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- PNNL-15303: Development of (Mn,Co)$_3$O$_4$ Protection Layers for Ferritic Stainless Steel Interconnects
- PNNL-15787: Analysis of Percent On-Cell Reformation of Methane in SOFC Stacks: Thermal, Electrical, and Stress Analysis
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PNNL-23397: Compliant Glass Seals for SOFC Stacks

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Presentations

SECA Core Program – Recent Development of Modeling Activities at PNNL (2002 SECA Core Technology Program Review Meeting)

SECA Core Technology Program – PNNL: SOFC Component Development (2002 SECA Core Technology Program Review Meeting)

SECA Core Program – Recent Development of Modeling Activities at PNNL (2003 SECA Core Technology Program Review Meeting)

SECA Core Technology Program - PNNL: SOFC Component Materials Development (2003 SECA Core Technology Program Review Meeting)

Compressive Seal Development for Solid Oxide Fuel Cells (2004 SECA Workshop)

SECA Core Program – Recent Development of Modeling Activities at PNNL (2004 SECA Workshop)


Development of Advanced SOFC Anodes (2004 SECA Workshop)

Cathode-Chromia Interactions (2004 SECA Workshop)
Advanced Metallic Interconnect Development (2004 SECA Workshop)

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SOFC Tolerance Limits for Phosphorus and Arsenic (2010 SECA Workshop)

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Modeling Tools for SOFC Design and Analysis: Recent PNNL Progress (2014 SECA Workshop)

Compliant Glass Seal Development (2014 SECA Workshop)
Executive Summary

This report summarizes results from experimental and modeling studies performed by researchers at Pacific Northwest National Laboratory on behalf of the Solid-State Energy Conversion Alliance (SECA) Core Technology Program. The work was performed from 1999 through 2014, under FWP 40552. PNNL’s scientific and technical contributions included development/evaluation of improved materials and fabrication processes for solid oxide fuel cell (SOFC) components, development/implementation of modeling tools to facilitate cell and stack design and optimization, and improved understanding/mitigation of SOFC performance degradation mechanisms. Key scientific and technical achievements included:

- Development of an optimized materials set and fabrication process for fabrication of thin electrolyte, anode-supported cells.
- Systematic evaluation and down-selection of candidate alloys for intermediate temperature, planar SOFC stacks.
- Development of protective spinel coatings for active interconnect regions; the spinel coatings were shown to reduce oxidation kinetics and chromium volatility.
- Development of a simple, cost-effective aluminization process for sealing regions of interconnects.
- Optimization/validation of physical surface modifications (e.g., surface blasting) to metallic interconnects which substantially improve oxide scale adhesion.
- A variety of sealing technologies allowing SOFC developers to tailor stack fabrication temperatures and mitigate thermal stresses during operation and thermal cycling.
- Improved understanding of effects of contaminants operating parameters on electrochemical and mechanical performance.
- 2D and 3D FEA-based modeling tools to analyze and optimize cell and stack design.
- A reduced order model (ROM) to accurately simulate stack performance in SOFC system simulations.
Introduction
From 1999 through 2014, under FWP 40552, Pacific Northwest National Laboratory (PNNL) provided R&D support to the Solid-state Energy Conversion Alliance (SECA) as a primary participant in SECA’s Core Technology Program (CTP). PNNL’s scientific and technical contributions included development/evaluation of improved materials and fabrication processes for solid oxide fuel cell (SOFC) components, development/implementation of modeling tools to facilitate cell and stack design and optimization, and improved understanding/mitigation of SOFC performance degradation mechanisms.

The scope of work was determined through regular consultation with SECA program management at National Energy Technology Laboratory (NETL) and representatives from the SECA industry teams. Transfer of results and technology to the industry teams was achieved through reporting of results (e.g., annual SECA Workshop, topical reports, peer-reviewed publications, presentations at technical society meetings, and one-on-one meetings with industry teams) and delivery of materials and software for in-house evaluation (e.g., coupons and stack components, software training workshops, and online software demonstrations).

Specific areas of contribution included:

- Materials and fabrication processes
  - Cell fabrication
  - Interconnect materials and coatings
  - Seals for SOFC stacks
  - Electrodes

- Modeling and simulation tools
  - Tools to support cell/stack design
  - Reduced order models (ROM) to support system modeling

- Understanding of degradation mechanisms
  - Interconnects
  - Seals
  - Cathodes

- New test protocols
  - SECA CTP stack test fixture
  - In-operando XRD

This report briefly summarizes some of the primary project accomplishments. Detailed descriptions of the project achievements can be found in the papers, reports, and patents referenced in this report, and in the appended topical reports and presentations.
Materials and Fabrication Processes

Cell Fabrication
In the early years of the SECA program, PNNL developed an optimized set of materials and processing conditions for fabrication of anode-supported thin electrolyte SOFC (Figure 1). In this work, PNNL selected commercial raw materials (oxide powders, binders, solvents, etc.), determined optimum materials processing conditions, and developed tape casting, screen printing, and sintering procedures for complete cell fabrication. The resulting technology was subsequently transferred to one of the SECA industry teams.

Interconnect Materials and Coatings
As interest in anode-supported SOFC grew due to their ability to operate at relatively low temperatures (e.g., 800°C), there was a need to develop alloy-based interconnects that could offer stable long-term performance. Following a comprehensive review of the properties of the most relevant alloy systems,1 systematic evaluations (e.g., thermal expansion, oxidation kinetics and electrical properties) were performed on selected candidate alloys. These tests led to the identification of several specific ferritic stainless steels as the preferred interconnect materials.2-5 While the selected ferritic stainless steels exhibited suitable interconnect properties, it was recognized that protective coatings would be required to improve their oxidation behavior and to mitigate volatilization of Cr from the steel surface. To protect interconnect surfaces in the “active” interconnect region, where high electrical conductivity is required, manganese-cobalt (MC) spinel coatings were developed. Properties optimization studies led to the selection of a specific composition: Mn1.5Co1.5O4, with a small amount of Ce added to improve oxide scale adhesion (Figure 2).6-11 Screen printing and aerosol spray procedures were developed for application of the spinel coatings.

In recent years, as test times were extended out to several thousands of hours, it was observed that the continued growth of oxide scale under the protective spinel coating eventually resulted in scale spallation during thermal cycling. To address this issue, a variety of surface modifications were applied to the stainless steel (AISI 441) prior to application of the protective spinel coating. Several of the modifications resulted in improved scale adhesion. The best results were achieved with surface blasting, with no scale spallation being observed even after 30,000 hours of oxidation at 800°C (Figure 3).12

To protect inactive interconnect regions (i.e., sealing areas and exposed surfaces), a novel aluminization process was developed. While commercial aluminization processes are available, they are expensive due to their reliance on exotic precursors and/or heat treatments. PNNL’s process, reactive air aluminization (RAA), is a simple aluminum powder based process requiring only a simple heat treatment in air.13 Both coatings (MC spinel and RAA) were validated for
6,000 hours at 800°C under realistic SOFC operating conditions in PNNL’s stack test fixture (described below).

While most of the interconnect work was directed towards metallic interconnects, PNNL also developed ceramic interconnect materials for high operating temperature SOFCs. Additions of modest levels of selected transition metal dopants to yttrium chromite-based compositions were found to be effective in reducing fabrication temperatures while maintaining low chemical expansion coefficients.

Seals for SOFC Stacks
A number of different sealing technologies were developed at PNNL on behalf of the SECA Core Technology Program:

**Compressive seals.** Compressive seals based on inexpensive mica-paper were developed for applications requiring sealing of materials with significant thermal expansion mismatch. These seals, which are simple to fabricate, exhibit excellent thermal cycle stability and low, stable long-term leak rates.

**Air brazes.** Brazes based on a liquid-phase oxide-silver melt provide joins with high rupture strength and high-temperature oxidation resistance. The brazing process is simple to perform, as it is conducted in air without the need for fluxes or inert cover gases. This technology was transferred to one of the SECA industry teams.

**Devitrifying glass seals.** A range of devitrifying glass seals were developed covering a wide range of stack sealing temperatures (85 – 1000°C). Advantages of these glasses include reduced reactivity and improved thermal expansion stability (over time) compared to conventional SOFC sealing glasses.

**Compliant glass seals.** As an alternative to devitrifying glass seals, compliant seals based on a glass with low Tg and low viscosity at SOFC operating temperatures were developed in a collaboration with Oak Ridge National Laboratory. Compliant glass seals can reduce thermo-mechanical stresses during stack operation and thermal cycling, and also exhibit self-healing of thermal cycle related damage. A composite compliant seal comprised of glass and zirconia fibers was validated for ~6,000 hours at 800°C under realistic SOFC operating conditions in PNNL’s stack test fixture.

Electrodes
A number of alternative cathode and anode materials and fabrication processes were developed and/or evaluated at PNNL for the SECA Core Technology Program, including:

- Pr2NiO4 cathodes
- Reaction-sintered cathode contact materials
- Dense ceria cathode interlayers
- Sulfur-tolerant ceramic anode materials

**Modeling and Simulation Tools**

**Tools to Support Cell/Stack Design**
PNNL developed the Solid Oxide Fuel Cell Multiphysics (SOFC-MP) solver to analyze and optimize cell and stack designs. This simulation tool performs coupled solution of the current density distribution, heat generation, and fuel/oxidant species concentrations in multi-cell planar stack geometries. The 3D module provides detailed evaluation of a full stack design (Figure 4) for transfer of the temperature profile to a finite element analysis (FEA) code for subsequent stress and reliability analysis. The 2D module (limited to co- and counter-flow designs) provides more rapid results for stack performance engineering studies. A custom graphical user interface supports model creation, job submission, post-processing, and results visualization with each module.

**Reduced order modes (ROM) to support system modeling**
PNNL developed a reduced order model (ROM) tool to incorporate the detailed knowledge obtained from SOFC-MP stack model results (e.g., voltage-current relationship, maximum temperature, temperature gradient, etc.) into system model simulations of SOFC-based power generation systems. This tool, based on response surface analysis, automates sampling of cases, model creation, job submission, data management, regression of results, visualization, error analysis, and ROM code export. The computationally efficient ROM approximation for the stack response was demonstrated to be a viable replacement for the typically simple stack models currently used in system simulations.

**Understanding of Degradation Mechanisms**

**Seals**
Modeling for various stack sealing technologies was performed by PNNL to characterize material response, improve thermal-mechanical reliability in stack designs, and aid adoption by industry team designers. Primary areas of focus included thermal cycling and damage of devitrifying glass-ceramic seals, behavior of bonded compliant seals, and influence of properties and reinforcement phase on damage and healing in compliant glass seals.

**Interconnects**
PNNL developed novel experimental methods and detailed finite element models to understand the drivers for long term performance of interconnect protective coatings and oxide scale layers. Experimental data from surface or interfacial indentation tests was used to characterize the strength of the interconnect-scale interface, while numerical models for delamination and spallation of the protective layer were combined with oxide scale growth kinetics to predict useful lifetimes for as-received and surface-modified interconnect materials.53-56

Cathodes
PNNL performed a number of studies intended to improve the SOFC community’s understanding of degradation mechanisms that can lead to reduced electrochemical performance of cathodes over time. For example, PNNL quantified the effects of humidity and volatile constituents of seals (e.g., B, Na, and K) on the chemical and electrochemical stability of LSCF and LSM/YSZ cathodes.57 PNNL also participated (in collaboration with Argonne National Laboratory and GE Energy) in a pioneering study on the effects of Cr volatility on SOFC cathodes. This study demonstrated that Cr poisoning was enhanced when cells were in direct contact with Cr-containing interconnect materials, and identified reaction products and possible degradation mechanisms. A summary report on this work was issued by GE Energy. PNNL was also among the first institutions to identify and study Sr segregation in LSCF cathodes; the results of this work led to subsequent studies by other SECA Core Technology Program researchers.58

New Test Capabilities

SECA Core Technology Program Stack Test Fixture
PNNL developed a test fixture and test protocols to allow for assessment of new materials and fabrication processes developed by PNNL and other SECA CTP participants in a realistic stack-like environment (Figure 5). This test capability, which has been used to evaluate new materials for up to 6,000 hours, serves as a technology bridge between lab scale tests (e.g., button cells) and the full size cells and stacks being developed by the SECA industry teams. The stack test fixture design and protocols were transferred to two other SECA CTP participants (NETL and U. of Connecticut) for implementation at their facilities.14, 59-62

In-operando XRD
PNNL designed and fabricated a custom test fixture that, when integrated with a high temperature XRD unit, performs XRD analysis on working SOFC cathodes (Figure 6). The fixture was used to measure changes in phase assemblage and lattice parameters for both LSCF and LSM/YSZ-based cathodes as a function of time, temperature, voltage, and cathode air humidity level.63

Summary
From 1999-2014, PNNL developed new technology and scientific understanding to support SECA industry teams in their development of cost-effective, highly efficient SOFC-based power systems. Primary areas of emphasis included a) improved materials for SOFC stack components, b) improved understanding of performance degradation mechanisms, and c) modeling tools to assist in cell, stack, and system design. Transfer of technology and scientific understanding was accomplished via individual meetings with SECA industry teams, the annual SECA Workshop, topical reports, peer-reviewed publications, presentations at technical society meetings, and delivery of materials and software to SECA industry teams for in-house evaluation and implementation.

Acknowledgments
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References


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Figure 1. SEM cross-section micrograph of anode-supported SOFC prepared using PNNL’s cell fabrication protocol.

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Figure 4. Process for use of SOFC-MP 3D temperature results for stack stress analysis.
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Figure 6. Test fixture developed by PNNL for in-operando XRD scanning of working SOFC cathodes on anode-supported cells.
Materials Properties Database for Selection of High-Temperature Alloys and Concepts of Alloy Design for SOFC Applications

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Materials Properties Database for Selection of High-Temperature Alloys and Concepts of Alloy Design for SOFC Applications

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November 2002

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Abstract

To serve as an interconnect / gas separator in an SOFC stack, an alloy should demonstrate the ability to provide (i) bulk and surface stability against oxidation and corrosion during prolonged exposure to the fuel cell environment, (ii) thermal expansion compatibility with the other stack components, (iii) chemical compatibility with adjacent stack components, (iv) high electrical conductivity of the surface reaction products, (v) mechanical reliability and durability at cell exposure conditions, (vi) good manufacturability, processability and fabricability, and (vii) cost effectiveness. As the first step of this approach, a composition and property database was compiled for high temperature alloys in order to assist in determining which alloys offer the most promise for SOFC interconnect applications in terms of oxidation and corrosion resistance.

The high temperature alloys of interest included Ni-, Fe-, Co-base superalloys, Cr-base alloys, and stainless steels. In the US alone, there are hundreds of commercial compositions produced, over 250 of which are listed in Appendix A. Two initial criteria (oxidation resistance and oxide scale electrical conductivity) were used to reduce the list of alloys to manageable proportions. Thermal expansion and fabrication characteristics were then considered to further reduce the list of stainless steels. Due to their outstanding oxidation resistance and their potential to be used in SOFC components that can exclude alumina scales from the stack electrical path, alloys with a sufficient amount of aluminum were classified into a separate alumina-forming alloy category. The down-selected compositions (approx. 130 in number) and their characteristics and/or applications are listed in the Selected Alloy Compositions tables (Appendix B).

Following the down-selection of alloy compositions, materials properties of interest corresponding to their functional requirements in SOFC stacks were compiled in a tabular form (Appendix C). For comparison, the properties of selected noble metals and intermetallics were also collected and compiled and are listed in a separate table in Appendix C.

Analysis of the pertinent literature indicated that, for a wide variety of alloys, there remains a lack of information on specific materials properties. Also, we have observed a large scatter in the reported database. For those cases, we employed general alloying principles as a tool of choice to approximate the unavailable data and to evaluate the reliability and consistency of collected data.

Though numerous high temperature alloys look promising, it is anticipated that there will be few, if any, “off the shelf” alloy compositions which could completely satisfy the materials requirements as an interconnect, especially for a long term in a specific SOFC design. Therefore, some concepts of alloy design, including composition, constitution, and structure, as well as their effects on properties relevant to SOFC applications, are elaborated in an attempt to provide guidance for modification of current compositions and development of new alloys.

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I. Introduction

Over the past several years, advances in planar anode-supported cell designs, along with improvements in the cell component materials and fabrication processes, have led to a steady improvement in the electrical performance, performance stability and reliability of planar SOFCs. The use of thin electrolytes and advanced cell electrode configurations and materials has led to a steady reduction in the operating temperatures to the 800ºC range or lower, without compromising the electrical performance or reliability.

Both metallic and ceramic interconnect materials have been used in SOFC stacks to demonstrate the feasibility of relatively long term operation of planar cells. Results indicate that although electronically conducting ceramic current collectors demonstrate superior chemical and structural stability; they remain very expensive and difficult to fabricate. Metallic current collectors, on the other hand, show surface oxide formation, increase in resistance and contamination of adjoining cell components. Metallic current collectors, however, remain highly cost effective and easy to fabricate when compared with ceramic counterparts.

In a planar SOFC configuration, the current collector / bipolar gas separator, as the name indicates, acts as a separator for the fuel and the oxidant gases and also serves as a current collector between cells. The fuel gas environment, consisting of H₂, H₂O, CO, CO₂, CHₓ, etc., has a low oxygen partial pressure (Log PO₂ (atm) = -14 to -20) and high carbon activity, while the oxidant gas environment usually consists of air. Exposure to this dual environment leads to oxidation and corrosion of metals and alloys resulting in the formation of various corrosion products. Bipolar separators also are exposed to peripheral gas seals (glass or compressive) and may experience chemical interaction with the seal materials.

Until recently, the leading candidate material for the SOFC interconnect was electronically conducting doped lanthanum chromite, LaCrO₃, a ceramic which could easily withstand the 1000°C operating temperature of an electrolyte or air electrode-supported SOFC design. CVD-EVD as well as high temperature sintering techniques were initially used for the fabrication of dense interconnections. Liquid phase sintering and dopants were also investigated to promote sintering at lower temperatures. However, difficulties with obtaining high-density chromite parts at reasonable sintering temperatures persisted. It was also found that the chromite interconnect tended to partially reduce at the fuel gas/interconnect interface, causing the component to warp and the peripheral seal to break. Development of the lower temperature anode supported cells which utilize nickel-based anode supports, thin electrolytes and highly active cathode structures have caused lanthanum chromite to be supplanted by metallic interconnects as the interconnect material of choice. Compared to doped lanthanum chromite, high temperature metallic materials also offer advantages such as improved manufacturability, significantly lower raw material and fabrication costs, and higher electrical and thermal conductivity. However, for a metallic alloy to be considered as a candidate material for the interconnect, it must satisfy the following requirements:

- Good surface stability (resistance to oxidation, sulfidation, and carburization) in both cathodic (air) and anodic (fuel gas plus
water vapor) atmospheres during isothermal and thermal cyclic operations.

- Thermal expansion matching to the other stack components (as least for a rigid seal design).
- Chemical compatibility with other materials in contact with the interconnect such as seals and cell materials.
- High electrical conductivity through both the bulk material and in-situ formed oxide scales.
- Mechanical reliability and durability at the device’s operating temperature.
- Strong adhesion or bond strength between the as-formed oxide scale and the underlying alloy substrate.
- Good manufacturability.

While there is a general agreement among the researchers in the SOFC technology development area that a suitable metal-based SOFC interconnect is needed for the overall cost reduction and faster start up, there is no agreement as to what alloy system might form the basis for this sub-component. Furthermore, there is no conclusive study that has been published in the open literature on suitable “lower” temperature SOFC interconnect materials that could serve as a reference. Long term degradation issues such as oxidation, carburization, sensitization, localized grain boundary penetration and oxide scale spallation still remain unresolved for a variety of alloys during their long term exposure under fuel cell operating conditions. The time, effort, and expense of developing a new alloy also needs basic understanding of the above degradation processes.

Considering the above materials requirements, oxidation-resistant alloys and several noble metals, such as platinum (including surface coatings), could be initially considered as potential candidates. The high cost of platinum and other noble metals, however, preclude their use as an interconnect in planar SOFCs. The remaining choices would be high temperature alloys that demonstrate oxidation resistance at elevated temperatures. The high temperature alloys of interest include Ni-, Fe- and Co-base superalloys, Cr-base alloys, and the stainless steels.

In the US alone, hundreds of commercial high temperature alloy compositions remain available for consideration for SOFC applications. To choose the best candidates for SOFC applications, and provide a reference for future research and development, the establishment of a materials database for the alloys of interest appeared to be mandatory.

As the first step to build the materials database for high temperature alloys, hundreds of commercial compositions, as listed in Appendix A, were collected from sources including textbooks, handbooks, electronic databases and producer Internet homepages. Both the alloy name and its UNS (Unified Numbering System) No., developed jointly by the U.S. Society of Automotive Engineers (SAE) and the American Society of Testing and Materials (ASTM), are listed with its composition. As the first cut, a selection criterion involving the content of critical elements (Cr, Al) in the alloys was established and applied to reduce the original composition lists to manageable proportions. The selected compositions with their characteristics and traditional applications are tabulated in Appendix B. The properties relevant to the functional requirements were defined and collected (as comprehensively as possible) for the
selected alloys (Appendix C). Given the wide range of data sources consulted, it was recognized that questions regarding the reliability and consistency of the collected data were likely to arise. Therefore, general background knowledge of alloying principles and the relationships between alloy composition, structure and properties were reviewed and used to help evaluate the real potential of compositions for SOFC applications.

The selection criteria for the different categories of alloy compositions are discussed below. Selected properties relevant to the interconnect materials requirements are also reviewed and discussed below in terms of general alloy principles. The concepts of alloy design are also elaborated, in an attempt to provide guidance for the modification of currently available compositions and future development of new alloy compositions exhibiting improved materials performance as an interconnect in SOFC.
II. Selection of Alloy Compositions

As mentioned above, the obvious choice for the current collector material would be a high temperature alloy that provides oxidation resistance under the high temperature exposure conditions that characterize the SOFC environment. Nominally, high temperature alloys can be classified into Ni-, Fe- and Co-based superalloys, Cr-based alloys and stainless steels. All of these alloys typically contain Cr and Al, which provide oxidation resistance by forming thin, adherent protective layers of Cr$_2$O$_3$ and Al$_2$O$_3$, respectively. Because of the overall higher resistance of alumina scales, it appears that Al$_2$O$_3$ forming alloys may not be suitable to be used as interconnects, at least for some designs, because of the performance loss (voltage loss across the insulating alumina scale). Thus, it is necessary to establish “critical” minimum Cr contents and “critical” maximum Al contents needed for long-term protection. (It should be noted that alumina formers may find application in SOFC stack designs which can exclude the alumina scale from the current collection function within the stack).

1. Ni-, Fe-, and Co-Base Superalloys

“Superalloys,” usually based on group VIIIA elements, have been developed for elevated temperature service where relatively severe mechanical stresses are encountered and high surface stability is required. These alloys are structurally characterized by the γ austenitic FCC matrix plus a variety of secondary phases. The principal secondary phases are the carbides MC, M$_2$C$_6$, M$_6$C and M$_7$C$_3$ (rare) in all Ni-, Fe-(Ni-) and Co-base alloys, and γ' FCC ordered Ni$_3$(Al,Ti) intermetallic compound in only Ni- and Fe-(Ni)- base compositions.

In the following, a selection criterion, mainly consisting of the “critical” minimum Cr content and “critical” maximum Al content is established for Ni-, Fe-, and Co-base superalloys.

1) “Critical Minimum” of Cr%

(i) Ni- and Fe-Base Superalloys:

As suggested by Robb, Wasielewski, Giggins and Pettit [1,2], the “critical” minimum Cr content to ensure the formation of a protective, continuous Cr$_2$O$_3$ scale is approximately 20-25 wt% chromium. This “critical” amount of Cr is also required to prevent the rupture of the protective scale, and internal oxidation due to the depletion of chromium at the sub-surface. This suggested “critical” minimum is consistent with the work of Birks and Rickert [12], who concluded that the oxide scale consists primarily of Cr$_2$O$_3$ when the Cr content in the alloy is greater that 20%; spinel (Cr,M)$_3$O$_4$ phases tend to form when the Cr concentration is less than 10%. Furthermore, a Cr content of more than 20 wt% in Ni-, Fe-, and Co-base alloys has been recommended as the principal method for combating hot corrosion [3]. For Ni-base alloys, Sims et al. [4] concluded that at least 15 wt% Cr
was needed for reasonable resistance to hot corrosion and that the optimum was 18-19 wt%.

It should also be noted that, in addition to Cr and Al, trace elements such as La, Ce, Y, etc., might also directly or indirectly contribute, sometimes significantly, to the oxidation and corrosion resistance. For Ni-base alloys with Cr contents less than 20%, an appropriate amount of Al is typically added to enhance the oxidation resistance.

Thus it appears that, for optimum oxidation and corrosion resistance, the Cr content in Ni- and Fe-base alloys should be more than ~18 wt%, which is therefore recommended as the “critical” minimum content for Ni- and Fe-base superalloys.

(ii) Co-Based Superalloys:

Experimental studies conducted by Kofstad and Hed [5-7] indicated that additions of 9% Cr decrease the already poor oxidation resistance of pure cobalt by a factor of three. The oxide scale is predominantly CoO, with some CoCr2O4. Upon further additions of Cr to 25%, the oxidation rate decreases to a minimum, and a protective scale of Cr2O3 is established. Sims et al. [4] mentioned an optimum content of 25-30% Cr in Co-base alloys for hot corrosion. It is also noted that oxidation and corrosion resistance of Co-base alloys could be further improved by additions of Al, B, Ca, and Zr. Therefore, the “critical” minimum content of Cr was set as 22% for Co-base alloys.

2) “Critical” Maximum of Al% 

(i) Ni- and Fe-Base Superalloys:

Based on the ratio of Cr and Al, Wasielewski and Rapp [1] classified superalloys containing both Cr and Al into the following three categories:

a) A NiO scale with Cr2O3 and Al2O3 internal oxides for both low Cr and Al contents-type I;

b) An Cr2O3 scale with Al2O3 internal oxides for high Cr (>15%) but low Al (1%<Al%<3%)-type II;

c) An exclusive α-Al2O3 scale for relatively high Cr (>15%), and high Al (>3%)-type III.

The steady-state parabolic rate constants are decreased by more than one order of magnitude in passing from type I to type II, and again in passing from type II to type III. The elimination of NiO as the steady-state scale is accomplished when the combined volume fraction of Cr2O3 and Al2O3 precipitates is sufficient to block inward diffusion of oxygen into the alloy matrix. Thus the sidewise growth of Cr2O3 particles can develop a “protective” inner scale of Cr2O3. The presence of an inner layer drastically reduces the local oxygen activity at the metal-interface so that an enrichment of Al2O3 particles occurs. For type III alloys, which have sufficient bulk Al or volume fraction of alumina, an α-
Al$_2$O$_3$ layer forms beneath the Cr$_2$O$_3$ inner scale, which dramatically enhances the oxidation resistance, but acts as an electrical insulating layer. Therefore, an Al content of 3 wt% was established here to be the “critical” maximum. It was found that in the original list (Appendix A), no Ni-base alloys with Cr content of higher that 18 wt% contain an Al content of higher than 3 wt%. For Fe-base alloys, application of this “critical” maximum only eliminates Incoloy MA956 with 4.5% Al, which is listed in the alumina forming alloys. Recent studies by Quadakkers et al [8] confirm that MA 956 is not suitable for typical SOFC interconnect applications due to the high electrical resistance of the formed alumina-scale.

(ii) Co-Base Superalloys:

Normally, conventional Co-base alloys do not contain Al and depend on $\alpha$-Cr$_2$O$_3$ for protection.

Note that, due to formability considerations, the casting alloys are left out for consideration at this stage. Only wrought alloys are listed here. Besides Cr and Al, Si is another alloy element that can provide oxidation resistance (by forming an insulating SiO$_2$ layer.) No criterion was established in term of Si content, but its effect on oxidation should be considered for some listed compositions that contain a fairly large amount of Si.

2. Cr-Base Alloys

The Cr-base alloys crystallize in the body-centered-cubic (BCC) structure and thus are not considered as superalloys by most metallurgists. As aluminum is not included in these compositions, no criterion was established, and thus all the Cr-alloys in the original list were considered to be selected for property collection.

3. Stainless Steels

Stainless steel is a generic term covering a large group of alloys, which are commonly known for their oxidation resistance. In terms of their structures, stainless steels are usually divided into four groups: (i) ferritic steels; (ii) austenitic stainless steels; (iii) martensitic steels and (iv) precipitation-hardening steels. It is noted that some FCC austenitic stainless steels, usually with significant amount of Ni addition, are classified into superalloys and listed in Fe-Ni-base superalloy tables.

The ferritic stainless steels typically have 11 to 30% chromium as the major alloy addition and are low in carbon. These compositions are substantially ferritic, a body-centered-cubic (BCC) structure at all temperatures and therefore can not be strengthened by heat treatment, although some of the “ferritic” grades do undergo some austenite formation at high temperatures and can transform into
Ductility and formability of ferritic compositions are less than that of the austenitic grades. Their corrosion resistance competes with the austenitic grades for certain applications. Ferritic stainless steels are magnetic, and resistance to high-temperature corrosion is better than that of martensitic types. They generally have good ductility and can be welded or fabricated without difficulty.

The aforementioned ferritic stainless steels also include pure or superferritic ones (refer to details in Part III, 5), such as 29-4, E-Brite 26-1, etc., and ferritic/austenitic duplex structures, such as Carpenter 7-Mo, AL 255, etc. The ratio of ferrite (BCC) to austenite (FCC) in duplex structures mainly depend on the nickel content, which is typically in the range of 4.5 to 8%. This nickel content is not sufficient to generate a fully austenitic structure, thus resulting in a combination of BCC ferritic and FCC austenitic structures.

Recently, some ferritic stainless steels have specifically been developed for glass sealing applications, where a close TEC match in the whole temperature range is required. Due to oxidation resistance considerations, only those with chromium content higher than the minimum are listed in the table of ferritic stainless steels.

Austenitic steels with a FCC structure are characterized by larger linear thermal expansion coefficients, which are typically in 18-20×10^{-6}/K (RT~800°C). For example, Project 70 Stainless and Carpenter 21Cr-6Ni-9Mn are common standard and non-standard austenitic stainless steels and have linear thermal expansion coefficients of 19.0×10^{-6}/K and 20.0×10^{-6}/K (RT~760°C)\cite{10}, respectively. Thus all standard and non-standard austenitic compositions are unlikely to be satisfactory candidates for rigid seal stack designs.

Martensitic and precipitation-hardening steels, which typically contain a Cr content of less than 18%,\cite{9} were not included in this study; their maximum service temperature without excessive scaling is usually less than 650°C\cite{11}.

Therefore only ferritic standard and non-standard steels, including duplex structures, are evaluated using the same criterion in chemical composition as established for superalloys, i.e. the “critical” minimum Cr content is set at 18 wt% and the “critical” maximum Al content at 3 wt%.

4. Alumina Forming Alloys

It has long been known that the oxidation resistance of alloys with a fairly high amount of Al is orders of magnitude higher than an alloy only containing Cr. It might be possible to make use of these alloys in SOFC stacks by designing the components to exclude the insulating alumina scale from the current conduction path. In this case, a “minimum” Al content (with reference to the Cr content) should be established. By referring to the previously mentioned Wasielewski and Robb rule\cite{11} for classification of superalloys, the following criteria were established to create an alumina forming alloy table:

i) High Cr (>18%) and high Al (>3%) - type I;
ii) High Cr (>18%) and fairly high Al (1<Al%<3%) – type II;
iii) Fairly high Cr % (15~18%) and high Al (>3%) - type III.
It is expected that both type I and III will form continuous Al2O3 inner layers. For type II, the Al content may not be enough to form a continuous Al2O3 layer, but might be a major component in the oxide scale to improve the oxidation resistance. In this work, alloys with Cr%≥15 and Al%≥3 are defined as alumina formers and separated into the Table of Alumina Forming Alloys.
III. Alloy Properties Relevant to the SOFC Interconnect Application

According to the materials functional requirements for a metallic interconnect in SOFCs, the following parameters or properties must be used to evaluate alloys: (i) thermal expansion coefficient; (ii) electrical conductivity of both bulk matrix and scale; (iii) oxidation resistance; (iv) corrosion resistance; (v) yield strength; (vi) elastic modulus; (vii) formability or tensile elongation; (ix) cost; (x) other properties, such as hydrogen embrittlement resistance, machinability, and etc. For this study, it was expected that it would not be possible to obtain all data required. Also, some data might not be reliable, particularly if considerable scatter existed in data taken from different sources. In those cases, knowledge of alloying principles can be used as a tool to approximate the unavailable data and to evaluate the reliability and consistency of collected data. In the following, the parameters or properties corresponding to the materials functional requirements will be reviewed and discussed in terms of general alloying principles.

1) Thermal expansion coefficient (TEC)

When available, the average linear TEC over the temperature range of RT-800°C has been collected from the available literature data for a large number of Ni, Fe, Co and Cr base alloys. The TEC of alloy systems largely depend on the crystal lattice structure. In term of matrix crystal structure, high temperature alloys can also be classified into BCC ferritic and FCC austenitic formers, as shown schematically in Figure 1. Ni-, Fe-, Co-base superalloys and austenitic stainless steels are FCC formers; ferritic stainless steels as well as Cr-base alloys are BCC formers. As a rule of thumb, BCC formers have a lower TEC than FCC formers. For example, the TEC of pure ferritic stainless steels are typically in the range of 12.0~13.0×10^{-6} K^{-1} from RT to 800°C, therefore having a better thermal expansion match to typical SOFC components. If the concentrations of substitutional elements are increased beyond the phase stability region, austenite may be formed in the ferritic matrix, resulting in a duplex structure. All duplex stainless compositions have shown higher TEC than their pure ferritic counterparts. Fully austenitic alloys with FCC structure possess higher thermal expansion coefficients than BCC formers. Austenite stainless steels and Fe-base superalloys usually have a TEC in the range of 15.0~20.0×10^{-6} K^{-1} from RT-800°C. Ni-base superalloys, also with FCC structure, tend to have TEC in the range of 14.0~19.0×10^{-6} K^{-1} from RT to 800°C. Co-base superalloy compositions normally possess a TEC of 14.0~17.0×10^{-6} K^{-1} from RT to 800°C.

The TEC data of different groups of alloys, along with other properties, is outlined in Table I.
Figure 1. Schematic of alloy design for SOFC applications.

Table I. Comparison of key properties of different alloy groups for SOFC applications

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Matrix structure</th>
<th>TEC ×10⁻⁶.K⁻¹</th>
<th>Oxidation resistance</th>
<th>Mechanical strengths</th>
<th>Manufacturability</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrBA</td>
<td>BCC</td>
<td>11.0-12.5 (RT-800°C)</td>
<td>Good</td>
<td>High</td>
<td>Difficult</td>
<td>Very expensive</td>
</tr>
<tr>
<td>FSS</td>
<td>BCC</td>
<td>11.5-14.0 (RT-800°C)</td>
<td>Good</td>
<td>Low</td>
<td>Fairly readily</td>
<td>Cheap</td>
</tr>
<tr>
<td>ASS</td>
<td>FCC</td>
<td>18.0-20.0 (RT-800°C)</td>
<td>Good</td>
<td>Fairly high</td>
<td>Readily</td>
<td>Cheap</td>
</tr>
<tr>
<td>FeBSA</td>
<td>FCC</td>
<td>15.0-20.0 (RT-800°C)</td>
<td>Good</td>
<td>High</td>
<td>Readily</td>
<td>Fairly expensive</td>
</tr>
<tr>
<td>NiBSA</td>
<td>FCC</td>
<td>14.0-19.0 (RT-800°C)</td>
<td>Good</td>
<td>High</td>
<td>Readily</td>
<td>Expensive</td>
</tr>
</tbody>
</table>
2) Electrical conductivity

For high temperature alloys, the electrical resistance increases with increasing temperature and is the sum of two parts, bulk resistance and scale resistance. The bulk electrical resistance, which usually can be easily found in handbooks and electronic sources, is collected and listed in Appendix C; typical values are 60-130×10^-6 Ω·cm at RT with only slight increases with temperature.

In the long term, the electrical resistance of the scale usually dominates the electrical behavior of high temperature alloys during SOFC operation. As mentioned earlier, the scale could be either Cr₂O₃ or Al₂O₃. Cr₂O₃ is an electronic conductor, which at 900°C has a conductivity of 10⁻²~10⁻¹ S·cm⁻¹ [16].

The temperature dependence of the conductivity can be expressed by:

\[ \sigma = \sigma_0 \exp \left(-\frac{E_a}{RT}\right) \]

where \( \sigma = \text{conductivity} \) (\( = 1/\rho \), where \( \rho = \text{resistivity} \)), \( E_a \) is the activation energy, \( R \) is the gas constant, and \( T \) is absolute temperature. \( \sigma_0 \) and \( E_a \) were reported by Kofstad et al. [15~17] at 0.04-0.06 S/cm and \( E_a=180 \) KJ/mol, respectively, in a temperature range of 800-1,000°C. Though the literature values of the electrical conductivity of alumina (\( \alpha \)-Al₂O₃) show large discrepancies and vary by many orders of magnitude [16], it is universally acknowledged to be an electrical insulator. Kofstad and Bredesen [21] concluded that the electrical conductivity of alumina is lower than that of chromia by a factor of 10⁵⁻¹⁰⁶. Accordingly, chromia formers rather than alumina formers should be considered as interconnect materials, unless the SOFC stack design excludes the Al₂O₃ scale from the electrical path.

In principle, the area specific resistance (ASR) can be evaluated according to Cr₂O₃ scale thickness, which is a function of the rate constant, temperature and time, assuming the scale growth follows the parabolic law. This ASR estimation however yields a lower value than those reported in most recent studies [14,18~20, 22]. Almost all of these studies concluded that the Cr₂O₃ scale growth and thus the electrical resistance would reach an unacceptable level in the long term under the SOFC operating conditions. It is believed that the discrepancy is caused by the complexity of Cr₂O₃ scale growth, which will be described in the next section. The growth of Cr₂O₃ scales on high temperature alloys in practical environments is much more complicated than the growth on pure chromium, which is generally used in lab-studies to obtain the rate constant.

Overall, it appears that, in the long term, the bulk and/or surface compositions of high temperature resistant alloys must be engineered to decrease the oxide scale growth rate and/or modify the scale chemistry so that the resistance of the scale can be limited to acceptable levels (refer to details in Part IV).
3) Oxidation resistance

In Wagner’s theory of oxidation \cite{23,24}, it is assumed that during the oxide growth, the transport of oxygen ions and/or metallic cations through the oxide scale takes place by lattice diffusion. Thus the growth of the surface oxide scale follows the well-known parabolic law:

\[ X^2 = kt + X_0^2 \]

where \(X\) and \(X_0\) is the thickness of the scale at time \(t\) and \(t=0\), respectively; \(k\) is rate constant. It has been experimentally shown that the parabolic law of the growth of scale is valid for essentially all cases in which the scale is adequately thick and homogeneous. It has been noted that\cite{13} the net current flow in SOFCs may cause some deviation from the parabolic law prediction.

Recent studies conducted on SOFC-related oxidation of high temperature alloys indicate that in most cases the oxidation of high temperature alloys still obeys the parabolic law under current flows appropriate for SOFC \cite{14}. Hence, in this study, the parabolic rate constant is selected as the parameter measuring the oxidation resistance of high temperature alloys. Our literature survey indicates that data collected from textbooks, handbooks, and electronic data sources exhibit considerable scatter.

In spite of the lack of consistent and complete data, the oxidation resistance can still be qualitatively understood in regard to alloy chemical composition. As stated previously, Cr and Al (and Si) are the major oxide scale formers to provide oxidation resistance in the high temperature alloys. The growth rate constant of Al containing alloys can be orders of magnitude lower than that of Cr containing alloys. Thus alumina formers typically have much higher oxidation resistance than alloys containing only chromium to provide protection. Besides, it is also common for the alumina formers to possess a stronger adherence between the scale and bulk matrix than chromia formers, and thus they demonstrate better scaling resistance against oxide spallation and cracking under thermal cycling.

Weak bonding of chromia scales with the underlying substrate is dictated by the following growth features \cite{15}:

(i) The scales grow predominantly by outward chromium diffusion along grain boundaries in the chromia scale. But, there is also some inward oxygen diffusion to result in formation of oxide within the scale, which can cause growth stress in the scale.

(ii) As the result of growth stress and the growth mechanism, the scales are often convoluted and contain cavities and porosity; furthermore, the scales often detach locally from the metal substrate.

(iii) Chromia scales may also exhibit extensive cracking at high temperatures and may also spall on cooling and thermal cycling.

The use of so called “reactive elements,” such as Ce, La and Y, or their oxide forms, has been found to greatly modify this growth behavior, which will be discussed in detail in Part IV. As a result, alloys with additions of reactive...
elements typically possess much improved oxidation, electrical and scaling resistance.

4) Corrosion resistance

The SOFC operates at high temperature (700-1,000°C) with fuel (such as H\textsubscript{2} or reformed natural gas) on the anode side and air on the cathode side. Moisture could be present on both the cathode and anode sides, and, therefore, in contact with the metallic interconnects. Sulfur impurities present in the fuel gas stream are also expected to exist, although upstream desulfurization has been commonly applied to decrease the sulfur impurity level to sub ppm or ppb levels. Thus, besides oxidation, the interconnect could also suffer from sulfidation, hot corrosion (in the presence of molten salt), and carburization, etc. Thermal stresses generated in the SOFC stack due to large temperature gradients across the current collector could also accelerate the corrosion process due to premature cracking and spallation of the oxide scale. The presence of complex gaseous species in the fuel environment also result in the establishment of grain boundary corrosion, internal oxidation and localized metal loss resulting in overall reduction of component life. Sulfidation refers to an aggressive attack resulting from the combined effects of oxidation plus reactions with sulfur, which may be present in the fuel gas stream. Our literature search indicated that no standardized data is available for quantitative comparison. Thus only qualitative classification is currently possible within the scope of this report. Generally, the degree of sulfidation or hot corrosion can be related to the chromium content and alloy chemistry in Ni-, Fe- and Co-base alloys. The effect of alloy elements on hot corrosion resistance is also discussed in the “Effects of Alloying Elements” section below.

5) Yield strength

The metallic interconnect is also required to have enough strength to help maintain the structural integrity of the stack during SOFC operation at high temperatures and under thermal cycling. Accordingly, the high temperature alloys for an interconnect should possess thermal fatigue resistance against possible structural fracture during thermal cycling, creep resistance to maintain the dimensional stability at high operating temperature, and rupture resistance to endure peak thermal stresses generated during SOFC operation. All the aforementioned strengths can be more or less correlated to the yield strength, \( \sigma_{\text{yield}} \). For stainless steels, the compositions with higher yield strength usually possess higher creep and fatigue strengths, so do superalloys. The high temperature mechanical properties of some superalloys and stainless steel compositions are collected in Table II.

Thus the yield strength, which is also easily available, was used to represent mechanical strength of the alloys. Since most alloys except annealed low carbon steels do not have obvious yielding strains, the stress at \( 0.2\% \) is defined as the yield strength, \( \sigma_{0.2} \). When possible, the yield strength from bar tests
at both RT and a high temperature (preferable around 800°C) was collected. If bar test data was not available, sheet test data was used.

The yield strength of an alloy is a function of alloy composition, phase constitution and structure/microstructure. The alloy can be strengthened through combinations of the following mechanisms:

(i) Solution strengthening;
(ii) Precipitation hardening;
(iii) Martensitic hardening;
(iv) Carbide or added oxide strengthening;
(v) Work hardening.

Different alloy groups could have different combinations of strengthening mechanisms. For example, strengthening mechanisms for ferritic stainless steels are limited to work hardening and solution strengthening, in order to maintain their BCC ferritic structure. Precipitation hardening may also be applicable, but may not be useful in improving the strength of an alloy at elevated temperatures (e.g., 800°C).

Overall, the superalloys and Cr-base alloys tend to have higher yield strengths than stainless steels; austenitic stainless and martensitic steels have higher yield strengths than ferritic stainless steels. The conventional ferritic stainless steels such as 430, 446, and 453 usually have a yield strength of about 300 MPa at RT. The yield strength of these stainless steels, however, drops quickly as the temperature increases over 700°C and usually ends up a number less than 50 MPa at 800°C. Consequently, these stainless compositions are typically characterized by substantially low creep and fatigue strength, which may be of concern for SOFC applications, especially in the long term.

In past years, numerous stainless alloy compositions have been developed for improved strength by increasing Cr content and adding other alloy elements, such as Mo. In order to maintain their ferritic structure, the interstitial elements of C and N are controlled at a very low level (usually <0.015%) by using novel refining process such as argon-oxygen decarburization (AOD) or vacuum melting. These structures with improved properties are called superferritic stainless steels. For instance, the AL 29-4 series, which are characterized by a high content of chromium, addition of molybdenum, and limited concentration of interstitial elements C and N through AOD refining, possess a yield strength almost twice of that of conventional ferritic stainless steels.
Table II. High temperature mechanical properties of superalloy and stainless steels

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Elastic modulus (GPa)</th>
<th>Yield strength $\sigma_{0.2}$ (MPa)</th>
<th>Creep strength $\sigma_{\varepsilon}$ (MPa)</th>
<th>Rupture strength $\sigma_{t}$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Superalloys</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carpenter 19-9DL</td>
<td>138 at 815°C</td>
<td>$\sigma_{732^\circ C} = 36$</td>
<td>$\sigma_{816^\circ C} = 59$</td>
<td></td>
</tr>
<tr>
<td>Incoloy 556™</td>
<td>148 at 800°C</td>
<td>220 at 760°C</td>
<td>$\sigma_{760^\circ C} = 59$</td>
<td></td>
</tr>
<tr>
<td>Aktiebolag 253 MA</td>
<td>115 at 760°C</td>
<td>110 at 750°C</td>
<td>$\sigma_{760^\circ C} = 29$</td>
<td></td>
</tr>
<tr>
<td>Haynes R-41</td>
<td>169 at 800°C</td>
<td>752 at 760°C</td>
<td>$\sigma_{760^\circ C} = 234$</td>
<td>$\sigma_{816^\circ C} = 165$</td>
</tr>
<tr>
<td>Inconel 625</td>
<td>160 at 760°C</td>
<td>421 at 760°C</td>
<td>$\sigma_{760^\circ C} = 234$</td>
<td>$\sigma_{816^\circ C} = 96$</td>
</tr>
<tr>
<td>Pyromet 680</td>
<td>144 at 816°C</td>
<td>241 at 760°C</td>
<td>$\sigma_{760^\circ C} = 55$</td>
<td>$\sigma_{816^\circ C} = 62$</td>
</tr>
<tr>
<td>Stainless steels</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL 446</td>
<td>200 at RT</td>
<td>275* at RT 55* at 760°C</td>
<td>$\sigma_{760^\circ C} = 7.6$</td>
<td>$\sigma_{760^\circ C} = 13.5$</td>
</tr>
<tr>
<td>Carpenter 443</td>
<td>200 at RT</td>
<td>345 at RT 41 at 760°C</td>
<td>$\sigma_{704^\circ C} = 7.0$</td>
<td></td>
</tr>
<tr>
<td>AL 439 HP™</td>
<td>200 at RT</td>
<td>310 at RT 48 at 760°C</td>
<td>$\sigma_{816^\circ C} = 7.0$</td>
<td></td>
</tr>
<tr>
<td>AL 441 HP™</td>
<td>200 at RT</td>
<td>290 at RT 58 at 760°C</td>
<td>$\sigma_{816^\circ C} = 11.0$</td>
<td></td>
</tr>
</tbody>
</table>

* Minimum as required.

6) Elastic modulus

The elastic modulus at RT and high temperature was collected and listed for most of the alloy compositions. Typically the superalloys have an elastic modulus in the vicinity of 200 GPa, although the moduli of specific polycrystalline alloys can vary from 170–240 GPa at room temperature depending on the alloy systems. Ferritic stainless steels also have moduli around 200 GPa. The elastic modulus decreases at high temperatures.

7) Joinability

No standard parameter and data are available to quantitatively measure the joinability of various metals or metals and ceramics of interest. Overall, alloys
with a FCC matrix structure, such as superalloys, have better joinability than those with a BCC matrix, such as Cr-base alloys. Ni- and Fe-Ni-base superalloys are considerably less weldable than the Co-based superalloys. Austenitic stainless steels have better joinability than ferritic stainless steels, which may be exhibit the following difficulties:

(i) Excessive grain growth at high temperature;
(ii) Sensitization when the steel is cooled from temperatures above 925°C;
(iii) Lack of ductility.

8) Formability

Conventionally, the Erichsen or Olsen cupping depth (mm) is used to measure the formability. If the E or O cupping depth at room temperature (RT) was not available, the elongation data from bar tests, which is available from many sources, is collected as an alternative for evaluation. Generally, alloys with higher elongation rate are expected to have better formability. Overall, superalloys and stainless steels are better than Cr-base alloys.

9) Cost

The price of stainless steel 446 (in ¼” mils sheet) is used as the basis. The cost factor is defined as the ratio of the price of a specified alloy to that of 446. Superalloys are more expensive than stainless steels and among various superalloys, Co-base alloys are more expensive than Ni-base; Ni-base alloys are more expensive than Fe-base. Mechanically alloyed compositions are more expensive than their conventional counterparts.

10) Others, including resistance to hydrogen embrittlement, and machinability.

BCC matrix alloys are typically more sensitive to hydrogen-induced embrittlement than FCC matrix alloys.
Machinability of alloys is expressed as a percentage by referring to Seco Tools AB. Decreasing values indicate increasing machining difficulty.
The machining ability of stainless steels can be summarized as the followings:

(i) The martensitic stainless steels are usually machined in the annealed conditions. Their machinability is generally intermediate to the ferritic and austenitic grades;
(ii) The ferritic grades are easiest to machine;
(iii) The austenitic grades are gummy and give the most difficulty;
(iv) Improved machinability (in all cases) can be obtained through addition of lead, sulfur, or phosphorus.
IV. Effects of Alloy Elements

Alloy properties are determined by alloying compositions, phase constitution, and structure. Alloyming elements and their quantity are the most important factors to be considered in the alloy design for the desired structure and thus the required properties. 

Cr, Ni and Fe are three major alloy elements in high temperature alloys. As shown in Figure 1, the quantities of these three elements in an alloy could decide the phase constitution, structure and thus properties.

As mentioned previously, Cr is a primary element for forming oxide scales for providing surface stability of high temperature alloys. To have enough oxidation and corrosion resistance at the SOFC operating temperatures, ideally the amount of Cr in most high temperature alloys should not be less than a number around 18%, as described previously. In addition, Cr is also an important element for improving mechanical properties through solid solution strengthening and carbide hardening by forming Cr₂C₃ and Cr₂₃C₆. In Fe-base high temperature alloys, including superalloys and stainless steels, Cr, by producing the gamma loop in Fe-Cr phase diagram (Figure 2), can be utilized to stabilize ferrites and destabilize austenite. For the pure Fe-Cr system, a minimum of 13 wt% Cr is required to maintain the BCC ferritic structure from RT to the melting point. For martensitic stainless steels, the Cr content cannot be too high, normally less than 18%, in order to generate austenite at high temperatures, which transforms to martensite during subsequent cooling. In Cr-base alloys, a BCC crystal structure is maintained which contributes to thermal expansion matching with other SOFC components.

Though the addition of more Cr increases the oxidation resistance and also helps stabilize the BCC ferritic structure for a TEC match, increased Cr concentration could also lead to some disadvantages for SOFC applications. As shown in the Fe-Cr phase diagram in Figure 2, a second phase, called the sigma phase, can precipitate along grain boundaries in the alloy matrix at a temperature in the range of 550~870°C when the concentration of Cr is higher than 14~15 wt% [11]. The formation of sigma phase along grain boundaries not only causes a lower ductility (sigma phase embrittlement), but also results in deteriorated oxidation resistance as well as thermal expansion mismatch in SOFC, as indicated in our recent studies[25]. It is also reported that increasing Cr contents in ferritic structures decrease the thermal expansion coefficient of alloy compositions, but also creates “knees” in the thermal expansion curves if the Cr concentration becomes too high [26].

As indicated by many studies [14,18~20, 22], the resistance of the chromia scale will reach an unacceptable level after hundreds of hours under current SOFC operating conditions. Accordingly, it appears that the high temperature alloys have to be modified so as to inhibit the growth of the chromia scale and decrease the resistance of the scale. One effective approach is to change the bulk or surface chemistry by adding reactive elements, such as Y, Ce, or La (or their oxide forms). These elements, when added as a trace amount (0~0.1%) to the alloys, significantly modify the growth behavior of the chromia scale, as listed by Kofstad [15] in the following:

(i) The preferential formation of chromia scales is enhanced;
(ii) The growth rate of chromia scales is reduced;
(iii) The adherence of chromia scales to the alloy substrate is improved;
(iv) The scales are denser.
Figure 2. Cr-Fe phase diagram and crystal structure data.
(After J.O. Anderson and B. Sundman\textsuperscript{[27]})

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pearson Symbol</th>
<th>Strukturbericht</th>
<th>Prototype</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc</td>
<td>cF4</td>
<td>A1</td>
<td>Cu</td>
<td>RK</td>
</tr>
<tr>
<td>α</td>
<td>tP30</td>
<td>D8\textsubscript{b}</td>
<td>α-CrFe</td>
<td>CE</td>
</tr>
<tr>
<td>fcc</td>
<td>cF4</td>
<td>A1</td>
<td>Cu</td>
<td>RK</td>
</tr>
</tbody>
</table>
As a result, these reactive trace elements significantly increase the oxidation resistance of alloys, decrease electrical resistance of the scale, and improve the scaling resistance under thermal cycling.

Another approach to inhibit the growth of the chromia scale is to modify the surface of currently available compositions by applying a dense coating, whose composition is usually a conductive oxide, acting as a diffusion barrier to decrease the growth of chromia layer. The coatings are also expected to decrease or prevent the evaporation of chromia scale [32,33]. Vaporized chromium species can deposit at the interface of the cathode and electrolyte, resulting in higher polarization by decreasing the active sites at the interface [34]. Ideally, the conductive oxide used for the coating should be an electronic conductor with very low ionic conductivity ion order to decrease cationic and anionic transport through the coating layer. Coatings with perovskite oxides traditionally used in SOFC have demonstrated promising results in improving the surface stability of chromia forming alloys [22, 28-31].

Besides Cr, Al and Si are the other two elements that can be used to provide oxidation resistance. It has been demonstrated that Al is much more effective than Cr in improving oxidation, corrosion and scaling resistance by forming an Al₂O₃ layer on the high temperature alloys. The alumina formed on the alloy surface is also thermodynamically stable and thus does not exhibit the poisoning effects associated with the evaporation of species from the chromia scale. The insulating nature of the alumina scale, however, may prevent any application of alumina formers in the active electrochemical area of the cell. Due to the lack of adherence and susceptibility to internal oxidation, Si is not commonly used in alloying to provide oxidation resistance. It is also postulated that the silica based or silica containing scale could become very insulating in the active cell region resulting in performance loss.

Ni acts to stabilize the austenite structure and form ordered γ’ precipitation for strengthening of Ni- and Fe-base superalloys. Thus in the ferritic structures, the Ni amount must be controlled at a lower level (typically less than about 2~3.0% for ferritic stainless steels, but dependent on content of Cr, C, N, etc.) in order to maintain their BCC crystal structure even at high temperatures. With increases in the amount of Ni, the alloy matrix will transform from BCC to FCC. The thermal expansion coefficients of FCC alloys might be too high for consideration for SOFC applications (at least for stacks utilizing rigid, bonded seals (e.g., glass, glass-ceramic seals)).

Fe is the base element for the stainless steels and Fe-base superalloys. Below 912°C, pure Fe has a BCC ferritic structure and transforms to FCC austenitic structure after this point. As discussed earlier, Cr helps to stabilize the BCC ferritic structure. By the contrast, Ni, Mn, Mo, Co and many other substitutional elements help stabilize the FCC austenitic structure by pushing the gamma loop in the Cr-rich direction. Another important function of Fe is to form Fe₃C in steels and also act as a solid solution strengthener.

Mo, W, Ti, Nb and Ta are carbide formers and usually used to improve mechanical strength.

Interstitial elements of C and N can also play important role in alloy design. Both elements can be used to strengthening alloy matrix through interstitial solution hardening mechanism and also helps formation of austenites by moving the gamma loop to the Cr
rich direction. So, in the ferritic structure, the content of these interstitial elements should be controlled at a limited level.

Some trace elements, such as phosphorus and sulfur, typically have detrimental effects on alloy properties, but could modify manufacturability. Their quantity is usually closely controlled in most compositions.

The effects of alloy elements are summarized in Table III.
### Table III. Effects of alloying elements on properties relevant to SOFC applications

<table>
<thead>
<tr>
<th>Alloying Elements</th>
<th>Composition range</th>
<th>Effects on properties relevant to SOFC applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Fe-BSA</td>
<td>Ni/Fe-BSA</td>
<td>These elements are the base elements for high temperature alloys. Besides they are used for strengthening and/or improving mechanical strength.</td>
</tr>
<tr>
<td>Base-elements</td>
<td>Base for NiBSA</td>
<td>Base element for NiBSA; Stabilizes FCC austenite and increase TEC; Be less that 2.0 for BCC ferritic structures with lower TEC; Form hardening precipitates to increase mechanical strength for Ni-/Fe-BSA.</td>
</tr>
<tr>
<td>Ni</td>
<td>0-22</td>
<td>Base element for NiBSA; Stabilizes FCC austenite and increase TEC; Be less that 2.0 for BCC ferritic structures with lower TEC; Form hardening precipitates to increase mechanical strength for Ni-/Fe-BSA.</td>
</tr>
<tr>
<td>Ni</td>
<td>0-20</td>
<td>Base element for FeBSA and SS, usually cheaper than Ni, Co- and Cr-bases; Improve mechanical strength through solid solution strengthening and carbide (Fe,C) formation.</td>
</tr>
<tr>
<td>Fe</td>
<td>Base for FeBSA</td>
<td>Base element for Co-base alloys, expensive; Raises solvus temperature to affect amount of precipitates; Improve mechanical strength w/ solid solution strengthening.</td>
</tr>
<tr>
<td>Fe</td>
<td>0-20</td>
<td>Base element for BCC Cr-base alloys, expensive and difficult in manufacturing; Improve oxidation/corrosion resistance, and mechanical strength through M7C3,M23C6 formation and solid solution strengthening.</td>
</tr>
<tr>
<td>Co</td>
<td>0-20</td>
<td>Base element for Co-base alloys, expensive and difficult in manufacturing; Improve oxidation/corrosion resistance, and mechanical strength through M7C3,M23C6 formation and solid solution strengthening.</td>
</tr>
<tr>
<td>Cr</td>
<td>5-25</td>
<td>Base element for BCC Cr-base alloys, expensive and difficult in manufacturing; Improve oxidation/corrosion resistance, and mechanical strength through M7C3,M23C6 formation and solid solution strengthening.</td>
</tr>
<tr>
<td>Carbide formers or strengthening elements</td>
<td>Mo</td>
<td>Increase mechanical strength through carbides (MC, M23C6, M6C) formation and solid solution strengthening; Improve pitting corrosion resistance.</td>
</tr>
<tr>
<td>Carbide formers or strengthening elements</td>
<td>W</td>
<td>Increase mechanical strength through carbides (MC, M23C6, M6C) formation and solid solution strengthening.</td>
</tr>
<tr>
<td>Carbide formers or strengthening elements</td>
<td>Ti</td>
<td>Improve mechanical strength through formation of carbide (MC) and precipitates γ’Ni3(Al,Ti).</td>
</tr>
<tr>
<td>Carbide formers or strengthening elements</td>
<td>Nb</td>
<td>Improve mechanical strength through carbide (MC) formation; precipitation strengthening and solution hardening.</td>
</tr>
<tr>
<td>Carbide formers or strengthening elements</td>
<td>Nb,Ta</td>
<td>Improve mechanical strength through carbides (MC) formation and solution hardening; Modify oxidation resistance.</td>
</tr>
<tr>
<td>Interstitial elements</td>
<td>C</td>
<td>Improve mechanical strength through carbide (Fe2C, M2C), M(CN) formation and solution strengthening; Causes grain boundary segregation by forming carbides. Austenite former and closely controlled in ferritic structures.</td>
</tr>
<tr>
<td>Interstitial elements</td>
<td>N</td>
<td>Improve mechanical strength through formation of M(C,N) carbonitrides and solution strengthening; Austenite stabilizer and closely controlled in ferritic structures for lower TEC.</td>
</tr>
</tbody>
</table>

- **Base-elements**
  - **Ni**: Base for NiBSA, used for strengthening and improving mechanical strength.
  - **Fe**: Base for FeBSA, used for Ni-Fe BSAs, and SS. Cost-effective compared to Ni, Co- and Cr-bases.
  - **Co**: Base for Co-base alloys, used for Ni- and Fe-BSAs.
  - **Cr**: Base for Cr-base alloys, used for Ni-, Ni-Fe-BSA.

- **Carbide formers or strengthening elements**
  - **Mo**: Improves mechanical strength through carbides (MC, M23C6, M6C) formation and solid solution strengthening.
  - **W**: Improves mechanical strength through carbides (MC, M23C6, M6C) formation and solid solution strengthening.
  - **Ti**: Improves mechanical strength through formation of carbide (MC) and γ’Ni3(Al,Ti).
  - **Nb, Ta**: Improve mechanical strength through carbides (MC) formation and solution hardening.

- **Interstitial elements**
  - **C**: Improves mechanical strength through carbides (Fe2C, M2C), M(CN) formation and solution strengthening.
  - **N**: Improves mechanical strength through formation of M(C,N) carbonitrides and solution strengthening.
Continue Table III.

<table>
<thead>
<tr>
<th>Alloying Elements</th>
<th>Composition range</th>
<th>Effects on properties relevant to SOFC applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Fe-BSA</td>
<td>CoBSA</td>
<td>SS</td>
</tr>
<tr>
<td><strong>Scale formers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>5-25</td>
<td>19-30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>0-6.0</td>
<td>0-4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0-5.0</td>
<td>0-6.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reactive elements</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re</td>
<td>0-0.200</td>
<td>0-0.200</td>
</tr>
<tr>
<td>Re$_2$O$_3$</td>
<td>0-2.0</td>
<td>0-2.0</td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;1.0 for NiBSA 0~5.0 for FeBSA</td>
<td>0-2.0</td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Re: rare earth elements, such as Y, La, Ce.
NiBSA: nickel based superalloy; FeBSA: iron based superalloy; CoBSA: co-base superalloys.
CrBA: Cr-base alloys.
SS: stainless steels; FSS: ferritic stainless steels; ASS: austenitic stainless steels.
V. Conclusions

Alloys showing high temperature oxidation resistance can be considered as potential interconnection / bipolar separator materials for SOFC application. The high temperature alloys of interest include Ni-, Fe-, Co-base superalloys, Cr-base alloys and stainless steels. The oxidation and corrosion resistance of selected alloy systems can be improved through the addition of alloying elements, such as Cr and Al, which can form an adherent scale on the alloy surface to provide the necessary protection of the metallic substrate and long term structural stability of the component. To form a continuous and adherent scale for long term oxidation and corrosion resistance, the Cr concentration in a high temperature alloy should not be less than about 18% in Ni- and Fe-base alloys (including stainless steels), and 22% for Co-base alloys. If an appropriate amount of Al (1~3.0 wt%) is added, the recommended minimum Cr content could be lower, but still must exceed about 15% in order to have enough internal oxidation resistance. As the Al concentration increases over 3% (but usually less than 5%), a continuous and adherent alumina layer will become the dominant component in the scale on the alloy surface. These alloys are classified as alumina formers, which demonstrate much more improved oxidation and scaling resistance than chromium formers. The insulating nature of the alumina scale may however prevent any application in SOFC, unless the stack is designed in such a way that the insulating alumina scale can be excluded from the electrical path.

In terms of TEC, ferritic stainless and Cr-base alloys offer better TEC match with other SOFC components than Ni-, Fe-, and Co-base superalloys and austenitic stainless steels. The high price and difficulty in fabrication of Cr- and Co-base alloys make them less favorable for intricate shape formation and large volume commercial application in SOFC power generation systems. Among the high temperature alloys, the stainless steels offer the lowest cost and reasonable manufacturability. A disadvantage of the ferritic stainless steels however is their lower mechanical strength, especially at the high temperatures required for operation of SOFC. Addition of more Cr and other alloying elements could lead to improved strength and corrosion resistance, but could also cause the sigma phase formation at the SOFC operating temperature around 800°C, resulting in embrittlement and possible TEC mismatch.

Though numerous alloy compositions are available for consideration, there are few if any compositions which will satisfy the functional requirements of the interconnect in SOFC. One of the biggest concern remains that the currently available alloys may not offer high enough oxidation resistance and electronic conductivity of the oxide scale.

As a result, it is likely that new alloy compositions and/or protective surface modifications or coatings will be required. To improve the oxidation resistance and control the electrical resistance of the oxide scale at an acceptable level in the long run, one effective approach may be to add reactive elements, such as Y, Ce, La or their oxide forms into the high temperature alloys. These elements can be added as a trace amount (0~0.1%) to the alloys, but significantly modify the growth behavior and consequently improve oxidation and scaling resistance, as well as the scale resistance. Another possible solution is to apply a dense, electrically conductive coating to inhibit the growth of chromia scale and decrease the resistance of the scale. Considerable development work
will be required in order to produce a completely satisfactory interconnect material for SOFCs operating at intermediate temperatures.

VI. Acknowledgement

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References

25. Z.G. Yang, K.S. Weil, and D.M. Paxton, private communication.
# Appendix A

## Compositions of High Temperature Alloys

### Ni-Cr or Ni-Cr-Fe Base Alloys

<table>
<thead>
<tr>
<th>Alloysa</th>
<th>Nominal composition, wt%</th>
<th>UNS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
</tr>
<tr>
<td>AF2-IDA</td>
<td>Bal</td>
<td>12.0</td>
</tr>
<tr>
<td>Alloy 713Cc</td>
<td>Bal</td>
<td>12.5</td>
</tr>
<tr>
<td>Alloy 713LCc</td>
<td>Bal</td>
<td>12.0</td>
</tr>
<tr>
<td>Astroloyd</td>
<td>Bal</td>
<td>15.0</td>
</tr>
<tr>
<td>B-1910</td>
<td>Bal</td>
<td>10.0</td>
</tr>
<tr>
<td>GMR-235f</td>
<td>Bal</td>
<td>15.5</td>
</tr>
<tr>
<td>GMR-235Df</td>
<td>Bal</td>
<td>15.5</td>
</tr>
<tr>
<td>Hastelloy C</td>
<td>56.0</td>
<td>16.5</td>
</tr>
<tr>
<td>Hastelloy C-4</td>
<td>Bal</td>
<td>16.0</td>
</tr>
<tr>
<td>Hastelloy C-22</td>
<td>51.6</td>
<td>21.5</td>
</tr>
<tr>
<td>Hastelloy C-276</td>
<td>Bal</td>
<td>15.5</td>
</tr>
<tr>
<td>Hastelloy C-2000</td>
<td>Bal</td>
<td>23</td>
</tr>
<tr>
<td>Hastelloy D-205™</td>
<td>Bal</td>
<td>20</td>
</tr>
<tr>
<td>Alloys²</td>
<td>Nominal composition, wt%</td>
<td>UNS</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------</td>
<td>----------</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
</tr>
<tr>
<td>Hastelloy G</td>
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</tr>
<tr>
<td>Hastelloy G-3</td>
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<td>22.0</td>
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<tr>
<td>Hastelloy G-30</td>
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<tr>
<td>Hastelloy G 50</td>
<td>Bal</td>
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</tr>
<tr>
<td>Hastelloy N</td>
<td>72.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Hastelloy S</td>
<td>Bal</td>
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</tr>
<tr>
<td>Hastelloy W</td>
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<td>5.0</td>
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<td>Haynes 75</td>
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<tr>
<td>Haynes 230</td>
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<tr>
<td>Haynes 214⁴</td>
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<tr>
<td>Haynes 242</td>
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<tr>
<td>Haynes R-41</td>
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<td>Haynes HR-160</td>
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<td>28</td>
</tr>
<tr>
<td>HAD 8077</td>
<td>Bal</td>
<td>16</td>
</tr>
<tr>
<td>Illium Ge</td>
<td>Bal</td>
<td>22.0</td>
</tr>
</tbody>
</table>

² Notes: a = alloy number, b = balance, -- = none
<table>
<thead>
<tr>
<th>Alloys&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>W</th>
<th>Cb</th>
<th>Ti</th>
<th>Al</th>
<th>B</th>
<th>Zr</th>
<th>Others</th>
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<tbody>
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<td>Illium 98c</td>
<td>Bal</td>
<td>28.0</td>
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<td>--</td>
<td>0.05</td>
<td>--</td>
<td>--</td>
<td>8</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>5Cu</td>
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<td>Illium B'</td>
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<td>--</td>
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<td>--</td>
<td>--</td>
<td>3.5</td>
<td>8</td>
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<td>--</td>
<td>--</td>
<td>5Cu</td>
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<td>0.08</td>
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<td>4</td>
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<td>3.0</td>
<td>--</td>
<td>--</td>
<td>4.7</td>
<td>5.5</td>
<td>0.014</td>
<td>0.06</td>
<td>1.0V</td>
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<td>--</td>
<td>0.06</td>
<td>0.75</td>
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<td>2.9</td>
<td>3.0</td>
<td>2.9</td>
<td>0.5</td>
<td>0.5</td>
<td>0.005</td>
<td>0.03</td>
<td>0.02Mg</td>
</tr>
<tr>
<td>IN-162'</td>
<td>Bal</td>
<td>10.0</td>
<td>0.5b</td>
<td>--</td>
<td>0.12</td>
<td>0.10</td>
<td>0.20</td>
<td>4.0</td>
<td>2.0</td>
<td>1.0</td>
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<td>6.5</td>
<td>0.020</td>
<td>0.10</td>
<td>2.0Ta</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>2.3</td>
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<td>0.003</td>
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<td>--</td>
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<tr>
<td>IN-597</td>
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<td>--</td>
<td>1.5</td>
<td>--</td>
<td>--</td>
<td>3.0</td>
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<td>0.012</td>
<td>0.05</td>
<td>0.02Mg</td>
</tr>
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<td>--</td>
<td>0.25</td>
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</tr>
<tr>
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<td>50</td>
<td>1.0</td>
<td></td>
<td></td>
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<tr>
<td>IN-731'</td>
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<td>9.5</td>
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<td>10</td>
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<td>0.2b</td>
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<td>--</td>
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<td>0.06</td>
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<td>0.3b</td>
<td>1.75</td>
<td>2.6</td>
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<td>3.4</td>
<td>0.01</td>
<td>0.10</td>
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<td>--</td>
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<td>2.0</td>
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<sup>a</sup> Alloys: BAL = balance

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## Nominal composition, wt%

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a : alloy number

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<sup>b</sup> N07001
Notes:
a. Some superalloys such as Inconel 718, Rene 41, Udimet 500, and others are made by more than one manufacturer;
b. Maximum composition;
c. Cast alloy.
d. Compositions of Astroloy, Rene 77, and Udimet 700 are very similar. Certain elements are controlled to prevent sigma phase formation.
e. Waspaloy A has a higher solution temperature and longer time at stabilization than Waspaloy B.

Note:
1) Many of the alloy designations are registered trademarks of producer companies. For example, Hastelloy, Haynes, and Multimet are registered trademarks of Cabot Co., and Incoloy and Inconel are trade marks of Huntington Alloys Co.
2) The Unified Numbering System (UNS) is being developed jointly by the U.S. Society of Automotive Engineers (SAE) and the American Society of Testing and Materials (ASTM). Each UNS number consists of a single letter prefix followed by five digits. The interested high-temperature alloys appearing here fall into four different UNS material groups and may have prefixes of K, N, R, and S. The prefixes K, N, R and S represent the following UNS number series:
   Kxxxxx: miscellaneous steels and ferrous metals;
   Nxxxxx: nickel and nickel alloy;
   Rxxxxx: reactive and refractory metals and alloys;
   Sxxxxx: heat and corrosion resistant (stainless) steels.
# Fe-Ni-Cr Base Alloys

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³Others = --

⁴UNS = S66286
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<sup>a</sup> Includes Al, B, Zr, Ti, and Cu. For Incoloy 800 and 802, 803, 825, and 840, Ti and Zr are not listed. For Incoloy 925, 802, and 803, Cu is not listed. For N-155, Multimet alloy, Pyromet 860 (carpenter), Pyromet 31 (carpenter), S-590, and Unitemp 212, Pb is not listed.
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\(^a\) Some alloys are made by more than one manufacturer
\(^b\) Maximum composition
\(^c\) Cast alloy.
## Standard Stainless Steels

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I. **Martensitic types** (hardenable)

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<th>Co</th>
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II. **Precipitation hardening** (Typically Cr% <18.0)

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<th>Si</th>
<th>Mo</th>
<th>W</th>
<th>V</th>
<th>Cu</th>
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<th>Al</th>
<th>Co</th>
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<td>4.0</td>
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Note: Some austenitic stainless steels are already listed in previous Fe-Ni-Cr Tables. Included here are ferritic stainless steels and some austenitic compositions.
### Nonstandard Stainless Steels

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<tr>
<th>Alloys&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Nominal composition, wt%</th>
<th>UNS</th>
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<tr>
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<td>Ni</td>
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<td>Austenitic types (Cr-Mn-Ni types-200 Series, and Cr-Ni-300 Series)</td>
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<td>AL 33</td>
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<td>AL 50 (XM-19) (22-13-5) Carpenter 21Cr-6Ni-9Mn Carpenter 22Cr-13Ni-5Mn</td>
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<td>6.50</td>
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<td>Bal</td>
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<td>Alloy 255 (AL)</td>
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<td>Armeo 18 SR</td>
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<td>AL 468&lt;sup&gt;TM&lt;/sup&gt;</td>
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<td>AL 441 HP&lt;sup&gt;TM&lt;/sup&gt;</td>
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<td>Fecralloy&lt;sup&gt;d&lt;/sup&gt;</td>
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<sup>a</sup>Alloys: Carpenter 443, AL 453<sup>TM</sup>, Carpenter 443, AL 433<sup>TM</sup>, Carpenter 444, AL 444<sup>TM</sup> (Alloy 18-2), Armeo 18 SR, AL 468<sup>TM</sup>, AL 441 HP<sup>TM</sup>, AL 439 HP<sup>TM</sup>, ODM 751, Fecralloy<sup>d</sup>

<sup>b</sup>Y<sub>2</sub>O<sub>3</sub>

<sup>c</sup>Ce+La

<sup>d</sup>Y<sub>2</sub>O<sub>3</sub>
### Nominal composition, wt%

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<th>Fe</th>
<th>Mo</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Cu</th>
<th>N</th>
<th>Others</th>
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</table>

- a. Some alloys are made by more than one manufacturer;
- b. Maximum composition;
- c. Cast alloy;
- d. Fecralloy is a group of alloy, in which Fe, Cr, Al and rare earth elements are major alloying elements.

* For glass-to-metal sealing applications, the thermal expansion characteristics of glass and metal are closely matched and the metal must also have an oxide which fluxes at high temperature with the glass to provide a hermetic and mechanically sound joint.
### Co Base Alloys

<table>
<thead>
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<th>Alloys&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Nominal composition, wt%</th>
<th>UNS</th>
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<td>AiResist 13&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;b&lt;/sup&gt; 21 2.5&lt;sup&gt;b&lt;/sup&gt; Bal 0.45 0.5&lt;sup&gt;b&lt;/sup&gt; -- -- 11 2.0 -- 3.5 -- -- 0.1&lt;sup&gt;Y&lt;/sup&gt;</td>
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<td>AiResist 213</td>
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<td>6.5Ta, 0.1Y</td>
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<td>7.5Ta, 0.17Y</td>
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<td>Haynes 21&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3 27 1 64 0.25 -- -- 5 -- -- -- -- -- --</td>
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<tr>
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<td>10 20 3.0&lt;sup&gt;b&lt;/sup&gt; Bal 0.10 1.50 0.50 -- 15 -- -- -- -- -- --</td>
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<td>Haynes 25 (WF-11, L 605)</td>
<td>3.0&lt;sup&gt;b&lt;/sup&gt; 28 20.0 Bal 0.08 0.65 0.35 1.5&lt;sup&gt;b&lt;/sup&gt; -- -- -- -- -- -- -- --</td>
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<td>3.0&lt;sup&gt;b&lt;/sup&gt; 28 20.0 Bal 0.10 1.25&lt;sup&gt;b&lt;/sup&gt; 0.3 -- 14 -- -- -- -- -- --</td>
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<tr>
<td>Haynes 188</td>
<td>22 22 3.0&lt;sup&gt;b&lt;/sup&gt; Bal 0.10 1.25&lt;sup&gt;b&lt;/sup&gt; 0.3 -- 14 -- -- -- -- --</td>
<td>0.04La</td>
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<td>Alloys(^a)</td>
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<td>----------------</td>
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<td>-----</td>
</tr>
<tr>
<td></td>
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<td>(Stellite)</td>
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<td>MAR-M322(^c)</td>
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<td>Alloys²</td>
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<td>X-40c</td>
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<tr>
<td>X-45c</td>
<td>10.5</td>
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a. Some alloys are made by more than one manufacturer
b. Maximum composition
c. Cast alloy.
## Cr Base Alloys

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<th>Ni</th>
<th>Cr</th>
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<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>W</th>
<th>Cb</th>
<th>Ti</th>
<th>Al</th>
<th>B</th>
<th>Zr</th>
<th>Others</th>
<th>UNS</th>
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<td>--</td>
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<td>--</td>
<td>0.1  (Y+La)</td>
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<tr>
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<td>--</td>
<td>--</td>
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<td>--</td>
<td>--</td>
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<td>--</td>
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<td>1.7 Ta</td>
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<tr>
<td>Chrome 30</td>
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<td>--</td>
<td>--</td>
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<td>0.1 Y</td>
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<td>3MgO, 2.5V</td>
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<tr>
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<td>--</td>
<td>1.0 Y,0.006La, 0.001S, 0.0066N</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

\(a\) Some alloys are made by more than one manufacturer  
\(b\) Maximum composition  
\(c\) Cast alloy.
## Appendix B
### Selected Compositions
### Ni-Cr or Ni-Cr-Fe Base Alloys

<table>
<thead>
<tr>
<th>Alloysa</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>W</th>
<th>Cb</th>
<th>Ti</th>
<th>Al</th>
<th>B</th>
<th>Zr</th>
<th>Other s</th>
<th>Characteristics, Typical applications</th>
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<tbody>
<tr>
<td>Inconel 671</td>
<td>53.5</td>
<td>46.0</td>
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<td>--</td>
<td>--</td>
<td>--</td>
<td>0.4</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>For extremely corrosive environments</td>
</tr>
<tr>
<td>IN-657c</td>
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<td>50</td>
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<td>0.6 Y2O3</td>
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<tr>
<td>Inconel MA 758</td>
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<td>--</td>
<td>0.05</td>
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<td>0.5</td>
<td>0.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>MAed, furnace skid rails at 1260°C, fuel atomizer in diesel engine</td>
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<tr>
<td>Nimonic 81</td>
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<td>30.0</td>
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<td>0.2</td>
<td>0.2</td>
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<td>2.0Cu</td>
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<td>Resist nitric/hydrofluoric acid</td>
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<td>Haynes HR-160</td>
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<td>2.0</td>
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<td>Developed for high temp. hot corrosion resistance</td>
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<tr>
<td>NA-224</td>
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<td>Nicrofer 6025HT-602CA</td>
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<td>Excl. resist. To oxidation &amp; carburising at high °C</td>
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<td>65.0</td>
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<td>1.25</td>
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<td>Combustion chamber, excep. Oxidation &amp; scaling resistance</td>
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<td>--</td>
<td>3.0</td>
<td>1.5</td>
<td>0.012</td>
<td>0.05</td>
<td>Stressed parts in turbines, Excl. oxidation &amp; corrosion resistance (&gt;900°C)</td>
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a: Alloys as per alloy designations.
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<th>Characteristics, Typical applications</th>
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<td>Alloys</td>
<td>Nominal composition, wt%</td>
<td>Characteristics, Typical applications</td>
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<td>--------------------------</td>
<td>--------------------------------------</td>
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<tr>
<td>Hastelloy G 50</td>
<td>Bal. 20.0 Ni 17.5 Cr 2.5 Co 1.0 Mn 0.02 Si 1.0 Mo 1.0 W 9.0 Cb 0.5 Ti 0.4 Al - B - Zr -</td>
<td>For appli. In severe sour gas env.</td>
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<tr>
<td>Hastelloy D-205 TM</td>
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<td>Outstanding corrosion resistance to concentrated acidic media, silica forming alloy</td>
</tr>
<tr>
<td>Nimonic 263 RollsRoyce263</td>
<td>Bal. 20 Ni 0.06 Cr 0.4 Mo 5.9 Cb 2.2 Ti 1.5 Al 0.007 B 2.0</td>
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<tr>
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<td>74.6 Ni 20.0 Cr 2.5 Co 0.05 Mo 0.5 Ti 0.3 Al 0.6</td>
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<tr>
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<td>Turbine rings, casings</td>
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<td>TDNiC</td>
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<td>Turbine rings, casings</td>
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<td>Turbine rings, casings</td>
</tr>
<tr>
<td>Haynes 75</td>
<td>Bal. 20 Ni 5.0 Cr 1.0 Mo 1.0 W 9.0 Cb 0.5 Ti 1.5 Al 0.007 B 2.0</td>
<td>Turbine rings, casings</td>
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<td>Nimonic 95</td>
<td>53.5 Ni 19.5 Cr 5.0 Mo 18.0 W 1.5 Ti 2.9 Al 2.0</td>
<td>Turbine blades &amp; discs, hot working tools</td>
</tr>
<tr>
<td>Nimonic 90</td>
<td>57.4 Ni 19.5 Cr 18.0 Mo 0.7 Ti 2.4 Al 2.0</td>
<td>Turbine blades &amp; discs, hot working tools</td>
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<tr>
<td>Waspaloy A4</td>
<td>Bal. 19.5 Ni 1.5 Cr 13.5 Mo 0.5 Ti 2.5 Al 2.0</td>
<td>Turbine blades &amp; discs, hot working tools</td>
</tr>
<tr>
<td>Waspaloy B4</td>
<td>Bal. 19.5 Ni 1.5 Cr 13.5 Mo 0.5 Ti 2.5 Al 2.0</td>
<td>Turbine blades &amp; discs, hot working tools</td>
</tr>
<tr>
<td>Nimonic 80</td>
<td>Bal. 19.5 Ni 3.0b Cr 2.0b Mo 0.1b Ti 2.25 Al 2.0</td>
<td>Turbine blades, rings and discs.</td>
</tr>
<tr>
<td>Nimonic 80A</td>
<td>74.7 Ni 19.5 Cr 1.0 Mo 0.7 Ti 2.5 Al 2.0</td>
<td>Turbine blades, rings and discs.</td>
</tr>
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<td>Udimet 500</td>
<td>Bal. 19.0 Ni 0.5b Cr 18.0 Mo 0.08 Ti 3.0 Al 3.0</td>
<td>Turbine blades, rings and discs.</td>
</tr>
<tr>
<td>Udimet 520</td>
<td>Bal. 19.0 Ni 12.0 Cr 1.0 Mo 6.0 Ti 3.0 Al 3.0</td>
<td>Turbine blades, rings and discs.</td>
</tr>
</tbody>
</table>

For appli. In severe sour gas env. | Outstanding corrosion resistance to concentrated acidic media, silica forming alloy | Turbine rings, casings |

Excl. corrosion resistance in a variety of enviro. | Oil tubular goods, | Turbine rings, casings |

Equivalent to alloy 600, low stress elevated temperature with reasonable oxidation resistance requirement. | Equivalent to alloy 600, low stress elevated temperature with reasonable oxidation resistance requirement. | Turbine rings, casings |

Jet engine blades | Jet engine discs | Turbine blades & discs, hot working tools |

Similar to Udimet 500, improved workability | Similar to Udimet 500, improved workability | Turbine blades & discs, hot working tools |
<table>
<thead>
<tr>
<th>Alloys&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Nominal composition, wt%</th>
<th>Characteristics, Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
</tr>
<tr>
<td>Rene 41</td>
<td>Bal</td>
<td>19.0</td>
</tr>
<tr>
<td>M-252, J1500</td>
<td>Bal</td>
<td>19.0</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>73.0</td>
<td>18.5</td>
</tr>
<tr>
<td>Udimet 710</td>
<td>Bal</td>
<td>18.0</td>
</tr>
<tr>
<td>Udimet 720</td>
<td>Bal</td>
<td>18.0</td>
</tr>
<tr>
<td>Nimonic PK 33</td>
<td>Bal</td>
<td>18.0</td>
</tr>
<tr>
<td>Nimonic PE.11</td>
<td>39.0</td>
<td>18.0</td>
</tr>
</tbody>
</table>

f. Some superalloys such as Inconel 718, Rene 41, Udimet 500, and others are made by more than one manufacturer.
g. Maximum composition
h. Compositions of Astroloy, Rene 77, and Udimet 700 are very similar. Certain elements are controlled to prevent sigma phase formation.
i. Waspaloy A has a higher solution temperature and longer time at stabilization than Waspaloy B.

Note: Many of the alloy designations are registered trademarks of producer companies. For example, Hastelloy, Haynes, and Multimet are registered trademarks of Cabot Co., and Incoloy and Inconel are trademarks of Huntington Alloys Co.
# Fe-Ni-Cr Base Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Nominal composition, wt%</th>
<th>Characteristics, Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
</tr>
<tr>
<td>Incoloy 028</td>
<td>31.5</td>
<td>27</td>
</tr>
<tr>
<td>Incoloy 803</td>
<td>34.5</td>
<td>27.0</td>
</tr>
<tr>
<td>Haynes HR-120</td>
<td>37</td>
<td>25</td>
</tr>
<tr>
<td>20Mo-4</td>
<td>37.5</td>
<td>23.75</td>
</tr>
<tr>
<td>20Mo-6</td>
<td>35.1</td>
<td>24.0</td>
</tr>
<tr>
<td>Pyromet 31 (carpenter)</td>
<td>55.5</td>
<td>22.7</td>
</tr>
<tr>
<td>Incoloy 864</td>
<td>34.0</td>
<td>22.5</td>
</tr>
<tr>
<td>Incoloy 556</td>
<td>20.0</td>
<td>22.0</td>
</tr>
<tr>
<td>Incoloy 825</td>
<td>42</td>
<td>21.5</td>
</tr>
<tr>
<td>Aktiebolag 253 MA</td>
<td>11</td>
<td>21</td>
</tr>
<tr>
<td>Incoloy 800</td>
<td>32.5</td>
<td>21</td>
</tr>
<tr>
<td>Incoloy 925</td>
<td>44.0</td>
<td>21.0</td>
</tr>
<tr>
<td>N-155, Multimet alloy</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>Incoloy 802</td>
<td>32.5</td>
<td>21</td>
</tr>
<tr>
<td>S-590</td>
<td>20</td>
<td>20.5</td>
</tr>
<tr>
<td>Incoloy 801</td>
<td>32</td>
<td>20.5</td>
</tr>
</tbody>
</table>

- Highloyed aus. SSS
- Excl. resistance to oxidizing & reducing environ.
- Excl. high temperature corrosion resist.
- Developed recently for more improved creep rupture strength.
- A sulfidation and corrosion resistant precipitation hardenable alloy
- Specially developed for auto-exhaust system.
- Heat exchanger, condenser tubing, stress-corrosion resistance
- Developed lately for oxidation resistance
- Furnace. Heat exchanger parts
- Surface & down-hole hardware in sour gas wells
- Gas turbine sheet parts
- Titanium creep-forming dies, ethylene furnace tubes
- Gas turbine parts, blades
- Petroleum hydrotreaters, heat exchangers
<table>
<thead>
<tr>
<th>Alloys</th>
<th>Nominal composition, wt%</th>
<th>Characteristics, Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
</tr>
<tr>
<td>Incoloy 840</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Armco 20-45-5</td>
<td>45.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Incoloy 25-6Mo</td>
<td>25.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Incoloy 020</td>
<td>35.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Incoloy 330</td>
<td>35.5</td>
<td>19.5</td>
</tr>
<tr>
<td>19-9DL</td>
<td>9.0</td>
<td>19</td>
</tr>
<tr>
<td>19-9DX</td>
<td>9.0</td>
<td>19</td>
</tr>
<tr>
<td>RA-330</td>
<td>35</td>
<td>19</td>
</tr>
<tr>
<td>RA-330 HC</td>
<td>35</td>
<td>19</td>
</tr>
<tr>
<td>Rolled Alloys</td>
<td>14.5</td>
<td>18.5</td>
</tr>
<tr>
<td>RA85H</td>
<td>14.5</td>
<td>18.5</td>
</tr>
<tr>
<td>Incoloy DS</td>
<td>38.0</td>
<td>18.0</td>
</tr>
</tbody>
</table>

- Some alloys are made by more than one manufacturer;
- Maximum composition;
- Cast alloy.
## Ferritic Stainless Steels

<table>
<thead>
<tr>
<th>Alloys&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Cu</th>
<th>N</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>29-4-2 (AL)</td>
<td>2.1</td>
<td>29.0</td>
<td>Bal.</td>
<td>4.0</td>
<td>0.003</td>
<td>0.05</td>
<td>0.1</td>
<td>--</td>
<td>0.025</td>
<td>0.02</td>
<td>--</td>
<td>--</td>
<td>0.015</td>
<td>Superferritic, and high strength and corrosion resistance</td>
</tr>
<tr>
<td>29-4C (AL)</td>
<td>0.15</td>
<td>29.0</td>
<td>Bal.</td>
<td>4.0</td>
<td>0.01</td>
<td>0.3</td>
<td>0.2</td>
<td>--</td>
<td>0.025</td>
<td>0.02</td>
<td>--</td>
<td>--</td>
<td></td>
<td>Superferritic, high strength and corrosion resistance</td>
</tr>
<tr>
<td>7-Mo Stainless Steel (Car)</td>
<td>5.2</td>
<td>29.0</td>
<td>Bal.</td>
<td>2.5</td>
<td>0.03</td>
<td>2.0</td>
<td>0.6</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.35</td>
<td>A duplex structure with 85% ferrite and 15% austenite.</td>
</tr>
<tr>
<td>Alloy 255 (AL)</td>
<td>6.5</td>
<td>27.0</td>
<td>Bal.</td>
<td>3.9</td>
<td>0.04</td>
<td>1.5</td>
<td>1.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>2.5</td>
<td>0.25</td>
<td></td>
<td>A duplex structure with 50% ferrite and 50% austenite. Designed for comb. of high strength and exc. coro. res.</td>
</tr>
<tr>
<td>E-Brite 26-1 Sea-cure/Sc-1</td>
<td>0.09</td>
<td>26.0</td>
<td>Bal.</td>
<td>1.0</td>
<td>0.001</td>
<td>0.01</td>
<td>.25</td>
<td>--</td>
<td>0.02</td>
<td>0.02</td>
<td>--</td>
<td>0.03</td>
<td>0.01</td>
<td>Superferritic, high corrosion resistance</td>
</tr>
<tr>
<td>Monit</td>
<td>4.5</td>
<td>26.0</td>
<td>Bal.</td>
<td>4.5</td>
<td>0.25</td>
<td>1.0</td>
<td>0.75</td>
<td>--</td>
<td>0.04</td>
<td>0.03</td>
<td>0.3</td>
<td>--</td>
<td>--</td>
<td>Superferritic</td>
</tr>
<tr>
<td>26-1 Ti</td>
<td>0.50</td>
<td>26.0</td>
<td>Bal.</td>
<td>1.00</td>
<td>0.06</td>
<td>0.75</td>
<td>0.75</td>
<td>--</td>
<td>0.04</td>
<td>0.02</td>
<td>0.6</td>
<td>0.2</td>
<td>0.04</td>
<td>A duplex structure</td>
</tr>
<tr>
<td>18-2FM</td>
<td>--</td>
<td>26.0</td>
<td>Bal.</td>
<td>--</td>
<td>0.08</td>
<td>2.5</td>
<td>1.00</td>
<td>--</td>
<td>0.04</td>
<td>0.15</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Free-machining alloy with corrosion resistance similar to that of 303</td>
</tr>
<tr>
<td>446</td>
<td>--</td>
<td>25</td>
<td>Bal.</td>
<td>--</td>
<td>0.20</td>
<td>1.5</td>
<td>1.00</td>
<td>--</td>
<td>0.04</td>
<td>0.03</td>
<td>--</td>
<td>--</td>
<td>0.25</td>
<td>More Cr than 442 for more improved scaling resistance</td>
</tr>
<tr>
<td>Carpenter 443</td>
<td>--</td>
<td>20.5</td>
<td>Bal.</td>
<td>--</td>
<td>0.2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>--</td>
<td>0.04</td>
<td>0.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>--</td>
<td>--</td>
<td>1.0Cu</td>
<td>Corrosion and mechanical properties close to 18-8 austenitic stainless steels</td>
</tr>
<tr>
<td>442</td>
<td>--</td>
<td>20.5</td>
<td>Bal.</td>
<td>--</td>
<td>0.20</td>
<td>1.00</td>
<td>1.00</td>
<td>--</td>
<td>0.04</td>
<td>0.03</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Equivalent to Carpenter 443</td>
</tr>
<tr>
<td>AL 453&lt;sup&gt;TM&lt;/sup&gt;</td>
<td>0.3</td>
<td>22.0</td>
<td>Bal.</td>
<td>--</td>
<td>0.03</td>
<td>0.3</td>
<td>0.3</td>
<td>0.6</td>
<td>0.02</td>
<td>0.03&lt;sup&gt;b&lt;/sup&gt;</td>
<td>--</td>
<td>--</td>
<td>0.10&lt;sup&gt;b&lt;/sup&gt; (Ce+La)</td>
<td>For SOFC applications due to its TEC match and excellent oxidation and scaling resistance</td>
</tr>
</tbody>
</table>

<sup>a</sup> Alloys are labeled with their composition standards.
Ferritic stainless steels (cont.)

<table>
<thead>
<tr>
<th>Alloys\a</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Cu</th>
<th>N</th>
<th>Others</th>
<th>Characteristics, Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL 433(TM)</td>
<td>0.25</td>
<td>20.0</td>
<td>Bal</td>
<td>--</td>
<td>0.01</td>
<td>0.30</td>
<td>0.39</td>
<td>--</td>
<td>0.021</td>
<td>0.001</td>
<td>--</td>
<td>--</td>
<td>0.019</td>
<td>0.54 Cb, 0.80\b</td>
<td>Superferritic, in the family of 409 and 439. Combining oxidation resistance and high temp. strength.</td>
</tr>
<tr>
<td>Carpenter 443 (18-2)</td>
<td>--</td>
<td>20.5</td>
<td>Bal</td>
<td>--</td>
<td>0.20</td>
<td>1.00</td>
<td>1.00</td>
<td>--</td>
<td>0.04\b</td>
<td>0.03\b</td>
<td>--</td>
<td>1.10</td>
<td>--</td>
<td>--</td>
<td>As modified type of 430 for higher corrosion resistance.</td>
</tr>
<tr>
<td>AL 468(TM)</td>
<td>0.22</td>
<td>18.25</td>
<td>Bal</td>
<td>--</td>
<td>0.009</td>
<td>0.40</td>
<td>0.55</td>
<td>0.03</td>
<td>0.024</td>
<td>0.001</td>
<td>0.10</td>
<td>--</td>
<td>0.016</td>
<td>0.25 Cb</td>
<td>Cb stabilized, reducing Ti and thus the Ti related defects as in 439</td>
</tr>
<tr>
<td>AL 441 HP(TM)</td>
<td>0.30</td>
<td>18.0</td>
<td>Bal</td>
<td>--</td>
<td>0.009</td>
<td>0.35</td>
<td>0.34</td>
<td>0.05</td>
<td>0.023</td>
<td>0.002</td>
<td>0.29</td>
<td>--</td>
<td>0.014</td>
<td>0.71 Cb, 0.8\b Ti+Cb</td>
<td>Good oxidation and corrosion resistance for auto. Exhaust application.</td>
</tr>
<tr>
<td>AL 439 HP(TM)</td>
<td>0.23</td>
<td>18.0</td>
<td>Bal</td>
<td>--</td>
<td>0.012</td>
<td>0.45</td>
<td>0.55</td>
<td>--</td>
<td>0.02</td>
<td>0.001\b</td>
<td>0.40</td>
<td>--</td>
<td>0.013</td>
<td>--</td>
<td>A titanium stabilized alloy, more weldable than 430.</td>
</tr>
</tbody>
</table>

Sealing glass stainless steels

| Carpenter “27” | 0.5\b | 28.0 | Bal | --  | 0.05 | 0.60 | 0.40 | --  | --   | --   | --  | --  | --  | --          | Sealing glass material. No phase transformation till 1050oC Modify 430 for sealing glass appl.      |
| AL 430Ti      | 0.0 | 20.0 | Bal | --  | 0.10 | 0.60 | 0.40 | --  | 0.40  | --   | --  | --  | --  | --          | Sealing glass composition with exactly TEC match                                                 |
| Carpenter “18” | 0.0 | 18.0 | Bal | --  | 0.10 | 0.60 | 0.40 | --  | 0.40  | --   | --  | --  | --  | --          |

\a Alloys: AL 433 TM, Carpenter 443, 444 (18-2), AL 468 TM, AL 441 HP TM, AL 439 HP TM, Carpenter “27”, AL 430Ti, Carpenter “18”

# Co Base Alloys

<table>
<thead>
<tr>
<th>Alloys&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>W</th>
<th>Cb</th>
<th>Ti</th>
<th>Al</th>
<th>B</th>
<th>Zr</th>
<th>Others</th>
<th>Characteristics,</th>
<th>Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haynes 6B</td>
<td>3.0</td>
<td>30.0</td>
<td>1.0</td>
<td>61.5</td>
<td>1.0</td>
<td>1.4</td>
<td>--</td>
<td>1.5</td>
<td>4.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Solid solution alloy, as L-605, Haynes 188, s-186</td>
<td></td>
</tr>
<tr>
<td>Haynes 6K</td>
<td>2.0</td>
<td>31.0</td>
<td>3.0b</td>
<td>59.0</td>
<td>1.6</td>
<td>2.0b</td>
<td>2.0b</td>
<td>1.50b</td>
<td>4.50</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Machine knives</td>
<td></td>
</tr>
<tr>
<td>UMCo-50</td>
<td>--</td>
<td>28.0</td>
<td>21.0</td>
<td>49.0</td>
<td>0.12&lt;sup&gt;b&lt;/sup&gt;</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Solid solution alloy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haynes 150</td>
<td>3.0&lt;sup&gt;b&lt;/sup&gt;</td>
<td>28</td>
<td>20.0</td>
<td>Bal</td>
<td>0.08</td>
<td>0.65</td>
<td>0.35</td>
<td>1.5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Resistant thermal shock, high temperature corrosion (air &amp; air-SO2)</td>
<td></td>
</tr>
<tr>
<td>ULTIMET</td>
<td>9</td>
<td>26</td>
<td>3</td>
<td>54</td>
<td>0.06</td>
<td>0.8</td>
<td>0.3</td>
<td>5.0</td>
<td>2.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Appli. For severe corrosive attack env.</td>
<td></td>
</tr>
<tr>
<td>Haynes 188</td>
<td>22</td>
<td>22</td>
<td>3.0&lt;sup&gt;0&lt;/sup&gt;</td>
<td>Bal</td>
<td>0.10</td>
<td>1.25&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.3</td>
<td>--</td>
<td>14</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.04La</td>
<td>High strength and oxidation resistance &gt;Hastelloy X; Aero-burner cans, after burner components</td>
<td></td>
</tr>
</tbody>
</table>

---

e. Some alloys are made by more than one manufacturer  
f. Maximum composition  
g. Cast alloy.
## Cr-Base Alloys

<table>
<thead>
<tr>
<th>Alloys&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Nominal composition, wt%</th>
<th>Characteristics, Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
</tr>
<tr>
<td>C207</td>
<td>--</td>
<td>Bal</td>
</tr>
<tr>
<td>Cl-41</td>
<td>--</td>
<td>Bal</td>
</tr>
<tr>
<td>IM-15</td>
<td>--</td>
<td>Bal</td>
</tr>
<tr>
<td>Chrome 30</td>
<td>--</td>
<td>Bal</td>
</tr>
<tr>
<td>Chrome 90</td>
<td>--</td>
<td>Bal</td>
</tr>
<tr>
<td>Chrome 90S</td>
<td>--</td>
<td>Bal</td>
</tr>
<tr>
<td>Ducrolloy (Plansee)</td>
<td>--</td>
<td>Bal</td>
</tr>
</tbody>
</table>

<sup>a</sup> Made by PM approach.
# Alumina Forming Alloys

<table>
<thead>
<tr>
<th>Alloys&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Nominal composition, wt%</th>
<th>Characteristics, Typical applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
</tr>
<tr>
<td>Ni-Cr-Fe Superalloys</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nimonic 115</td>
<td>Bal</td>
<td>15.0</td>
</tr>
<tr>
<td>IN MA-6000E</td>
<td>68.5</td>
<td>15.0</td>
</tr>
<tr>
<td>Haynes 214&lt;sup&gt;TM&lt;/sup&gt;</td>
<td>Bal</td>
<td>17.6</td>
</tr>
<tr>
<td>Astroloy&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Bal</td>
<td>15.0</td>
</tr>
<tr>
<td>Udiment 700</td>
<td>Bal</td>
<td>15.0</td>
</tr>
<tr>
<td>Rene 77&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Bal</td>
<td>15.0</td>
</tr>
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<td>HAD 8077</td>
<td>Bal</td>
<td>16</td>
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<td>Udiment 500</td>
<td>Bal</td>
<td>19.0</td>
</tr>
<tr>
<td>Fe-Ni-Cr Superalloys</td>
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<tr>
<td>Incoloy MA 956</td>
<td>0.50&lt;sup&gt;s&lt;/sup&gt;</td>
<td>20</td>
</tr>
<tr>
<td>Alloys&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Nominal composition, wt%</td>
<td>Characteristics, Typical applications</td>
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<tr>
<td></td>
<td>Ni</td>
<td>Cr</td>
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<td><strong>Ferritic Stainless Steels</strong></td>
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<tr>
<td>Kanthal (APM)</td>
<td>--</td>
<td>22</td>
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<td>Fecralloy</td>
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<td>15.8</td>
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<tr>
<td>Armco 18 SR</td>
<td>0.25</td>
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<td><strong>Co Base Superalloys</strong></td>
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<tr>
<td>AiResist 215&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.0b</td>
<td>19</td>
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<tr>
<td>AiResist 13c</td>
<td>1.0b</td>
<td>21</td>
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<tr>
<td>AiResist 213</td>
<td>--</td>
<td>19</td>
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# Appendix C  
Properties of Selected Alloys

## I. Ni-Cr or Ni-Cr-Fe Base Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>TEC $\times 10^{-6}$ K$^{-1}$</th>
<th>Electrical resistivity (bulk) $\times 10^{-6}$ Ω.cm</th>
<th>Yield strength $\sigma_{0.2}$ (bar) (MPa)</th>
<th>Elastic modulus (GPa)</th>
<th>Oxidation Resistance $\times 10^{-6}$ mg$^2$.cm$^{-4}$.s$^{-1}$</th>
<th>Corrosion resistance: Hot corr.:=HCR  Carburiz.:=CR  Stress corr.:=SCR</th>
<th>Joinability</th>
<th>Formability or Elongation</th>
<th>Cost factor</th>
<th>Others</th>
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<tbody>
<tr>
<td>Inconel 671</td>
<td>15.0</td>
<td>86.9</td>
<td>225</td>
<td>216</td>
<td>14.6 1,000°C</td>
<td>Super,  Esp. HCR</td>
<td>25%</td>
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<tr>
<td>IN 657</td>
<td>~15.0</td>
<td>~80-90</td>
<td>114</td>
<td>560</td>
<td>600°C</td>
<td>Exc. HCR</td>
<td>24%</td>
<td></td>
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<tr>
<td>Inconel MA 758</td>
<td>15.0</td>
<td>114</td>
<td>560</td>
<td>228</td>
<td>288 760°C</td>
<td>Exc. HCR</td>
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<tr>
<td>Nimonic 81</td>
<td>11.1 20-100-800°C</td>
<td>127</td>
<td>184</td>
<td>158</td>
<td>184 538°C</td>
<td>538°C</td>
<td>41%</td>
<td></td>
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</tr>
<tr>
<td>Haynes G-30</td>
<td>16.0 30-760°C</td>
<td>~160-100</td>
<td>202</td>
<td>184</td>
<td>184 538°C</td>
<td>538°C</td>
<td>41%</td>
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<tr>
<td>Inconel 690</td>
<td>16.5 20-760°C</td>
<td>115</td>
<td>170</td>
<td>211</td>
<td>170 800°C</td>
<td>538°C</td>
<td>41%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IN-587</td>
<td>~16-17 20-800°C</td>
<td>112</td>
<td>663</td>
<td>&gt;556, 800H</td>
<td>663 760°C</td>
<td>&gt;556, 800H</td>
<td>28%</td>
<td></td>
<td></td>
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<tr>
<td>Haynes HR-160</td>
<td>~16-17 RT-800°C</td>
<td>112</td>
<td>215</td>
<td>&gt;556, 800H</td>
<td>215 760°C</td>
<td>&gt;556, 800H</td>
<td>28%</td>
<td></td>
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<tr>
<td>NA-224</td>
<td>~16-17 RT-800°C</td>
<td>118</td>
<td>220</td>
<td>&gt;556, 800H</td>
<td>220 800°C</td>
<td>&gt;556, 800H</td>
<td>30%</td>
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<tr>
<td>Nicrofer 602SHT-602CA</td>
<td>16.6 RT-800°C</td>
<td>118</td>
<td>220</td>
<td>&gt;556, 800H</td>
<td>220 800°C</td>
<td>&gt;556, 800H</td>
<td>30%</td>
<td></td>
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</table>

H resistance=HR  Scaling resist.=SR
<table>
<thead>
<tr>
<th>Alloys</th>
<th>TEC ×10^(-6)K^-1</th>
<th>Electrical resistivity (bulk) ×10^(-6)Ω.cm</th>
<th>Yield strength σ0.2 (bar) (MPa)</th>
<th>Elastic modulus (GPa)</th>
<th>Oxidation Resistance ×10^(-6)mg^2.cm^-4.s^-1</th>
<th>Corrosion resistance: Hot corr.:=HCR Carbariz.:=CR Stress corr.:=SCR</th>
<th>Join-ability</th>
<th>Formability or Elongation</th>
<th>Cost factor</th>
<th>Others</th>
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</thead>
<tbody>
<tr>
<td>Nimonic 86</td>
<td>~15-16 RT-800°C</td>
<td>~100-120</td>
<td></td>
<td></td>
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<td></td>
<td>Exc. HCR</td>
<td>41%</td>
<td>20%</td>
<td></td>
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<tr>
<td>RA-333</td>
<td>~17-18 RT-800°C</td>
<td>~100-120</td>
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<td>Excellent HCR</td>
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<tr>
<td>IN-597</td>
<td>~16-17 RT-800°C</td>
<td>~100-120</td>
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<td>Low in NaCl env&lt;N.80A,90</td>
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<tr>
<td>Nimonic 101</td>
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<td>~100-120</td>
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<td>Good HCR</td>
<td>15%</td>
<td>10%</td>
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</tr>
<tr>
<td>Inconel 601</td>
<td>16.5 27-760°C</td>
<td>~100-120</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Good CR</td>
<td></td>
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<tr>
<td></td>
<td>14.0 20-700°C</td>
<td>~100-120</td>
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<td>Exc. HCR, CR in Both ox &amp; re env</td>
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<tr>
<td></td>
<td>119 200 sp</td>
<td>663 760°C</td>
<td>129 800°C</td>
<td>12.2 1,000°C</td>
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<td>Readily</td>
<td>45% in 2in</td>
<td>20%</td>
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</tr>
<tr>
<td></td>
<td>690 760°C</td>
<td>372 RT</td>
<td>155 760°C</td>
<td>150 800°C</td>
<td></td>
<td></td>
<td>Readily</td>
<td>63%</td>
<td></td>
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<tr>
<td></td>
<td>285 760°C</td>
<td>164 800°C</td>
<td>211 RT</td>
<td>5.5 2.2</td>
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<td></td>
<td>Readily</td>
<td>3.5%</td>
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<tr>
<td>Inconel 601</td>
<td>12.5 25-800°C</td>
<td>285 760°C</td>
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<td>Exc.</td>
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<tr>
<td></td>
<td>112 250°C</td>
<td>164 800°C</td>
<td>199 RT</td>
<td>5.5 2.2</td>
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<td></td>
<td>Readily</td>
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<td>Haynes 230</td>
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<td>690 760°C</td>
<td>129 800°C</td>
<td>5.5 2.2</td>
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<td>Readily</td>
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<td>Inconel 617</td>
<td>15.2 25-800°C</td>
<td>350 RT</td>
<td>129 800°C</td>
<td>5.5 2.2</td>
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<td>Readily</td>
<td></td>
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<tr>
<td></td>
<td>11.6 20-100°C</td>
<td>164 800°C</td>
<td>150 800°C</td>
<td>5.5 2.2</td>
<td></td>
<td></td>
<td>Readily</td>
<td></td>
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<tr>
<td>Hastelloy G</td>
<td>16.4 21-650°C</td>
<td>690 760°C</td>
<td>129 800°C</td>
<td>5.5 2.2</td>
<td></td>
<td></td>
<td>Readily</td>
<td></td>
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<tr>
<td>Hastelloy G-3</td>
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<td>~100-120</td>
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<td>Exc.</td>
<td></td>
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<tr>
<td></td>
<td>118 262 s</td>
<td>220 s 760°C</td>
<td>320 RT</td>
<td>5.5 2.2</td>
<td></td>
<td></td>
<td>Readily</td>
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<tr>
<td>Hastelloy X</td>
<td>16 26-816°C</td>
<td>~100-120</td>
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<td>Exc.</td>
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<tr>
<td>Hastelloy HX</td>
<td>16.1 26-816°C</td>
<td>~100-120</td>
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<td>Exc.</td>
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<tr>
<td></td>
<td>116 261</td>
<td>320 RT</td>
<td>196 RT</td>
<td>5.5 2.2</td>
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<td>Readily</td>
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<td>Pyromet 680</td>
<td>16 26-816°C</td>
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<td>Readily</td>
<td></td>
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<tr>
<td></td>
<td>241 760°C</td>
<td>144 RT</td>
<td>143 RT</td>
<td>5.5 2.2</td>
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<td></td>
<td>Readily</td>
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Note: Machinability (%) H resistance=HR Scaling resist.=SR
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<tr>
<th>Alloys</th>
<th>TEC  $\times 10^{-6} \cdot K^{-1}$</th>
<th>Electrical resistivity (bulk) $\times 10^{-6} \cdot \Omega \cdot cm$</th>
<th>Yield strength $\sigma_{0.2}$ (bar) (MPa)</th>
<th>Elastic modulus (GPa)</th>
<th>Oxidation Resistance $\times 10^{-6} \cdot mg^2 \cdot cm^{-4} \cdot s^{-1}$</th>
<th>Corrosion resistance: Hot corr.=$HCR$ Carbariz.=$CR$ Stress corr.=$SCR$</th>
<th>Join-ability</th>
<th>Formability or Elongation</th>
<th>Cost factor</th>
<th>Others</th>
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<tbody>
<tr>
<td>Hastelloy C-22</td>
<td>15.3  21-760°C</td>
<td>114</td>
<td>269 s 760°C</td>
<td>163 760°C</td>
<td>69.4 1,100°C</td>
<td>Exc. $HCR$, $SCR$</td>
<td>Superior</td>
<td>62%</td>
<td>20%</td>
<td>Machinability (%)</td>
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<td>128</td>
<td>421 760°C</td>
<td>160 760°C</td>
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<td>Exc. $HCR$</td>
<td>Readily</td>
<td>50%</td>
<td>16-18%</td>
<td>H resistance=$HR$</td>
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<td>12.0 ~16.5  20-100-800°C</td>
<td>123.7</td>
<td>245 s 530°C</td>
<td>192 RT</td>
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<td>Exc. $HCR$</td>
<td>Readily</td>
<td>60%</td>
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<td>Stable with temp.</td>
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<td>Inconel 725™</td>
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<td>~100-120</td>
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<td>35%</td>
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<td>Hastelloy G-50</td>
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<td>16%</td>
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<td>56.5%</td>
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<td>115</td>
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<td>166 800°C</td>
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<td>9%</td>
<td>16%</td>
<td>16%</td>
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<tr>
<td>RollsRoyce263</td>
<td>~16-17  RT-800°C</td>
<td>~100-120</td>
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<td>20%</td>
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<td>16%</td>
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<td>108</td>
<td>400 760°C</td>
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<td>20%</td>
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<td>Inconel MA 754</td>
<td>~15  26-93-800°C</td>
<td>~100-120</td>
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<td>20%</td>
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<td>Inconel 050</td>
<td>16.2  20-760°C</td>
<td>119</td>
<td>262 s 760°C</td>
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<td></td>
<td>41%</td>
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<tr>
<td>TDNiC</td>
<td>~15  26-93-800°C</td>
<td>~100-120</td>
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<td>15%</td>
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<td>119</td>
<td>265 760°C</td>
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<td>6%</td>
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<td>Nimonic 95</td>
<td>~15  RT-800°C</td>
<td>~100-120</td>
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<td>6%</td>
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<tr>
<td>Alloys</td>
<td>TEC $\times 10^{-6}, \text{K}^{-1}$</td>
<td>Electrical resistivity (bulk) $\times 10^{-6}, \Omega \cdot \text{cm}$</td>
<td>Yield strength $\sigma_{0.2}$ (bar) (MPa)</td>
<td>Elastic modulus (GPa)</td>
<td>Oxidation Resistance $\times 10^{-6}, \text{mg}^2, \text{cm}^{-2}\cdot \text{s}^{-1}$</td>
<td>Corrosion resistance: Hot corr. = HCR Carboriz. = CR Stress corr. = SCR</td>
<td>Join-ability</td>
<td>Formability or Elongation</td>
<td>Cost factor</td>
<td>Others</td>
</tr>
<tr>
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<tr>
<td>Nimonic 90</td>
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<td>114</td>
<td>538</td>
<td>214</td>
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<td>Good in NaCl &gt; N.101, 91</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>(pyromet 90)</td>
<td>20-760$^\circ\text{C}$</td>
<td>760$^\circ\text{C}$</td>
<td>676</td>
<td>RT</td>
<td>164</td>
<td>Good</td>
<td>Readily</td>
<td>25%</td>
<td>14%</td>
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<tr>
<td>Waspaloy A</td>
<td>15.4 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>124</td>
<td>582</td>
<td>214</td>
<td>16</td>
<td>Good</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
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<tr>
<td>Waspaloy B</td>
<td>20-800$^\circ\text{C}$</td>
<td>760$^\circ\text{C}$</td>
<td>676</td>
<td>RT</td>
<td>164</td>
<td>Good</td>
<td>Readily</td>
<td>25%</td>
<td>14%</td>
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<tr>
<td>Nimonic 80A</td>
<td>12.7 $\times 10^{-6}, \text{K}^{-1}$</td>
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<td>660</td>
<td>504</td>
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<td>Readily</td>
<td>23%</td>
<td>10%</td>
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<tr>
<td>Nimonic 80</td>
<td>20-100$^\circ\text{C}$</td>
<td>117</td>
<td>504</td>
<td>760$^\circ\text{C}$</td>
<td>164</td>
<td>Good</td>
<td>Readily</td>
<td>25%</td>
<td>14%</td>
<td></td>
</tr>
<tr>
<td>Udimet 520</td>
<td>16.5 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>~15</td>
<td>660</td>
<td>504</td>
<td>169</td>
<td>Good in NaCl &gt; N.101, 91</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Haynes R-41</td>
<td>5-8 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>~100-120</td>
<td>752</td>
<td>760$^\circ\text{C}$</td>
<td>169</td>
<td>Good</td>
<td>Readily</td>
<td>25%</td>
<td>14%</td>
<td></td>
</tr>
<tr>
<td>Pyromet M-252,</td>
<td>15.2 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>130.8</td>
<td>752</td>
<td>760$^\circ\text{C}$</td>
<td>169</td>
<td>Good in NaCl &gt; N.101, 91</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>(carpenter)</td>
<td>20-800$^\circ\text{C}$</td>
<td>~100-120</td>
<td>718</td>
<td>760$^\circ\text{C}$</td>
<td>156</td>
<td>Good</td>
<td>Readily</td>
<td>25%</td>
<td>14%</td>
<td></td>
</tr>
<tr>
<td>Inconel 718</td>
<td>14.0 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>~15-16</td>
<td>718</td>
<td>760$^\circ\text{C}$</td>
<td>169</td>
<td>Good HCR</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Udimet 710</td>
<td>20-816$^\circ\text{C}$</td>
<td>~100-120</td>
<td>718</td>
<td>760$^\circ\text{C}$</td>
<td>156</td>
<td>Good HCR</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Udimet 720</td>
<td>~15-16 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>~100-120</td>
<td>829</td>
<td>760$^\circ\text{C}$</td>
<td>156</td>
<td>Good HCR</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Nimonic PK 33</td>
<td>12.1 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>126</td>
<td>739</td>
<td>760$^\circ\text{C}$</td>
<td>154</td>
<td>Good HCR</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Nimonic 718</td>
<td>16.0 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>121 aged</td>
<td>739</td>
<td>760$^\circ\text{C}$</td>
<td>154</td>
<td>Good HCR</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Udimet 710</td>
<td>~15-16 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>~100-120</td>
<td>829</td>
<td>760$^\circ\text{C}$</td>
<td>154</td>
<td>Good HCR</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Udimet 720</td>
<td>~15-16 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>~100-120</td>
<td>814</td>
<td>760$^\circ\text{C}$</td>
<td>154</td>
<td>Good HCR</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Nimonic PK 33</td>
<td>12.1 $\times 10^{-6}, \text{K}^{-1}$</td>
<td>126</td>
<td>620</td>
<td>800$^\circ\text{C}$</td>
<td>154</td>
<td>Good HCR</td>
<td>Readily</td>
<td>23%</td>
<td>10%</td>
<td></td>
</tr>
</tbody>
</table>

Close to Waspaloy A, except no addition of 0.02S and 0.1 Cu for improved machinability.
## II. Fe-Ni-Cr Base Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>TEC (RT)~800°C $\times10^{-6}$ K$^{-1}$</th>
<th>Electrical resistivity (bulk) $\times10^6$ Ω.cm</th>
<th>Yield strength $\sigma_{0.2}$ (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Oxidation Resistance $\times10^{-6}$ mg$^2$. cm$^{-4}$. s$^{-1}$</th>
<th>Corrosion resistance: Hot corr.:HCR Carbariz.:CR Stress corr.:SCR</th>
<th>Join-ability</th>
<th>Formability or Elongation</th>
<th>Cost factor</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incoloy 028</td>
<td>16.7</td>
<td>20-426°C</td>
<td>99</td>
<td>214 RT</td>
<td>200 RT</td>
<td>Exc. in both Oxi. &amp; red. Env.</td>
<td></td>
<td></td>
<td>40%</td>
<td>Exc. resist. To cyclic oxidation</td>
</tr>
<tr>
<td>Incoloy 803</td>
<td>17.1</td>
<td>21-649°C</td>
<td>103</td>
<td>215 760°C</td>
<td>195 RT</td>
<td>Exc. HCR, CR Good SCR</td>
<td></td>
<td></td>
<td>46%</td>
<td></td>
</tr>
<tr>
<td>Haynes HR-120</td>
<td>17.3</td>
<td>26-800°C</td>
<td>105</td>
<td>375 s RT</td>
<td>197 RT</td>
<td>Exc. HCR, CR Good SCR</td>
<td></td>
<td></td>
<td>50%</td>
<td>Good SCR</td>
</tr>
<tr>
<td>20Mo-6</td>
<td>16.87</td>
<td>26-800°C</td>
<td>108</td>
<td>275 RT</td>
<td>186 RT</td>
<td>Exc. HCR, CR Good SCR</td>
<td></td>
<td></td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>20Mo-4</td>
<td>16.87</td>
<td>26-800°C</td>
<td>106</td>
<td>262 RT</td>
<td>186 RT</td>
<td>Exc. HCR, CR Good SCR</td>
<td></td>
<td></td>
<td>41%</td>
<td></td>
</tr>
<tr>
<td>Pyromet 31</td>
<td>16.1</td>
<td>21-816°C</td>
<td>122</td>
<td>669 760°C</td>
<td>154 RT</td>
<td>Exc. HCR, SCR</td>
<td></td>
<td></td>
<td>41%</td>
<td></td>
</tr>
<tr>
<td>Incoloy 864</td>
<td>16.4</td>
<td>21-649°C</td>
<td>104</td>
<td>140 760°C</td>
<td>195 RT</td>
<td>Exc. HCR, SCR</td>
<td></td>
<td></td>
<td>41%</td>
<td></td>
</tr>
<tr>
<td>Incoloy 556™</td>
<td>16.7</td>
<td>26-800°C</td>
<td>95.2</td>
<td>220 760°C</td>
<td>148 RT</td>
<td>Exc. HCR, CR Good SCR</td>
<td></td>
<td></td>
<td>41%</td>
<td></td>
</tr>
<tr>
<td>Incoloy 825</td>
<td>17.1</td>
<td>26-760°C</td>
<td>113</td>
<td>183 760°C</td>
<td>206 RT</td>
<td>Exc. HCR, CR Good SCR</td>
<td></td>
<td></td>
<td>47.7%</td>
<td>8.5</td>
</tr>
<tr>
<td>Aktiebolag 253 MA</td>
<td>19.0</td>
<td>26-760°C</td>
<td>84</td>
<td>110 760°C</td>
<td>115 RT</td>
<td>Exc. HCR, CR Good SCR</td>
<td></td>
<td></td>
<td>45%</td>
<td></td>
</tr>
<tr>
<td>Incoloy 800</td>
<td>14.4</td>
<td>20-100°C</td>
<td>99</td>
<td>213 550°C</td>
<td>193 RT</td>
<td>Exc. HCR, CR Good SCR</td>
<td></td>
<td></td>
<td>51%</td>
<td>2.3</td>
</tr>
<tr>
<td>Incoloy 925</td>
<td>13.2</td>
<td>25-93°C</td>
<td>116</td>
<td>640 ps 639°C</td>
<td>3.3 1,000°C</td>
<td>Exc. both reduc. &amp; oxid.</td>
<td></td>
<td></td>
<td>44%</td>
<td>16%</td>
</tr>
<tr>
<td>N-155, Multimet alloy</td>
<td>17.5</td>
<td>26-800°C</td>
<td>93</td>
<td>393 RT</td>
<td>2.7 1,000°C</td>
<td>Exc. HCR, CR Good SCR</td>
<td></td>
<td></td>
<td>24%</td>
<td>16%</td>
</tr>
<tr>
<td>Incoloy 802</td>
<td>~16-18</td>
<td>RT-800°C</td>
<td>~100-120</td>
<td>~100-120</td>
<td></td>
<td>6.5</td>
<td></td>
<td></td>
<td>43%</td>
<td>16-20%</td>
</tr>
<tr>
<td>Alloys</td>
<td>TEC RT-800°C ×10⁻⁶ K⁻¹</td>
<td>Electrical resistivity (bulk) ×10⁻⁶ Ω.cm</td>
<td>Yield strength σ₀.₂ (MPa)</td>
<td>Elastic Modulus (GPa)</td>
<td>Oxidation Resistance ×10⁻⁶ mg².cm⁻².s⁻¹</td>
<td>Corrosion resistance: Hot corr.=HCR Carburiz.=CR Stress cor.=SCR</td>
<td>Join-ability</td>
<td>Formability or Elongation</td>
<td>Cost factor</td>
<td>Others</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------------</td>
<td>------------------------------------------</td>
<td>---------------------------</td>
<td>-----------------------</td>
<td>---------------------------------</td>
<td>------------------------------------------------</td>
<td>---------------</td>
<td>-----------------------------</td>
<td>-------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>S-590</td>
<td>~16-18</td>
<td>~100-120</td>
<td>197 RT</td>
<td>207 RT</td>
<td>Same as 801</td>
<td>Same as 801</td>
<td>53%</td>
<td>20%</td>
<td></td>
<td>Machinability (%) H resistance=HR Scaling resist.=SR</td>
</tr>
<tr>
<td>Incoloy 801</td>
<td>~16-18</td>
<td>~101.2</td>
<td>RT</td>
<td>RT</td>
<td>RT</td>
<td>RT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Incoloy 840</td>
<td>~16-18</td>
<td>~100-120</td>
<td>197 RT</td>
<td>207 RT</td>
<td>Same as 801</td>
<td>Same as 801</td>
<td>53%</td>
<td>20%</td>
<td></td>
<td>Machinability (%) H resistance=HR Scaling resist.=SR</td>
</tr>
<tr>
<td>Armco 20-45-5</td>
<td>~16-18</td>
<td>~100-120</td>
<td>197 RT</td>
<td>207 RT</td>
<td>Same as 801</td>
<td>Same as 801</td>
<td>53%</td>
<td>20%</td>
<td></td>
<td>Machinability (%) H resistance=HR Scaling resist.=SR</td>
</tr>
<tr>
<td>Incoloy 020</td>
<td>~16.9</td>
<td>80</td>
<td>170 760°C</td>
<td>188 RT</td>
<td>Exc. in natural &amp; acidic env.</td>
<td>Exc. HCR, CR Good SCR</td>
<td>42%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19-9DX</td>
<td>~16-18</td>
<td>~100-120</td>
<td>197 RT</td>
<td>207 RT</td>
<td>Same as 801</td>
<td>Same as 801</td>
<td>53%</td>
<td>20%</td>
<td></td>
<td>Machinability (%) H resistance=HR Scaling resist.=SR</td>
</tr>
<tr>
<td>19-9DL</td>
<td>~16-18</td>
<td>~100-120</td>
<td>197 RT</td>
<td>207 RT</td>
<td>Same as 801</td>
<td>Same as 801</td>
<td>53%</td>
<td>20%</td>
<td></td>
<td>Machinability (%) H resistance=HR Scaling resist.=SR</td>
</tr>
<tr>
<td>RA-330</td>
<td>18.0</td>
<td>77</td>
<td>138 816°C</td>
<td>117 760°C</td>
<td>Exc. upto 677°C</td>
<td>Exc. HCR, CR Good SCR</td>
<td>42%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RA-330 HC</td>
<td>18.0</td>
<td>77</td>
<td>138 816°C</td>
<td>117 760°C</td>
<td>Exc. upto 677°C</td>
<td>Exc. HCR, CR Good SCR</td>
<td>42%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rolled Alloys</td>
<td>18.0</td>
<td>101.7</td>
<td>138 816°C</td>
<td>117 760°C</td>
<td>Exc. HCR, CR Good SCR</td>
<td>Good SCR</td>
<td>42%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RA85H</td>
<td>18.0</td>
<td>101.7</td>
<td>138 816°C</td>
<td>117 760°C</td>
<td>Exc. HCR, CR Good SCR</td>
<td>Good SCR</td>
<td>42%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Incoloy DS</td>
<td>18.0</td>
<td>101.7</td>
<td>138 816°C</td>
<td>117 760°C</td>
<td>Exc. HCR, CR Good SCR</td>
<td>Good SCR</td>
<td>42%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Low Ni alloy developed for the manufacture of the seam-welded tubing used for the sheathing of electrical resistance heating elements.
### III. Ferritic Stainless Steels

<table>
<thead>
<tr>
<th>Alloys</th>
<th>TEC RT~800°C ×10⁻⁶.K⁻¹</th>
<th>Electrical Resistivity (bulk) ×10⁶Ω.cm</th>
<th>Yield strength σ₀.₂ (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Oxidation Resistance ×10⁻⁶ mg².cm⁻⁴.s⁻¹</th>
<th>Corrosion resistance: Hot corr.=HCR Stress cor.=SCR Carbariz.=CR</th>
<th>Join-ability</th>
<th>Formability or Elongation</th>
<th>Cost factor</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>29-4-2 (AL)</td>
<td>9.4</td>
<td>~60-80</td>
<td>655 605</td>
<td>207 RT</td>
<td>Exc. &gt;E-Bite, 446 at 800°C</td>
<td>Exc. Comp. to supera</td>
<td>Fairly</td>
<td>25%</td>
<td>Good SR</td>
<td>Exc. SR</td>
</tr>
<tr>
<td>29-4C (AL)</td>
<td>10.4</td>
<td>~60-80</td>
<td>500 RT</td>
<td>207 RT</td>
<td></td>
<td>Ex. HCR, SCR</td>
<td>Fairly</td>
<td>&gt;20%</td>
<td></td>
<td>Good SR</td>
</tr>
<tr>
<td>7-Mo Stainless</td>
<td>13.3 14.7</td>
<td>77.5</td>
<td>565 RT</td>
<td>200 RT</td>
<td></td>
<td>Ex. HCR, SCR</td>
<td>Readily</td>
<td>31%</td>
<td></td>
<td>Good SR</td>
</tr>
<tr>
<td>(Carpenter)</td>
<td>25-538-760°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy 255 (AL)</td>
<td>13.8</td>
<td>82.1</td>
<td>&gt;480 RT</td>
<td></td>
<td>5.4 1,000°C</td>
<td>Ex. &lt;29-4-2</td>
<td>Fairly</td>
<td>&gt;20%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-Brite 26-1</td>
<td>~13</td>
<td>~60-80</td>
<td>&gt;275 RT</td>
<td></td>
<td></td>
<td>Ex. HCR, SCR</td>
<td>Fairly</td>
<td>&gt;20%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea-cure/Sc-1</td>
<td>11.8</td>
<td>~60-80</td>
<td>&gt;380 RT</td>
<td></td>
<td></td>
<td>Ex. HCR, SCR</td>
<td>Readily</td>
<td>&gt;20%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monit</td>
<td>~13-14</td>
<td>~60-80</td>
<td>&gt;550 RT</td>
<td></td>
<td></td>
<td>Ex. HCR, SCR</td>
<td>Fairly</td>
<td>&gt;20%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26-1 Ti</td>
<td>~12</td>
<td>~60-80</td>
<td>&gt;275 RT</td>
<td></td>
<td></td>
<td>Ex. HCR, SCR</td>
<td>Fairly</td>
<td>&gt;20%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18-2FM</td>
<td>~12</td>
<td>~60-80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>446</td>
<td>10.4 11.2</td>
<td>67</td>
<td>&gt;275 &lt;55* RT 760°C</td>
<td>200 RT</td>
<td>2.6 1,000°C</td>
<td>Ex.</td>
<td>Fairly</td>
<td>&gt;20%</td>
<td>1</td>
<td>Good SR</td>
</tr>
<tr>
<td>AL 453™</td>
<td>11.4 12.3</td>
<td>73.3</td>
<td>310 39</td>
<td>200 RT (est.) 760°C</td>
<td>0.22</td>
<td>Ex. HCR, SCR</td>
<td>Fairly</td>
<td>35%</td>
<td>1</td>
<td>Exc. SR</td>
</tr>
<tr>
<td>Carpenter 443</td>
<td>12.1</td>
<td>68</td>
<td>275 RT</td>
<td>200 RT</td>
<td>760°C</td>
<td>Good</td>
<td>Fairly</td>
<td>&gt;20%</td>
<td>1</td>
<td>Good SR</td>
</tr>
<tr>
<td></td>
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<td></td>
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## Ferritic stainless steels (cont.)

<table>
<thead>
<tr>
<th>Alloys</th>
<th>TEC</th>
<th>Electrical Resistivity (bulk) $\times 10^{-6}$ $\Omega \cdot \text{cm}$</th>
<th>Yield strength $\sigma_{0.2}$ (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Oxidation Resistance $\times 10^{-6}$ mg$^2$.cm$^{-4}$.s$^{-1}$</th>
<th>Corrosion resistance: Hot corr.=HCR Stress cor.=SCR Carburiz.=CR</th>
<th>Join-ability</th>
<th>Form-ability or Elongation</th>
<th>Cost factor</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL 433™</td>
<td>11.80</td>
<td>65</td>
<td>325 $\times 10^{-6}$ $\text{K}^{-1}$</td>
<td>80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>200 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$</td>
<td>Good</td>
<td></td>
<td></td>
<td>32%</td>
<td></td>
</tr>
<tr>
<td>Carpenter</td>
<td>12.10</td>
<td>~ 60-70</td>
<td>345 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>200 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>0.10 80 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$</td>
<td>Good</td>
<td>Good</td>
<td></td>
<td>22%</td>
<td></td>
</tr>
<tr>
<td>AL 443</td>
<td>12.50</td>
<td>63</td>
<td>328 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>200 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>0.17 80 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$</td>
<td>Good</td>
<td>Good</td>
<td></td>
<td>33%</td>
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</tr>
<tr>
<td>Carpenter</td>
<td>12.00</td>
<td>58.7</td>
<td>290 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>200 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>0.10 80 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$</td>
<td>Good</td>
<td>Fairly</td>
<td></td>
<td>31%</td>
<td>Good SR</td>
</tr>
<tr>
<td>AL 441 HP™</td>
<td>63</td>
<td>63</td>
<td>310 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
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<td>0.10 80 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$</td>
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<td>34%</td>
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</tr>
<tr>
<td>AL 439 HP™</td>
<td>12.50</td>
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<td>200 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>0.10 80 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$</td>
<td>Good</td>
<td>Good</td>
<td></td>
<td>34%</td>
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<tr>
<td>AL 439 Ti</td>
<td>9.9</td>
<td>60</td>
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<td>200 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>0.10 80 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$</td>
<td>Good</td>
<td>Good</td>
<td></td>
<td>25%</td>
<td>Exactly TEC match with glass</td>
</tr>
<tr>
<td>Carpenter</td>
<td>10.0</td>
<td>63</td>
<td>345 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>200 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>0.10 80 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$</td>
<td>Good</td>
<td>Good</td>
<td></td>
<td>25%</td>
<td>Exactly TEC match with glass</td>
</tr>
<tr>
<td>Carpenter</td>
<td>11.0</td>
<td>63</td>
<td>345 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>200 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$</td>
<td>0.10 80 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$</td>
<td>Good</td>
<td>Good</td>
<td></td>
<td>25%</td>
<td></td>
</tr>
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</table>

### Sealing-glass alloys

| AL 430Ti      | 9.9 11.3     | 60                                                                              | 310 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$ | 200 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$ | 0.10 80 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$ | Good                                                      | Good         |                             | 25%        |                             |
| Carpenter    | 10.0 11.0    | 63                                                                              | 345 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$ | 200 80 $\times 10^{-6}$ $\text{Ω} \cdot \text{cm}$ | 0.10 80 $\times 10^{-6}$ $\text{mg}^2$.cm$^{-4}$.s$^{-1}$ | Good                                                      | Good         |                             | 25%        |                             |
## VI. Co-Base Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>TEC RT–800°C $\times 10^{-6} , K^{-1}$</th>
<th>Electrical resistivity (bulk) $\times 10^6 , \Omega \cdot cm$</th>
<th>Yield strength $\sigma_{0.2}$ (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Oxidation Resistance $\times 10^{-6} , mg^2 \cdot cm^{-4} \cdot s^{-1}$</th>
<th>Hot Corrosion resistance</th>
<th>Join-ability</th>
<th>Form-ability or Elongation</th>
<th>Cost factor</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haynes 6B (Stellite)</td>
<td>16.3 0-800°C</td>
<td>91.0</td>
<td>260 860°C</td>
<td></td>
<td></td>
<td>Exc. SCR, HCR</td>
<td>Readily</td>
<td>17%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haynes 6K (Stellite)</td>
<td>14.5 0-800°C</td>
<td>~60-90</td>
<td>82.5 87</td>
<td>310 815°C 150 700°C 275 538°C 290 s 760°C</td>
<td>215 RT 180 649°C 169 s 800°C</td>
<td>Close 230 &gt;X,617,625</td>
<td>Exc. SCR, HCR</td>
<td>Readily 4%</td>
<td>8% 38% 56%</td>
<td>Welding mater.</td>
</tr>
<tr>
<td>UMCo-50</td>
<td>16.8 20-1000°C</td>
<td></td>
<td>101</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Readily 56%</td>
<td>12-14%</td>
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</tr>
<tr>
<td>Haynes 150</td>
<td>16.9 25-760°C</td>
<td></td>
<td>101</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Readily 56%</td>
<td>12-14%</td>
<td></td>
</tr>
<tr>
<td>Haynes 188</td>
<td>16.5 20-800°C</td>
<td></td>
<td>101</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Readily 56%</td>
<td>12-14%</td>
<td></td>
</tr>
</tbody>
</table>

- TEC: Thermal expansion coefficient
- Yield strength: $\sigma_{0.2}$
- Elastic Modulus: $E$
- Oxidation Resistance: $R$
- Hot Corrosion resistance: $H$
- Join-ability: J
- Form-ability or Elongation: F
- Cost factor: Cost
- Others: Machinability (%), H resistance=HR, Sealing resist.=SR

- ±: Variation range
- °C: Temperature range
- s: Time in seconds
- RT: Room temperature
- SCR: Solid corrosion resistance
- HCR: High corrosion resistance
- Welding mater.: Welding material
- Excellent HCR: Excellent high corrosion resistance
## V. Cr-Base Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>TEC RT~800°C $\times 10^{-6}$K$^{-1}$</th>
<th>Electrical resistivity (bulk) $\times 10^{-6}$Ω.cm</th>
<th>Yield strength $\sigma_{0.2}$ (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Oxidation Resistance $\times 10^{-6}$mg$^2$.cm$^{-4}$.s$^{-1}$</th>
<th>Hot Corrosion resistance</th>
<th>Joinability</th>
<th>Form-ability or Elongation</th>
<th>Cost factor</th>
<th>Others Machinability (%)</th>
<th>H resistance=HR</th>
<th>Scaling resist.=SR</th>
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<tbody>
<tr>
<td>C207</td>
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<td>IM-15</td>
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<td>Chrome 30</td>
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<tr>
<td>Chrome 90</td>
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<td></td>
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<tr>
<td>Ducrolloy (Plansee)</td>
<td>11.8</td>
<td>20-1000°C</td>
<td></td>
<td></td>
<td>4.60</td>
<td>1.000°C</td>
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<td></td>
<td></td>
<td>&lt;10%</td>
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VI. Alumina Forming Alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>TEC RT~800°C ×10⁻⁶ K⁻¹</th>
<th>Electrical resistivity (bulk) ×10⁻⁶ Ω.cm</th>
<th>Yield strength σ₀.₂ (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Oxidation Resistance ×10⁻⁶ mg².cm⁻⁴.s⁻¹</th>
<th>Hot Corrosion resistance</th>
<th>Join-ability</th>
<th>Form-ability or Elongation</th>
<th>Cost factor</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nimonic 105</td>
<td>~16-18 20-800°C 16.6</td>
<td>~120-140 134</td>
<td>~120-140 640.5 760°C 16 800°C</td>
<td>162 800°C Super &gt;&gt; alloy 230</td>
<td>Excl. SCR, HCR Super. SCR, HCR Excl. SCR, HCR Excl. SCR, HCR Good. SCR, HCR Good. SCR, HCR Good. SCR, HCR</td>
<td>Readily</td>
<td>Readily</td>
<td>36.8%</td>
<td>Good SR, HR 18% Good SR, HR</td>
<td></td>
</tr>
<tr>
<td>Haynes 214™</td>
<td>~16-18 20-800°C 16.6</td>
<td>~120-140 134</td>
<td>~120-140 640.5 760°C 16 800°C</td>
<td>162 800°C Super &gt;&gt; alloy 230</td>
<td>Excl. SCR, HCR Super. SCR, HCR Excl. SCR, HCR Excl. SCR, HCR Good. SCR, HCR Good. SCR, HCR Good. SCR, HCR</td>
<td>Readily</td>
<td>Readily</td>
<td>36.8%</td>
<td>Good SR, HR 18% Good SR, HR</td>
<td></td>
</tr>
<tr>
<td>IN MA-6000E</td>
<td>~16-18 20-800°C 16.6</td>
<td>~120-140 134</td>
<td>~120-140 640.5 760°C 16 800°C</td>
<td>162 800°C Super &gt;&gt; alloy 230</td>
<td>Excl. SCR, HCR Super. SCR, HCR Excl. SCR, HCR Excl. SCR, HCR Good. SCR, HCR Good. SCR, HCR Good. SCR, HCR</td>
<td>Readily</td>
<td>Readily</td>
<td>36.8%</td>
<td>Good SR, HR 18% Good SR, HR</td>
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<tr>
<td>Astroloy⁴</td>
<td>~16-18 20-800°C 16.6</td>
<td>~120-140 134</td>
<td>~120-140 640.5 760°C 16 800°C</td>
<td>162 800°C Super &gt;&gt; alloy 230</td>
<td>Excl. SCR, HCR Super. SCR, HCR Excl. SCR, HCR Excl. SCR, HCR Good. SCR, HCR Good. SCR, HCR Good. SCR, HCR</td>
<td>Readily</td>
<td>Readily</td>
<td>36.8%</td>
<td>Good SR, HR 18% Good SR, HR</td>
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<tr>
<td>Udiment 700</td>
<td>~16-18 20-800°C 16.6</td>
<td>~120-140 134</td>
<td>~120-140 640.5 760°C 16 800°C</td>
<td>162 800°C Super &gt;&gt; alloy 230</td>
<td>Excl. SCR, HCR Super. SCR, HCR Excl. SCR, HCR Excl. SCR, HCR Good. SCR, HCR Good. SCR, HCR Good. SCR, HCR</td>
<td>Readily</td>
<td>Readily</td>
<td>36.8%</td>
<td>Good SR, HR 18% Good SR, HR</td>
<td></td>
</tr>
<tr>
<td>Rene 77⁴</td>
<td>~16-18 20-800°C 16.6</td>
<td>~120-140 134</td>
<td>~120-140 640.5 760°C 16 800°C</td>
<td>162 800°C Super &gt;&gt; alloy 230</td>
<td>Excl. SCR, HCR Super. SCR, HCR Excl. SCR, HCR Excl. SCR, HCR Good. SCR, HCR Good. SCR, HCR Good. SCR, HCR</td>
<td>Readily</td>
<td>Readily</td>
<td>36.8%</td>
<td>Good SR, HR 18% Good SR, HR</td>
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<td>HAD 8077</td>
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<td>~120-140 134</td>
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<td>162 800°C Super &gt;&gt; alloy 230</td>
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<td>Readily</td>
<td>Readily</td>
<td>36.8%</td>
<td>Good SR, HR 18% Good SR, HR</td>
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<tr>
<td>Udiment 500</td>
<td>~16-18 20-100°C 13.3</td>
<td>~120-140 134</td>
<td>~120-140 640.5 760°C 16 800°C</td>
<td>162 800°C Super &gt;&gt; alloy 230</td>
<td>Excl. SCR, HCR Super. SCR, HCR Excl. SCR, HCR Excl. SCR, HCR Good. SCR, HCR Good. SCR, HCR Good. SCR, HCR</td>
<td>Readily</td>
<td>Readily</td>
<td>36.8%</td>
<td>Good SR, HR 18% Good SR, HR</td>
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VI. Ni base superalloys

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<th>Alloys</th>
<th>TEC RT~800°C ×10⁻⁶ K⁻¹</th>
<th>Electrical resistivity (bulk) ×10⁻⁶ Ω.cm</th>
<th>Yield strength σ₀.₂ (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Oxidation Resistance ×10⁻⁶ mg².cm⁻⁴.s⁻¹</th>
<th>Hot Corrosion resistance</th>
<th>Join-ability</th>
<th>Form-ability or Elongation</th>
<th>Cost factor</th>
<th>Others</th>
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<tbody>
<tr>
<td>MA956</td>
<td>11.3 20-100°C 131</td>
<td>120 800°C</td>
<td>Super. SCR, HCR</td>
<td>9%</td>
<td>Exc. SR, HR</td>
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Fe base superalloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>TEC RT~800°C ×10⁻⁶ K⁻¹</th>
<th>Electrical resistivity (bulk) ×10⁻⁶ Ω.cm</th>
<th>Yield strength σ₀.₂ (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Oxidation Resistance ×10⁻⁶ mg².cm⁻⁴.s⁻¹</th>
<th>Hot Corrosion resistance</th>
<th>Join-ability</th>
<th>Form-ability or Elongation</th>
<th>Cost factor</th>
<th>Others</th>
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<tbody>
<tr>
<td>MA956</td>
<td>11.3 20-100°C 131</td>
<td>120 800°C</td>
<td>Super. SCR, HCR</td>
<td>9%</td>
<td>Exc. SR, HR</td>
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<tr>
<td>Alloys</td>
<td>TEC RT–800°C $\times 10^{-6}.K^{-1}$</td>
<td>Electrical resistivity (bulk) $\times 10^{-6} , \Omega \cdot \text{cm}$</td>
<td>Yield strength $\sigma_{0.2}$ (MPa)</td>
<td>Elastic Modulus (GPa)</td>
<td>Oxidation Resistance $\times 10^6 , \text{mg}^2. \text{cm}^{-4} \cdot \text{s}^{-1}$</td>
<td>Hot Corrosion resistance</td>
<td>Join-ability</td>
<td>Form-ability or Elongation</td>
<td>Cost factor</td>
<td>Others Machinability (%)</td>
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<td>VII. Ferritic Stainless Steels</td>
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<tr>
<td>Kanthal (APM)</td>
<td>16.3</td>
<td>11.1</td>
<td>12.2*</td>
<td>~120-140</td>
<td>134</td>
<td>&gt;550 RT 800°C 200 (est) 1.0 1,000°C</td>
<td>Super. SCR, HCR</td>
<td>&lt;25%</td>
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<td>Exc. SR</td>
</tr>
<tr>
<td>Fecralloy</td>
<td>20-100</td>
<td>20-100</td>
<td>650°C</td>
<td>134</td>
<td>12.2</td>
<td>100-200</td>
<td>800°C</td>
<td>200 (est)</td>
<td>1.0 1,000°C</td>
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* Tested at PNNL
## VI. Selected Elemental Metals and Intermetallics

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<tr>
<th>Alloys</th>
<th>TEC RT~800°C ×10⁻⁶ K⁻¹</th>
<th>Electrical resistivity (bulk) ×10⁻⁶ Ω.cm</th>
<th>Yield strength σ₀.₂ (MPa)</th>
<th>Vapor pressure (Pa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Oxidation Resistance ×10⁻⁶ mg².cm⁻⁴.s⁻¹</th>
<th>Melting point (°C)</th>
<th>Join-ability</th>
<th>Form-ability or Ductility</th>
<th>Cost factor</th>
<th>Others</th>
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<tbody>
<tr>
<td>Silver FCC</td>
<td>20.61</td>
<td>1.7</td>
<td>55 RT</td>
<td>10² 800°C</td>
<td>71 RT</td>
<td>1064</td>
<td>961</td>
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<td>Gold FCC</td>
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<td>2.4</td>
<td>125 RT</td>
<td>10⁻² 800°C</td>
<td>74.5 RT</td>
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<td>Platinum FCC</td>
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<td>150 RT</td>
<td>1.3x10⁻³ 946°C</td>
<td>156 RT</td>
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<td>13.3</td>
<td>6.8</td>
<td>&gt;150 RT</td>
<td>10⁻⁴ 965°C</td>
<td>207 RT</td>
<td>1084</td>
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<td>Copper FCC</td>
<td>16.5</td>
<td>10</td>
<td>10</td>
<td>10⁻⁵ 800°C</td>
<td>68 RT</td>
<td>1875</td>
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<td>Chromium BCC</td>
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<td>68</td>
<td>282 RT</td>
<td>26.5</td>
<td>62</td>
<td>660</td>
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<td>Aluminum FCC</td>
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<td>Titanium HCP</td>
<td>8.4</td>
<td>420</td>
<td>10–35 (annealed) 140</td>
<td></td>
<td>178 Limited &gt;650°C</td>
<td>1390</td>
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<tr>
<td>Fe₃Al Ordered BCC</td>
<td>12.3</td>
<td>500 (est) 800°C</td>
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Notes:

1. Yield strength $\sigma_{0.2}$ (bar) (MPa): yield strength at 0.2% offset. Normally data from bar tests at a temperature around 800°C is collected. If bar test data is not available, the sheet test data is used and marked as B in tables. Typically a yield strength from a bar test is higher than that from a sheet test.
2. Oxidation resistance is measured by the parabolic rate constant in unit of $\text{mg}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$.
3. Corrosion resistance: including hot corrosion (sulfidation) and carburization resistance, abbreviated as HCR and CR respectively.
4. Formability: measured by Erichsen or Olsen cupping depth (mm), marked as E and O, respectively. If the E or O cupping depth at room temperature (RT) is not available, the elongation data from bar tests is collected as alternatives for comparison. The data from sheet tests will be used and marked as S in case bar test data is not available.
5. The (bulk) electrical resistance at room temperature is used here. The resistance usually increases with temperature, but normally the resistance (increasing) coefficient is small. The resistance at room temperature provides enough information for evaluation of electrical resistance of alloys.
6. Cost factor is the ratio of ($/\text{lb of alloy}) / ($/\text{lb of stainless steel 446}) in ¼” mils sheet.
7. Machinability of alloys is expressed as a percentage by referring Seco Tools AB. Decreasing values indicate increasing machining difficulty.

Abbreviations:
RT: room temperature
ST: solution treated;
PT: precipitation treated;
SP: solution + precipitation treated;
OCD: typical Olsen cup depth;
SSS: stainless steel;
“~”: Estimated by authors.
Development of (Mn,Co)$_3$O$_4$ Protection Layers for Ferritic Stainless Steel Interconnects

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SP Simner  JW Stevenson
P Singh

July 2005

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(9/2003)
Development of (Mn,Co)$_3$O$_4$ Protection Layers for Ferritic Stainless Steel Interconnects

Executive Summary

A spinel-based surface protection layer has been developed for alloy SOFC current collectors and bi-polar gas separators. The (Mn,Co)$_3$O$_4$ spinel with a nominal composition of Mn$_{1.5}$Co$_{1.5}$O$_4$ demonstrates an excellent electrical conductivity and thermal expansion match to ferritic stainless steel interconnects. A slurry-coating technique provides a viable approach for fabricating protective layers of the spinel onto the steel interconnects. Thermally grown protection layers of Mn$_{1.5}$Co$_{1.5}$O$_4$ have been found not only to significantly decrease the contact resistance between a LSF cathode and stainless steel interconnect, but also inhibit the sub-scale growth on the stainless steel. The combination of the inhibited sub-scale growth, good thermal expansion matching between the spinel and the stainless steel, and the closed-pore structure contribute to the excellent structural and thermomechanical stability of these spinel protection layers, which was verified by a long-term thermal-cycling test. The spinel protection layers can also act effectively to prevent outward diffusion of chromium from the interconnect alloy, preventing subsequent chromium migration into the cathode and contact materials. PNNL is currently engaged in studies intended to optimize the composition, microstructure, and fabrication procedure for the spinel protection layers.

Introduction

Given the reduction in solid oxide fuel cell (SOFC) operating temperatures to the 600-800°C temperature range, it has become possible to consider cost-effective high temperature oxidation-resistant alloys as replacements for conventional lanthanum chromite ceramics for construction of interconnects in SOFC stacks [1-3]. Chromia-forming ferritic stainless steels are considered to be among the most promising candidate materials due to their electrically conducting oxide scale, appropriate thermal expansion behavior, and low cost [3-6]. However, several issues potentially hinder their application, including increasing electrical resistance over time, and the migration of chromium via chromia scale evaporation into SOFC cathodes [7-10], which can lead to degradation in cell electrochemical performance [9-13]. Newly developed alloys such as Crofer22 APU, which is protected at elevated temperatures via formation of a
unique scale comprised of a (Mn,Cr)_3O_4 spinel top layer and chromia or chromia-rich sub-layer [14-16], may offer some improvement in this regard due to the lower volatility of Cr from spinel than from chromia. However, volatility measurements at PNNL indicate that the chromium volatility from the spinel may be only a factor of 2 lower than that from chromia (at 850°C in air with 3%H_2O), so Cr volatility from the spinel as well as any exposed chromia that is not covered by the spinel layer, particularly during the early stages of oxidation, may still result in an unacceptable degradation in cell performance [13,16-18]. Also, it appears that a further improvement in long-term scale stability is needed, particularly for SOFC stacks with an operating temperature >700°C [16,19,20].

As an alternative approach to bulk alloy modification, the interconnect can be surface-modified via application of a protection layer of conductive oxide(s) on the cathode-side. The protection layer is intended to serve as a barrier to both chromium cation outward and oxygen anion inward diffusion, so that it can decrease the alloy oxidation kinetics, mitigate or even prevent chromium migration from the chromium-containing alloy substrate, and minimize the interfacial contact area specific resistance (ASR) between the cathode and the interconnect by limiting the growth of the Cr-based oxide scale, which has relatively low conductivity. Accordingly, the material(s) selected for the protection layer should possess high electrical conductivity coupled with low chromium cation diffusivity. Low oxygen ion diffusivity is also desirable to limit oxidation of the substrate alloy and therefore the subsequent growth of a chromia or chromia-rich scale or interlayer between the protection layer and the bulk alloy. In addition, the thermal expansion behavior of the protection layer material should match that of the substrate alloy and its scale to enhance thermomechanical integrity, particularly during thermal cycling.

Reported examples of protection layers include overlay coatings of conductive perovskite compositions, such as Sr doped lanthanum manganite, ferrite and chromite, which are often used as cathode and interconnect materials in SOFCs [21-24]. These coatings help lower the interfacial contact resistance, but cell performance may still be degraded by chromium migration from either chromium-containing perovskites (e.g. (La,Sr)CrO_3) or non-chromium-containing compositions via chromium cation diffusion through the coatings [9,25]. Other potential challenges associated with perovskite overlay coatings include limited thermomechanical stability due to extensive sub-scale growth resulting from oxygen ion inward diffusion. Spinel
protective layers have also been investigated. Previous work of Larring and Norby [25] on Plansee Ducrolloy (Cr-5%Fe-1%Y₂O₃), an interconnect alloy for high temperature (900-1,000°C) SOFCs, indicated that a (Mn,Co)₃O₄ spinel layer could be a promising barrier to chromium migration. PNNL has investigated thermal growth of (Mn,Co)₃O₄ spinel layers, with a nominal composition of Mn₁.₅Co₁.₅O₄, onto candidate ferritic stainless steels for interconnect applications in SOFCs [26-30]. Both short and long term tests were carried out, demonstrating the effectiveness of the spinel protection layers in improving the metallic interconnect surface stability, mitigating chromium migration, and minimizing interfacial ASR.

This report summarizes PNNL’s ongoing efforts on the development, characterization, and testing of (Mn,Co)₃O₄ spinel-based protection layers for application in the electrochemically active area of the SOFC current collector and gas separator. Coating chemistry, fabrication details, properties, and test results are presented.

1. Structure and Properties of (Mn,Co)₃O₄ Spinels

An ideal spinel oxide consists of a cubic close-packed configuration of O²⁻ ions with metal cations filling one eighth of the tetrahedral sites and one-half of the octahedral sites. Due to lattice distortion, the cubic spinel often transforms to a tetragonal spinel. This is particular true for (Mn,Co)₃O₄ or Mn₁₊δCo₂₋δO₄ (-1.0≤δ≤2.0) systems. Naka, et al [31], reported that, for 0.3<δ<1.9, cubic spinel co-existed with the tetragonal spinel, while generally a single phase of cubic spinel was found for δ in the range of -0.9–0.3. Consistent with those results, the primary spinel prepared and studied at PNNL, which had a nominal composition of Mn₁.₅Co₁.₅O₄, was found by XRD analysis (see Figure 1) to consist of two phases, MnCo₂O₄ and Mn₂CoO₄, reported in JCPDS as #18-1237 [34] and #23-0408 [35], respectively. MnCo₂O₄ is a cubic spinel [31-33], with Mn occupying octahedral interstitial sites and Co occupying both tetrahedral and octahedral interstitial sites in the close packed oxygen ion lattice; while Mn₂CoO₄ possesses a tetragonal spinel structure [35]. To further verify the structure of the synthesized “Mn₁.₅Co₁.₅O₄” spinel, spinels with a Mn/Co ratio of 1:2, i.e. MnCo₂O₄, and a ratio of 2:1, i.e. Mn₂CoO₄, were prepared. XRD analyses on these two compounds indicated that the XRD pattern of the synthesized MnCo₂O₄ matched with JCPDS #18-1237, while the synthesized Mn₂CoO₄ matched with JCPDS #23-0408. Thus the synthesized Mn₁.₅Co₁.₅O₄ spinel was a dual phase material comprised of cubic Mn₁₊δCo₂₋δO₄ and tetragonal Mn₂₋εCo₁+εO₄. δ and ε represent a small
deviation and are reported [31] to be less than 0.3 and 0.1 for the cubic and tetragonal spinels, respectively. (For simplicity, MnCo$_2$O$_4$ and Mn$_2$CoO$_4$ are used in this report to represent the cubic and tetragonal spinels, respectively). A similar combination of spinels was also observed by Aukrust and Muan during their phase-diagram study of the cobalt oxide – manganese oxide system in air [36].

As shown in Figure 2, the Mn$_{1.5}$Co$_{1.5}$O$_4$ spinel demonstrated a good thermal expansion match to ferritic stainless steels such as Crofer22 APU and AISI430, as well as perovskite cathode compositions such as La$_{0.8}$Sr$_{0.2}$FeO$_3$ and La$_{0.8}$Sr$_{0.2}$FeO$_3$. Electrical conductivity tests on the Mn$_{1.5}$Co$_{1.5}$O$_4$ spinel (see Figure 3) indicated an electrical conductivity of ~60 Scm$^{-1}$ at 800$^\circ$C in air, which is 3~4 orders of magnitude higher than Cr$_2$O$_3$ [38], and 2~3 orders higher than MnCr$_2$O$_4$ [37], which is the dominant phase in the top layer of scales grown on Mn-containing oxidation resistance alloys such as Crofer22 APU.

2. Fabrication of Spinel Protection Layers

Several approaches are being pursued at PNNL as potential means of fabricating an adherent spinel protection layer on ferritic stainless steels. One approach that has proven successful is slurry coating. Figure 4 shows a flow chart of the slurry coating process, which starts with powder synthesis and is followed by slurry preparation, coating, and a subsequent heat treatment in a reducing environment. The spinel protection layer is finally formed via thermal growth during heat treatment in air. Two powder synthesis approaches were used:

- Solid-state reaction of MnCO$_3$ and Co$_3$O$_4$
- Glycine-nitrate combustion synthesis process (GNP) [39].

The two synthesis approaches generated powders with different properties which greatly affected the quality of the spinel protection layer and its performance. In particular, the glycine-nitrate process yielded finer, more homogeneous powders than the solid-state approach, leading to improved quality and performance of the spinel protection layers.

To synthesize the spinel via the glycine-nitrate process, appropriate amounts of Mn(NO$_3$)$_2$ and Co(NO$_3$)$_3$ solutions were mixed with glycine and then slowly heated to the combustion point to form the precursor ash. The ash was calcined in air at 800$^\circ$C for 4 hours, attrition-milled, and then fabricated into a screen-printing ink by mixing it with a binder system (Ferro BV-111-2) on a three-roll mill. The ink was applied onto stainless steel coupons by
painting or screen-printing (e.g., 165mesh screen, 0.05mm emulsion). After being dried in an oven in air at 80°C for 1~2 hours, the coated stainless steel coupons were heat-treated in an Ar/3%H\textsubscript{2}O/2.75%H\textsubscript{2} environment at 800°C for 2 hours or more. During the heat-treatment in the reducing environment, the organic binder and solvent were removed and the spinel was reduced into Co and MnO, as confirmed by the XRD analysis shown in Figure 5(a). SEM analysis (see Figure 6(a)) revealed a uniform, porous layer comprised of MnO and metal Co, as well as a thin oxide scale grown between that layer and the substrate Crofer22 APU. (Note that the manganese cobaltite spinels are not stable in fuel environments, and their application as a protection layer is limited to the cathode-side of metallic interconnects). During subsequent oxidation in air, the MnO and Co reacted with oxygen to re-form the spinel phases. This is confirmed by the XRD analysis shown in Figure 5(b) that shows a protection layer grown in air at 800°C after 100 hours. The pattern in Figure 5(b) matched very well with that of as-synthesized Mn\textsubscript{1.5}Co\textsubscript{1.5}O\textsubscript{4} powder (Figure 1(b)). A cross-section SEM image (Figure 6(b)) after the oxidizing heat-treatment shows that the spinel protection layer was well bonded to the Crofer22 APU substrate via an ~1.0 \(\mu\)m thick sub-scale layer that was grown between the spinel protection layer and the metal substrate. A significant amount of (apparently closed) porosity is present in the spinel layer. The densification of the spinel layer from the highly porous layer of MnO and Co is attributed to a sintering process that is enhanced by the spinel formation reactions occurring during the oxidizing heat-treatment. Thus it appears that the reducing heat treatment is an important intermediate step for the thermal growth of spinel protection layers with good adhesion to the ferritic stainless steel. The closed pore microstructure in the protection layer may also be beneficial by providing strain tolerance to improve thermomechanical stability during SOFC operation. As no obvious boundary was discernible between the sub-scale layer and the spinel protection layer, it appears that the Mn-Co spinel and the native oxide scale grown on Crofer22 APU, which is comprised of (Mn,Cr)\textsubscript{3}O\textsubscript{4} spinel and Cr\textsubscript{2}O\textsubscript{3} [4,16], are mutually compatible. Importantly, EDS analysis on the cross-section indicated that no detectable chromium penetration into the protection layer had occurred after a duration of 100 hours at 800°C.

The same approach was also used to fabricate a Mn\textsubscript{1.5}Co\textsubscript{1.5}O\textsubscript{4} protection layer onto AISI430 (Figure 7). As in the case for Crofer22APU, the protection layer acted as an effective Cr barrier during the 100 hours of heat treatment.
3. Performance and Stability

(A) Electrical Performance and Thermomechanical Stability

Stainless steel samples with spinel protection layers were first evaluated in a configuration (described in Reference 26) which simulates the interconnect/cathode structure in SOFC stacks. Porous LSF layers, representing the cathodes, were fabricated onto both sides of a dense, 2mm thick LSF substrate via screen-printing of LSF ink and subsequent sintering at 1150°C in air. (For the balance of this paper, these porous LSF layers will be referred to as cathodes, although in these symmetrical ASR tests, no cathodic processes were occurring). The LSF substrate with cathodes was then sandwiched symmetrically between two Crofer22 APU coupons, representing the interconnects, that had been screen-printed with the spinel-forming ink and subsequently heat-treated in a reducing environment. A contact layer of LSCM (La$_{0.6}$Sr$_{0.2}$Co$_{0.5}$Mn$_{0.5}$O$_3$) ink was applied between the Crofer22 APU coupons and cathodes. During tests, a dead load of 6.5 psi was uniformly applied to the “sandwich” in order to promote interfacial contact. A four point resistance technique was adopted to determine the resistance of the interconnect/cathode assembly. A current density of 0.5A.cm$^{-2}$ was applied during the test, while the voltage was monitored as a function of time. The contact area-specific resistance (ASR) between a cathode and an interconnect was obtained by dividing the measured ASR by two (due to the symmetrical test design). Both isothermal and thermal cyclic (from room temperature to 800°C at a rate of 5°C/min) tests were performed.

Figure 8 shows the contact ASR for Crofer22 APU with the spinel protection layer as a function of time at 800°C in air, in comparison with that of unprotected Crofer22 APU. For the unprotected Crofer22 APU, the contact ASR increased steadily to 39 mohm.cm$^2$ after 400 hours. In contrast, the ASR for the Crofer22 APU with the spinel protection layer had a low initial value (~17 mohm.cm$^2$) which subsequently decreased to ~13 mohm.cm$^2$ after 400 hours. The lower interfacial ASR and its decreasing trend with time is tentatively attributed to the high electrical conductivity of the manganese cobalt spinel, and interactions between the protection layer and the contact material, which led to an improved electrical contact over time between these two layers. The observed contact ASR was lower than previously reported for perovskite overlay coatings, which increased with time [40,41].
After the short-term test, SEM analysis on the cross-section of the tested sample confirmed that the spinel layer was well-bonded to the Crofer22 APU and free of spallation or cracks. A smooth, continuous interface was observed between the protection layer and the sub-scale grown on the stainless steel. Again EDS found no evidence of Cr penetration through the protection layer into either the L SCM contact layer or the LSF cathode. In contrast, 6.0~10.0 wt% Cr was generally detected in the L SCM contact layer between the bare (unprotected) Crofer22 APU and LSF cathode, and 2.0~3.0 wt% Cr in the LSF cathode, after 400 hours of testing.

To examine its long-term performance and thermomechanical stability, Crofer22 APU with the thermally grown spinel protection layers was further tested for a period of six months under a total of 125 thermal cycles (plus three occurrences of unscheduled power failure). During this test (see Figure 9), the contact ASR between the LSF cathode and the metallic interconnect at 800ºC steadily decreased from the starting value of 15.0 mohm.cm² to 14.3 mohm.cm², demonstrating excellent stability. SEM analysis on the cross-section of the tested sample at the edge areas, where there was no contact paste applied, as shown in Figure 10(a), indicated good thermomechanical stability of the thermally-grown protection layers. No spallation or chipping was observed, and the sub-scale only grew to a thickness ~2.0 µm. In contrast, as shown in Figure 10(b), spallation or chipping was observed on the portion of the Crofer22 APU without a protection layer, and the scale grew to a thickness over 10 µm, which is consistent with previous work [16]. The spalled fragments were identified by EDS point analysis to be primarily (Mn,Cr)₃O₄ spinel. Thus, the spinel protection layer on Crofer22 APU not only drastically reduced the interfacial ASR, but also inhibited the scale growth on the ferritic stainless steel by limiting oxygen ion diffusion inward through the spinel layer. The excellent thermomechanical stability and stable electrical performance are attributed to the inhibited sub-scale growth, an improved strain tolerance of the porous microstructure, and a good thermal expansion match between the spinel and the metal substrate.

Also, unlike many overlay coatings such as perovskites [9,25,41], the spinel protection layer acted as an effective mass transport barrier in stopping chromium migration from the metal. EDS analysis (see Figure 11) revealed a sharp Cr profile across the interface between the sub-scale and the spinel protection layer, with no chromium detectable in the spinel protection layer and at its surface after the six months thermal cycling test. No Cr was found in the L SCM
contact and the LSF cathode. For example, the EDS analysis of the contact layer at point “A” in Figure 7 indicated 18% Mn, 6.0% Co, 17.0% La, 7.0% Sr, 52% O, and no Cr.

As verified by both the short- and long-term tests, the manganese cobaltite spinel protection layers thermally grown on ferritic stainless steel interconnects appear to be very effective in improving the surface stability and electrical conductivity of these metallic interconnect materials, and in preventing outward chromium cation diffusion to the interconnect surface.

(B) Stability During Cell Test

In addition to the ASR and thermomechanical stability evaluations, the spinel protection layers were further examined for their effect on the stability of electrochemical performance of an anode-supported SOFC. The cell was fabricated with a Ni-YSZ anode, thin-film YSZ electrolyte, and a La0.8Sr0.2FeO3 (LSF) cathode, as well as a Ce0.8Sm0.2O1.9 interlayer (~5 µm sintered thickness) between the cathode and electrolyte. A piece of stainless steel with the Mn1.5Co1.5O4 protection layer [18] was used as the cathode current collector, and applied to the cathode (under a compressive load) with Pt paste. Precise cell fabrication and testing techniques are detailed in an earlier publication [42].

Overall the cell tests indicated the effectiveness of the (Mn,Co)3O4 spinel protection layers in stopping chromium migration from the ferritic stainless steel interconnects and thus preventing cathode poisoning. As an example, Figure 12 shows the electrochemical performance of a cell with a Crofer22 APU cathode current collector with the spinel protection layer, in comparison with that of a cell with an unprotected Crofer22 APU current collector. The data (obtained at 0.7V/750°C) show a rapid degradation of the cell with the unprotected Crofer22 APU current collector. SEM/EDS analysis on the cross-section of the tested sample indicated 1~3 atomic % Cr in the LSF cathode and the ceria interlayer between the cathode and the YSZ electrolyte. Chromium migration into a LSF cathode was also observed by Simner et al. [43] when a perovskite conductive oxide contact material was used. In contrast, the cell with the Crofer22 APU that was protected by the thermally grown Mn1.5Co1.5O4 spinel layer also experienced an initial drop in performance but then exhibited a cathode conditioning effect [44], which was followed by stable performance. SEM/EDS analysis on the cross-section of this cell
found no Cr deposition or migration into the LSF cathode and the ceria interlayer. While the mechanisms behind the behavior of the two cells are complicated [45], the correlation between stable/unstable performance and the absence/presence of Cr in the cell is apparent.

Thus it appears that the thermally grown Mn$_{1.5}$Co$_{1.5}$O$_4$ spinel protection layer on the ferritic stainless steel acted effectively as a barrier to outward diffusion of chromium from the steel. Both the prevention of chromium migration and decreased ASR (as indicated by the ASR tests described above) likely contributed to the improved electrochemical performance observed in the cell with the spinel-protected current collector.

**Summary**

The (Mn,Co)$_3$O$_4$ spinel with a nominal composition of Mn$_{1.5}$Co$_{1.5}$O$_4$ demonstrates an excellent electrical conductivity and thermal expansion match to ferritic stainless steel interconnects. A slurry coating approach appears to a viable means of fabricating protective layers of the spinel onto the steel interconnects. Thermally grown protection layers of Mn$_{1.5}$Co$_{1.5}$O$_4$ not only significantly decreased the contact resistance between a LSF cathode and the stainless steel interconnect, but also inhibited the sub-scale growth on the stainless steel. The combination of the inhibited sub-scale growth, good thermal expansion matching between the spinels and the stainless steel, and the closed-pore structure may contribute to the excellent structural and thermomechanical stability of these spinel protection layers, which was verified by a long-term thermal-cycling test. The spinel protection layers can also act effectively to prevent outward diffusion of chromium from the interconnect alloy, preventing subsequent chromium migration into the cathode and contact materials. PNNL is currently engaged in studies intended to optimize the composition, microstructure, and fabrication procedure for the spinel protection layers.

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Figure 1. X-ray diffraction patterns of (a) MnCo$_2$O$_4$, (b) Mn$_{1.5}$Co$_{1.5}$O$_4$, and (c) Mn$_2$CoO$_4$, all of which were synthesized via a glycine-nitrate process, followed by calcination at 800ºC for 4 hours in air.
Figure 2. Thermal expansion behavior of Mn$_{1.5}$Co$_{1.5}$O$_4$, in comparison with that of La$_{0.8}$Sr$_{0.2}$MnO$_3$, La$_{0.8}$Sr$_{0.2}$FeO$_3$, Crofer22 APU and AISI430.
Figure 3. Electrical conductivity of transition metal oxide spinels measured at PNNL, in comparison with reported data [37].
Figure 4. Flow chart for fabrication of spinel protection layers on ferritic stainless steel interconnects via slurry coatings.
Figure 5. X-ray diffraction patterns of protection layers on Crofer22 APU: (a) after a heat-treatment at 800°C for 24 hours in 2.75%H2/bal. Ar, (b) after the subsequent oxidation at 800°C in air for 100 hours.
Figure 6. SEM images of cross-sections of protection layers on Crofer22 APU: (a) after a heat-treatment at 800°C for 24 hours in 2.75%H₂/bal. Ar, (b) after the subsequent oxidation at 800°C in air for 100 hours.
Figure 7. SEM images of cross-sections of protection layers on AISI430: (a) after a heat-treatment at 800°C for 24 hours in 2.75%H₂/bal. Ar, (b) after the subsequent oxidation at 800°C in air for 100 hours.
Figure 8. Interfacial ASR between a LSF cathode and a Crofer22 APU current collector with and without the spinel protection layer. Temperature - 800°C, Exposure atmosphere - air.
Figure 9. Contact ASR of $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3||\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_3||\text{Crofer22 APU}$ as a function of thermal cycle numbers. The Crofer22 APU was screen-printed with the $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ spinel paste and then heat-treated at 800°C in the reducing environment for 24 hours before being placed in the test stand and continuously tested for six months.
Figure 10. SEM images of the cross-section of Crofer22 APU after testing for 6 months including over 125 thermal cycles: (a) at the side with a thermally grown Mn$_{1.5}$Co$_{1.5}$O$_4$ spinel protection layer and (b) at the side without protection.
Figure 11. Microstructural and compositional analyses on the Mn$_{1.5}$O$_{1.5}$O$_4$ protection layer subjected to a contact ASR measurement for a period of six months including thermal cycling.
Figure 12. Electrical performance behavior of cells utilizing bare and protected current collectors:

With unprotected current collector, cell shows rapid performance degradation
With spinel protected current collector, cell performance improves with time.

Cell attributes: Crofer22 APU cathode current collector, La$_{0.8}$Sr$_{0.2}$FeO$_3$ cathode, Sm-doped ceria interlayer, YSZ electrolyte and Ni/YSZ anode.
Analysis of Percent On-Cell Reformation of Methane in SOFC Stacks: Thermal, Electrical, and Stress Analysis

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Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830
Analysis of Percent On-Cell Reformation of Methane in SOFC Stacks: Thermal, Electrical, and Stress Analysis

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Work Performed under
SECA Core Technology Program and
Contract DE-AC05-76RL01830

Report Submitted to:
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Executive Summary

This report summarizes a parametric analysis performed to determine the effect of varying the percent on-cell reformation (OCR) of methane on the thermal, electrical, and mechanical performance for a generic, planar solid oxide fuel cell (SOFC) stack design. OCR of methane can be beneficial to an SOFC stack because the reaction (steam-methane reforming) is endothermic and can remove excess heat generated by the electrochemical reactions directly from the cell. The heat removed is proportional to the amount of methane reformed on the cell. Rapid reaction kinetics provided by the high-temperature SOFC operation and excess steam over the nickel-based anode catalyst ensure complete methane conversion. Thus, the thermal load varies with methane concentration entering the stack. The endotherm due to the fast reformation reaction can cause a temperature depression on the anode near the fuel inlet, resulting in large thermal stresses. This effect depends on factors that include inflowing methane concentration, local temperature, and stack geometry.

The analysis assumed the fuel would be partially to fully pre-reformed in an external reformer such that the desired fuel compositions would be delivered to the stack, where the remaining percentage of the reformation reaction would be completed on-cell. Simulations were performed using an SOFC stack modeling tool developed at PNNL and validated for the prediction of fuel use, on-cell methane reforming, and distribution of temperature. The study was performed using three-dimensional stack model geometries. Cross-flow, co-flow, and counter-flow configuration stacks of 10x10- and 20x20-cm cell sizes were examined. Thermal performance was evaluated based on the predicted maximum temperature difference on the anode. Electrical performance was based on the predicted power output. Mechanical performance was based on the maximum principal stress on the anode. Fuel utilization was established at 75%. The effect of cathode air cooling was included in the study by examination of 30% and 15% air utilizations.

The analysis showed for the counter-flow and cross-flow stacks of 10x10-cm size the stress and temperature difference would be minimized when between 40 and 50% of the reformation reaction occurred on the anode. Gross electrical power density was virtually unaffected by %OCR. For all stack configurations and sizes the inflow temperature increased with %OCR as the subsequent heat load decreased. Cooling provided by the cathode airflow associated with 30% air utilization was not substantially improved upon by 15% air use for the smaller (10x10-cm) stack size. The increased airflow associated with 15% air utilization was needed for cooling the larger (20x20-cm) stacks. The co-flow stack exhibited the largest benefit from the additional cathode air cooling and had the lowest anode stresses of the 20x20-cm stacks. For the conditions and particular generic stacks of this study, the results suggest 40 to 50% OCR should be considered for cross-flow and counter-flow stacks, and higher percentages may be desirable in co-flow stacks. Results of this study also suggest that 30% air utilization may be sufficient for 10x10-cm cell stacks, and 15% air utilization should be considered for 20x20-cm cell stacks.
Acknowledgments

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1.0 Introduction

The solid oxide fuel cell (SOFC) industry continues to develop larger, more powerful cell stacks for stationary power applications, and thermal management remains a critical issue for the reliable operation of these stacks. On-cell reforming (OCR) of methane is an effective means of removing excess heat generated within an SOFC stack. OCR refers to reforming the fuel directly on the anode. Of the various heat removal methods available for use in SOFC stacks, OCR has the potential to be the most beneficial to the overall system. The reformation reaction is endothermic and, when used on the anode, immediately removes excess heat generated by the electrochemical oxidation reactions. The demand on an external fuel reformer (and associated heat exchanger) decreases as the percentage of the reformation reaction that takes place on-cell increases. Thus, the size of the external reformer and related heat exchanger could be decreased while also decreasing the thermal load experienced by the stack.

In the reformation reaction, methane combined with steam is converted at high temperature to hydrogen and carbon monoxide in the presence of a nickel catalyst such as the typical nickel-based (Ni-YSZ) SOFC anode (Eq. 1). The hydrogen and carbon dioxide gas products can be consumed electrochemically in the oxidation reactions (Eq. 2 and 3) and are also subject to the rapid water-gas shift reaction (Eq. 4).

$$CH_4 + H_2O \Rightarrow 3H_2 + CO$$  \hspace{1cm} (1)

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + 2e^-$$  \hspace{1cm} (2)

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 + 2e^-$$  \hspace{1cm} (3)

$$CO + H_2O \leftrightarrow CO_2 + H_2$$  \hspace{1cm} (4)

On-cell reformation is attractive because of the decreased thermal load it can provide as well as the cost benefits of decreased reformer size. However, the kinetics of the reformation reaction on a standard Ni-YSZ anode is rapid, and with increasing %OCR, the resultant endotherm can cause a significant local temperature depression near the fuel inlet on the anode. Cooling near the fuel inlet and subsequently increased heating downstream due to increased hydrogen concentration and electrical current density can set up a large difference between the minimum and maximum temperatures on the cell ($\Delta T$). Along with the cell $\Delta T$ there can be and increase in the thermal stresses on the anode\(^1\) creating an unreliable condition for cell operation.

The objective of this report is to analyze the effect of varying the percentage of the reformation reaction occurring on-cell on the stack performance. In particular, this work addresses the effect that variable %OCR has on the thermal, electrical, and mechanical performance of a generic stack design with co-flow, counter-flow, and cross-flow configurations
and 10x10- and 20x20-cm active cell sizes. The thermal performance is evaluated based on the predicted cell $\Delta T$ with analysis of the heat load and balances. The electrical performance is based on the predicted output power density. The mechanical performance is based on the maximum principal anode stress.
2.0 Methodology

A computational modeling tool for simulating the multi-physics of SOFC operation was used in this study. The PNNL developed SOFC-MP code solves the equations for mass transport, energy, and electrochemistry required to predict the fluid flow, temperature, species, and current density distributions in a three-dimensional SOFC geometry.\(^2,3,4\) The electrochemistry model used was described by Chick et al.,\(^5\) calibrated\(^6,7\) for application to planar stack simulations, and updated to provide an improved anode concentration polarization model.\(^8\) The capabilities of these tools have also been expanded to incorporate steam-methane reformation for simulating on-cell reforming\(^9\) and have been updated with a rate expression derived experimentally at PNNL:\(^10\)

\[
(-r_{CH_4})(mol / gm_{cat} / s) = (2.188E8)e^{-\frac{E_{act}}{RT}} C_{CH_4} C_{CO_2}^{-0.0134}
\]

The temperature, T, is in Kelvin, the universal gas constant, R is 8.314 J/mol-K, the activation energy, \(E_{act}\), is 94,950 J/mol, and the concentrations, \(C_i\), are in units of mol/cc. A steam-to-carbon ratio of at least 1.0 (S:C=1.0) was used in all of King’s tests. While the methane conversion rate showed no dependence on the steam concentration, a slight hindering effect was identified due to the concentration of CO\(_2\). This expression (Eq. 5) represents fast kinetics although it does include a self-leveling effect. As the temperature decreases locally due to the endotherm, the reaction slows as a consequence. The rate increases with increased methane concentration. Hence, larger endothermic effects are expected with increased OCR.

In the study it was assumed the unreformed fuel mixture containing methane, steam, and nitrogen passed through a fuel stream pre-heater to an external reformer using excess steam (S:C = 2.0) ultimately to prevent coking of the anode. In Eq. (1) through (4), one mole of CH\(_4\) is converted to three moles of H\(_2\) and one mole of CO. In the shift reaction, one mole of CO (and H\(_2\)O) is converted to one mole of H\(_2\) (and CO\(_2\)); or the CO can be oxidized directly, as H\(_2\) is for generating electrical current. Thus the fuel content of gas mixtures that contain CO and CH\(_4\) (on a mol/s basis) is the sum of mol/s H\(_2\), mol/s CO and four times the mol/s CH\(_4\).

This study examined fuels with compositions representing 0 to 80% OCR. Regardless of the fuel feed composition, the fuel content in all cases was 4.15E-06 mol/s/cm\(^2\). Table 2.1 summarizes the molar compositions of partially reformed fuel mixtures supplied from an external reformer to the stack for the simulations (see the appendix for mass compositions of the fuel mixtures). Methane made up 28% of the total unreformed fuel mixture. When the fuel was 20% pre-reformed (in preparation for 80% OCR) the resulting mixture, as shown in Table 2.1, contained 20.2% methane, 11.8% hydrogen, 48.8% steam, etc. As the OCR decreased to zero, the methane was fully converted and the hydrogen and steam concentrations were 53.8% and 18.1%, respectively.
Table 2.1.  Molar Compositions of Partially Reformed Fuel Mixtures Supplied from an External Reformer to the Stack (mole fraction)

<table>
<thead>
<tr>
<th>%OCR</th>
<th>H2</th>
<th>CO</th>
<th>H2O</th>
<th>CO²</th>
<th>CH4</th>
<th>N²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.538</td>
<td>0.127</td>
<td>0.181</td>
<td>0.052</td>
<td>0.000</td>
<td>0.101</td>
</tr>
<tr>
<td>10</td>
<td>0.503</td>
<td>0.112</td>
<td>0.205</td>
<td>0.056</td>
<td>0.019</td>
<td>0.105</td>
</tr>
<tr>
<td>20</td>
<td>0.465</td>
<td>0.096</td>
<td>0.232</td>
<td>0.059</td>
<td>0.039</td>
<td>0.109</td>
</tr>
<tr>
<td>30</td>
<td>0.423</td>
<td>0.080</td>
<td>0.262</td>
<td>0.061</td>
<td>0.060</td>
<td>0.114</td>
</tr>
<tr>
<td>40</td>
<td>0.376</td>
<td>0.064</td>
<td>0.295</td>
<td>0.062</td>
<td>0.084</td>
<td>0.118</td>
</tr>
<tr>
<td>50</td>
<td>0.324</td>
<td>0.049</td>
<td>0.333</td>
<td>0.061</td>
<td>0.110</td>
<td>0.124</td>
</tr>
<tr>
<td>60</td>
<td>0.264</td>
<td>0.033</td>
<td>0.377</td>
<td>0.058</td>
<td>0.137</td>
<td>0.129</td>
</tr>
<tr>
<td>70</td>
<td>0.196</td>
<td>0.020</td>
<td>0.428</td>
<td>0.052</td>
<td>0.168</td>
<td>0.136</td>
</tr>
<tr>
<td>80</td>
<td>0.118</td>
<td>0.008</td>
<td>0.488</td>
<td>0.042</td>
<td>0.202</td>
<td>0.142</td>
</tr>
</tbody>
</table>

After the electrochemical solution was obtained, the temperature profile was used as a load in a structural analysis to evaluate the stresses in the cell. The maximum principal stress of the anode was then evaluated for each of the cases.
3.0 Modeling Approach

3.1 Model Geometry

Multiple model geometries were used in this work. Generic cross-flow, co-flow, and counter-flow planar SOFC three-dimensional stack models were created in 10x10- and 20x20-cm cell sizes. The footprints for the geometries are shown in Figure 3.1. Each model comprised 53,312 computational elements within the footprint of the three-dimensional stack. The models included 1-mm-tall fuel and air flow regions, 0.66-mm-thick PEN, 2-mm- (~80 mil-) thick separator/interconnect plates top and bottom, and 0.2-mm-thick by 6-mm-wide glass-ceramic seals at the stack perimeter. The computational grid used within the active area consisted of 50 elements in both the X and Y planar coordinates.

![Figure 3.1. Exploded Assemblies for the a) Co- and Counter-Flow Configuration for the 10x10- and 20x20-cm Cases and b) Cross-Flow Configuration for the 10x10- and 20x20-cm Cases. Geometries consist of (bottom to top) lower separator plate, cathode flow region/interconnect, lower seal, cell, upper seal, anode flow region/interconnect, and upper separator plate.](image)

3.2 Boundary Conditions

Each model was constructed to represent a single repeating cell unit located at the mid-level of a large, multiple-cell stack, and gradients in the vertical direction were assumed small; thus cyclic boundaries were used at the top and bottom surfaces of the model to represent this condition. It was assumed the stack was operating within an insulated enclosure with an air gap between the stack and enclosure walls. Wall boundaries at the stack perimeter accounted for
natural convection of air surrounding the stack and radiation across the gap to the container walls. Constant mass inflow boundaries were used for the air and fuel streams.

The solutions were adjusted to achieve average cell temperature and current density to 750°C and 0.6 A/cm, respectively. In the simulations, the iterative solutions for all cases were well converged with respect to mass, momentum, energy, chemistry, and electrochemistry. Because all cases simulated stack operation at the same average temperature and current density except for variations in the output power, the differences in net heat load were attributable to the heat removed by OCR. Subsequently, the thermal performance of each stack could be compared directly.

For the structural evaluation, minimal displacement support boundary conditions were used at the bottom of the cell. These simplified boundary conditions do not constrain the unit cell model as well as if it was within a full stack and thus enable more component deflection, which can contribute to the stress.

### 3.3 Electrochemical Performance and Material Properties

For these analyses, the electrochemical performance of a cell operating on the fully pre-reformed fuel was taken to be 0.60 A/cm² at 0.68 V and 75% fuel utilization, at an average cell temperature of 750°C. Two air flow rates were used to examine the cooling effect of air at 30% and 15% air utilization. In the electrochemistry model, the Butler-Volmer parameters were set as $\alpha_{BV} = 0.6$, $k_{BV} = 150,000$ A/cm² and $E_{act,BV} = 118,000$ J/mole. Anode, electrolyte, and cathode thicknesses were 600, 10, and 50 microns, respectively. The anode and cathode porosity was 30%, and the tortuosity was 2.5 for both electrodes. Thermal properties used in the model are summarized in Table 3.1. The temperature dependent elastic modulus (Pascals) and coefficients of thermal expansion (1/T) for the stack materials are shown in Figures 3.2 and 3.3, respectively.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg/m³)</th>
<th>Thermal Conductivity (W/m-K)</th>
<th>Specific Heat (J/kg-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases (air, fuel)</td>
<td>Ideal gas: $\rho = \rho(T)$</td>
<td>Multicomponent mass weighted</td>
<td>Multicomponent mass weighted</td>
</tr>
<tr>
<td>PEN</td>
<td>4300</td>
<td>3</td>
<td>0.06 (steady)</td>
</tr>
<tr>
<td>430-SS picture frame, separator plate, spacers</td>
<td>7700</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Seal (glass)</td>
<td>2800</td>
<td>1.05</td>
<td>0.06</td>
</tr>
<tr>
<td>Cathode flow space (effective)</td>
<td>Same as cathode air</td>
<td>13 (~half that of I/C uniform channel/rib pitch)</td>
<td>Same as cathode air</td>
</tr>
<tr>
<td>Anode flow space (effective)</td>
<td>Same as anode fuel</td>
<td>9.1</td>
<td>Same as anode fuel</td>
</tr>
</tbody>
</table>

Table 3.1. Thermal Properties Used in the Simulations
Figure 3.2. Temperature-Dependent Elastic Modulus (Pascals)

Figure 3.3. Temperature-Dependent Coefficient of Thermal Expansion (1/T)
4.0 Results for 10x10-cm Cell Size

To analyze the effect of %OCR in the 10x10-cm cell size, model geometries of cross-flow, co-flow, and counter-flow configurations were created as described in Section 3. For each flow configuration, cases simulating OCR ranging from 0 to 80% per compositions summarized in Table 3.1, and air flow rates associated with air utilizations of 30% and 15% were performed. Enough fuel mixtures were simulated to identify the thermal and power output behavior trends for each flow configuration, but not all of the fuel mixtures were simulated for all geometries.

4.1 Cross Flow 10x10 cm

Figure 4.1 shows the cell $\Delta T$ (triangular icons), and the maximum principal stress (S1) in the anode (red square or green “x” icons) for each 10x10-cm cross-flow case versus %OCR. The scale for the cell $\Delta T$ is at left in the figure and that for the stress is at right. Cell $\Delta T$ for this generic 10x10 cross-flow stack and 30% air utilization varied between 74° and 82°C with a minimum at 50% OCR. The anode stress somewhat followed the trend of $\Delta T$ and exhibited a minimum value at intermediate %OCR for 30% air use. As shown in the figure, when more air was supplied to the stack (15% air use) the variation of stress was decreased, but the magnitude of the stress was not decreased substantially. For both air utilizations, the minimum anode stress was about 14-MPa. These results are summarized in Table 4.1.

![Figure 4.1. Cell Temperature Difference ($\Delta T$) and Maximum Principal Stress (S1) Versus %OCR for 10x10-cm Cross-Flow Cases](image-url)
Table 4.1. Summary of Results for 10x10-cm Cell Size (75/30% fuel/air utilization). Cases below the dashed line in each block of data are results for 15% air utilization.

<table>
<thead>
<tr>
<th>Case</th>
<th>%OCR</th>
<th>Temperature, °C</th>
<th>Anode Stress</th>
<th>Power</th>
<th>Heat In</th>
<th>Heat Out, W</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inflow Min Max</td>
<td>AT S1max, MPa</td>
<td>W/cm² Total Air Fuel Walls Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cross-Flow Cases: 10x10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>550 699 778 79</td>
<td>17.2 0.404</td>
<td>40.5 -12.1 -16.7 -11.7 -40.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>651 700 774 74</td>
<td>14.8 0.403</td>
<td>30.3 -3.4 -15.7 -11.2 -30.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>677 701 775 74</td>
<td>14.2 0.403</td>
<td>27.9 -1.2 -15.5 -11.2 -27.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>701 701 775 74</td>
<td>13.9 0.403</td>
<td>25.4 0.9 -15.2 -11.2 -25.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>748 696 778 82</td>
<td>15.1 0.403</td>
<td>20.7 4.8 -14.6 -11.0 -20.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>644 703 779 77</td>
<td>15.3 0.405</td>
<td>40.4 -14.4 -14.4 -11.6 -40.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>709 708 774 66</td>
<td>14.0 0.405</td>
<td>27.8 -2.0 -14.7 -11.1 -27.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>746 697 777 80</td>
<td>14.1 0.404</td>
<td>20.6 4.9 -14.5 -11.0 -20.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-Flow Cases: 10x10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>559 699 776 77</td>
<td>18.4 0.404</td>
<td>40.4 -11.6 -17.5 -11.3 -40.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>665 703 777 74</td>
<td>17.9 0.403</td>
<td>30.3 -3.4 -16.0 -11.0 -30.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>50</td>
<td>691 704 777 73</td>
<td>17.7 0.403</td>
<td>27.9 -1.3 -15.6 -10.9 -27.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>60</td>
<td>716 705 777 72</td>
<td>17.6 0.403</td>
<td>25.5 0.6 -15.2 -10.9 -25.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>80</td>
<td>758 704 779 74</td>
<td>17.2 0.402</td>
<td>20.8 3.7 -14.6 -9.8 -20.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>645 707 774 68</td>
<td>16.2 0.406</td>
<td>40.3 -13.9 -15.4 -11.0 -40.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>50</td>
<td>722 712 775 63</td>
<td>15.4 0.404</td>
<td>27.8 -1.9 -14.9 -11.0 -27.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>80</td>
<td>759 711 777 66</td>
<td>14.8 0.403</td>
<td>20.8 3.3 -14.4 -9.7 -20.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Counter-Flow Cases: 10x10</td>
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<td>529 696 781 85</td>
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<td>40.2 -13.6 -15.3 -11.3 -40.2</td>
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<tr>
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<td>20</td>
<td>572 710 772 62</td>
<td>19.9 0.406</td>
<td>35.2 -9.0 -15.3 -10.8 -35.2</td>
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<tr>
<td>19</td>
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<td>617 723 768 45</td>
<td>13.8 0.405</td>
<td>30.2 -4.4 -15.3 -10.5 -30.2</td>
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<tr>
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<td>50</td>
<td>640 721 768 47</td>
<td>14.7 0.404</td>
<td>27.8 -2.1 -15.3 -10.4 -27.8</td>
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<td></td>
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<tr>
<td>21</td>
<td>60</td>
<td>663 715 769 54</td>
<td>16.3 0.404</td>
<td>25.4 0.1 -15.2 -10.3 -25.4</td>
<td></td>
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<tr>
<td>22</td>
<td>70</td>
<td>685 709 771 62</td>
<td>17.8 0.404</td>
<td>23.0 2.4 -15.1 -10.2 -23.0</td>
<td></td>
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</tr>
<tr>
<td>23</td>
<td>80</td>
<td>705 704 773 69</td>
<td>19.0 0.403</td>
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<td>710 712 769 57</td>
<td>14.9 0.405</td>
<td>20.6 3.9 -14.4 -10.1 -20.6</td>
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<td></td>
</tr>
</tbody>
</table>

The inflow temperature increased linearly with increasing %OCR. Table 4.1 provides a summary of results from the 10x10 cross-flow, as well as co-, and counter-flow cases. In the table, for cases 1–5 as indicated in the left-most column, the total stack heat load column labeled “Heat In” shows a linear decrease with increasing %OCR. The linear inflow temperature increase was coincident with the linear decrease of heat load. As the heat load decreased, the inflow temperature was increased to maintain the average cell temperature.
The heat flow out of the stack (for cases 1–5 in Table 4.1) through the perimeter walls and the heat removed by the fuel stream decreased only slightly with increasing %OCR, while heat removed by the air stream decreased sharply. The direction of heat flow associated with the air became positive (net Heat In) for %OCR above 50%; hence, the air had shifted from providing cooling to the stack to providing net heat into the stack. This was also predicted for the 15% air use cases (cases 6-8). Independent of the air flow rates, temperature differences, and %OCR, the gross output power density for each case (including cross-, co-, and counter-flow stacks) was virtually constant at 0.40 W/cm². Hence the electrical performance was stable for all 10x10-cm stack cases.

4.2 Co-Flow 10x10 cm

Figure 4.2 plots the cell $\Delta T$ and maximum principal stress in the anode for the 10x10-cm co-flow stack cases. The figure shows little change to the magnitudes of $\Delta T$ and the anode stress over the range of %OCR. However, this 10x10-cm co-flow stack benefited from increased cathode air flow (15% air use) in the form of decreased $\Delta T$ and stress over the full range of %OCR. Stresses in the anode for this co-flow case were similar in magnitude to those predicted for the cross-flow stack.

![Figure 4.2](image)

**Figure 4.2.** Cell Temperature Difference ($\Delta T$) and Maximum Principal Stress (S1) Versus %OCR for 10x10-cm Co-Flow Cases
4.3 Counter-Flow 10x10 cm

The 10x10-cm counter-flow cases plotted in Figure 4.3 show a definite thermal benefit for intermediate %OCR because the models predicted the anode stress to decrease from 25 MPa at 0%OCR to a minimum of 13.8 MPa at 40% OCR. The minimum stress was comparable to that predicted for cross-flow and co-flow stacks. Similarly, ΔT decreased from 85°C at 0% OCR to 45°–47°C at 40–50% OCR. The 45°–47°C temperature differences were substantially less than those exhibited by either the cross- or co-flow configuration stacks in the 10x10-cm cell size. However, the maximum cell temperature was not substantially lower than the other stacks. The counter-flow stack benefited from 15% air use because the stresses were less than those of the 30% air utilization cases. While the benefit of intermediate %OCR is apparent for the counter-flow stack, the results indicate the thermal performance is also more sensitive to the effect of OCR than the cross- and co-flow stacks.

![Figure 4.3. Cell Temperature Difference (ΔT) and Maximum Principal Stress (S1) Versus %OCR for 10x10-cm Counter-Flow Cases](image)

4.4 Temperature Distributions and Stress: 10x10 cm

The distribution of thermally induced stresses in a planar SOFC anode depends on the distribution of temperature. The temperature distribution is affected by the stack flow configuration (geometry), air utilization, and %OCR. Other variables affecting the temperature that were not addressed by this study include the thermal conductivity, thickness of stack components, fuel utilization, and stack wall boundary conditions, to name a few. Even without the effect of these other variables, the temperature distribution was unique for each simulation case. As was demonstrated above, the temperature and anode stress were particularly sensitive to %OCR in

4.4
the 10x10-cm counter-flow stack. This result, due to changes in the temperature distribution, is illustrated in Figure 4.4, which shows distributions of anode temperature and stress for cases 17, 19, and 23 from Table 4.1. In the orientation shown in the figure, air flowed across the cell from the left, and fuel flowed from the right. With 0% OCR, the distribution of temperature (a) indicated that the primary cooling came from the air (at left). Subsequently, the maximum temperature and maximum stress (b) occurred near the air outflow (at right). With 40% OCR, cooling was provided by the air and by the reformation of methane (at right). In this case the distributions of temperature (c) and stress (d) were more centrally located on the anode. With 80% OCR, less cooling was provided by the air, and a larger portion was provided by the reformation of methane. Hence maximums in temperature (e) and stress (f) occurred nearer the air inflow edge of the cell (at left). This suggests that the symmetric temperature profile with the maximum at the center is the most beneficial regarding anode stresses.

**Figure 4.4.** Distributions of Anode Temperature (top) and Maximum Principal Stress (bottom) within a 10x10-cm Counter-Flow Stack Operating with (a,b) 0% OCR, (c,d) 40% OCR, and (e,f) 80% OCR. Temperature color scale is 958K to 1054K (685°-781°C). Stress color scale is -1.75 to 25.8 MPa.
5.0 Results: 20x20-cm Cell Size

To analyze the effect of %OCR in the 20x20-cm cell size, model geometries of cross-flow, co-flow, and counter-flow were created. For each flow configuration, cases simulating OCR ranging from 0 to 80% and air flow rates associated with air utilizations of 30 and 15% were performed. A sufficient number of fuel mixtures were simulated to identify the behavior trends of each flow configuration; thus, not all of the fuel mixtures were simulated for all geometries.

5.1 Cross-Flow 20x20 cm

Figure 5.1 plots cell ΔT and maximum principal stress in the anode for the 20x20-cm cross-flow cases. Legends and labeling are consistent with the figures in Section 4. Cell temperature differences for this generic cross-flow stack with 15% air utilization were very large, varying in magnitude from 236°C to 310°C with a minimum ΔT in the 40 to 50% OCR range. The anode stress was also quite large with 30% air utilization (red squares in Figure 5.1) and featured a minimum value of 60.2-MPa at 50% OCR. The stresses decreased substantially and were less varied with 15% air use, indicating that increased air flow represents an improvement in the operating conditions for this 20x20-cm stack.

Table 5.1 summarizes the simulation results from the 20x20-cm cross-flow, co-flow, and counter-flow cases. As with the smaller cell size, the inflow temperature increased linearly with increasing %OCR. As the heat load decreased, the inflow temperature increased to maintain the

![Figure 5.1. Cell Temperature Difference (ΔT) and Maximum Principal Stress (S1) Versus %OCR for 20x20-cm Cross-Flow Cases](image-url)
Table 5.1. Summary of Results for 20x20-cm Cell Size (75/30% fuel/air utilization). Cases below the dashed line in each block of data are results for 15% air utilization.

<table>
<thead>
<tr>
<th>Case</th>
<th>%OCR</th>
<th>Temperature, °C</th>
<th>Anode Stress</th>
<th>Power Heat In</th>
<th>Heat Out, W</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inflow Min Max AT</td>
<td>S1max, MPa</td>
<td>W/cm² Total</td>
<td>Air Fuel Walls Total</td>
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<td></td>
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<td>0.399</td>
<td>113.3</td>
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<tr>
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<td>718 600 878 278</td>
<td>65.5</td>
<td>0.406</td>
<td>81.2</td>
</tr>
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<td>0.397</td>
<td>165.2</td>
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<td>52.5</td>
<td>0.407</td>
<td>81.3</td>
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<td>Co-Flow Cases: 20x20</td>
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<tr>
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<tr>
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<td>29.8</td>
<td>0.407</td>
<td>160.5</td>
</tr>
<tr>
<td>39</td>
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<td>724 690 817 127</td>
<td>27.0</td>
<td>0.405</td>
<td>110.6</td>
</tr>
<tr>
<td>40</td>
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<td>766 693 817 124</td>
<td>25.5</td>
<td>0.404</td>
<td>82.3</td>
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<tr>
<td>Counter-Flow Cases: 20x20</td>
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<td>71.7</td>
<td>0.409</td>
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<td>78.8</td>
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<td>45.4</td>
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<td>55.2</td>
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<td>656 679 816 137</td>
<td>56.5</td>
<td>0.409</td>
<td>80.9</td>
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</table>

average cell temperature at 750°C. Also, the heat flow from the stack through the perimeter walls and the heat removed by the fuel stream were roughly constant, while heat removed by the air stream decreased sharply with increasing %OCR. As in the smaller cell size cases, the heat removed by the air became positive (net heat in) for OCR above 50%; hence, the air had shifted from cooling the stack to heating the stack.

5.2 Co-Flow 20x20 cm

Figure 5.2 plots cell ΔT and maximum principal stress in the anode for the 20x20-cm co-flow cases. Over the range of %OCR, the magnitude of the anode stress decreased without a minimum from 46.9 MPa at 0% to 40.0 MPa at 80% OCR for 30% air use. The results also show a performance benefit from operating the stack at 15% air utilization (cases 38–40 in Table 5.1)
as the anode stresses were further decreased to 25.5-MPa at 80%OCR. These anode stresses were considerably lower than those of the cross-flow stack. Likewise, the cell ΔT was decreased to 148°C at 0% and 124°C at 80% OCR, decreasing continuously with increasing %OCR.

5.3 Counter-Flow 20x20 cm

The 20x20-cm counter-flow stack was predicted to have the largest anode stresses of the three 20x20-cm stack geometries examined. Figure 5.3 plots the cell ΔT and maximum principal stress in the anode for this stack. Anode stress ranged from 87.6 MPa at 0% OCR to 71.7 MPa at 60% OCR at 30% air utilization. Figure 5.4 shows distributions of the anode temperature and stress for 0, 60, and 80% OCR and 30% air use (cases 41, 44, and 45 from Table 5.1). The distributions of temperature and stress were very similar to those of the 10x10-cm counter-flow cases (Figure 4.4). Anode stress was lowest for an intermediate (60%) OCR case. This case had a symmetric temperature profile with the maximum at the center. However, the stress increased while the cell ΔT continued to decrease as the OCR approached 80%. While the 80% OCR case also had a symmetric temperature profile with the maximum at the center, the elevated anode stress may be attributable to the more closely spaced isotherms (or larger thermal gradients) in the anode (Figure 5.4e) compared to the 60% OCR case (Figure 5.4c).

Stresses were less but still large with 15% air use, ranging from a minimum of 45.4 MPa at 0% to a maximum of 56.5 MPa at 80% OCR. The predicted cell temperature difference was quite large (304°C) at 0% OCR and 30% air utilization and consistently decreased with
Figure 5.3.  Cell Temperature Difference ($\Delta T$) and Maximum Principal Stress ($S_1$) Versus %OCR for 20x20-cm Counter-Flow Cases

Figure 5.4.  Distributions of Anode Temperature (top) and Maximum Principal Stress (bottom) within a 20x20-cm Counter-Flow Stack Operating with (a,b) 0% OCR, (c,d) 60% OCR, and (e,f) 80% OCR. Temperature color scale is 839 to 1155K (566°-882°C). Stress color scale is -3.65 to 87.6 MPa.
increasing %OCR and increased air flow (15% air utilization). The counter-flow stack did not perform as well as the co-flow stack.

In both the co-flow and counter-flow configurations, $\Delta T$ was predicted to decrease without minimum with increasing %OCR and 15% air utilization (double air flow). However, the magnitude of the cell $\Delta T$ was consistently and considerably smaller in the co-flow stack (see cases 35-40 in Table 5.1). More importantly, it was shown that the anode stresses resulting from the temperature distributions were substantially smaller in the co-flow stack.

### 5.4 Power Density 20x20 cm

Power density was nearly invariant within the 10x10-cm cases independent of %OCR and flow configuration. However, within the 20x20-cm cases, cross-flow with 0% OCR and 30% air utilization (Case 27, Table 5.1) had conspicuously low power density (7% low relative to similar co- and counter-flow cases) and a very large temperature difference (310°C). Increased air flow and 15% air utilization (Case 31, Table 5.1) enabled a large increase in the inflow temperature, which helped to substantially decrease the cell $\Delta T$ and boost the Nernst potential. The average Nernst potential (and power listed in Table 5.1) increased to within 2% of the average of all 20x20-cm cases.

### 5.5 Cathode Air Utilization

In this study, the nominal pressure drop for one of the 20x20-cm cells with 30% air utilization, with 1-mm-tall by 1-mm-wide channels, spaced by 1-mm-wide fins on the interconnect, would be approximately 0.34 psi. Cases in which the cathode air flow rate was doubled (15% air utilization) would have increased cathode channel pressure drop proportional to 0.68 psi if the cathode channel height was left unaltered. Assuming a pumping efficiency of 0.5 for a 100-cell stack, this would increase the power required to pump air through the cathode by a factor of 4. Similarly low efficiencies are often suffered when relatively low flow rates and high head losses are required. Higher efficiencies could be possible if larger high-speed pumps were used to provide air for multiple stacks.\(^{11}\) The benefit that increased air flow can provide in the form of decreased thermal stress must be balanced with the increased cathode pressure drop and blower power requirement. However, the 20x20-cm cell stacks examined in this study required increased air flow (15% air utilization) to achieve reasonably low stresses and anode temperatures.
6.0 Conclusions

The following observations were drawn from the results of this study:

- The analysis showed that the anode stress was a minimum along with the temperature difference on the cell when 40 to 50% of the reformation reaction took place on-cell in counter-flow and cross-flow stacks of 10x10-cm size.

- Gross electrical power density of 0.40 W/cm² was virtually unaffected for each 10x10-cm case. Each of the 20x20-cm cases that exhibited reasonable thermal performance also had power densities that varied from the average of 0.40 W/cm² by at most -1% to +2%.

- Inflow gas temperature increased linearly with linearly increasing %OCR to offset the decreasing heat load and maintain the average cell temperature at 750°C. Examination of the heat load data showed that the air had shifted roles from providing stack cooling to providing net stack heat for OCR above 50%. An exception to this was the 20x20-cm counter-flow stack in which the air continued to provide net cooling over the full range of OCR.

- The co-flow stack showed substantial thermal benefit due to increased air flow (and 15% air utilization) as the anode stress and cell temperature difference was decreased over the full range of OCR. Cross-flow and counter-flow stacks did not show the same consistent benefit.

- Within the 20x20-cm cases the co-flow configuration stack had the smallest anode stresses and cell temperature difference both of which had no minimum, but rather were continuously decreased with increasing OCR.

- For the conditions and particular generic stacks of this study, the results suggest 40 to 50% reformation on-cell should be considered for cross-flow and counter-flow stacks, and higher percentages may be desirable in co-flow stacks.

- Air utilization of 15% provided a consistent thermal benefit in the form of decreased anode stress, cell ΔT, and maximum temperature compared with 30% air utilization. Although doubling the air flow can result in a factor of 4 increase in the air blower power requirement, a maximum of 15% air utilization may be necessary in 20x20-cm cell stacks to achieve acceptably low stresses and anode temperatures.
7.0 References


Appendix A

Molar Compositions of Partially Reformed Fuel Mixtures
Appendix A

Molar Compositions of Partially Reformed Fuel Mixtures

Table A.1. Mass Compositions of Partially Reformed Fuel Mixtures Supplied from an External Reformer to the Stack (mass fraction)

<table>
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<tr>
<th>OCR</th>
<th>0%</th>
<th>10%</th>
<th>20%</th>
<th>30%</th>
<th>40%</th>
<th>50%</th>
<th>60%</th>
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Topical Report

Effects of Oxide Thickness on Scale and Interface Stresses under Isothermal Cooling and Micro-Indentation

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Pacific Northwest National Laboratory
Richland, WA 99354

May 2006

Work Performed Under:
SECA Core Technology Program
Contract DE-AC05-76RL01830

Report Submitted to:
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Pacific Northwest National Laboratory
Richland, WA 99354
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PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTHELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830
Executive Summary

The effects of various oxide scale thickness on bulk and interface stresses are predicted for the ferritic stainless steel interconnect material, Crofer 22 APU, under isothermal cooling condition and micro-indentation. The goal of the study is to utilize the measurement methodology and the associated quantified interfacial strength developed by other SECA team members in predicting possible scale spallation for different scale thickness, therefore indicating the possible interconnect life under isothermal cooling conditions. A very high level of compressive stress is predicted for the oxide scale upon isothermal cool due to CTE mismatches between the oxide and the alloy substrate. The predicted magnitude of thermal stresses is in good agreement with experimental measurements reported in the literature. It is also found that interfacial shear stress increases with increasing oxide scale thickness, therefore the possibility for scale delamination also increases with scale growth. Finite element computational simulations of micro-indentation test were performed to quantify the interfacial shear stress levels at different indentation depths. These results will be compared with experimental indentation measurements to quantify the interfacial shear strength. The shear strength will then be compared with the shear stress generated upon cooling to predict the life of interconnect at different stage of oxide scale growth.
Acknowledgements

The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the United States Department of Energy under Contract DE-AC06-76RL01830. The work summarized in this report was funded as part of the Solid-State Energy Conversion Alliance (SECA) Core Technology Program by the U.S. Department of Energy’s National Energy Technology Laboratory (NETL).

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1.0 Introduction

Interconnects in solid oxide fuel cells (SOFCs) provide cell to cell electrical connection, and also serve as gas separator for the separation of the fuel (anode) from the oxidant (cathode). In order to perform their intended functionalities, interconnects must demonstrate or possess the following materials characteristics:

(1) Excellent electrical conductivity
(2) Corrosion resistance in oxidizing and reducing environment
(3) Corrosion resistance in bi-polar exposure condition
(4) Matched thermal expansion coefficient (CTE) with other SOFC components
(5) Good thermal conductivity for thermal management
(6) Bulk and interface stability with electrodes
(7) Low/negligible solubility for hydrogen, carbon and oxygen
(8) Low cost and easy to fabricate

Over the past several decades, researchers have primarily spent their efforts in finding proper complex ceramic oxides as interconnect materials. The doped rare earth chromites ((La, Sr, Ca)(Cr, Mg)O₃, (Y, Ca)CrO₃) are found to have most of the desired properties as interconnects. Lanthanum chromite (LaCrO₃) exhibits relatively high electronic conductivity in both fuel and oxidant atmospheres, moderate to good chemical stability in the fuel cell environments and excellent CTE compatibility with other cell components. Lanthanum chromite is a p-type electrical conductor. Its conductivity decreases as it becomes oxygen deficient, LaCrO₃₋δ [1]. The conductivity of pure lanthanum chromite is not sufficiently high for use as an interconnect material, but can be increased by doping. The most common dopants for lanthanum chromite are alkaline-earth elements, among which researches on strontium and calcium dopants [1] are the most often reported. For fabrication of lanthanum chromite-based interconnect material, electrochemical vapor deposition (EVD), plasma spray and tape casting seem to be the only well developed fabrication methods [2]. The most challenge for LaCrO₃ or doped LaCrO₃ is easy volatilization of Cr at sintering temperatures.
It is attributed to a volatile species, such as CrO₃. These species will be reduced to solid Cr₂O₃, which inhibits sintering of the particles [3].

LaCrO₃ exhibits sufficient conductivity only when the working temperature is above 800°C. The recently developed anode-supported planar SOFCs design allows reduction of working temperature to go below 800°C, which led to the proposed use of alloys as interconnects and current collectors in SOFC systems. Compared with ceramic, alloys are much cheaper and easier to fabricate. They also meet several other requirements for good interconnect materials, such as good electrical conductivity, low cost and ease of fabrication etc.

An oxide layer inevitably forms on the surface of metals and alloys in atmospheres representative of SOFC. Al₂O₃, SiO₂, Cr₂O₃, etc. are the most common component of alloy oxide. It is noted that Al₂O₃, and SiO₂ are the most insulting oxides at elevated temperatures, while Cr₂O₃ is reported to have relatively good electrical conductivity under the similar exposure environment. Another important aspect is that the oxide scale protects the alloy substrate from further oxidation. While this conductive oxide layer is necessary, it also limits the useful life of these interconnect components if it grows too thick. The oxide layer grows thicker over time, and therefore the resistance increases with oxide thickness. On the other hand, under thermal cycling or cooling down to room temperature, thick oxide scale remains prone to spallation and lose its protective effect [4]. In addition, Cr₂O₃ reacts with H₂O to form a more easily evaporated CrO₂(OH)₂ phase [5]. This chromium oxyhydroxide can diffuse in the cathode and to the electrolyte interface where it can be reduced back to Cr₂O₃. The deposition of Cr₂O₃ within the cathode bulk and at the cathode/electrolyte interface leads to the poisoning and degradation of cathodes, resulting in increased overvoltage and loss of electrical performance.

To eliminate or reduce the aforementioned disadvantages of using Cr contained alloy as interconnect materials, enormous attempts have been undertaken. It has been found, that the addition of thin layers of surface dopants or coating of reactive element such as Yttrium [6, 7], Ruthenium [8], Neodymium [9], Praseodymium [9], Lithium [10], Erbium [11] can change the growth mechanism of the oxide scale, effectively improving the adhesion of oxide and
slowing the rate of growth. Thinner and denser oxide scales have been observed for the reactive-element doped alloy. These differences in morphology could be explained by selective oxidation of the protective oxide forming element [9]. The reasons of growth-rate reduction are proposed. It has also been suggested that the reduction may be because of the larger ionic radii of reactive elements, which may be mainly segregated at the grain boundary of oxide scale [12].

Others suggest the reactive elements act as nucleation sites for the first-formed oxides, thereby decreasing the inter-nuclei spacing [4]. The controlled growth of the oxide layer also results in less surface area of the Cr2O3 and therefore the evaporation rate of Cr species is slowed. Another approach is to let the interfacial oxide layer grow, but to dope it with another material that decreases the area specific resistance (ASR). There are several dopants that decrease the resistance of Cr2O3, [13]. According to Chen et al. [14], the effect of the densified Mn-Co spinel coating is to significantly reduce Cr2O3 sub-scale formation, lower the thermal expansion mismatch, and increase the electronic conductivity of the scale. For 850°C, an ASR can be predicted of approximately 0.5 Ωcm².

Yet another approach is to coat interconnects with conducting oxide layers. This has been attempted with various perovskites [15], all these coatings lead to improved scale adherence and scale electronic conductivity, while reducing oxide growth rate and Cr volatility. Two approaches of synthesizing a perovskite thin film, reactive formation and sol-gel processing, are compared by Zhu et al. [16]. As a simple, cost-effective method for synthesizing the LaCrO3-based coatings on interconnect alloy, the sol-gel chelating precursor approach is preferred.

Interconnect materials development has mostly focused on nickel-based alloys, chromium-based alloys and iron-based alloys. Nickel-based alloys have considerably higher thermal expansion than those of other fuel cell components. Chromium-based alloys are attractive with stable oxides, but are relatively costly to fabricate. Compared to chromium-based alloys, iron-based alloys have advantages in terms of high ductility, good workability and low cost.
By far, iron-based alloys, especially Cr-Fe based alloy, e.g. Crofer 22 APU, are the most attractive metallic interconnect material for SOFCs.

Considerable amount of experimental work has been focused on developing a conductive oxide coating on metallic interconnects for improved surface stability and life time. The coatings have been commonly used by SOFC developers to improve the interconnect performance, i.e., electrical and thermal, and to mitigate chromium evaporation into cells at the cathode side. For example, coating made from (Mn,Co)3O4 based compositions have been found to be promising in terms of electrical performance and thermo-mechanical stability. However, to ensure that such coating can meet the SECA performance life target of 40,000 hours, an accelerated testing/modeling combined approach is needed.

Results from thermal mechanical modeling of the Fe-Cr substrate(scale/spinel protection coating will identify the sensitivities of interconnect structural integrity to various manufacturing factors such as bond strength, layer thickness combination, etc. Such a simulation tool can eventually be used to guide the materials development activities to achieve certain life target and also to forecast the productive lifetime of interconnect under certain operating condition and thermal cycles. Such information is also useful to manufacturers for strategic and economic planning. If supplemented by a companion effort to characterize the uncertainties in the degradation model, a ‘coarse life prediction methodology’ can also be established such that confidence levels can be assigned to these forecasts.

Long term performance and structural integrity of interconnect can be characterized into two main issues: creep of the ferritic stainless steel interconnect and the associated loss or reduction of electrical contact with anode/cathode and the change of air/fuel flow path/pattern; and the spallation/crack of the surface oxide formed on the Crofer22 APU substrate with loss of substrate protection.

In order to predict the spallation/crack of the surface oxide layer on the Crofer22 APU substrate, strength for different interfaces in the interconnect system needs to be quantified, and stresses at various interfaces need to be predicted and compared with the corresponding
strength. To this end, the micro-indentation based interfacial adhesion strength characterization technique developed by Beuth et al. [18] will be used. Thermal shock tests developed at ORNL will also be used to quantify the effects of spatial temperature gradients on different interfacial strength.

This report is the first of a series of reports on interconnect degradation and life predictions. Its objective is to present our results-to-date on the effects of different interconnect thickness and oxide layer thickness on the structural stability and integrity of the oxide layer during isothermal cooling. The final goal is to quantify the interface adhesion strength between the oxide layer and the substrate material. As a next step, the interface strength between the protective coating and the oxide layer will be characterized to predict the interconnect life under normal and thermal cyclic operating conditions.

### 2.0 Technical Approach and Model Description

High-temperature oxidation of metals and alloys with the formation of surface oxide involve the development of mechanical stresses. Sources of stress in the scale are:

1. Thermal stresses induced by temperature changes and differences in the thermal expansion coefficients of the scale and the substrate.
2. Stresses resulting from oxidation and scale growth.
3. External stresses induced by deformation of the oxide scale/metal substrate system.

Thermal stresses produced during isothermal cooling will be addressed in this report. A separate report on prediction of growth stress (2nd source) will be issued in the near future.

Oxide scale spallation has been observed on the surface of uncoated Crofer 22 APU coupons under extended period of oxidation exposure [19]. To investigate the mechanisms of cracking and oxide layer spallation of interconnect during the temperature change from the operating temperature of 800°C to room temperature of 25°C, numerical analyses were performed to determine the stress distributions caused by the mismatch of CTEs of the interconnect
substrate material and its scale. The effects of the scale thickness on the normal stress inside
the scale as well as the shear stress on the interface between the scale and substrate are
investigated. The shear stress on the interface is considered to be the driving force for
delamination and the normal stress in the scale layer is considered to be the driving force for
scale local buckling once delamination occurs.

It should be mentioned that the oxide scale structure for Crofer 22 APU is rather complex and
Quadakker et al. [28] and Yang et al. [20] provide good descriptions on its evolution during
the oxidation process. For example, Figure 1 shows the SEM cross-sectional microstructure
and elemental distributions of Crofer22 APU after oxidation at 800°C for 1200 h in air. From
the EDXS and XRD analysis, it is clear that the top layer was mainly composed of an (Mn,
Cr)$_3$O$_4$ spinel phase, and the sublayer mainly consisted of chromia.

The CTE and mechanical properties of Crofer22 APU substrate are temperature dependent
and are shown in Figure 3 and 4 [21, 22]. Temperature dependent CTE and mechanical
properties for the complex oxide scale formed on the metal surface are not currently available.
Since the interface between the substrate and the oxide mainly consists of chromia and that
scale composition and microstructure tended to become homogeneous after long term
oxidation [20], the CTE and Young’s modulus used for stress analysis is based on the
temperature independent data for Cr$_2$O$_3$ only [23, 24], see Table 1.

The initial thickness of the interconnect substrate is 500 $\mu$m. Scale thickness ranging from
2 $\mu$m to 30 $\mu$m is considered. The upper limit of 30 $\mu$m is chosen based on the extrapolated
scale thickness at 40,000 hour using the experimental results of Kurokowa et al. [25]. The
boundary of the interconnect sheet is assumed to be simply supported, see Figure 2. At
operating temperature 800°C, the interconnect and the oxide layer are considered to be stress
free and the stress generated during isothermal cool-down is predicted based on the CTE
mismatch of the substrate and the chromia scale.
Figure 1 SEM cross-sectional microstructure and elemental distributions of Crofer22 APU after oxidation at 800°C for 1200 h in air [20]

It should be noted that, theoretically, the total thickness of substrate and oxide at different stages of the oxide growth should be different from the initial substrate thickness because the oxide to metal volume ratio, typically referred to as Pilling-Bodworth ratio (PBR), is usually different from 1.0 [26]. Since the PBR of chromia (Cr$_2$O$_3$) to chromium is 2.07 and the maximum scale thickness considered is 30 $\mu$m, the total thickness change due to oxide growth is very small compared with the initial substrate thickness. Hence, for computational purposes, we kept the total thickness of the substrate and the oxide to be constant during the simulation, and only varied the thickness of the oxide layers. It should also be noted that a uniform metal oxide/metal substrate interface is assumed for this simulation case. It is also assumed that the oxide formation is only on one surface.
The finite element (FE) mesh used in the stress analysis is shown in Figure 5, which includes 32000 8-nodes brick elements and 35301 nodes. The mesh near the interface of the scale and substrate is refined in order to obtain accurate stress predictions.

Figure 3 Temperature dependent CTE of Crofer 22 APU [21]
Figure 4 Temperature dependent elastic modulus of Crofer 22 APU [22]

Table 1 Mechanical properties of materials

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus(GPa)</th>
<th>Poisson’s ratio</th>
<th>CTE (x10⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scale</td>
<td>250</td>
<td>0.27</td>
<td>5.7</td>
</tr>
</tbody>
</table>

(a) FE mesh of a quarter of structure          (b) Local mesh close to the interface

Figure 5 FE mesh for stress prediction upon cooling
Micro-indentation test has been used in measurement of interfacial properties of coatings to substrate by many researchers [18, 27]. For example, indentation test is being used by the Carnegie Mellon University team in measuring the fracture toughness of chromia/substrate interfaces. In the test, the chromia scale is penetrated by the indenter, and the plastic deformation of the underlying substrate induces compressive radial strains in the substrate. The interfacial toughness was then determined from the results of mechanics analysis of the indentation problem and measurement of the delamination radius.

Following similar methodology, finite element computational analysis is used to simulate the indentation test in order to quantify the interfacial shear strength, and to compare with the shear stress generated due to SOFC cooling for different scale thickness in order to predict the life of interconnect. In this analysis, thickness of substrate is 500 μm and thickness of the oxide scale ranges from 2 μm to 30 μm. The indenter used is Brale C, which has a 120° tip angle with tip radius of 200 μm. The finite element model is shown in Figure 6.

Indentation generated shear stresses on the oxide/substrate interface during micro-indentation tests are predicted for different oxide thickness. Interface stress evolution for different scale thickness will be discussed in the next section.

Figure 6 FE mesh for interface stress prediction upon micro-indentation
3.0 Results Discussions

**Thermal Stress**

Figure 7 shows the von Mises stress contour in the scale and the substrate upon cooling for scale thickness of 5 \(\mu m\). Figure 8(a) shows the thru-thickness normal stress distribution for the interconnect away from its free edge. Very low thermally induced normal stress is predicted throughout the entire substrate thickness, and a very high level of compressive stress is predicted in the thin oxide scale. The predicted thermal stress magnitude in the oxide scale is in good quantitative agreement with typical experimental measurements as shown in Figure 8(b). Results for other scale thickness have the same qualitative trend: Very high compressive stresses are predicted for the scale upon cooling, this is due to CTE mismatch between the oxide scale and the substrate material.

Figure 9 (a) and (b) show the contours of shear stress on the substrate/oxide interface, and the normal stresses in the scale. Normal stress in the oxide scale is compressive and reaches to zero at the free edge. Shear stress on the interface obtains its highest value at the sample free edge, and it decreases to zero at the sample center because of symmetry. Figure 10 shows the thermal stress distribution on the interface and in the oxide scale. If one assumes interface shear stress is the driving force for delamination, then the free edges of interconnect are the area most prone to delamination. In addition, the very high compressive stress level in the scale indicates that small imperfections on the scale/substrate interface can lead to scale buckling and spallation.

![Figure 7 von Mises stress contour in the scale and substrate upon cooling](image-url)
The effects of scale growth on the resulting thermal stress levels are presented in Figure 11 for the center of the sample (a) and the edge of the sample (b). Even though the numerical scales for the interface shear stress are different for the two plots, similar trend with increasing scale thickness can be observed: magnitude of compressive normal stress in the scale decreases with increasing scale thickness; interfacial shear stress increases with increasing scale thickness. Again, if one were to consider interfacial shear stress as the
driving force for delamination, then there is a growing tendency for delamination with scale growth. This is true for both the center and the free edge of the interconnect.

![Stress from center to edge](image)

Figure 10 Thermal stress distribution in the scale and shear stress distribution on the interface

![Effects of scale growth on thermal stress](image)

(a) Center of sample  
(b) Edge of sample

Figure 11 Effects of scale growth on thermal stress

**Indentation Stress**

Figure 12 shows the typical stress field for the indentation tests: a field of very high shear stress is generated by the indentation process at the interface of the scale/substrate right outside the contact radius of the indenter with the scale. The location and magnitude of the maximum shear stress on the interface evolve with the indentation depth and the thickness of
the oxide scale. For example, Figures 13 to 16 show the progression of shear stress location and magnitudes for the scale’s thickness ranging from 2 \( \mu m \) to 30 \( \mu m \).

![Figure 12 Typical shear stress field during indentation](image)

**Figure 12** Typical shear stress field during indentation

![Figure 13 Shear stress contour in 2 \( \mu m \) thick scale](image)

**Figure 13** Shear stress contour in 2 \( \mu m \) thick scale
Figure 14 Shear stress contour in 5 \( \mu m \) thick scale

Figure 15 Shear stress contour in 15 \( \mu m \) thick scale
Figure 17 depicts the relationship between maximum shear stress on the interface with increasing indentation depths for different scale thickness. At the initial stage of indentation, interfacial shear stress is the highest for the thinnest oxide scale, which indicates that this type of indentation test is more suitable for thinner scale adhesion characterization at low indentation depth. With increasing scale thickness, the highest shear stress point moves inside the scale layer, Figure 16(d). Results from these simulations will be compared with experimental indentation measurements to quantify the interfacial shear strength.

Figure 18 shows the influence of thermal stress on the indentation stress by performing the virtual indentation test on a sample with thermal stress due to cool down. With the thermal stresses, higher magnitude of compressive normal stress is predicted but the interfacial shear stress due to indentation remains the same. This result indicates that effect of thermal stress is negligible in quantifying the interfacial shear strength using indentation tests.
Figure 17. Evolution of interfacial shear stress during 5 µm indentation test for various scale thickness

Figure 18. Influence of thermal stress on indentation stress
4.0 Conclusions

Thermal stresses generated in the oxide scale as well as at the scale/substrate interface during isothermal cooling and indentation stresses generated by micro-indentation tests have been predicted for various oxide scale thickness in the oxide scale as well as on the scale/substrate interface to examine the influence of scale thickness on various stress components. The purpose is to quantify the interfacial strength by comparing the prediction with experimental indentation measurements. Interconnect surface oxide integrity at different operation time, i.e., with different oxide thickness, will be predicted based on the interfacial strength and the stresses generated during isothermal cooling. The conclusions of the current study are:

1. Compressive thermal stresses of high magnitude are predicted in the scale upon isothermal cooling. The predicted stress level is in quantitative agreement with experimentally measured residual stress;

2. Upon isothermal cooling, magnitude of the compressive normal stress in the scale decreases with increasing scale thickness;

3. Upon isothermal cooling, magnitude of interfacial shear stress at the scale/substrate interface increases with increasing scale thickness;

4. A field of very high shear stress is generated by the micro-indentation process at the interface between the scale/substrate outside the contact radius;

5. We will use the interfacial shear stress prediction to compare with the experimental indentation measurement in quantifying the interfacial strength;

6. The effect of thermal stress is negligible in quantifying the interfacial shear strength using indentation tests.
5.0 References


22. *Young’s modulus of Crofer 22 APU*, Jan., 2006, ThyssenKrupp VDM.


Topical Report

Effects of Interconnect Creep on Long-Term Performance of One-Cell and Multi-Cells Stacks

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PACIFIC NORTHWEST NATIONAL LABORATORY
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Executive Summary

Creep deformation becomes relevant for a material when the operating temperature is near or exceeds half of its melting temperature (in degrees of Kelvin). The operating temperatures for most of the solid oxide fuel cells (SOFC) under development in the SECA program are 800°C-1000°C with emphasis on intermediate temperature operations. High temperature ferritic alloys are potential candidates as interconnect (IC) materials and spacers due to their low cost and CTE compatibility with other SOFC components. Since the melting temperature of most ferritic stainless steels is around 1500°C, possible creep deformation of IC under the typical cell operating temperature should not be neglected. In this report, the effects of interconnect creep behavior on stack geometry change and stress redistribution of different cell components are predicted and summarized. The goal of the study is to investigate the performance of the fuel cell stack by obtaining the fuel and air channel geometry changes due to creep of the ferritic stainless steel interconnect, therefore indicating possible SOFC performance change under long term operations. IC creep models were incorporated into SOFC-MP and Mentat FC, and finite element analyses were performed to quantify the deformed configuration of the default SOFC stack design under the long term steady state operating temperature. The purpose is to quantify the long term SOFC stack geometry change by investigating the changes in air and fuel flow paths and the corresponding stress re-distribution among various cell components. It is found that creep behavior of the ferritic stainless steel IC contributes to narrowing of both the fuel and the air flow channels. In addition, stress re-distribution of the cell components suggests the need for a compliant sealing material that also relaxes at operating temperature.
Acknowledgements

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1.0 Introduction

Interconnects in solid oxide fuel cells (SOFCs) provide cell to cell electrical connection, and also serve as gas separator for the separation of the fuel (anode) from the oxidant (cathode). In order to perform their intended functionalities, interconnects must demonstrate or possess the following materials characteristics:

(1) Excellent electrical conductivity
(2) Corrosion resistance in oxidizing and reducing environment
(3) Corrosion resistance in bi-polar exposure condition
(4) Matched thermal expansion coefficient (CTE) with other SOFC components
(5) Good thermal conductivity for thermal management
(6) Bulk and interface stability with electrodes
(7) Low/negligible solubility for hydrogen, carbon and oxygen
(8) Low cost and easy to fabricate

Recently, SECA funded interconnect materials development has been mostly focusing on ferritic stainless steels. Compared to chromium-based alloys, iron-based alloys have advantages in terms of high ductility, good workability and low cost [1]. By far, iron-based alloys, especially Fe-Cr based alloy, e.g. Crofer 22 APU, are the most attractive metallic interconnect material for SOFCs [2, 3].

Creep deformation becomes relevant for a material when the operating temperature is near or exceeding half of its melting temperature (in degrees of Kelvin) [4, 5, 6]. The operating temperatures for most of the solid oxide fuel cells (SOFC) under development are in the range of 800°C-1000 °C. Since the melting temperature of most stainless steel is around 1500°C, creep deformation of IC under the typical cell operating temperature should not be neglected. In this report, the effects of interconnect creep behavior on stack geometry changes and stress redistributions in various cell components are predicted and summarized. The goal of the study is to investigate the long term performance of the fuel cell stack by obtaining the fuel and air channel geometry changes due to the creep behavior of the ferritic stainless steel
interconnect. IC creep laws have been incorporated into SOFC-MP and Mentat FC, and finite element analyses were performed to quantify the deformed configuration of the SOFC under the long term steady state operating temperature. It is found that creep behavior of the ferritic stainless steel IC contributes to narrowing of both the fuel and the air flow channels. In addition, stress re-distribution of the cell components suggests the need for a compliant sealing material that relaxes at operating temperature.

2.0 Technical Approach and Model Description

The temperature differential between the initial, stress-free fabrication temperature and SOFC operating temperature will cause stresses and deformation of various cell components. Moreover, under long term operation, the stresses and deformation are expected to relax and re-distribute due to the anticipated creep behavior of the interconnect material.

To investigate the effects of interconnect creep on the long-term geometry change and stress re-distribution of various cell components, finite element electrochemical analyses were first performed to determine the steady-state operating temperature profile using SOFC-MP. Default planar design in SOFC-MP is used and the associated geometry parameters are listed in Table 1. Results on both 1-cell stack and 3-cell stack will be discussed in this report. Creep law for the ferritic stainless steel was incorporated into Mentat-FC, and finite element analyses were used to predict the long term creep behavior of the SOFC. Anode creep and seal creep have not been considered in the current study. Results including seal creep will be summarized in a subsequent report.

It should be mentioned that the exact creep behavior for Crofer 22 APU can not be found in the open literature. The mechanical properties of a commonly used high temperature ferritic alloy SS430 is used in the current numerical analyses. The temperature dependent Young’s modulus and CTE for SS430 are shown in Figures 1 and 2 [7]. Since the creep behaviors of SS430 or Crofer 22 APU are not available in the open literature, the complete creep behaviors of Fecralloy stainless steel under various initial stresses are used, see Figure 3. It should be mentioned that even though the exact creep rate vs. temperature curves could be different
from Crofer 22 APU to Fecralloy, the trend of the creep curves should be similar between the two materials with increasing temperature.

Table 1. Default SOFC Stack geometry factors

<table>
<thead>
<tr>
<th>SOFC component</th>
<th>Material</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Ni:YSZ</td>
<td>118.0</td>
<td>118.0</td>
<td>0.60</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>YSZ</td>
<td>118.0</td>
<td>118.0</td>
<td>0.01</td>
</tr>
<tr>
<td>Cathode</td>
<td>LSM</td>
<td>118.0</td>
<td>118.0</td>
<td>0.05</td>
</tr>
<tr>
<td>Picture Frame</td>
<td>SS-430</td>
<td>126.3</td>
<td>149.5</td>
<td>0.50</td>
</tr>
<tr>
<td>Separator Plate</td>
<td>SS-430</td>
<td>126.3</td>
<td>149.5</td>
<td>1.20</td>
</tr>
<tr>
<td>Seals</td>
<td>G18</td>
<td>5.0</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 Temperature dependent modulus of SS 430 [7]
Figure 2 Temperature dependent CTE of SS430 [7]

Figure 3 Arrhenius plots for Fecralloy steel under initial stress [4]
The creep rate shown in Figure 3 may be expressed as [4]

For $\sigma < 100\text{MPa}$

$$\dot{\varepsilon}_c = \begin{cases} 1.72\sigma^{5.5}e^{-277400/RT} & \text{for } T \geq 725^\circ\text{C} \\ 1.65 \times 10^{11}\sigma^{5.8}e^{-488700/RT} & \text{for } T \leq 710^\circ\text{C} \end{cases}$$

and for $\sigma > 100\text{MPa}$

$$\dot{\varepsilon}_c = \begin{cases} > 10^{-3} & \text{for } T \geq 725^\circ\text{C} \\ 28.2 \times \sigma^{10.5}e^{-488700/RT} & \text{for } T \leq 710^\circ\text{C} \end{cases}$$

This creep law has been implemented in Mentat-FC using a user-defined material subroutine.

The initial geometry of a 1-cell and 3-cell stack is illustrated in Figures 4 and 5, respectively. Its in-plane dimensions are 157.9mm by 149.5mm, and the total thickness for the 1-cell stack is 5mm, and the total thickness for the 3-cell stack is 12.6mm. This is the default geometry in SOFC-MP with cross flow.
Figure 4 Illustration of 1-cell stack:
(a) full structure, (b) cross section view, (c) enlarged view of the cross section
To obtain the steady-state operating temperature profile, SOFC-MP was used to perform the electro-chemical-thermal analyses. Figure 6 shows the FE model used in the SOFC-MP analysis. Figures 7 and 8 depict the steady state IC temperature distributions on the surfaces with and without air/fuel in/outlets, respectively.
Three cell stack

Figure 6 FE model used in electro-chemical thermal analysis

IC steady state temperature distribution on surface without air/fuel in/outlet
IC steady state temperature distribution on surface with air/fuel in/outlet

Figure 7 Steady state temperature distribution for 1-cell stack

IC steady state temperature distribution on surface without air/fuel in/outlet
IC steady state temperature distribution on surface with air/fuel in/outlet

Figure 8 Steady state temperature distribution for 3-cell stack

Since the SOFC components are considered to be stress free at its assembly temperature of 800°C, different degrees of thermal stresses will be generated at the steady state operating temperature due to the CTE mismatch of various cell components. Figure 9 shows the finite element model used in the thermal-mechanical analysis.
Three Cell Stack

Figure 9 Illustration of finite element model used in thermal-mechanical analysis

3.0 Results and Discussions

Changes of Air and Fuel Flow Channels

One cell stack

The deformed configurations of the fuel and air flow channels at $t=0.01\text{hour}$ are shown in Figures 10 and 11, respectively, with deformation magnification factor of 100. From Figure 10(b), it can be seen that the height of the flow channel narrows down with the temperature differential from the stress-free temperature to the steady-state temperature due to the mismatch and creep behavior of IC materials. This channel geometry change after reaching operating condition is caused by the CTE mismatches of various cell components such as anode, seal and interconnects. As schematically illustrated in Figure 12, the temperature differential will lead to different levels of shrinkage for various layers due to different CTE. Such a non-uniform shrinkage results in non-uniform bending of various cell structures as illustrated in Figure 13, which leads to the changes in air and fuel channel geometry.
Figure 10 Deformed configuration of fuel flow channel

Figure 11 Deformed configuration of air flow channel
Figures 14 and 15 illustrate the configurations of deformed IC and PEN assembly at 0.01 h and 1000h, respectively. At the end of 0.01 hour, the z-displacement of the bottom IC is the highest at the center of the cell, while the z-displacement of the PEN is the least at the same location. Therefore, the air flow channel is reduced and fuel flow channel is expanded due to the initial CTE mismatch. At the end of 1000 hours (Figure 15), however, more IC creep behavior is observed: at the center of the cell, the z-displacement of the bottom IC is the
largest, but the top IC is the least. This means that both the air flow channel and fuel flow channel are reduced due to the creep behavior of the IC under the operating temperature.

Figure 14 Deformed IC and PEN at 0.01hr

Figure 15 Deformed IC and PEN at 1000hr

Figure 16 shows the changes of the air and fuel flow channel widths at the center of the cell within the first hour of SOFC operation after cooling down from initial stress-free condition. Initially, CTE mismatch reduces the height of air flow channel but expands the height of fuel flow channel slightly. Subsequently, the creep behavior of IC begins to contribute to the height reductions of both air and fuel flow channels. The effect of IC creep on the changes of flow channels is shown in Figure 17 for the first one-thousand hour operating period.
Figure 16 Effect of creep of IC on flow channels within initial one hour
(a) air flow channel, (b) fuel flow channel

Figure 17 Effect of creep of IC on flow channels within 1000 hour
(b) air flow channel, (b) fuel flow channel

The effect of IC creep on the flow channel height changes is not monotonous. The reason is due to the different stress level in the bottom and top IC. The non-uniform temperature distribution and different temperature value in the bottom and top IC, as shown in Figure 7 and 8, create the different stress level in the bottom and top IC (shown in Figure 18 and 19, respectively). Based on the creep law described in the previous section, it caused the different creep strain rate, re-distributed the stresses in various components, and contributed to the deformed configuration of the IC and PEN in individual manner. Therefore, it results in the
non-monotonous change of stress levels (see Figures 18-19) in various components, as well as the non-monotonous changes in height of the air and fuel flow channels.

\[ \sigma_{11}^T = 39.1 \text{MPa} \quad \sigma_{11}^C = -42.2 \text{MPa} \]

Time: 0.01hr  

\[ \sigma_{11}^T = 300 \text{MPa} \quad \sigma_{11}^C = -33.3 \text{MPa} \]

Time: 0.21hr  

\[ \sigma_{11}^T = 198 \text{MPa} \quad \sigma_{11}^C = -35.8 \text{MPa} \]

Time: 1000hr

Figure 18 Stress \( \sigma_{11} \) distributions in bottom IC

\[ \sigma_{11}^T = 342 \text{MPa} \quad \sigma_{11}^C = -17.7 \text{MPa} \]

Time: 0.01hr  

\[ \sigma_{11}^T = 195 \text{MPa} \quad \sigma_{11}^C = -7.4 \text{MPa} \]

Time: 28hr  

\[ \sigma_{11}^T = 185 \text{MPa} \quad \sigma_{11}^C = -15.1 \text{MPa} \]

Time: 1000hr

Figure 19 Stress \( \sigma_{11} \) distributions in top IC

Three Cell Stack

For the 3-cell stack considered here, creep deformation of interconnect plates narrows down the air flow channels, similar as those observed for 1-cell stack, see Figure 20. Figure 20(a) and 20(b) show the deformed air flow channels at 0.01 hr and 1000hr, which illustrate the effects of CTE mismatch and long-term creep of interconnect steel plate, respectively. Mismatch of CTE under temperature drop from the operating temperature to room temperature narrows the air flow channel. In addition, the long-term creep of the interconnect steel plate also contributes to further narrowing of the air flow channels.
Figure 20 Deformed air flow channel (magnification factor=100)
It should be noted that the mismatch of CTE and the steel interconnect plate creep display
different influence on the fuel flow channel geometries for different fuel flow layer. Figure
21(a) and 21(b) show the deformed fuel flow channels at 0.01 hr and 1000hr, respectively.
The different effects of CTE mismatch and long-term creep of interconnect steel plate are
shown individually. It may be seen from Figure 21(a) that all the fuel channels are broadened
due to CTE mismatch during cooling from the operating temperature to the room temperature.
However, interconnect creep narrows the bottom fuel channel significantly, similar as those
observed in the 1-cell stack. The middle fuel channel is narrowed down, too. However, the
top fuel channel widens as the result of interconnect creep. The underlying reason for the
air/fuel flow channel geometry is the varying degrees of PEN deformation to accommodate
interconnect plate geometry change due to CTE mismatch and long-term creep. Figure 22
reveals the inconsistent bending deformation of the PEN and interconnect steel plate induced
by the CTE mismatch and long-term creep of the interconnect, narrowing down or broadening the air and fuel flow channel geometry respectively.

**Stress Re-distribution as a Result of IC Creep**

Figures 23 to 24 illustrate the effects of IC creep on stress evolutions in various cell components in the first 68 hours of operation for one-cell stack. It may be observed that the stresses in both the bottom and the top ICs are relaxed due to creep, the stresses in the PEN structure are also reduced due to the IC stress relaxation. However, PEN seal stresses remain at a relatively high level during operation without considering its creep behaviors. The maximum Von Mises stresses in various components of the one-cell stack are listed in Table 2 at three time points.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Top IC</th>
<th>Bottom IC</th>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>31.2</td>
<td>47.2</td>
<td>61.6</td>
<td>52.6</td>
<td>61.6</td>
</tr>
<tr>
<td>68</td>
<td>7.2</td>
<td>7.8</td>
<td>55.3</td>
<td>49.5</td>
<td>55.3</td>
</tr>
<tr>
<td>1000</td>
<td>4.8</td>
<td>5.0</td>
<td>54.3</td>
<td>49.1</td>
<td>54.3</td>
</tr>
<tr>
<td>Time (h)</td>
<td>PEN seal</td>
<td>Picture frame</td>
<td>Anode spacer</td>
<td>Anode seal</td>
<td>Cathode spacer</td>
</tr>
<tr>
<td>0.01</td>
<td>52.3</td>
<td>30.1</td>
<td>21.8</td>
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<td>49.1</td>
<td>5.8</td>
<td>5.0</td>
<td>5.0</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 2 Maximum Von Mises stresses in various components of one cell stack (MPa)
On bottom surface

$T = 0.01\text{hr}$  \hspace{1cm}  $T = 68\text{hr}$

Figure 23 Effect of creep on stress in bottom IC

On top surface

$T = 0.01\text{hr}$  \hspace{1cm}  $T = 68\text{hr}$

Figure 24 Effect of creep on stress in top IC
Figure 25 Effect of creep on stress in electrolyte

Figure 26 Effect of creep on stress in cathode
Figure 27 Effect of creep on stress in anode

Figure 28 Effect of creep on stress in PEN seal
Figure 29 Effect of creep on stress in spacer 1

Figure 30 Effect of creep on stress in spacer 2
4.0 Conclusions

The effects of interconnect creep on the change in air and fuel flow channel shapes and dimensions were predicted under the SOFC steady state operating condition for a period of 1000 hours. The purpose of this effort is to quantify the long term SOFC stack geometry.
changes by investigating the changes in air and fuel flow paths and the corresponding stress re-distribution among various cell components. The conclusions of the current study are:

1. Mismatch of CTE of the different components in SOFC causes the bending of various components such as interconnects and PEN structure;

2. Non-uniform bending deformations of various cell components cause the change of air and fuel flow path at the initial stage of SOFC operation: the height of air flow channel was reduced, but the height of fuel flow channel was enlarged slightly, for both one cell and three cell stacks;

3. Over the course of 1000 hours of operating time, creep behavior of the interconnect contributes to the height reductions of the air fuel flow channels, for both 1-cell and 3-cell stacks;

4. Over the course of 1000 hours of operating time, creep behavior of the interconnect has different influence on different fuel flow channels: (a) interconnect creep narrows the bottom fuel channel significantly, similar as those observed in the 1-cell stack; (b) the middle fuel channel is also narrowed, but with less magnitude; however, (c) the top fuel channel widens as the result of interconnect creep;

5. Effect of the creep of IC on the height of both the air and fuel flow channels is not monotonous due to the different stress levels in the interconnects, which create different stain rates under creep deformation;

6. Creep of the interconnect releases the stress in the interconnect, and reduces the stress level in the PEN structures;

7. Stress in the PEN seal remains at relatively high level without considering seal creep.

8. Seal creep should be considered and incorporated in future creep studies.
5.0 References


Fabrication of (Mn,Co)$_3$O$_4$ Surface Coatings onto Alloy Substrates

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Pacific Northwest National Laboratory, Richland, WA

March 2007
Abstract
Ferritic stainless steels are promising candidates for IT-SOFC interconnect applications due to their low cost and resistance to oxidation at SOFC operating temperatures. However, several challenges remain, including long term electrical conductivity and surface stability under interconnect exposure conditions and chromia scale evaporation. One means of extending interconnect lifetime and improving performance is to apply a protective coating, such as (Mn,Co)\textsubscript{3}O\textsubscript{4} spinel, to the cathode side of the interconnect. These coatings have proven effective in reducing scale growth kinetics and Cr volatility. This report describes several procedures developed at PNNL for fabricating (Mn,Co)\textsubscript{3}O\textsubscript{4} spinel coatings onto ferritic stainless steels.

Introduction
In recent years, progress in materials and fabrication techniques have allowed for a reduction in SOFC operating temperatures to a range (e.g., 650-800ºC) in which commonly used oxidation-resistant alloys, such as ferritic stainless steels, can be considered as replacement materials for the traditional ceramic interconnect materials used in high temperature (900-1,000ºC) SOFC stacks. Compared to doped lanthanum chromites, ferritic stainless steels offer advantages such as improved manufacturability, higher thermal conductivity, and lower material and fabrication costs. However, to demonstrate satisfactory durability and performance as interconnects, the selected alloys must satisfy a set of stringent material requirements, including:

- Excellent surface stability during simultaneous exposure to both cathodic (air) and anodic (fuel gas) atmospheres at elevated temperatures.
- Strong scale adhesion to the metal substrate and low Cr volatility from the scale to avoid potential cell poisoning.
- Good thermal expansion matching to other stack components (particularly for stacks using a rigid seal design).
- High electrical conductivity through both the bulk material and in situ formed oxide scales.
- Chemical compatibility with other materials in contact with the interconnect, such as seals, contacts and cell materials.
- Satisfactory mechanical reliability and durability at the device’s operating temperatures.
- Ease of manufacture.

In the past, conventional high-temperature oxidation-resistant alloys were developed for a range of applications that required excellent surface and/or structural stability, but not high scale electrical conductivity, which is important for SOFC interconnect applications. Recently, however, several ferritic stainless steels, including Crofer22APU (ThyssenKrupp) and ZMG232 (Hitachi), have been specifically developed for the interconnect application. Overall, these alloys demonstrate improved performance over traditional compositions, but several challenges remain, including long term electrical conductivity and surface stability under interconnect exposure conditions, chromia scale evaporation, and compatibility with the adjacent stack components, such as electrical contact layers and seals.
One means of extending interconnect lifetime and improving performance during exposure to air (oxidant) is to apply a protective coating, such as \((\text{Mn,Co})_3\text{O}_4\) spinel, to the cathode side of the interconnect.\(^1\) In addition to investigating the properties of a number of compositions in the \((\text{Mn,Co})_3\text{O}_4\) spinel family, PNNL has also developed techniques for fabricating spinel coatings which have proven effective in reducing scale growth kinetics and Cr volatility when applied onto ferritic stainless steels.\(^3\) This document, which contains specific details regarding PNNL’s slurry-based coating process, is intended to a) assist SECA participants in preparing and evaluating the performance of these coatings, and b) provide a basis from which SECA participants can tailor formulations and application procedures to meet the specific requirements of their SOFC development activities.

Fabrication Procedure

A simplified process schematic of the coating process is shown in Figure 1. Most of the coatings at PNNL are prepared using \(\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4\) powder which is attrition milled to a particle size distribution similar to that shown in Figure 2. The coating process begins with the preparation of a slurry with a viscosity that is appropriate for the chosen application method, such as painting, screen-printing, dip-coating, or spraying. Screen-printing has been found to be convenient for coating of flat parts, but other methods may be better suited for coating of shaped parts. After application of the slurry, the coated substrate is dried and then heat-treated in a reducing environment to decompose the spinel powder into a mixture of MnO and Co (see Figure 3, taken from Reference 3). During subsequent heat treatment in air, reaction-assisted sintering (during which the MnO and Co react to re-form the spinel phase) produces the final coating on the substrate (see Figure 4, taken from Reference 3). Specific details for several application methods are described below:

1. **Painting or Screen-Printing**
   a. Prepare a slurry by mixing the spinel powder with a binder system (e.g., Ferro B-75717) using a three-roll mill. A typical weight ratio of powder to binder is 1.0 : 0.6.
   b. Coat the alloy part with slurry. Alloy parts are typically cleaned by degreasing in acetone in an ultrasonic bath followed by washing with 2-propanol. This can be accomplished by painting with a brush or, for flat parts, by screen-printing, which allows for better control of the coating thickness. At PNNL, 165 mesh screens with 2 mil emulsion thickness are typically used to obtain coatings ~10-15 microns thick. The coated sample should be dried in air at ~100°C for 1-2 hours.
   c. Heat the coated sample under reducing conditions at 800°C for at least 2 hours; at PNNL, coatings are typically reduced for 4 hours. A 5°C/min heating and cooling rate is commonly used. The typical reducing gas is dilute hydrogen (2.75%H\(_2\)+in Ar) with ~3%H\(_2\)O (added by flowing the gas through a water bubbler at room temperature).
   d. Heat the coated sample in air at 800°C for 4 hours to complete the coating fabrication.

2. **Dip Coating**
   a. Prepare a slurry by mixing the spinel powder, Ferro B-75717 binder, and 2-propanol. A typical weight ratio for the mixture is spinel : B-75717 : 2-propanol = 1.0 : 0.6 : 1.0-1.5.
   b. Dip-coat the alloy part. At PNNL, the slurry is typically shaken for ~1 hour to assure homogeneity prior to dipping. Figure 5 shows a typical relationship between part
withdrawal rate and normalized coating mass after drying. After dip-coating, the coated part is typically dried at 80°C in a vacuum oven for ten minutes.

c. Perform the reducing and oxidizing heat treatments described in Steps 1c and 1d above.

3. Spray Coating

a. Prepare a slurry by mixing the spinel powder with B-75717 binder and carbitol or 2-propanol. A typical weight ratio for a carbitol-based slurry is spinel : B-75717 : carbitol = 1.0 : 0.3-0.6 : 0.6-1.0. A typical weight ratio for a 2-propanol-based slurry is spinel : B-75717 : 2-propanol = 1.0 : 0.6 : 0.75-1.0. If carbitol is used as the solvent, overnight stirring is recommended. All slurries are typically shaken for at least 1 hour before spray-coating.

b. Spray-coat the alloy part. At PNNL, spraying is performed using an air brush (Model 100-LGF, Badger Air Brush Co.) with a diaphragm compressor (Model 80-2, Badger Air Brush Co.). The distance between the nozzle and the substrate is kept at ~6 cm. The coating mass (and therefore thickness) is controlled by adjusting the spray-duration time; typical results are shown in Figure 6. Coated parts are typically dried overnight at room temperature, and then dried at 120°C in a vacuum oven for 8 hrs.

c. Perform the reducing and oxidizing heat treatments described in Steps 1c and 1d above.

Conclusion

(Mn,Co)3O4 spinel coatings prepared according to procedures developed at PNNL have proven effective in reducing scale growth kinetics and Cr volatility when applied onto ferritic stainless steels. It should be noted that PNNL’s experimental validation of the coating formulations and application processes was primarily conducted on small specimens (e.g., 1.2 cm x 2.5 cm). Investigations into the process consistency and reproducibility for larger sample sizes and various shapes (e.g., with integrated gas distribution and flow channels, manifolds, etc.) would be required to understand and optimize the coating thickness uniformity, microstructural consistency, and adherence.

References:


Acronyms

IT-SOFC: Intermediate temperature Solid Oxide Fuel Cell
PNNL: Pacific Northwest National Laboratory
SECA: Solid-State Energy Conversion Alliance
SOFC: Solid Oxide Fuel Cell
Figure 1. Schematic diagram of spinel coating fabrication process.

Figure 2. Typical particle size analysis for spinel powder used in slurry preparation.
Figure 3. SEM micrograph of cross-section of spinel coating on Crofer22APU after heat-treatment at 800°C for 24 hours in 2.75%H₂/bal. Ar (Reference 3).

Figure 4. SEM micrograph of cross-section of spinel coating on Crofer22APU after heat-treatment at 800°C in air for 100 hours (Reference 3).
Figure 5. Normalized dry weight of dip-coated spinel coating as a function of withdrawal speed from slurry.

Figure 6. Normalized dry weight of sprayed spinel coating as a function of spray duration time. Slurry recipe (weight basis) was spinel powder : B-75717 : 2-propanol = 1.0 : 0.6 : 1.0.
Topical Report

Effect of IC Surface Quality on Interfacial Strength and Life Quantification of Coated Metallic IC Using an Integrated Experimental/Modeling Approach

W. N. Liu
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E. Stephens
M. A. Khaleel

January 2008

Prepared for the SECA Core Technology Program
National Energy Technology Laboratory, Pittsburgh, Pennsylvania
under Contract DE-AC05-76RL01830
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Prepared for the SECA Core Technology Program
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Pacific Northwest National Laboratory
Richland, Washington 99352
Executive Summary

In PNNL report 16610(a), an integrated experimental/modeling methodology was developed to quantify the interfacial strength between oxide-scale and the Crofer substrate. The technique was applied to quantify interfacial strength and to predict possible delamination and subsequent spallation at the scale/substrate interface, therefore indicating the possible interconnect (IC) life under isothermal cooling or thermal cycling conditions. The purposes of the current report are to 1) report the decrease of interfacial strength with oxide growth, 2) report the effect of the metallic IC surface quality on the interfacial strength, 3) report on the interfacial strength at the different interfaces in the spinel coating/oxide scale/metallic substrates tri-layer systems, and 4) report the methodology for predicting life for spinel coated metallic interconnect.

Under the typical SOFC operating environment, the thickness of the oxide scale will continue to grow with operating time, even with protective coatings. First, the method presented by Sun et al. [5] was applied to oxide scale/Crofer 22 samples, which were oxidized for five different times, 300 h, 600 h, 900 h, 1200 h, and 1500 h, respectively. It was found that the interfacial strength between the oxide scale and Crofer22 substrate decreases with the growth of the oxide scale. For the samples with short oxidization time and thin oxide scale, the interfacial strengths measured were not consistent using the indentation test. It was found that the surface roughness of the metallic substrate plays a great influence on the consistency of the indentation results. When the ratio of the oxide scale thickness over the mean surface roughness is larger than 5.2, consistent indentation results, therefore interfacial adhesion strength, can be obtained. When the ratio of the oxide scale thickness over the mean surface roughness is less than 5.2, less consistent indentation results were observed.

The integrated experimental/modeling method was then applied to the spinel coated Crofer 22 and SS441 tri-layer systems to determine the adhesion strength of various interfaces. It is found that the oxide adhesion strength of as received SS441 is lower than that of Crofer 22. One possible reason is its higher surface roughness level. The methodology was then applied to a spinel coated Crofer 22 APU to predict the life of this coated IC system under isothermal cooling condition.

(a) X Sun, W Liu, EV Stephens, and MA Khaleel. 2007. Interfacial Strength and IC Life Quantification Using an Integrated Experimental/Modeling Approach. PNNL-16610, Pacific Northwest National Laboratory, Richland, WA [Limited Distribution].
### Acronyms

<table>
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<th>Acronym</th>
<th>Description</th>
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<td>CTE</td>
<td>Coefficient of thermal expansion</td>
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<td>FE</td>
<td>Finite element</td>
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<td>IC</td>
<td>Interconnect</td>
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<td>National Energy Technology Laboratory</td>
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<td>SECA</td>
<td>Solid-State Energy Conversion Alliance</td>
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<td>Scanning electron microscopy</td>
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<td>SOFC</td>
<td>Solid-oxide fuel cell</td>
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Acknowledgements

Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC05-76RL01830. The work summarized in this report was funded as part of the Solid-State Energy Conversion Alliance Core Technology Program by the U.S. Department of Energy’s National Energy Technology Laboratory. We would like to acknowledge the technical directions from Wayne Surdoval and Travis Shultz. Technical discussions with Dr. Z. Gary Yang are also gratefully acknowledged.
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1.0 Introduction

Interconnects (ICs) in solid-oxide fuel cells (SOFCs) provide cell-to-cell electrical connection and also serve as gas separators to separate the fuel (anode) from the oxidant (cathode). Recently, the IC materials development effort funded by the Energy Conversion Alliance (SECA) has been mostly focusing on ferritic stainless steels. Compared to chromium-based alloys, iron-based alloys have advantages in terms of high ductility, good workability, and low cost [1]. By far, iron-based alloys, especially Cr-Fe based alloys, e.g., Crofer 22 APU and SS441, are the most attractive metallic IC materials for SOFCs [2, 3].

It should be noted that the oxidation reaction of the metallic ICs in the SOFC working environments is unavoidable. The appearance and growth of the oxide scale will cause growth stress in the oxide scale [2,3]. In addition, the coefficient of thermal expansion (CTE) mismatch between the oxide and the substrate creates stresses in the scale and on the scale/substrate interface during cooling [4], leading to scale delamination/buckling and eventual spallation. The interfacial strength between the oxide scale and the substrate is therefore crucial to the reliability and durability of the metallic IC in SOFC operating environments. A methodology for quantifying the interfacial strength between the oxide scale and the Crofer substrate was presented by Sun et al. [5], it was also used to predict possible delamination and subsequent spallation at the scale/substrate interface, therefore indicating the possible uncoated IC life under isothermal cooling or thermal cycling conditions. The purposes of the current report are to 1) report the decrease of interfacial strength with oxide growth, 2) report the effect of the metallic IC surface quality on the interfacial strength, 3) report on the interfacial strength at the different interfaces in the spinel coating/oxide scale/metallic substrates tri-layer systems, and 4) report the methodology for predicting life for spinel coated metallic interconnect.

The thickness of the oxide scale will grow under the SOFC operating environment. First, the method presented in [5] was applied to oxide scale/Crofer22 samples, which were oxidized for five different times, 300 h, 600 h, 900 h, 1200 h, and 1500 h, respectively. It was found that the interfacial strength between the oxide scale and the Crofer22 substrate decreases with the growth of the oxide scale. For the samples with a short oxidization time and a thin oxide scale, the interfacial strengths measured were not consistent using the indentation test. It was found that the surface roughness of the metallic substrate plays a great influence on the consistency of the indentation results. When the ratio of the oxide scale thickness over the mean roughness is larger than 5.2, consistent indentation results, therefore interfacial adhesion strength, can be obtained. When the ratio of the oxide scale thickness over the mean roughness of the metal surface is less than 5.2, indentation results will be inconsistent.

The integrated experimental/modeling method was then applied to the spinel coated Crofer 22 and SS441 tri-layer systems to determine the adhesion strength of various interfaces. It is found that the oxide adhesion strength of as received SS441 is lower than that of Crofer 22. One possible reason is its higher surface roughness level.

An illustrative example is shown next demonstrating the application of this integrated methodology in life prediction for a spinel coated Crofer 22 APU under isothermal cooling condition.
2.0 Technical Approach and Model Description

This section discusses the structure and material properties of the oxide scale, and the Crofer/stainless steel substrate.

Figure 2.1 shows the cross-sectional microstructures of Crofer 22 APU after oxidation at 800°C without and with spinel coating materials, respectively. The cross-sectional microstructures of SS441 after oxidation at 800°C without and with spinel coating materials are shown in Figure 2.2. The thickness of the oxide scale and coating are assumed to be uniform. The oxide scale and spinel coating materials for Crofer 22 APU and SS441 are considered as similar and possess same mechanical properties. The mechanical property of the oxide scale of Crofer 22 APU and SS441 under high temperature is not currently available. The main composition of the oxide scale is Cr₂O₃; therefore, the values of Cr₂O₃ are used here, i.e., \( \nu = 0.27 \) and \( E = 250 \text{GPa} \) [6, 7]. The main spinel coating materials are Mn₁.₅Co₁.₅O₄, its modulus and Poisson’s ratio are measured as \( \nu = 0.36 \) and \( E = 124.7 \text{GPa} \) [8].

Temperature dependent material properties are used for Crofer 22 APU and SS441. Figure 2.3 through Figure 2.5 illustrate the Young’s modulus, CTE, and yield strength of Crofer 22 APU used in the numerical analyses [9-11], respectively. The corresponding temperature-dependent Young’s modulus, CTE, and yield strength of SS441 are shown in Figure 2.6 through Figure 2.8. [12, 13]
Figure 2.1. Cross-Sectional Microstructures of Crofer 22 APU After Oxidation at 800°C (a) Bare Crofer; (b) with Spinel Coating
Figure 2.2. Cross-Sectional Microstructures of SS441 After Oxidation at 800°C (a) Bare SS441; (b) with Spinel Coating
Figure 2.3. Temperature-Dependent Modulus of Crofer 22 APU

Figure 2.4. Temperature-Dependent CTE of Crofer 22 APU
Figure 2.5. Temperature-Dependent Yield Strength of Crofer 22 APU

Figure 2.6. Temperature-Dependent Modulus of SS 441
Figure 2.7. Temperature-Dependent CTE of SS 441

Figure 2.8. Temperature-Dependent Yield Strength of SS 441

Figure 2.9 shows a schematic of the indentation test. Figure 2.10 and Figure 2.11 depict the typical finite element (FE) model used for the Crofer/scale bi-layer system and Crofer/scale/coating tri-layer system, respectively. The typical FE mesh used for the SS441/scale bi-layer system and SS441/scale/coating tri-layer system are illustrated in Figure 2.12 and Figure 2.13, respectively. Taking advantage of the symmetrical nature of the indentation test, axisymmetric models were used for computational efficiency.
The thicknesses of the Crofer and SS441 substrates used in the indentation test, and therefore in the subsequent simulations, were different: the thickness of Crofer22 APU sample is 0.5 mm; the thickness of SS441 sample is 1.6mm. Very fine mesh was used within the indenter contact zone and near the interfaces between the substrate/scale and scale/coating to ensure accurate stress predictions at these locations.

![Figure 2.9. Schematic of Indentation Test](image)

![Figure 2.10. FE Mesh Used for Crofer/Scale Bi-Layer System](image)
Figure 2.11. FE Mesh Used for Crofer/Scale/Coating Tri-Layer System

Figure 2.12. FE Mesh Used for SS441/Scale Bi-Layer System
Figure 2.13. FE Mesh Used for SS441/Scale/Coating Tri-Layer System
3.0 Experimental Indentation Test

This section discusses the experimental procedures used in the indentation test and the corresponding experimental indentation results.

3.1 Experimental Procedures

The experimental procedures have been described in details by Sun et. al [5]. A hardness tester was used to apply the indentation load on the oxide scale of the metallic IC using a Rockwell 1/16-in.-diameter ball indenter. The loads were stair-stepped between 60 kgf and 150 kgf (load range of the hardness tester used in the indentation test) to determine the load that caused spallation to occur on each specimen. When spallation was observed, the load was typically reduced and the indentation repeated, continually increasing the load with each indent until failure was observed again.

Room-temperature indentation tests were performed first on oxidized bare Crofer specimens to quantify the interfacial strength between the oxide scale and the Crofer substrate. With different thicknesses of the oxide scale, i.e., different oxidation time, the corresponding interfacial strength could be calculated, and the effects of the scale thickness or oxidation time on the interfacial strength were studied. After determining the interfacial strength of the Crofer and oxide scale, room-temperature indentation tests on the spinel-coated Crofer specimens were followed. The interfacial strength between the oxide scale and the spinel-coating layer was determined.

In the indentation tests on bare SS441 samples, a larger diameter indenter tip (Rockwell 1/8-in.-diameter ball) had to be used because oxide scale spallation occurred at the minimum admissive load of the hardness tester using the Rockwell 1/16-in.-diameter ball indenter. Even with a larger diameter indenter, the indentation results are still less consistent than those for Crofer 22. It was found that the surface roughness of the SS441 sample is much higher than that of the Crofer 22. Surface modification (polishing) was then performed on the as-received SS441 sample to achieve a comparable surface roughness level as that of the Crofer 22. Indentation tests were then performed on the oxidized, surface modified samples to quantify the influence of surface quality on its scale/substrate interfacial adhesion strength.

Figure 3.1 is a scanning electron microscopy (SEM) image representative of the oxide scale observed on the specimens. This particular image is a 300-hour oxidized Crofer specimen with a measured scale thickness of 1.38 μm. Figure 3.2 includes a SEM image of a cross-section of the Crofer/scale/coating. All specimens were oxidized at 800°C. Metallography was performed to determine the oxide-scale thickness and the spinel-coat thickness for each specimen.
Figure 3.1. SEM Image Representative of the Oxide Scale Observed on the Crofer Specimens—300-Hour Oxidized Specimen with a Measured Scale Thickness of 1.38 μm

Figure 3.2. SEM Image of Cross-Section of Crofer/Scale/Coating—600-Hour Oxidized Specimen with a Measured Scale Thickness of 1.50 μm and Coating Thickness of 12.93 μm
3.2 Experimental Indentation Results

Table 3.1 lists the indentation test results for bare Crofer with different oxide scale thicknesses. Seven specimens oxidized at varying lengths of oxidation time were tested. These test results were reported in [5]. In our preliminary analyses, relatively coarse meshes were used in the finite element analysis to determine the interfacial stress: the mesh size used was about 3 μm at the scale/substrate interface [5]. In the current report, a much smaller mesh size of 0.5 μm is used at the interface to ensure more accurate stress calculations. The indentation results in Table 3.1 are included here again for the completeness of this report.

Table 3.2 lists the indentation test results for the spinel-coated Crofer with different thicknesses of oxide scale and the spinel coating. The respective indentation test results for bare SS441 and spinel-coated SS441 are listed in Table 3.3 and Table 3.4, together with the thicknesses of the oxide scale and the spinel coating. In the tables, the number of indents that either spalled or did not spall at each load condition tested along with the corresponding specimen scale thickness is tabulated.

### Table 3.1. Indentation Test Results for Bare Crofer with Oxide Scale

<table>
<thead>
<tr>
<th>Spec #</th>
<th>Scale Thickness (μm)</th>
<th>Load (Kgf)</th>
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<th>75</th>
<th>90</th>
<th>100</th>
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### Table 3.2. Indentation Test Results for Spinel-Coated Crofer with Oxide Scale

<table>
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<th>Spec #</th>
<th>Thickness (μm)</th>
<th>Load (Kgf)</th>
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<th>75</th>
<th>90</th>
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Table 3.3. Indentation Test Results for Bare SS441 with Oxide Scale

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<th>Load (Kgf)</th>
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<th>Spall</th>
<th>No Spall</th>
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<td>1</td>
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Table 3.4. Indentation Test Results for Spinel Coated SS441 with Oxide Scale

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<th>Load (Kgf)</th>
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<td>2</td>
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</table>

In Table 3.1, relatively consistent indentation results have been obtained for oxidized bare Crofer 22 with scale thickness greater than 2.06 μm. In general, at a particular scale thickness, the number of spalled samples increases with indentation load. On the other hand, under a specific indentation load, more spalled samples are observed with increasing oxide scale thickness. For specimens with scale thickness of 2.04 μm and 1.50 μm, no spallation was observed. However, for the sample with the thinnest scale of 1.38 μm, the indentation test results were not consistent. In other word, no spallation and spallation alternatively occur for specimen #1 with an increase of the indentation load from 90Kgf to 150Kgf.

In Table 3.3, the indentation test results for bare SS441 with oxide scale were also not consistent, see results listed in Table 3.3. The surface roughness of the bare Crofer 22 APU and SS441 were then studied to gain some better understanding of the factors influencing interfacial failure.

Table 3.5 includes the measured results of the surface roughness of the bare Crofer 22 APU, where $R_s$ refers to mean of absolute values of the profile deviations from the mean line, $R_y$ represents the sum of the height of highest peak and depth of deepest valley from mean line, $R_q$ is the square root of the mean
of the squares of the profile deviations from the mean line, and $R_z$ is the sum of the mean height of the five highest peaks and the mean depth of the five deepest valleys. Table 3.6 lists the similar surface roughness measurements for the as-received SS441 samples.

**Table 3.5.** Surface Roughness Measurements of As-Received Bare Crofer 22 APU

<table>
<thead>
<tr>
<th>Profile #</th>
<th>$R_a$ ($\mu m$)</th>
<th>$R_y$ ($\mu m$)</th>
<th>$R_q$ ($\mu m$)</th>
<th>$R_z$ ($\mu m$)</th>
</tr>
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<tbody>
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<td>1</td>
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<td>1.69</td>
<td>1.61</td>
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<td>2</td>
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<td>1.82</td>
<td>1.64</td>
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<td>2.02</td>
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<td>2.20</td>
<td>0.38</td>
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<td>6</td>
<td>0.35</td>
<td>2.25</td>
<td>2.07</td>
<td>0.44</td>
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<td>7</td>
<td>0.26</td>
<td>1.97</td>
<td>1.70</td>
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<td>Average</td>
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<td>1.86</td>
<td>0.36</td>
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</table>

**Table 3.6.** Surface Roughness Measurements of As-Received Bare SS441

<table>
<thead>
<tr>
<th>Profile #</th>
<th>$R_a$ ($\mu m$)</th>
<th>$R_y$ ($\mu m$)</th>
<th>$R_q$ ($\mu m$)</th>
<th>$R_z$ ($\mu m$)</th>
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<tr>
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<td>0.66</td>
<td>6.20</td>
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<tr>
<td>Average</td>
<td>0.73</td>
<td>6.83</td>
<td>4.95</td>
<td>0.96</td>
</tr>
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</table>

Comparing the surface roughness measurements of the as-received samples, it is seen that Crofer 22 APU has a much better surface finish quality with an average $R_a$ level of only 0.29 $\mu m$. On the other hand, the as-received SS441 has a much poorer surface finish, with an average $R_a$ level of 0.73 $\mu m$.

Correlating the surface quality of Crofer 22 APU with the indentation test results shown in Table 3.1, it is indicative that when the oxide scale is too thin, cooling induced local residual stresses can dominate the indentation results, causing them to be inconsistent over the various loading ranges and indentation locations. For Crofer 22 APU, when $H_o / R_a < 5.2$ ($H_o$ refers to the thickness of the oxide scale), the indentation results becomes inconsistent.
Applying the same rational to the indentation results on bare SS441 in Table 3.2, it is found that the ratio of $H_o / R_o$ is less than 5.2 for all the oxidized samples except specimen #7. Again, surface roughness induced local interfacial stresses may dominate the indentation results, causing them to be inconsistent. In order to further investigate the effects of IC surface roughness on interfacial strength and IC life, surface modified SS441 is currently being investigated. The indentation results will be presented in our next report.
4.0 Interfacial Strength Quantification

Interface of Oxide/Crofer 22 Substrate

In Table 3.1, the indentation loads for the experimental results highlighted in yellow are taken as the critical indentation loads to determine the interfacial strength of the oxide scale and Crofer substrate for different oxide thicknesses. Finite element simulations of the corresponding Rockwell 1/16-in.-diameter ball indentation tests on the oxide scale/substrate bi-layer system with different scale thickness were performed. The interfacial shear stresses at the critical indentation loads are quantified as the interfacial strengths for various oxide thicknesses. The typical finite element mesh used is shown in Figure 2.11. The characteristic mesh size at the location for maximum shear stress is around 0.5 micron. The Crofer 22 APU substrate is considered to be elastic-plastic based on the properties in Ref. [9]. This is also based on the observed permanent deformation on the indented samples.

The predicted interface shear strength versus the oxide scale thickness is depicted in Figure 4.1. The results here indicate that the interfacial strength changes with the increase of oxide thickness. The maximum interfacial shear strength of 395 MPa is predicted for the specimen with 2.41 \( \mu \text{m} \) thick scale at the critical indentation load of 100 Kgf. With further growth of the oxide scale, the interfacial strength decreases. Similar observations of decreasing interfacial toughness with increasing scale thickness have been reported on SS441 in Ref. [14]. The potential reasons for the interfacial strength degradation are: 1) change of the elemental composition along the scale interface with oxidation time and 2) change of the growth stress with oxidation time. Further work in these areas is being pursued to quantify these effects.

![Figure 4.1. Predicted Interfacial Shear Strength Versus Oxide Scale Thickness for Crofer 22 APU](image)

Interface of Spinel Coating/Oxide for the Spinel-Coating/Oxide/Crofer Tri-Layer System

In order to determine the interfacial strength of the spinel coating to the oxide layer, finite element simulations are performed for the indentation tests in Table 3.2 on spinel-coating/oxide/Crofer tri-layer systems. Typical finite element mesh is shown in Figure 2.11.
The predicted maximum interfacial shear stresses at the scale/Crofer and Spinel/scale interfaces under the critical indentation loads (highlighted in yellow in Table 3.2) are depicted in Figure 4.2. The predicted interfacial shear stresses between the oxide scale and Crofer for the two cases are both less than the oxide scale/Crofer interfacial strength determined in the previous section. Therefore, indentation failure will not occur at this interface. Detailed SEM cross section of the failed spinel-coated Crofer in Figure 4.4 confirms this prediction.

On the other hand, the interfacial shear stress in the interface of the oxide scale and the spinel-coating layer is much higher than that on the oxide scale/Crofer interface, see Figure 4.2. Figure 4.3 shows the shear stress distribution at indentation load of 130Kgf for the spinel-coated Crofer tri-layer system. During indentation, very high magnitude of shear stress is predicted in the spinel coating as well as at the coating/oxide scale interface. Therefore, failure in the spinel coating caused by this high shear stress may precede the coating/oxide interface failure. The SEM cross section of the failed spinel-coated Crofer in Figure 4.4 again confirms this prediction. When failure occurs first in the spinel coating, the subsequent interfacial failure at the spinel coating/oxide interface can be considered as the results of crack propagation. Therefore the predicted interfacial stress at the spinel/oxide interface at corresponding critical indentation loads can be considered as the lower bounds of the true interfacial strength at that interface. Results in Figure 4.3 indicate that the lower bound of this interfacial strength is 886 MPa.

![Figure 4.2. Maximum Interfacial Shear Stress on the Interfaces for Spinel-Coated Crofer System](image)
As discussed earlier, the indentation test results for as-received SS441 with oxide scale are not consistent due to the poor surface quality. Even so, one test result (highlighted in yellow in Table 3.3) for the specimen with 2.32 μm thick oxide scale has been chosen to calculate the interfacial strength. This case is chosen because the indentation results show an increasing number of spallations with increasing indentation load, even though failure was also observed at the minimum indentation load. The corresponding strength obtained can therefore be considered as the upper bound of the actual interfacial strength between the as received SS441 and its oxide scale. The calculated maximum interfacial shear stress at the oxide/SS441 for this case is about 348 MPa. Therefore, the actual interfacial strength of the oxide scale and as-received SS441 should be less than 348 MPa.
Interfaces in Spinel-Coating/Oxide/SS441 Tri-Layer Systems

Figure 4.5 shows the predicted maximum interfacial shear stresses for the spinel-coated SS441 systems highlighted in Table 3.4. The predicted shear stresses at the oxide scale/SS441 interface for both cases are quite close to the upper bound of the interfacial strength quantified in the previous section, i.e., 348 MPa.

The predicted maximum interfacial shear stresses at the oxide scale/spinel-coating interface are slightly larger than the lower bound of the interfacial strength determined by the indentation test, i.e. 886 MPa. Even though it is impossible to exactly pinpoint the failure locations for the tri-layer systems using these data, it is possible to suggest that the interfacial failure will likely to occur on the oxide scale/SS441 interface based on the upper and lower bound strengths at different interfaces illustrated in Figure 4.5.

Figure 4.6 shows an SEM cross-section of a failed spinel-coated SS441 under critical indentation load. The indentation failure did occur on the oxide scale/SS441 interface, suggesting that the interfacial strength of the oxide scale and spinel-coating layer should be higher than the value previously determined by the indentation results on Crofer/oxide/spinel system. In fact, it should be higher than 1005 MPa since failure did not occur at the oxide/spinel interface. On the other hand, because failure occurred at the oxide/SS441 interfaces for both the tri-layer systems, interfacial strength of the oxide/SS441 can be quantified as 314 MPa for the as received SS441.

![Figure 4.5](image_url)  
**Figure 4.5.** Maximum Interfacial Shear Stresses on the Interfaces for Spinel-Coated SS441 (as received) System
Figure 4.6. SEM Image of Cross-Section of Failed Spinel-Coated SS441 (as received)
5.0 Life Prediction of Spinel-Coated Metallic Interconnect

The interfacial strengths determined in the previous sections for various interfaces can now be used to quantify the life of spinel coated metallic interconnect by comparing them with the interfacial stresses developed during stack cooling process. Based on the predicted interface shear stress with different oxide scale thicknesses developed during isothermal cooling from the operating temperature to room temperature, the critical thickness of the oxide scale was determined by comparing with the interfacial strength. The corresponding oxidation time required to form this critical thickness of the oxide scale can be determined using the oxide growth kinetics curve with spinel coating. Interconnect life can then be quantified. Similar analyses procedure was reported in PNNL Report 16610 for uncoated interconnect systems.

Assuming the thickness of spinel coating is 15-micron, the maximum interfacial shear stresses at the scale/substrate interface and scale/spinel interface caused by isothermal cooling (from 800°C to room temperature) are calculated for various subscale thickness as shown in Figure 5.1. At both interfaces, the cooling-induced maximum interfacial shear stress increases with scale growth. It is also illustrated that the interfacial shear stresses on the oxide scale/Crofer interface is much higher than that on the oxide scale/spinel coating interface. Meanwhile, the quantified interfacial strength at the oxide scale/Crofer interface is much lower than that of the oxide scale/spinel coating interface. Therefore, cooling induced spallation will occur at the oxide/Crofer interface. Assuming a constant interfacial strength of 395 MPa, the critical oxide scale thickness at which interfacial fracture/delamination will occur during isothermal cooling is identified as 4.2-microns.

The critical oxide thickness can then be used together with a typical oxide-growth kinetics law, such as that described in Figure 5.2, to estimate the IC life under a normal operating temperature of 800°C. For example, the oxide-growth kinetics for spinel-coated Crofer 22 APU can be expressed as

\[ h = 0.0277 \cdot t^{1/2} + 0.751 \]

Taking the critical oxide thickness as 4.2 microns, the life for the spinel coated Crofer can be calculated as 15504 h.

It should be mentioned that the interconnect life predictions discussed here and in PNNL Report 16610 have not considered the effects of surface roughness related local stresses generated by the cooling process. Both analyses assume a perfectly smooth interface between the metallic interconnect and its oxide layers. The effect of surface roughness/finish on interconnect life prediction is the subject of our future studies.
Figure 5.1. Increase of Interfacial Shear Stress with Growth of Oxide Scale Under Isothermal Cooling Conditions
Figure 5.2. Oxide Growth Kinetics for Bare Crofer 22 and Spinel Coated Crofer 22

\[ T \text{ (mïrons)} = 0.0277t^{0.5} + 0.751 \]

\[ R^2 = 0.9961 \]
6.0 Conclusions

In this report, the shear strengths of the oxide/substrate interface and the oxide scale/spinel coating interfaces are quantified using a combined experimental/analytical approach. First, stair-stepping indentation tests are performed to quantify the critical indentation loads at which scale spallation occurs for various scale thicknesses. Then corresponding finite element indentation tests are performed to calculate the interfacial shear strength at the critical indentation load at different interfaces.

Based on the analyses of combined experimental and modeling results, some conclusions can be summarized as follows.

(1) The interfacial strength between the oxide scale and the Crofer22 substrate decreases with the growth of the oxide scale, indicating that the growth of the oxide scale will degrade the IC reliability and therefore influence the long-term stack performance.

(2) Interconnect surface roughness/finish influences the consistency of the indentation results. For those samples with \( H_s / R_s < 5.2 \), inconsistent indentation results were observed. When this ratio is greater than 5.2, consistent interfacial strength can be obtained. The effects of surface roughness/finish on interfacial strength and interconnect life prediction are the subjects of our current studies.

(3) The surface roughness of the as received SS441 is roughly three times higher than that of the Crofer22.

(4) The oxide adhesion strength of as received SS441 is lower than that of the Crofer22. One possible reason is its higher surface roughness.

(5) The interfacial adhesion strength of the oxide scale/spinel-coating interface is much higher than that of the oxide scale/substrate interface.

(6) The interfacial strengths determined by this integrated experimental/modeling approach can be used to quantify the life of the spinel-coated metallic IC. The predicted life of the Crofer 22 APU coated with 15-micron spinel coating is around 15500 h.

Our future work include applying similar methodology in identifying the interfacial strength of oxide layer with surface modified SS441 to confirm the effects of surface roughness/finish on interfacial strength and interconnect life prediction. We will also continue to investigate the degradation mechanisms of interfacial strength with oxide scale growth.
7.0 References


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Investigation of AISI 441 Ferritic Stainless Steel and Development of Spinel Coatings for SOFC Interconnect Applications

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Investigation of AISI 441 Ferritic Stainless Steel and Development of Spinel Coatings for SOFC Interconnect Applications

Abstract
As part of an effort to develop cost-effective ferritic stainless steel-based interconnects for solid oxide fuel cell (SOFC) stacks, both bare and spinel coated AISI 441 were studied in terms of metallurgical characteristics, oxidation behavior, and electrical performance. The conventional melt metallurgy used for the bulk 441-alloy fabrication leads to significant processing cost reduction, and the alloy chemistry, which includes minor alloying additions of Nb and Ti, facilitates strengthening by precipitation and formation of Laves phase both inside grains and along grain boundaries during exposure in the intermediate SOFC operating temperature range. The Laves phase formed along the grain boundaries also ties up some of the Si. No formation of an insulating silica layer at the scale/metal interface was observed during prolonged exposure at SOFC operating temperatures. Nevertheless, substantial increases in ASR observed during long-term oxidation due to oxide scale growth suggested the need for a conductive protection layer, which could also minimize Cr evaporation. In particular, Mn$_{1.5}$Co$_{1.5}$O$_4$ based surface coatings on planar coupons substantially improved the electrical performance of the 441, yielding stable ASR values at 800°C for over 5,000 hours. Ce-modified spinel coatings retained the advantages of the unmodified spinel coatings, and appeared to alter the scale growth behavior beneath the coating, leading to a more adherent scale. The spinel protection layers also appeared to improve the surface stability of 441 against the anomalous oxidation that has been observed for ferritic stainless steels exposed to dual atmosphere conditions similar to SOFC interconnect environments. Hence, it is anticipated that, compared to unmodified spinel coatings, the Ce-modified coatings may lead to superior structural stability and electrical performance. There is, however, a need to develop and validate the coating for larger, shaped interconnects. It should also be noted that the alloy oxidation and corrosion resistance in fuel compositions (syngas, hydrocarbons, etc) and fuel utilizations (up to 85%, for example) of practical interest have not yet been studied.

I. Introduction
Oxidation resistant ferritic stainless steels are considered to be promising candidate materials for interconnect applications in SOFC stacks operating in the intermediate temperature range of 650-850°C. One issue associated with the use of conventional steels in this application, however, is the high electrical resistance and physical degradation that can result from the growth of the oxide scale on the alloy surface during high temperature exposure. For steels containing sufficient residual silicon, such as AISI 430, electrical resistance can be further increased by the formation of a continuous insulating silica layer at the scale/alloy interface. Low Si ferritic alloys have been developed for interconnect applications (e.g., Crofer22APU), but the required additional processing to remove the Si substantially increases the material cost.

Alternatively, modification of the alloy chemistry can potentially be used to avoid silica layer formation without the need for expensive vacuum refining steps. For example,
Dulieu et al.\textsuperscript{1} reported that alloy 1.4509 (German specification, analogous to AISI 441), which is similar in many respects to 1.4016 (AISI 430), did not form a silica sub-layer at the scale/alloy interface, in spite of the presence of over 0.5% residual Si in both alloys. The primary difference in the composition of the two alloys is the presence of small amounts of Nb and Ti in 1.4509, suggesting that these additives played a key role in preventing Si from forming an insulating oxide layer at the scale/alloy interface.

Based on this encouraging result, the metallurgical characteristics, oxidation behavior, and electrical performance of AISI 441 were evaluated. In addition, benefits of protective air-side interconnect coatings were examined by applying spinel-based coatings to AISI 441, and comparing the behavior of the coated steel to that of uncoated steel. Results of these investigations are summarized in this report.

II. Experimental Procedure

ATI Allegheny Ludlum provided test samples of AISI 441 (referred to hereafter as 441). The chemical analysis provided by the manufacturer is detailed in Table I. As received steel coupons (25 mm x 12.5 mm x 1.5 mm) were cleaned in an ultrasonic acetone bath for five minutes and then rinsed with alcohol prior to oxidation or electrical testing, or application of a spinel coating. Mn\textsubscript{1.5}Co\textsubscript{1.5}O\textsubscript{4} (MC) and Ce\textsubscript{0.05}Mn\textsubscript{1.475}Co\textsubscript{1.475}O\textsubscript{4} (Ce-MC) spinel powders were prepared via glycine-nitrate combustion synthesis and applied to selected alloy coupons using a slurry-based approach.\textsuperscript{2} After coating, the dried coupons were first heat-treated in a reducing environment (2.75% H\textsubscript{2}/3% H\textsubscript{2}O/balance Ar) for two hours and then oxidized in ambient air at 800\textdegree C for one hour.

Bare and coated steel coupons were evaluated via isothermal oxidation tests in ambient air. The isothermal oxidation testing in air was performed by suspending the bare or coated coupons from an alumina rod in a tube furnace. A steady flow of ambient air (~1-2% water) was provided throughout the oxidation tests. The oxidized coupons were weighed before and after heat treatment, and then subjected to microstructural characterization. Dual atmosphere tests (simultaneous exposure to air and hydrogen, both with ~3% H\textsubscript{2}O) were also performed, following the procedure described in Ref. 3. The electrical resistance of bare and coated 441 was measured using a four-probe DC technique. (La\textsubscript{0.8}Sr\textsubscript{0.2})\textsubscript{0.98}MnO\textsubscript{3} (LSM) contact paste was applied between two identical steel coupons and Pt leads were spot-welded to the coupons. During the resistance tests, a constant current density of 500 mA.cm\textsuperscript{-2} was applied to the coupons. Details of the test arrangement were reported in a previous publication.\textsuperscript{4} XRD, SEM/EDS, and TEM/EDS analyses were performed on selected samples.

III. Results and Discussion

A. Properties of Ferritic Stainless Steel 441

1. Metallurgy of 441

The steel studied was representative of AISI 441, a commercially available ferritic stainless steel (i.e., body-centered cubic crystal structure) specified as UNS S44100. A similar material is specified by DIN 1.4509. The compositional ranges for these alloys are shown in Table I. Alternatively; a very similar grade with a somewhat more restrictive compositional range is produced and sold as18CrCb. These two variants
together find large volume applications in the construction of heat-resistant components for automotive exhaust systems.

Overall, AISI 441 is similar to AISI 430, a very common mid-level Cr ferritic steel. However, it also contains important additions of Nb and Ti which result in improved high temperature strength, weld ductility, and resistance to inter-granular corrosion in weld heat affected zones. The improved high temperature strength is a consequence of the formation of dispersed Laves phase (Fe2Nb) precipitates.

Table I. Compositional ranges of UNS S44100 and DIN 1.4509, along with typical AISI 441 chemistry and the chemical analysis of AISI 441 tested in this study.

<table>
<thead>
<tr>
<th>Element</th>
<th>UNS S44100 (Ref.5)</th>
<th>DIN 1.4509</th>
<th>Typical 441 heat chemistry (Ref. 5)</th>
<th>Test Material (actual)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.03 max.</td>
<td>0.030 max.</td>
<td>0.009</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>17.5-19.5</td>
<td>17.5-18.5</td>
<td>18.0</td>
<td>17.6</td>
</tr>
<tr>
<td>Mn</td>
<td>1.0 max.</td>
<td>1.0 max.</td>
<td>0.35</td>
<td>0.33</td>
</tr>
<tr>
<td>Si</td>
<td>1.0 max.</td>
<td>1.0 max.</td>
<td>0.34</td>
<td>0.47</td>
</tr>
<tr>
<td>Nb</td>
<td>0.3 + 9xC min; 0.9 max.</td>
<td>0.3 + 3xC min; 1.0 max.</td>
<td>0.50</td>
<td>0.46</td>
</tr>
<tr>
<td>Ti</td>
<td>0.1-0.5</td>
<td>0.1-0.6</td>
<td>0.22</td>
<td>0.18</td>
</tr>
<tr>
<td>Ni</td>
<td>1.0 max.</td>
<td>1.0 max.</td>
<td>0.30</td>
<td>0.20</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td>0.05</td>
<td>0.045</td>
</tr>
<tr>
<td>P</td>
<td>0.04 max.</td>
<td>0.040 max.</td>
<td>0.023</td>
<td>0.024</td>
</tr>
<tr>
<td>S</td>
<td>0.03 max.</td>
<td>0.015 max.</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe</td>
<td>balance</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Experimental Observations:**

Figure 1 shows an SEM image of a polished cross section of the as-received 441. Differences in contrast resulting from different crystal orientations revealed that the grains ranged in size from around 20 to 60 microns. Second phases (lighter in appearance) were observed to be randomly distributed within the grains. SEM/EDS point analysis indicated that the second phase precipitates were rich in Nb and Ti, but contained little, if any, Si. This was further confirmed by TEM analysis, which indicated that the intra-grain precipitates were a Laves phase, which is consistent with the Fe2Nb Laves phase reported in the manufacturer’s technical data “blue sheet” for 441.

After oxidation in air at 800°C for 300 hours, second phase formation was observed at the grain boundaries, as shown in the SEM image in Figure 2. Subsequent TEM analysis indicated that the grain boundary phase was a Laves phase rich in both Nb and Si, in contrast to the initial intra-grain precipitates, which contained little, if any, Si.

**Thermodynamic Calculations:**

ThermoCalc software (using the TCFe5 database) was used to gain insight into the equilibrium phase constitution of the 441 alloy. Weight fraction of phases vs. Temperature is plotted in Figure 3 using typical 441 heat chemistry (see column 3 of Table I), with the exception of S and P, which were set to 0. This calculation shows 441 to solidify over a narrow range with BCC and MC carbides (FCC_A1#2) forming directly from the melt. The solidus occurs at about 1466°C. The BCC and MC carbides phases are the only stable phases from the solidus to about 833°C, where the first Laves phase (LAVES_PHASE_C14) formation is indicated. (It will be noted that, in fact,
Experimental results have verified the formation of the Laves phase at a somewhat higher temperature: 850°C. The amount of Laves phase increases as the temperature falls. At about 626°C, Sigma phase formation is predicted. It should be noted that the kinetics for Sigma phase formation are slower than those for Laves phase formation. As such, Sigma phase may not be observed in the short term even if it is predicted thermodynamically. However, Sigma phase formation may need to be taken into account during the projected 40,000h life cycle of the SOFC (especially with lower temperature operation or a more Sigma phase favoring alloy chemistry). Sigma phase can reduce the Cr content of the surrounding, resulting in localized breakdown of the protective oxide scale. The effect of individual alloy constituents on Laves phase formation was also evaluated using ThermoCalc; those results, and their possible implications for future alloy development, are summarized in Appendix A.

2. Oxidation Behavior of 441

Figure 4 shows the oxidation behavior, in terms of weight gain as a function of time, of 441 at 800°C in flowing air. The weight gain due to the surface oxide scale growth approximately followed the classic Wagner parabolic relationship with time. The oxidation rate was similar to that previously measured for Crofer22APU, and slightly lower than that reported for AISI 430 under similar testing conditions. X-ray diffraction and cross-sectional SEM/EDS analysis on the oxidized samples confirmed that, as in the case of Crofer22APU, the scale grown on 441 had a bi-layer structure with a Mn-Cr spinel top layer and a chromia-rich sub-layer. No spallation was observed in the early stages of oxidation, but after 900 hours, localized scale spallation was observed, with the spallation edges coinciding with grain boundaries (Figure 5). Occasional delamination observed at the scale/alloy interface during cross-sectional analysis provided qualitative evidence that the bonding of the scale to the steel substrate was weaker than that previously observed for Crofer22APU, possibly due to the absence of rare earth elements in the 441 substrate (see discussion below). Exposure to a low oxygen partial pressure (pO₂) environment (moist hydrogen) resulted in predominantly compact scale formation very similar in structure and chemistry to that observed after air exposure. Selected areas indicated porosity near the scale–metal interface. The scale did not show any evidence of spallation. This observation is in agreement with the observations on 441 by Chandra-Ambhorn et al., who also found higher adhesion energy for the scale in the low pO₂ environment compared to the adhesion energy for the air-grown scale.

3. Electrical Performance of 441

In addition to satisfactory structural and surface stability, candidate interconnect alloys must also provide low electrical resistance in order to minimize power loss. Figure 6 shows the area specific resistance (ASR) of 441 as a function of time, measured in air at 800°C. The 441 exhibited an initially low ASR that increased steadily over time due to oxide scale growth, reaching ~20 mΩ.cm² after 500 hours. Figure 7 shows an SEM cross-section image of the 441 and LSM contact material after the electrical measurement. A uniform scale was grown on the 441 substrate, which appeared to have reacted with the LSM contact material at their interface to form a dense interfacial layer. Importantly, there was no silica layer formation at the scale/metal interface, in spite of the relatively
high residual Si content (0.47%) in the steel. This is partly attributable to the observed incorporation of Si into the grain boundary Laves phase.

B. Properties of Spinel-Coated Ferritic Stainless Steel 441

As mentioned above, chromia-forming ferritic stainless steels such as 441 are promising candidate materials for interconnects in SOFC stacks. During long-term operation, however, materials-related challenges may arise, including surface instability (including oxidation, spallation, and reactions with neighboring components), increasing electrical resistance due to continuous oxide scale growth, and chromia-scale evaporation, which may lead to cathode poisoning.

One promising approach to overcome these issues is surface-modification of the metallic interconnects with conductive oxide coatings. For example, (Mn,Co)₃O₄ spinel coatings on stainless steel interconnects have been demonstrated to be effective in limiting inward oxygen and outward chromium diffusion.2,4,8-11 As a result, spinel coatings are expected to improve stack performance by enhancing oxidation resistance and avoiding Cr poisoning. To fully utilize these advantages of the coatings, however, adequate adherence at the interfaces between the coating, the scale grown beneath the coating, and the metal substrate is also required.

One well-established way to improve scale adherence to stainless steel substrates is to add small amounts of rare earth (RE) element(s) into the alloy. An alternative approach is to modify the alloy surface by deposition or coating with RE, usually in the form of oxides.12-15 For example, Alman el al.16,17 reported improved oxidation resistance after surface treatment of ferritic stainless steels with Ce, via a pack cementation-based process. Preliminary testing at PNNL indicated that the surface treatment led to reduced ASR, at least in the hundreds of hours time frame. However, to obtain satisfactory long-term oxidation resistance, and to minimize Cr volatility, a protective coating (either on a bare or Ce surface-modified alloy) may be required. Recently, PNNL has worked to obtain the benefits of a spinel coating and a Ce surface treatment in a single fabrication step by the application of spinel coatings modified with Ce. Specifically, Mn₁.₅Co₁.₅O₄ spinel was modified by addition of Ce (the nominal composition was Ce₀.₀₅₀Mn₁.₄₇₅Co₁.₄₇₅O₄) and then applied as a coating onto 441, which, as noted above, contains no RE additions. The properties of 441 with the Ce-modified spinel coating (Ce-MC) were investigated and compared to the properties of both uncoated 441 and 441 coated with the “standard” Mn₁.₅Co₁.₅O₄ spinel (MC).

1. Oxidation Behavior of Spinel-Coated 441

Figure 4 shows the oxidation behavior, in terms of weight gain as a function of time, of MC and Ce-MC coated 441 at 800°C in air. It is clear that, during the 1200 hours of testing, the oxidation rate of the 441 was substantially reduced by the presence of the spinel coatings. Since the coatings appeared to provide a diffusion barrier to air (i.e., with closed pore microstructure), the observed weight change of the coated samples is attributed to oxygen ion inward diffusion through the coating leading to subsequent scale growth beneath the coating.

Further insight into the effects of the coatings can be gained from Figure 8, which shows the oxidation behavior of bare and coated 441 at 850°C in air. During the early stages of the oxidation, the weight gain due to scale growth beneath the coatings was
similar, but, after ~600 hours of oxidation, the net weight gain of the samples with the MC coatings leveled off and dropped to near zero after 900 hours. Spallation of the MC coating was visually observed after the test, and SEM analysis indicated that the spallation occurred along the scale/metal interface. In comparison, the weight of the samples with the Ce-MC coatings continued to increase (at a much lower rate than the uncoated 441) during the whole test, and no spallation was observed on the Ce-MC coated samples, either visually and microscopically. These results suggest that the addition of Ce to the coating material led to a beneficial RE effect of scale adherence.

2. Electrical Performance of Spinel-Coated 441

Figure 6 shows ASR of bare, MC, and Ce-MC spinel-coated 441 as a function of time at 800°C in air. The beneficial effect of the spinel coatings on ASR is clearly apparent. While the electrical performance of the MC and Ce-MC spinel coated coupons was similar, the structure and properties of the interface between the metal substrate and the oxide scale grown beneath the coatings appeared to differ. SEM cross-section analyses on tested samples with the MC coating revealed cracks or gaps along the scale/metal interface (Figure 9(a)). Though the cracks were likely generated during the cooling at the end of the test or during sample polishing for SEM analysis, they are qualitative indicators of relatively poor bonding at the scale/metal interface, and were consistent with other test results described above. In contrast, the scale grown beneath the Ce-MC coating (Figure 9(b)) remained adherent to the metal substrate, with no noticeable cracks or detachment along the interface. Both the MC and Ce-MC coatings were effective barriers to Cr-outward diffusion, though some Fe diffusion into the spinel coatings was evident, as indicated by SEM/EDS analyses shown in Figure 10. Although the EDS line scan did not clearly reveal Ce in the Ce-MC coating, point EDS analyses indicated the presence of ceria as a second phase (shown as white spots in Figure 10(b)) finely dispersed in the coating matrix. Thus, it appears that there was limited, if any, solubility of Ce in (Mn,Co)₃O₄, leading to subsequent precipitation of the second phase. Overall, the most important difference between the MC and Ce-MC coatings is the apparent improvement in scale adherence and thus scale/metal interfacial stability when Ce was included in the spinel coating composition.

Figure 11 shows ASR of bare, MC, and Ce-MC spinel-coated 441 as a function of time at 850°C in air. Once again, the beneficial effect of the spinel coatings on ASR is evident. SEM analysis of the tested samples clearly demonstrated the benefit of the Ce addition to the coating. The MC coating, and the scale grown beneath it, exhibited buckling on the 441 surface (see Figure 12(a)), and detachment occurred along the scale/metal interface, as shown in the inset in Figure 12(a). The buckling and detachment likely occurred during the cooling after the end of the test, as the electrical performance remained stable throughout the test. In contrast, the Ce-MC coating, and the scale grown beneath it, was well adherent to the metal substrate, and no cracking was observed along the scale/metal interface (see Figure 12(b)). SEM/EDS analysis found no evidence of Cr penetration into either the MC or Ce-MC coatings.

In addition to the above tests, long-term ASR tests on bare and spinel-coated 441 are also in progress. As shown in Figure 13, the ASR of bare 441 increased to ~60 mΩ.cm² after ~5,000 hours in air at 800°C. In contrast, the samples coated with MC spinel and Ce-MC spinel exhibited stable ASR of ~10-13 mΩ.cm². It should be noted
that the tests were interrupted twice by unscheduled power outages at around 650 and 2,800 hours. The unscheduled thermal events resulted in a step change and increase in the ASR of bare 441, possibly indicating damage to the interfacial contact or detachment of the scale from the metal substrate. In contrast, the ASRs of the coated samples returned to their previous level, suggesting that the coatings improved the stability of the contact material/coating/steel interface. For comparison, ASR results for MC spinel-coated Crofer22APU tested previously under identical conditions are also shown in Figure 13. Clearly, the electrical performance of the two coated alloys was very similar.

3. Dual Atmosphere Testing of Spinel-Coated 441

Previous studies found that the oxidation behavior of ferritic stainless steels under the dual atmosphere conditions experienced by SOFC interconnects can differ significantly from the behavior observed under single atmosphere conditions. In particular, when ferritic stainless steels were simultaneously exposed to air on one side and moist hydrogen at the other, the scale growth on the air side differed from the scale growth observed during exposure to air only. AISI430, with ~17% Cr, suffered localized accelerated oxidation via the formation of iron oxide-rich nodules on the air side when exposed to ambient air (~1-2% H2O) vs. moist hydrogen (~3% H2O) at 800ºC. Crofer22APU, with a higher Cr content (~23% Cr) did not exhibit localized nodule growth under those conditions. However, iron oxide-rich nodules did nucleate and grow in the air side scale when ambient air was replaced by moist air (~3% H2O). MC spinel coatings applied to the air side have been found to be effective in suppressing this anomalous oxidation behavior in Crofer22APU. Recently, PNNL performed similar tests (moist air vs. moist hydrogen) on 441 with an air side Ce-MC coating. It should be noted that the 441 coupons were approximately 3x thicker (1.5 mm vs. 0.5 mm) than the previously tested Crofer22APU. As in the case of MC-coated Crofer22APU, no anomalous oxidation behavior (such as nodule formation) was observed on the air side of the Ce-MC coated 441 after 1000 hours of heat treatment at either 800 or 850ºC. Figure 14 shows the SEM/EDS analysis on the air side of Ce-MC coated 441 that was simultaneously exposed to 97%H2 + 3% H2O on the other side during the 1,000 hours tests at 850ºC. For the purpose of comparison, the analysis on Ce-MC coated 441 that was exposed to air on both sides during the same test is also included. The Ce-MC coating on the air side appeared to be less dense than the coating on the sample that was exposed to air on both sides. The higher density of the coating on the sample exposed to air only may be related to the diffusion of Fe into the coating during the oxidation test, as diffusion of Fe appeared to be inhibited under the dual atmosphere exposure conditions. Nevertheless, air side coating on the dual atmosphere sample, which consisted of a dense inner layer and a porous outer layer, appeared to be effective in preventing spallation and detachment along the coating/scale/metal interfaces.

IV. Conclusions

Investigations into the metallurgy, oxidation behavior, and electrical performance indicate that the alloy metallurgy and chemistry of 441 ferritic stainless steel remains promising for SOFC interconnect applications.

- The conventional melt metallurgy used for the bulk alloy fabrication leads to significant processing cost reduction and the alloy chemistry with the presence of
minor alloying additions of Nb and Ti facilitate the strengthening by precipitation and formation of Laves phase both inside grains and along grain boundaries during exposure in the intermediate SOFC operating temperature range. The Laves phase formed along the grain boundaries also ties up some of the Si. No formation of an insulating silica layer at the scale/metal interface was observed during prolonged exposure at SOFC operating temperatures.

- The substantial increase in ASR during long-term oxidation due to oxide scale growth suggested the need for a conductive protection layer, which could also minimize Cr evaporation. In particular, air side Mn$_{1.5}$Co$_{1.5}$O$_4$ based surface coatings on planar coupons drastically improved the electrical performance of the ferritic stainless steel 441, yielding stable ASR values at 800°C for over 5,000 hours. There is a need to develop and validate the coating for larger, shaped interconnects.

- Ce-modified spinel coatings retained the advantages of the unmodified spinel coatings, and also appeared to alter the scale growth behavior beneath the coating, leading to a more adherent scale. Hence, it is anticipated that, compared to unmodified spinel coatings, the Ce-modified coatings may lead to superior structural stability and electrical performance when applied to commercial grade ferritic stainless steels (such as 441) for SOFC interconnect applications.

- The spinel protection layers appeared also to improve the air side surface stability of 441 against the anomalous oxidation that has been observed for ferritic stainless steels exposed to dual atmosphere conditions similar to SOFC interconnect environments. It should be noted that the alloy oxidation and corrosion resistance have not yet been evaluated in fuel compositions (syn gas, hydrocarbons, etc) and fuel utilizations (up to 85%, for example) of practical interest.

Acknowledgements

The authors would like to thank Jim Rakowski at ATI Allegheny Ludlum for providing the 441 alloy samples and for helpful discussions. Nat Saenz, Shelly Carlson, and Jim Coleman at PNNL performed metallographic sample preparation and SEM analysis. The authors would also like to acknowledge helpful discussions with Wayne Surdoval, Ayyakkannu Manivannan, and Briggs White at the National Energy Technology Laboratory (NETL) regarding the initiation and implementation of this study. The work summarized in this paper was funded by the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program. PNNL is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.
References
Figure 1. SEM image of polished 441 (as-received).

Figure 2. SEM image of polished 441 after oxidation in air for 300 hours at 800°C.
Figure 3. ThermoCalc Results: Weight fraction of phase (BPW) vs. Temperature (°C) for typical 441 chemistry. Note that the weight fraction phase scale only goes to 0.050 in this plot.

Figure 4. Weight gain, expressed as $(\Delta m)^2$, of bare 441, MC spinel-coated 441, and Ce-MC spinel-coated 441 as a function of time during oxidation in air at 800°C.
Figure 5. SEM surface image of 441 after oxidation at 800°C in air for 900 hours. Note surface oxide spallation.

Figure 6. Area specific resistance (ASR) of bare 441, MC spinel-coated 441, and Ce-MC spinel-coated 441 as a function of time during oxidation in air at 800°C. LSM was used as the contact paste.
Figure 7. SEM cross-section image, with EDS line scan, of 441 after electrical evaluation at 800°C in air for 500 hours. Alloy is on left; LSM contact paste is on right.

Figure 8. Weight gain, expressed as $(\Delta m)^2$, of bare 441, MC spinel-coated 441, and Ce-MC spinel-coated 441 as a function of time during oxidation in air at 850°C.
Figure 9. SEM cross-section images of (a) MC spinel-coated 441, and (b) Ce-MC spinel-coated 441 after 1,000 hours of electrical resistance testing in air at 800°C. Alloy is on left; coating is in center; LSM contact paste is on right.
Figure 10. SEM/EDS cross-section images of (a) MC spinel-coated 441, and (b) Ce-MC spinel-coated 441 after 1,000 hours of electrical resistance testing in air at 800°C. Alloy is on left; coating is in center; LSM contact paste is on right.
Figure 11. Area specific resistance (ASR) of bare 441, MC spinel-coated 441, and Ce-MC spinel-coated 441 as a function of time during oxidation in air at 850°C. LSM was used as the contact paste. Tests were interrupted by an unscheduled power outage at 180 hours.
Figure 12. SEM cross-section images of (a) MC spinel-coated 441, and (b) Ce-MC spinel-coated 441 after 700 hours of electrical resistance testing in air at 850°C.
Figure 13. Area specific resistance (ASR) of bare 441, MC spinel-coated 441, and Ce-MC spinel-coated 441 as a function of time during oxidation in air at 800°C. LSM was used as the contact paste. Tests were interrupted by unscheduled power outages at ~650 and 2800 hours. Previous ASR results for MC spinel-coated Crofer22APU are also shown for purposes of comparison.
Figure 14. SEM/EDS of 441 coated with Ce-MC protection layers, after 1,000 hours of dual atmosphere exposure at 850°C: (a) one side of the sample that was exposed to air on both sides; (b) the air side of the sample that was simultaneously exposed to 97%H₂ / 3% H₂O on the other side.
Appendix A

The calculated effects of changes in alloy chemistry on the Laves solvus temperature are summarized in Table A1. The alloy balance chemistry is found in the table (Column 2). Note that N and Al were dropped from the formulation (in addition to S and P, which were dropped earlier). Each element was individually considered within its specification range. If the specification was given as “less than” the minimum was taken as zero. Niobium was found to have the greatest effect on the Laves solvus (~178°C) and its effect was positive. The next greatest positive effect was observed with Ti (~50°C). The greatest negative effect was observed with C (~63°C). These results are logical in that the Laves phase chemistry is an Fe₂X composition where ‘X’ is mainly Nb and Ti. Thus, with additional C, both Nb and Ti are removed from availability to form Laves by preferentially forming additional MC carbides instead.

Figure A1 shows a vertical section through the 441 alloy phase diagram as a function of temperature (T) and weight percent Nb. This figure shows graphically the stabilizing effect that Nb has on the Laves phase. A similar result was observed with Ti (Figure A2). Note that both Nb and Ti have very little impact on the Sigma phase stability. Figure A3 shows a vertical section through the 441 alloy phase diagram as a function of T and weight percent Cr. While Cr is seen to have only a minor effect on the Laves phase stability (~7°C over the specification range), Cr is found to have a significant effect on the Sigma phase formation. For example, at 25 wt percent Cr, Sigma phase is stabilized to ~750°C, which could have a detrimental impact on the sections of an SOFC stack operating under this temperature if such a modified alloy were used. Figure A4 shows a vertical section through the 441 alloy phase diagram as a function of T and weight percent Si. As in the case of Cr, only a minor effect on the Laves phase stability was observed, in comparison to a very significant increase in Sigma phase stability. Thus, high Si in combination with high Cr should be avoided in this alloy when used for SOFC applications.

Table A1: Changes in the Laves phase formation temperature over the range of allowable chemistries for each alloying constituent for UNS S44100 (other elements held constant). The symbol in brackets indicates whether increasing this constituent increases (+) or decreases (−) the solvus temperature for Laves phase.

<table>
<thead>
<tr>
<th>Element</th>
<th>Chemistry for Calculations</th>
<th>ΔT (°C) for Laves</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.009</td>
<td>63(-)</td>
</tr>
<tr>
<td>Cr</td>
<td>18.0</td>
<td>7(+))</td>
</tr>
<tr>
<td>Mn</td>
<td>0.35</td>
<td>3(-)</td>
</tr>
<tr>
<td>Si</td>
<td>0.34</td>
<td>14(-)</td>
</tr>
<tr>
<td>Nb</td>
<td>0.50</td>
<td>178(+)</td>
</tr>
<tr>
<td>Ti</td>
<td>0.22</td>
<td>50(+)</td>
</tr>
<tr>
<td>Ni</td>
<td>0.30</td>
<td>4(-)</td>
</tr>
<tr>
<td>Fe</td>
<td>Balance</td>
<td></td>
</tr>
</tbody>
</table>
Figure A1: A vertical section through the 441 alloy phase diagram as a function of T and weight percent Nb. The two vertical lines encompass the specification range.

Figure A2: A vertical section through the 441 alloy phase diagram as a function of T and weight percent Ti. The two vertical lines encompass the specification range.
Figure A3: A vertical section through the 441 alloy phase diagram as a function of T and weight percent Cr. The two vertical lines encompass the specification range.

Figure A4: A vertical section through the 441 alloy phase diagram as a function of T and weight percent Si. The vertical line indicates the specification maximum (minimum is zero).
Topical Report

Effect of Spinel Coating Thickness on Interfacial Stresses and Life Quantification of Coated Metallic IC

W. N. Liu
X. Sun
E.V. Stephens
M. A. Khaleel

August 2008

Prepared for the SECA Core Technology Program
National Energy Technology Laboratory, Pittsburgh, Pennsylvania under Contract DE-AC05-76RL01830
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under Contract DE-AC05-76RL01830
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Pacific Northwest National Laboratory
Richland, Washington 99352
Executive Summary

In PNNL report 17357(a), an integrated experimental/modeling methodology was applied to quantify interfacial strength and to predict possible delamination and subsequent spallation at the scale/substrate interface. The purposes of the current report are: 1.) to report the effects of the spinel coating thickness on the cooling-induced interfacial stresses; 2.) to provide a methodology in quantifying the life of coated metallic interconnect.

Oxidation reaction of the ferritic stainless interconnects in a typical SOFC working environment is unavoidable and the thickness of the oxide scale will continue to grow with operating time. To control the growth of the oxide scale, a spinel protection layer is usually coated on the surface of the ferritic stainless interconnects. In the meantime, the presence of an additional spinel coating layer also changes the interfacial stresses during cooling for various interfaces. The influence of the thickness of the spinel coating layer on the interfacial stresses is studied this quarter using finite element analyses. Three different spinel coating thicknesses and four different subscale thicknesses have been considered for SS441. Based on the interfacial strength of the oxide scale and SS441, predicted interfacial shear stress over a range of subscale thickness for various spinel coating thickness, as well as the experimentally determined oxide scale growth kinetics for different thickness of the spinel coating layer, the optimal thickness of the spinel coating layer can be determined for the expected life of SS441 in the SOFC operating environment.

## Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>CTE</td>
<td>coefficient of thermal expansion</td>
</tr>
<tr>
<td>FE</td>
<td>finite element</td>
</tr>
<tr>
<td>IC</td>
<td>interconnect</td>
</tr>
<tr>
<td>NETL</td>
<td>National Energy Technology Laboratory</td>
</tr>
<tr>
<td>SECA</td>
<td>Solid-State Energy Conversion Alliance</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>SOFC</td>
<td>solid-oxide fuel cell</td>
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</table>
Acknowledgements

Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle under Contract DE-AC05-76RL01830. The work summarized in this report was funded as part of the Solid-State Energy Conversion Alliance Core Technology Program by the U.S. Department of Energy’s National Energy Technology Laboratory. We would like to acknowledge the technical directions from Wayne Surdoval and Travis Shultz. Technical discussions with Dr. Z. Gary Yang are also gratefully acknowledged.
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1.0 Introduction

Oxidation reaction of the ferritic stainless interconnects in a typical SOFC working environment is unavoidable and the thickness of the oxide scale will continue to grow with stack operation time. The appearance and growth of the oxide scale will cause growth stress in the oxide scale [1, 2]. In addition, the coefficient of thermal expansion (CTE) mismatch between the oxide and the substrate creates stresses in the scale and on the scale/substrate interface during cooling [3], leading to scale delamination/buckling and eventual spallation. The interfacial strength between the oxide scale and the substrate is therefore crucial to the reliability and durability of the metallic IC in SOFC operating environments. To control the oxide scale growth, spinel protection layer is usually coated on the surface of the ferritic stainless interconnects. In PNNL 16610 [4], an integrated experimental/modeling methodology was developed to quantify the interfacial strength between oxide-scale and the Crofer substrate. The technique was applied to quantify interfacial strength and to predict possible delamination and subsequent spallation at the scale/substrate interface, therefore indicating the possible interconnect (IC) life under isothermal cooling or thermal cycling conditions as in PNNL report 17357 [5].

In general, the procedures for IC life prediction can be summarized as follows:

1. First, the interfacial strength at various interfaces needs to be quantified by the stair-stepping indentation test and the corresponding finite element analyses;

2. Second, the stack cooling induced interfacial shear stresses are calculated for given IC thickness with different subscale thickness using finite element analyses. For a given coating thickness, the critical thickness of the oxide scale can be determined by comparing the predicted interfacial shear stress with the interfacial strength quantified in the previous step;

3. The corresponding oxidation time required to form this critical thickness of the oxide scale can then be determined using the oxide growth kinetics charts for the given ferritic interconnect with and without spinel coating layer. Interconnect life can then be determined.

The spinel protection coating layer on the IC surface can effectively slow down the sub-scale oxide growth but cannot completely stop it. In the meantime, the presence of the spinel coating
layer also changes the interfacial stresses on the various interfaces during iso-thermal cooling. Kinetic growth of the oxide scale and interfacial stresses at various interfaces in coated metallic IC are closely dependent on the thickness of the spinel coating layer. The thickness of the spinel coating layer therefore should be chosen optimized to meet the design life of the SOFC stack. The influence of the thickness of the spinel coating layer on cooling-induced interfacial stress is first studied in this report. Again, we focus our attention on SS441. Based on the interfacial strength of the oxide scale and SS441, predicted interfacial shear stress over a range of subscale thickness for various spinel coating thickness, as well as the experimentally determined oxide scale growth kinetics for different thickness of the spinel coating layer, the optimal thickness of the spinel coating layer can be determined for the expected life of SS441 in the SOFC operating environment.
2.0 Technical Approach and Model Description

For the completeness of the report, this section discusses the structure and material properties of the spinel coating, oxide scale, and SS441 substrate.

Figure 1 shows the cross-sectional microstructures of as-received SS441 after oxidation at 800°C with spinel coating layer. The thickness of the oxide scale and coating are assumed to be uniform. The mechanical properties of the oxide scale of SS441 under high temperature are not currently available. The main composition of the oxide scale is Cr₂O₃; therefore, the values of Cr₂O₃ are used here, i.e., \( \nu = 0.27 \) and \( E=250 \text{GPa} \) [6, 7]. The main spinel coating materials used here are similar to that for Crofer 22 APU and are Mn₁₅Co₁₅O₄, its modulus and Poisson’s ratio are measured as \( \nu = 0.36 \) and \( E=124.7 \text{GPa} \) [8]. It should be emphasized that the coating material examined in this report is the same as those used for Crofer 22 APU, and it is not the cerium or lanthanum doped coatings recently developed by SECA Core Task 1.

Temperature dependent material properties of SS441 are used in this report. Figure 2 through Figure 4 illustrate the Young’s modulus, CTE, and yield strength of SS441 used in the numerical analyses [9, 10], respectively.
Figure 1. Cross-sectional microstructures of SS441 after oxidation at 800°C with spinel coating

Figure 2. Temperature-dependent modulus of SS 441
Figure 3. Temperature-dependent CTE of SS 441

Figure 4. Temperature-dependent yield strength of SS 441
3.0 Parametric Study of Spinel Coating Thickness

This section discusses the finite element model and numerical results. Figure 5 shows the geometry model used in the analysis. The thickness of SS441 sample is 1.6mm. Taking advantage of the symmetrical nature of the sample, only quarter sample is considered here.

Three different spinel coating thicknesses and four different subscale thicknesses have been considered for SS441. The thicknesses of the oxide scale and spinel coating layer studied in the report are listed in Table 1. For each spinel coating thickness given, the oxide scale varies its thickness from 2 μm, 5 μm, 10 μm, up to 15 μm, respectively.

The typical FE mesh used for SS441/scale/coating tri-layer system is illustrated in Figure 6. Very fine mesh was used near the interfaces between the substrate/scale and scale/coating to ensure accurate stress predictions at these locations. Very fine FE mesh is also used near the sample edge to ensure accurate interfacial shear stress predictions at these locations.

![Geometry model](image)

Figure 5. Geometry model
Table 1 Thicknesses of oxide scale and spinel coating layer considered

<table>
<thead>
<tr>
<th>Spinel coating (μm)</th>
<th>10</th>
<th>25</th>
<th>50</th>
<th>--</th>
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</thead>
<tbody>
<tr>
<td>Oxide Scale (μm)</td>
<td>2</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Cases studied</td>
<td>All combinatorial of the above cases</td>
<td></td>
<td></td>
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</tr>
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</table>

Figure 6. FE mesh used for SS441/scale/coating tri-layer system

Figures 7 to 9 illustrate the maximum shear stresses on the interfaces of the scale/SS441 substrate and scale/coating layer over the thickness of the oxide scale for different thickness of the spinel coating. For initial growth of the oxide scale in which the thickness of the oxide scale
is less than 5 μm, the maximum shear stress on the interfaces increase quickly. After the thickness of the oxide scale exceeds 5 μm, the maximum shear stress on the interfaces increases slowly even decreases slightly for the thin spinel coating. It is clear that the maximum shear stress on the interface of the scale and SS441 substrate is always larger than that of the scale and spinel coating layer. However, the interfacial shear strength of the scale and SS441 is much less than that of the interface between the oxide scale and spinel coating layer. The failure will always happen on the interface of the oxide scale and SS441 substrate.

Figure 10 and 11 shows the curves of the interfacial shear stresses over the thickness of the spinel coating layer. It is found that for the same sub-scale thickness, the cooling-induced interfacial stresses only slightly increase with coating thickness. This is because of the subtle CTE differences among the tri-layers. As expected, the interfacial stresses at both interfaces increase with the increase of sub-scale thickness. Based on the previously quantified strength of 886MPa for the interface between the sub-scale and the spinel coating, results predicted here indicate that the interfaces between the scale and the spinel coating are safe during cooling for all the cases considered. On the other hand, higher cooling induced interfacial stresses are consistently predicted at the interfaces between the scale and SS441. Comparing these stresses with the strength quantified for that interface, i.e., 320MPa, it is clear that cooling induced failure will occur at that interface, even for SS441 with the thinnest sub-scale.
**Figure 7.** Curves of the maximum shear stresses on the interfaces of scale/SS441 and scale/coating over thickness of oxide scale with 10 $\mu$m of coating material.

**Figure 8.** Curves of the maximum shear stresses on the interfaces of scale/SS441 and scale/coating over thickness of oxide scale with 25 $\mu$m of coating material.
Figure 9. Curves of the maximum shear stresses on the interfaces of scale/SS441 and scale/coating over thickness of oxide scale with 50 μm of coating material.

Figure 10. Curves of the maximum shear stresses on the interfaces of scale/SS441 over thickness of spinel coating.
Based on the analysis mentioned above, the interfacial failure on the oxide scale and the SS 441 substrate will always occur even with the spinel coating layer. Possible methods of improving the life of coated SS441 are currently being examined.

**Effects of SS441 Substrate Thickness**

It should be mentioned that the thickness of the as-received SS 441 in this study is 1.6 mm. Since the interfacial shear stresses during cooling are induced by the different CTE of the oxide scale and the SS 441 substrate, the thicker the IC substrate, the higher the interfacial stress will be. To this end, the effect of SS 441 substrate thickness is investigated here. Table 2 lists the maximum interfacial shear stresses for SS 441 with two different thicknesses, 0.5 mm and 1.6 mm, respectively. It is clear that decreasing the thickness of SS 441 substrate will significantly lower the interfacial stresses. Therefore, reducing the bulk thickness of metallic IC should be one simple and effective way of reducing the failure driving force, i.e., interfacial stresses.
Table 2 Effect of SS 441 thickness on interfacial stresses

<table>
<thead>
<tr>
<th>Substrate thickness</th>
<th>1.6mm</th>
<th>0.5mm</th>
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<tbody>
<tr>
<td>Coating thickness</td>
<td>10 um</td>
<td>10 um</td>
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<tr>
<td>Scale (um)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scale/441</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scale/Coat</td>
<td></td>
<td></td>
</tr>
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</tr>
<tr>
<td>Scale/Coat</td>
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<td>2</td>
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</tr>
<tr>
<td>5</td>
<td>487 MPa</td>
<td>350 MPa</td>
</tr>
<tr>
<td>10</td>
<td>489 MPa</td>
<td>360 MPa</td>
</tr>
<tr>
<td>15</td>
<td>485 MPa</td>
<td>345 MPa</td>
</tr>
</tbody>
</table>

Other options for improving the IC life include improving the interfacial adhesion strength between the oxide scale and the substrate through Ce-doped spinel coatings, possibly by surface modifications of the SS 441.

With the effect of the spinel coating thickness on the interfacial stresses, its potential influence on the life of the ferritic interconnect is considered here. Figure 12 depicts the short term oxide scale kinetics of SS441 at 800 °C. Longer term oxide growth kinetics in terms of subscale thickness is currently being generated by SECA Core Task 1. Experimental results show that with 15 μm thickness of the spinel coating layer, the growth of the oxide scale is much slower than that of the bare SS441. It is clear that with increase of the spinel coating layer, the growth of the oxide scale will be decelerated, therefore, longer life can be expected because the different thickness of the spinel coating layer does not significantly change the interfacial stresses. The optimal selection of the spinel coating layer thickness will be closely dependent on the oxide growth kinetics of the different ferritic interconnect substrate.
Figure 12 Short term oxide growth kinetics measured for SS441

\[ \delta w^2 = 5.0 \times 10^{-14}t \]
\[ R^2 = 0.9941 \]

\[ \delta w^2 = 2.0 \times 10^{-14}t \]
\[ R^2 = 0.9726 \]
4.0 Conclusions

In this report, influence of the thickness of the spine coating on the interfacial shear stresses on the oxide/substrate interface and the oxide scale/spinel coating interfaces is studied using finite element analyses. Three different spinel coating thicknesses and four different subscale thicknesses have been considered for SS441.

Based on the analyses results, following observations and conclusions can be made:

(1) For the same sub-scale thickness, the cooling-induced interfacial stresses only slightly increase with coating thickness. This is because of the subtle CTE differences among the tri-layers.

(2) The interfacial stresses at both interfaces increase with the increase of sub-scale thickness.

(3) Interfacial stresses on the oxide scale and SS441 interface is always larger than the interfacial stresses on the oxide scale and the spinel coating interface.

(4) Based on the previously quantified strength of 886MPa for the interface between the sub-scale and the spinel coating, results predicted here indicate that the interfaces between the scale and the spinel coating are safe during cooling for all the cases. On the other hand, Comparing these interfacial stresses of the oxide scale and SS441 substrate with the strength quantified for that interface, i.e., 320MPa, it is clear that cooling induced failure will occur at that interface, even for SS441 with the thinnest sub-scale.

(5) The life of the ferritic interconnect is dominated by the oxide growth kinetics.

Our future work includes the examination of possible methods of improving the life of coated SS441. The options include reducing the sheet thickness of SS441, surface modification, as well as improving the interfacial adhesion strength between the oxide scale and the substrate through Ce-doped spinel coatings. Further works in these areas are currently underway.
5.0 References


3. X Sun, WN Liu, P Singh and MA Khaleel. 2006. \textit{Effects of Oxide Thickness on Scale and Interface Stresses under Isothermal Cooling and Micro-Indentation}. PNNL-15794, Pacific Northwest National Laboratory, Richland, WA.


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Summary

This report provides instructions for use of the two-dimensional solid oxide fuel cell multi-physics (2D SOFC-MP) modeling code developed at Pacific Northwest National Laboratory (PNNL). This research software package evaluates the electrochemical performance and temperature distribution of multi-cell co-flow and counter-flow solid oxide fuel cell (SOFC) stacks. These types of analyses are useful to stack designers to evaluate the effect of cell design, geometric parameters, material properties, electrochemical properties, thermal boundary conditions, and operating conditions on stack performance. This report briefly presents an overview of the code followed by detailed instructions and examples for installation, model pre-processing, usage, solution, and results post-processing with the software. Several demonstration cases are presented which highlight the types of engineering analyses that can be performed with the software.
Acknowledgements

Preparation of this manual was sponsored by the U.S. Department of Energy’s National Engineering Technology Laboratory (NETL) as part of the Solid State Energy Conversion Alliance (SECA) program. The author’s gratefully acknowledge the helpful discussions and feedback provided by NETL program management.
Acronyms and Abbreviations

2D two dimensional
3D three dimensional
AR aspect ratio
$\Delta T$ temperature difference
GUI graphical user interface
IC interconnect
I-V current-voltage
NETL National Energy Technology Laboratory
OCR On-cell reformation
PNNL Pacific Northwest National Laboratory
SECA Solid-State Energy Conversion Alliance
SOFC solid oxide fuel cell
SOFC-MP solid oxide fuel cell multi-physics
UA air utilization
UF fuel utilization
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1.0 Introduction
Numerical modeling has played an important role in solid oxide fuel cell (SOFC) development within the Solid-State Energy Conversion Alliance (SECA) program. Modeling of stacks provides insights to SOFC design, materials, and operation which can help to reduce the required number of costly experimental studies. PNNL developed the SOFC-MP (Solid Oxide Fuel Cell Multi-Physics) model to evaluate the flow, electrochemical, thermal, and structural performance of planar cells (Khaleel et al. 2004). This model operates on the full three-dimensional (3D) geometry of the stack using a finite element framework. The modeling approach was later adapted to evaluate a simpler representation of tall co/counter-flow stack geometries (Lai et al. 2010). This model has sufficiently fast solution times so that it can be used by the fuel cell designer to quickly evaluate different operating scenarios for multi-cell stacks. After a brief overview of the model capabilities, this document presents detailed instructions and demonstrations for the practical use of this code to evaluate SOFC stacks.

2.0 Model Overview
SOFC-MP 2D software is a quasi-two dimensional (2D) numerical model for the efficient computation of the current density, species concentration, and temperature distributions in planar symmetric solid oxide fuel cell stacks. It assumes fully developed steady flow of the fuel and oxidant through a multi-cell SOFC stack. The brief overview of the model capabilities in this document should be supplemented by the detailed discussions of the algorithms and capabilities provided in Lai et al. (2010).

2.1 Capabilities
The modeling code is designed to provide the following simulation capabilities:
• Co- or counter-flow geometry
• Mixed fuel compositions containing H₂, H₂O, CO, CO₂, CH₄, and N₂
• User-defined electrochemistry and methane reforming models
• Analysis of large area cells
• Analysis of multi-cell tall stacks
• Adiabatic or radiation/convection thermal boundary conditions

2.2 Assumptions
The modeling approach has the following primary assumptions:
• The model domain includes only the active area of the cells (i.e. manifold and cell support frames are not explicitly included).
• Variation of in-plane cell quantities normal to the flow direction is negligible.
• The working voltage is uniform for each cell but varies along the stack height.
• The water-gas shift equation is in equilibrium for carbon-containing fuels.
• Fuel and inlet gas temperatures along the cell height are known.

2.3 Numerical Overview
SOFC-MP 2D solves multi-physics phenomena for a fully developed steady laminar flow in a multi-cell SOFC stack. The model solves the fully coupled governing equations for
electrochemistry, heat transfer, and fluid flow in a simplified 2D plane with user-defined boundary conditions. The solution provides detailed distributions of the temperature field, current density, and species partial pressures for each cell in the stack.

The solution starts with an initial guess for the temperature field and cell voltage based on inlet air and fuel temperatures as well as the average cell voltage specified from the input file. It then performs four numerical steps in two iteration loops.

The model follows a control volume marching scheme along the fuel flow direction from the control volumes in the inlet area toward the outlet area. In each control volume, the air and fuel gas composition is assumed known from the previous control volume. The oxygen and hydrogen consumption rates are then calculated based on the current density computed from the user-specified current-voltage (I-V) relationship, the remaining species content will be calculated, and then the gas partial pressure is rebalanced to give the new fuel and air composition for the subsequent volume. Thermal equilibrium is required for each control volume in the mesh and thus a matrix equation is created to solve the temperature distribution. The coefficients in the matrix equation depend on the current density, partial pressures, and temperature fields; therefore the solution scheme is an iterative one. Solution convergence is considered achieved when the temperature difference at every control volume from two consecutive iteration steps is within the user preset tolerance (e.g., 0.1°C). The calculation of temperature distribution for a given cell voltage distribution constitutes the inner iteration loop for the model.

For this given cell voltage distribution, the current for each cell in the stack is calculated by integrating the current density along the flow direction. Because all cells are connected in series in the same circuit, each cell must have the same total current. The difference of current in each cell indicates that the cell voltage must be redistributed. This voltage rebalance activity forms the outer loop iteration that converges when the current difference among cells is within the user-specified tolerance (e.g., 1% of the total current).

The model reaches the final solution when convergence criteria for both the inner temperature loop and the outer voltage-current loop are achieved. Further details of the model solution are provided in Lai et al (2010).

### 3.0 Installation of SOFC-MP 2D

The SOFC-MP code has been compiled for both the MS Windows and Linux environments.

### 3.1 Installation Compact Disk

A compact disk (CD) containing the installation files, software, demonstration problems, and documentation is available for use with this document.

### 3.2 Microsoft Windows Platform

System requirement: Windows XP or Windows 7 server, with minimum 1G RAM and 10G free space.
Third party software requirement: None.
Double click setup.exe or SOFC_Mp.msi and follow the instructions. The default installation destination directory is C:\PNNL\SOFC_MP, but you are free to specify a different one. The installation procedure will copy the following files to the installed directory:

1. EC_IntegralModel.exe
2. libmmd.dll
3. libifcoremd.dll
4. ButlerVolmer.inp
5. trans.lib
6. thermo.lib

After installation, the installation directory should be added to the system PATH variable. Go to Windows System Properties -> Environment Variables and add the installed directory to the PATH variable. (Note: the default path to add is C:\PNNL\SOFC_MP unless changed by the user).

The installation compact disk (CD) provides a /Utilities directory that users can also copy to the installation directory. In the directory, there are two batch files which will facilitate the simulation executions, and one Microsoft Excel spreadsheet which can be used for simulation result post processing if desired.

The installation disk also provides eighteen example cases for use with SOFC-MP 2D, each in its own directory, from /2Dcase01 to /2Dcase18. The file CaseDescriptions.txt in the /Documents directory provides the detailed descriptions of those eighteen cases. Copy all directories included with the installation disk to the installed directory if needed.

### 3.3 Linux Platform

On a Linux platform, the file sofc.tar contains all compressed files the SOFC-MP 2D model requires. Assuming $HOME/SOFC-MP as the installation directory, run the tar command:

```
$ tar -xvf sofc.tar
```

A few files will be uncompressed in directory $HOME/SOFC-MP:

- sofc – the main executable for SOFC-MP 2D
- trans.lib – a library of species transport properties
- thermo.lib – a library of species thermodynamic properties
- ButlerVolmer.inp – parameter file for electrochemistry calculations

The same tar command will also create eighteen sample directories under $HOME/SOFC-MP. The following library setting statement must be inserted in the Linux shell startup setting file (such as .bashrc depending on the user’s operating system):

```
export LD_LIBRARY_PATH=/share/apps/gcc-4.4.1/lib64:/share/apps/gcc-4.4.1/lib:$LD_LIBRARY_PATH
```
To run SOFC-MP 2D in a directory other than the installed directory, the same .bashrc file should contain the following PATH setting statement:

```
Export PATH=$HOME/SOFC_MP/bin:$PATH
```

### 4.0 Usage of SOFC-MP 2D

The SOFC-MP model was developed to quickly evaluate the sensitivity of stack performance to geometric and operational parameter changes. The model is useful for initial design of stacks to characterize the expected temperature field based on the electrochemical response and stack thermal boundary conditions. It is also useful for simulation of stack experiments to more fully understand observed trends during physical testing of actual stacks. The generation of the numerical model for a stack simulation is described in the following subsections.

#### 4.1 Pre-Processing

##### 4.1.1 Model Geometry

The model uses a simplified geometrical representation of the stack for the computations. This simplified geometry provides the benefits of numerical efficiency while being applicable to general planar stack designs. The model domain consists of the cell active area, where the geometry of the manifolds is not included and the fuel/oxidant inlet flows are assumed to be provided uniformly across each cell. The user provides the active cell width and length and indicates the flow orientation (co-flow or counter-flow). The thicknesses of the cell components are also necessary to account for the in-plane thermal heat transfer. The user provides the total cell thickness (anode + electrolyte + cathode), the thickness of a simple flat interconnect, and the thicknesses of the upper and lower load plates constraining the stack. The heights of the fuel and oxidant channels are also required. If a multi-cell stack is desired, the total number of cells is then input. These are the primary geometry parameters for the stack. If the model is to consider an insulation enclosure around the stack, the thickness of the insulation layer on each side is also required. If the model is to consider the thermal effects of manifold geometry, equivalent thermal links at the inlet and outlet of the stack can be used to include additional heat conduction between adjacent cells.

##### 4.1.2 Operating Parameters

The operating parameters of the stack consist of the inlet fuel definition, inlet oxidant definition, and the solution target for the mode of electrical operation. For the fuel definition, the total molar flow rate, species molar fractions (consisting of \( \text{H}_2, \text{H}_2\text{O}, \text{CO}, \text{CO}_2, \text{CH}_4, \text{and N}_2 \) species), and inlet temperature is required. For the oxidant definition, the total molar flow rate, species molar fractions (consisting of \( \text{O}_2 \) and \( \text{N}_2 \) species), and inlet temperature is required. The temperature of the inlet gases can also be varied linearly along the stack height if necessary to account for heating of the gases in the manifold. Finally, the inlet system pressure of the fuel and oxidant is provided, but the model currently performs no additional calculations for pressurized operation.

To define the electrical operating target, several options are available. The user can select the total voltage for the stack, the average voltage of the cells, the average current density for the stack, or the overall fuel utilization. Based on the assigned current-voltage relationship, the program will iterate to find the voltage and current distribution that satisfies the selected target.
Supplementary spreadsheet tools are provided for the user to pre-calculate values for the conditions of interest (e.g. compute the fuel and oxidant flow rates necessary to obtained desired utilizations for a given stack current).

### 4.1.3 Thermal Parameters

The model accounts for thermal conduction within the solid component layers, radiation between solid component layers, convection between the solid components and fluid domains, and external heat loss to the surrounding environment. For the conduction calculation, the thermal conductivity is required for the cell, interconnect, top plate, bottom plate, and insulation layer. For the internal radiation exchange, the total emissivity values of the cell and interconnect are required. For the solid-fluid heat exchange, the film coefficients for the fuel and oxidant streams are required. Presently, only single values (i.e. no dependence on temperature, composition, flow rate, etc.) are permitted for the film coefficient parameters.

By using the external boundary conditions, the heat transfer from the stack via convection and radiation can be simulated. The user assigns values for the total emissivity of the stack, total emissivity of the insulation, convection coefficient between the stack and insulation, convection coefficient between the insulation and the ambient environment, and the temperature of the ambient environment. For example, the ambient environment can be either a high temperature furnace (representative of a typical laboratory testing condition) or room temperature (representative of the self-heating mode for an installation). These boundary conditions parameters can also be varied independently for the top, bottom, front, back, and sides of the stack. Supplementary spreadsheet tools are provided for the user to calculate these boundary condition coefficients.

### 4.1.4 Material Properties

The only required material properties for the thermal solution are the thermal conductivities and total emissivities of the solid components as described above. The material properties required for the electrochemical solution are described in the following section.

### 4.1.5 Electrochemistry

The electrochemical response of the cell was made to be flexible for the user. The simplest option is to use the default internal electrochemistry model. This model is based on the semi-empirical approach established by Chick et al. (2000) and computes the working voltage from the Nernst voltage and various cell polarizations. The open circuit Nernst voltage is provided by Eq. (1) for the O₂ partial pressure at the anode/electrolyte interface given in Eq. (2) and computed from the change in Gibbs free energy of formation for the hydrogen oxidation reaction as shown in (3). Eq. (4)-(12) provide the ohmic loss due to contact resistance, the ohmic loss due to electrolyte ionic resistance, the ohmic loss due to anode electrical resistance, the ohmic loss due to cathode electrical resistance, the ohmic loss due to interconnect electrical resistance, a Butler-Volmer activation loss for the cathode, a concentration loss for the cathode, a concentration loss for the anode, and an empirical linear over-potential, respectively. The working voltage is then obtained from these voltage losses (computed as a function of the given current density, temperature, and species concentrations) according to Eq. (13).
\[ E = \frac{R_G T}{4F} \ln \left( \frac{P_{O_2}^{\text{cathode}}}{P_{O_2}^{\text{anode}}} \right) \]  
(1)

\[ p_{O_2}^{\text{anode}} = \left( \frac{P_{H_2O}}{\exp(-\Delta G_f / R_G T) P_{H_2}} \right)^2 \]  
(2)

\[-\Delta G_f = -56930 + 6.75 \ast T \ast \log_{10}(T) - 0.64 \ast \frac{T^2}{1000} - 0.08 \ast \frac{100000}{T} - 8.74T\]  
(3)

\[ \eta_{\text{contact}} = \frac{i t_{\text{contact}}}{P_e \exp(E_a / RT)} \]  
(4)

\[ \eta_{\text{electrolyte}} = \frac{i t_{\text{electrolyte}}}{\sigma_{YSZ}} \]  
(5)

\[ \eta_{\text{anode ohmic}} = \frac{i t_{\text{anode}}}{\sigma_{Ni,YSZ}} \]  
(6)

\[ \eta_{\text{cathode ohmic}} = \frac{i t_{\text{cathode}}}{\sigma_{LSM}} \]  
(7)

\[ \eta_{\text{int erconnect ohmic}} = \frac{i t_{\text{int erconnect}}}{\sigma_{\text{steel}}} \]  
(8)

\[ \eta_{\text{cathode activation}} = \frac{RT}{\alpha F} \sinh \left( \frac{i}{2i_0} \right) \]  
(9)

\[ \eta_{\text{cathode concentration}} = iP_{\text{cop}} \exp(k_{\text{cop}} P_{O_2}^{\text{cathode}}) \]  
(10)

\[ \eta_{\text{anode concentration}} = \max\left(\exp(B_{\text{anop}} + D_{\text{anop}} (i + C_{\text{anop}}) - A_{\text{anop}}), 0\right) \]  
(11)

\[ \eta_{\text{lop}} = \max\left(M_{\text{lop}} i + B_{\text{lop}}, 0\right) \]  
(12)

\[ V(i) = E - \eta_{\text{contact}} - \eta_{\text{electrolyte}} - \eta_{\text{anode ohmic}} - \eta_{\text{cathode ohmic}} - \eta_{\text{int erconnect ohmic}} - \eta_{\text{cathode activation}} - \eta_{\text{cathode concentration}} - \eta_{\text{anode concentration}} - \eta_{\text{lop}} \]  
(13)
The most flexible approach for modeling the electrochemistry is through a user subroutine where a custom current-voltage relationship can be created. This subroutine is called frequently during solution to compute the electrochemical response at every computational point on the cells. The solution call to the subroutine provides the present current density, fuel partial pressures, oxidant partial pressures, and temperature for the EC computations. The subroutine must then return the appropriate voltage value based on the programmed electrochemistry algorithm. The subroutine uses simple structures in the programming language called Lua (2011). The user should be able to start from the provided demonstration electrochemistry routines and adapt as necessary.

4.1.6 Units
The required units for the input parameters and user subroutines are indicated. The program uses SI units for most but not all parameters. Since the code is a research tool that supports existing users while undergoing development, mixed units still exist in various places as noted.

4.1.7 Numerical Solution Controls
Several parameters for control of the numerical solution are available to the user; however, most of these will not need to be altered. The primary parameter of interest is the number of computational points along the domain. The resolution of the model may be changed as needed to obtain finer results at the cost of longer computations, but generally a minimum of 100 solution points are suggested. If high gradients occur due to reforming, then greater resolution will be beneficial for better capturing the endothermic reaction. Other advanced parameters for solution control include temperature relaxation factors, time step, temperature limits, and iteration limits.

The solution is obtained when the temperature and current are converged. The tolerances for the temperature and total current are required. The demonstration values should be sufficient for most cases, but tolerances can be loosened to speed convergence.

TimeStep is a parameter introduced to stabilize the thermal computations. For co-flow cases, the value can be set to 0.1 or even larger. For counter-flow cases, due to the more unstable nature of the numerical approach, the value should be smaller, e.g., 0.001. When TimeStep value is very small, the speed of the numerical iterations toward the real thermal solution is artificially reduced so that even when the tolerances for temperature and current are met, the thermal solution is still not valid because the energy has not been balanced. Users are advised to check the energy balance, tighten the tolerance parameters and re-run the simulation until the energy is balanced.

A flag named SmartIterations is available for the model to automatically adjust TimeStep value. If SmartIterations is not set, or set to 0, the iterations will proceed as is. If SmartIterations is set to 1, the model will adjust TimeStep value when it sees necessary. This usually brings a faster convergence to an energy-balanced solution.

4.1.8 Input File Creation
The model input is provided by a simple text file called EC_Dimension1_InputTable.dat with a keyword format. Values are assigned to each of the pre-defined keywords described in the following section. The user should begin by modifying an existing demonstration input file. Comment lines in the input file are indicated with the # symbol at the beginning of the line.
### 4.1.9 Input File Keyword Descriptions

The available keywords, keyword descriptions, and example values are described in the following tables. These parameters define the model geometry (Table 1), fuel and oxidant definitions (Table 2), electrochemical operating parameters (Table 3), numerical model options (Table 4), material properties (Table 5), thermal boundary conditions (Table 6), in-progress electrode diffusion calculations (Table 7), and the default electrochemistry model (Table 8).

#### Table 1 Input File Keywords for Cell Geometry Definition

<table>
<thead>
<tr>
<th>Keyword</th>
<th>Description</th>
<th>Example Values (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CELL PARAMETERS</td>
<td>Flag for 2D model input</td>
<td></td>
</tr>
<tr>
<td>CoFlowFlag</td>
<td>Flow orientation of the cell</td>
<td>0 = counter-flow</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 = co-flow</td>
</tr>
<tr>
<td>Ax</td>
<td>Cell length</td>
<td>0.25 (m)</td>
</tr>
<tr>
<td>Ay</td>
<td>Cell width</td>
<td>0.25 (m)</td>
</tr>
<tr>
<td>nCells</td>
<td>Number of cells in stack</td>
<td>96</td>
</tr>
<tr>
<td>BottomPlateH</td>
<td>Thickness of bottom plate</td>
<td>0.005 (m)</td>
</tr>
<tr>
<td>PEN_H</td>
<td>Thickness of positive electrode/electrolyte/negative electrode</td>
<td>0.0005 (m)</td>
</tr>
<tr>
<td>InterConnPlateH</td>
<td>Thickness of interconnect</td>
<td>0.0005 (m)</td>
</tr>
<tr>
<td>TopPlateH</td>
<td>Thickness of top plate</td>
<td>0.005 (m)</td>
</tr>
<tr>
<td>AirFlowH</td>
<td>Height of oxidant channel</td>
<td>0.001 (m)</td>
</tr>
<tr>
<td>FuelFlowH</td>
<td>Height of fuel channel</td>
<td>0.0005 (m)</td>
</tr>
<tr>
<td>InletArea</td>
<td>Inlet manifold area in contact between cells</td>
<td>0.0001 (m$^2$)</td>
</tr>
<tr>
<td>InletL</td>
<td>Effective height of inlet manifold area in contact</td>
<td>0.003 (m)</td>
</tr>
<tr>
<td>OutletArea</td>
<td>Outlet manifold area in contact between cells</td>
<td>0.0001 (m$^2$)</td>
</tr>
<tr>
<td>OutletL</td>
<td>Effective height of outlet manifold area in contact</td>
<td>0.003 (m)</td>
</tr>
</tbody>
</table>

#### Table 2 Input File Keywords for Fuel and Oxidant Definitions

<table>
<thead>
<tr>
<th>Keyword</th>
<th>Description</th>
<th>Example Values (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SystemPressure</td>
<td>Inlet pressure for fuel/oxidant</td>
<td>1.0 (atm)</td>
</tr>
<tr>
<td>FuelFlowRate</td>
<td>Total molar flow rate</td>
<td>0.4 (mol/s)</td>
</tr>
<tr>
<td>FuelTemperature</td>
<td>Fuel inlet temperature</td>
<td>973 (°K)</td>
</tr>
<tr>
<td>FuelTonTop</td>
<td>Option fuel inlet temperature at top of stack</td>
<td>1003 (°K)</td>
</tr>
<tr>
<td>FuelH2</td>
<td>Mole fraction of H$_2$</td>
<td>0.7</td>
</tr>
<tr>
<td>FuelH2O</td>
<td>Mole fraction of H$_2$O</td>
<td>0.2</td>
</tr>
<tr>
<td>FuelCO</td>
<td>Mole fraction of CO</td>
<td>0.005</td>
</tr>
<tr>
<td>FuelCO2</td>
<td>Mole fraction of CO$_2$</td>
<td>0.005</td>
</tr>
<tr>
<td>FuelCH4</td>
<td>Mole fraction of CH$_4$</td>
<td>0.08</td>
</tr>
<tr>
<td>FuelN2</td>
<td>Mole fraction of N$_2$</td>
<td>0.01</td>
</tr>
</tbody>
</table>
### Table 3 Input File Keywords for Electrochemical Operation Definition

<table>
<thead>
<tr>
<th>Keyword</th>
<th>Description</th>
<th>Example Values (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation_Option</td>
<td>Solution mode for the desired electrical target</td>
<td>0 = solve for voltage</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 = solve for current density</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 = solve for fuel utilization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 = solve for stack I-V</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 = solve for stack I-V at fixed %UF</td>
</tr>
<tr>
<td>Average_CellVoltage</td>
<td>Solve for mean cell voltage (option 0)</td>
<td>0.75 (V)</td>
</tr>
<tr>
<td>StackVoltage</td>
<td>Solve for total stack voltage (option 0)</td>
<td>72.0 (V)</td>
</tr>
<tr>
<td>Average_CurrentDensity</td>
<td>Solve for mean cell current density (option 1)</td>
<td>5000 (A/m²)</td>
</tr>
<tr>
<td>Fuel_Utilization</td>
<td>Solve for fixed fuel utilization (option 2)</td>
<td>0.65</td>
</tr>
<tr>
<td>Average_CellVoltage_Low</td>
<td>Lower voltage on sweep for I-V curve (option 3)</td>
<td>0.4 (V)</td>
</tr>
<tr>
<td>Average_CellVoltage_High</td>
<td>Upper voltage on sweep for I-V curve (option 3)</td>
<td>1.0 (V)</td>
</tr>
<tr>
<td>Average_CellVoltage_Increment</td>
<td>Voltage increment on sweep for I-V curve (option 3)</td>
<td>0.05 (V)</td>
</tr>
<tr>
<td>EC_Model_Option</td>
<td>Method to compute electrochemistry</td>
<td>0 = internal default</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 = user subroutine</td>
</tr>
<tr>
<td>ShortCurrent</td>
<td>(work in progress)</td>
<td></td>
</tr>
<tr>
<td>CH4_Option</td>
<td>Method to compute CH₄ reforming rate</td>
<td>0 = equilibrium path length</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 = Achenbach rate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 = user subroutine</td>
</tr>
<tr>
<td>EquilibriumPathCO</td>
<td>Distance over which CO shift reaction reaches equilibrium</td>
<td>0.001 (m)</td>
</tr>
<tr>
<td>EquilibriumPathCH4</td>
<td>Distance over which CH₄ reforming reaction reaches equilibrium</td>
<td>0.01 (m)</td>
</tr>
</tbody>
</table>

### Table 4 Input File Keywords for Numerical Model Options

<table>
<thead>
<tr>
<th>Keyword</th>
<th>Description</th>
<th>Example Values (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nx</td>
<td>Number of solution increments along flow</td>
<td>100</td>
</tr>
<tr>
<td><strong>Keyword</strong></td>
<td><strong>Description</strong></td>
<td><strong>Example Values (units)</strong></td>
</tr>
<tr>
<td>---------------------------</td>
<td>--------------------------------------------------------------------------------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>TimeStep</td>
<td>A stabilizing coefficient for thermal computations</td>
<td>0.1 for co-flow (&lt;(3/Nx)) for counter-flow</td>
</tr>
</tbody>
</table>
| SmartIterations           | A flag indicating whether the model will automatically adjust TimeStep value for the purpose of speeding up the convergence | 0 = do not adjust TimeStep  
1 = allow model to adjust TimeStep |
| T_Relaxation              | Relaxation factor for temperature calculation                                   | 0.9                       |
| T_TopLimit                | Upper limit for temperature iterations                                          | 950 ('C)                  |
| T_BottomLimit             | Lower limit for temperature iterations                                          | 650 ('C)                  |
| VoltageIncrement          | Maximum increment of voltage between iterations                                 | 0.001 (V)                 |
| H2_Threshold              | Lower threshold for H\(_2\) partial pressure                                    | 0.0001 (Pa)               |
| H2_Threshold_Current      | Current generated at H\(_2\) lower threshold                                   | 0.0001 (A/m\(^2\))       |
| VoltageIterationLimit     | Maximum number of voltage/current iterations                                    | 100                       |
| LimitTIterations          | Maximum number of temperature iterations                                         | 20                        |
| UserDefinedHeat           | Use user defined thermal conductivities                                          | 0 = default  
1 = user subroutine |
| QuasiTransient            | (work in progress)                                                              |                           |
| HaveConductionOnInlet     | Flag for thermal conduction between cells at inlet/outlet                       | 0 = ignore  
1 = include |
| PrintBalances             | Flag to print species balances                                                  | 0 = do not print  
1 = print |
| NoDiffusion               | Flag to activate electrode diffusion calculations                                | 0 = include  
1 = do not include |
| PrintDiffusionDifference  | Flag to print electrode diffusion results                                        | 0 = do not print  
1 = print |
| T_precision               | Convergence criterion for maximum temperature variation between iterations       | 0.2 (V)                   |
| CurrentTolerance          | Convergence criterion for maximum current density variation from the average    | 0.2 (A/m\(^2\))          |

**Table 5 Input File Keywords for Material Property Definitions**
<table>
<thead>
<tr>
<th>Keyword</th>
<th>Description</th>
<th>Example Values (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BoundaryFlag</td>
<td>Flag indicating type of external environment</td>
<td>1 = ambient temperature 2 = insulated enclosure</td>
</tr>
<tr>
<td>TopEnvironmentT</td>
<td>Top ambient temperature</td>
<td>750 (°C)</td>
</tr>
<tr>
<td>TopFilmCoefficient</td>
<td>Film coefficient for top insulation convection</td>
<td>12 (W/m²-K)</td>
</tr>
<tr>
<td>TopEmissivity</td>
<td>Emmissivity for top insulation radiation</td>
<td>0.9</td>
</tr>
<tr>
<td>TopSIFilmCoefficient</td>
<td>Film coefficient for top stack-insulation convection</td>
<td>12 (W/m²-K)</td>
</tr>
<tr>
<td>TopSIEmissivity</td>
<td>Emmissivity for top stack-insulation radiation</td>
<td>0.9</td>
</tr>
<tr>
<td>TopIsolationH</td>
<td>Thickness of top insulation</td>
<td>0.05 (m)</td>
</tr>
<tr>
<td>TopIsolationHC</td>
<td>Thermal conductivity of top insulation</td>
<td>1.0 (W/m-K)</td>
</tr>
<tr>
<td>TopGeometryScale</td>
<td>Scale factor for top area</td>
<td>1.2</td>
</tr>
<tr>
<td>BottomEnvironmentT</td>
<td>Bottom ambient temperature</td>
<td>750 (°C)</td>
</tr>
<tr>
<td>BottomFilmCoefficient</td>
<td>Film coefficient for bottom insulation convection</td>
<td>12 (W/m²-K)</td>
</tr>
<tr>
<td>BottomEmissivity</td>
<td>Emmissivity for bottom insulation radiation</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>BottomSIFilmCoefficient</strong></td>
<td>Film coefficient for bottom stack-insulation convection</td>
<td>12 (W/m(^2)-K)</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-------------------------------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td><strong>BottomSIEmissivity</strong></td>
<td>Emmissivity for bottom stack-insulation radiation</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>BottomIsolationH</strong></td>
<td>Thickness of bottom insulation</td>
<td>0.05 (m)</td>
</tr>
<tr>
<td><strong>BottomIsolationHC</strong></td>
<td>Thermal conductivity of bottom insulation</td>
<td>1.0 (W/m-K)</td>
</tr>
<tr>
<td><strong>BottomGeometryScale</strong></td>
<td>Scale factor for bottom area</td>
<td>1.2</td>
</tr>
<tr>
<td><strong>FrontEnvironmentT</strong></td>
<td>Front ambient temperature</td>
<td>750 (°C)</td>
</tr>
<tr>
<td><strong>FrontFilmCoefficient</strong></td>
<td>Film coefficient for front insulation convection</td>
<td>12 (W/m(^2)-K)</td>
</tr>
<tr>
<td><strong>FrontEmissivity</strong></td>
<td>Emmissivity for front insulation radiation</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>FrontSIFilmCoefficient</strong></td>
<td>Film coefficient for front stack-insulation convection</td>
<td>12 (W/m(^2)-K)</td>
</tr>
<tr>
<td><strong>FrontSIEmissivity</strong></td>
<td>Emmissivity for front stack-insulation radiation</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>FrontIsolationH</strong></td>
<td>Thickness of front insulation</td>
<td>0.05 (m)</td>
</tr>
<tr>
<td><strong>FrontIsolationHC</strong></td>
<td>Thermal conductivity of front insulation</td>
<td>1.0 (W/m-K)</td>
</tr>
<tr>
<td><strong>FrontGeometryScale</strong></td>
<td>Scale factor for front area</td>
<td>1.2</td>
</tr>
<tr>
<td><strong>BackEnvironmentT</strong></td>
<td>Back ambient temperature</td>
<td>750 (°C)</td>
</tr>
<tr>
<td><strong>BackFilmCoefficient</strong></td>
<td>Film coefficient for back insulation convection</td>
<td>12 (W/m(^2)-K)</td>
</tr>
<tr>
<td><strong>BackEmissivity</strong></td>
<td>Emmissivity for back insulation radiation</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>BackSIFilmCoefficient</strong></td>
<td>Film coefficient for back stack-insulation convection</td>
<td>12 (W/m(^2)-K)</td>
</tr>
<tr>
<td><strong>BackSIEmissivity</strong></td>
<td>Emmissivity for back stack-insulation radiation</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>BackIsolationH</strong></td>
<td>Thickness of back insulation</td>
<td>0.05 (m)</td>
</tr>
<tr>
<td><strong>BackIsolationHC</strong></td>
<td>Thermal conductivity of back insulation</td>
<td>1.0 (W/m-K)</td>
</tr>
<tr>
<td><strong>BackGeometryScale</strong></td>
<td>Scale factor for back area</td>
<td>1.2</td>
</tr>
<tr>
<td><strong>SideEnvironmentT</strong></td>
<td>Side ambient temperature</td>
<td>750 (°C)</td>
</tr>
<tr>
<td><strong>SideFilmCoefficient</strong></td>
<td>Film coefficient for side insulation convection</td>
<td>12 (W/m(^2)-K)</td>
</tr>
<tr>
<td><strong>SideEmissivity</strong></td>
<td>Emmissivity for side insulation radiation</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>SideSIFilmCoefficient</strong></td>
<td>Film coefficient for side stack-insulation convection</td>
<td>12 (W/m(^2)-K)</td>
</tr>
<tr>
<td><strong>SideSIEmissivity</strong></td>
<td>Emmissivity for side stack-insulation radiation</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>SideIsolationH</strong></td>
<td>Thickness of side insulation</td>
<td>0.05 (m)</td>
</tr>
<tr>
<td>Keyword</td>
<td>Description</td>
<td>Example Values (units)</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>SideIsolationHC</td>
<td>Thermal conductivity of side insulation</td>
<td>1.0 (W/m-K)</td>
</tr>
<tr>
<td>SideGeometryScale</td>
<td>Scale factor for side area</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Table 7 Input File Keywords for Electrode Diffusion Computation**

<table>
<thead>
<tr>
<th>Keyword</th>
<th>Description</th>
<th>Example Values (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nLayers</td>
<td>Number of layers for electrode diffusion calculation (work in progress)</td>
<td>3</td>
</tr>
<tr>
<td>nSpecies</td>
<td>Number of species</td>
<td>6</td>
</tr>
<tr>
<td>Thickness</td>
<td>Total PEN thickness</td>
<td>560 (µm)</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>Electrode tortuosity</td>
<td>1.1</td>
</tr>
<tr>
<td>Porosity</td>
<td>Electrode porosity</td>
<td>55 (%)</td>
</tr>
<tr>
<td>PoreRadius</td>
<td>Electrode pore radius</td>
<td>0.5 (µm)</td>
</tr>
<tr>
<td>ElectrolyteThickness</td>
<td>Electrolyte thickness</td>
<td>10 (µm)</td>
</tr>
<tr>
<td>InterconnectThickness</td>
<td>Interconnect thickness</td>
<td>1500 (µm)</td>
</tr>
<tr>
<td>CathodeThickness</td>
<td>Cathode thickness</td>
<td>50 (µm)</td>
</tr>
<tr>
<td>CathodePorosity</td>
<td>Cathode porosity</td>
<td>55 (%)</td>
</tr>
<tr>
<td>CathodeTortuosity</td>
<td>Cathode tortuosity</td>
<td>1.1</td>
</tr>
<tr>
<td>AnodeThickness</td>
<td>Anode thickness</td>
<td>500 (µm)</td>
</tr>
<tr>
<td>AnodePorosity</td>
<td>Anode porosity</td>
<td>55 (%)</td>
</tr>
<tr>
<td>Anode Tortuosity</td>
<td>Anode tortuosity</td>
<td>1.1</td>
</tr>
</tbody>
</table>

**Table 8 Input File Keywords for Default Electrochemistry Definition**

<table>
<thead>
<tr>
<th>Keyword</th>
<th>Description</th>
<th>Example Values (units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScaleThickness</td>
<td>Interconnect scale thickness</td>
<td>0.3 (µm)</td>
</tr>
<tr>
<td>PreExponent</td>
<td>Scale resistance pre-exponential constant</td>
<td>10</td>
</tr>
<tr>
<td>ActivationEnergy</td>
<td>Scale resistance activation energy</td>
<td>0.2</td>
</tr>
<tr>
<td>CathodePreExponent</td>
<td>Pre-exponential coefficient for cathode resistance</td>
<td>575955</td>
</tr>
<tr>
<td>CathodeActivationEnergy</td>
<td>Activation energy for cathode resistance</td>
<td>0.117</td>
</tr>
<tr>
<td>BV_AlphaCoefficient</td>
<td>$\alpha$ for Butler-Volmer activation polarization</td>
<td>0.55</td>
</tr>
<tr>
<td>BV_ActivationEnergy</td>
<td>$E_a$ for Butler-Volmer activation polarization</td>
<td>1.2</td>
</tr>
<tr>
<td>BV_PreExponent_a</td>
<td>Pre-exponential coefficient a for Butler-Volmer activation polarization</td>
<td>-120</td>
</tr>
<tr>
<td>BV_PreExponent_b</td>
<td>Pre-exponential coefficient b for Butler-Volmer activation</td>
<td>2.3e5</td>
</tr>
</tbody>
</table>
4.1.10 Creation of Custom Electrochemistry Subroutine

The subroutine file VoltageOnCurrent.dat contains the required user subroutines for the electrochemistry calculations. The subroutine VoltageValue contains the coding necessary to input the current-voltage relationship for the model. The subroutine must return the voltage based on the supplied temperatures, fuel partial pressures, oxygen partial pressure, and requested current density. Using the inherent mathematical functions available in Lua (or even high level programming constructs), the user should be able to replicate their electrochemistry routine or experimental data for use in the model. The equations or data should cover the entire expected range of operation within the stack. Specifically, the iterations begin with requests for voltage at extreme currents of 1e-5 and 5e3 A/cm², so the routine should return a voltage value for these limits (e.g. if the requested current is above a calculated limiting current then the routine should return a voltage of 0.0). The arguments for the subroutine are shown in Table 9.

**Table 9 Available Arguments in the I-V User Subroutine**

<table>
<thead>
<tr>
<th>Subroutine Arguments</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CathodeDepletionCoefficient_a</td>
<td>Cathode concentration overpotential coefficient</td>
</tr>
<tr>
<td>CathodeDepletionCoefficient_b</td>
<td>Cathode concentration overpotential coefficient</td>
</tr>
<tr>
<td>LOP_slope</td>
<td>Linear overpotential coefficient</td>
</tr>
<tr>
<td>LOP_is</td>
<td>Linear overpotential coefficient</td>
</tr>
<tr>
<td>LOP_ii</td>
<td>Linear overpotential coefficient</td>
</tr>
<tr>
<td>AOP_ns</td>
<td>Anode concentration overpotential coefficient</td>
</tr>
<tr>
<td>AOP_ni</td>
<td>Anode concentration overpotential coefficient</td>
</tr>
<tr>
<td>AOP_qs</td>
<td>Anode concentration overpotential coefficient</td>
</tr>
<tr>
<td>AOP_qi</td>
<td>Anode concentration overpotential coefficient</td>
</tr>
<tr>
<td>AOP_ms</td>
<td>Anode concentration overpotential coefficient</td>
</tr>
<tr>
<td>AOP_mi</td>
<td>Anode concentration overpotential coefficient</td>
</tr>
<tr>
<td>AOP_ps</td>
<td>Anode concentration overpotential coefficient</td>
</tr>
<tr>
<td>AOP_pi</td>
<td>Anode concentration overpotential coefficient</td>
</tr>
<tr>
<td>VTC</td>
<td>(work in progress)</td>
</tr>
</tbody>
</table>
4.1.11 Creation of Custom Reforming Rate Subroutine

If the fuel contains methane for on-cell reforming, the reforming rate of the methane can also be customized with the subroutine `CH4ReformingRate`. The solver assumes the rate of methane reformation is kinetically controlled, so this subroutine returns the maximum rate of reforming. If used, the appropriate flag in the `EC_Dimension1_InputTable.dat` file must be set and the subroutine is placed in the same `VoltageOnCurrent.dat` file that contains the I-V user subroutine. The subroutine arguments are shown in Table 10.

<table>
<thead>
<tr>
<th>Subroutine Arguments</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>fuelT</td>
<td>Temperature of fuel (°K)</td>
</tr>
<tr>
<td>pCH4</td>
<td>Fuel partial pressure CH₄ (atm)</td>
</tr>
<tr>
<td>Ch4_Usage</td>
<td>Rate of reformation to be returned (mol/s)</td>
</tr>
</tbody>
</table>

4.2 Solution

The solution is obtained by running the single executable file on the input file. This can be done using the provided execution scripts or directly from the command line. The solution procedure creates output files that provide solution status, final results, results summary, and model debugging information.

4.2.1 Submission on MS Windows Platform

To run a job on the Windows platform, it is assumed that the executable is installed correctly and in the system path so that it is accessible from any working directory. If the PATH variable was not set as indicated, then the user needs to copy the executable file and all the DLL files to the runtime directory. Then, the case can be run by the following steps:
1. To run SOFC-MP for each case, go to the appropriate directory of the selected demonstration case and double click the batch file named "\^\^2D_Run_First_Time\^\^\^\^\^.bat". It will copy all necessary files to the current directory and start the SOFC-MP 2D simulation.
2. To use an input file other than the default “EC_Dimension1_InputTable.dat”, for example, “myInput.dat”, type command “EC_IntegralModel.exe myInput.dat” in a DOS command prompt.
3. Check the status of the program: Depending on the size of the model, the program can last anywhere from 1 minute to up to 1 hour. Check a debugging file named “RunMonitor.dat”, if the last line writes “Two Dimensional program ends at xx:xx:xx”, then the program has finished. An alternative is to check the Windows Task Manager, under Processes tab, wait until “EC_IntegralModel.exe” disappears.

4.2.2 Submission on Linux Platform
Once the environment variables are set as described in Section 3.2, to run SOFC-MP 2D in the input directory simply type:

```
$ sofc [inputFile]
```

Note, without the optional parameter [inputFile], the model will assume the input file as EC_Dimension1_InputTable.dat.

4.2.3 Description of Output Files
Several output files are created upon completion of the solution. These text files may be viewed directly if needed, but usually they are simply read into the spreadsheet tool created for automated post-processing. The files are as follows:

- ModelOutput.dat – the main output file containing major result matrix such as electrical performance, temperature metrics, flow characteristics.
- CurrentInCellsLatest.dat – a result file, containing active voltage and current at each cell.
- StackTemperature.txt – a result file containing temperature at each node.
- StackFractions.txt – a result file containing fuel and air composition at each node.
- IterFl.dat – a debugging file detailing the convergence on temperature field matrix equation residual.
- Stack1D.txt – a result file containing temperature and fuel composition data.
- SavedState.dat – voltage and temperature data saved from last program run. If the program runs again, the data in the file will be read in and used as the initial condition. A subsequent run with SavedState.dat usually has much faster convergence.
- RunMonitor.dat – main debugging file. Useful information includes the numerical iteration and performance data.
- Solidstat.dat – a debugging file containing information on temperature matrix solver.
- WatchInitFl_00.dat – a debugging file containing information about gas species.
- FlowStat.dat – a debugging file containing fuel flow information during the numerical iteration process.
• AirStat.dat – a debugging file containing air flow information during the numerical iteration process.
• CurrentInCells.dat – a debugging file containing current distribution during the numerical iteration process.
• Cea2.out – output file from the CEA library.
• Cea_message.dat – debugging information for CEA interfacing.

4.3 Post-Processing

The model output results are contained within simple ASCII text files, so they can be viewed by the user or read into a spreadsheet if desired. However, the simplest approach is to use the provided post-processing spreadsheet tool created with Microsoft Excel 2007 for use with SOFC-MP 2D. The spreadsheet reads in the results data files from SOFC-MP 2D and automatically calculates the performance metrics of interest to the designer. The objective of this tool was to provide a mechanism for rapid evaluation and understanding of the numerical results. The file 2D_template_rev18_distribute.xlsm is provided on the demonstration CD under the /Utilities directory. For simulations ran on Linux, all result files can be copied to Windows file system for this post-processing purpose.

4.3.1 Open the Excel Spreadsheet Tool

Copy the spreadsheet to a convenient location and open it with Excel 2007 (the worksheet apparently works with Excel 2003, but it becomes a very large file size and all calculation features are not supported). The spreadsheet provides a method to select the working directory where the results are located, so it does not need to be re-copied to the working directory for every analysis. Upon opening the spreadsheet, a warning window may appear or the information bar at the top of the spreadsheet cells may indicate “Security Warning: Some active content has been disabled.” The spreadsheet makes considerable use of Data Connections (to read in the results files) and Macros (to perform calculations and control the data input), so these advanced features must be enabled for the worksheet to function properly. Select “Enable this content” for both Macro and Data Connection.

4.3.2 Worksheets in the Excel Spreadsheet Tool

The user will primarily work with the Summary worksheet for their analysis as described in detail below. The preceding worksheets in the workbook are first briefly explained. The Info worksheet contains some basic description of the worksheet contents, and the next few worksheets hold the imported results data. The spreadsheet reads the results files and places the data into the tool’s worksheets as shown in Table 11. The user generally does not need to utilize these sheets directly.

Table 11. Results Files Read Into the Post-Processing Tool

<table>
<thead>
<tr>
<th>Results Filename</th>
<th>Worksheet</th>
<th>Data Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC_Dimension1_InputTable.dat</td>
<td>Import1</td>
<td>All model input parameters</td>
</tr>
<tr>
<td>CurrentInCellsLatest.dat</td>
<td>Import2</td>
<td>Voltage and current for each cell</td>
</tr>
<tr>
<td>StackTemperature.txt</td>
<td>Import3</td>
<td>Temperature and current density distributions along each cell</td>
</tr>
<tr>
<td>StackFractions.txt</td>
<td>Import4</td>
<td>Species distributions along each cell</td>
</tr>
</tbody>
</table>
The computations for data reduction and synthesis are performed on the worksheets listed in Table 12. The user generally does not need to utilize these sheets directly.

**Table 12. Calculation Worksheets in the Post-Processing Tool**

<table>
<thead>
<tr>
<th>Worksheet Name</th>
<th>Calculations and Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc1</td>
<td>Min/Max/Average temperatures for components at cell and stack level</td>
</tr>
<tr>
<td>Calc2</td>
<td>Min/Max/Average current, current density, and voltage</td>
</tr>
<tr>
<td>Calc3</td>
<td>Average outlet species compositions at cell and stack level</td>
</tr>
<tr>
<td>Calc4</td>
<td>Manual calculation to verify energy balance computations</td>
</tr>
<tr>
<td>Calc5</td>
<td>Selected distribution data for plotting</td>
</tr>
</tbody>
</table>

The *Summary* worksheet is the primary sheet of interest. This ‘dashboard’ shows all of the calculated metrics based on the latest SOFC-MP run and will be described in detail below. The remaining worksheets contain various calculators to support modeling cases or calculations used for development and verification of the model (Table 13).

**Table 13. Supplementary Worksheets in the Post-Processing Tool**

<table>
<thead>
<tr>
<th>Worksheet Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saved_Cases</td>
<td>Archival of saved results</td>
</tr>
<tr>
<td>Calculators</td>
<td>Supplementary calculation tools to aid the user</td>
</tr>
<tr>
<td>EnergyCheck</td>
<td>Simple energy balance check for the stack</td>
</tr>
</tbody>
</table>

### 4.3.3 Import Data to the Excel Spreadsheet Tool

Two large buttons on the *Summary* worksheet are used to automatically read in the results data (Figure 1). The “Change working directory and re-import all data files!” button allows the user to navigate their file system using a conventional explorer window to select the working directory where SOFC-MP 2D results are located. Upon selection, the data import process proceeds, all calculations are performed, and a window confirms successful data import. The second button entitled “Re-import all data files!” performs the same import and calculation function from the previous working directory shown above the buttons in cell L17. This option would be used for subsequent runs of the same model. The following discussion about the results all focus on content within this *Summary* worksheet.
4.3.4 Convergence Check

Before evaluating model results, the user should always ensure the model is fully converged. If the model did not have sufficient iterations to solve or did not converge due to other reasons, any results are likely erroneous and should be ignored. Some important indicators are shown in the lower left side of the Convergence Assessment block (Figure 2). The values for the current and temperature imbalance are shown along with the assigned tolerance limit. These are the most important values to check regarding solution convergence. If the final value is greater than the limit, then the corresponding current or temperatures are not fully converged and indicated with a warning message. The model likely needs to be run again with additional iterations. Next, the maximum and minimum model temperatures are indicated along with the assigned upper and lower limits on the solution iteration. If the solution values are near these limits, a warning message is indicated and the model may be ill defined or the limits need to be expanded. The next two values indicate the number of voltage and temperature iterations compared to the assigned limits. Usually, if the iterations reach the assigned limit, then the current and temperature is not yet converged and the model should be run with additional iterations.

<table>
<thead>
<tr>
<th>Convergence Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current converged within assigned limit</td>
</tr>
<tr>
<td>Final value: 0.2320 Limit: 0.3</td>
</tr>
<tr>
<td>Temperature converged within assigned limit</td>
</tr>
<tr>
<td>Final value: 0.02 Limit: 0.05</td>
</tr>
<tr>
<td>Global temperatures within user upper limit</td>
</tr>
<tr>
<td>Maximum value: 848.6 Limit: 900</td>
</tr>
<tr>
<td>Global temperatures within user lower limit</td>
</tr>
<tr>
<td>Minimum value: 707.9 Limit: 650.0</td>
</tr>
<tr>
<td>Voltage iterations within assigned limit</td>
</tr>
<tr>
<td>Final value: 1 Limit: 20</td>
</tr>
<tr>
<td>Temperature iterations within assigned limit</td>
</tr>
<tr>
<td>Final value: 0 Limit: 10</td>
</tr>
</tbody>
</table>

Figure 2. Convergence parameters and criteria to assess solution convergence

4.3.5 Model Data

Selected model data are summarized to verify the model under consideration. The flow orientation for the fuel and air is shown in B3:D3 (Figure 3a). The number of cells and cell
geometry is shown in C6:C11 (Figure 3b). The inlet mole fractions of the fuel are shown in B28:E36, and the corresponding molar flow rates are shown in G27:J35.

### 4.3.6 Performance Metrics

Many performance metrics of interest are shown on the Summary worksheet. The electrical performance is shown in C15:D26 (Figure 4). Here the total current, average current density, average power density, total voltage, average voltage, and total power are reported. The fuel and air utilizations are shown F16:J24 (Figure 5). The net output fuel mole fractions and flow rates are shown in B28:E36 (Figure 6) and G27:J35 (Figure 7), respectively. If CH₄ is present in the fuel, the percentage of on-cell reforming is shown in J36. The temperature results including average cell temperature, cell temperature difference, cathode air temperature change, and anode fuel temperature change are shown in F2:K13 (Figure 8). The energy balance including the change of fuel enthalpy, electrical power, change in air enthalpy, and external loss to the environment is shown in M2:P12 (Figure 9). These are expected to be the primary metrics needed by the user, although others can be easily added.

### Electrical Performance

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>total = 312.425</td>
<td>81.7920</td>
</tr>
<tr>
<td>average =</td>
<td>0.8520</td>
</tr>
<tr>
<td>min = 312.193</td>
<td>0.8419</td>
</tr>
<tr>
<td>max = 312.447</td>
<td>0.8574</td>
</tr>
<tr>
<td>max delta from total = 0.2320</td>
<td>0.0155</td>
</tr>
<tr>
<td>%delta = 0.07%</td>
<td>1.82%</td>
</tr>
</tbody>
</table>

| avg current density = 0.4999 (A/cm²) |
| max current density = 0.6198 (A/cm²) |
| avg power density = 0.4259 (W/cm²) |
| total power = 25553.9 (W) |

Figure 4. Stack electrical performance summary
### Fuel/Oxidant Flow

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>inlet air flow rate</td>
<td>2.47E+00 mole/s</td>
</tr>
<tr>
<td>inlet air flow rate</td>
<td>3319.680 slpm</td>
</tr>
<tr>
<td>O2 current</td>
<td>7.77E-02 mole/s</td>
</tr>
<tr>
<td>stoichs oxidant</td>
<td>6.67</td>
</tr>
<tr>
<td>air utilization</td>
<td>14.98%</td>
</tr>
<tr>
<td>inlet fuel flow rate</td>
<td>2.47E-01 mole/s</td>
</tr>
<tr>
<td>inlet fuel flow rate</td>
<td>331.968 slpm</td>
</tr>
<tr>
<td>outlet fuel flow rate</td>
<td>2.47E-01 mole/s</td>
</tr>
<tr>
<td>fuel utilization</td>
<td>64.87%</td>
</tr>
</tbody>
</table>

#### Figure 5. Stack air and fuel utilization

### Species Mole Fractions

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Inlet</th>
<th>Cell edge</th>
<th>Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.9700</td>
<td>0.9638</td>
<td>0.3408</td>
</tr>
<tr>
<td>H2O</td>
<td>0.0300</td>
<td>0.0362</td>
<td>0.6592</td>
</tr>
<tr>
<td>CO</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>CO2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>CH4</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>N2</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>total</td>
<td>1.0000</td>
<td>1.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>fuel value</td>
<td>0.9700</td>
<td>0.9638</td>
<td>0.3408</td>
</tr>
</tbody>
</table>

#### Figure 6. Stack inlet and outlet fuel molar fractions

### Species Molar Flow Rates

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Inlet (mol/s)</th>
<th>Cell edge (mol/s)</th>
<th>Outlet (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>2.40E-01</td>
<td>2.38E-01</td>
<td>8.42E-02</td>
</tr>
<tr>
<td>H2O</td>
<td>7.41E-03</td>
<td>8.94E-03</td>
<td>1.63E-01</td>
</tr>
<tr>
<td>CO</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>CO2</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>CH4</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>N2</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>total</td>
<td>2.47E-01</td>
<td>2.47E-01</td>
<td>2.47E-01</td>
</tr>
<tr>
<td>fuel flow</td>
<td>2.40E-01</td>
<td>2.38E-01</td>
<td>8.42E-02</td>
</tr>
<tr>
<td>OCR</td>
<td>N.A.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Figure 7. Stack inlet and outlet fuel molar flow rates
Energy Balance  

<table>
<thead>
<tr>
<th>(negative = heating the stack)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>heat loss top</td>
<td>271.800 (W)</td>
</tr>
<tr>
<td>heat loss bottom</td>
<td>222.373 (W)</td>
</tr>
<tr>
<td>heat loss front</td>
<td>-197.017 (W)</td>
</tr>
<tr>
<td>heat loss back</td>
<td>590.065 (W)</td>
</tr>
<tr>
<td>heat loss sides</td>
<td>1348.070 (W)</td>
</tr>
<tr>
<td>total ext heat loss</td>
<td>2235.291 (W)</td>
</tr>
<tr>
<td>net chemical energy</td>
<td>35650.200 (W)</td>
</tr>
<tr>
<td>electrical energy</td>
<td>-25553.900 (W)</td>
</tr>
<tr>
<td>heat removed by air</td>
<td>-7862.110 (W)</td>
</tr>
<tr>
<td>external heat removed</td>
<td>-2235.291 (W)</td>
</tr>
<tr>
<td>imbalance</td>
<td>-1.101 (W)</td>
</tr>
</tbody>
</table>

Figure 8. Stack energy balance

4.3.7 Distributions and Plotting

The Summary worksheet also permits the plotting of distributions of quantities along the cell length to aid understanding. The worksheet is created to allow the user to plot quantities for three different cells from the multi-cell stack. The green numbers in R3:R5 can be changed to indicate the cell data to be plotted (Figure 9). The directions of fuel and air flow in the cell plots are shown in R8:T9 where cell #1 is at the bottom of the stack by definition. The plots include:

- fuel mole fractions as a function of path length
- working voltage as a function of cell number
- current density as a function of path length
- cell temperature as a function of path length
- fuel temperature as a function of cell length
- air temperature as a function of cell length
- minimum, maximum, and average cell temperature as a function of cell number
- cell temperature difference as a function of cell number

Example plots are shown in Figure 10-Figure 13. The user may control the plotting ranges in the conventional way, but additional buttons for semiautomatic range control of the figures are included in O45:U54 (Figure 14).

Results Plotting by Cell

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cell #1</td>
</tr>
<tr>
<td>24</td>
<td>Cell #24</td>
</tr>
<tr>
<td>48</td>
<td>Cell #48</td>
</tr>
</tbody>
</table>

Flow Directions for Path Plots

----->>> Fuel Flow ----->>>
----->>> Air Flow ----->>>

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bottom of Stack</td>
</tr>
<tr>
<td>96</td>
<td>Top of Stack</td>
</tr>
</tbody>
</table>

Figure 9. Selection of different cells for results distribution plotting
Figure 10. Contours of a) fuel mole fractions along the cell and b) distribution of the cell voltage through the stack height.

Figure 11. Contours of the a) current density and b) cell temperature along the cell.

Figure 12. Contours of the a) fuel and b) air temperature along the cell.
Figure 13. Distribution of the a) minimum, maximum, and average cell temperatures and b) cell temperature difference through the stack height

<table>
<thead>
<tr>
<th>x_min</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>x_max</td>
<td>96</td>
<td>96</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>x_ticks</td>
<td>10</td>
<td>10</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>y_min</td>
<td>650</td>
<td>0.8</td>
<td>1000</td>
<td>650</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>y_max</td>
<td>850</td>
<td>0.9</td>
<td>7000</td>
<td>850</td>
<td>1</td>
<td>0.04</td>
</tr>
<tr>
<td>y_ticks</td>
<td>100</td>
<td>0.02</td>
<td>1000</td>
<td>50</td>
<td>0.1</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table showing the range and number of ticks for the x and y axes.

Figure 14. Buttons to control axes for results graphs.

4.3.8 Data Archival

The Summary worksheet also permits the user to archive results data. Buttons to archive the current results set or clear the archive are located on the Summary worksheet (Figure 15). This button calls a macro which most of the calculated results metrics on a single line in the Saved_Cases worksheet. The data can then be recalled if needed or used for plotting and comparisons between multiple cases in a sensitivity analyses.

Figure 15. Buttons to archive solution data.

5.0 Demonstration Cases

Several cases are explained in further detail here to demonstrate how to use the tool to solve stack problems.
5.1 Single Co-Flow Cell with H\textsubscript{2} Fuel

The first example is a single cell co-flow model reported by the International Energy Agency (Achenbach 1996) and used subsequently as an informal benchmark in the SOFC community (Ferguson et al 1996, Braun 2002, Zhang et al 2006, Li et al 2010). This represents the simplest case that can be considered by using only a single cell, wet hydrogen fuel, adiabatic boundary conditions, and the co-flow orientation which is generally more numerically stable than counter-flow. Model development involves definition of two primary files: the input data file EC_Dimension1_InputTable.dat and the user subroutine VoltageOnCurrent.dat containing the electrochemistry routine.

5.1.1 Creation of EC_Dimension1_InputTable.dat File for Example Case 1

This file contains all of the cell geometry, thermal material properties, fuel/oxidant input conditions, thermal boundary conditions, and solution controls for the stack model. The easiest way to create this file is to modify an existing input file. Specifically, the definition of this example requires assignment of the following keywords:

### Table 14 Keyword Assignments for Example Case 1

<table>
<thead>
<tr>
<th>Keyword Assignment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFlowFlag = 1</td>
<td>Co-flow cell</td>
</tr>
<tr>
<td>nCells=1</td>
<td>Use a single cell</td>
</tr>
<tr>
<td>Ax = 0.1</td>
<td>Cell length along flow direction is 10 cm</td>
</tr>
<tr>
<td>Ay = 0.1</td>
<td>Cell width is 10 cm</td>
</tr>
<tr>
<td>PEN_H = 0.00025</td>
<td>Cell thickness = 50 (\mu)m anode + 50 (\mu)m cathode + 150 (\mu)m electrolyte = 250 (\mu)m</td>
</tr>
<tr>
<td>InterConnectPlateH = 0.001393</td>
<td>Effective interconnect thickness accounting for ribs = 0.5 mm + 2.42/5.42*2 mm = 1.393 mm</td>
</tr>
<tr>
<td>BottomPlateH = 0.000946</td>
<td>Effective bottom plate thickness accounting for ribs = 0.5 mm + 2.42/5.42 mm = 0.946 mm</td>
</tr>
<tr>
<td>TopPlateH = 0.000946</td>
<td>Effective top plate thickness accounting for ribs = 0.5 mm + 2.42/5.42 mm = 0.946 mm</td>
</tr>
<tr>
<td>AirFlowH = 0.000554</td>
<td>Effective air flow height = 1*3/5.42 = 0.554 mm</td>
</tr>
<tr>
<td>FuelFlowH = 0.000554</td>
<td>Effective fuel flow height = 1*3/5.42 = 0.554 mm</td>
</tr>
<tr>
<td>CoFlowFlag = 1</td>
<td>Flag = 1 for co-flow, 0 for counter-flow</td>
</tr>
<tr>
<td>FuelFlowRate = 0.00020325</td>
<td>2.0325e-4 mol/s fuel to give 85% utilization</td>
</tr>
<tr>
<td>FuelTemperature = 1173</td>
<td>900°C inlet fuel temperature</td>
</tr>
<tr>
<td>FuelH2 = 0.90</td>
<td>90% hydrogen</td>
</tr>
<tr>
<td>FuelH2O = 0.10</td>
<td>10% water</td>
</tr>
<tr>
<td>OxidantFlowRate = 0.0030485</td>
<td>3.0485e-3 mol/s air to give 12.15% utilization</td>
</tr>
<tr>
<td>OxidantTemperature = 1173</td>
<td>900°C inlet air temperature</td>
</tr>
<tr>
<td>OxidantO2 = 0.21</td>
<td>Standard air composition</td>
</tr>
<tr>
<td>OxidantN2 = 0.79</td>
<td>Standard air composition</td>
</tr>
<tr>
<td>OxidantSolidFilmCoefficient = 1035</td>
<td>Effective film coefficient</td>
</tr>
<tr>
<td>FuelSolidFilmCoefficient = 1500</td>
<td>Effective film coefficient</td>
</tr>
<tr>
<td>InterConnectPlateHC = 2.0</td>
<td>Thermal conductivity of interconnect</td>
</tr>
<tr>
<td>PENEmittance = 0.5</td>
<td>Effective PEN emissivity</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>InterConnectEmittance = 0.5</td>
<td>Effective interconnect emissivity</td>
</tr>
<tr>
<td>BottomPlateHC = 2.0</td>
<td>Thermal conductivity of bottom plate</td>
</tr>
<tr>
<td>TopPlateHC = 2.0</td>
<td>Thermal conductivity of top plate</td>
</tr>
<tr>
<td>PEN_HC = 2.0</td>
<td>Thermal conductivity of cell</td>
</tr>
<tr>
<td>StackVoltage = 0.70875</td>
<td>Solve for assigned voltage to obtain a current density of 0.3 A/cm²</td>
</tr>
</tbody>
</table>

The values above include effective values for the components, channel heights, and heat transfer parameters to account for the ribbed interconnect. The effective thickness for the simple plate interconnect provides the same cross-sectional area as the ribbed interconnect design for the same in-plane heat transfer by thermal conduction. The effective height for the simple flow channel provides the same cross-sectional flow area as the ribbed channel design for the same volumetric flow rate. The effective film coefficients provide the appropriate heat transfer between solid and fluid to account for both the convection through the ribbed interconnect channels and the conduction through the rib. The effective emissivities account for the different view areas between the ribbed interconnect and the simple interconnect. A pre-processing calculator to compute these effective properties based on the nominal material properties and rib geometry is included in the spreadsheet. The full details of the input file are provided in Appendix A.

### 5.1.2 Creation of VoltageOnCurrent.dat File for Example Case 1

The subroutine file `VoltageOnCurrent.dat` contains the required user subroutines for the electrochemistry calculations necessary to input the current-voltage relationship for the model. The subroutine returns the voltage based on the supplied temperatures, fuel partial pressures, oxygen partial pressure, and requested current density. The `VoltageOnCurrent.dat` file for the user subroutine is then created and placed in the working directory. The example subroutine `VoltageValue()` for the Achenbach benchmark case with H₂ fuel is shown in Figure 16. Upon being called from the main program, the code sets various parameters necessary for the computations including the ideal gas constant, Faraday’s constant, a pressure conversion factor, and thickness values for the anode, electrolyte, cathode, and interconnect. Note that this model simulates an older electrolyte-supported technology which had much lower power densities than modern cell designs. Next, the reaction temperature is computed from the average of the oxidant and fuel temperatures. The partial pressures of the fuel species are then converted to units of bar to be consistent with the benchmark, and the input current density is converted from A/m² to A/cm². Next, the ohmic resistances of the cell layers are computed based on their thicknesses and resistivities, and these values are summed for the total ohmic loss. Next, the open circuit voltage is computed based on the change in Gibbs free energy of formation and adjusted for the actual partial pressures of the reactants. For this benchmark, the concentration and activation losses were not computed and it was assumed for simplicity that these polarization losses are equal to the ohmic loss. Therefore, the working voltage is then computed by subtracting the polarization losses from the Nernst voltage. The voltage is then checked, and any negative values are assigned a small positive value for improved numerical stability. Finally, the computed working voltage is returned to the solver.
function VoltageValue()
-- Assign Constants/Conversions/Geometry/Material Data
R=8.3145; F=96485.3; atm2bar=1.01325
th_a=50.0e-6; th_e=150.0e-6; th_c=50.0e-6; th_ic=2500.0e-6
--
-- Compute the local cell temperature
Tk=(oT+fT)/2.0
--
-- Compute the total pressure & convert to bar
pO2airc=pO2air*atm2bar; pN2airc=pN2air*atm2bar
pH2c=pH2*atm2bar; pH2Oc=pH2O*atm2bar; pCOc=pCO*atm2bar
pCO2c=pCO2*atm2bar; pCH4c=pCH4*atm2bar; pN2c=pN2*atm2bar
pTotal=pH2c+pH2Oc+pCOc+pCO2c+pCH4c+pN2c
--
-- Convert the passed current density
Jcalc=J*10000.
--
-- Calculate ohmic resistance
siga=95.0e6/Tk*math.exp(-1150.0/Tk)
sigc=42.0e6/Tk*math.exp(-1200.0/Tk)
sige=3.34e4*math.exp(-10300.0/Tk)
sigic=9.3e6/Tk*math.exp(-1100.0/Tk)
RohmIC=0.0025/sigic
Rohm=th_a/siga+th_c/sigc+th_e/sige+RohmIC
--
-- Calculate the open cell voltage
U00H2O=(241.106-3.804e-2*Tk-1.402e-5*Tk^2+3.551e-9*Tk^3)*1000.0/2.0/F
U0H2=U00H2O-R*Tk/2.0/F*math.log(pH2Oc/pH2c/pO2airc^0.5)
--
-- Calculate the working voltage
UH2=U0H2-(Rohm*Jcalc+Rohm*Jcalc+Rohm*Jcalc)
Z=UH2
--
-- Return the voltage value (not less than zero)
if Z<0.0 then
  Z=0.001
end
return Z
end

Figure 16. I-V user subroutine for example Case 1.

5.1.3 Results for Example Case 1
Selected results for this case are shown in Figure 17. These species distribution indicates consumption of the H\textsubscript{2} fuel along the cell (Figure 17a) resulting in a current density distribution that is highest at the fuel rich inlet (Figure 17c) and a temperature distribution that is hottest at the outlet due to the heat removal from the oxidant and fuel gases (Figure 17d). The results predictions were also compared to the metrics in the literature (Figure 18, Figure 19) and found that the model results fall well within the range of the reported values. More details on the model validation and comparisons are found in Lai et al (2010).
Figure 17. Contours of the species distribution for a) H₂ and b) CH₄ fuels, the current density distribution for c) H₂ and d) CH₄ fuels, and the cell temperature for the e) H₂ and f) CH₄ fuels.
Figure 18. Comparison of minimum and maximum a) current densities and b) cell temperatures between the model and the benchmark cases.

Figure 19. Comparison of a) cell voltage, b) fuel outlet temperature, and c) oxidant outlet temperature between the model and the benchmark cases.

5.2 Single Co-Flow Cell with CH₄ Fuel
The next example is identical to the previous case except that a fuel with methane is used. Carbon-based fuels are widely available from natural gas, gasification processes, generation processes for biological materials, etc. and of interest for the SOFC. The nickel in the anode acts as a catalyst for steam reformation of the methane on the cell. The reformation reaction of methane along with the water-gas shift reaction of carbon monoxide produces four models of hydrogen from each mole of methane. Also favorably, the reformation reaction is endothermic which can be utilized to beneficially remove heat from the stack. Therefore, the modeling tool must handle carbon-based fuels also.

5.2.1 Creation of EC_Dimension1_InputTable.dat File for Example Case 2
The input file is very similar to the H₂ case. The additional changes to the file are shown in Figure 16 and the full input file is provided in Appendix B. The fuel flow rate is smaller because the H₂ content of the methane fuel is greater and will result in the same utilization after on-cell
reforming. Next, the fuel composition is appropriately updated. Finally, the stack voltage for the required current density is slightly lower because of a lower Nernst voltage with the methane.

### Table 15: Keyword Assignments for Example Case 2

<table>
<thead>
<tr>
<th>Keyword Assignment</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FuelFlowRate = 0.00018741</td>
<td>1.8741e-4 mol/s fuel to give 85% utilization</td>
</tr>
<tr>
<td>FuelH2 = 0.2626</td>
<td>26.26% hydrogen</td>
</tr>
<tr>
<td>FuelH2O = 0.4934</td>
<td>49.34% water</td>
</tr>
<tr>
<td>FuelCO = 0.0294</td>
<td>2.94% carbon monoxide</td>
</tr>
<tr>
<td>FuelCO2 = 0.0436</td>
<td>4.36% carbon dioxide</td>
</tr>
<tr>
<td>FuelCH4 = 0.1710</td>
<td>17.1% methane</td>
</tr>
<tr>
<td>StackVoltage = 0.6374</td>
<td>Solve for assigned voltage to obtain a current density of 0.3 A/cm²</td>
</tr>
</tbody>
</table>

#### 5.2.2 Creation of VoltageOnCurrent.dat File for Example Case 2

The I-V calculation for the carbon-based fuel is the same as the H₂ case. In general, this may not be true because the possibility for oxidation of H₂, CO, and CH₄ exists in the cell, where each of these reactions proceed such that the total anode current consists of contributions from each oxidation reaction. However, in this model it is assumed that the methane is not oxidized and converted to H₂ via on-cell steam reformation. It is also assumed that the relatively fast water-gas shift equation is always in equilibrium everywhere on the cell. With these assumptions, the working voltage for the H₂ and CO oxidation has been shown to be identical, so the predicted open circuit voltage considering only H₂ oxidation is acceptable. The steam reformation reaction is kinetically controlled though, so a rate expression is required. The Achenbach rate (1994) is implemented in the `CH4ReformingRate()` subroutine and placed in the `VoltageOnCurrent.dat` file as shown in Figure 20.

```python
function CH4ReformingRate()
    GasConstant=8.3144
    Ch4_Usage=4274.0*pCH4*math.exp(-82000.0/fuelT/GasConstant)
    return Ch4_Usage
end
```

Figure 20. CH₄ reforming rate subroutine for the example Case 2.

#### 5.2.3 Results for Example Case 2

The results for the Achenbach case 3 are also shown in Figure 17–Figure 19. The species distribution indicates the production of H₂ at the inlet from reformed CH₄ (Figure 17b). This reduces the temperature at the inlet region (Figure 17f) which reduces the current density (Figure 17d). The current density increases further downstream as the cell becomes hotter but then reduces again due to low fuel concentration. Overall, the cell temperature is lower due to the on-cell reformation. Comparison of the total output power indicates about a 10% loss from the H₂ case.
5.3 Multi-Cell Co-Flow Cell with H₂ Fuel

While many models for single SOFC cells exist in the literature and have been used for studies, very few have been demonstrated for tall stack analyses. The SOFC-MP 2D model is well suited for evaluating distributions and performance of tall stacks. A tall stack consisting of 96 625 cm² cells was created by increasing the number of cells and flow rates in the model definition. This stack assumes an anode-supported cell with much higher performance (Figure 21). The input files for this case are shown in Appendix C.

![Figure 21. I-V curve for the modeled H₂ and CH₄ fuels.](image)

Various results are shown in Figure 22 and Figure 23. Several observations can be made about the stack performance:

- The voltage varies ~2% along the stack height with the highest value near the top of the stack (which is hotter and reduces the electrolyte ionic conductivity).
- The current density profile varies along the stack height. Due to hotter inlet gases at the top of the stack, the peak current density shifts toward the inlet compared to the bottom of the stack. The center cells in the stack are hotter because they see less influence from the top and bottom boundary conditions, so the peak current density for these cells occurs at the middle of the cell.
- The temperature difference is greatest for cell #15 (130°C) compared to the end cells (50-70), which is important for structural reliability.

Clearly the effect of the boundary conditions and stack size will affect the response in different cells, indicating that single cell models do not provide all the necessary information for design and operation of realistic tall stacks.
Figure 22. Comparison of the predicted results between the a) cell voltage and c) current density distribution for the H₂ fuel case and the b) cell voltage and d) current density distribution for the CH₄ fuel case.
The tall stack example was also repeated with a carbon-based fuel composition which gave the performance shown in Figure 21. The input files for this case are provided in Appendix D. The results are shown in Figure 22 and Figure 23. Several observations can be made about these stack results:

- The voltage varies ~2% along the stack height with the highest value near the top of the stack (which is hotter and reduces the electrolyte ionic conductivity).
- The current density profile varies along the stack height. Due to hotter inlet gases at the top of the stack, the peak current density shifts toward the inlet compared to the bottom of the stack. The center cells in the stack are hotter because they see less influence from the top and bottom boundary conditions, so the peak current density for these cells occurs at the middle of the cell.
- The temperature difference is greatest for cell #15 (130°C) compared to the end cells (50-70), which is important for structural reliability.

5.5 Effect of Cell Aspect Ratio

The primary driver for thermal-mechanical stresses in the SOFC is the temperature profile of the cells and associated mismatches in component thermal expansion
coefficients. The SOFC-MP software was used to evaluate the effect of cell aspect ratio on the stack thermal profile. The influence of cell aspect ratio (AR) values of 0.2-5.0 on the thermal temperature difference (ΔT) was evaluated, where the AR is defined as the ratio of the cell length along the flow direction to the cell width. The temperature field was more uniform with high aspect ratios due to stronger thermal influence of either the inlet flow gas temperature (AR=0.2) or heat transfer with the furnace (AR=5.0). The maximum cell ΔT and global ΔT were 128°C and 139°C respectively for AR=1.0. For AR=0.2, the cell ΔT decreased by 12°C and the global ΔT decreased by 10°C. For AR=5.0, the cell ΔT decreased by 7°C and the global ΔT decreased by 11°C. This type of analyses could aid the stack engineers with potential changes to the cell design to minimize thermal stresses.

![Figure 24. Effect of cell aspect ratio on stack temperature difference.](image)

### 5.6 Effect of Interconnect Thickness

The effect of interconnect thickness (IC) on the stack thermal profile was also evaluated. Thinner ICs may provide cost reduction; however, thermal management will be impacted because the IC also conducts the electrochemical heat from the stack interior. Thinner IC’s with the same thermal conductivity have less ability to conduct heat laterally. IC thickness reduction from 1.5 mm to 0.5 mm resulted in an undesirable increase of peak temperature by 11°C, global stack ΔT by 17°C, and maximum cell ΔT by 16°C. This type of analyses could help the stack engineers identify potential impacts on the stress state due to cost reduction strategies.
6.0 Summary

An efficient numerical tool was developed to evaluate the effects of cell design, geometric parameters, material properties, electrochemical properties, thermal boundary conditions, and operating conditions on stack performance. Detailed instructions for installation, model development, usage, and post-processing were provided. Various example cases using the software were demonstrated. This manual should provide the user with enough knowledge to construct their own model and perform independent analyses.

7.0 References


Appendix A

EC_Dimension1_InputTable.dat for Example Case 1

Description: Achenbach single cell co-flow benchmark with H₂ fuel

```
CELL PARAMETERS
nLayers = 10
nSpecies = 6
Thickness = 250.0
Tortuosity = 2.5
Porosity = 30.0
PoreRadius = 0.5
ElectrolyteThickness = 150.0
InterconnectThickness = 1500.0
CathodeThickness = 50.0
CathodePorosity = 30.0
CathodeTortuosity = 2.5
AnodeThickness = 50.0
AnodePorosity = 30.0

CONTACT RESISTANCE PARAMETERS
ScaleThickness = 30.0
PreExponent = 10.0
ActivationEnergy = 0.20

CATHODE RESISTANCE PARAMETERS
CathodePreExponent = 575955.0
CathodeActivationEnergy = 0.117

CATHODE BUTLER-VOLMER PARAMETERS
BV_AlphaCoefficient = 0.55
BV_PreExponent_a = -120
BV_PreExponent_b = 2.3e5

CATHODE O₂ DEPLETION PARAMETERS
CathodeDepletionCoefficient_a = 3
CathodeDepletionCoefficient_b = -35

ANODE DEPLETION POLARIZATION PARAMETERS
LOP_slope = 0.2027
LOP_is = -8.897e-4
LOP_ii = 0.5221
AOP_ns = 2.439e-3
AOP_ni = -2.3598
AOP_qs = 1.747e-2
AOP_qi = -17.73
AOP_ms = -1.158e-2
AOP_m = 11.06
AOP_pe = 6.560e-4
AOP_pi = -1.152

SystemPressure = 1.0

FUEL PARAMETERS (FLOW RATE IS MOLE/SEC; TEMP IS K)
FuelFlowRate = 0.00020325
FuelTemperature = 1173
FuelTopTemp = 1173
FuelH2 = 0.90
FuelH2O = 0.10
FuelCO = 0.00
FuelCO2 = 0.00
```
FuelCH4 = 0.00
FuelN2 = 0.00

OXIDANT PARAMETERS (FLOW RATE IS MOLE/SEC; TEMP IS K)
OxidantFlowRate = 0.00030485
OxidantTemperature = 1173
OxidantTonTop = 1173
OxidantO2 = 0.21
OxidantN2 = 0.79

DIMENSION IN DIRECTION OF GAS FLOW (M)
Ax = 0.1

DIMENSION PERPENDICULAR TO GAS FLOW (M)
Ay = 0.1

NUMBER OF INCREMENTS PER CELL
Nx = 1000

NUMBER OF CELLS IN STACK
nCells=1

--Average_CurrentDensity=3000
StackVoltage=0.7082
--Average_CellVoltage=0.7098
ShortCurrent=0.0

DISTANCE REQUIRED TO REACH GAS EQUILIBRIUM
EquilibriumPathCO = 0.001
EquilibriumPathCH4 = 0.01

EMISSIVITY OF INTERCONNECT AND CELL
InterConnectEmittance = 0.5
PENEmittance = 0.5

THICKNESSES OF BOTTOM, INTERCONNECT, TOP PLATE AND PEN
BottomPlateH = 0.000946
InterConnectPlateH = 0.001393
TopPlateH = 0.000946
PEN_H = 0.00025

THERMAL COND. OF BOTTOM, INTERCONNECT, TOP PLATE AND PEN
BottomPlateHC = 2.0
InterConnectPlateHC = 2.0
TopPlateHC = 2.0
PEN_HC = 2.0

HEIGHT OF GAS FLOW PASSAGES
AirFlowH = 0.000554
FuelFlowH = 0.000554

OxidantSolidFilmCoefficient = 134.0
FuelSolidFilmCoefficient = 510.0

SWITCH:COFLOW IS 1, COUNTERFLOW IS 0
CoFlowFlag = 1

relaxation parameter between old T distribution and new T distribution
T_Relaxation = 0.5
T_precision = 0.05

maximum temperature admissible in iterations (C)
T_TopLimit = 1420.0
minimum temperature admissible in iterations (C)
T_BottomLimit = 580.0

maximum admissible total current difference in the cells in stack
CurrentTolerance = 0.001

voltage increment for the cell during multicell stack solution
VoltageIncrement = 0.001
VoltageIterationLimit = 5
TopEnvironmentT = 950
TopFilmCoefficient = .00010
TopEmissivity = 0.00003
TopSIFilmCoefficient = .010000
TopSIEmissivity = 0.009
TopIsolationH = 0.2
TopIsolationHC = 0.006
TopGeometryScale = 10e-8

BottomEnvironmentT = 950
BottomFilmCoefficient = .00010
BottomEmissivity = 0.00003
BottomSIFilmCoefficient = .010000
BottomSIEmissivity = 0.009
BottomIsolationH = 0.2
BottomIsolationHC = 0.006
BottomGeometryScale = 10e-8

FrontEnvironmentT = 950
FrontFilmCoefficient = .00010
FrontEmissivity = 0.00003
FrontSIFilmCoefficient = .010000
FrontSIEmissivity = 0.009
FrontIsolationH = 0.2
FrontIsolationHC = 0.006
FrontGeometryScale = 10e-8

BackEnvironmentT = 950
BackFilmCoefficient = .00010
BackEmissivity = 0.00003
BackSIFilmCoefficient = .010000
BackSIEmissivity = 0.009
BackIsolationH = 0.2
BackIsolationHC = 0.006
BackGeometryScale = 10e-8

SideEnvironmentT = 950
SideFilmCoefficient = 0.000010
SideEmissivity = 0.000003
SideSIFilmCoefficient = 0.000010
SideSIEmissivity = 0.000003
SideIsolationH = 0.20000111
SideIsolationHC = 0.0006
SideGeometryScale = 10e-8

InletArea = 0.0001
InletHC = 20.0
InletL = 0.003
OutletArea = 0.0001
OutletHC = 20.0
OutletL = 0.003
BoundaryFlag = 2

CP_pen = 400.0
CP_plate = 400.0

EC_Model_Option = 4
VTC = -0.017
UserDefinedHeat = 1
QuasiTransient = 0
TimeStep=0.01
LimitTiterations = 40
PrintBalances = 1
HaveConductionOnInlet = 0

H2_Threshold=0.01
H2_Threshold_Current=0.01
VoltageOnCurrent.dat for Example Case 1

```plaintext
-- EC based on Achenbach benchmark paper for H2 fuel
-- function VoltageValue()
--
-- Assign Constants/Conversions/Geometry/Material Data
R=8.3145; F=96485.3; atm2bar=1.01325
th_a=50.0e-6; th_e=150.0e-6; th_c=50.0e-6; th_ic=2500.0e-6
--
-- Compute the local cell temperature
Tk=(oT+fT)/2.0
--
-- Compute the total pressure & convert to bar
pO2airc=pO2air*atm2bar; pN2airc=pN2air*atm2bar
pH2c=pH2*atm2bar; pH2Oc=pH2O*atm2bar; pCOc=pCO*atm2bar
pCO2c=pCO2*atm2bar; pH4c=pCH4*atm2bar; pN2c=pN2*atm2bar

Ptotal=pH2c+pH2Oc+pCOc+pCO2c+pCH4c+pN2c
--
-- Convert the passed current density
Jcalc=J*10000.
--
-- Calculate ohmic resistance
siga=95.0e6/Tk*exp(-1150.0/Tk)
sigc=42.0e6/Tk*exp(-1200.0/Tk)
sige=3.34e4*Tk*exp(-10300.0/Tk)
sigic=9.3e6/Tk*exp(-1100.0/Tk)
RohmIC=0.0025/sigic
Rohm=th_a/siga+th_c/sigc+th_e/sige+RohmIC
--
-- Calculate the open cell voltage
U00H2O=(241.106-3.804e-2*Tk-1.402e-5*Tk^2+3.551e-9*Tk^3)*1000.0/2.0/F
U0H2=U00H2O-R*Tk/2.0/F*math.log(pH2Oc/pH2c/pO2airc^0.5)
--
-- Calculate the working voltage
UH2=UOH2-(Rohm*Jcalc+Rohm*Jcalc+Rohm*Jcalc)
Z=UH2
--
-- Return the voltage value (not less than zero)
if Z<0.0 then
    Z=0.001
end
return Z
end
```

**Appendix B**

**EC_Dimension1_InputTable.dat for Example Case 2**

Description: Achenbach single cell co-flow benchmark with CH$_4$ fuel

<table>
<thead>
<tr>
<th>CELL PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>nLayers = 10</td>
</tr>
<tr>
<td>nSpecies = 6</td>
</tr>
<tr>
<td>Thickness = 250.0</td>
</tr>
<tr>
<td>Tortuosity = 2.5</td>
</tr>
<tr>
<td>Porosity = 30.0</td>
</tr>
<tr>
<td>PoreRadius = 0.5</td>
</tr>
<tr>
<td>ElectrolyteThickness = 150.0</td>
</tr>
<tr>
<td>InterconnectThickness = 1500.0</td>
</tr>
<tr>
<td>CathodeThickness = 50.0</td>
</tr>
<tr>
<td>CathodePorosity = 30.0</td>
</tr>
<tr>
<td>CathodeTortuosity = 2.5</td>
</tr>
<tr>
<td>AnodeThickness = 50.0</td>
</tr>
<tr>
<td>AnodePorosity = 30.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CONTACT RESISTANCE PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScaleThickness = 30.0</td>
</tr>
<tr>
<td>PreExponent = 10.0</td>
</tr>
<tr>
<td>ActivationEnergy = 0.20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CATHODE RESISTANCE PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CathodePreExponent = 575955.0</td>
</tr>
<tr>
<td>CathodeActivationEnergy = 0.117</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CATHODE BUTLER-VOLMER PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>BV_AlphaCoefficient = 0.55</td>
</tr>
<tr>
<td>BV_ActivationEnergy = 1.2</td>
</tr>
<tr>
<td>BV_PreExponent_a = -120</td>
</tr>
<tr>
<td>BV_PreExponent_b = 2.3e5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CATHODE O$_2$ DEPLETION PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CathodeDepletionCoefficient_a = 3</td>
</tr>
<tr>
<td>CathodeDepletionCoefficient_b = -35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ANODE DEPLETION POLARIZATION PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOP_slope = 0.2027</td>
</tr>
<tr>
<td>LOP_is = -8.897e-4</td>
</tr>
<tr>
<td>LOP_ii = 0.5221</td>
</tr>
<tr>
<td>AOP_ns = 2.439e-3</td>
</tr>
<tr>
<td>AOP_ni = -2.358</td>
</tr>
<tr>
<td>AOP_qs = 1.747e-2</td>
</tr>
<tr>
<td>AOP_qi = -1.158e-2</td>
</tr>
<tr>
<td>AOP_ms = 11.06</td>
</tr>
<tr>
<td>AOP_mi = -1.152</td>
</tr>
<tr>
<td>AOP_ps = 6.560e-4</td>
</tr>
<tr>
<td>AOP_pi = -1.152</td>
</tr>
</tbody>
</table>

| SystemPressure = 1.0 |

<table>
<thead>
<tr>
<th>FUEL PARAMETERS (FLOW RATE IS MOLE/SEC; TEMP IS K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FuelFlowRate = 0.0001873849</td>
</tr>
<tr>
<td>FuelTemperature = 1173</td>
</tr>
<tr>
<td>FuelTonTop = 1173</td>
</tr>
<tr>
<td>FuelH2 = 0.2626</td>
</tr>
<tr>
<td>FuelH2O = 0.4934</td>
</tr>
<tr>
<td>FuelCO = 0.0294</td>
</tr>
<tr>
<td>FuelCO2 = 0.0436</td>
</tr>
<tr>
<td>FuelCH4 = 0.1710</td>
</tr>
<tr>
<td>FuelN2 = 0.00</td>
</tr>
</tbody>
</table>
OXIDANT PARAMETERS (FLOW RATE IS MOLE/SEC; TEMP IS K)
OxidantFlowRate = 0.0030485
OxidantTemperature = 1173
OxidantTonTop = 1173
OxidantO2 = 0.21
OxidantN2 = 0.79

DIMENSION IN DIRECTION OF GAS FLOW (M)
Ax = 0.1

DIMENSION PERPENDICULAR TO GAS FLOW (M)
Ay = 0.1

NUMBER OF INCREMENTS PER CELL
Nx = 1000

NUMBER OF CELLS IN STACK
nCells = 1

--Average_CurrentDensity = 3000
StackVoltage = 0.64645
--Average_CellVoltage = 0.7098
ShortCurrent = 0.0

DISTANCE REQUIRED TO REACH GAS EQUILIBRIUM
EquilibriumPathCO = 0.001
EquilibriumPathCH4 = 0.01

EMISSIVITY OF INTERCONNECT AND CELL
InterConnectEmittance = 0.5
PENEmittance = 0.5

THICKNESSES OF BOTTOM, INTERCONNECT, TOP PLATE AND PEN
BottomPlateH = 0.000946
InterConnectPlateH = 0.001393
TopPlateH = 0.000946
PEN_H = 0.00025

THERMAL COND. OF BOTTOM, INTERCONNECT, TOP PLATE AND PEN
BottomPlateHC = 2.0
InterConnectPlateHC = 2.0
TopPlateHC = 2.0
PEN_HC = 2.0

HEIGHT OF GAS FLOW PASSAGES
AirFlowH = 0.000554
FuelFlowH = 0.000554

OxidantSolidFilmCoefficient = 132.0
FuelSolidFilmCoefficient = 321.0

SWITCH: COFLOW IS 1, COUNTERFLOW IS 0
CoFlowFlag = 1

relaxation parameter between old T distribution and new T distribution
T_Relaxation = 0.5
T_precision = 0.05
maximum temperature admissible in iterations (C)
T_TopLimit = 1420.0

minimum temperature admissible in iterations (C)
T_BottomLimit = 580.0

maximum admissible total current difference in the cells in stack
CurrentTolerance = 0.001

voltage increment for the cell during multicell stack solution
VoltageIncrement = 0.001
VoltageIterationLimit = 5

TopEnvironmentT = 950
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>TopFilmCoefficient</td>
<td>.00010</td>
</tr>
<tr>
<td>TopEmissivity</td>
<td>0.00003</td>
</tr>
<tr>
<td>TopSIFilmCoefficient</td>
<td>.010000</td>
</tr>
<tr>
<td>TopSIEmissivity</td>
<td>0.009</td>
</tr>
<tr>
<td>TopIsolationH</td>
<td>0.2</td>
</tr>
<tr>
<td>TopIsolationHC</td>
<td>0.006</td>
</tr>
<tr>
<td>TopGeometryScale</td>
<td>10e-8</td>
</tr>
<tr>
<td>BottomEnvironmentT</td>
<td>950</td>
</tr>
<tr>
<td>BottomFilmCoefficient</td>
<td>.00010</td>
</tr>
<tr>
<td>BottomEmissivity</td>
<td>0.00003</td>
</tr>
<tr>
<td>BottomSIFilmCoefficient</td>
<td>.010000</td>
</tr>
<tr>
<td>BottomSIEmissivity</td>
<td>0.009</td>
</tr>
<tr>
<td>BottomIsolationH</td>
<td>0.2</td>
</tr>
<tr>
<td>BottomIsolationHC</td>
<td>0.006</td>
</tr>
<tr>
<td>BottomGeometryScale</td>
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</tr>
<tr>
<td>FrontEnvironmentT</td>
<td>950</td>
</tr>
<tr>
<td>FrontFilmCoefficient</td>
<td>.00010</td>
</tr>
<tr>
<td>FrontEmissivity</td>
<td>0.00003</td>
</tr>
<tr>
<td>FrontSIFilmCoefficient</td>
<td>.010000</td>
</tr>
<tr>
<td>FrontSIEmissivity</td>
<td>0.009</td>
</tr>
<tr>
<td>FrontIsolationH</td>
<td>0.2</td>
</tr>
<tr>
<td>FrontIsolationHC</td>
<td>0.006</td>
</tr>
<tr>
<td>FrontGeometryScale</td>
<td>10e-8</td>
</tr>
<tr>
<td>BackEnvironmentT</td>
<td>950</td>
</tr>
<tr>
<td>BackFilmCoefficient</td>
<td>.00010</td>
</tr>
<tr>
<td>BackEmissivity</td>
<td>0.00003</td>
</tr>
<tr>
<td>BackSIFilmCoefficient</td>
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<tr>
<td>BackSIEmissivity</td>
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<tr>
<td>BackIsolationH</td>
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<tr>
<td>BackIsolationHC</td>
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<tr>
<td>BackGeometryScale</td>
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<tr>
<td>SideEnvironmentT</td>
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<tr>
<td>SideFilmCoefficient</td>
<td>0.00010</td>
</tr>
<tr>
<td>SideEmissivity</td>
<td>0.000003</td>
</tr>
<tr>
<td>SideSIFilmCoefficient</td>
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</tr>
<tr>
<td>SideSIEmissivity</td>
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</tr>
<tr>
<td>SideIsolationH</td>
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</tr>
<tr>
<td>SideIsolationHC</td>
<td>0.006</td>
</tr>
<tr>
<td>SideGeometryScale</td>
<td>10e-8</td>
</tr>
<tr>
<td>InletArea</td>
<td>0.0001</td>
</tr>
<tr>
<td>InletHC</td>
<td>20.0</td>
</tr>
<tr>
<td>InletL</td>
<td>0.003</td>
</tr>
<tr>
<td>OutletArea</td>
<td>0.0001</td>
</tr>
<tr>
<td>OutletHC</td>
<td>20.0</td>
</tr>
<tr>
<td>OutletL</td>
<td>0.003</td>
</tr>
<tr>
<td>BoundaryFlag</td>
<td>2</td>
</tr>
<tr>
<td>CP_pen</td>
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<tr>
<td>CP_plate</td>
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<tr>
<td>EC_Model_Option</td>
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<tr>
<td>VTC</td>
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<tr>
<td>UserDefinedHeat</td>
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<tr>
<td>QuasiTransient</td>
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<tr>
<td>TimeStep</td>
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<tr>
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<tr>
<td>PrintBalances</td>
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</tr>
<tr>
<td>HaveConductionOnInlet</td>
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</tr>
<tr>
<td>H2_Threshold</td>
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</tr>
<tr>
<td>H2_Threshold_Current</td>
<td>0.01</td>
</tr>
<tr>
<td>CH4_Option</td>
<td>2</td>
</tr>
</tbody>
</table>
VoltageOnCurrent.dat for Example Case 2

--- EC based on Achenbach benchmark paper for CH4 fuel
--- assume no CH4 oxidation, just steam reforming
--- assume not CO oxidation, just water-gas shift
---
function VoltageValue()
---
--- Assign Constants/Conversions/Geometry/Material Data
R=8.3145; F=96485.3; atm2bar=1.01325
th_a=50.0e-6; th_e=150.0e-6; th_c=50.0e-6; th_ic=2500.0e-6
---
--- Compute the local cell temperature
Tk=(oT+fT)/2.0
---
--- Compute the total pressure & convert to bar
pO2airc=pO2air*atm2bar; pN2airc=pN2air*atm2bar
pH2c=pH2*atm2bar; pH2Oc=pH2O*atm2bar; pCOc=pCO*atm2bar
pCO2c=pCO2*atm2bar; pCH4c=pCH4*atm2bar; pN2c=pN2*atm2bar
Ptotal=pH2c+pH2Oc+pCOc+pCO2c+pCH4c+pN2c
---
--- Convert the passed current density
Jcalc=J*10000.
---
--- Calculate ohmic resistance
siga=95.0e6/Tk*math.exp(-1150.0/Tk)
sigc=42.0e6/Tk*math.exp(-1200.0/Tk)
sige=3.34e4*math.exp(-10300.0/Tk)
sigic=9.3e6/Tk*math.exp(-1100.0/Tk)
RohmIC=0.0025/sigic
Rohm=th_a/siga+th_c/sigc+th_e/sige+RohmIC
---
--- Calculate the open cell voltage
U00H2O=(241.106-3.804e-2*Tk-1.402e-5*Tk^2+3.551e-9*Tk^3)*1000.0/2.0/F
U0H2=U00H2O-R*Tk/2.0/F*math.log(pH2Oc/pH2c/pO2airc^0.5)
---
--- Calculate the working voltage
UH2=U0H2-((Rohm+Jcalc+Rohm)*Jcalc+Rohm*Jcalc)
Z=UH2
---
--- Return the voltage value (not less than zero)
if Z<0.0 then
Z=0.001
end
return Z
end

---------------------------------------------------------------------------------------------------
-- CH4 conversion rate for on-cell reformation
--
function CH4ReformingRate()
GasConstant=8.3144
Ch4_Usage=4274.0*pCH4*math.exp(-82000.0/fuelT/GasConstant)
return Ch4_Usage
end
### Appendix C

**EC_Dimension1_InputTable.dat for Example Case 3**

Description: Tall stack co-flow example with H$_2$ fuel

```plaintext
#CELL PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFlowFlag</td>
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</tr>
<tr>
<td>Ax</td>
<td>0.25</td>
</tr>
<tr>
<td>Ay</td>
<td>0.25</td>
</tr>
<tr>
<td>nCells</td>
<td>96</td>
</tr>
<tr>
<td>BottomPlateH</td>
<td>0.005</td>
</tr>
<tr>
<td>PEN_H</td>
<td>0.0005</td>
</tr>
<tr>
<td>InterConnectPlateH</td>
<td>0.0005</td>
</tr>
<tr>
<td>TopPlateH</td>
<td>0.005</td>
</tr>
<tr>
<td>AirFlowH</td>
<td>0.001</td>
</tr>
<tr>
<td>FuelFlowH</td>
<td>0.0005</td>
</tr>
<tr>
<td>InletArea</td>
<td>0.0001</td>
</tr>
<tr>
<td>InletL</td>
<td>0.003</td>
</tr>
<tr>
<td>OutletArea</td>
<td>0.0001</td>
</tr>
<tr>
<td>OutletL</td>
<td>0.003</td>
</tr>
<tr>
<td>Cell_Variation</td>
<td>0</td>
</tr>
</tbody>
</table>

# STACK GEOMETRY PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ax</td>
<td>0.25</td>
</tr>
<tr>
<td>Ay</td>
<td>0.25</td>
</tr>
<tr>
<td>nCells</td>
<td>96</td>
</tr>
<tr>
<td>BottomPlateH</td>
<td>0.005</td>
</tr>
<tr>
<td>PEN_H</td>
<td>0.0005</td>
</tr>
<tr>
<td>InterConnectPlateH</td>
<td>0.0005</td>
</tr>
<tr>
<td>TopPlateH</td>
<td>0.005</td>
</tr>
<tr>
<td>AirFlowH</td>
<td>0.001</td>
</tr>
<tr>
<td>FuelFlowH</td>
<td>0.0005</td>
</tr>
<tr>
<td>InletArea</td>
<td>0.0001</td>
</tr>
<tr>
<td>InletL</td>
<td>0.003</td>
</tr>
<tr>
<td>OutletArea</td>
<td>0.0001</td>
</tr>
<tr>
<td>OutletL</td>
<td>0.003</td>
</tr>
<tr>
<td>Cell_Variation</td>
<td>0</td>
</tr>
</tbody>
</table>

# AIR-FUEL FLOW PARAMETERS

<table>
<thead>
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<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SystemPressure</td>
<td>1.0</td>
</tr>
<tr>
<td>FuelTemperature</td>
<td>973</td>
</tr>
<tr>
<td>FuelTonTop</td>
<td>1003</td>
</tr>
<tr>
<td>FuelFlowRate</td>
<td>0.0147</td>
</tr>
<tr>
<td>FuelH2</td>
<td>0.485</td>
</tr>
<tr>
<td>FuelH2O</td>
<td>0.03</td>
</tr>
<tr>
<td>FuelCO</td>
<td>0.0</td>
</tr>
<tr>
<td>FuelCO2</td>
<td>0.0</td>
</tr>
<tr>
<td>FuelCH4</td>
<td>0.0</td>
</tr>
<tr>
<td>FuelN2</td>
<td>0.0</td>
</tr>
<tr>
<td>FuelFlowRate</td>
<td>0.247</td>
</tr>
<tr>
<td>FuelH2</td>
<td>0.97</td>
</tr>
<tr>
<td>FuelH2O</td>
<td>0.03</td>
</tr>
<tr>
<td>FuelCO</td>
<td>0.0</td>
</tr>
<tr>
<td>FuelCO2</td>
<td>0.0</td>
</tr>
<tr>
<td>FuelCH4</td>
<td>0.0</td>
</tr>
<tr>
<td>FuelN2</td>
<td>0.0</td>
</tr>
</tbody>
</table>
```

C-1
# Fuel Flow Rate = 0.0147
# Fuel H2 = 0.538
# Fuel H2O = 0.181
# Fuel CO = 0.127
# Fuel CO2 = 0.052
# Fuel CH4 = 0.101
# Fuel N2 = 0.0

Oxidant Flow Rate = 2.47
Oxidant Temperature = 973
Oxidant Ton Top = 1003
Oxidant O2 = 0.21
Oxidant N2 = 0.79

# oxidant inlet state

#---------------------------#
# STACK SOLUTION MODE      #
# Comment out all modes except one! #
#---------------------------#

# Mode 1: cell average voltage (V)
Average_CellVoltage = 0.852

# Mode 2: total stack voltage (V)
#StackVoltage = 0.64175

# Mode 3: current density (A/m^2)
#Average_CurrentDensity = 3000

# Mode 4: fixed fuel utilization
#Fuel_Utilization = 0.65

# Mode 5: solve the stack V-I curve
#Average_CellVoltage_Low = 0.4
#Average_CellVoltage_High = 1.0
#Average_CellVoltage_Increment = 0.05

#---------------------------#
# ELECTROCHEMISTRY OPTIONS #
#---------------------------#

# I-V relation: internal is 0, subroutine is 4
EC_Model_Option = 4

# short current switch?
ShortCurrent = 0.0

# CH4 consumption option
# 0 is path length, 2 is Achenbach rate expression, 3 is user subroutine
CH4_Option = 3

# species equilibrium distance (m)
EquilibriumPathCO = 0.001
EquilibriumPathCH4 = 0.01

#---------------------------#
# SOLUTION CONTROL PARAMETERS #
#---------------------------#

# number of increments
Nx = 100

# timestep for counter-flow
TimeStep = 0.5

# temp iteration relaxation factor
T_Relaxation = 1.0

# temperature iteration limits (C)
T_TopLimit = 900.0
T_BottomLimit = 650.0

# multicell voltage increment
VoltageIncrement = 0.001

# minimum threshold on H2
H2_Threshold = 0.0001
H2_Threshold_Current = 0.0001

# maximum voltage/temperature iterations
VoltageIterationLimit = 30
<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LimitTiterations</td>
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<tr>
<td>UserDefinedHeat</td>
<td>1</td>
</tr>
<tr>
<td>QuasiTransient</td>
<td>0</td>
</tr>
<tr>
<td>HaveConductionOnInlet</td>
<td>0</td>
</tr>
<tr>
<td>PrintBalances</td>
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<tr>
<td>PrintDiffusionDifference</td>
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</tr>
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<td>T_precision</td>
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<tr>
<td>CurrentTolerance</td>
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<tr>
<td>OxidantSolidFilmCoefficient</td>
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<tr>
<td>FuelSolidFilmCoefficient</td>
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</tr>
<tr>
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</tr>
<tr>
<td>PENEmittance</td>
<td>0.5</td>
</tr>
<tr>
<td>BottomPlateHC</td>
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</tr>
<tr>
<td>InterConnectPlateHC</td>
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</tr>
<tr>
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<tr>
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<tr>
<td>CP_pen</td>
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<td>CP_plate</td>
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<tr>
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<tr>
<td>TopFilmCoefficient</td>
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</tr>
<tr>
<td>TopEmissivity</td>
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<tr>
<td>TopSIFilmCoefficient</td>
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<tr>
<td>TopSIEmissivity</td>
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<td>BottomEmissivity</td>
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</tr>
<tr>
<td>BottomSIFilmCoefficient</td>
<td>1000.0</td>
</tr>
</tbody>
</table>
BottomSIEmissivity = 0.9
BottomIsolationH = 0.25
BottomIsolationHC = 25.0
BottomGeometryScale = 2.5
# front
FrontEnvironmentT = 750
FrontFilmCoefficient = 0.3
FrontEmissivity = 0.7
FrontSIFilmCoefficient = 1000.0
FrontSIEmissivity = 0.9
FrontIsolationH = 0.12
FrontIsolationHC = 25.0
FrontGeometryScale = 1.3
BackEnvironmentT = 750
BackFilmCoefficient = 0.3
BackEmissivity = 0.7
BackSIFilmCoefficient = 1000.0
BackSIEmissivity = 0.9
BackIsolationH = 0.12
BackIsolationHC = 25.0
BackGeometryScale = 1.3
# sides
SideEnvironmentT = 750
SideFilmCoefficient = 0.3
SideEmissivity = 0.7
SideSIFilmCoefficient = 1000.0
SideSIEmissivity = 0.9
SideIsolationH = 0.03
SideIsolationHC = 25.0
SideGeometryScale = 2.0

#----------------------------------------#
#           ELECTRODE DIFFUSION          #
# thickness and radius in (micron)       #
# porosity in (%)                        #
#----------------------------------------#
nLayers = 3
nSpecies = 6
Thickness = 250.0
Tortuosity = 1.1
Porosity  = 55.0
PoreRadius  = 0.5
ElectrolyteThickness = 150.0
InterconnectThickness = 1500.0
CathodeThickness = 50.0
CathodePorosity = 55.0
CathodeTortuosity = 1.1
AnodeThickness = 50.0
AnodePorosity = 55.0

#----------------------------------------#
#     INTERNAL I-V CURVE PARAMETERS      #
#----------------------------------------#
ScaleThickness  = 30.0
PreExponent = 10.0
ActivationEnergy = 0.20
# cathode resistance
CathodePreExponent = 575955.0
CathodeActivationEnergy = 0.117
# cathode BV activation
BV_AlphaCoefficient = 0.55
BV_ActivationEnergy = 1.2
BV_PreExponent_a = -120
BV_PreExponent_b = 2.3e5
# cathode O2 depletion
CathodeDepletionCoefficient_a = 3
CathodeDepletionCoefficient_b = -35
VoltageOnCurrent.dat for Example Case 3

--- B Koeppel
--- 4-1-11
---
--- Available Local Inputs From SOFC-MP
---
--- 0T Temperature oxidant (K)
---  fT Temperature fuel (K)
---  J Current density (A/cm²)
---  po2air Air side partial pressure O₂ (atm)
---  pN2air Air side partial pressure N₂ (atm)
---  pH2 Fuel side partial pressure H₂ (atm)
---  pH2O Fuel side partial pressure H₂O (atm)
---  pCO Fuel side partial pressure CO (atm)
---  pCO2 Fuel side partial pressure CO₂ (atm)
---  pCH4 Fuel side partial pressure CH₄ (atm)
---  pN2 Fuel side partial pressure N₂ (atm)
---  nActiveCell Cell number
---  DistanceFromTheEdge Distance along path (m)
---  DistanceFromTheEdgeRatio Relative distance along the path
---
--- Required Subroutine Outputs
---  Z Voltage (V)
---
--- User-Assigned Geometry/Material Inputs
---  th_a Thickness anode (microns)
---  th_e Thickness electrolyte (microns)
---  th_c Thickness cathode (microns)
---  th_ic Thickness interconnect (microns)
---  por_a Porosity anode (%)
---  por_c Porosity cathode (%)
---  tort_a Tortuosity anode
---  tort_c Tortuosity cathode
---  BV_alpha Butler-Volmer 'alpha' constant
---  BV_prexp Butler-Volmer pre-exponential constant
---  BV_Eact Butler-Volmer activation energy
---  R_cont Contact resistance
---
--- User-Assigned Constants/Conversions
---  R Ideal gas constant
---  F Faraday's constant
---  atm2Pa Conversion for pressure atm -> Pa
-- mic2m Conversion for length micron -> m
--

function VoltageValue()
--
-- Assign Constants/Conversions
R=8.3145
F=96485.0
atm2Pa=101325.0
mic2m=1.0e-6
--

-- Assign Flags
BVflag=1 -- 0-old method, 1-pressurized method
--

-- Assign Geometry/Material Data
th_a= 450.0
th_e= 10.0
th_c= 40.0
th_ic= 500.0
por_a= 40.0
por_c= 40.0
tort_a= 2.5
tort_c= 2.5
BV_alpha= 0.3
BV_prexp= 105000.0
BV_Eact= 107489.0
R_cont= 0.0
BV_alpha2a= 2.0
BV_prexp2a= 465000.0
BV_Eact2a= 125000.0
BV_alpha2f= 0.5
BV_prexp2f= 75000000.0
BV_Eact2f= 110000.0
BV_gamma2a= 0.133
V_loss= 0.0
--

-- Compute the local cell temperature
-------------------------------
Tk=(oT+fT)/2.0
To=Tk-273.0
--

-- Compute the Nernst open circuit voltage
------------------------------------------
Keq_dHo=-56930.0
Keq_A=6.75
Keq_B=0.64
Keq_C=0.08
Keq_L=-8.74
Keq_dG=Keq_dHo+Keq_A*Tk*math.log10(Tk)+Keq_B*Tk/Tk+Keq_C*100000/Tk+Keq_L*Tk
Kequb=math.exp(-Keq_dG*4.184/R/Tk)
pO2anode=(pH2O/Kequb/pH2)^2
Voc=(R*Tk/4.0/F)*math.log(pO2air/pO2anode)
--

-- Compute the ohmic polarization
---------------------------------
-- Compute the electrolyte conductivity
s_eA=8.588e-10
s_eB=-1.101e-6
s_eC=4.679e-4
s_eD=0.0654
s_e=s_eA*Tc^3+s_eB*Tc^2+s_eC*Tc+s_eD
-- Compute the interconnect conductivity
s_icA=0.069
s_icB=70.9
s_ic=1000000.0/(s_icA*s_c+s_icB)
-- Compute the cathode conductivity
s_ca=575955.0
s_cEa=0.117
s_c=(s_ca/Tk)*math.exp(-s_cEa/0.00008617/Tk)*(1.0-(0.018*por_c))
-- Compute the anode conductivity
\[ s_{aA}=1000 \]
\[ s_{a}=s_{aA}*(1.0-(0.018*\text{por}_{a})) \]

-- Compute the effective cell resistivity
\[ R_{\text{cont}}+(\text{th}_{e}/s_{e}+\text{th}_{a}/s_{a}+\text{th}_{ic}/s_{ic}+\text{th}_{c}/s_{c})*0.0001 \]

-- Compute the total ohmic loss
\[ \text{Ohmic}=R_{i} J \]

-- Compute the activation polarization (old method or new pressurized method)

\[
\text{if BVflag==0 then}
\]
-- Old method
\[ \text{10=BV}_{\text{prexp}}*\text{math}.\text{exp}(-\text{BV}_{\text{Eact}}/R/Tk) \]
\[ \text{BV}=(R*Tk/BV_{\text{alpha}}/F)\text{math}.\text{log}((\text{J}/2.0/10)+\text{math}.\text{sqrt}((\text{J}/2.0/10)^2+1)) \]

else
-- New method
\[ \text{i}_{\text{eff}}_{f}=\text{BV}_{\text{prexp}}2f*\text{math}.\text{exp}(-\text{BV}_{\text{Eact}}2f/R/Tk)*\text{pO2anode}\text{BV}_{\gamma2f} \]
\[ \text{i}_{\text{eff}}_{a}=\text{BV}_{\text{prexp}}2a*\text{math}.\text{exp}(-\text{BV}_{\text{Eact}}2a/R/Tk)*\text{pO2air}\text{BV}_{\gamma2a} \]
\[ \eta_{f}=R\text{TK}/BV_{\alpha2f}/F\text{math}.\text{log}((\text{J}/2.0/i_{\text{eff}}_{f})+\text{math}.\text{sqrt}((\text{J}/2.0/i_{\text{eff}}_{f})^2+1)) \]
\[ \eta_{a}=R\text{TK}/BV_{\alpha2a}/F\text{math}.\text{log}((\text{J}/2.0/i_{\text{eff}}_{a})+\text{math}.\text{sqrt}((\text{J}/2.0/i_{\text{eff}}_{a})^2+1)) \]
\[ \text{BV}=\eta_{f}+\eta_{a} \]
end

-- Compute the diffusion coefficients

-- Make 0.0 species non-zero to make equations defined
\[
\text{if pCO<=0 then}
\]
\[ \text{pCO}=1e-16 \]
\[
\text{else}
\]
\[ \text{pCO}=\text{pCO} \]
end
\[
\text{if pCO2<=0 then}
\]
\[ \text{pCO2}=1e-16 \]
\[
\text{else}
\]
\[ \text{pCO2}=\text{pCO2} \]
end

\[ \text{P}_{\text{total}}=\text{pH}_{2}+\text{pH}_{2O}+\text{pCO}+\text{pCO2}+\text{pN}_{2}+\text{pCH}_{4} \]
\[ \text{H}_{2}\text{mf}=\text{pH}_{2}/\text{P}_{\text{total}} \]
\[ \text{H}_{2O}\text{mf}=\text{pH}_{2O}/\text{P}_{\text{total}} \]
\[ \text{CO mf}=\text{pCO}/\text{P}_{\text{total}} \]
\[ \text{CO}_{2}\text{mf}=\text{pCO2}/\text{P}_{\text{total}} \]
\[ \text{N}_{2}\text{mf}=\text{pN}_{2}/\text{P}_{\text{total}} \]
\[ \text{CH}_{4}\text{mf}=\text{pCH}_{4}/\text{P}_{\text{total}} \]

-- Diffusion constants (empirical radii and molecular weights)
\[ \text{H}_{2}i=1.92 \]
\[ \text{H}_{2O}i=2.33 \]
\[ \text{COi}=2.66 \]
\[ \text{CO}_{2}i=3.0 \]
\[ \text{N}_{2}i=2.62 \]
\[ \text{O}_{2}i=2.55 \]
\[ \text{CH}_{4}i=2.9 \]
\[ \text{H}_{2}ii=2.0 \]
\[ \text{H}_{2O}ii=18.0 \]
\[ \text{COi}=28.0 \]
\[ \text{CO}_{2}i=44.0 \]
\[ \text{N}_{2}ii=28.0 \]
\[ \text{O}_{2}ii=32.0 \]
\[ \text{CH}_{4}ii=16.0 \]

-- Compute anode binary diffusion constants
\[ \text{H}_{2}\text{H}_{2O}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{H}_{2}i\text{+H}_{2}ii)/(\text{H}_{2}i\text{+H}_{2O}i)^{2})) \]
\[ \text{H}_{2}\text{CO}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{H}_{2}i\text{+COi)/(H}_{2}i\text{+CO}_{2}i)^{2})) \]
\[ \text{H}_{2}\text{CO}_{2}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{H}_{2}i\text{+CO}_{2}i)/(\text{H}_{2}i\text{+CO}_{2}i)^{2})) \]
\[ \text{H}_{2}\text{N}_{2}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{H}_{2}i\text{+N}_{2}i))/(\text{H}_{2}i\text{+N}_{2}i)^{2}) \]
\[ \text{H}_{2}\text{CH}_{4}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{H}_{2}i\text{+CH}_{4}i)/(\text{H}_{2}i\text{+CH}_{4}i)^{2})) \]
\[ \text{O}_{2}\text{N}_{2}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{O}_{2}i\text{+N}_{2}i)/(\text{O}_{2}i\text{+N}_{2}i)^{2})) \]
\[ \text{H}_{2}O\text{CO}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{H}_{2}Oi\text{+COi)/(H}_{2}Oi\text{+COi})^{2})) \]
\[ \text{H}_{2}O\text{CO}_{2}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{H}_{2}Oi\text{+CO}_{2}i)/(\text{H}_{2}Oi\text{+CO}_{2}i)^{2})) \]
\[ \text{H}_{2}O\text{N}_{2}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{H}_{2}Oi\text{+N}_{2}i)/(\text{H}_{2}Oi\text{+N}_{2}i)^{2})) \]
\[ \text{H}_{2}O\text{CH}_{4}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{H}_{2}Oi\text{+CH}_{4}i)/(\text{H}_{2}Oi\text{+CH}_{4}i)^{2})) \]
\[ \text{N}_{2}\text{CH}_{4}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{N}_{2}i\text{+CH}_{4}i)/(\text{N}_{2}i\text{+CH}_{4}i)^{2})) \]
\[ \text{CO}_{2}\text{CH}_{4}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{COi}\text{+CH}_{4}i)/(\text{COi}\text{+CH}_{4}i)^{2})) \]
\[ \text{CON2}=((\text{le}^{-3}/\text{P}_{\text{total}})\text{*(Tk}^{1.75}\text{)*math}.\text{sqrt}(\text{1}/(\text{COi}\text{+N}_{2}i)/(\text{COi}\text{+N}_{2}i)^{2})) \]
COCH4=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/COii+1/CH4ii)/((COi+CH4i)^2)
CO2N2=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/CO2ii+1/N2ii)/((CO2i+N2i)^2)
CO2CH4=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/CO2ii+1/CH4ii)/((CO2i+CH4i)^2)
-- Compute anode unitary diffusion constants
H2_UD=(1-H2_mf)/(H2O_mf/H2H2O+CO_mf/H2CO+CO2_mf/H2CO2+N2_mf/H2N2+CH4_mf/H2CH4)
H2O_UD=(1-H2O_mf)/(H2_mf/H2H2O+CO_mf/H2CO+CO2_mf/H2CO2+N2_mf/H2N2+CH4_mf/H2CH4)
CO_UD=(1-CO_mf)/(H2_mf/H2CO+N2_mf/H2N2+CO2_mf/H2CO2+N2_mf/H2N2+CH4_mf/H2CH4)
CO2_UD=(1-CO2_mf)/(H2_mf/H2CO2+H2O_mf/H2CO2+CO_mf/H2CO+CO2_mf/H2CO2+N2_mf/H2N2+CH4_mf/H2CH4)
N2_UD=(1-N2_mf)/(H2_mf/H2N2+H2O_mf/H2N2+CO_mf/H2N2+CO2_mf/H2N2+CH4_mf/H2N2)
CH4_UD=(1-CH4_mf)/(H2_mf/H2CH4+H2O_mf/H2CH4+CO_mf/H2CH4+CO2_mf/H2CH4+N2_mf/H2CH4)
-- Compute anode adsorption and surface diffusion modifications
area_H2=math.pi*(H2i*10^-10)^2
area_H2O=math.pi*(H2Oi*10^-10)^2
area_CO=math.pi*(COi*10^-10)^2
area_CO2=math.pi*(CO2i*10^-10)^2
area_N2=math.pi*(N2i*10^-10)^2
area_O2=math.pi*(O2i*10^-10)^2
area_CH4=math.pi*(CH4i*10^-10)^2
pres_H2=math.max(0,pH2-J*82.058*Tk*(th_a/10000)/(2*F)*(tort_a/(H2_UD*por_a/100)))
pres_H2O=math.max(0,pH2O+J*82.058*Tk*(th_a/10000)/(2*F)*(tort_a/(H2O_UD*por_a/100)))
pres_CO=math.max(0,pCOc-J*82.058*Tk*(th_a/10000)/(2*F)*(tort_a/(CO_UD*por_a/100)))
pres_CO2=math.max(0,pCO2c+J*82.058*Tk*(th_a/10000)/(2*F)*(tort_a/(CO2_UD*por_a/100)))
pres_N2=math.max(0,pN2)
pres_O2=math.max(0,pO2anode)
pres_CH4=max(0,pCH4)
Qev_H2=0.425
Qev_H2O=0.549
Qev_CO=0.5
Qev_CO2=0.5
Qev_N2=0.5
Qev_O2=0.5
Qev_CH4=0.5
bP_H2=6.023*10^23*area_H2*10^-13/math.sqrt(2*math.pi*R*Tk*H2ii)*math.exp(Qev_H2/(0.026*Tk/298))*pres_H2
bP_H2O=6.023*10^23*area_H2O*10^-13/math.sqrt(2*math.pi*R*Tk*H2Oii)*math.exp(Qev_H2O/(0.026*Tk/298))*pres_H2O
bP_CO=6.023*10^23*area_CO*10^-13/math.sqrt(2*math.pi*R*Tk*COii)*math.exp(Qev_CO/(0.026*Tk/298))*pres_CO
bP_CO2=6.023*10^23*area_CO2*10^-13/math.sqrt(2*math.pi*R*Tk*CO2ii)*math.exp(Qev_CO2/(0.026*Tk/298))*pres_CO2
bP_N2=6.023*10^23*area_N2*10^-13/math.sqrt(2*math.pi*R*Tk*N2ii)*math.exp(Qev_N2/(0.026*Tk/298))*pres_N2
bP_CH4=6.023*10^23*area_CH4*10^-13/math.sqrt(2*math.pi*R*Tk*CH4ii)*math.exp(Qev_CH4/(0.026*Tk/298))*pres_CH4
cov_H2=bP_H2/(1+bP_sum)
cov_H2O=bP_H2O/(1+bP_sum)
cov_CO=bP_CO/(1+bP_sum)
cov_CO2=bP_CO2/(1+bP_sum)
cov_N2=bP_N2/(1+bP_sum)
cov_O2=bP_O2/(1+bP_sum)
cov_CH4=bP_CH4/(1+bP_sum)
cov_sum=cov_H2+cov_H2O+cov_CO+cov_CO2+cov_N2+cov_O2+cov_CH4
fij_H2=cov_H2/cov_sum
fij_H2O=cov_H2O/cov_sum
fij_CO=cov_CO/cov_sum
fij_CO2=cov_CO2/cov_sum
fij_N2=cov_N2/cov_sum
fij_O2=cov_O2/cov_sum
fij_CH4=cov_CH4/cov_sum
DsurfH2th1=0.1
DsurfH2th2=4.51e-5
D_H2=H2_UD^fij_H2*((DsurfH2th1^(1-fij_H2)*DsurfH2th2^fij_H2)/(1-fij_H2))^1-fij_H2
D_H2O=H2O_UD^fij_H2O*(10^-4)^(1-fij_H2O)
D_CO=CO_UD^fij_CO*(10^-4)^(1-fij_CO)
D_CO2=CO2_UD^fij_CO2*(10^-4)^(1-fij_CO2)
D_N2=N2_UD^fij_N2*(10^-4)^(1-fij_N2)
D_O2=O2_UD^fij_O2*(10^-4)^(1-fij_O2)
D_CH4=CH4_UD^fij_CH4*(10^-4)^(1-fij_CH4)
```plaintext
-- Compute the cathode concentration polarization
------------------------------------------------------------------
Deffc = 0.01 * por_c * O2N2 / tort_c
ics = 1.0e-8 * (4.0 * F * Ptotal * atm2Pa * Deffc) / (R * Tk * th_c * mic2m) * math.log(1.0 / (1.0 - pO2air))
Cath = (R * Tk / 4.0 / F) * math.log(1.0 - (J / ics))
-- Compute the anode concentration polarization
------------------------------------------------------------------
DeffH2 = D_H2
DeffH2O = 0.01 * H2O_UD * por_a / tort_a
DeffCO = 0.01 * CO_UD * por_a / tort_a
DeffCO2 = 0.01 * CO2_UD * por_a / tort_a
alim = 2 * F * pH2 / atm2Pa * DeffH2 / (831.45 * Tk * th_a)
blim = 2 * F * pH2O / atm2Pa * DeffH2O / (831.45 * Tk * th_a)
clim = 2 * F * pCOc / atm2Pa * DeffCO / (831.45 * Tk * th_a)
dlim = 2 * F * pCO2c / atm2Pa * DeffCO2 / (831.45 * Tk * th_a)
-- Adjust calculation for iteration case of too high current requested
if J > (alim + clim) then
  Jcalc = (alim + clim) * 0.99
else
  Jcalc = J
end
OPa_A = (Jcalc + blim + dlim) / blim / dlim
OPa_B = (Jcalc * (alim * dlim + blim * clim) + blim * clim * dlim + alim * blim * clim + clim * dlim
  - alim * blim * clim) / alim / blim / clim / dlim
OPa_C = (Jcalc - alim - clim) / alim / clim
holdA1 = OPa_A
holdB1 = OPa_B
holdC1 = OPa_C
stabcheck = OPa_B^2 - 4.0 * OPa_A * OPa_C
stabcheck2 = (-OPa_B + math.sqrt(OPa_B^2 - 4.0 * OPa_A * OPa_C)) / 2.0 / OPa_A
if stabcheck > 0 then
  if stabcheck2 > 0 then
    Anod = (R * Tk / 2.0 / F) * math.log((-OPa_B + math.sqrt(OPa_B^2 - 4.0 * OPa_A * OPa_C)) / 2.0 / OPa_A)
  end
  holdA2 = 0
  holdB2 = 0
  holdC2 = 0
  DeffH2 = 0.01 * H2O_UD * por_a / tort_a
  DeffH2O = 0.01 * H2O_UD * por_a / tort_a
  DeffCO = 0.01 * CO_UD * por_a / tort_a
  DeffCO2 = 0.01 * CO2_UD * por_a / tort_a
  alim = 2 * F * pH2 / atm2Pa * DeffH2 / (831.45 * Tk * th_a)
  blim = 2 * F * pH2O / atm2Pa * DeffH2O / (831.45 * Tk * th_a)
  clim = 2 * F * pCOc / atm2Pa * DeffCO / (831.45 * Tk * th_a)
  dlim = 2 * F * pCO2c / atm2Pa * DeffCO2 / (831.45 * Tk * th_a)
  OPa_A = (Jcalc + blim + dlim) / blim / dlim
  OPa_B = (Jcalc * (alim * dlim + blim * clim) + blim * clim * dlim + alim * blim * clim + clim * dlim
    - alim * blim * clim) / alim / blim / clim / dlim
  OPa_C = (Jcalc - alim - clim) / alim / clim
  holdA2 = OPa_A
  holdB2 = OPa_B
  holdC2 = OPa_C
  Anod = (R * Tk / 2.0 / F) * math.log((-OPa_B + math.sqrt(OPa_B^2 - 4.0 * OPa_A * OPa_C)) / 2.0 / OPa_A)
end
end
-- Compute the final voltage result
------------------------------------------------------------------
V = (Voc - Ohmic - BV + Cath + Anod) + V_loss
Z = V
-- return the voltage value
return Z
end
```

Appendix D

EC_Dimension1_InputTable.dat for Example Case 4

Description: Tall stack co-flow example with CH₄ fuel

<table>
<thead>
<tr>
<th>#CELL PARAMETERS</th>
<th>#CELL PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFlowFlag = 1</td>
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<table>
<thead>
<tr>
<th>#FLOW GEOMETRY SWITCH</th>
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<tbody>
<tr>
<td>Ax = 0.25</td>
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</tr>
<tr>
<td>Ay = 0.25</td>
<td></td>
</tr>
<tr>
<td>nCells=96</td>
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</tr>
<tr>
<td>BottomPlateH = 0.005</td>
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</tr>
<tr>
<td>PEN_H = 0.0005</td>
<td></td>
</tr>
<tr>
<td>InterConnectPlateH = 0.0005</td>
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</tr>
<tr>
<td>TopPlateH = 0.005</td>
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</tr>
<tr>
<td>AirFlowH = 0.001</td>
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</tr>
<tr>
<td>FuelFlowH = 0.0005</td>
<td></td>
</tr>
<tr>
<td>InletArea = 0.0001</td>
<td></td>
</tr>
<tr>
<td>InletL = 0.003</td>
<td></td>
</tr>
<tr>
<td>OutletArea = 0.0001</td>
<td></td>
</tr>
<tr>
<td>OutletL = 0.003</td>
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</tr>
<tr>
<td>Cell_Variation = 0</td>
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</tbody>
</table>

<table>
<thead>
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<th>#STACK GEOMETRY PARAMETERS</th>
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</thead>
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<td>SystemPressure = 1.0</td>
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<tr>
<td>FuelTemperature = 973</td>
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</tr>
<tr>
<td>FuelTonTop = 1003</td>
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</tr>
<tr>
<td>FuelFlowRate = 0.0147</td>
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</tr>
<tr>
<td>FuelH2 = 0.485</td>
<td></td>
</tr>
<tr>
<td>FuelH2O = 0.03</td>
<td></td>
</tr>
<tr>
<td>FuelCO = 0.0</td>
<td></td>
</tr>
<tr>
<td>FuelCO2 = 0.0</td>
<td></td>
</tr>
<tr>
<td>FuelCH4 = 0.0</td>
<td></td>
</tr>
<tr>
<td>FuelN2 = 0.485</td>
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</tr>
<tr>
<td>FuelFlowRate = 0.294</td>
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</tr>
<tr>
<td>FuelH2 = 0.324</td>
<td></td>
</tr>
<tr>
<td>FuelH2O = 0.333</td>
<td></td>
</tr>
<tr>
<td>FuelCO = 0.049</td>
<td></td>
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</tbody>
</table>
FuelCO2 = 0.061
FuelCH4 = 0.110
FuelN2 = 0.124
#FuelFlowRate = 0.0147
#FuelH2 = 0.538
#FuelH2O = 0.181
#FuelCO = 0.127
#FuelCO2 = 0.052
#FuelCH4 = 0.101
#FuelN2 = 0.0

# oxidant inlet state

OxidantFlowRate = 2.47
OxidantTemperature = 973
OxidantTonTop = 1003
OxidantO2 = 0.21
OxidantN2 = 0.79

#---------------------------
# STACK SOLUTION MODE
# Comment out all modes except one!
#---------------------------

Average_CellVoltage=0.7841
#Mode 1: cell average voltage (V) #
#Mode 2: total stack voltage (V) #
#Mode 3: current density (A/m^2) #
#Mode 4: fixed fuel utilization #
#Mode 5: solve the stack V-I curve #

#---------------------------
# ELECTROCHEMISTRY OPTIONS
#---------------------------

EC_Model_Option = 4
# short current switch? #
ShortCurrent=0.0
# CH4 consumption option #
CH4_Option=3
# species equilibrium distance (m) #
EquilibriumPathCO = 0.001
EquilibriumPathCH4 = 0.01

#---------------------------
# SOLUTION CONTROL PARAMETERS
#---------------------------

Nn = 100
# timestep for counter-flow #
TimeStep=0.5
# temp iteration relaxation factor #
T_Relaxation = 1.0
# temperature iteration limits (C) #
T_TopLimit = 900.0
T_BottomLimit = 650.0
# multicell voltage increment #
VoltageIncrement = 0.001
# minimum threshold on H2 #
H2_Threshold=0.0001
# maximum voltage/temperature iterations
VoltageIterationLimit = 30
LimitTiterations = 10

# gas heat capacity
UserDefinedHeat = 1

# quasi-transient switch
QuasiTransient = 0

# manifold conduction?
HaveConductionOnInlet = 0

# Electrode diffusion calculations
NoDiffusion = 1

# print diffusion results (1 is yes)
PrintDiffusionDifference = 1

# max temp variation between iterations
T_precision = 0.05

# max cell current density variation
CurrentTolerance = 0.1

# OxidantSolidFilmCoefficient = 2700.0
FuelSolidFilmCoefficient = 2700.0

# emissivity
InterConnectEmittance = 0.5
PENEmittance = 0.5

# thermal conductivity (W/m-K)
BottomPlateHC = 25.0
InterConnectPlateHC = 25.0
TopPlateHC = 25.0
PEN_HC = 4.0
InletHC = 25.0
OutletHC = 25.0

# specific heat capacity (J/kg-K)
CP_pen = 400.0
CP_plate = 400.0

# top
BoundaryFlag = 2
TopEnvironmentT = 750
TopFilmCoefficient = 1.5
TopEmissivity = 0.7
TopSIFilmCoefficient = 1000.0
TopSIEmissivity = 0.9
TopIsolationH = 0.25
TopIsolationHC = 25.0
TopGeometryScale = 2.5

# bottom
BottomEnvironmentT = 750
BottomFilmCoefficient = 0.3
BottomEmissivity = 0.7
BottomSIFilmCoefficient = 1000.0
BottomSIEmissivity = 0.9
BottomIsolationH = 0.25
BottomIsolationHC = 25.0
BottomGeometryScale = 2.5

# front
FrontEnvironmentT = 750
FrontFilmCoefficient = 0.3
FrontEmissivity = 0.7
FrontSIFilmCoefficient = 1000.0
FrontSIEmissivity = 0.9
FrontIsolationH = 0.12
FrontIsolationHC = 25.0
FrontGeometryScale = 1.3

# back
BackEnvironmentT = 750
BackFilmCoefficient = 0.3
BackEmissivity = 0.7
BackSIFilmCoefficient = 1000.0
BackSIEmissivity = 0.9
BackIsolationH = 0.12
BackIsolationHC = 25.0
BackGeometryScale = 1.3

# sides
SideEnvironmentT = 750
SideFilmCoefficient = 0.3
SideEmissivity = 0.7
SideSIFilmCoefficient = 1000.0
SideSIEmissivity = 0.9
SideIsolationH = 0.03
SideIsolationHC = 25.0
SideGeometryScale = 2.0

#----------------------------------------#
#           ELECTRODE DIFFUSION          #
# thickness and radius in (micron)       #
# porosity in (%)                        #
#----------------------------------------#
nLayers = 3
nSpecies = 6
Thickness = 250.0
Tortuosity = 1.1
Porosity  = 55.0
PoreRadius  = 0.5
ElectrolyteThickness = 150.0
InterconnectThickness = 1500.0
CathodeThickness = 50.0
CathodePorosity = 55.0
CathodeTortuosity = 1.1
AnodeThickness = 50.0
AnodePorosity = 55.0

#----------------------------------------#
#     INTERNAL I-V CURVE PARAMETERS      #
#----------------------------------------#
ScaleThickness  = 30.0
PreExponent     = 10.0
ActivationEnergy = 0.20

CathodePreExponent = 575955.0
CathodeActivationEnergy = 0.117

BV_AlphaCoefficient = 0.55
BV_ActivationEnergy = 1.2
BV_PreExponent_a = -120
BV_PreExponent_b = 2.3e5
CathodeDepletionCoefficient_a = 3
CathodeDepletionCoefficient_b = -35

LOP_slope = 0.2027
LOP_is = -8.897e-4
LOP_ii = 0.5221
AOP_ns = 2.439e-3
AOP_ms = -2.358
AOP_qs = 1.747e-2
AOP_ps = 6.560e-4
VTC = -0.17

VoltageOnCurrent.dat for Example Case 4

B Koeppel
-- 4-1-11

VoltageValue()

Available Local Inputs From SOFC-MP
- oT Temperature oxidant (K)
- fT Temperature fuel (K)
- J Current density (A/cm2)
- pO2air Air side partial pressure O2 (atm)
- pN2air Air side partial pressure N2 (atm)
- pH2 Fuel side partial pressure H2 (atm)
- pH2O Fuel side partial pressure H2O (atm)
- pCO Fuel side partial pressure CO (atm)
- pCO2 Fuel side partial pressure CO2 (atm)
- pCH4 Fuel side partial pressure CH4 (atm)
- pN2 Fuel side partial pressure N2 (atm)
- nActiveCell Cell number
- DistanceFromTheEdge Distance along path (m)
- DistanceFromTheEdgeRatio Relative distance along the path

Required Subroutine Outputs
- Z Voltage (V)

User-Assigned Geometry/Material Inputs
- th_a Thickness anode (microns)
- th_e Thickness electrolyte (microns)
- th_c Thickness cathode (microns)
- th_ic Thickness interconnect (microns)
- por_a Porosity anode (%)
- por_c Porosity cathode (%)
- tort_a Tortuosity anode
- tort_c Tortuosity cathode
- BV_alpha Butler-Volmer 'alpha' constant
- BV_prexp Butler-Volmer pre-exponential constant
- BV_Eact Butler-Volmer activation energy
- R_cont Contact resistance
-- User-Assigned Constants/Conversions
-- R  Ideal gas constant
-- F  Faraday's constant
-- atm2Pa Conversion for pressure atm -> Pa
-- mic2m Conversion for length micron -> m

---

function VoltageValue()
---

--- Assign Constants/Conversions
R=8.3145
F=96485.0
atm2Pa=101325.0
mic2m=1.0e-6
---

--- Assign Flags
BVflag=1 -- 0=old method, 1=pressurized method
---

--- Assign Geometry/Material Data
th_a=  450.0
th_e=  10.0
th_c=  40.0
th_ic=  500.0
por_a=  40.0
por_c=  40.0
tort_a=  2.5
tort_c=  2.5
BV_alpha=  0.3
BV_prexp=  105000.0
BV_Eact=  107489.0
R_cont=  0.0
BV_alpha2a=  2.0
BV_prexp2a=  465000.0
BV_Eact2a=  125000.0
BV_gamma2a=  0.5
BV_alpha2f=  1.0
BV_prexp2f=  75000000.0
BV_Eact2f=  110000.0
BV_gamma2f=  0.133
V_loss=  0.0
---

--- Compute the local cell temperature
Tk=(oT+fT)/2.0
Tc=Tk-273.0
---

--- Compute the Nernst open circuit voltage
---

Keq_dHo=-56930.0
Keq_A=6.75
Keq_B=-0.64
Keq_C=-0.08
Keq_L=-8.74
Keq_dG=Keq_dHo+Keq_A*Tk*math.log10(Tk)+Keq_B*Tk*Tk/1000+Keq_C*100000/Tk+Keq_L*Tk
Kequib=math.exp(-Keq_dG*4.184/R/Tk)
pO2anode=(pH2O/Kequib/pH2)^2
Voc=(R*Tk/4.0/F)*math.log(pO2air/pO2anode)
---

--- Compute the ohmic polarization
---

--- Compute the electrolyte conductivity
s_eA=8.588e-10
s_eB=-1.301e-6
s_eC=4.679e-4
s_eD=-0.0654
s_e=s_eA*Tc^3+s_eB*Tc^2+s_eC*Tc+s_eD
---

--- Compute the interconnect conductivity
s_icA=0.069
s_icB=70.9
s_ic=1000000.0/(s_icA*Tc+s_icB)
---

--- Compute the cathode conductivity
---

---
s_cA=575955.0
s_c Ea=0.117
s_c=(s_cA/Tk)*math.exp(-s_cEa/0.00008617/Tk)*(1.0-(0.018*por_c))
    -- Compute the anode conductivity
s_aA=1000
s_a=s_aA*(1.0-(0.018*por_a))
    -- Compute the effective cell resistivity
Ri=R_cont+(th_e/s_e+th_a/s_a+th_ic/s_ic+th_c/s_c)*0.0001
    -- Compute the overall ohmic loss
Ohmic=Ri*J
    -- Compute the activation polarization (old method or new pressurized method)
------------------------------------------------------------------
if BVflag==0 then
    -- Old method
    i0=BV_prexp*math.exp(-BV_Eact/R/Tk)
    BV=(R*Tk/BV_alpha/F)*math.log((J/2.0/i0)+math.sqrt((J/2.0/i0)^2+1))
else
    -- New method
    ioff_f=BV_prexp2f*math.exp(-BV_Eact2f/R/Tk)*pO2anode^BV_gamma2f
    ioff_a=BV_prexp2a*math.exp(-BV_Eact2a/R/Tk)*pO2air^BV_gamma2a
    eta_f=R*Tk/BV_alpha2f/F*math.log((J/2.0/ioff_f)+math.sqrt((J/2.0/ioff_f)^2+1))
    eta_a=R*Tk/BV_alpha2a/F*math.log((J/2.0/ioff_a)+math.sqrt((J/2.0/ioff_a)^2+1))
    BV=eta_f+eta_a
end
------------------------------------------------------------------
-- Compute the diffusion coefficients
------------------------------------------------------------------
if pCO<=0 then
    pCOc=1e-16
else
    pCOc=pCO
end
if pCO2<=0 then
    pCO2c=1e-16
else
    pCO2c=pCO2
end
Ptotal=pH2+pH2O+pCOc+pCO2c+pN2+pCH4
H2_mf=pH2/Ptotal
H2O_mf=pH2O/Ptotal
CO_mf=pCOc/Ptotal
CO2_mf=pCO2c/Ptotal
N2_mf=pN2/Ptotal
CH4_mf=pCH4/Ptotal
    -- Diffusion constants (empirical radii and molecular weights)
H2i=1.92
H2oi=2.33
COi=2.66
CO2i=3.0
N2i=2.62
O2i=2.9
H2ii=2.0
H2Oi=18.0
COii=28.0
CO2ii=44.0
N2ii=28.0
O2ii=32.0
CH4ii=16.0
    -- Compute anode binary diffusion constants
H2H20=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/H2ii+1/H2Oi)/((H2i+H2Oi)^2)
H2CO=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/H2ii+1/COii)/((H2i+COii)^2)
H2CO2=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/H2ii+1/CO2ii)/((H2i+CO2ii)^2)
H2N2=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/H2ii+1/N2ii)/((H2i+N2ii)^2)
H2CH4=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/H2ii+1/CH4ii)/((H2i+CH4ii)^2)
O2N2=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/O2ii+1/N2ii)/((O2i+N2ii)^2)
H2OCCO=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/H2O1i+1/COii)/((H2O1i+COii)^2)
H2OCCO2=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/H2O1i+1/CO2ii)/((H2O1i+CO2ii)^2)
H2ON2=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/H2O1i+1/N2ii)/((H2O1i+N2ii)^2)
H2ON2=(1e-3/Ptotal)*(Tk^1.75)*math.sqrt(1/H2O1i+1/N2ii)/((H2O1i+N2ii)^2)
$$H_{2}OCH_{4}=(1e^{-3}/P_{total})*(T_{k}^{1.75})*\mathbf{sqrt}(1/H_{2}O_{ii}+1/CH_{4}ii)/((H_{2}Oi+CH_{4}i)^{2})$$
$$N_{2}CH_{4}=(1e^{-3}/P_{total})*(T_{k}^{1.75})*\mathbf{sqrt}(1/N_{2}ii+1/CH_{4}ii)/((N_{2}i+CH_{4}i)^{2})$$
$$CO_{2}CH_{4}=(1e^{-3}/P_{total})*(T_{k}^{1.75})*\mathbf{sqrt}(1/CO_{ii}+1/CH_{4}ii)/((CO_{i}+CH_{4}i)^{2})$$
$$CO_{2}N_{2}=(1e^{-3}/P_{total})*(T_{k}^{1.75})*\mathbf{sqrt}(1/CO_{2}ii+1/N_{2}ii)/((CO_{2}i+N_{2}i)^{2})$$

-- Compute anode unitary diffusion constants
$$H_{2}UD=(1-H_{2}_{mf})/(H_{2}O_{mf}/H_{2}H_{2}O+CO_{mf}/H_{2}CO+CO_{2}_{mf}/H_{2}CO_{2}+N_{2}_{mf}/H_{2}N_{2}+CH_{4}_{mf}/H_{2}CH_{4})$$
$$H_{2}OUD=(1-H_{2}O_{mf})/(H_{2}_{mf}/H_{2}H_{2}O+CO_{mf}/H_{2}CO+CO_{2}_{mf}/H_{2}CO_{2}+N_{2}_{mf}/H_{2}N_{2}+CH_{4}_{mf}/H_{2}CH_{4})$$
$$COUD=(1-CO_{mf})/(H_{2}_{mf}/H_{2}CO+N_{2}_{mf}/N_{2}H_{2}O+CO_{2}_{mf}/CO_{2}H_{2}+N_{2}_{mf}/N_{2}CH_{4}+CH_{4}_{mf}/CH_{4}N_{2})$$
$$CO_{2}UD=(1-CO_{2}_{mf})/(H_{2}_{mf}/H_{2}CO_{2}+N_{2}_{mf}/N_{2}CH_{4}+CO_{mf}/CO_{2}H_{2}+CO_{2}_{mf}/CO_{2}H_{4}+N_{2}_{mf}/N_{2}CO_{2})$$

-- Compute anode adsorption and surface diffusion modifications
$$area_{H_{2}}=\pi*(H_{2}i*10^{-10})^{2}$$
$$area_{H_{2}O}=\pi*(H_{2}Oi*10^{-10})^{2}$$
$$area_{CO}=\pi*(COi*10^{-10})^{2}$$
$$area_{CO_{2}}=\pi*(CO2i*10^{-10})^{2}$$
$$area_{N_{2}}=\pi*(N_{2}i*10^{-10})^{2}$$
$$area_{O_{2}}=\pi*(O_{2}i*10^{-10})^{2}$$
$$area_{CH_{4}}=\pi*(CH_{4}i*10^{-10})^{2}$$

$$pres_{H_{2}}=\max(0,p_{H_{2}}-J*82.058*T_{k}*(th_a/10000)/(2*F)*(tort_a/(H_{2}UD*por_a/100)))$$
$$pres_{H_{2}O}=\max(0,p_{H_{2}O}+J*82.058*T_{k}*(th_a/10000)/(2*F)*(tort_a/(H_{2}OUD*por_a/100)))$$
$$pres_{CO}=\max(0,p_{CO}c-J*82.058*T_{k}*(th_a/10000)/(2*F)*(tort_a/(COUD*por_a/100)))$$
$$pres_{CO_{2}}=\max(0,p_{CO_{2}}c+J*82.058*T_{k}*(th_a/10000)/(2*F)*(tort_a/(CO_{2}UD*por_a/100)))$$
$$pres_{N_{2}}=\max(0,p_{N_{2}})$$
$$pres_{O_{2}}=\max(0,p_{O_{2}anode})$$
$$pres_{CH_{4}}=\max(0,p_{CH_{4}})$$

$$Q_{ev_{H_{2}}}=0.425$$
$$Q_{ev_{H_{2}O}}=0.549$$
$$Q_{ev_{CO}}=0.5$$
$$Q_{ev_{CO_{2}}}=0.5$$
$$Q_{ev_{N_{2}}}=0.5$$
$$Q_{ev_{O_{2}}}=0.5$$
$$Q_{ev_{CH_{4}}}=0.5$$

$$bP_{H_{2}}=6.023*10^{23}*area_{H_{2}}*10^{-13}/\mathbf{sqrt}(2*\pi*R*T_{k}*H_{2}{ii})*\exp(Q_{ev_{H_{2}}}/(0.026*T_{k}/298))\times\text{pres}_{H_{2}}$$
$$bP_{H_{2}O}=6.023*10^{23}*area_{H_{2}O}*10^{-13}/\mathbf{sqrt}(2*\pi*R*T_{k}*H_{2}O_{ii})*\exp(Q_{ev_{H_{2}O}}/(0.026*T_{k}/298))\times\text{pres}_{H_{2}O}$$
$$bP_{CO}=6.023*10^{23}*area_{CO}*10^{-13}/\mathbf{sqrt}(2*\pi*R*T_{k}*CO_{ii})*\exp(Q_{ev_{CO}}/(0.026*T_{k}/298))\times\text{pres}_{CO}$$
$$bP_{CO_{2}}=6.023*10^{23}*area_{CO_{2}}*10^{-13}/\mathbf{sqrt}(2*\pi*R*T_{k}*CO_{2}{ii})*\exp(Q_{ev_{CO_{2}}}/(0.026*T_{k}/298))\times\text{pres}_{CO_{2}}$$

$$cov_{H_{2}}=bP_{H_{2}}/(1+bP_{sum})$$
$$cov_{H_{2}O}=bP_{H_{2}O}/(1+bP_{sum})$$
$$cov_{CO}=bP_{CO}/(1+bP_{sum})$$
$$cov_{CO_{2}}=bP_{CO_{2}}/(1+bP_{sum})$$
$$cov_{N_{2}}=bP_{N_{2}}/(1+bP_{sum})$$
$$cov_{O_{2}}=bP_{O_{2}}/(1+bP_{sum})$$
$$cov_{CH_{4}}=bP_{CH_{4}}/(1+bP_{sum})$$

$$cov_{sum}=cov_{H_{2}}+cov_{H_{2}O}+cov_{CO}+cov_{CO_{2}}+cov_{N_{2}}+cov_{O_{2}}+cov_{CH_{4}}$$

D$_{H_{2}}$=H$_{2}$UD*(1-fij$_{H_{2}}$)*(Dsurf$_{H_{2}th_{1}}$*(1-fij$_{H_{2}}$)*Dsurf$_{H_{2}th_{2}}$*fij$_{H_{2}}$)/(1-fij$_{H_{2}}$)
```
D_CO2=CO2_UD^{(1-fij_CO2)}(1-fij.CO2)
D_N2=N2_UD^{(1-fij.N2)}(1-fij.N2)
D_O2=O2(*(1-fij.O2)
D_CH4=CH4_UD^{(1-fij.CH4)}(1-fij.CH4)

-- Compute the cathode concentration polarization
-----------------------------------------------

Deffic=0.01*por_c*O2/(tort_c
ics=1.0e-8*(4.0*F*Ptotal*atm2Pa*Deffic)/(R*Tk*th_c*mic2m)*math.log(1.0/(1.0-pO2air))
Cath=(R*Tk/4.0/F)*math.log(1.0-(J/ics)}

-- Compute the anode concentration polarization
-----------------------------------------------

DeffH2=D_N2
DeffH2O=D_O2
DeffCO=0.01*CO2_UD*por_a/tort_a
DeffCO2=0.01*CO2_UD*por_a/tort_a
alim=2*F*pH2*atm2Pa*DeffH2/
blim=2*F*pH2O*atm2Pa*DeffH2O/
clim=2*F*pCO*atm2Pa*DeffCO/
lim=2*F*pCO2*atm2Pa*DeffCO2/

-- Adjust calculation for iteration case of too high current requested
if J>(alim+clim) then
    Jcalc=(alim+clim)*0.99
else
    Jcalc=J
end

OPa_A=(Jcalc+blim+clim)/blim/clim
OPa_B=(Jcalc+alim+clim)/alim/clim
OPa_C=(Jcalc-alim-clim)/alim/clim

holdA1=OPa_A
holdB1=OPa_B
holdC1=OPa_C

if stabcheck>0 then
    if stabcheck2>0 then
        Anod=(R*Tk/2.0/F)*math.log((-OPa_B+math.sqrt(OPa_B^2-4.0*OPa_A*OPa_C))/2.0/OPa_A)
        holdA2=0
        holdB2=0
        holdC2=0
    else
        DeffH2=0.01*H2O_UD*por_a/tort_a
        DeffH2O=0.01*H2O_UD*por_a/tort_a
        DeffCO=0.01*CO_UD*por_a/tort_a
        DeffCO2=0.01*CO2_UD*por_a/tort_a
        alim=2*F*pH2*atm2Pa*DeffH2/
        blim=2*F*pH2O*atm2Pa*DeffH2O/
        clim=2*F*pCO*atm2Pa*DeffCO/
        lim=2*F*pCO2*atm2Pa*DeffCO2/
        OPa_A=(Jcalc+blim+clim)/blim/clim
        OPa_B=(Jcalc+alim+clim)/alim/clim
        OPa_C=(Jcalc-alim-clim)/alim/clim
        Anod=(R*Tk/2.0/F)*math.log((-OPa_B+math.sqrt(OPa_B^2-4.0*OPa_A*OPa_C))/2.0/OPa_A)
        holdA2=0
        holdB2=0
        holdC2=0
    end
else
    DeffH2=0.01*H2O_UD*por_a/tort_a
    DeffH2O=0.01*H2O_UD*por_a/tort_a
    DeffCO=0.01*CO_UD*por_a/tort_a
    DeffCO2=0.01*CO2_UD*por_a/tort_a
    alim=2*F*pH2*atm2Pa*DeffH2/
    blim=2*F*pH2O*atm2Pa*DeffH2O/
    clim=2*F*pCO*atm2Pa*DeffCO/
    lim=2*F*pCO2*atm2Pa*DeffCO2/
    OPa_A=(Jcalc+blim+clim)/blim/clim
    OPa_B=(Jcalc+alim+clim)/alim/clim
    OPa_C=(Jcalc-alim-clim)/alim/clim
    Anod=(R*Tk/2.0/F)*math.log((-OPa_B+math.sqrt(OPa_B^2-4.0*OPa_A*OPa_C))/2.0/OPa_A)
end

-- Compute the final voltage result
-----------------------------------------------

V=(Voc+Ohmic-BV+Cath+Anod)+V_loss
Z=V

-- return the voltage value
return Z
```
function CH4ReformingRate()
GasConstant=8.3144
Ch4_Usage=4274.0*pCH4*math.exp(-82000.0/fuelT/GasConstant)
return Ch4_Usage
end
### Distribution

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Refractory Glass Seals for SOFC

Y.S. “Matt” Chou and J.W. Stevenson
Pacific Northwest National Laboratory, Richland, WA

February 2009 (Released July 2011)
Introduction
One of the critical challenges facing planar solid oxide fuel cell (SOFC) technology is the need for reliable sealing technology. Seals must exhibit long-term stability and mechanical integrity in the high temperature SOFC environment during normal and transient operation. Several different approaches for sealing SOFC stacks are under development, including glass or glass-ceramic seals, metallic brazes, and compressive seals. Among glass seals, rigid glass-ceramics, self-healing glass, and composite glass approaches have been investigated under the SECA Core Technology Program. The U.S. Department of Energy’s Pacific Northwest National Laboratory (PNNL) has developed the “refractory” glass approach in light of the fact that higher sealing temperatures (e.g., 930-1000ºC) may enhance the ultimate in-service bulk strength and electrical conductivity of contact materials, as well as the bonding strength between contact materials and adjacent SOFC components, such as interconnect coatings and electrodes. This report summarizes the thermal, chemical, mechanical, and electrical properties of the refractory sealing glass.

Materials and fabrication
The PNNL refractory glasses are alkaline-earth based silicate glasses fabricated by conventional glass melting processes using commercially available raw materials such as oxide and carbonate powders. The glasses contain alkaline earths (Ba, Sr, Ca, and/or Mg), Y or Al modifiers, and Si and B glass formers. After evaluating a number of formulations which exhibited a wide range of thermal properties, several preferred compositions have been selected which offer sealing temperatures in the range of 930-1000ºC, and CTE in the 11.5 – 12.5 ppm/ºC range.

Crystal structure and thermal stability
As noted above, the refractory sealing glasses are designed to seal at higher temperatures than conventional SOFC sealing glasses (e.g., PNNL’s G18, sealing T ~830ºC). Table I shows the thermal expansion of a refractory sealing glass (YSO1, sealing T ~1000ºC) before and after an accelerated isothermal aging test at 900ºC in air or a wet reducing environment. For comparison, the CTE behavior of G18 in air is also listed. It is apparent that the refractory sealing glass exhibited improved CTE stability compared to G18. The aged refractory glass was also characterized with x-ray diffraction. Figure 1 shows the diffraction patterns for refractory glass after 4, 1000, and 2000 hrs of aging (green, blue, and red plots, respectively). It is apparent that the refractory sealing glass was very stable in terms of crystalline phase formation, as no new phases or significant changes in relative amounts of phases were observed after the initial 4 hr heat treatment. The major phase was SrSiO3 with lesser amounts of Ca3SiO5, Ca2SiO4, and Y2SiO5 also present. The observed stability in the XRD patterns is consistent with the stability observed in the CTE measurements.

Electrical stability
Results of an electrical stability test on a representative refractory glass (YSO75, sealing T ~975ºC) are shown in Figure 2. The test was performed under 0.7V DC loading in dual environments at 850ºC; 850ºC was chosen to accelerate any potential reactions. The test was run with dilute fuel (2.7 H2/Ar + 30% H2O) for the first 432 hrs and then with pure H2 + 30% H2O for the rest of the test. The glass exhibited an electrical resistivity greater than 10⁶ ohm-m, about 5 orders of magnitude higher than YSZ (~2.5x10⁻¹ ohm-m @ 800ºC) and 9 orders higher than...
cathode (LSM $\sim 6 \times 10^{-5}$ ohm-m @ 800°C) or anode materials (Ni/YSZ $\sim 1 \times 10^{-5}$ ohm-m @ 800°C). The high electrical resistivity clearly indicates that no significant electrical loss through the sealing glass would be expected.

**Volatility**

Since most of the refractory glasses contain $\sim 7-10$ mol% of B$_2$O$_3$ and an appreciable amount of SiO$_2$ as the glass former, the potential weight loss, especially in reducing environments, needs to be addressed. The volatility of glass may have two impacts. First, electrochemical performance may be degraded if the volatile species deposit onto active electrochemical sites. In addition, excessive evaporation of sealing material could weaken the seal and cause leakage. Volatility of two refractory sealing glasses was evaluated in a wet reducing environment at 800°C for $\sim$1600 hrs; weight loss results are shown in Figure 3. Following an initial period ($\sim$600 hrs) of rapid weight loss, the volatility decreased significantly. The second stage volatility rates ($3.2-3.6 \times 10^{-8}$ g/cm$^2$-hr) were similar to estimated values for SiO$_2$ ($4.3-14 \times 10^{-8}$ g/cm$^2$-hr) based on published activation energies. Using the measured volatility and assuming a typical seal geometry, it is estimated that the total material loss for 40,000 hr operation at 800°C would be less than 0.1 wt%.

**Mechanical integrity**

Butt joint testing was performed to study the mechanical integrity of the refractory sealing glass. Stainless steel squares (1/2”x1/2”) were joined with the sealing glass at elevated temperatures (e.g., 950°C) in air. After joining, the couples were tested in uni-axial tension at room temperature. Some samples were aged in air or a wet reducing environment to study environmental effects. In addition to the as-received steel, aluminized steel coupons were also tested. The strengths are shown in Figure 4. It is evident that the seal strength degraded greatly when aged in air, while no degradation resulted from aging in a reducing environment. The loss of strength resulted from tensile residual stresses due to CTE mismatch between an interfacial reaction product (SrCrO$_4$, CTE $\sim$22 ppm/°C) and the other materials (CTE $\sim$11.5-12.5 ppm/°C). Aluminization was effective in preventing this loss of strength during air aging.

**Glass validation in a single-cell stack assembly**

To further evaluate the performance of the refractory sealing glass in a realistic manner, the glass (YSO77 sealing, T $\sim$950°C) was tested in a single-cell stack assembly. A commercial 50mm x 50mm anode-supported cell with LSM/YSZ cathode was tested for thermal cycle stability and baseline performance stability using 97% H$_2$ + 3%H$_2$O vs. air at 800°C. The cell was first sealed onto an aluminized SS441 cell frame at 950°C 2h in air. The sealed couple was then assembled with SS441 anode and cathode plates, contact pastes, perimeter seals, and fuel and air heat-exchangers. Figure 5 shows the open circuit voltage (OCV) versus thermal cycles. For each cycle the sample was heated from room temperature to 750°C in 3 hrs, held for 3 hrs, then cooled to near room temperature. The total time for each cycle was 24 hr. Throughout the thermal cycle testing, the measured OCV was very close to the theoretical Nerst potential, suggesting no fracture of the refractory sealing glass. The structural integrity of the seal was further verified during post-test analysis. Results from an electrochemical performance stack fixture test are shown in Fig. 6. This test again used refractory sealing glass for the cell-to-frame frame. Overall, the $\sim$1400 hr test showed very good stability in electrochemical performance, with degradation (calculated from observed power density after 300 hr) about 1.3%/1000 hr. The final
OCV before terminating the test was 1.089V (@800°C), suggesting that good sealing was achieved for the entire test.

**Post-test interfacial analysis**
Figure 7 shows the sealing glass/YSZ interfacial region of a cell tested in the stack test fixture. Clearly there are reactions between the sealing glass and YSZ electrolyte as demonstrated by “needle” formation along the interface. Thermodynamic calculations indicated the formation of BaZrO₃ or SrZrO₃, which was consistent with EDS chemical analysis. The presence of the needles is not expected to be an issue, since the CTEs of the zirconates are very close to YSZ. At the interface between the glass and the aluminized AIS 441 (Fig. 8), no chromate phase was identified. An aluminum-rich band was observed at the glass/metal interface due to substantial dissolution of the alumina surface layer, but no distinct evidence of crystalline phase formation was observed.

**Acknowledgements**
The work described in this report was funded through the Solid-State Energy Conversion Alliance (SECA) Core Technology Program by the US Department of Energy’s National Energy Technology Laboratory (NETL). Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RL01830.

**Contacts**
PNNL currently has several candidate refractory sealing glasses with sealing temperature ranging from ~930-1000°C. For more information, please contact:

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509-375-2527

**Dr. Jeff Stevenson**
jeff.stevenson@pnnl.gov
509-372-4697
Table I. CTE of sealing glass before and after aging.

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<th>2000hr</th>
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<td>11.62</td>
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<td>air</td>
<td>12.50</td>
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Figure 1. XRD patterns of refractory glass (YSO1) before and after accelerated aging at 900°C.

Figure 2. Electrical stability of refractory glass (YSO75) during isothermal aging under a 0.7 V DC loading and dual environments (pure H₂+30%H₂O vs. air) at 850°C. Resistivity data were not recorded during the first ~400 hrs of the test.
Figure 3. Weight loss versus aging time at 800°C in flowing wet and reducing gas (30% H₂O+70%(2.7%H₂/Ar)) for 2 refractory sealing glasses.

Figure 4. Effect of environmental aging on the tensile strength of joined steel/glass/steel coupons. The glass used for this test was YSO75 with sealing T ~975°C.
Figure 5. Thermal cycle stability test of refractory sealing glass (YSO77).

Figure 6. Electrochemical performance of anode-supported cell tested at 800°C and 0.7 V using 97% H₂+3%H₂O vs. air.
Figure 7. Interfacial microstructure along the glass/YSZ interface after 2325 hr test at 800°C and 0.7V; YSZ is on the right.

Figure 8. Interfacial microstructure along the glass/aluminized AISI 441 interface after 2325 hr test at 800°C and 0.7V; the aluminized AISI 441 is on the left.
Reactive Air Aluminization

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Y.S. Chou
J.W. Stevenson

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October 2011
Introduction
Ferritic stainless steels and other alloys are of great interest to SOFC developers for applications such as interconnects, cell frames, and balance of plant components. While these alloys offer significant advantages (e.g., low material and manufacturing cost, high thermal conductivity, and high temperature oxidation resistance), there are challenges which can hinder their utilization in SOFC systems; these challenges include Cr volatility and reactivity with glass seals. To overcome these challenges, protective coatings and surface treatments for the alloys are under development. In particular, aluminization of alloy surfaces offers the potential for mitigating both evaporation of Cr from the alloy surface and reaction of alloy constituents with glass seals. Commercial aluminization processes are available to SOFC developers, but they tend to be costly due to their use of exotic raw materials and/or processing conditions. As an alternative, PNNL has developed Reactive Air Aluminization (RAA), which offers a low-cost, simpler alternative to conventional aluminization methods.1,2

RAA Fabrication Process
The Reactive Air Aluminization (RAA) process consists of four primary steps: 1) preparation of aluminum (Al) powder slurry, 2) application onto the alloy surface, 3) heat treatment in air, and 4) cleaning of the aluminized surface. These steps are illustrated schematically in Figure 1. The slurry is prepared using a mixture of Al powder and a commercial organic binder system. Application to the alloy surface can be performed via screen-printing, brush painting, dip coating, or spray coating. A typical heating schedule consists of heating in air (3°C/min) to 1000°C, a one hour hold at 1000°C, and then cooling at 3°C/min. During the heat treatment, the surfaces of the Al particles oxidize, creating an aluminum oxide (alumina) shell around a metallic Al core. As the temperature exceeds the melting point of Al (660°C), the cores of the particles become molten. As a result of the volumetric expansion associated with that phase change, the liquid Al fractures the oxide shells, and flows to the alloy surface. As the heat treatment proceeds, some of the Al diffuses into the alloy while the Al at the surface is oxidized. After the heat treatment is completed, the surface region of the alloy consists of an Al diffusion layer in the alloy substrate, a thin alumina layer at the surface, and residual alumina shells above the surface. During post-heat treatment cleaning, the residual shells are removed, typically through a brushing process.

Properties of RAA
Surface composition
Figure 2 shows an aluminized ferritic stainless steel (Crofer22APU) surface. Results of EDS analysis are summarized on the ternary alloy diagram in Figure 3. While oxidized, non-aluminized Crofer22APU develops a Cr-rich oxide scale, the aluminized alloy exhibits a surface composition highly enriched in Al (the detected Fe content is likely a result of electron beam penetration through the surface layer into the bulk alloy).

Effect of Al particle size
Variations in the initial Al particle size can lead to significantly different surface composition and morphology of the aluminized alloy. Morphology differences resulting from different aluminum particle sizes are shown in Figure 4. Surface layer characteristics are summarized in Table I. In general, for large particle sizes, the oxidized volume fraction is less than that the amount of molten aluminum, resulting in more extensive diffusion into the alloy substrate, and
increased surface roughness. On the other hand, if the Al particle size is too small, the oxidized volume ratio is much larger than the amount of molten aluminum, resulting in minimal diffusion into the alloy substrate. Also, due to the thermal expansion difference at the faying interface, the thick alumina layer may de-adhere.

**Effect of initial coating thickness**
Differences in the thickness of the applied slurry layer can result in differences in the final surface composition and morphology. For example, Table II shows results for two different coating thicknesses (10 and 160 microns); both were prepared using the same Al powder (3 microns). While both coatings had similar surface roughness and alumina layer thickness, the thicker coating resulted in a much deeper Al diffusion zone inside the alloy substrate. At present, aluminization is frequently performed using ultrasonically sprayed precursor coatings of ~3-5 microns thickness. After heat treatment, an Al diffusion depth of 10-15 microns, and a surface roughness of 2-3 microns, is typically observed (see SEM image in Figure 5).

**Effect on thermal expansion**
Due to the high coefficient of thermal expansion (CTE) of Al, the diffusion of Al into the alloy substrate tends to increase its thermal expansion. For example, Figure 6 shows dilatometric results for Crofer22APU (0.5 mm thick) with aluminization treatments based on -325 mesh (44 microns), 3 microns, and 0.1 micron Al powder. Results for non-aluminized Crofer22APU are also shown. The use of -325 mesh Al powder resulted in a relatively thick coating of variable thickness, resulting in a highly variable CTE, as shown for two nominally identical samples in Figure 6. As expected, decreasing thickness of the Al diffusion layer reduced the difference in CTE compared with the original bare stainless steel (see plots for 3 and 0.1 micron Al particle size in Figure 6).

**Oxidation behavior**
Results of oxidation testing of bare and aluminized Crofer22APU at 800ºC in air are shown in Figure 7. While the bare Crofer22APU showed the expected parabolic mass gain due to Cr-based oxide scale growth, the aluminized steel exhibited no measurable mass gain due to the increased oxidation resistance provided by the alumina surface layer. Representative SEM surface images and cross-section images are shown in Figures 8 and 9 for bare and aluminized Crofer22APU, respectively.

**Self-healing behavior**
The presence of a “reservoir” of diffused Al in the alloy substrate allows for self-healing of surface damage due to scratching, abrasion, etc. Results of a scratch-healing test are shown in Figure 10. For this test, scratches were introduced into the surface of an aluminized Crofer22APU coupon. As shown in the figure, healing of the scratch occurred during a subsequent heat treatment at 800ºC for 4 hours, although the aluminum content in the healed region was not quite as high as that in the undamaged surface.
Long-Term Performance of RAA

To evaluate the long-term performance of the RAA process, AISI441 ferritic stainless steel cell frames and interconnects were aluminized and tested in the SECA CTP stack test fixture for 6,000 hours at 800ºC. After the test, the stack was disassembled, sectioned, and polished for microstructure and interfacial characterization. Four areas of the aluminized AISI 441 were selected for analysis: the fuel side sealing glass/aluminized AISI441 interface, the air side sealing glass/aluminized AISI441 interface, aluminized AISI441 exposed to fuel, and aluminized AISI441 exposed to air. Results of microstructural and chemical analyses are discussed below.

Sealing glass/aluminized AISI441 interface at the fuel side
Figure 11A shows a typical microstructure of a sealing glass/aluminized AISI441 interface near the seal edge exposed to fuel. The sealing glass was an alkaline earth silicate glass developed at PNNL. A high magnification view of the interface with elemental analysis is shown in Figure 11B. The alumina coating was dense and continuous with relatively uniform thickness of ~1-2 microns. EDS spot analysis of the dark gray layer (arrow in Figure 11A) confirmed that the major components were Al and O, with minor amounts of Fe, Cr, Ti, Nb, and Sr. No debonding of the thin coating was observed. The dense and continuous nature of the alumina appeared to effectively block the diffusion of Cr and Fe into the glass matrix. However, there was some interaction between the alumina protective coating and the glass, as evidenced by the substantial amount of Al in the glass adjacent to the alumina layer (see line scan in Figure 11B). Five spots of Figure 11B were selected for EDS analysis in order to better understand the local chemistry. The results are listed in Table III.

Sealing glass/aluminized AISI441 interface at the air side
The microstructure of the alumina coating at the air side was different from that on the fuel side, as shown in Figure 12A. Instead of a continuous, dense Al2O3 layer, there were dark gray precipitates along the glass/metal interface, tentatively identified as SiO2 (spots #1 and #5 Table IV). An elemental line scan across the interface (shown in Figure 12B) indicated that Cr (green line), Fe (dark blue line), and Mn (light blue line) diffused from the alloy into the glass. Overall, it appeared that the sealing glass had corroded the alumina protection layer severely, as evidenced by the presence of Al throughout the 10-15 micron region next to the interface. EDS confirmed the presence of Ba, Sr, Cr, Ti, and Al in the white precipitates in the sealing glass. Although the glass/metal interface appeared to have remained intact for the duration of the test, it should be noted that BaCrO4 and SrCrO4 can potentially form at the air side due to chemical reaction between oxygen, Cr in the steel, and the alkaline earth silicate sealing glass. The formation of these chromate phases is undesirable due to their very high CTE, which can degrade the mechanical integrity of the glass/steel interface during thermal cycling, especially if a continuous interfacial layer of chromite is formed.

Aluminized AISI441 exposed to fuel
In addition to the aluminized region sealed with refractory sealing glass, the fuel side area not covered by sealing glass was also subjected for analysis. A typical alumina coating microstructure at the fuel side is shown in low magnification and high magnification in Figure 13A and Figure 13B, respectively. The alumina coating appeared to be composed of discrete particles of varying color contrast (Figure 13B), as compared to the dense and homogeneous
color/contrast alumina layer found in regions covered with sealing glass (Figure 11B). Chemical analysis by EDS of selected spots showed that Al and O were the major constituents, with minor amounts of Fe, Cr, Ti, and Ba (Table V). The presence of Ba is likely due to vapor phase transport or surface diffusion from the nearby sealing glass. The alumina layer appeared to be well-bonded to the metal substrate, with no de-bonding or spallation observed.

**Aluminized AISI441 exposed to air**

For comparison, the aluminized area at the air side without sealing glass was also characterized. The coating and metal interface is shown in low and high magnification in Figure 14A and Figure 14B, respectively. The alumina layer appeared to be continuous, and more homogeneous than the fuel side layer with its discrete particle-like microstructure. The alumina thickness ranged from ~5 to ~10 microns, which was similar to the fuel side. Ti and Al oxide particles were also evident (dark grey precipitates; see arrows in Figure 14B). Spot EDS analysis near the metal substrate showed primarily Al and O with a minor amount of Cr (0.1 at%; see Table VI). At the outer surface, small amounts (< 1 at %) of K, Mn, Sr, Ba, Ca, and Fe were detected. The Sr, Ba, and Ca were likely from the nearby sealing glass, while K may have come from the phlogopite mica spacer. The relatively thick alumina layer appeared to be well-bonded after the metallurgical preparation, indicating good adhesion strength.

**Summary**

Reactive air aluminization (RAA), developed at PNNL, provides a simple, inexpensive method for creating a protective surface layer of aluminum oxide on alloys such as ferritic stainless steel. The process improves long-term surface stability at elevated temperatures (e.g., 800ºC) by reducing the oxidation rate, chemical reactivity, and volatilization of chromium. For more information, please contact Jeff Stevenson (509-372-4697; jeff.stevenson@pnnl.gov).

**Acknowledgement**

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**References**

1. U.S. Published Pending Application #2010/029734.
Table I. Effect of Al particle size on surface properties; unit: micron.

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<th>-325 mesh</th>
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Table II. Effect of coating thickness on surface properties; unit: micron.

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Table III. EDS spot analysis of selected spots in Figure 11B (atomic %).

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**A New Concept: Reactive Air Aluminizing**

1. Application & Drying
2. Heat treatment in Air
3. Removal of loose material (leaving behind an adherent, protective coating)

Figure 1. Schematic illustration of the Reactive Air Aluminizing process.

Figure 2. Surface SEM micrograph of aluminized Crofer22APU.
Figure 3. Results of EDS analysis on aluminized and non-aluminized Crofer22APU.
Figure 4. Cross section SEM images of aluminized Crofer22APU. Three different Al particle sizes were used in the aluminization process: (a) -325 mesh, (b) 3µm, (c) 0.1µm
Figure 5. Cross-sectional SEM image of aluminized surface fabricated from ultrasonically sprayed Al coating.

Figure 6. Thermal expansion measurements with various coating starting material sizes.
Figure 7. Oxidation kinetics test results for bare and aluminized Crofer22APU.
Figure 8. Bare Crofer22APU oxidized at 800°C for the indicated times: a) SEM surface images and b) SEM cross-section images.
Figure 9. Aluminized Crofer22APU oxidized at 800ºC for the indicated times: a) SEM surface images and b) SEM cross-section images.
Figure 10. Results of self healing test (800°C, 4 hours).
Figure 11. (A) Typical microstructure at the sealing glass/aluminized AISI441 interface at fuel side; (B) a high magnification of the circled area with elemental line scans. Chemical analyses of five selected spots (1-5) are listed in Table III.
Figure 12. (A) Typical microstructure at the sealing glass/aluminized AISI441 interface at air side; (B) a high magnification of the circled area with elemental line scans. Chemical analyses of four selected spots (1-4) are listed in Table IV.
Figure 13. (A) Typical microstructure of the fuel side aluminized AISI441; (B) a high magnification of the outer surface. Chemical analyses of three selected spots (1, 2, and 3) are listed in Table V.
Figure 14. (A) Typical microstructure of the air side aluminized AISI441; (B) a high magnification of the circled area with elemental line scans. Chemical analyses of two selected spots (1 and 2) are listed in Table VI. Arrows in 14A shows the typical Al or Ti containing precipitates from internal oxidation.
Enhanced Densification of SDC Barrier Layers

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September 2011
Introduction
A samaria-doped ceria (SDC) barrier layer separates the lanthanum strontium cobalt ferrite (LSCF) cathode from the yttria-stabilized zirconia (YSZ) electrolyte in a solid oxide fuel cell (SOFC) to prevent the formation of electrically resistive interfacial SrZrO$_3$ layers that arise from the reaction of Sr from the LSCF with Zr from the YSZ. However, the sintering temperature of this SDC layer must be limited to ~1200°C to avoid extensive interdiffusion between SDC and YSZ to form a resistive CeO$_2$-ZrO$_2$ solid solution. Therefore, the conventional SDC layer is often porous and therefore not as impervious to Sr-diffusion as would be desired. In the pursuit of improved SOFC performance, efforts have been directed toward increasing the density of the SDC barrier layer without increasing the sintering temperature.

Dense SDC Barrier Layer Prototype
Figure 1 compares SEM micrographs of a conventional screen printed SDC barrier layer to a pulsed laser deposited (PLD) SDC barrier layer. The PLD SDC barrier layers used in this study were prepared by Alex Ignatiev and Naijuan Wu at the University of Houston. Figure 1a, it can be seen that the screen printed layer is porous. The PLD SDC layer in Figure 1b, on the other hand, is a prototype of the ideally dense SDC barrier layer pursued in this study. Figure 2 compares the electrochemical performance of a cell with the dense PLD SDC to a cell that was similar in all aspects except that it had a conventional screen printed SDC barrier layer. At 0.8V, the cell with the dense SDC layer generated over 1.1 W/cm$^2$ while the cell with the screen printed layer generated less than 0.7 W/cm$^2$. The ohmic and polarization resistances extracted from the impedance spectroscopy data through fitting to an equivalent circuit model are presented in Table 1. While the polarization resistances of the two cells were quite similar at each temperature, the ohmic resistances were significantly lower in the cell with the PLD SDC. Figure 3a plots the total ohmic resistances of the cells as a function of temperature together with the ohmic contribution of the YSZ electrolyte. In Figure 3b, it can be seen that after the ohmic contribution of the YSZ has been subtracted, there is still a significant ohmic resistance of the other components in the cells. However, the improved density of the PLD SDC has greatly reduced this additional ohmic resistance. This is largely due to the increased effectiveness of the dense PLD SDC as a barrier to Sr-diffusion. In Figure 4, it can be seen that SrZrO$_3$ formation at the SDC/YSZ interface in cells with conventional SDC layers increased with the temperature at which the LSCF cathode was sintered, until a thick layer was present after 1200°C cathode sintering. However, in Figure 5, after sintering the LSCF cathode on a dense PLD SDC layer at 1200°C, no SrZrO$_3$ layer was visible. Unfortunately, PLD is an expensive and time consuming process that is not fit for large-scale, high-volume SOFC production, thus other, more cost effective means of enhancing the density of the SDC layer were investigated.

Enhancing SDC Barrier Layer Density

Decreasing the average particle size. Various approaches to improving densification of the SDC layer were explored. Dilatometry results of powder compacts containing mixtures of various ratios of nano- to submicron-sized powders are shown in Figure 6. It can be seen that by increasing the ratio of nano-sized powders, the sinterability improved. However, in practice, when the powder mixtures were incorporated into a paste, screen printed onto the SOFC bilayers, and sintered at 1200°C for 2 hours, they exhibited severe cracking as shown in the micrographs in Figure 7.

Sintering aids and optimized ink formulation. The dilatometry results in Figure 8 illustrate the effect on sinterability of doping the SDC with 2 mol% of various sintering aids. It can be seen that Cu was the most effective additive for improving sinterability. Therefore, the effects of various Cu doping levels were examined, as shown in Figure 9. The sintering shrinkage did not exhibit a strong dependency on Cu concentration. Upon determining that Cu-doping enhanced the sintering of SDC without the extensive cracking problem that was seen when the nano-sized powder was introduced, a parametric study was undertaken to examine the effects of the solids loading and binder system used when making the screen print ink. It was determined that the highest densities were obtained by using 2 mol% Cu-doped SDC at a
level of 70% solids loading in Ferro B-75717 binder. A micrograph of the resulting SDC layer after sintering at 1200°C for 2 hours is shown in Figure 10.

**Electrochemical Testing and X-ray Diffraction (XRD)**

Unlike the cells with PLD SDC, repeated electrochemical tests of cells with SDC layers made using the optimized ink formulation described above showed no improvement in performance over cells with conventional SDC layers. To understand why this may be the case, powders composed of YSZ and various SDC formulations, including undoped, 2 mol% Co-doped, and 2 mol% Cu-doped SDC, were mixed together. XRD was performed on each powder mixture before heat treatment, after firing at 1000°C for 2 h, and after firing at the typical SDC barrier layer sintering condition of 1200°C for 2 h. The results are shown in Figures 11 – 13. The propensity for solid solution formation increased with the sinterability of the SDC composition that was measured by dilatometry (see Figure 8). This is most evident when the XRD scans taken after 1000°C sintering (in red in each of the figures) are compared. In Figure 11, XRD of the mixture containing undoped SDC determined that the major peak for SDC at ~28.6° and the major peak for YSZ at ~30.2° are largely unchanged after 1000°C sintering. Then, in Figure 12, the mixture containing Co-doped SDC exhibits a small peak that has begun to form at ~29.6° between the two original peaks after 1000°C sintering, indicating the beginnings of solid solution formation. Additionally, the two original peaks have decreased in intensity and the YSZ peak has shifted ~0.1° toward the SDC. Finally, in Figure 13 showing the mixture containing Cu-doped SDC, the original peaks have largely disappeared and a fully formed solid solution peak is present at ~29.6° after 1000°C sintering. There is no sign of the YSZ peak and the only remnant of the SDC peak is a small shoulder on the solid solution peak at around ~29°.

**Conclusions**

The density of the SDC barrier layer can be greatly increased through small amounts of Cu-doping of the SDC powder together with increased solids loading and use of an appropriate binder system in the screen print ink. However, the resulting performance of cells with these barrier layers did not exhibit the expected increase in accordance with that achieved with the prototypical PLD SDC layer. It was determined by XRD that increased sinterability of the SDC also results in increased interdiffusivity between the SDC and YSZ, resulting in formation of a highly resistive solid solution.

**Acknowledgements**

The work described in this report was funded through the Solid-State Energy Conversion Alliance (SECA) Core Technology Program by the US Department of Energy’s National Energy Technology Laboratory (NETL). Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC06-76RL01830.

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**Table 1:** Comparison of the resistances determined from equivalent circuit modeling of impedance spectroscopy performed on cells with PLD and screen printed SDC layers.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Laser-deposited SDC (W.cm²)</th>
<th>Screen-printed SDC (W.cm²)</th>
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<tbody>
<tr>
<td></td>
<td>( R_\Omega )</td>
<td>( R_p )</td>
</tr>
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<td>750</td>
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</tr>
<tr>
<td>700</td>
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<td>1.18</td>
</tr>
<tr>
<td>600</td>
<td>0.27</td>
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Figure 1: SEM micrographs of cross-sections of fuel cells with (a) screen-printed and (b) laser-deposited SDC interlayers.

Figure 2: Comparison of the I-V curves and impedance spectroscopy of cells with screenprinted (top) and PLD (bottom) SDC barrier layers.
Figure 3: Ohmic resistances of fuel cells with screen-printed and laser-deposited SDC interlayers (a) before and (b) after deduction of the contribution from the YSZ electrolyte.

Figure 4: Cross-sectional SEM images of fuel cells with cathodes sintered at (a) 1200°C, (b) 1150°C, (c) 1100°C, and (d) 1050°C for 2h on conventional screen printed SDC barrier layers.
Figure 5: Cross-sectional SEM images of fuel cells with laser-deposited SDC interlayer and LSCF cathodes sintered at 1200°C for 2h. No SrZrO3 formation is observed.

Figure 6: Dilatometric results of compact SDC powders with various ratios of nano-sized powder to submicron-sized powder.
Figure 7: SEM images of SDC interlayers sintered at 1200°C for 2 h with various ratios of nano-sized powder to micro-sized powder.

Figure 8: Dilatometric results of the effects of 2 mol% of various sintering aids in SDC on sinterability.
Figure 9: Dilatometric results of SDC powders with various concentrations of Cu-doping.

Figure 10: SEM micrograph of a cell with the SDC layer made from screen print ink with 2 mol% Cu-doped SDC in Ferro B-75717 binder at 70% solids loading.
Figure 11: XRD diffraction patterns of undoped SDC+YSZ composite powder sintered at different temperatures.

Figure 12: XRD diffraction patterns of Co-doped SDC+YSZ composite powder sintered at different temperatures.
Figure 13: XRD diffraction patterns of Cu-doped SDC+YSZ composite powder sintered at different temperatures.
Compliant Glass Seals for SOFC Stacks

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April 30, 2014
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Executive Summary

This report summarizes results from experimental and modeling studies performed by participants in the Solid-State Energy Conversion Alliance (SECA) Core Technology Program, which indicate that compliant glass-based seals offer a number of potential advantages over conventional seals based on de-vitrifying glasses, including reduced stresses during stack operation and thermal cycling, and the ability to heal micro-damage induced during thermal cycling. The properties and composition of glasses developed and/or investigated in these studies are reported, along with results from long-term (up to 5,800h) evaluations of seals based on a compliant glass containing ceramic particles or ceramic fibers.
Introduction

The functional requirements of seals for solid oxide fuel cell (SOFC) stacks depend on the specific design and configuration, but in general they include:

- Prevent mixing of fuel and oxidant or mixing of reactants with the ambient environment
- Mechanical bonding of components
- Electrical insulation between stack components

Seal materials must be chemically and physically stable at operating conditions. In some applications (e.g., vehicles), seals must also be able to withstand acceleration forces associated with vibration and shock. Finally, seal materials must be low in cost and amenable to low-cost stack manufacturing methods.

Most SOFC seal research has focused on glasses which, after the sealing process, devitrify into a rigid glass-ceramic mixture. In particular, alkaline earth-based aluminosilicate glasses have been extensively studied due to their appropriate coefficient of thermal expansion (CTE) and sealing temperatures. Recently, an alternative sealing technology based on glasses resistant to de-vitrification has been developed by participants in the SECA Core Technology Program. The primary advantage of this “compliant glass” approach lies in the fact that, in contrast to conventional glass seals that develop a rigid microstructure, a de-vitrification resistant sealing glass with relatively low glass transition temperature \( T_g \) may retain relatively compliant behavior at SOFC operating temperatures, thereby minimizing thermal stress generation during operation. Also, the low \( T_g \) will help to minimize thermal stress generation during stack cooldown, and, if damage (such as micro-crack formation) does occur during cooling to room temperature, there is the potential for self-healing when the SOFC stack is reheated. Finally, compliant glass seals, consisting of crystallization-resistant glass and reinforcing phases, may assist in accommodating stack displacements, thus enabling the assembly and operation of SOFC stacks based on cells having large active surface area, for which dimensional tolerances of flatness and parallelism will be difficult to meet. The purpose of this report is to summarize:

- Properties of candidate compliant glasses and glass/filler composites developed and/or characterized under the SECA Core Technology Program
- Results of long-term testing of compliant glass-based seals under realistic SOFC stack conditions
- Results of modeling of compliant glass seal performance in SOFC stacks

Development and Characterization of Self-Healing Glasses within the SECA Core Technology Program

A number of organizations including Mo-Sci Corporation, Alfred University, Missouri University of Science & Technology-Rolla, Sandia National Laboratories, the University of Cincinnati, and Pacific Northwest National Laboratory (PNNL) have developed and characterized glass compositions for SOFC sealing applications as part of the Solid-State Energy Conversion Alliance (SECA) Core Technology Program.

Table I lists the chemical composition and properties of several glasses recently developed at Mo-Sci Corporation (Rolla, MO). Among those glasses, the preferred candidate for a viscous sealing glass for SOFC sealing applications is G102, an alkali-free barium borosilicate glass.
Glass. G102 exhibits stable thermo-mechanical/thermo-chemical properties and excellent thermal stability against crystallization within the SOFC operating temperature range. No bulk crystals were observed in samples of G102 isothermally held at 650, 750, and 850°C for up to 2000 hours in air. Even when G102 samples were thermally cycled for 21 days (84 cycles) through a temperature range (610-800°C) that covers the nucleation and growth regions, only surface crystallization was observed. There were no significant changes in the composition or properties (CTE and viscosity) for samples of G102 held for 2000 hours at 800°C in air. The long-term (2000 hrs) volatility of G102 was minimal and comparable to that of other sealing glasses at operational temperatures. Al-SS441/G102/YSZ-bilayer sandwich seals remain hermetic after 148 thermal cycles (between room temperature and 800°C, total process time about 5200 hours) in dry air and wet forming gas. Self-healing of G102 seals cracked by thermal shock was also demonstrated. A seal cracked by thermal shock (>25°C/s) was resealed after two hours at temperatures as low as 744°C in air, and this seal held pressure to 2 psi when cooled to room temperature.

Table II lists the chemical composition and properties of several glasses recently developed at Alfred University (Alfred, NY). Three preferred glasses were identified; all contained Ga₂O₃ up to 15 mole percent to modify the alkaline earth borosilicate base compositions. Testing out to 1000 hours in air, dry 4% H₂ in N₂, and wet 100% H₂ showed that all three crystallized extensively but retained some amorphous phase to provide viscous behavior. Testing against alumina-coated stainless steel, YSZ, and spinel coated stainless steel demonstrated excellent compatibility with alumina and YSZ, but not with spinel.¹⁻³

**Development of Compliant Glass Seals at ORNL and PNNL**

While a broad range of chemical compositions were developed and investigated as part of these SECA-funded projects, in recent work at PNNL and Oak Ridge National Laboratory (ORNL), two commercially available multicomponent silicate glasses containing barium and alkali metals, SCN-1 (SEM-COM, Toledo, OH) and G6 (GE Healthcare Bio Sciences, Pittsburgh, PA), have also been found to exhibit excellent behavior in terms of physical and mechanical properties and long-term stability, including resistance to crystallization. The main constituents and properties of these glasses are listed in Table III.

Studies on these glasses included determination of the chemical composition of the glasses⁴ and characterization of chemical composition evolution as a function of time of exposure to SOFC-relevant environments, such as air and gas mixtures of H₂+H₂O+N₂. The compositions of the SCN-1 and G6 glasses are listed in Table IV. Based on the composition of these glasses, their Young’s modulus was calculated using the Makishima-Mackenzie model.⁵ In turn, these values allow for calculation of residual stresses in glass seals at temperatures below the glass transition temperature, when the glass behaves as a solid. Values of Young’s modulus for SCN-1 and G6 glasses are plotted in Figure 1 as a function of temperature.

Values for the temperature dependence of the coefficient of thermal expansion, the glass transition temperature and the softening temperature of SCN-1 and G6 glasses were determined using a thermomechanical analyzer, as shown in Figure 2 and described in detail elsewhere⁵. These values are presented in Table III. The viscosity of these glasses was determined using the parallel plate method according to test method ASTM C1351, and is described using the Vogel-Fulcher-Tammann (VFT) model between 550°C and 750°C (see Table V).
The microstructural stability of the glass, in particular its resistance to crystallization, is one of the main considerations for the long-term functionality of these glasses in sealing applications. Glasses are in a metastable condition with respect to their crystalline form, so there exists a driving force toward reaching a crystalline state. The time to reach this state will depend on the kinetics of crystallization. Knowledge about these mechanisms is important because glasses containing a significant amount of crystalline phases have shown sluggish healing kinetics even at temperatures much higher than the glass softening temperatures.6

The long-term stability of SCN-1 and G6 glasses was investigated in air and in gas mixtures of H2+H2O+N2. These studies, which are described in detailed elsewhere,7 were performed by sintering test specimens of these two glasses on alumina or YSZ substrates, followed by monitoring the evolution of the microstructure and the composition of these glasses as a function of time of exposure. Figure 3 shows a collection of micrographs of the cross-sectional area of glass beads of SCN-1 and G6 glasses after different periods of time of exposure up to 10,000 hrs at 800°C. These micrographs show that at the bulk level, the glasses remain amorphous, although evidence of precipitation of crystalline phases within the glass or on the outer surface of the glass beads is observed. From X-ray diffraction measurements and chemical analyses, KAlSi3O8, barium oxide and a calcium-rich silicate were found to be the main crystalline phases that precipitated from the glass and the volume fraction of KAlSi3O8 in SCN-1 glass increases with exposure time. While the time dependence of the volume concentration follows the classical Johnson–Mehl–Avrami (JMA) kinetics at exposure times below 5000 hrs, at longer exposure times, deviation from the JMA behavior is observed. This behavior is similar to the crystallization behavior in other glass seal systems.8 There are several reasons for deviation from JMA kinetics including the heterogeneous nature of nucleation sites and in the case of SCN-1 glass, the possible exhaustion of potassium and aluminum from the glass matrix at longer exposure times. These micrographs also reveal that the initial distribution of pores in the glass will change with time of exposure. Detailed quantitative analyses of the distribution of pore sizes as a function of time of exposure indicate that small pores will coalesce into larger pores, but that the total porosity remains effectively constant.

**Engineered Glass Seals**

One approach for developing megawatt-size SOFC planar systems involves the use of cells with large active area (hundreds of square centimeters). Considering the state of the art for processes to manufacture planar cells, it will be very difficult to fabricate large active area cells with tight tolerances of flatness and parallelism. One potential strategy to enable the use of large surface area cells is to design and use seals with the necessary compliance to accommodate the lack of flatness or parallelism of the cells. ORNL, PNNL, and the National Energy Technology Laboratory (NETL) have developed engineered glass seals that incorporate crystallization-resistant glasses and structural features to accommodate deformation to compensate for the lack of flatness or parallelism.

The engineered glass seals incorporate frangible ceramic particles or ceramic fibers that are chemically and thermoelastically compatible with the crystallization-resistant glass. Among the many options, successful results have been obtained with commercially available hollow zirconia spheres and zirconia fibers (Zircar Ceramics, Florida, NY). The series of schematics in Figure 4 illustrate the principle by which engineered glass seals can seal surfaces that are not parallel or flat. In this case the application of compressive stresses in the direction normal to the
surfaces to be bonded will fracture the frangible hollow ceramic particles and induce flow of the mixture of glass, ceramic particles and organic binder towards the gaps between the surfaces to be sealed.

One of the positive attributes of engineered glass seals is that their viscosity and mechanical properties can be tailored by varying the concentration of secondary phases in the glass. Figure 5 shows a plot with the temperature dependence of the viscosity of engineered glass seals consisting of SCN-1 glass and different volume concentration of calcia-stabilized zirconia frangible hollow particles. These results show that it is possible to tailor the viscosity of the seal by orders of magnitude over the range of temperatures of interest for the operation of SOFCs by controlling the concentration of secondary ceramic phases (e.g., frangible ceramic particles or ceramic fibers). This is an important attribute that permits sealing a stack with large temperature gradients not just along the length of a stack, but also on the plane of individual cells. This implies that if the temperature distribution in a stack is known in advance, then it is possible to design engineered glass seals with the appropriate value of viscosity depending on the region of the stack where the seal will operate. This would be accomplished by adding a greater concentration of secondary ceramic phases to the crystallization-resistant glass to obtain higher viscosity to seal regions of the cell/stack that are expected to experience higher temperatures than other regions, where a seal with lower viscosity would be used.

Seal materials must be low in cost and amenable to low-cost stack manufacturing methods. Four methods were investigated for the manufacture of engineered glass seals:

- Tape casting
- Screen printing
- Paste extrusion
- Fused deposition

Tape casting is a well-established method in which a slurry is cast onto a moving carrier surface, while a smooth knife edge spreads the slurry to a specified thickness. In this case the slurry consists of a mixture of an organic binder, glass particles and ceramic particles or ceramic fibers. The resulting tape can be cut into different shapes, as shown in Figure 6, which shows a photograph of a tape of organic binder, hollow calcia-stabilized zirconia particles and SCN-1 glass.

Screen-printing is also a well-established process for manufacturing seals. According to this method a woven mesh over an ink-blocking stencil is used. The stencil forms open areas of mesh that transfer a mixture of a liquid organic binder, glass particles and ceramic particles or fibers, through the mesh as a sharp-edged image onto a substrate. A fill blade or squeegee is moved across the screen stencil, forcing or pumping ink through the mesh openings to wet the substrate during the squeegee stroke. Figure 7 shows a photograph of two patterns of glass (SCN-1 and G6), organic binder and ceramic particles printed onto an YSZ substrate. Each pattern contains two half-moon sections each containing different ratios of ceramic to glass particles (either 3:1 or 5:1). The objective was to demonstrate the feasibility of printing continuous patterns of engineered glass seal containing different concentrations of ceramic particles and therefore, different viscosity. Figure 8 shows the cross-section of the area where the two patterns meet and demonstrates that it is possible to obtain a dense and continuous seal with different concentrations of secondary phases, in this case frangible calcia-stabilized YSZ hollow spheres. This feature, i.e., the ability of having continuous sealing patterns with variable concentration of secondary ceramic particles or fibers, constitutes an advantage of screen
printing over tape casting. Furthermore, screen printing makes a more effective use of material with minimum waste in contrast to tape casting. A similar method, paste extrusion, uses slurries similar to screen printing slurries. In this process, the sealing paste is applied directly to the sealing regions via extrusion through a nozzle. The process is amenable to automation through the use of computer controlled slurry pumps and X-Y stages.

Fused deposition has been the focus of much interest as part of additive manufacturing processes. The operating principle in fused deposition is the extrusion of a thermoplastic material through a heated nozzle maintained above the glass transition temperature of the thermoplastic. To obtain complex shapes, the nozzle can be moved in three axes according to a preprogrammed pattern as illustrated in Figure 9. The object being fabricated is resting on top of a table and it is being built by moving the nozzle in the X-Y-Z axes. Upon extrusion of the thermoplastic material, it is deposited to build the next layer of the model, where it cools down and solidifies.

Using a mixer extruder, it has been possible to prepare mixtures of glass, ceramic particles and an organic binder, such as PLA (poly-lactic acid), as illustrated in the micrograph in Figure 10, which shows the cross-section of a wire containing 30% volume fraction of SCN-1 glass particles embedded in a matrix of PLA. When the wire is fed through the heated nozzle at temperatures above the glass transition of the organic binder, this will flow along with the glass and ceramic particles and will be deposited according to a predetermined design. When the deposited material is heated to temperatures above the softening point of the glass, the organic binder will burn out and the glass will melt and sinter, forming a continuous seal. At the time of the preparation of this report wires containing PLA, SCN-1 or G6 glass and ceramic particles or ceramic fibers have been successfully prepared and are being deposited using a 3D printer operating according to the fuse deposition process. The advantage of this approach over tape casting and screen printing is that it is possible to print arbitrary patterns with prescribed concentrations of ceramic particles or ceramic fibers and in turn, specific values of viscosity.

Fabrication of Seal Materials

Fabrication of glass/zirconia tapes at ORNL

Polymer tapes loaded with a mixture of glass and zirconia spheres were prepared using conventional non-aqueous tape casting methods.

Fabrication of glass and glass/zirconia pastes at PNNL

Mixtures of SCN-1 glass powder (sieved through #100 mesh) and short zirconia fibers (ZYBF-5, Zircar Ceramics, Inc., NY) were ball-milled with iso-propanol for 30 minutes. Pastes were prepared by mixing the glass powder or the glass/fiber mixture with 20-25 wt% organic binder (ESL450, ElectroScience Laboratories, PA). After homogenization with a 3-roll mill, the paste was de-aired and placed in a syringe for application.
Testing of Seal Materials

After promising results were achieved with thermal cycle leak tests performed on small (1” x 1”) test coupons, validation tests of plain glass seals and glass/zirconia seals were performed on a larger scale using PNNL’s SECA Core Technology Program “single cell stack” test fixture (shown schematically in Figure 11). These single cell tests used commercial Ni-YSZ anode-supported thin YSZ electrolyte cells (5 cm x 5 cm) with LSM cathodes. AISI 441 interconnect plates (with protective MnCo spinel and alumina coatings in the appropriate areas) were placed on both sides of the cells. Hybrid mica seals were used for the perimeter seal at a compressive load of ~20-30 psi. Three versions of the compliant seal material were evaluated as cell-to-frame seals. Seals based on plain SCN-1 glass or glass with 15% zirconia fibers were applied in paste form, while seals based on glass with 17 vol% crushed zirconia hollow spheres were applied in tape form. A three-step heating profile was used to fabricate the seals: binder burn-out (500°C for 2h), densification (630°C for 2h), and final wetting (850°C for 2h).

The sealed cell-to-frame assemblies were tested for hermeticity (i.e., no evidence of seal penetration by iso-propanol) prior to the assembly of the test stack. (La0.8Sr0.2)0.95MnO3 (LSM20) powder (Fuel Cell Materials, OH) and NiO powder (JT Baker, PA) were mixed with organic binders (ESL450, ElectroScience, PA) to form a paste and were applied as cathode and anode contact materials, respectively. Nickel mesh (70x80 of diameter 0.006”) was spot-welded onto the anode-side of the AISI 441 interconnect. Pt lead wires were used for voltage sensing, and Inconel 600 rods were used as current leads. The stack assembly was heated to 800°C in air, followed by anode reduction in 5% H2/N2 for 2h before switching to the final fuel of H2:N2=1:1 with ~3% H2O. Air was used as the oxidant.

Two types of cell tests were conducted. The first type - a combined ageing and thermal cycling test - was performed on three versions of the compliant seal: plain SCN-1 glass, glass with 15 vol% zirconia fibers, and glass with 17 vol% crushed zirconia hollow spheres. In these tests, the cells were operated in constant current mode at 800°C for a total of 1500h, with an interruption for a deep thermal cycle every 500h. The second type of cell test was a long-term validation test, which was achieved by continuing the test of the glass with 15 vol% zirconia fibers beyond 1500h until a total test time of 5800h was reached. Results of the tests are described below.

Combined Ageing and Thermal Cycling Tests

Cell voltage versus time for the three different seal tests (plain SCN-1 glass, glass with 15 vol% zirconia fibers, and glass with 17 vol% crushed zirconia hollow spheres) is shown in Figure 12. The average degradation rates between thermal cycles were 9.1%/kh, 4.1%/kh, and 5.2%/kh for plain SCN-1 glass. For glass with 15% zirconia fibers, they were 7.5%/kh, ~0%/kh, and 2.0%/kh, and for glass with crushed zirconia hollow spheres they were 9.5%/kh, 5.5%/kh, and 3.6%/kh. The degradation rate of the test with the best overall performance (glass seal with zirconia fibers) was similar to that of a previous test using a devitrifying glass seal (~1.1%/kh from t=500 to 1500h). While all of the tests showed significant degradation in electrochemical performance over time, it is unlikely that the degradation was related to the seals, given that the open circuit voltages remained stable for the duration of the tests, and room temperature testing of the seals, performed by flowing only one gas (fuel or oxidant) to look for cross-over to the other gas bubbler, gave no indication of leakage. After 1500h, two of the tests (plain SCN-1 glass and glass with crushed zirconia spheres) were terminated and dis-assembled for post-test...
analysis. Liquid penetration tests with iso-propanol indicated hermetic sealing, which is consistent with the high open circuit voltage and lack of gas crossover observed during the test. SEM/EDS analyses of cathode and anode active areas indicated either no presence of alkalis or, at most, a very small amount near the detection limit of 0.5%. As discussed in the next section, the test of the glass seal with zirconia fibers was continued for a longer period of time.

Long-Term Validation Test

One of the abovementioned aging/thermal cycling tests (the test with a glass/zirconia fiber seal), was selected for continuation as a long-term validation test. The primary motivation for selecting the glass/fiber seal was related to the issue of pore coarsening. Studies at both PNNL and ORNL found that small pores initially present in plain SCN-1 glass coalesced during isothermal aging at elevated temperatures to form very large voids. In an attempt to hinder the pore coarsening processes, inert fillers such as zirconia fibers or crushed zirconia hollow spheres were evaluated. While both forms of inert filler performed well in the 1500 tests described above, supplemental pore coarsening studies indicated that the fibers were the most effective in limiting void growth, so the seal with zirconia fibers was selected for the long-term test.

The results of the test (cell voltage vs. time) are shown in Figure 13. (For comparison, results from a previous test with a devitrifying glass seal are also shown). The first 1500h of the test duplicate the results discussed in the previous section. Note that at t=1750h, the cell suffered some damage due to an unscheduled power outage during which the cathode air was shut off and no compressive loading was maintained, in addition to furnace cooling. This disruption led to an abrupt increase in ohmic resistance (as determined by electrochemical impedance spectroscopy) that led to a significant drop in cell voltage. This increase in ohmic resistance was likely due to a loss of contact at the cathode side, so again it is unlikely that the degradation was related to the seals. The open circuit voltage remained stable for the duration of the test, and room temperature testing of the seals, performed by flowing only one gas (fuel or oxidant) to look for cross-over to the other gas bubbler, gave no indication of leakage.

At the conclusion of the test, room temperature leak testing revealed no evidence of gas cross-over. The cell assembly was then dis-assembled for post-test analysis. Liquid penetration tests with iso-propanol indicated hermetic sealing, and examination with optical microscopy found no evidence of seal damage or failure. The anode appeared to be completely reduced, without any discoloration or greenish color indicative of Ni oxidation. One potential concern when using non-crystallizing glasses for SOFC sealing applications is the possibility of squeezing the glass out of the bonding area because of compressive loading either externally applied or resulting from the weight of the stack. No spreading of the glass was observed after the long-term test, but if this issue arises in larger scale cells and stacks, it could be addressed by using spacers (e.g., mica paper) to maintain the desired seal thickness.

Cross-section SEM/EDS was used to characterize the microstructure and chemistry of the anode and cathode. Except for a small amount of Na (<1 at%) that was detected in the cathode current collection layer, levels of Na, K, and Si were at or below the detection limit. Glass interactions with the two mating materials were also examined along the glass/YSZ electrolyte and glass/aluminized AISI441 cell frame interfaces. Two typical microstructure images of the glass/YSZ electrolyte interface are shown in Figure 14. Five areas were selected for EDS chemical analysis; the results are listed in Table VI. The interaction between the glass and YSZ electrolyte was minimal, as evidenced by the absence of Zr in the glass. This is consistent with
the smooth YSZ/glass interface and the homogeneous appearance of the YSZ electrolyte, which indicates no leaching or corrosion along the YSZ grain boundaries.

Two typical microstructure images along the glass/aluminized AISI441 interconnect are shown in Figure 15; results of EDS spot analysis are listed in Table VII. Overall, the alumina protection layer was intact, with no evidence of de-bonding from the metal substrate. Only minute concentrations of metal species were detected in the glass matrix. In addition, no significant precipitation was found in the glass along the glass/alumina interface, indicating good chemical compatibility with the alumina protection layer. Figure 16A shows a lower magnification image of a typical portion of the engineered glass seal after the long-term stability test. Note that the majority of the pores are somewhat irregular in shape, indicating the effectiveness of the zirconia fibers in hindering the coalescence of pores. For comparison, an SEM image of plain SCN-1 glass (no fillers) sealed between two bilayers and aged for only 500h at 800°C shows the presence of large spherical pores that in some cases span the width of the seal (Figure 16B). This indicates the potential benefit of including inert fillers in the compliant glass SCN-1 when designing seals for SOFC stacks.

Compliant Glass Seal Modeling

The thermo-mechanical performance of compliant glass seals in SOFC stacks under various operating conditions was systematically investigated through numerical models. A fully three-dimensional thermo-visco-elastic-damage-healing constitutive model was developed to capture the unique stress-strain material behavior of the glass. The evolution kinetics of the two major damage sources, i.e. CTE mismatch-induced mechanical cracks and changes in seal porosity, are described in detail in Appendix A and Reference.10 The proposed material model was calibrated with experimentally obtained properties and then implemented in finite element (FE) analyses through user-subroutines in the commercial FE code ABAQUS. The mechanical performance of single- and multi-cell SOFC stacks was then examined. The major findings from this study are summarized below and in Appendix A.

Two types of SOFCs were modelled. One corresponded to PNNL’s SECA Core Technology Program stack test fixture, while the other corresponded to a larger 10x10 cm planar design that more closely resembled full-sized SECA cells and stacks. In both cases, glass seals joined the electrolyte layer to the metallic cell frame. Multi-cell stack models were generated by sequentially repeating the single-cell units.

A typical damage accumulation and dissipation response of the seal glass during a single thermal cycle (cooling from the fabrication temperature to room temperature, followed by re-heating to the operating temperature) is shown in Figure 17, with the volume-averaged damage due to cracks and pores separately exhibited. In this study, “damage” is defined as the fractional reduction in elastic modulus. Overall, the damage generated within the sealant was found to be trivial and unlikely to result in noticeable performance reduction, which is consistent with experimental observations with the SECA stack test fixture. Furthermore, the relatively low viscosity of the glass at operating temperature would likely lead to healing of any minor damage caused by thermal cycling. Overall, as might be expected, the rate of temperature change and loading conditions dominated damage behavior, with less damage occurring with lower stresses and more gradual temperature changes.

The seal reliability of a three-cell SOFC stack (PNNL stack fixture) during multiple thermal cycles was also evaluated. Similar to previous experimental measurements,11 the
mechanical integrity of the glass seal was predicted to be minimally impacted by 10 deep thermal cycles, as shown in Figure 18. Although pore-related damage was initially lower in magnitude than cracking damage, its continuous increase with increasing number of cycles could eventually lead to a loss of seal integrity. Furthermore, the continuous increase in pore-related damage (primarily represented by increased pore size due to pore coalescence), may enhance crack initiation, as evidenced by the increasing height of the crack damage peaks. However, predicted results also indicate that the pore damage rate tends to saturate over time which would suggest a more optimistic projection on the long-term performance of the seal. Further experimental and modeling analyses focused on long-term operations and performance are expected to strengthen such confidence.

Since the electrochemical reactions that occur during SOFC operation can strongly affect the temperature fields within SOFC stacks, the effects of associated operating parameters were also investigated by integrating the FE analysis with the SOFC-MP multi-physics computational capabilities. Operational variables such as thermal boundary conditions, current density, fuel utilization, and fuel composition were considered. Figure 19 shows results for a single thermal cycle of a single cell repeat unit representative of a commercial-scale SOFC stack.

As shown in the figure, although the repeat unit behaved quite similarly under adiabatic, furnace, and insulated self-heating conditions, the non-adiabatic case showed slightly less pore-related damage and slower healing because of the lower internal temperatures (3a). Although increases in fuel utilization and power density tend to yield larger temperature gradients which can introduce more stress concentrations and damage, seal damage for both a low power/fuel utilization and high power/fuel utilization case were similar (3b). The difference between methane-powered and hydrogen-powered SOFCs also appeared to be trivial, although the comparatively more uniform temperature field for methane produced slightly less mechanical degradation (3c).

The predicted seal performance of a larger three-cell SOFC stack during multiple thermal cycles is shown in Figure 20. It is apparent that the mechanical degradation within the seal is quite low even after 10 deep thermal cycles, following a trend similar to that of the PNNL stack fixture.

The viscosity and the elastic modulus are both important design metrics for compliant glass. For example, higher values of elastic modulus can promote damage due to the intensified stress field. Glass viscosity influences the damage response in a mechanism-dependent manner. Figures 21(a)-(b) show the predicted variation of damage with viscosity for cases where different damage sources dominate. It was found that, when cracking is dominant, higher viscosity results in more damage because of the hindered stress relaxation. On the other hand, when pore evolution is dominant, increasing viscosity will reduce damage by preventing flow-driven pore coarsening until a limiting viscosity corresponding to the increase in the stress concentration effect is met. These findings could potentially reconcile the contradictory experimental observations reported in the open literature and can also provide guidance to material customization, i.e. addition of a reinforcement phase to mitigate pore coarsening.

A comparison between mechanical responses of the compliant SCN-1 glass and a state-of-the-art devitrifying glass (PNNL’s G18), shown in Figure 22, illustrates the benefits that compliant glass seals can bring to SOFC technology. It is clear that the compliant glass accumulates much less damage than the devitrifying glass under the same thermo-mechanical operations. The compliant nature of the SCN-1 glass is believed to be the underlying root cause,
as stress concentrations can be quickly relaxed. Moreover, with its healing capability upon re-heating, most of the lost structural integrity can be effectively recovered.

The main findings from the modeling study can be summarized as follows:

1) The present 3D thermo-visco-elastic coupled continuum damage-healing glass model is able to capture the essential nonlinear material behaviors of SOFC glass sealant under short-term stack operating conditions including the underlying mechanisms accounting for different mechanical degradation and recovery physics. The overall damage within the compliant seal was found to be trivial even under aggressive operating conditions.

2) It has also been found that cracking damage occurring during thermal cycling can be completely repaired at high temperature due to the prevailing inter-diffusion while pore coarsening-induced material degradation tends to accumulate over the time/operational cycles. The addition of reinforcement phases to prevent the viscous flow is a conceptually viable solution to reduce pore growth, although its effectiveness and applicability should be quantitatively characterized through further high-fidelity modeling.

3) Thermo-electro-chemical conditions such as thermal boundary conditions, power density, and fuel composition are important operating parameters, and internal cracking damage can be further eliminated through more gradual environmental temperature changes.

4) Compared to a rigid devitrifying glass-ceramic such as G18, the SCN-1 compliant glass is found to have clear advantages in terms of the ability to minimize and mitigate damage by effectively relaxing the stress concentrations.

Conclusions

Experimental and modeling studies performed by participants in the Solid-State Energy Conversion Alliance (SECA) Core Technology Program indicate that compliant glass-based seals offer a number of potential advantages over conventional seals based on de-vitrifying glasses, including reduced stresses during stack operation and thermal cycling, and the ability to heal micro-damage induced during thermal cycling. Subsequent to the development of a comprehensive understanding of the thermo-physical and mechanical properties of a variety of candidate sealing glasses, seals based on one of the candidate glasses (SCN-1, with and without modifying fillers) were fabricated and tested under stack-like conditions. The seal tests, which included a long-term (5800h) validation test, demonstrated the viability of the compliant glass seal approach for SOFC stack sealing applications. This viability was further demonstrated through modeling of multi-cell SOFC stacks, which indicated minimal damage within the seals during thermal cycling and self-healing capability upon returning the seals to operating temperature. While most of the validation testing was focused on one specific glass (SCN-1), other glasses developed and/or characterized by participants in the SECA Core Technology Program would also merit consideration when designing a compliant glass seal for a specific stack design and set of operating conditions.
Acknowledgments

The work summarized in this report was funded by the DOE Office of Fossil Energy’s Solid-state Energy Conversion Alliance (SECA). The authors appreciate helpful discussions with the NETL SECA Program management team, and thank Scott Misture (Alfred University) and C.W. Kim (Mo-Sci Corporation) for providing information regarding their compliant glass development. The following contributors at ORNL are also acknowledged: Beth Armstrong, Valerie Garcia-Negron, John Henry, Melanie Kirkham, Andres Marquez, Dana McClurg, Roberta A. Meisner, Amit Shyam, Hannah Stokes, Rosa Trejo, Yanli Wang, and Shirley Waters.

References


Tables

Table I. Chemical composition and properties of silicate glasses developed by Mo-Sci Corporation as part of the SECA Core Technology Program. Primary constituents are designated in blue.

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Table II. Chemical composition and properties of silicate glasses developed by Alfred University as part of the SECA Core Technology Program. Primary constituents are designated in blue.

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Table III. Chemical composition and properties of commercial glasses SCN (SEM-COM, Inc., Toledo, OH) and G6 (GE Healthcare Bio-Sciences, Pittsburgh, PA). Primary constituents are designated in blue.

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<td></td>
<td></td>
<td></td>
<td>508</td>
<td>600</td>
<td>7.25x10⁻⁶ + (6.67x10⁻³) T</td>
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Table IV. Chemical composition of SCN and G6 glasses. Values were determined by inductively coupled plasma mass spectrometry (ICPMS) and inductively coupled plasma-Atomic Emission Spectrometry (ICPAES).

<table>
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<tr>
<th>Element</th>
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<th>ICP-AES</th>
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<tr>
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<tr>
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<td>Zn</td>
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<td>53.4</td>
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<td>Fe</td>
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Table V. Temperature dependence of viscosity of selected glasses.

a) Temperature dependence of viscosity of Mo-Sci glasses between 600°C and 800°C.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$m$</th>
<th>$T_g$ (°C)</th>
<th>$\log \eta_\infty$</th>
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</thead>
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<tr>
<td>G73</td>
<td>64.13</td>
<td>606</td>
<td>-3.5</td>
</tr>
<tr>
<td>G102</td>
<td>57.18</td>
<td>593</td>
<td>-3.3</td>
</tr>
</tbody>
</table>

\[
\log \eta (T) = \log \eta_\infty + (12 - \log \eta_\infty) \frac{T_g}{T} \exp \left[ \left( \frac{m}{12 - \log \eta_\infty} - 1 \right) \left( \frac{T_g}{T} - 1 \right) \right]
\]

b) Temperature dependence of viscosity of SCN glass (Vogel-Fulcher-Tammann (VFT) model) between 550°C and 750°C. Temperature in °C.

\[
\log \eta (T) = -6.007 + \frac{9129.7}{T + 33.46}
\]

c) Temperature dependence of viscosity of G6 glass (Vogel-Fulcher-Tammann (VFT) model) between 550°C and 750°C. Temperature in °C.

\[
\log \eta (T) = -3.126 + \frac{3917.5}{T - 295.45}
\]
Table VI. Chemical analyses of selected areas shown in Figure 14A and 14B.

from figure 14A

<table>
<thead>
<tr>
<th>Area</th>
<th>O</th>
<th>Mg</th>
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<th>Ca</th>
<th>Ni</th>
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<th>Ba</th>
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from figure 14B

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Table VII. Chemical analyses of selected spots shown in Figure 15A and 15B.

from figure 15A

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<th>Ca</th>
<th>Ti</th>
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from figure 15B

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</table>
Figures

Figure 1. Young’s modulus of SCN (circles) and G6 (squares) glasses as a function of temperature using resonant ultrasound spectroscopy. The onset of the rapid decrease of Young’s modulus coincides with the value of the glass transition temperature determined from thermal expansion measurements.

Figure 2. Photograph of thermomechanical analyzer used to determine the thermal expansion and the glass transition and softening temperatures of glasses.
Figure 3. Micrographs of the cross-section of both SCN and G6 glass beads sintered onto YSZ substrates at 800°C as a function of time of exposure in air or gas mixtures of H₂+H₂O+N₂.
Figure 4. Schematic illustrations of the principle by which engineered glass seals can seal surfaces that are not parallel or flat.
Figure 5. Temperature dependence of the viscosity of engineered glass seals consisting of SCN glass and different volume concentrations of calcia-stabilized zirconia frangible hollow particles.

Figure 6. Photograph of a tape consisting of organic binder, hollow calcia-stabilized zirconia particles and SCN glass.
Figure 7. Two patterns of glass (SCN and G6), organic binder and ceramic particles printed onto a YSZ substrate. Each pattern contains two half-moon sections each containing different ratios of ceramic to glass particles (either 3:1 or 5:1).

Figure 8. Cross-section of the area where the two patterns meet, demonstrating that it is possible to obtain a dense and continuous seal with different concentrations of secondary phases (in this case, frangible calcia-stabilized YSZ hollow spheres).
Figure 9. Schematic illustration of the fused deposition process. To obtain complex shapes, the nozzle can be moved in three axes according to a preprogrammed pattern.

Figure 10. Cross-section images of a wire containing 30% volume fraction of SCN glass particles embedded in a matrix of PLA.
Figure 11. Schematic illustration of the SECA Core Technology Program stack test fixture (not to scale).
Figure 12. Results of single cell stack fixture tests with three different seals: plain SCN-1 glass, SCN-1 with 15 vol% zirconia fiber, and SCN-1 with 17 vol% crushed zirconia hollow spheres (5 to 1 volume ratio). The cell tests were interrupted every 500h for a deep thermal cycle.

Figure 13. Long-term evaluation of an engineered compliant glass seal (SCN-1 with 15 vol% ZrO₂ fibers) in a single cell stack fixture test.
Figure 14. Typical microstructures at the seal/electrolyte interface after the long-term validation test. EDS analyses of 5 areas (#1-#5) are listed in Table VI.
Figure 15. Typical microstructures at the seal/aluminized AISI 441 interface after the long-term validation test. EDS analyses of the indicated spots are listed in Table VII.
Figure 16. (A) Typical microstructure of engineered compliant glass seal (SCN-1 + 15% zirconia fibers) after long-term stability test (800°C/5830h); (B) plain SCN-1 glass aged 500h in air at 800°C between two bilayers.
Figure 17. Transient damage distribution within the glass sealant.

Figure 18. Damage evolution for a multi-cell PNNL stack during multiple thermal cycles.
Figure 19. Effects of electrochemical operating parameters (a) thermal boundary conditions (b) power density/fuel utilization (c) fuel composition.

Figure 20. Damage evolution for larger multi-cell SOFC stack during multiple thermal cycles.
Figure 21. Effects of glass viscosity when (a) cracking or (b) pore evolution is dominant.

Figure 22. Comparison between SCN-1 and G18.
Appendix: Modelling of glass seal behavior

The temperature-dependent and rate-sensitive mechanical behavior of the compliant glass materials originates from its amorphous, liquid-like but rigidly bounded molecular structure. In order to capture the structural precursors of such immediate-range positioning symmetry and long-range conformational disorder, the overall stress response can be resolved into two components: an equilibrium time-independent stress element accounts for the entropic molecular configuration rearrangement, while an inelastic history-dependent stress element is assumed to describe the stiff macroscopic deformation due to the enthalpic stretching of intermolecular and intramolecular bonds. The one-dimensional rheological analog shown in Figure A1 is used to illustrate such a thermo-viscoelastic concept with the Maxwell component capturing the viscous response and the parallel linear Hookean spring representing the elastic characteristic. The following constitutive model description summarizes the development described in [1].

The deformation can be decomposed into thermal and mechanical parts as \( \mathbf{\varepsilon} = \mathbf{\varepsilon}_T + \mathbf{\varepsilon}_M \) with the latter further split into the elastic and viscous components as \( \mathbf{\varepsilon}_M = \mathbf{\varepsilon}_{eq} + \mathbf{\varepsilon}_n \), where \( \mathbf{\varepsilon}_T = \mathbf{\varepsilon}(T)(T - T_0)I \) describes the isotropic thermal expansion, \( \mathbf{\varepsilon}_M \) denotes the mechanical strain, \( \mathbf{\varepsilon}_{eq} \) measures the equilibrium atomic packing coordination, and \( \mathbf{\varepsilon}_n \) and \( \mathbf{\varepsilon}_v \) correspond to the non-equilibrium elastic and viscous deformation, respectively.

The constitutive relations then yield \( \mathbf{\sigma}_M = \mathbf{\sigma}_v + \mathbf{\sigma}_{eq} \) with \( \mathbf{\sigma}_v = (1 - \varphi)C_{eq} : \mathbf{\varepsilon}_{eq} \), \( \mathbf{\sigma}_n = \mathbf{\sigma}_n : \mathbf{\varepsilon}_n \), \( \mathbf{\sigma}_v = \mu(T) \mathbf{\varepsilon}_v \). Here, \( \mathbf{\sigma}_M \) represents the overall mechanical response, \( \mathbf{\sigma}_v \) defines the non-equilibrium stress acting on the viscoelastic component, \( \mathbf{\sigma}_{eq} \) characterizes the equilibrium stress, and \( C_{eq} \) and \( C_n \) denote the isotropic elasticity tensors.

The temperature dependence of the material viscosity \( \mu(T) \) can be described by the Vogel-Fulcher-Tammann (VFT) equation \( \log \mu(T) = \log \mu_0 + \frac{A}{T - T_v} \) with \( \mu_0 \) is the reference viscosity, \( A \) is a material constant, and \( T_v \) is the Vogel temperature representing the ideal glass transition temperature at which flow can no longer occur and the free volume drops to zero.

Since the deterioration and recovery in glass materials typically refers to the formation, accumulation, and reduction of mechanical cracks and internal pores, the scalar damage variable \( \varphi \) can then be divided into \( \varphi = \varphi_c + \varphi_p \) where \( \varphi_c \) and \( \varphi_p \) account for the damages induced by cracks and pores respectively. To be inclusive, they can be generally written as \( \varphi_c = \varphi_{c}^n + \varphi_{c}^g + \varphi_{c}^h \) and \( \varphi_p = \varphi_{p}^n + \varphi_{p}^g + \varphi_{p}^h \), in which the superscripts \( n, g, \) and \( h \) represent the terms of nucleation, growth, and healing, respectively.

For a randomly oriented micro-crack filled solid medium in which the micro-crack nucleates under critical stress, the crack nucleation can be interpreted as \( \varphi_c^n = \lambda \Sigma m^\Sigma m \) where \( \Sigma \) denotes the first stress invariant, \( \lambda \) refers to the proportionality constant, and \( m \) factorizes the load effects. Moreover, since crack growth is mainly driven by the change of the elastic energy, its propagation can be captured by \( \varphi_c^g = \frac{\partial F_c(\varphi_c, T)}{\partial \varphi_c} \) where the damage threshold function \( F_c(\varphi_c, T) \) characterizes the critical energy state for the cracking and can be numerically determined from the experimental stress-strain curves as shown in Figure A2.

The self-healing morphological changes of the cracked compliant glass at elevated temperatures such as blunting and pinching of crack tips, rounding and grooving of radial cracks, receding and breaking up of lateral and median cracks that later turn into cylindrical or spherical closed cavities and ultimately disappear are believed to be driven by the combined viscous flow- and diffusional mass transport. In other words, the whole crack healing process essentially consists of two locally sequential phenomenological stages: 1) the geometrical crack closure induced by the creep deformation and 2) the re-establishment of the physical bonding across the crack interface due to the surface diffusion. The
former is captured by the material viscous flow behavior, while the latter is determined from the lower-length scale simulation, specifically, the kinetic Monte Carlo (kMC) model.

As a typical computational tool in simulating the time evolution of natural physical processes, the kMC model is naturally effective to describe the inter-diffusion healing stage in the current study. Figure A2 shows the \((M \times \Delta S) \times (M \times \Delta S)\) 2D lattice model used in the kMC simulation, where the non-dimensional lattice spacing is denoted by \(\Delta S\). If \(\Delta x\) takes the covalent bond length of the glass, the model then actually represents a specimen with an already closed but not healed crack. Convergence studies further demonstrate that \(M = 1000\) is able to ensure sufficient prediction accuracy.

The healing probability of an arbitrary bond follows

\[
P = \omega h \cdot \exp\left(-\frac{E_h}{kT}\right)
\]

where \(k\) is Boltzmann constant, \(\omega_h\) is the frequency and \(E_h\) is the activation energy. The model is then calibrated by controlled healing experiments where two rectangular SCN-1 glass bars with dimensions of \(4 \text{ mm} \times 3 \text{ mm} \times 23 \text{ mm}\) were placed vertically in a fixture as shown in Figure A3(a) and exposed to different elevated temperatures for varying time periods before being taken out for flexural strength measurements following ASTM C1161-02 (Figure A3(c)). Since no gap is left between the specimens, the two bars together can be perceived as one SCN-1 glass bar of double length but with an already closed cross-sectional crack in the middle of the span. The healing experiments actually record the fracture surface inter-diffusion and physical bonding re-establishment evolution in the healing stage. The scale damage variable \(\varphi\) is determined by the ratio of the total of remaining broken bonds to the initial amount of broken bonds in the kMC model and by the measured flexural strength divided by that of the virgin glass in the experiments. In that way, the probability function for the kMC model was then calibrated and the temperature dependence of the crack healing rate could be formulated as

\[
\dot{\varphi}_h^c = -\exp(\vartheta T + \zeta)\varphi_c
\]

where \(\vartheta\) and \(\zeta\) are temperature dependent parameters. Since \(\dot{\varphi}_h^c\) drops exponentially with the decrease in \(T\), there could be a lower bound temperature below which no observable healing would occur within any practical time frame.

Since pore accumulation is commonly perceived as the main phenomenon associated with the inelastic deformation process which generally originates from the simultaneous growth of both pre-existing interstitial voids and the newly nucleated cavities at the internal imperfection sites, a general equation for pore nucleation can be given as

\[
\dot{\varphi}_p^N = \chi \left(\frac{\exp(\omega (\Sigma - \Sigma_m))}{1 - \varphi_p}\right)
\]

where \(\chi\) represents the coalescence effect and \(\omega[\Sigma - \Sigma_m]\) describes the nucleation energy barrier with \(\Sigma_m\) denoting the threshold hydrostatic stress and \(\omega\) weighing the stress influence. Furthermore, due to mass conservation, the growth of the internal pores yields

\[
\dot{\varphi}_p^B = (1 - \varphi_p)\frac{\alpha}{\Sigma}\text{tr}(\dot{\varepsilon}_v)
\]

where \(\dot{\varepsilon}_v\) is typically considered as a constant describing the compressibility of the matrix material. As no pore healing has been observed in experiments, \(\dot{\varphi}_p^B\) is neglected.

The present glass material damage-healing model is then implemented into finite element analyses through commercial engineering software ABAQUS user subroutines to simulate the thermo-mechanical performance of the glass sealant within the SOFC stacks. Although geometrical features or specifics may vary between different SOFC stacks, the essential mechanical components are typically the same, including the interconnect plates, PEN, glass seal, and metallic window frame. Sequentially repeating the cell units between two heat exchanger/compression blocks then forms the multi-cell SOFC stack. Figure A5 shows the finite element model of an in-house three-cell SOFC stack that has been tested, in which the cells are separated by window-frames and interconnect plates made of SS441 stainless steel, and the compliant glass seal is applied to attach the cell to the window-frame.

Numerical simulations were then performed to predict the structural response of this multi-cell SOFC stack when exposed to deep thermal cycling loads. The stack is simply supported at the bottom with slight compressive load on the top as suggested by the experiments. During a rapid cooling-heating cycle, the ambient temperature decreases from the normal operating temperature to the room temperature in 20 minutes and then bounces back in 50 minutes. This procedure has repeated for a total of 10 cycles.
Figure A6(a)-(d) show the contours of the transient stress and damage distribution over the three seals. It is found that all of the seals appear to result in almost identical thermo-mechanical loading and degradation conditions. As the most degraded areas coincide with the locations of stress concentrations, it indicates and verifies the speculation that the cooling-induced mechanical mismatch is primarily responsible for damage. However, the predicted results also show that even under such aggressive thermal loading circumstance, the overall structural damage is still trivial and within the expected tolerance for development of a possible leak path, demonstrating the effectiveness of the novel SCN-1 glass.

Besides the damage typically concentrating near the edges, it is also noticed that the seal attached to the middle cell shows slightly higher degradation than the other two, which is relatively more revealing in the porosity distribution contour. It could be caused by the double mechanical constraints that the middle cell has to comply with from the top and bottom interconnects. Such effects may be even more pronounced in a larger stack size.

The time evolution of the average damage along with the temperature profile is shown in Figure A7. It can be seen that the amount of damage induced by porosity starts lower than that caused by mechanical cracking especially during the first 1 or 2 cycles. However, unlike the cracking damage that can be healed every time upon heating, the pores occupied by the entrapped air bubbles are prevented from annealing. Therefore, as thermal cycling continues, the glass sealant material keeps being further degraded, which makes it increasingly easier for cracks to initiate and accumulate as demonstrated by the predicted results for the subsequent loading cycles.

Since the electrochemical reactions occurring within the cell typically have prominent influence on the working temperature environment of the SOFC stack, its effects on the long-term functionality and reliability of the compliant glass sealant has also been investigated by integrating the FEM analyses with the PNNL-developed SOFC-MP multi-physics calculations.

A 10 × 10cm industrial characteristic co-flow SOFC single-cell stack is used in the numerical simulations, in which the fuel and air enter from the left side at a temperature of 700ºC. Crucial parameters such as fuel utilization, fuel composition, and thermal boundary conditions, i.e. adiabatic, furnace, and insulation have been examined. Here two types of fuels, specifically wet hydrogen and a reforming composition containing methane, have been considered. For the adiabatic condition, no heat transfer is allowed between the SOFC stack and its surroundings; for the furnace condition, the SOFC stack is assumed to be placed in a constantly heated furnace; and the insulated condition describes a SOFC stack in an enclosure container made of low thermal conductivity insulation materials whose outer boundaries are kept at room temperature.

Figure A8 shows the temperature maps that correspond to different fuel utilization and composition conditions, where it can be seen that high fuel-utilization operation leads to the largest temperature gradient over the stack. Similar plots for the temperature profiles yielded by different thermal boundary conditions are also presented in Figure A9. Unlike the adiabatic condition where the temperature monotonically increases from the left to right, the furnace and insulated conditions appear to localize the heated zones within the central region with temperatures decreasing radially outwards. It is also noticed that furnace and insulated conditions generally result in lower temperature fields and narrower temperature gradients.

The resultant damage evolution behaviors as responses to the CTE-mismatch induced thermal stresses have been shown in Figure A10. Although the SOFC stacks under adiabatic, furnace, and insulated conditions behave quite similarly, non-adiabatic cases tend to show slightly lower pore damage and slower healing because of the cooler internal environment. Similar behavior was also observed for different fuel utilizations as aggressive high power operation yields larger temperature gradients which can introduce more stress concentrations and damage. The difference between methane-powered and hydrogen-powered SOFCs appears to be trivial for these cases, although the comparatively more uniform temperature field for methane produces slightly lower mechanical degradation.

As one of the most important physical properties in the glass, viscosity can substantially affect the material’s mechanical behaviors. However, unlike the elastic modulus of which the increase promotes the
damages due to the intensified stress field, the glass viscosity influences the damage response in a mechanism-dependent manner. Figure A11(a)-(b) show the predicted variation of damage with viscosity for cases where different damage sources dominate. It is found that, when cracking is dominant, higher viscosity results in more damage because of the hindered stress relaxation; while when pore evolution is dominant, increasing viscosity will reduce damage by preventing the flow driven pore coarsening until a limiting viscosity corresponding to the rise of the stress concentration effect is met. These findings could potentially reconcile the contradictive experimental observations reported in the open literature [2, 3] and will also provide guidance to material customizations, i.e. addition and dispersion of reinforcement phase such as ceramic fibers/particles to mitigate pore coarsening.

Since such material strengthening customization is likely to introduce non-uniform material properties, further studies have been conducted to evaluate such heterogeneity effects. As shown in Figure A12, a distribution of viscosities has been considered within the glass sealant with the specific properties of material points randomly assigned.

It is found in Figure A13 and A14 that the non-uniform viscosity field can strongly elevate the mechanical resistance of the glass seal. It can be seen that both average cracking damage and pore growth are sharply reduced. A wider damage peak appears in the crack evolution probably because of the scattered material properties. After further examining the stress conditions, it was demonstrated that the relaxation of stress in the inhomogeneous configuration is the essential driving force for the drastic damage reduction.

Furthermore, a compliant glass mechanical response in terms of characteristic material properties, i.e. elastic modulus and viscosity has been established in Figure A15 where the relative deviations of the material properties that describe the heterogeneity fall into the range of 1e-2 to 1e2. It can be observed that cracking damage is highly sensitive to stiffness but less affected by viscosity, while pore growth is strongly influenced by both characteristics. It is thus concluded that an optimal material design configuration with a high viscosity and low stiffness would be most likely to result in the lowest overall damage. Tailored material properties through the addition of reinforcement phases could help to achieve such a desirable property combination.

References
Figure A1. Linear analog of the thermo-inelastic model

Figure A2. Experimental calibration of crack propagation kinetics
Figure A3. (a) illustration of kMC model (b) kMC prediction of crack healing kinetics

Figure A4. (a) controlled healing test fixture (b) post-healing glass bar (c) four-point bending test fixture
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Figure A6. Seal performance under thermal loading predictions (a) stress distribution (b) total damage distribution (c) porosity distribution (d) crack distribution
Figure A7. Average damage evolution of the three cell-frame SCN-1 glass seals

Figure A8. Temperature contours of the SOFC stacks operated with different fuel utilization and compositions
Figure A9. Temperature contours of the SOFC stack under different thermal boundary conditions

Figure A10. Effects of electrochemical operation parameters (a) thermal boundary conditions (b) fuel utilization (c) fuel composition

Figure A11. Effects of glass viscosity when (a) cracking (b) pore evolution is dominant
Figure A12. Compliant glass sealant with a heterogeneous viscosity field

Figure A13. Comparison of crack evolution: heterogeneous glass vs. homogeneous glass
Figure A14. Comparison of pore evolution: heterogeneous glass vs. homogeneous glass

Figure A15. Mechanical response surface of the compliant glass sealant (a) resistance to cracking damage and (b) resistance to pores
Mitigation and Prediction of Spallation of Oxide Scales on Ferritic Stainless Steel

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Executive Summary

This report, which supplements and updates a previous interim report (PNNL-22191), summarizes results from experimental and modeling studies performed by researchers at Pacific Northwest National Laboratory on behalf of the Solid-State Energy Conversion Alliance (SECA) Core Technology Program. The results indicate that application of physical surface modifications, such as surface blasting, prior to application of protective surface coatings can substantially increase oxide scale spallation resistance during long-term exposure to elevated temperatures (e.g., 800-850°C). To better understand and predict the benefits of surface modification, an integrated modeling framework was developed and applied to the obtained experimental results.
Introduction
In recent years, progress in materials and fabrication techniques have allowed for a reduction in SOFC operating temperatures to a range in which commonly used oxidation-resistant alloys, such as ferritic stainless steels, can be considered as replacement materials for the traditional ceramic interconnect materials used in high temperature SOFC stacks. One candidate steel, which offers appropriate CTE, good oxidation resistance, an electrically conductive oxide scale, and relatively low cost, is AISI 441. AISI 441 is prepared via conventional melt metallurgy and is therefore less expensive than candidate steels that utilize vacuum processing to reduce the Si content to very low levels. Additions of Nb and Ti to the AISI 441 tie up residual Si in Laves phase at grain boundaries, eliminating the need for expensive processing. To reduce Cr volatility and improve scale adhesion and oxidation resistance, protective coatings, such as Ce-modified (Mn,Co)3O4 (Ce-MC) spinel, have been developed for application to the cathode side of the interconnect. Long-term testing of AISI 441 coupons coated with Ce-MC spinel has indicated stable, low area-specific resistance (ASR) for over 25,000 hours at 800°C in air. However, it was also observed that thermal cycling of spinel-coated coupons after long-term oxidation (e.g., ≥4,000 hours at 800°C) can result in spallation of the oxide scale (and the spinel coating above it) from the underlying steel substrate. The interfacial strength between the oxide scale and the substrate is crucial to the reliability and durability of the metallic interconnect in SOFC operating environments, as scale spallation could lead to increased Cr volatility and a substantial increase in electrical resistance.

To further investigate this issue, a study was initiated in order to determine whether surface treatments applied to AISI 441 prior to application of a spinel coating could result in improved oxidation/spallation resistance. Long-term oxidation tests were performed on spinel-coated steel coupons, which led to a down-selection to a preferred surface treatment (surface blasting). Subsequently, a long-term validation test of surface-blasted, spinel-coated AISI 441 was performed under realistic SOFC stack conditions using the Solid-state Energy Conversion Alliance (SECA) Core Technology Program stack test fixture. In parallel, an integrated experimental/analytical methodology for quantifying the interfacial strength between the oxide scale and metallic interconnect materials was developed, thereby establishing a modeling tool that is able to predict the life of interconnect candidate materials under typical SOFC operating conditions. This integrated approach can also be used to quantify the effects of different surface finishes, coating/oxide layer thicknesses, and different coating materials such that an optimized coating thickness and surface condition for interconnect candidates can be developed to satisfy SECA life requirements.
Surface Modification Approaches
A variety of physical surface modifications to AISI 441 were investigated to assess their potential for mitigating spallation issues. ATI Allegheny Ludlum provided sheet stock (0.02” thick) of AISI 441 with the following five surface conditions:

1. Mill reference (unmodified, except for hand polishing with #1200 grit paper)
2. De-siliconized (treated to sequester and remove silicon from the near surface of the sheet; an alternative to decreasing the Si content of the alloy)
3. Surface blasted (subjected to a grit/shot blast process to produce surface deformation)
4. Surface ground (subjected to surface abrasion to produce surface deformation)
5. Temper-rolled (subjected to a cold rolling process)

Coupons of the surface-treated steel were coated with Ce-MC spinel and subjected to oxidation testing in stagnant air at 800°C and 850°C. At 2,000 hour intervals, the coupons were cooled down to room temperature and examined. In some instances, a coupon representing one or more of the surface treatments was removed from the study for SEM/EDS evaluation, while the remaining coupons were reheated for continued testing.

Results of Long-term Oxidation Tests
Results of the oxidation study are summarized in Tables I and II for coupons oxidized at 800 and 850°C, respectively. Each row of the table summarizes observations after the designated cumulative oxidation time. The “Macrosopic Spallation” columns indicate whether or not visual inspection revealed any spallation at the scale/steel interface on any of the coupons subjected to a given surface treatment. A green color indicates that none of the coupons exhibited spallation, while an “X” with a red background indicates that spallation was observed on at least one of the coupons. A “XX” with a red background indicates that, after the listed time, no unspalled coupons remained for the given surface condition. For example, after 10,000 hours, all of the mill reference coupons being tested at 800°C had exhibited visual spallation of the oxide (and accompanying coating) from the steel substrate. The “Microscopic De-bonding” columns apply to coupons removed from the study for cross-section SEM analysis; these columns indicate whether or not the cross-section SEM analysis revealed any localized or complete (i.e., along entire length of cross section) de-bonding at the scale/steel interface. A green color indicates that the coupon exhibited no de-bonding, while an “L” with a red background indicates that localized de-bonding was observed, and a “C” with a red background indicates that complete de-bonding was observed.

The results of the oxidation tests indicated that all of the surface treatments resulted in improved spallation resistance relative to the unmodified mill reference condition. Surface blasting produced the best results, as none of the spinel-coated, surface-blasted coupons exhibited either localized de-bonding or macroscopic spallation, despite the fact that the surface blasted coupons
tended to exhibit a higher scale growth rate than most of the other surface treatments (Figure 1). A representative low magnification cross-section SEM image of a coupon oxidized for 30,000 hours at 800°C, shown in Figure 2, reveals the roughened surface morphology created by the surface blasting process, which may be at least partly responsible for the improved spallation resistance.

Cross-section SEM/EDS analysis was also performed to evaluate compositional changes in the coating over time. As would be expected thermodynamically, diffusion of Cr and Fe into the coating from the underlying scale and alloy led to an increased concentration of both elements over time. As shown in Figure 3 and Table III, after 30,000 hours at 800°C the Cr concentration in the coating was ~7-10 at%. Although this is substantial, it is much lower than would be the case for an exposed chromia-based scale. Results of Cr volatility experiments on Cr-containing MnCo spinel (being performed by a partner institution) will be reported when they become available.

**Results of Long-Term Stack Fixture Tests**

Following up on the encouraging results observed with small surface-blasted coupons, two long-term tests were performed in PNNL’s stack test fixture (Figure 4). These tests allowed the surface modification to be evaluated at a larger scale under conditions that resemble the operating conditions and environment of real-world SOFC stacks. Two tests were performed: one with an AISI 441 interconnect plate that was surface-blasted with #40 (coarse) grit, and one with a plate that was surface-blasted with #80 (fine) grit. Surface roughness measurements indicated that the #40 and #80 grits resulted in average surface roughness of 4.62 and 3.30 µm, respectively. (The roughness of the interconnect blasted with #80 grit was similar to that of the material originally provided by Allegheny Ludlum). Both interconnect plates were coated (via aerosol spray deposition) with Ce-MC spinel after the surface blasting was performed. Other stack test components included commercial anode-supported cells (5 cm x 5 cm) with LSM-based cathodes, LSM and NiO contact pastes, and de-vitrifying glass seals. The tests were performed in constant current mode at 800°C for ~6,000 hours, followed by 9 deep thermal cycles to assess the spallation resistance. While some degradation in cell performance was observed during the test, there was no indication that the degradation was related to instability of the coated interconnects. Upon completion of the tests, the cells were dis-assembled for post-test analysis. No evidence of coating or scale spallation was observed during visual inspection of the interconnect plates. Similarly, cross-section SEM analyses revealed no evidence of de-bonding at either the coating(scale or scale/steel interfaces (Figure 5).

**Interfacial Indentation Experiments**

Interfacial indentation testing has been reported as an alternative to characterize the adhesive properties for thermal spray coatings. A Vickers indenter is applied to a sample cross section to generate and propagate a crack along the interface between the coating and the substrate.
materials. The indentation load and the length of the cracks generated at the interface are then measured from a series of tests. These values can then provide a quantitative measure of the apparent fracture toughness, or interfacial strength, of the “interface material” which represents the coating adhesion. Figure 6 shows a schematic of the interfacial indentation test. The induced crack is located in the plane of the interface and has a half-penny shape.

This indentation methodology was applied to the surface-blasted (SB) and surface-ground (SG) spinel-coated AISI 441 specimens from the long-term oxidation studies at 800 and 850°C. Micro- and nano-indentation was performed on cross-sections of the SB and SG surface modified populations for which no coupons had exhibited spallation or delamination at the end of a given thermal cycle. Up to five different loads, \( P = 0.2, 0.375, 0.8, 1.2 \) and \( 1.8 \) N, were applied to each specimen with a minimum of three indents at each load. Note that the greater load ranges were not always feasible due to the indent size created. After indentation, the crack lengths, \( a \), the local oxide thickness, and the half-diagonal of each indent were measured optically as illustrated in Figure 7. Three local thickness measurements were also performed and then averaged for each indentation. The crack lengths induced on each side of the indent were also averaged.

According to Chicot et al., the relation between the crack length, \( a \), and the applied load, \( P \), is represented by a straight line for a given substrate and each coating thickness, \( e \), on a logarithmic scale. These lines will converge and intersect at a critical load \( (P_c) \) and a critical crack length \( (a_c) \) that corresponds to the cracking ability of the interface for each surface condition. It must be noted that only results obtained where the generated crack remains in the interface plane are valid. Any deviation of the crack into the coating does not correspond to delamination of the interface. Hence in our data, results with cracks that violated this condition were discarded and only indentation results where the crack remained in the interface were analyzed. The natural log of the average crack length and load applied was determined for all valid indentation data and plotted.

Also according to the proposed theory, plotting of the relationship between the applied load and the indentation diagonal for indents that do not generate cracks will produce another straight line that passes through the critical point. These data points represent the relationship corresponding to the Vickers hardness (HV) of the interface. Therefore, a linear fit of these data points at the defined slope value of 0.5 from the standard Vickers hardness (HV) equation provides another line to identify the critical intersection point.

Due to the time intensive nature of obtaining sufficient indentation data, two adaptations of the Chicot et al. methodology were made to improve the data analysis. First, local scale thickness for any given specimen did not vary enough to distinguish oxide scale thickness effects on the generated indentation crack size. Therefore, scale thickness was neglected and all cracked
Indents for a given specimen were used to obtain the first fitted line. Second, the number of indents which did not crack for a given specimen was sometimes small. Therefore, indentation data with and without cracks were used to obtain the hardness line for a given specimen when necessary. This increased the fitting statistics without significantly changing the predicted interface hardness. The intersection of the indentation data linear fit and the apparent hardness then defines the critical parameters, \(P_c\) and \(a_c\), as shown in Figure 8.

By combining the critical parameters for cracking, \(P_c\) and \(a_c\), with the interface mechanical properties, the apparent interface fracture toughness \((K_{in})\) may be defined as

\[
K_{in} = 0.015 \frac{P_c}{a_c^{3/2}} \left( \frac{E}{H} \right)^{1/2}
\]

(1)

where \(P_c\) and \(a_c\) are the coordinates of the critical point. A \((P_c, a_c)\) couple defines the visible interfacial crack initiation, where \(P_c\) is the applied load and \(a_c\) is the imprint diagonal of the indenter which equals to the crack length at this load level. The relationship \((E/H)_I\) is defined by

\[
\left( \frac{E}{H} \right)_I^{1/2} = \frac{\left( \frac{E}{H} \right)_S^{1/2}}{1 + \left( \frac{H_S}{H_c} \right)^{1/2}} + \frac{\left( \frac{E}{H} \right)_C^{1/2}}{1 + \left( \frac{H_c}{H_S} \right)^{1/2}}
\]

(2)

where \(E\) is the Young modulus, \(H\) is the hardness and the subscripts, \(S\), \(C\) and \(I\) stand for the substrate, coating and interface, respectively.

**Oxide Scale Spallation Model**

Cooling of the SOFC stack from normal operating temperatures can result in delamination, buckling and spallation of the coating system due to mismatch of coefficients of thermal expansion (CTE) between the substrate, oxide scale, and coating layers. Therefore, a general modeling framework based on stress analysis and fracture mechanics was developed to predict the mechanical reliability and lifetime of the spinel-coated surface-modified specimens under isothermal cooling and thermal cycling.

The developed framework is shown in Figure 9, where the left half indicates the required physical testing and the right half indicates the fracture mechanics-based modeling. For physical testing, the interfacial fracture toughness \(K_{ic}\) and oxide growth kinetics are used as model inputs. Using metallographically prepared specimens from the long-term heat treatment experiments, the scale growth kinetics are determined by optical measurements of scale thicknesses and the fracture toughness is estimated by the interfacial indentation experiments described above.

For the fracture mechanics-based modeling, analytical solutions were formulated to evaluate the scale/substrate interfacial toughness \(r\) and the energy release rate \(G\) for buckling driven delamination under isothermal cooling, both of which are functions of the oxide thickness \(h\). The interfacial fracture toughness \(K_{ic}\) from material testing is used to calculate the interfacial
toughness $r$. The critical oxide thickness $h_c$ at which oxide scale fails can then be found from the failure criteria $G > r$. The predicted interconnect lifetime, i.e. the time required for oxide scale to grow to the thickness $h_c$, can then be inferred from the oxide growth kinetic curves. Due to uncertainties associated with the fracture toughness derived from the indentation, a systematic method to incorporate this uncertainty into the lifetime prediction was also developed. Complete details of the analytical model developed are provided in the Appendix.

**Results of Interconnect Lifetime Sensitivity Analysis**

Using the developed experimental/analytical methodology, a parametric study was performed on the effects of various design factors such as interfacial fracture toughness $K_{ic}$, thermal expansion coefficients, coating thickness, and compressive stress on the mean interconnect (IC) lifetime. Summary results of the sensitivity analysis are:

- IC lifetime increases significantly with increasing interface fracture toughness $K_{ic}$ as expected.
- IC lifetime increases slightly with CTE of the coating layer, but decreases significantly with CTE of the substrate due to larger thermal mismatch stresses.
- IC lifetime increases almost linearly with coating layer thickness due to the additional elastic energy adsorbed by the coating layer during buckling.
- Compressive stress applied to the coating surface is beneficial to improve the interconnect lifetime, suggesting that IC regions in the active area subjected to stack preload will have a longer lifetime than unsupported regions.

**Results of Interconnect Surface Modification Analysis**

The methodology was then applied to the surface modified SS441 specimens from long-term testing at 800°C and 850°C. The predicted lifetimes and uncertainty of the various specimen conditions are shown in Figure 10. It is observed that SG specimens exhibited the highest individual strength/lifetime but also the widest range of predicted lifetime. Further analysis of the sample data indicated that no obvious trend in the predicted strength/lifetime was observed over the duration of the long term heat treatment. Also, no apparent difference between the 800°C and 850°C conditions was observed, and local oxide thickness variation at the indentation locations was not responsible for the observed strength differences. It was therefore concluded that all of the indentation data could be reasonably consolidated into SB and SG datasets.

The distributions of the interfacial stress intensity factor and critical oxide scale thickness for the SB and SG consolidated data are shown in Figure 11. The SG distribution contains two strong peaks suggesting that two different surface topologies may be present (i.e., regions of ‘good’ and ‘poor’ surface grinding). This is consistent with observations from microscopy which suggested that some regions of the SG material did not receive the same amount of grinding as others. Optimization of the SG process to eliminate the lower strength regions could result in a more uniform improvement similar to that observed in the SB material.
The predicted probability and cumulative distribution functions for both treatments are shown in Figure 12. The predicted results indicate that, if the specimen data is representative of the overall interconnect response, neither material would experience any failures through 25k hours at 800°C. The predicted failure rate of the unsupported interconnect would be ~10% at 30k hours and ~40% at 40k hours. Comparing to the long term heat treatment experiments, the model is conservative for the SB treatment as no failures were observed through 32k hours. The model is not conservative for the SG treatment. The cumulative distribution taken from the experimental SG results, where failures at 12k, 20k, and 22k hours were observed, is also shown in Figure 12b. This further supports the hypothesis that the SG application was undesirably not uniform, leading to some regions experiencing premature failure.

Conclusions

The main results from the long term heat treatment experiments and developed experimental/analytical lifetime methodology can be summarized as follows:

1. Physical surface modification of ferritic stainless steel prior to application of protective spinel coatings can significantly improve resistance to spallation at the oxide scale/steel substrate interface during long-term exposure to elevated temperatures (e.g., 800-850°C).
2. An integrated modeling framework combined with interfacial indentation experiments was established to predict the mean interconnect lifetime and its uncertainty.
3. For the specific surface modifications studied experimentally, the surface blast modification was found to be more uniform and superior to surface grinding. The predicted operating duration of an unsupported surface-modified interconnect is ~30k hours, at which point local buckling delamination may occur, possibly leading to degradation of interconnect performance. The model results are conservative relative to the experimental results, as no failures were observed through 32k hours.

In summary, a quantitative prediction of interconnect lifetime together with the associated uncertainty was implemented in a combined experimental/analytical framework to support SECA’s material development and design efforts.

Acknowledgements

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References:

Table I. Summary of results of 800°C oxidation study.

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<th>Time (h)</th>
<th>Mill Reference (1200 grit)</th>
<th>Temper Rolled</th>
<th>De-siliconized</th>
<th>Surface Grind</th>
<th>Surface Blast</th>
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X - spallation on at least one coupon
XX - no unspalled coupons left in study
C - complete de-bonding of scale of SEM/EDS sample
L - localized de-bonding of scale of SEM/EDS sample
# - coupon not removed for analysis due to limited number of coupons remaining in study
Table II. Summary of results of 850°C oxidation study.

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<td>14000</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>L</td>
<td></td>
</tr>
<tr>
<td>16000</td>
<td>XX</td>
<td>XX</td>
<td>#</td>
<td>#</td>
<td>#</td>
</tr>
<tr>
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<td>XX</td>
<td>XX</td>
<td>#</td>
<td>#</td>
<td>#</td>
</tr>
<tr>
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<tr>
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<td>XX</td>
<td>XX</td>
<td>XX</td>
<td>#</td>
<td>L</td>
</tr>
</tbody>
</table>

X - spallation on at least one coupon  
XX - no unspalled coupons left in study  
C - complete de-bonding of scale of SEM/EDS sample  
L - localized de-bonding of scale of SEM/EDS sample  
# - coupon not removed for analysis due to limited number of coupons remaining in study
Table III. EDS results for the regions shown in Figure 3 (atomic %).

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>58.74</td>
<td>0.69</td>
<td></td>
<td></td>
<td></td>
<td><strong>6.63</strong></td>
<td>16.81</td>
<td>3.90</td>
<td>13.06</td>
<td>0.18</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>58.09</td>
<td>0.67</td>
<td></td>
<td></td>
<td></td>
<td><strong>7.50</strong></td>
<td>16.58</td>
<td>3.89</td>
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<tr>
<td>Spectrum 3</td>
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<td>0.61</td>
<td></td>
<td></td>
<td></td>
<td><strong>8.15</strong></td>
<td>15.60</td>
<td>3.70</td>
<td>12.83</td>
<td>0.09</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>57.98</td>
<td>0.42</td>
<td>0.56</td>
<td></td>
<td></td>
<td><strong>9.57</strong></td>
<td>15.12</td>
<td>3.52</td>
<td>12.66</td>
<td>0.17</td>
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<tr>
<td>Spectrum 5</td>
<td>58.03</td>
<td>0.26</td>
<td>0.54</td>
<td></td>
<td></td>
<td><strong>11.55</strong></td>
<td>13.91</td>
<td>3.23</td>
<td>12.34</td>
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<td>Spectrum 6</td>
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<td>0.68</td>
<td></td>
<td></td>
<td></td>
<td><strong>9.09</strong></td>
<td>15.29</td>
<td>3.65</td>
<td>12.66</td>
<td>0.21</td>
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<td>Spectrum 7</td>
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<td>0.31</td>
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<td></td>
<td><strong>8.37</strong></td>
<td>16.28</td>
<td>3.83</td>
<td>12.99</td>
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<td>Spectrum 8</td>
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<td></td>
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<td></td>
<td><strong>35.98</strong></td>
<td>0.76</td>
<td>0.22</td>
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<tr>
<td>Spectrum 9</td>
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<td>0.26</td>
<td>0.23</td>
<td></td>
<td></td>
<td><strong>36.45</strong></td>
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<td></td>
</tr>
<tr>
<td>Spectrum 10</td>
<td>61.80</td>
<td>0.33</td>
<td></td>
<td></td>
<td></td>
<td><strong>37.00</strong></td>
<td>0.58</td>
<td>0.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum 11</td>
<td>59.46</td>
<td>0.68</td>
<td>0.66</td>
<td>0.14</td>
<td></td>
<td><strong>37.47</strong></td>
<td>0.53</td>
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<td>Spectrum 12</td>
<td>5.44</td>
<td>0.45</td>
<td>1.00</td>
<td>0.77</td>
<td></td>
<td><strong>18.07</strong></td>
<td>74.27</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Spectrum 13</td>
<td>0.51</td>
<td>1.09</td>
<td>0.65</td>
<td></td>
<td></td>
<td><strong>17.69</strong></td>
<td>80.05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Average oxide scale thickness of spinel-coated AISI 441 with the indicated surface conditions as a function of time. Samples were oxidized in air at 800°C.

Figure 2. SEM micrograph of spinel-coated AISI 441 after 30,000 hours of oxidation in air at 800°C. Deep thermal cycles were performed every 2,000 hours. The chromia-based scale (dark gray) is visible between the spinel coating (top layer, light gray) and steel substrate (bottom).
Figure 3.  SEM/EDS analysis of surface blasted, spinel-coated AISI 441 after 30,000 hours of oxidation in air at 800°C. EDS results for the indicated regions are listed in Table III.
Figure 4. Photographs showing the cell assembly for single cell stack fixture test: (A) cell sealed onto aluminized AISI 441 cell frame plate; (B) anode-side interconnect plate with welded Ni mesh, and cathode-side spinel-coated, aluminized interconnect plate; (C) hybrid mica perimeter seals; (D) assembled view with top porous alumina and bottom Inconel 600 load block and heat-exchangers.
Figure 5. Representative microstructures of the spinel-coated AISI 441 after long-term stability and thermal cycling test at 800°C: a) surface blasted with coarse grit; b) surface blasted with fine grit.
Figure 6. A schematic of the Vickers indentation test for interfacial analysis.

Figure 7. Representative image of a surface ground specimen indented at 375 mN indicating crack length measurement.

Figure 8. Representation of the cracking ability of an SB specimen exposed to 20,000h at 850°C where the critical load, $P_c$, and critical crack length, $a_c$, were determined.
Figure 9. Flow chart for IC life prediction methodology.

Figure 10. Measured mean lifetimes for SB and SG surface modified SS441 specimens at a) 800°C and b) 850°C.

Figure 11. Expected distributions of the a) interfacial stress intensity factor and b) critical oxide scale thickness for the SB and SG specimen based on experimental measurements.
Figure 12. Expected a) probability density function and b) cumulative distribution function for the SB and SG modified SS441 specimens.
Appendix

Integrated modeling framework

A schematic plot of a coated metallic interconnect (IC) with multilayers of dissimilar materials is illustrated in Figure 1. The elastic response of each layer subjected to a uniform temperature decrease \( \Delta T \) during isothermal cooling can then be given as

\[
\sigma_s = E_s \frac{E_1 h_1 (\alpha_s - \alpha_1) + E_2 h_2 (\alpha_s - \alpha_2)}{E_1 h_1 + E_2 h_2 + E_3 h_3} \Delta T
\]

\[
\sigma_1 = E_1 \frac{E_2 h_2 (\alpha_1 - \alpha_2) + E_3 h_3 (\alpha_1 - \alpha_3)}{E_1 h_1 + E_2 h_2 + E_3 h_3} \Delta T
\]

\[
\sigma_2 = E_2 \frac{E_3 h_3 (\alpha_2 - \alpha_3) + E_1 h_1 (\alpha_2 - \alpha_1)}{E_1 h_1 + E_2 h_2 + E_3 h_3} \Delta T
\]

where \( E \) is the elastic modulus, \( \alpha \) denotes the coefficient of thermal expansion (CTE), \( h \) represents the thickness, and the subscripts \( s \), 1, and 2 correspond to the substrate, oxide scale, and coating respectively.

As interfacial failures of ICs generally stem from these accumulated CTE mismatch-induced thermal stresses, two failure modes, namely buckling driven blistering and edge delamination, are commonly observed, where the first is primarily driven by the compressive stress in the adhesive thin film and the latter is caused by CTE mismatch induced shear stress. Since significant shear traction is found to be limited to the near-corner regions of the films, the buckling driven blistering is considered to be of major concern to the interfacial cracking, for which the failure criteria is typically defined as

\[
G \geq \Gamma
\]

with \( G \) denoting the energy release rate that represents the released elastic energy per unit of newly created fracture surface area and \( \Gamma \) is a critical value of \( G \).
Accounting for the buckling driven blistering of a multi-layer structure in which the substrate is significantly thicker than the adhesive thin film, an analytical plane-strain solution for the energy release rate $G$ is

$$G = \frac{(1-v_f^2)h_fE_f}{2E_f}(1 - \frac{\sigma_c}{\sigma_f})(1 + 3\frac{\sigma_c}{\sigma_f})$$

Here $v_f$ is the Poisson’s ratio and $\sigma_c$ is the critical buckling stress given by

$$\sigma_c = \frac{\pi^2}{12(1-v_f^2)} \left( \frac{h_f}{b} \right)^2$$

with $b$ denoting the size of the intrinsic interfacial blister. It should be noted that Eq. (6) is only valid when $\sigma_f \geq \sigma_c$.

One can then extend the present formulation to include the additional effects of the coating layer on the overall fracture resistance following a similar energy approach.

![Figure 2. Auxiliary buckling problem of a coated IC.](image)

The auxiliary buckling problem of a coated metallic IC illustrated in Figure 2 shows an oxide scale and a coating film clamped along their edges with no separation/slip between the coating and scale. The thermally induced compressive stress in the oxide scale brings a change to the multilayer curvature for which the corresponding deformation is given by the nonlinear Von Karman plate theory as:

$$\Delta = \frac{1}{2} \int_0^b w^2 dy = 2b^{\frac{1}{2}}(\sigma_1 - \sigma_c)$$

Therefore, the in-plane strain due to such buckled shape deformation imposed onto the coating layer can then be expressed as

$$\varepsilon^* = \frac{\Delta}{2b} = \frac{1-v_f^2}{E_f} (\sigma_1 - \sigma_c)$$

If we further denote the thermal strain within the coating layer to be $\varepsilon_2$, the elastic energy build-up in the coating layer caused by the oxide scale buckling is given as
\[ S_e = \frac{E_2}{1-\nu_2^2} \left( (\varepsilon_1 + \varepsilon_2)^2 - \varepsilon_2^2 \right) b h_2 \]  

where \( \varepsilon_2 = \frac{1-\nu_2^2}{E_2} \sigma_2 \) with \( E_2, \nu_2, \) and \( h_2 \) corresponding to the elastic modulus, Poisson’s ratio, and thickness of the coating layer.

As a result, the energy available for the buckling driven blistering fracture process is accordingly reduced. If we now re-define the original bi-layer energy release rate shown in Eq. \((5)\) as \( G_0 \), the updated \( G \) for the three-layer coated IC yields

\[ G = G_0 - \frac{1}{2} \frac{\partial S_e}{\partial b} = \frac{1}{2} \frac{1-\nu_2^2}{E_2} \left( \sigma_1 - \sigma_e \right) \left[ h_1 \left( \sigma_1 + 3\sigma_e \right) \frac{E_2}{E_1} \frac{1-\nu_2^2}{1-\nu_1^2} h_2 \left( \sigma_1 - \sigma_e \right) - 2\sigma_2 h_2 \right] \]  

It should be noted that here the critical buckling stress \( \sigma_e \) is currently assumed to be independent of the coating layer as \( h_1 \) is usually far greater than \( h_2 \) although expressions of enhanced accuracy for \( \sigma_e \) can be obtained through further finite element analyses.

Defined as the critical \( G \) for the crack tip to advance, \( \Gamma \) has been found to be strongly dependent on the mode mixity that can be expressed as: \(^5\)

\[ \Gamma = \Gamma_1 (1 + \tan^2 [(1 - \lambda)\psi]) \]  

where \( \Gamma_1 = \frac{1-\nu_2^2}{E_2} K_{IC}^2 \) is related to the apparent interfacial fracture toughness measurement \( K_{IC} \) which can be determined from indentation test, and \( \psi \) is the phase angle describing the mixity of the fracture failure Mode I and II for which a functional form can be written as

\[ \tan \psi = \frac{4 + \sqrt{3} \xi \tan \omega}{-4 \tan \omega + \sqrt{3} \xi} \]  

Here \( \xi = \sqrt{\frac{2}{3} \left( \frac{\sigma}{\sigma_e} - 1 \right)} \) and \( \omega = \omega(D_\alpha) \) is a function of the Dundurs mismatch parameter \( D_\alpha \). When similar elastic properties of the substrate and the film materials hold, \( D_\alpha = 0 \) can be approximated and \( \omega = 52.07^\circ \). \( \lambda \) reflects the mode-dependency of \( \Gamma \) and has been reported to be able to capture trends for the available experimental data sets with a value between 0.1 and 0.3. \(^3\)

Given material properties (Table 1) of the other IC components, i.e. substrate and coating, as well as the SOFC operating conditions, a typical plot of \( G \) and \( \Gamma \) with oxide scale thickness \( h_1 \) can be presented in Figure 3. Since it appears that due to the mode mixity \( \Gamma \) decreases with \( h_1 \) while \( G \) approaches to the opposite, a critical scale thickness \( h_c \) for interfacial cracking failure can then be identified based on Eq. \((4)\). Furthermore, by correlating the predicted \( h_c \) to the growth kinetics measurement of the oxide scale (shown in Figure 4), the IC lifetime to spallation failure can be finally estimated.

In the present study, the lifetime of a metallic SOFC IC of Cr-Fe-based alloy coated with a spinel protective layer has been evaluated, for which the material properties and geometric parameters are listed in Table 1 and two different surface modifications, surface ground (SG) and surface blast (SB), have been applied.
Figure 3. Typical variation of $G$ and $\Gamma$ with $h_1$.

With the $K_{IC}$ measurements given by the interfacial nano-indentation tests for SB and SG samples to be $2.5 \text{ MPa}\cdot\text{m}^{0.5}$ and $2.2 \text{ MPa}\cdot\text{m}^{0.5}$, the critical thickness $h_{cr}$ can be identified as $10.5 \mu\text{m}$ and $9.5 \mu\text{m}$ respectively.

Since the measurements of oxidation kinetics for the two types of samples shown in Figure 4 yield the linear scale thickness growth functions as

$$
    h_1 = \begin{cases} 
        1.56e^{-4}t + 4.13 & \text{coated SB sample} \\
        1.73e^{-4}t + 3.17 & \text{coated SG sample} 
    \end{cases}
$$

(15)
where $t$ is in the duration time in hours, their expected lifetime can be determined accordingly as

$$t_L = \begin{cases} 44783 & \text{coated SB sample} \\ 31173 & \text{coated SG sample} \end{cases}$$

(16)

Table 1 Material properties and geometric parameters used in the present IC lifetime estimation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Physical meaning</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_s$</td>
<td>Young’s modulus (substrate)</td>
<td>200</td>
<td>GPa</td>
</tr>
<tr>
<td>$E_1$</td>
<td>Young’s modulus (oxide)</td>
<td>250</td>
<td>GPa</td>
</tr>
<tr>
<td>$E_2$</td>
<td>Young’s modulus (coating)</td>
<td>124.7</td>
<td>GPa</td>
</tr>
<tr>
<td>$\nu_s$</td>
<td>Poisson’s ratio (substrate)</td>
<td>0.3</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>Poisson’s ratio (oxide)</td>
<td>0.27</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>Poisson’s ratio (coating)</td>
<td>0.36</td>
<td>Dimensionless</td>
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<tr>
<td>$\alpha_s$</td>
<td>Coefficient of thermal expansion (substrate)</td>
<td>$12.4\times10^{-6}$</td>
<td>1/K</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>Coefficient of thermal expansion (oxide)</td>
<td>$5.7\times10^{-6}$</td>
<td>1/K</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>Coefficient of thermal expansion (coating)</td>
<td>$11.5\times10^{-6}$</td>
<td>1/K</td>
</tr>
<tr>
<td>$h_s$</td>
<td>Thickness (substrate)</td>
<td>$5\times10^{-4}$</td>
<td>m</td>
</tr>
<tr>
<td>$h_3$</td>
<td>Thickness (coating)</td>
<td>$1.5\times10^{-5}$</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>Temperature change during stack cooling</td>
<td>775</td>
<td>K</td>
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</table>
Effects of interfacial fracture toughness $K_{IC}$ and coefficients of thermal expansion

The interfacial fracture toughness $K_{IC}$ is considered to be of major significance to the mechanical reliability of the multilayered structure.

Figure 5. Effects of interfacial fracture toughness $K_{IC}$.

Figure 5 shows the variation of $h_c$ with $K_{IC}$ for both coated and uncoated specimens, where higher $K_{IC}$ has been generally observed to yield greater $h_c$ because of the enhanced interface strength and material fracture resistance. As the protective coating layer is able to provide additional confinement to tolerate the buckling instability induced by the oxide scale, it benefits the mechanical integrity and leads to significantly larger critical thickness of oxide scale. Because the spallation induced IC failure originates from the accumulated thermal stresses during operational stack cooling, the CTEs of individual IC design components, i.e. the substrate alloy and the coating layer, are critical factors in raw material selection.

As shown in Figure 6, the predictions of the critical scale thickness $h_c$ against the thermal expansion coefficients of the substrate ($\alpha_s$) and the coating ($\alpha_2$) appear to follow opposite trends. It has been found that for both SG and SB IC specimens the critical scale thickness $h_c$ (or interconnect life) is proportionally increasing with $\alpha_2$ and significantly decreasing with $\alpha_s$, the substrate coefficient of thermal expansion.

The uncertainty associated with the lifetime prediction.

Although the measurement accuracy can be improved with advanced evaluation techniques, statistical observational errors are still usually inevitable. Quantification of the influence of such input uncertainties on the outcome projections then becomes important to evaluate the predictive confidence level. The uncertainty in interconnect life prediction introduced from the indentation data can be quantitatively determined. The proposed methodology is able to predict both the mean value and the associated uncertainty for critical scale thickness and interconnect life time. The current modeling methodology takes the fracture toughness values measured from indentation test as the input to predict the lifetime of
interconnect. Uncertainties associated with the calculation of the interfacial roughness from the indentation data can be important to the prediction of interconnect lifetime. A systematic method to incorporate this uncertainty into the lifetime prediction was developed. In this section, indentation results from 10,000 h 800°C specimens are used as an example to demonstrate the method (Figure 7).

Figure 6. Effects of thermal expansion coefficient.

Figure 7. Determination of $a_c$ and $p_c$ from indentation data.
First, we have classified the indentation data into the data set “No Crack” and the data set “w/ Crack”. Two lines are obtained by linear fitting the “No Crack” and the “w/ Crack” data. The critical indentation load \( p_c \) and crack length \( a_c \) can be obtained as the interception of the two lines. The mean and the variance of the interception and slope of each line can be obtained from the linear regression analysis that was shown in the following table.

<table>
<thead>
<tr>
<th></th>
<th>Intercept (mean)</th>
<th>Intercept (std)</th>
<th>Slope (mean)</th>
<th>Slope (std)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Crack</td>
<td>2.30199</td>
<td>0.04866</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>W/ Crack</td>
<td>2.97471</td>
<td>0.2499</td>
<td>0.87692</td>
<td>0.38978</td>
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</table>

Next, from the mean and the standard deviation of slope and intercept of two lines, a Monte Carlo simulation can be run to generate replicas. For each replica, the critical indentation load \( p_c \) and the crack length \( a_c \) can be computed. The fracture toughness value can be further calculated for each set of \( p_c \) and \( a_c \) from Eq. (13). The mean and standard deviation of \( p_c \), \( a_c \), and \( K_I \) for 10,000 hrs at 800°C are summarized in the next table. The probability distributions of \( p_c \), \( a_c \), and \( K_I \) are also shown in Figure 8.

\[
K_{II} = 0.015 \frac{p_c}{a_c^{3/2}} \left( \frac{E}{H} \right)^{1/2}
\]

(13)

<table>
<thead>
<tr>
<th></th>
<th>ln(( p_c ))</th>
<th>ln(( a_c ))</th>
<th>( K_I )</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
<td>-1.7826</td>
<td>1.4106</td>
<td>2.9937</td>
</tr>
<tr>
<td>std</td>
<td>0.6753</td>
<td>0.3501</td>
<td>0.5121</td>
</tr>
</tbody>
</table>

Figure 8. Probability distribution function of \( p_c \), \( a_c \) and toughness \( K_I \).
Thirdly, the critical scale thickness $h_c$ can be calculated for each fracture toughness value $K_I$ using the interconnect lifetime model. For a given coating thickness and lateral stress, the calculated mean and standard deviation of $h_c$, and its probability distribution are shown in Figure 9 and the accompanying table.

![Probability distribution of critical thickness $h_c$.](image)

<table>
<thead>
<tr>
<th>$h_c$ (µm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
<td>12.76</td>
</tr>
<tr>
<td>std</td>
<td>2.51</td>
</tr>
</tbody>
</table>

Finally, the interconnect lifetime mean, standard deviation and its probability distribution can be determined from the oxidation kinetic curves (shown in Figure 4) with computed critical scale thickness $h_c$. The oxidation kinetics measured from experiment was shown in Figure 4 for both surface blast (red symbol) and surface ground (green symbol). Therefore, the predicted interconnect lifetime and associated uncertainty can be estimated from the indentation data at 10,000hrs and 800C. The probability distribution and the cumulative distribution of interconnect lifetime were shown in the Figures 10 and 11. Up to this stage, we have demonstrated the methodology to predict the lifetime of interconnect using the indentation data with associated uncertainty of the prediction.
Figure 10. Probability distribution function of predicted interconnect life time.

Figure 11. Cumulative distribution function of predicted interconnect life time.

**Effect of coating thickness on the interconnect lifetime**

Since it has been demonstrated that two beneficial effects on interconnect lifetime can be typically expected from the coating layer, i.e. slower oxide growth rate and improved mechanical stability, the overall effect of the coating layer on the critical scale thickness can be studied. The variations of critical scale thickness $h_c$ with coating thickness $h_2$ for the two surface modifications, i.e. SG and SB, are shown in Figure 12. A monotonic proportional correlation between these two metrics has been observed, indicating that the thicker coating will generally strengthen the structure and increase the interconnect life time.
Effect of lateral compressive stress on the oxide scale failure and interconnect lifetime

There could be lateral compressive stress applied on the coating for in-situ SOFC, as shown in Figure 13. In order to quantitatively consider the effect of this lateral compressive stress on the scale failure and interconnect lifetime, the energy release rate must be reformulated to include the terms due to the lateral compressive stress.

First, the work done by the lateral compressive stress, or equivalently the increase in the potential energy while buckling is

\[ S_w = \int_{-b}^{b} \sigma_z w(x) \, dx \]  \hspace{1cm} (14)
\[ S_w = \sigma_z \delta b \]  

\[ \frac{\partial S_w}{2 \partial b} = \frac{\sigma_z \delta}{2} \]  

(15)

where \( \sigma_z \) is the lateral compressive stress, \( w \) is the lateral deformation due to buckling, \( \delta \) is the maximum deformation and \( b \) is the half size of the blister.

The energy release rate due to the lateral compressive stress can be written as:

\[ G = G^0 - \frac{1}{2} \frac{\partial S_w}{\partial b} - \frac{1}{2} \frac{\partial S_w}{\partial b} \]  

(17)

The total energy release rate can be written as:

with the first term representing the contribution from the scale, second term for the coating, and the third term from lateral stress, respectively. The modified interconnect model was implemented numerically. The modeling results are plotted in the next three figures.

Figure 14 shows the variation of the scale critical thickness with the coating thickness for different level of later compressive stresses. With increasing lateral compressive stress, the critical thickness (or equivalently the interconnect lifetime) is increasing. For a compressive stress of 0.2MPa, there is negligible increase in the critical thickness. The can also be shown in Figures 15 and 16, where critical thickness and lifetime were plotted against the lateral stress directly.

Figure 14. Variations of scale critical thickness with coating thickness for different later stresses.
Critical scale thickness ($\mu$m)

Lateral stress (MPa)

$K_c = 2.2 \text{MPa m}^{1/2}$

$h_c = 15 \mu m$

Figure 15. Variation of critical thickness $h_c$ with lateral stress.

Interconnect Life at 800 °C, Surface Blast

Life (Hours)

Lateral Stress (MPa)

Figure 16. Variation of interconnect life time with lateral stress.

References

SECA Core Program – Recent Development of Modeling Activities at PNNL

MA Khaleel
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KP Recknagle, DR Rector, J Deibler, RT Pagh, RE Williford, LA Chick

Pacific Northwest National Laboratory
Richland, WA 99352

June 19, 2002
Technical Issues and R&D Objectives

- Technical Issues
  - Concurrent management and control of thermal, physical, chemical and electrochemical processes over various SOFC operational parameters.

- Objectives
  Develop modeling and simulation tools to be used by the SECA vertical teams as an integral part of the design process. Tools to be used for:
    - System design requirements roll-out
    - Sub-system component design
    - Microstructural and material design/optimization
    - Control design
    - Life prediction
**Technical Approach**

Flow Analysis

Thermal Analysis

Stress Analysis

**Electrical Power System**

**Tools and Methodologies for Rapid start-up**

Modeling levels

**Thermal system**

**Stack**

**Validation and Property measurement**

**Cell**

**Cell-level**

**Continuum-level electrochemistry**

**Flow, thermal & Electrochemistry analysis**

**Power density profile**

**H2O concentration**

**Methane distribution**

**Thermal Shock**

**Battelle**

**HEAT GENERATION**

- H2 97.0% 0.970 W/cm²
- CO 0.0% -0.2088 W/cm²
- H2O 3.0% (Minus sign denotes exotherm)
- CO2 0.0% i = 0.5 A/cm²
- N2 0.0% Vi = 0.869 volts
- Total 100.0% P= 0.00 kW 1.65 W

**Fraction of CO that is water-gas shifted** = 0.5
**Fuel Utilization** = 6.82%

**Molar %**

- H2 1.44E-04 97.00%
- CO 9.64E-10 0.00%
- H2O 4.46E-06 3.00%
- CO2 3.64E-11 0.00%
- N2 4.13E-21 0.00%
- CH4 0.00E+00 0.00%

**Electrolyte** = 10 na na

**Active cell area** = 3.8 cm²

**Electrode**

- Anode = 600 30 2.50
- Cathode = 50 30 2.50

**Contact Resistance** = 0 Ohm-cm²

**Average Stack Temp** = 750 °C

**Inlet Temp** 1023 K 750 °C

**Outlet Temp** 1023 K

**B-V Parameters**:

- α = 0.518
- Px = 127
- QH₂ = 0.425
- Eact = 110
- Dsurf-H₂ = 0.0107 mol/sec

**O₂**

- 4.50E-05 0.21
- 4.01E-05 0.19

**N₂**

- 1.69E-04 0.79
- 1.69E-04 0.81

**Total**

- 0.0002 1.00
- 2.09E-04 1.00

**Temperature**

- 200 sccm
- 1.49E-04 mol/s

- 100.0%
Cell Electrochemistry Performance Model

### Input Parameters:
- Fuel composition and flow rate
- Temperature
- Adjustable cell parameters

### Output Data:
- I-V curve and power
- Heat generation
- Fuel utilization and exhaust composition

#### Fuel Gas Input Parameters

<table>
<thead>
<tr>
<th>Fuel Stream</th>
<th>mol/sec</th>
<th>Molar %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>1.44E-04</td>
<td>97.00%</td>
</tr>
<tr>
<td>CO</td>
<td>9.64E-10</td>
<td>0.00%</td>
</tr>
<tr>
<td>H2O</td>
<td>4.46E-06</td>
<td>3.00%</td>
</tr>
<tr>
<td>CO2</td>
<td>3.64E-11</td>
<td>0.00%</td>
</tr>
<tr>
<td>N2</td>
<td>4.13E-21</td>
<td>0.00%</td>
</tr>
<tr>
<td>CH4</td>
<td>0.00E+00</td>
<td>0.00%</td>
</tr>
<tr>
<td>PO2</td>
<td>------</td>
<td>1.67E-23</td>
</tr>
<tr>
<td>Total</td>
<td>1.49E-04</td>
<td>1.00E+00</td>
</tr>
</tbody>
</table>

#### Active cell area:
- 3.8 cm²

#### Fraction of CO that is water-gas shifted = 0.5

#### Fuel Utilization = 6.82%

#### Fuel Stream Parameters:
- 750 °C Inlet Temp
- 1023 K
- 750 °C Inlet Temp
- 1023 K

#### Cathode Inlet Gas Stream:
- O2: 4.50E-05, P: 0.21 atm
- N2: 1.69E-04, P: 0.79 atm
- Total: 0.0002, P: 1.00 atm

#### Cathode Outlet Gas Stream:
- O2: 4.01E-05, P: 0.19 atm
- N2: 1.69E-04, P: 0.81 atm
- Total: 2.09E-04, P: 1.00 atm

#### Contact Resistance:
- 0 Ohm-cm²

#### Offset voltage due to leak:
- -0.06

#### B-V Parameters:
- α = 0.518
- Pₓ = 127
- Qₓ² = 0.425
- Eact = 110
- Dsurf = 0.0107

#### Electric Work

#### HEAT GENERATION
- -0.2088 W/cm²

(Minus sign denotes exotherm)
Model Output

- Cell parameters can be adjusted so that one set of cell parameters provide excellent fit of a family of IV curves for a “unit” cell operated over a range of temperatures and a range of hydrogen concentrations.
- The “calibrated” model can then be used to predict large stack performance by applying it within a CFD code to computational unit cells.
Topics for Continuum Electrochemistry Modeling

- Calculation Flow Diagram For 1-Cell Stack
- Generic Cross-Flow Case
- Alternate Flow Configurations
- Transition from Transient Heating to Steady State
- Calculation Flow Diagram For Multiple-Cell Stacks
- Multiple Cell Stack Modeling Results
STAR-CD/EC (1-Cell Stack) Flow Diagram

- **STAR-CD**
  - Temperature, Gas Chemistry (mass conc.), Model Geometry
  - Source Terms: SORSCA, FLUINJ, SORENT
    - Scalar, Mass, Enthalpy

- **POSDAT**
  - T, pp(i)
  - Cell Voltage
  - (Source Terms)

- **EC**
  - Current, Scalar (molar), and Enthalpy source terms
MARC/EC (1-Cell Stack) Flow Diagram

MARC
Flow - Thermal - Electrical - Mechanical

FLUX
Heat Flux
Update State Variables

PLOT

ELEVAR

STRESSES
Model Geometry, Temperature, Current Distribution

EC
Cell Voltage
Gas, Chemistry, Heat Generation

T, pp(i)
Cross-Flow Case: Conditions

- Inflow Air & Fuel Temperature = 625°C
- Air delivery rate = 15 gm/sec/60cells
- Fuel delivery rate = 1.08 gm/sec/60cells (9.5x10^-4 moles/sec)
  - Composition: shifted to equilibrium at 625 °C
    - [H2] = 0.37443
    - [H2O] = 0.03449
    - [CO] = 0.33662
    - [CO2] = 0.06759
    - [N2] = 0.18687
- Cell Voltage = 0.7 (as in all other cases)
- Cyclic boundary conditions at top and bottom of unit cell.
Cross-Flow Case: Results

62% Fuel Utilization Case:
- Current Density = 0.300-1.46 (0.687 A/cm²)
- Heat Generation = 0.21 - 0.99 (0.477 W/cm²)
- PEN Temperature = 643 - 912 (769 °C)

Fuel Utilization = 61.7%
Cross-Flow Case: Results (Continued)

CO\textsubscript{2}, Mass Fraction

H\textsubscript{2}O, Mass Fraction

CO, Mass Fraction

Heat Generation, W/cm\textsuperscript{2}

PROSTAR 3.10
31 Dec 60
GC S-CO
TIME = 24:3100
LOCAL MIN. = 2236
LOCAL MAX. = 3486-01
PRESENTATION GRID

PROSTAR 3.10
31 Dec 60
GC S-CO2
TIME = 24:3100
LOCAL MIN. = 5504
LOCAL MAX. = 1336
PRESENTATION GRID

PROSTAR 3.10
31 Dec 60
GC H2O
TIME = 24:3100
LOCAL MIN. = 1015
LOCAL MAX. = 3486-01
PRESENTATION GRID

PROSTAR 3.10
31 Dec 60
GC W/cm\textsuperscript{2}
TIME = 24:3100
LOCAL MIN. = 2300
LOCAL MAX. = 3486
PRESENTATION GRID
## Alternate Flow Configurations – Steady State

<table>
<thead>
<tr>
<th>Flow Configuration</th>
<th>Conditions</th>
<th>Results</th>
<th>Fuel Utilization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air delivery, gm/s @ °C</td>
<td>Fuel delivery, gm/s @ °C</td>
<td>∆T&lt;sub&gt;PEN&lt;/sub&gt;, °C</td>
</tr>
<tr>
<td>Cross-flow</td>
<td>0.25 @ 625</td>
<td>0.018 @ 625</td>
<td>269</td>
</tr>
<tr>
<td>Co-flow</td>
<td>0.25 @ 625</td>
<td>0.018 @ 625</td>
<td>184</td>
</tr>
<tr>
<td>Counter-flow</td>
<td>0.25 @ 595</td>
<td>0.018 @ 595</td>
<td>267</td>
</tr>
</tbody>
</table>
Alternate Flow Configurations – Steady State

CROSS-FLOW

CO-FLOW

COUNTER-FLOW

Temperature, Degrees C
(\Delta T=180 \text{ co-} \Delta T=270 \text{ cross-})

Current Density, A/cm²

H₂ Mass Conc., kg/kg

Battelle
Modeling of Transition from Transient to Steady State – Cross Flow Case

Start with Transient Temperatures (temperature range ~900-1075K)

- Is the heating method sound?
- Will start of reaction cause instabilities?
- Can we actually shorten the “startup” time?

(temperature range = 931-1185K)
STAR-CD/EC (Multiple-Cell) Flow Diagram

1-cell stack

- STAR-CD
  - Temperature, Gas Chemistry (mass conc.)
  - Model Geometry
- Source Terms
  - SORSCA
  - FLUINJ
  - SORENT
  - T, pp(i)
  - Current, Scalar (molar), and Enthalpy source terms

Adjust Cell Voltage

Sum over cell to get total cell current
Cell Current = Stack Current?

Multiple-Cell Stack
Is an extension of
The 1-cell stack calculation
Steady State: 16-Cell Stack Model

Fuel Delivery: 8E-6 kg/s/cell @ 944K
Air Delivery: 0.25 kg/s/cell @ 944K

Output:
245 mW/cm²
Tcell(ave) = 751°C

Full 3-D Temperature dataset available for computing thermal stress
Topics for Microstructural Electrochemistry

- Method.
- Advantages.
- Sample simulation results.
  - Reaction zones in the anode
  - Internal reformation
Effective Property Method

- Discretize gas channels, electrodes and electrolyte into nodes with 5-25 µm thickness
- Each node has effective transport and reaction properties (gas diffusion, surface diffusion, surface area density, TPB density, etc.)
- Solve flow and transport equations using lattice Boltzmann to obtain three-dimensional distributions for
  - Gas velocity, density
  - Gas species concentrations
  - Adsorbed species, solid diffusing species (oxygen)
  - Energy, temperature
Microstructural Electrochemistry Method

- Geometry may be generated using statistical data taken from digitized pictures of the porous material.
- Properties include effective gas diffusion, surface diffusion, solid diffusion, triple phase boundary density, etc.
- Effective properties may be determined using lattice Boltzmann simulations of the discrete microstructure.
Advantages

- Spatially varying electrode properties
- Parallel transport paths for oxygen (gas, surface, solid)
- Distributed reaction zones (TPB, internal reformation)
- Link cell performance to electrode microstructure
Simulation Results from Effective Property Model

- Fuel Channel
- Anode
- Cathode
- Air Channel

800 nodes

\[ \Delta X = 10\mu m \]
Internal Reformation

- Methane distribution
  - Methane is continually depleted
  - Gradient is driving it to surface
  - Methane is reformed upon contact with Anode surface
  - High diffusion into the channel
  - And low diffusion into the anode

- Hydrogen distribution
Topics for Start-up

- Start-up issues and challenges.
- Computational tools for start-up simulations and stack design.
- Thermal controller for rapid heating of stacks.
- Structural parametric results.
- Optimization studies
- Experimental validation of structural models.
Rapid Start-up Issues for SOFC

- Flow through stack must be “uniformly” distributed.
- Maintain thermal stresses within material set strength.
- Stack pressure drop to be small.
- Minimize time to heat stack to initiation temperature of 700 °C (within a few minutes ultimately)
- Issues necessitate survey of designs, with given material set, to discover working options ...Stack Geometry, Gas channel and manifold dimensions, flow configurations.
Transient simulations
Target Structure – Basic Planar Stack Design

Design Variables
• Gas flow distribution channel dimensions/types
• Ceramic or metallic interconnect
• Material thickness
• PEN strength
• Rigid or compression seals
• Manifold dimensions
• Flow configuration
Transient - Rapid Start-up
Thermal-Fluids Stack Model

Air - Inflow manifold
Air - (porous media)
2.5mm channel ht
Fuel - Outflow manifold
Metallic or Ceramic Interconnect
Positive-Electrolyte-Negative (PEN) Composite in Model

470,000 computational cells
36 hours (x8 CPU) for 5 min

Fluid cells removed
Stack Model with Temperature Control, Modified Geometry and Boundary Conditions

Non-Uniform stack flow and heating.....

Would also mean non-uniform reactions and heating during steady operation.

Fix: increased outlet manifold dimension

- Flow channel height shortened to (1.5mm)
- User routine defined free convection BC at walls (T_e)
- User routine defined temperature control
Prediction of Temperature Distribution and Subsequent Thermal Stresses

Temperatures from CFD model

Stresses in various Components From FEA Models

Guidance for Modifications:
• Heating Method
• Flow Channels
• Manifold Dimensions

Updated Geometry or Boundary Conditions. New CFD Prediction of Flow and Temperature
Temperature Controller

- CFD model is run with standard controller to generate temperature distribution
- FEA modeling performed using temperature distribution to determine maximum PEN ΔT allowed based upon strength of material
- CFD model is re-run using optimized temperature controller to meet the maximum ΔT at each average PEN temperature

<table>
<thead>
<tr>
<th>Ave Pen</th>
<th>Pen ΔT</th>
</tr>
</thead>
<tbody>
<tr>
<td>523</td>
<td>504</td>
</tr>
<tr>
<td>640</td>
<td>380</td>
</tr>
<tr>
<td>724</td>
<td>245</td>
</tr>
</tbody>
</table>
Optimization studies

- Controller for heat-up time optimization
- Geometrical optimization
- Optimization of mesh stiffness

Bounding (minimum) heat-up is the order of 10 minutes (heat rate of 19.6 KJ/sec and total heat input of 6.81 MJ)
Effect of Temperature Profile and Seal Compliance on Stresses in the PEN

- Linear - PEN
- Parabolic - PEN
- Linear - stack
- Parabolic - stack

1:1 100/10 Stack (18.4 MPa)
1:1 Linear Temp Stack (15.7 MPa)
Effect of Temperature Profile and Seal Compliance on Stresses in the PEN

CROSS-FLOW

CO-FLOW

COUNTER-FLOW

Tave = 771°C
\(\Delta T = 250°C\)

T ave = 761°C
\(\Delta T = 183°C\)

T ave = 756°C
\(\Delta T = 265°C\)

\[\sigma \text{ MPa} \]

\[\kappa \]

Counter flow

Co flow

Cross flow
## Layered model results

<table>
<thead>
<tr>
<th>Design</th>
<th>Anode stress (MPa)</th>
<th>Vertical Deflection (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross flow</td>
<td>27.3</td>
<td>0.031</td>
</tr>
<tr>
<td>Co - flow</td>
<td>10.3</td>
<td>0.035</td>
</tr>
<tr>
<td>Counter flow</td>
<td>26.3</td>
<td>0.063</td>
</tr>
</tbody>
</table>

**PEN out-of-plane deflection**

**Anode principal stress (Pa)**
## Results 3-Stack Simulations

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Bottom</th>
<th>Top</th>
<th>Anode $\sigma_1$ MPa</th>
<th>SS $\sigma_{eqv}$ MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% (A)</td>
<td>24</td>
<td>22</td>
<td>370</td>
<td>547</td>
</tr>
<tr>
<td>0.001% (D)</td>
<td>49.6</td>
<td>32.4</td>
<td>313</td>
<td>609</td>
</tr>
<tr>
<td>0.001% (E)</td>
<td>56.4</td>
<td>33.8</td>
<td>410</td>
<td>585</td>
</tr>
<tr>
<td>Simple BC</td>
<td>52.5</td>
<td>28.9</td>
<td>326</td>
<td>617</td>
</tr>
</tbody>
</table>

- Will the stack survive thermal stresses? (based on stress/strength failure criteria)
- What is the effect of out of plane stiffness?
- Will softer glass reduce stresses?
- How do the B.C.’s change stress profiles?
Experimental Validation of Structural Modeling

Rapid (<30 sec.) heating of ceramic PEN to 700°C with 20 KW infrared heaters. Temperature profile controlled with parabolic shaped mask.

Infrared image of temperature profile

Finite element modeling of test
Applicability to SOFC Commercialization

- Modeling tools developed by PNNL for design, optimization and operation of SOFC materials, stacks and systems.
- Engineering insights and guidance regarding SOFC materials, stacks and systems.
Future Activities

- Enhancement of continuum level electrochemistry models for full stacks and steady state parametric studies.
- Micro-structural level electrochemistry for microstructural optimization and simulating internal reformation
- Predictive models for strength and life
- Material properties and model correlation/validation.
Jeff Stevenson
Pacific Northwest National Laboratory
Richland, WA 99352

Presented at the SECA CTP Review Meeting
Pittsburgh, PA, June 18, 2002
Topical Outline

- SOFC Component Development Activities
  - 1. Cells
    - Advanced Cathode Materials Development – Steve Simner
    - Advanced Anode Materials Development – Olga Marina
  - 2. Metallic Interconnect Development – Gary Yang (Scott Weil, Dean Paxton)
  - 3. Compressive Seal Development – Matt Chou

- (SOFC Modeling discussed in Moe Khaleel’s presentation)
SOFC Cathode Materials Development
Cathode Materials Development

- **Objective:** Develop and optimize high performance, stable cathode materials for intermediate temperature SOFC.

- **Approach:**
  - Synthesis (glycine-nitrate) and characterization of candidate cathode powders (XRD, dilatometry, SEM, PSA, TGA, electrical conductivity)
  - Fabrication of cathodes on anode-supported membranes via screen printing and sintering
  - Evaluation of cathode performance by electrochemical testing and SEM
SOFC Cathode Material Challenges

- Intrinsic Properties
  - High electrocatalytic activity towards oxygen reduction
    - High ionic conductivity, high surface exchange kinetics
  - Thermal expansion compatible with other SOFC materials
  - Minimal chemical interaction with the electrolyte and interconnect materials during fabrication and operation
  - High electronic conductivity

- Processing Related
  - Porous, stable microstructure to allow gas transport
  - Optimized interfacial microstructure to maximize oxygen reduction kinetics:
    - \( \frac{1}{2} O_2 (g) + 2 e^- (\text{cathode}) \rightarrow O^2- (\text{electrolyte}) \)
  - Stability (chemical, phase, microstructural, dimensional) at high temperature in oxidizing atmosphere (1 to 10^{-6} \text{ atm.} P(\text{O}_2))
  - Adhesion to electrolyte surface – dependent on sintering temperature
  - Ease of fabrication
  - Low cost
Gas Flow Rates
Anode: 200 sccm H₂-3%H₂O
Cathode: 300 sccm air
Advantages of LSF Cathode

- Mixed ionic-electronic conduction
  - High oxygen diffusion coefficient, $D$, and surface exchange coefficient, $k$, relative to LSM.

- Potentially reduces cathodic polarization by extending the cathodic reaction sites beyond the triple phase boundaries (TPB).

Data from PNNL and other sources
Advantages of LSF Cathode

- TEC is compatible with other cell/stack components
- High electronic conductivity (similar to LSM)

PNNL Data
Introduction of a ceria interlayer substantially improves the performance.

Mixtures of LSF and YSZ, heated to 1300°C for 2 h, showed no evidence of zirconate formation. LSF peaks were shifted somewhat, possibly due to change in oxygen nonstoichiometry. Enhanced performance may be due to high ionic conductivity and surface exchange kinetics of the ceria vs. zirconia.
Anode-supported cell w/ LSF-20 cathode

Cell: LSF Cathode / SDC Interlayer / YSZ Electrolyte / Ni-YSZ anode

Fuel: 97% H₂ / 3% H₂O (Low Fuel Utilization)

Oxidant: Air

Achieving Further Improvement

- LSF demonstrates good performance and stability, but requires further improvement:
  
  1) LSF – SDC mixtures
     - Optimize composition and morphology
  
  2) Engineering ceria layer
     - Optimize density, thickness, surface texture
  
  3) Compositional modification of LSF: e.g., B-site dopants

Advantage of LSF-SDC mixtures:
no “burn-in” period during initial operation
SOFC Anode Materials Development
SOFC Anodes:
Advantages and Disadvantages of Ni/YSZ Anode

Advantages:
- Relatively inexpensive; chemically and physically compatible with YSZ electrolyte
- High electronic conductivity
- High catalytic activity for fuel oxidation and for steam reforming of methane
- With these advantages, conventional Ni/YSZ cermet has proven adequate for operation on clean H₂ or fully reformed fuels

Disadvantages:
- Unstable in oxidizing atmosphere at high temperatures
- Easily poisoned by sulfur
- Tends to promote carbon deposition during internal reforming; high catalytic activity for steam reforming can cause excessive thermal gradients
- Sintering during operation (particularly at high steam partial pressures occurring at high fuel utilization) may decrease activity of anode-electrolyte interface; may cause warping in anode-supported cells
Advanced Red/Ox Tolerant Anode

Objective: Develop alternative to Ni-based anode that offers higher tolerance to oxidizing environments (to allow fuel to be turned off during system startup and shutdown) and tolerance to sulfur-containing environments

Approach:
- Synthesis (glycine-nitrate) and characterization of candidate anode powders
- Fabrication of anodes on electrolyte-supported cells via screen printing and sintering
- Evaluate candidate oxide materials using electrical conductivity measurements, 2- and 3-electrode cell tests (I-V, impedance spectroscopy), dilatometry, XRD, SEM
Candidate Material for Oxidation Tolerant Anodes

- La-doped SrTiO$_3$
  - Reasonable electrical conductivity (up to 15 S/cm)
  - Dimensional and chemical stability under redox cycling
  - TEC match to SOFC components
  - But, LST exhibits poor activity for hydrogen oxidation

I: Exposure to reducing environment at 1000ºC (corresponding to SOFC anode environment during operation)

II: Exposure to air during thermal cycling (corresponding to conditions an unprotected anode would experience during system startup and shutdown)
Half-cell polarization curves

- LST exhibits poor anodic performance
  - low catalytic activity
- Approaches to improve performance:
  - Adding a catalytically active second phase
  - B-site doping
### Polarization resistances at the doped SrTiO$_3$ / YSZ interface at 850°C in H$_2$/H$_2$O=97/3 vs. Pt/air

<table>
<thead>
<tr>
<th>Anode composition</th>
<th>$T_{sint}$, °C</th>
<th>$R_p$, Ωcm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.35}$Sr$</em>{0.65}$TiO$_3$</td>
<td>1000</td>
<td>52</td>
</tr>
<tr>
<td>La$<em>{0.4}$Sr$</em>{0.6}$TiO$_3$</td>
<td>1000</td>
<td>44</td>
</tr>
<tr>
<td>5 wt% Ni+ La$<em>{0.4}$Sr$</em>{0.6}$TiO$_3$</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>La$<em>{0.35}$Sr$</em>{0.65}$Ti$<em>{0.8}$Ni$</em>{0.2}$O$_3$</td>
<td>1000</td>
<td>48</td>
</tr>
<tr>
<td>La$<em>{0.35}$Sr$</em>{0.65}$Ti$<em>{0.8}$Co$</em>{0.2}$O$_3$</td>
<td>1000</td>
<td>39</td>
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<tr>
<td>La$<em>{0.35}$Sr$</em>{0.65}$Ti$<em>{0.8}$Cu$</em>{0.2}$O$_3$</td>
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<td>60</td>
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<tr>
<td>La$<em>{0.35}$Sr$</em>{0.65}$Ti$<em>{0.8}$Cr$</em>{0.2}$O$_3$</td>
<td>1000</td>
<td>47</td>
</tr>
<tr>
<td>La$<em>{0.35}$Sr$</em>{0.65}$Ti$<em>{0.8}$Fe$</em>{0.2}$O$_3$</td>
<td>1000</td>
<td>21</td>
</tr>
<tr>
<td>(La,Sr)(Ti,Ce)O$_3$, Ti/Ce=19</td>
<td>1000</td>
<td>1.5</td>
</tr>
<tr>
<td>(La,Sr)(Ti,Ce)O$_3$, Ti/Ce=9</td>
<td>1000</td>
<td>0.4</td>
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<tr>
<td>(La,Sr)(Ti,Ce)O$_3$, Ti/Ce=5.7</td>
<td>1000</td>
<td>0.3</td>
</tr>
<tr>
<td>(La,Sr)(Ti,Ce)O$_3$, Ti/Ce=4</td>
<td>1000</td>
<td>0.2</td>
</tr>
<tr>
<td>(La,Sr)(Ti,Ce)O$_3$, Ti/Ce=1</td>
<td>1000</td>
<td>3.6</td>
</tr>
<tr>
<td>(La,Sr)(Ti,Ce)O$_3$, Ti/Ce=4, Sr/La=9</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>(Y,Sr)(Ti,Nd)O$_3$</td>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>(Y,Sr)(Ti,Pr)O$_3$</td>
<td>1000</td>
<td>43</td>
</tr>
<tr>
<td>(Y,Sr)(Ti,Ce)O$_3$</td>
<td>1000</td>
<td>16</td>
</tr>
</tbody>
</table>
XRD patterns (calcined 1200°C/1h)
All-ceramic SOFCs: Electrochemical Performance

**Fuel:** H₂/H₂O = 97/3 (Low Utilization)

**Oxidant:** Air
Work in progress / Future work

- Optimize composite phases for electrical conductivity and electrocatalytic activity
- Perform sulfur tolerance tests
- Perform long-term carbon tolerance test
- Test steam-reforming of methane and higher hydrocarbon fuels
- Determine mechanical properties
SOFC Interconnect Development
SOFC Interconnects: Challenges

Mechanical and chemical stability:

- High temperature oxidation/corrosion resistance
- Multi component gas streams (H₂O, CO₂, O₂ etc.)
- Changing fuel composition (as result of fuel utilization)
- Simultaneous fuel and oxidant gas exposures
- Isothermal (high temperature) and thermal cyclic exposures

Low resistance path for electric current
Low materials and fabrication cost

Preferred high temperature interconnect material: Doped lanthanum chromite
High temperature alloys may satisfy these requirements for lower temperature (<800°C) SOFC stacks
Metallic Interconnects for SOFC

Objectives:
1. Identify and quantify degradation processes in candidate alloys
2. Develop a cost effective optimized material (bulk and/or coatings development) for intermediate temperature operation.

Approach:
- Pre-screening of candidate alloys (completed)
- Screen testing (evaluation of chemical, electrical, mechanical properties)
- Materials development
Overall, heat resistant alloys could be potential candidates, including:

- Ferritic stainless steels
- Austenitic stainless steels
- Fe-Ni-base superalloys
- Ni-Fe-base superalloys
- Cr-base alloys
- Co-base superalloys
Pre-selection process

Data collection/
Literature studies

From handbooks, textbook, journal
publications, producer’s WebPages, etc

Properties Database*

Compilation of composition and property
information of about three hundred heat
resistant alloys.

Pre-selection of
Candidate Alloys

Composition criteria for pre-selection
➢ Chromia formers
\[ Cr \geq 18 \text{ wt}\% \text{ for Ni- and Fe-bases;} \]
\[ Cr \geq 22 \text{ wt}\% \text{ for Co-bases;} \]
➢ Alumina formers
\[ Al \geq 3\sim4 \text{ wt}\% \]
\[ Cr \geq 15 \text{ wt}\% \]

*Available upon request
Screen testing of candidate alloys

**Selected alloys**
- Ni-Fe-base superalloys: G-30, Nicrofer 6025, Haynes 230, Haynes 214, Rene 41;
- Fe-Ni-base superalloys: Haynes 120, Pyromet, Haynes 556;
- Ferritic stainless steels: 430, 446, Ebrite, 29-4C, Al 453
  - Advantages: CTE match, cost, ease of fabrication

**Screen testing**

| Chemical Screen | Oxidation in fuel and oxidant environment  
|                 | Chemical compatibility with barium-calcium-aluminosilicate base glass seals  
|                 | Oxide scale thermodynamic stability  
| Electrical Screen | ASR measurements under cell exposure conditions (air & dual atmosphere)  
| Mechanical Screen | Investigation of thermal expansion  
|                 | Interfacial bonding strength with glass seals  

CTE of Ferritic Stainless Steels

TEC Comparison Normalized to Reduced Anode at 640°C

Fraction Elongation ($\Delta L/L$)

Temperature (°C)

PNNL Data

Reduced anode

Fe-29Cr-4Mo
Fe-21Cr-6.3Al
Fe-25Cr-4.5Al-0.1Y
Fe-17Cr

Reduced Anode

29-4C
SS 430
FeCrAlloy
alpha-4

U.S. Department of Energy
Pacific Northwest National Laboratory
Oxidation Resistance of 446 and AL 453

Oxidation resistance was measured as a function of time at 550, 700 and 800°C in air.

ANSI 446

- 800°C, Kg=1.2×10^{-13} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}
- 700°C, Kg=0.9×10^{-14} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}
- 550°C, Kg=10^{-15-16} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}

AL 453

- 800°C, Kg=1.9×10^{-13} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}
- 700°C, Kg=1.3×10^{-14} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}
- 550°C, Kg=10^{-15-16} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}
Oxidation Study – Surface Analysis of Scale

ANSI 446: Preoxidized for 300 hours in air at 550, 700 and 800°C.

XRD – 800°C - MnCr2O4, Cr2O3

AL 453: Preoxidized for 300 hours in air at 550, 700 and 800°C.

XRD – 800°C – Cr2O3, MnCr2O4
Scale microstructures of 446 and AL 453

Samples were pre-oxidized at 800°C for 300 hours in air.

Cr$_2$O$_3$, (Cr,Mn)$_3$O$_4$  
Cr$_2$O$_3$, Fe$_2$O$_3$, (Cr,Mn)$_3$O$_4$  
Cr$_2$O$_3$, (Cr,Mn)$_3$O$_4$, SiO$_2$  
Cr$_2$O$_3$, (Cr,Mn)$_3$O$_4$, Fe$_2$O$_3$, …  
Al$_2$O$_3$, Cr$_2$O$_3$, Fe$_2$O$_3$
Measured ASR of SS446 and AL 453

ASR was measured as a function of temperature, after heat treatment at 550, 700 and 800°C for 300 hours in air.

*ANSI 446*

*AL 453*
2-Atmosphere Oxidation/Conductivity Test

Temperature: R.T. - 1000°C
Current Density: 0 - 4.0 A/cm²
Time at Temperature: Variable
Atmospheres: Air and Various Fuels
Sample Type/Thickness: Variable
Issues / Future Work

- Ferritic stainless steels offer best CTE match to PEN
  - Concerns include thickness and integrity of scale, resistance of scale, volatilization of chromium species, and strength of interfacial bonds (oxide/metal, oxide/glass)
  - May require modification of alloy bulk, modification of alloy surface, and/or application of protective coatings

- Future work:
  - Complete screening study (oxidation, scale resistance)
  - Bulk modification
  - Surface modification (oxide coatings, surface alloying)
SOFC Seal Development
SOFC Seals: Challenges

Requirements for seals in planar SOFC stacks
- High degree of sealing (hermetic or allowable leak rate) under minimal compressive load
- Matching CTE (especially for rigid seals)
- Electrically insulating
- Long-term stability at high T in oxidizing/reducing and humid environments
- Inexpensive
- Thermal cycle stability
- Chemically and physically stable
- Thermal shock resistance

Rigid seals (i.e., glass-ceramic) require very close TEC matching of all stack components to minimize stresses; Compressive seals may relax these requirements somewhat by providing compliance in “x-y” plane.
Compressive seals for SOFC

Objective: to develop inexpensive, reliable compressive seal materials, offering adequate sealing and stable performance under minimal compressive load, as an alternative to glass or glass-ceramic seals.

Approach:
- Evaluate “hybrid” seal concept (combination of mica and compliant material, e.g., glass)
- Leak rate measurements on simulated SOFC seals
- Post-test evaluation (SEM)
Basis of seal: Mica

- Muscovite: $\text{KAl}_2 (\text{AlSi}_3\text{O}_{10}) (\text{F,OH})_2$
- Phlogopite: $\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$

Single crystal sheet

Paper: Discrete flakes with binders

Layered silicate structure
Concept of hybrid compressive seal

Simple mica layer yields excessively high leak rates through interfaces

Mica: compliant in 2-D (x-y plane)

Metal/glass interlayer: compliant in 3-D; seals off interfaces
Reduction of leak rate by insertion of glass interlayers

Orders of magnitude reduction in leak rate (vs. plain mica) for single crystal type mica in hybrid design with glass interlayers
Results for larger (3” square) compressive seal test

Inconel/glass/MSC/glass/alumina, 800°C air
Consistent results with small (1.3”) sample
Thermal cycling of hybrid seal

Abrupt increase in leak rate during initial cycles –
Modest increase in leak rate subsequently

SS430(#800)/G6/MSCx1/G6/IC, 800°C, 100psi cycling

with glass
no glass (32G)
no glass (#800)
Thermal cycling degradation with hybrid seals

Frictional damage is limited to the first several sub-layers below glass/mica interface; CTE of mica (~6.9 ppm/K) substantially less than CTE of SS or glass (10-13 ppm/K)
Degradation to mica after thermal cycling

MSC after 24 thermal cycling to 800°C in air (applied stress: 100 psi (SS430/G6/MSC-ar/G6/IC))

Future Work: Extend leak rate experiments from coupon testing in air to testing of SOFC single cells under typical operating conditions.

• Leak rate measurements
• Effects of leaks on SOFC OCV and I-V behavior
Summary / Status

- **Cathode Development**
  - LSF cathodes exhibit low polarization losses, stable performance in anode-supported cell tests

- **Anode Development**
  - La-Sr-Ti-Ce oxide anodes exhibit redox and sulfur tolerance, and low anodic polarization losses

- **Interconnect Development**
  - Database of high temperature alloy properties completed / screen testing in progress

- **Seal Development**
  - Glass/mica “hybrid” compressive seals exhibit very low leak rates under moderate applied loads (25-100 psi)
SECA Core Program – Recent Development of Modeling Activities at PNNL

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KP Recknagle, DR Rector, Z Lin, B Koeppel, RE Williford, John Deibler

Pacific Northwest National Laboratory
Richland, WA 99352

Don Collins
National Energy Technology Laboratory

February 18-19, 2003
Technical Issues and R& D Objectives

Technical Issues
- Concurrent management and control of thermal, physical, chemical and electrochemical processes over various SOFC operational parameters.

Objectives
Develop modeling and simulation tools to be used by the SECA vertical teams as an integral part of the design process. Tools to be used for:
- System design requirements roll-out
- Sub-system component design
- Microstructural and material design/optimization
- Control design
- Life prediction
Integrated Modeling of Solid Oxide Fuel Cells

The development of modeling tools for the analysis of fuel cells is essential for the design process. These tools must include the coupling between the fluid, thermal, electrochemical, and structural behavior. Issues peculiar to SOFC design include elevated operating temperatures, CTE mismatch, flow uniformity and start-up time. The tools being developed will address these issues. They will be used to optimize the design, predict the performance, and assess the reliability and lifetime of the cell. PNNL is taking an integrated approach to incorporate all these effects.

Experimental Validation of Modeling

- Rapid (<30 sec.) heating of ceramic PEN to 700°C with 20 KW infrared heaters. Temperature profile controlled with parabolic shaped mask
- Infrared image of temperature profile
- Finite element modeling of test

Continuum Electrochemistry Results

- Microstructural electrochemistry modeling shows the hydrogen concentration as the fuel traverses the length of the cell and diffuses through the electrodes.
An integrated set of modeling tools is invaluable in the design of fuel cells. The physical phenomena to be modeled include fluid flow, heat transfer, and mechanical response. The methodologies being developed at PNNL provide a unified method for considering these aspects.

A common geometric database provides commonality between CFD and FEA meshes. The CFD analysis provides flow uniformity results and the temperature distribution through the stack. The coupling logic applies the temperatures to the corresponding FEA mesh. Stress levels and component safety factors can be evaluated in FEA results. A custom temperature controller can be designed for the SOFC start-up procedure.

**Flow Uniformity Results**
- Cathode-Side Velocities
  - bulk mean velocity in channels = 1.83 m/s
  - max = 2.19 m/s (20% above mean)
  - min = 1.37 m/s (25% below mean)
- Anode-Side Velocities
  - bulk mean velocity in channels = 1.13 m/s
  - max = 1.24 m/s (10% above mean)
  - min = 1.09 m/s (3.5% below mean)

Anode side flow is within 10% of mean => small channel height

**Start-up Temperature Controller**
- Ave PEN temp
- ΔT allow
- Time to reach 20°C - 0.98 min
- Time to reach 650°C - 13.2 min
- Time to reach 700°C - 14.8 min
- max DT - 424K

Optimized temperature controller safely provides additional heat early in the start-up resulting in greatly reduced start-up times.

**Rapid Start-up – Stress Analysis Results**
- Platinum
- Platinum electrodes
- separated from gas channels
- Multi-element seals
- subdivide PEN into layers

**Flow Chart**
- Fluid/Thermal
- Temperature Controller
- Structural Models

**SOFC Flow – Thermal – Stress Modeling**
- Start-Up Transient
  - Modeling demonstrates that temperature profiles are non-isothermal during start-up.
Electrochemistry Modeling of Solid Oxide Fuel Cells

Fuel cells are projected to play an important role in energy production in the future. Solid oxide fuel cells offer attractive benefits in high power density and fuel flexibility. Electrochemical modeling provides a means of assessing the steady state behavior of the cell. Modeling is being conducted at the continuum level for inclusion in the stack engineering analyses. Microstructural modeling is being performed to evaluate the effects of electrode porosity, tortuosity, and grain size. The combination of these two approaches provides a comprehensive method for evaluating electrochemistry.

Approach:
Integrated multi-level models with experimental validation

Electrochemistry Basics

- High Po2 environment
- Low Po2 environment
- Anode reaction: O2 = 2e- + 2H+ = H2O
- Cathode reaction: 2H+ + 2e- = H2
- Combustion reactions: O= = ½O2 + 2e-

Development of electrochemical models.

Continuum Modeling

Comparison of cross-flow, co-flow and counter-flow designs demonstrates the advantages of the co-flow design. The temperature gradient decreases which lowers the stress in the cell. The current density is also more uniform, decreasing the potential for fuel depletion.

Microstructural Modeling

- 2D model designed to capture the variation in gas concentration through the PEN microstructure and in the flow direction.
- Gas concentration increases if the reactive surfaces extend into the electrolyte rather than only at the electrode – electrolyte interface.
- Hydrogen distribution is a function of the flow rate and diffusion through the PEN.
Electrochemistry Analysis

Activity 1: Temperature control for 1-Cell stack models in CFD framework.
- Suitable for cases using both serial and parallel processing
- Dynamic simulation control (DSC) of the inflow boundary temperature to expedite the convergence to a predetermined, average cell temperature.
- Speeds parametric simulation.

Activity 2: An efficient modeling tool for SOFC development of coupled thermochemical stress and electrochemistry analysis in MARC.
Activity 1: Temperature Control

- Simulation of stack in insulated box (i.e. Not in heated oven)
  - Requires large flow rate of oxidant to ensure best power density.
  - Fuel Utilization controlled by fuel delivery rate.
  - Therefore: cell temperature is controlled by temperature of inflowing fuel and oxidant.

- Previously in simulations a desired cell temperature was achieved by:
  - Running constant boundary temperature cases
  - Iterating on boundary temperature to give desired cell temperature.

- With a temperature control scheme that allows the boundary temperature to adjust during simulation, the desired average cell temperature can be achieved with one simulation run.
Activity 1: (continued)
Temperature Control Scheme

Steps to controlling boundary temperature

- Cell Temperature (Tgoal) is chosen prior to STAR-CD simulation run
- Initial boundary temperature set (Tinflow)
- Calculate average cell temperature at each iteration (Tnew)
- Store average cell temperature of previous iteration (Told)
- Determine increment to add or subtract from Tinflow (dTin):
  - Magnitude of deviation from goal temperature: (dTgoal) = Tnew - Tgoal
  - Rate of temperature change per iteration: (Tdelt) = Tnew - Told
  - The change made to Tinflow (dTin) is proportional to both dTgoal and Tdelt
- Tinflow = Tinflow + dTin
- Proceede to next STAR-CD iteration
Activity 1: (continued)
Using Temperature Control

An Example Case Study: The following slides will show:
The Effect of Fuel Flow Rate on the Fuel Utilization and Electric Current Density for a Typical Cross-Flow SOFC operating at 750 degrees C and 0.7 Volts.

- Fuel Composition: 37%H2, 3%H2O, 34%CO, 7%CO, and 18%N2.
- Oxidant Composition (air): 21%O2, 79%N2
- 112 cm² active cell area
- Cell Performance model used was that of cell I-6 (ie. 0.442 A/cm² @ 0.7 Volts)
Activity 1: (continued) Using Temperature Control - Plotted Results

A quick inspection of the plots at left show the relationship of fuel utilization and fuel flow rate as well as how to best attain large current density and manageable delta-T on the cell depending on the inflow temperature - all at cell temperature 750°C.
Activity 1: (continued)
Cell Temperature Distributions

All five cases have volume average Temperature of 750°C ± 0.01°C

Low Utilization Case (large fuel flow)
High Utilization Case (small fuel flow)

ABOVE: Results include the distribution of temperature on the cell area (and the surrounding stack structure) for prediction of thermally induced stress.

Distributions of other variables are also available for plotting and analysis.
Activity 2: Motivations for EC in FEA Framework

Fuel cell operations involve multi-physics processes; the constitutive thermal, chemical, electrochemical and transport processes are strongly coupled => requiring versatile multi-physics tool for realistic description.

Technology development involves design optimization of various geometric, material and operation parameters; the cost of such parametric studies increases exponentially with the number of the working parameters and there are many such parameters involved.

=> Computational efficiency is critically important.
**Sample results:** Snapshot for startup to steady state transition

- \( T_0 = 0 \text{C}, \ T_{\text{air/fuel}} = 700 \text{C}, \ V_{\text{air}} = 0.33 \text{l/s}, \ V_{\text{fuel}} = 0.0825 \text{l/s}, \ V = 0.7 \text{Volt} \)
- \( t: \ a) 12 \text{s}; \ b) 60 \text{s}; \ c) 300 \text{s}; \ d) 600 \text{s}; \ e) 900 \text{s}; \ f) 1200 \text{s} \)
- Transient results almost identical for time steps from 0.2s to 12s
Comparison of different flow design

- Temperature profile for cross-, co-, counter-flow
- H$_2$+CO fuel; $V_{\text{fuel}}$=0.055 & 0.0275l/s, respectively.
Sample Results for Multi-cell Stacks

- Cell voltage variation for a 30-cell stack ($V_{tot}=21V$)
- Only the outmost top and bottom 2-3 cells deviate substantially from the average; similar results for 8- & 15- cell stacks
CPU time requirement

- Table 1, CPU time when specifying total current
  - # of cells 2 3 4 5 8 15 30
  - Time/inc(s) 0.45 0.68 0.91 1.15 1.83 3.48 6.93

- Table 2, CPU time when specifying total voltage
  - # of cells 2 3 4 5 8 15 30
  - Time/inc(s) 14.0 26.8 36.3 51.8 53.0 149 326

- CPU time increases roughly linearly with the number of cells in the stacks
- Typically 20-40 increments are needed for a steady state run
Micro Structural Analysis Activities

**Activity 1:** Develop a one-dimensional single cell model with the following features:
- Oxygen vacancy and electron transport through MIECs
- Charge transfer kinetics
- Surface adsorption, diffusion and reactions

**Activity 2:** Predict cell performance under different operating conditions

**Activity 3:** Create a three-dimensional microscopic model of cathode using digitized information from SEM images.
Single Cell Model (cont.)

- **LSF Cathode**: 30 µm (5x25µm; 25x0.2µm)
- **Sm-Doped Ceria**: 5µm (25x0.2µm)
- **YSZ (dense)**: 8µm (40x0.2µm)
- **Active anode (50% Ni/50% YSZ)**: 10µm (25x0.2µm; 5x1µm)
- **Bulk anode (40% Ni/60% YSZ)**: 500µm (50x10µm)
Single Cell Model (cont.)

Predicted fields:
- Gas concentrations (O$_2$, H$_2$, H$_2$O, CO, CO$_2$, CH$_4$)
- Surface concentrations (O$_2$, H$_2$, H$_2$O)
- Oxygen chemical potential (µ$_O$)
- Electron electrochemical potential (η$_e$)

Connection to Continuum Models
- Results may be used to define parameters for continuum electrochemistry model.
- This model may be extended to include flow in the air and fuel channels and arranged in a 2D matrix (e.g., 20x20) to form a three-dimensional cell model.
The purpose of this model is to predict cell performance based on material specific properties. Once the basic parameter set (surface specific kinetic rates, transport coefficients) have been established, the model will predict performance changes for:

- Change in electrolyte layer thicknesses
- Change in cathode or anode microstructure
- Change in electrode materials
Charge Transfer (Cathode)

- The oxygen exchange across the surface occurs through the reaction:

\[
\frac{1}{2} O_2 + V_O \xleftrightarrow{k_f, k_r} O^X_O + 2\dot{h}
\]

- The forward and reverse reaction rates are given by (\(E=E_{eq}+\eta\))

\[
i_f = Fk_f \exp \left[ \frac{\alpha F E_{eq}}{RT} \right] \exp \left[ \frac{\alpha F \eta}{RT} \right] P^{\frac{1}{2}} O_2 c_v
\]

\[
i_r = Fk_r \exp \left[ \frac{-(1-\alpha) F E_{eq}}{RT} \right] \exp \left[ \frac{-(1-\alpha) F \eta}{RT} \right]
\]

- Redefine in terms of a exchange current density, \(i_0 (\eta=0)\)

\[
i_0 = Fk_f \exp \left[ \frac{\alpha F E_{eq}}{RT} \right] P^{\frac{1}{2}} O_2 c_v = Fk_r \exp \left[ \frac{-(1-\alpha) F E_{eq}}{RT} \right]
\]
Charge Transfer (Cathode)

The net reaction rate then becomes

\[ i_{\text{net}} = i_f + i_r = i_0 \left[ \exp \left( \frac{\alpha F \eta}{RT} \right) - \exp \left( \frac{-(1 - \alpha) F \eta}{RT} \right) \right] \]

which is the same form as the global Butler-Volmer expression, but there are separate expressions for the cathode and anode which are defined in terms of local kinetic coefficients and concentrations.
Gas Diffusion

Diffusion of gas species through porous media is given by

\[ q = -D_{\text{eff}} \nabla c = -\frac{\varepsilon}{\tau} D \nabla c \]

where \( \varepsilon \) is the porosity and \( \tau \) is the tortuosity.

For small pores (diameter \( d \)) or low pressure, the Knudsen diffusion is given by

\[ D_K = \frac{d \left[ \frac{8RT}{\pi M} \right]^{\frac{1}{2}}}{3} \]

The transition between molecular and Knudsen diffusion is given by

\[ D = \frac{1}{\left(1/D_M + 1/D_K \right)} \]
Electrolyte and MIEC Transport

- The electrochemical potential for a given species is
  \[ \mu = \mu_0 + RT \ln c + nF\phi \]

  where \( \mu_0 \) is the reference potential, and \( \phi \) is the electrical potential.

- The oxygen ion and electron fluxes are given by the expressions
  \[ J_{O_2} = -\frac{\sigma_{O_2}}{F^2} \nabla \mu_{O_2} ; \quad J_e = -\frac{\sigma_e}{F^2} \nabla \mu_e \]

  where \( \sigma_{O_2} \) and \( \sigma_e \) are the ion and electron conductivities.
Electrolyte Transport (cont.)

- The electron (or hole) conductivity has the form

\[
\sigma_e = \sigma_{e0} P_{O_2}^{\frac{1}{4}}, \quad \sigma_h = \sigma_{h0} P_{O_2}^{\frac{3}{4}};
\]

where \( P_{O_2} \) is the equivalent partial pressure corresponding to the local oxygen electrochemical potential.

- At lower temperatures, the oxygen ion conductivity is expressed in the form

\[
\sigma_o T = A \exp \left( -\frac{E_a}{kT} \right)
\]
Anode Model

- The active triple phase boundary concentration (length/volume) is expressed as a function of location. Active means that the nickel, YSZ and gas regions are contiguous.
- The active YSZ volume available for oxygen ion conduction is expressed as a function of location.
- Macroscopic surface diffusion is calculated based on the surface area per unit volume and the surface tortuosity.
- The surface reaction site concentration (sites/unit area) is required for surface reactions.
Anode Reactions

The reaction set on the anode side is

\[ O_{YSZ} + V_{ad} \leftrightarrow O_{ad} \]  
\[ H_2(g) + 2V_{ad} \leftrightarrow 2H_{ad} \]  
\[ H_2O_{ad} \leftrightarrow H_2O(g) + V_{ad} \]  
\[ 2H_{ad} + O_{ad} \xrightarrow{k_f,k_r} H_2O_{ad} + 2V_{ad} \]

We assume that water formation (Eq. 4) is the rate limiting step. This reaction is used to create a Bulter-Volmer expression similar to that used for the cathode.

The other three reactions are treated as Langmuir adsorption.
Langmuir Adsorption

The rates of adsorption and desorption are given by the expressions

\[ R_{\text{ads}} = \frac{f(\theta)P}{\sqrt{2\pi nkT}} \exp\left(-\frac{E_a^{\text{ads}}}{RT}\right) = C_{\text{ads}} Pf(\theta) \exp\left(-\frac{E_a^{\text{ads}}}{RT}\right) \]

\[ R_{\text{des}} = C_{\text{des}} g(\theta) \exp\left(-\frac{E_a^{\text{des}}}{RT}\right) \]

The function dependence on surface coverage depends on the type of reaction. For simple adsorption/desorption, as in the case of water, the functions \( f \) and \( g \) have the form

\[ f(\theta) = 1 - \theta; \quad g(\theta) = \theta \]

and for dissociative adsorption of a homonuclear diatomic molecule, such as oxygen or hydrogen

\[ f(\theta) = (1 - \theta)^2; \quad g(\theta) = \theta^2 \]
Langmuir Adsorption (cont.)

The net rate of adsorption is given by the expression

\[
\frac{ds}{dt} = R_{ads} - R_{des} = C_{ads} P f(\theta) \exp\left(-\frac{E_{ads}}{RT}\right) - C_{des} g(\theta) \exp\left(-\frac{E_{des}}{RT}\right)
\]

The surface coverage at equilibrium for simple adsorption and dissociative adsorption

\[
\theta = \frac{bP}{1 + bP}; \quad \theta = \frac{\sqrt{bP}}{1 + \sqrt{bP}}
\]

where

\[
b = \frac{c_{ads}}{c_{des}} \exp\left(-\frac{\Delta E}{RT}\right)
\]
Model Status

- Using test data to define parameters for charge transfer and adsorption reactions

- Testing regions of the model, such as oxygen transport through composite electrolyte

Operating Conditions
- Temperature - 800 °C
- Current - 0.5 A/cm²
- Fuel Composition - 97% H₂, 3% H₂O
Composite Electrolyte Behavior

Oxygen Chemical Potential (atm) vs. Position (microns)
Microstructure Geometry Reconstruction

- Digitize a representative portion of a photographic image of the electrode to obtain an array of grayscale values for each pixel
- Developed computer program to convert to a two-dimensional solid map (filter to remove artifacts)
- Collect statistics such as autocorrelation function (variogram) and solid chord length distribution
- Construct a three-dimensional geometry through a stochastic computational method which matches the statistical information taken from the two-dimensional image
Cathode SEM Image

SEM image

Digitized image
A (100)\(^3\) node model was constructed to represent a (15 \(\mu\)m)\(^3\) section of cathode material based on the variogram and chord length distributions.

Model Geometry

2-D Slice
Model Applications

- Detailed three-dimensional transport simulations are performed to determine effective properties

- The single component geometry model will be used to determine
  - Effective gas diffusion parameters (tortuosity)
  - Effective surface diffusion parameters
  - Effective electrical and ionic conductivities

- A multicomponent anode model (with Ni and YSZ solids as well as gas phase) may be used to determine the active TPB distribution as a function of position
Thermal-Mechanical Modeling Objectives

- Improved constitutive relations for cell/seal materials
  - Include effects of reduction, creep, defects, thermal cycling

- Predict stresses/deformations at seal interfaces
  - Glass and mica seals
  - Leak rate estimate
  - Parametric analysis

- Improved FEA models
  - Thermal cycling
  - Residual fabrication stresses

- Catalog defects in cell materials
  - Predict crack growth
  - Reliability analysis
Thermal-Mechanical Modeling Example Reliability Analysis

PEN Deformation

Co-flow Design

In-plane Displacement Parallel to flow (UX)

Flow

In-plane Displacement Perpendicular to Flow (UY)

Out-of-plane Displacement (UZ)
Thermal-Mechanical Modeling
Example Reliability Analysis

Temperature Distribution

Principal Stress (S1) Cathode

Principal Stress (S1) Electrolyte

Principal Stress (S1) Anode

High Stresses at Edges (36 MPa)
Thermal-Mechanical Modeling
Example Reliability Analysis

- Risk of rupture intensity for PEN at steady-state operating conditions
- 2.1% failure probability due to fast-fracture

Electrolyte

Cathode

Anode

High on edge as expected
Plans for Remainder of FY03 Continuum Electrochemistry

► Software transfer and SECA vertical team training
► Temperature Control of Multiple Cell Stacks Running on Multiple Processors.
► Expand Simulation Capability of STAR-CD multiple-cell stack model to include current leakage from a selected cell within the stack to enable prediction of effect of one (or more) faulty cells on the overall stack performance.
► Implement additional, local electrical resistance related to life expectancy of the cell/stack (provide hook to MARC for resistance term which is yet to be defined).
Planned Activities for FY03
Micro Structural Electrochemistry

► Software transfer and SECA vertical team training

► Three-dimensional Electrode Models
  ● Determine effective properties using reconstructed geometry
  ● Continue to improve reconstruction process

► One-dimensional Cell Model
  ● Determine charge transfer and adsorption reaction parameters based on comparison of performance data for different cell designs
  ● Validate using experimental data
  ● Predict cell performance for a variety of cell design changes
Plans for the Reminder of FY03 Thermal-Mechanical Modeling

- Examine ORNL experimental results on PEN materials after reduction
  - Catalog defects
  - Develop constitutive relations (as directed by test data)

- Identify material data required to model high temperature behavior of seals
  - Coordinate with thermal gradient/cyclic testing (PNNL Task 3 and others)

- Construct improved FEA model
  - Higher resolution in the seal interface regions
  - Capability to analyze thermal cycling

- Established methods and models for predicting leak rates in compressive or hybrid seals.

- Update reliability analysis with available test data.
Applicability to SOFC Commercialization

- Modeling tools developed by PNNL for design, optimization and operation of SOFC materials, stacks and systems.

- Engineering insights and guidance regarding SOFC materials, stacks and systems.
SECA Core Technology Program - PNNL: SOFC Component Materials Development

Jeff Stevenson
Pacific Northwest National Laboratory
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Presented at the SECA CTP Review Meeting
Sacramento, CA, Feb. 19, 2003
SECA Core Technology Program - PNNL: SOFC Component Materials Development

Program Scope:
- Intermediate Temperature Cathode Materials Development
- Advanced Anode Materials Development
- Metallic Interconnect Materials Evaluation and Development
- SOFC Stack Seal Development
Presentation Outline

- Intermediate Temperature Cathode Materials Development
- Metallic Interconnect Materials Evaluation and Development

For each task:
- Objective
- Previous Status
- Results
- Future Work
Intermediate Temperature Cathode Materials Development
Cathode Materials Development

Objective: Develop and optimize high performance, stable cathode materials for intermediate temperature SOFC

Variables:
- Base composition, type and amount of dopant
- Initial particle size distribution (calcination and milling conditions), fugitive phases
- Sintering temperature and time

Approach:
- Synthesis (glycine-nitrate) and characterization of candidate cathode powders (XRD, dilatometry, SEM, PSA, TGA, electrical conductivity)
- Fabrication of cathodes on anode-supported membranes via screen printing and sintering
- Evaluation of cathode performance by electrochemical testing and SEM
Sr-Doped LaFeO$_3$ Cathode Development

Advantages:

• High ionic conductivity
• Rapid oxygen surface exchange kinetics
• TEC match to other components
• High electronic conductivity
• Iron is inexpensive B-site constituent

Introduction of doped ceria layer improves performance

La(Sr)FeO$_3$ 30-50µm  Ce(Sm)O$_2$ 3µm  YSZ 7µm  Anode ~550µm
Anode-supported cell w/ LSF-20 cathode (Previous status)

Cell: LSF Cathode / SDC Interlayer / YSZ Electrolyte / Ni-YSZ anode

Fuel: 97% H₂ / 3% H₂O (Low Fuel Utilization)

Oxidant: Air

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Power at 0.7V (W/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>0.36</td>
</tr>
<tr>
<td>700</td>
<td>0.63</td>
</tr>
<tr>
<td>750</td>
<td>0.85</td>
</tr>
<tr>
<td>800</td>
<td>1.21</td>
</tr>
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</table>
Role of ceria layer: Prevention of reaction between YSZ and LSF?

Mixtures of LSF and YSZ, heated to 1400°C for 2 h, showed no evidence of zirconate formation. (Contrary to case with LSCo and YSZ).
Role of ceria layer: Prevention of reaction between YSZ and LSF?

However, for $T \geq 1000^\circ C$, LSF peaks were shifted, indicating expansion of lattice due to change in composition of perovskite phase.

Results using $\text{ZrO}_2$ and $\text{Y}_2\text{O}_3$ indicate $\text{Zr}^{4+}$ from YSZ incorporated onto B-site of perovskite lattice; conclusion is supported by EDX results.
Impact of Zr$^{4+}$ on LSF Conductivity

Significant reduction in electrical conductivity of LSF w/ increasing Zr content:

\[ \left[ \text{Sr}_{La}^{+} \right] + \left[ \text{Fe}_{Fe}^{+} \right] = \left[ \text{Fe}^{0}_{Fe} \right] + 2\left[ \text{V}_{O}^{2+} \right] + \left[ \text{Zr}_{Fe}^{0} \right] \]

Conclusion: Ceria interlayer required for LSF cathodes sintered at $T \geq 1000^\circ$C
Enhancing LSF Sinterability

Goal: Modify the LSF cathode to sinter onto YSZ below 1000°C to avoid the LSF-YSZ interaction. Compositions of the type \((\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{Fe}_{0.98}\text{M}_{0.02}\text{O}_3\) are being considered.
Initial performance data indicates significantly improved power density (1.4-1.8 W/cm² at 750°C and 0.7V) for the new cathode material sintered on YSZ at 950°C.
Metallic Interconnect Materials
Evaluation and Development
Metallic Interconnects for SOFC

Objectives:
- Identify and quantify degradation processes in candidate alloys
- Develop a cost-effective optimized material for intermediate temperature interconnect applications

Approach:
- Screen testing of candidate alloys (chemical, electrical, mechanical properties)
- Materials development
  - Surface modification (surface doping, protective coatings)
  - Bulk modification
Screen testing of candidate alloys

Emphasis on “Chromia-forming” Ferritic Stainless Steels:
- CTE match, conductive oxide scale, low cost, ease of fabrication

Screening Studies

| Screening Screen   | \- Oxidation in air, fuel, and dual atmosphere environments (scale thickness, composition, and microstructure)  
|                    | \- Chemical compatibility with alkaline earth-aluminosilicate glass seals  
|                    | \- Oxide scale thermodynamic stability  
| Electrical Screen  | \- ASR measurements under SOFC exposure conditions  
| Mechanical Screen | \- Investigation of thermal expansion  
|                    | \- Interfacial bonding strength with glass seals  

Pacific Northwest National Laboratory  
U.S. Department of Energy
Selected alloys offer good CTE match to SOFC components

Temperature (C)

ΔL/L

AL453
Crofer 22
Ebrite
Reduced anode
Electrical Resistance of Scales on Selected FSS

Coupon samples were pre-oxidized in air at 800°C for 100h before carrying out tests in air at 800°C.
Scale Resistance for Crofer22APU at 700, 800°C (in air)
Microstructures of cross-sections of samples from conductivity tests (in air)

800°C, 500h

700°C, 500h

Note: Reduced Cr volatility due to (Cr,Mn)₃O₄ outer scale
Both bare and coated samples were pre-oxidized in air at 800°C for 100h before carrying out tests in air at 800°C.
Oxidation Behavior of Crofer22APU: Dual Atmosphere vs. Air

Air exposure at both sides

Air-side of dual exposure

Repeated EDX analyses on Crofer22APU tested under dual exposure indicate the presence of Fe in the scale
Thermal cycling tests:
5ºC/min to 800ºC, 100h dwell
3 cycles

XRD patterns from the airside of dual test vs. air exposure only
Airside under dual exposure w/ cycling
Elemental mapping of scale formed at the air side
Future Work (Short-term)

- Continue to study role of dual atmosphere exposure on corrosion of alloys
- Extend screening studies to include ZMG232, a new ferritic stainless composition developed by Hitachi Steel for SOFC applications
- Study the evaporation of scale on metallic interconnect
- Investigate the feasibility of doping interconnect surface to minimize scale growth / electrical resistance
Acknowledgements

- Cathode Development: Steve Simner, Mike Anderson
- Interconnect Development: Gary Yang, Prabhakar Singh, Matt Walker

- Financial Support:
  - Solid-State Energy Conversion Alliance Core Technology Program (SECA)
## Compositions of FSS

<table>
<thead>
<tr>
<th>FSS</th>
<th>Fe</th>
<th>Cr</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>Ti</th>
<th>Al</th>
<th>P</th>
<th>S</th>
<th>La+Ce</th>
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<tbody>
<tr>
<td>AISI430</td>
<td>Bal.</td>
<td>16.0</td>
<td>0.1</td>
<td>1.0</td>
<td>1.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.03</td>
<td>0.03</td>
<td>--</td>
</tr>
<tr>
<td>AISI446</td>
<td>Bal.</td>
<td>26.0</td>
<td>0.2</td>
<td>1.5</td>
<td>1.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.04</td>
<td>0.03</td>
<td>--</td>
</tr>
<tr>
<td>E-brite</td>
<td>Bal.</td>
<td>26.0</td>
<td>0.001</td>
<td>0.01</td>
<td>0.025</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
<td>AL453</td>
<td>Bal.</td>
<td>22.0</td>
<td>0.03</td>
<td>0.3</td>
<td>0.3</td>
<td>--</td>
<td>0.02</td>
<td>0.6</td>
<td>0.02</td>
<td>0.03</td>
<td>0.1</td>
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<tr>
<td>Crofer22 APU</td>
<td>Bal.</td>
<td>22.0</td>
<td>0.005</td>
<td>0.5</td>
<td>--</td>
<td>--</td>
<td>0.08</td>
<td>--</td>
<td>0.016</td>
<td>0.002</td>
<td>0.06La</td>
</tr>
<tr>
<td>ZMG232</td>
<td>Bal.</td>
<td>22.0</td>
<td>+ other elements</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
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</table>

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Pacific Northwest National Laboratory
U.S. Department of Energy

27
Compressive Seal Development
for Solid Oxide Fuel Cells

Y-S Matt Chou, Jeffry W. Stevenson
and Prabhakar Singh

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Funded under the SECA Core Technology Program
through US Department of Energy’s
National Energy Technology Laboratory (NETL)
Outline

- Technical issues
- R&D Objectives and Approach
- Results to Date
  - Long-term thermal cycling of hybrid micas: OCV results
  - Effect of compressive stress on leak rate versus thermal cycling
  - Effect of stack size on the fuel loss
  - Effect of temperature gradient on leak rate versus thermal cycling
  - Thermal cycling of large sample in pure hydrogen environment
  - Allowable leak rate: electrochemical consideration
- Applicability to SOFC commercialization
- Activities for the next 18 months
Current technical issues for compressive mica seals

- Will hybrid mica seals survive long-term thermal cycling ($10^2$-$10^3$ cycles) in SOFC environments?
- Will hybrid mica seals have sufficiently low leak rates after repeated thermal cycling?
- How low can the applied compressive load be?
- Will they survive thermal cycling with temperature gradients?
- How low a leak rate is allowable, both electrochemically and mechanically?
- Does the hybrid mica seal have long-term ($40 \times 10^3$ hrs) mechanical, thermal, and chemical stability in SOFC environments?
- Will the compressive stresses cause undesirable creep or plastic deformation of the metallic stack components?
- Will they cause degradation or corrosion to mating materials?
The R&D objective of this project is to develop a *durable* and *low-cost* compressive seal technology with properties to meet all SOFC stack requirements at very *low compressive stresses*. 
R&D Approaches

- Hybrid mica seals were developed after identification of major leak path at interfaces of compressive mica gasket seals. The concept was tested successfully with a glass or metallic inter-layers.

- Infiltrated Phlogopite micas can further lower the leak rates while maintaining thermal cycle stability. Good chemicals for infiltration yet to be identified.

- Concept of “infiltrated” mica was also successfully demonstrated on glass-mica composites at lower stresses. Processing technique yet to be identified.

- Evaluation of the hybrid micas and glass-mica composites under long-term thermal cycling in a simulated SOFC environments is in progress.

- Testing hybrid micas in a temperature gradient profile.

- Leak rate data is being obtained for hybrid micas and glass-mica composites over a wide range of compressive stresses (6 to 100 psi).
Results update
OCV v.s. long thermal cycle test

2”x2” 8YSZ dense plate with hybrid mica seals at 100 psi
Ag electrodes, Pt lead wire, and Inconel600 or SS430 block on alumina block
Long-term thermal cycling and OCV tests

Loss of ~1.4% (OCV=0.919 V) after 864 thermal cycles (@ 100 psi)
At 63 sccm of 2.55% H₂/Ar + ~3% H₂O versus air

2"x2" 8YSZ hybrid mica, 2.55%H₂/Ar+~3 % H₂O,
@64sccm, e.q. 80% fuel utilization, 100psi

Hybrid mica seal:
As-received mica paper sandwiched between 2 glass interlayers
Hybrid micas
Leak rate determination of 2”x2” hybrid mica (100psi) after 671 thermal cycles

Leak rate = 0.018 sccm/cm @ 0.2 psig
Comparison measured and calculated leak rate and at 864th cycle

Theoretical (Nernst) voltage @ 800°C of 2”x2” hybrid mica 100psi = 0.932 V (2.55% H₂/Ar + ~3% H₂O versus air)

Measured OCV = 0.919 V (@ flow rate = 63 sccm)  
Measured leak rates @0.2 psi = 0.018 sccm/cm

At 0.919 V, 800C and 63 sccm fuel (2.55% H₂/Ar)  
Calculated air leak rate = 0.027 sccm/cm

May suggest some background leaks.
THERMAL CYCLING AT LOWER STRESSES (50 psi)

Loss of ~3% (OCV=0.906V) after 451 thermal cycles, 8YSZ fractured 484 cycle

Estimated leak rate @ cycle #484
3.64 sccm or ~1.4 sccm/cm from OCV=0.72 V
OCV=0.927 V after 250 thermal cycles (0.5% loss). Hybrid seal based on glass-mica composite

Pt wire broke after 250 cycles. Estimated leak rate=0.011 sccm/cm from OCV=0.927 V
Effect of compressive stress on the leak rates of hybrid mica (4mil) at high (2 psi) helium pressure

2"x2" hybrid (G18) Ph4mil @800C, leak by He @ 2psig

- 6psi
- 12psi
- 25psi
- 50psi
- 100psi

leak rate, sccm/cm

number of thermal cycles
Effect of compressive stress on the leak rates, 4mil thick @ 2psig

hybrid 4mil mica by He at 2 psid

leak rate, sccm/cm @ 800C

Metal interconnect
ceramics
Effect of compressive stress on the leak rate of hybrid mica (4mil) at low (0.2 psi) helium pressure

hybrid 4mil mica by He at 0.2 psid

leak rate, sccm/cm @ 800°C

compressive stress (psi)
Fuel loss for hybrid mica at low differential pressure (0.2 psid)

Consider square stack with square active area and 1” space between active side and edge of stack

Leak length (inch) =
18” (5”x5” stack)
22” (6”x6” stack)
26” (7”x7” stack)
30” (8”x8” stack)
Fuel loss for hybrid mica at low pressure gradient (0.2 psid) and 80% fuel utilization

Assume 0.7 V, 0.75 A/cm², and 0.5 W/cm² @ 800°C with pure hydrogen

![Graph showing fuel loss vs stack size for different pressure gradients at 800°C. The graph includes data points for 100 psi, 50 psi, 25 psi, 12 psi, and 6 psi.]
Allowable leak rate is design-specific

- Stack-size dependent:
  fuel needed @ certain power density is $\alpha d^2$
  Leak rate (mica seal) is $\alpha d$
- Leak location dependent: e.g., inlet and outlet
- Fuel concentration dependent
- Electrochemical and mechanical consideration
- Mica seal may be more robust from mechanical point of view since the leak is rather uniform while rigid seals are prone to localized leaks, which can lead to catastrophic failure.
**OCV loss for hybrid mica at low pressure gradient (0.2 psid) and 80% fuel utilization**

A 6”x6” stack with a 4”x4” active area and total leak length 22” (per cell)
Cell power density of 0.5 W/cm², 0.75 A/cm² (0.7 V and 800°C)
Need 650 sccm (pure H2) and 1547 sccm air for a 80% fuel utilization

<table>
<thead>
<tr>
<th>leak rate, sccm/cm @0.2psi</th>
<th>0.02</th>
<th>0.04</th>
<th>0.06</th>
<th>0.08</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>total fuel leak, sccm</td>
<td>1.1</td>
<td>2.2</td>
<td>3.4</td>
<td>4.5</td>
<td>5.6</td>
</tr>
<tr>
<td>% of fuel loss</td>
<td>0.17</td>
<td>0.34</td>
<td>0.52</td>
<td>0.69</td>
<td>0.86</td>
</tr>
<tr>
<td>initial H2 conc. air side</td>
<td>0.000701</td>
<td>0.001402</td>
<td>0.002102</td>
<td>0.002803</td>
<td>0.003504</td>
</tr>
<tr>
<td>initial O2 conc. At fuel side</td>
<td>0.000361</td>
<td>0.000722</td>
<td>0.001083</td>
<td>0.001444</td>
<td>0.001805</td>
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<tr>
<td>OCV (V)</td>
<td>1.1009</td>
<td>1.0998</td>
<td>1.0987</td>
<td>1.0977</td>
<td>1.0966</td>
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<tr>
<td>loss OCV (mV)</td>
<td>0.88</td>
<td>2.03</td>
<td>3.15</td>
<td>4.13</td>
<td>5.21</td>
</tr>
<tr>
<td>loss OCV %</td>
<td>0.08</td>
<td>0.18</td>
<td>0.29</td>
<td>0.38</td>
<td>0.47</td>
</tr>
<tr>
<td>Eq. PO2 at air side</td>
<td>0.2097</td>
<td>0.2094</td>
<td>0.2092</td>
<td>0.2089</td>
<td>0.2086</td>
</tr>
</tbody>
</table>
Thermal cycling with temperature gradient

Temperature gradient of 30-100°C across 3.5”x3.5” sample during cycle
Effect of temperature gradient

3.5”x3.5” hybrid mica @100psi and cycling between 200-800°C

With T gradient

Without T gradient
Thermal cycling in pure hydrogen fuels of large (3.5”x3.5”) hybrid micas @ 12.5psi

Nernst voltage = 1.102 V @800°C for (97% H₂/3% H₂O vs air), flow rate 284 sccm ~ 80% fuel utilization
Summary and Conclusions

- Hybrid micas have demonstrated excellent thermal cycle stability under several different loading conditions: 864 cycles (100psi), 450 cycles (50 psi), and 250 cycles (26 psi) in OCV tests.

- The effect of compressive stress on the leak rate was studied from 6 psi to 100 psi. At all stresses, the hybrid micas showed fairly constant leak rates after ~10-20 thermal cycles.

- The leak rates were linearly proportional to the differential gas pressure.

- Leak test on large (3.5”x3.5”) hybrid mica showed no effect from ~30º-80ºC temperature gradients.

- Good thermal cycle stability was demonstrated on large (3.5”x3.5”) hybrid mica in 97% hydrogen / 3% water environment for 85 thermal cycles.

- Fuel loss was estimated for various stacks at different fuel utilizations, and found to be minimal (~0.1%) at low compressive stresses if the stack is to be operated at ambient or small differential pressures.
The developed hybrid mica seals could be quickly adapted for commercialization since the mica layers are commercially available, and the glass interlayers can be easily fabricated by tape casting or other automatic processes.

The glass-mica composite seal will require further processing optimization to improve distribution of large mica flakes, and the selection of an optimum glass or glass-ceramic to meet SOFC requirements.
Activities for the next 18 months

- Evaluate the low (3 psi) compressive stresses on hybrid micas
- Optimization of glass-mica composite seals by using two different glasses at various volume fractions: a Ba-Al silicate glass (a rigid glass-ceramics) and a glass which tends to remain vitreous instead of crystallizing. Evaluate forming techniques for making thin and uniform thickness mica-glass composites.
- Combined aging (1 month) and thermal cycling (100 cycles) tests of various hybrid micas in a simulated SOFC environment or pure hydrogen versus ambient air conditions.
- Testing leak rate versus limited (30-50) thermal cycles at various low loads (3, 6, and 12 psi) for various hybrid micas and glass-mica composites.
- Evaluate allowable leak rates from thermal-mechanical considerations.
- Design an accelerated aging test for evaluating the long-term stability of candidate hybrid mica seals in a simulated SOFC environments.
- Evaluate the degradation by hybrid micas or glass-mica composite seals on various candidate metallic interconnect materials in a simulated SOFC environment: e.g., coated/uncoated ferritic stainless steel, Haynes230, Inconel600 or others.
SECA Core Program – Recent Development of Modeling Activities at PNNL

MA Khaleel  
Email: moe.khaleel@pnl.gov  Phone (509) 375-2438  
KP Recknagle, Z Lin, B Koeppel, S Moorehead, KI Johnson, N Nguyen, D Rector, and G Grant  

Pacific Northwest National Laboratory  
Richland, WA 99352

Travis Shultz  
National Energy Technology Laboratory
Integrated Modeling of Solid Oxide Fuel Cells

Consolidated Computational Modeling for SECA

Thermo-mechanical cycling

Experimental Validation

Experimental data for models (seals)

Battelle

System models and controls

Stack

Controls and system dynamics

GUIs for continuum EC

On Cell Reforming

Microstructural electrochemistry Fracture and Electrochemistry

Pacific Northwest National Laboratory
SECA Computational Resource

- Provides SECA partners access to a high-performance computer for numerical analysis of fuel cell designs
- Commercial software packages and PNNL developed fuel cell sub-models are installed
- Platform for continued sub-model development and testing
- Silicon Graphics Inc
  - 3700 Altix Server
  - Linux based
  - 24 Intel “Madison” CPUs
  - Expandable to 32 CPUs in current chassis
  - 64 GBytes RAM - Shared Memory - also greatly expandable
  - Binary compatibility with PNNL 128 CPU SGI computer
Offsite Access for SECA Industrial Team Members

- All offsite non-PNNL users will need to be hosted by a PNNL staff member.
- Host will complete a Computer Access Request Form and Smartcart Request.
- Offsite computers must have a Hardware Firewall (PNNL staff use Linksys), or a software Firewall (Hardware Firewall is preferred).
- Access is via:
  - VPN software for PC or Macintosh Platforms (provided by PNNL).
  - ssh (secure shell) for Unix/Linux.
  - Users connect into PNNL using Smartcard (transient passwords in sync with PNNL base station).
Solid-State Energy Conversion Alliance (SECA) Modeling and Simulation Training Session Week of July 12, 2004

AGENDA

Day 1: Fluent
Morning: Introduction to Fluent Basics
CFD Modeling of SOFCs
Afternoon: Fluent on Newton Computer
Hands-on modeling activity

Day 2: MARC
Morning: Introduction to Marc basics
MARC SOFC GU
Afternoon: MARC on Newton Computer
Hands-on modeling activities with MARC

Day 3: Star CD
Morning: Introduction to Star CD basics
ES-SOFC
Afternoon: Star CD on Newton
Hands-on CFD Modeling

Day 4: Miscellaneous SOFC Modeling
Controls, system modeling.
Structural modeling, stress, strain, thermal cycling
Materials database
Lattice Boltzman models

August 28th and 29th, 2003
Experimental Validation of Electrochemistry Models

**Fuel Utilization:**
- **Experiment:** 20%  
  - **Model:** 22%
  - *(current \(\times 6.96 = \text{cm}^3/\text{min H}_2\) burned)*

**Predicted Temperature -**
- **Inflow range:** 744-749°C
- **Outflow range:** 747-752°C

**Gas Flow Temperatures**

- **Measured**
- **Predicted**

**Power & Fuel Utilization**
- **Experimental:** Power = 40 W (57 Amps @ 0.7 Volts), [20% fuel utilization]
- **Predicted:** Power = 44 W (63 Amps @ 0.7 Volts), [22% fuel utilization]
Tests on Joined Assemblies for Fundamental Properties

Test modified from adhesives industry (ASTM D2095) to carefully handle seal alignment

Specimen fabrication fixture

- Inconel fixture allows for 9 specimen to be fabricated in one furnace run.
- Sealing surface pressures can be achieved from 1 to 20 psi through the use of different size weights.
- Fixture can be used to fabricate glass seals, bonded compliant seals, or braze joints to 1100°C

Sample construction

0.020” Crofer 22 washer (Ni brazed to 430) on both sides

Dispensed Glass

Sealing surface
Shear Strength of the Interfaces and Seals
(modified ASTM F734-95 (2001))

Advantages of a torsion test for shear strength

- Torsion tests are among the ‘cleanest’ tests for pure shear.
- Bending and axial loads easy to control with misalignment couplers
- Test sample easy to machine from bar stock
- Test sample easy to align during seal cure and during testing
- No stress concentration issues normally seen in other types of flexural or shear testing methods
- Apparatus and specimen design easily adaptable to shear fatigue testing (esp. reverse shear)
- Multi-interface tests easy to assemble and align

- Device capable of testing up to 5000 in-lbs at temperatures up to 1200 C.
- Data acquisition records torque and angular displacement.
- Device can also apply axial load and torque simultaneously (strength, leak etc. of a loaded and cycled seal)
- New capability is currently being added for fuel gas or atmosphere introduced to inner cavity during test (inside the sealed annulus)
Flexure Strength G18 glass

Four point bend testing
- Fully articulated SiC fixture
- Cross-head speed = 0.5 mm/min
- Sample size 3 mm x 4mm x 50 mm

- Linear elastic up to 600C, Brittle failure
- Nonlinear (plastic deformation) at 800C

Flexure strength of G18 glass

Average of 8 to 10 bend bars

<table>
<thead>
<tr>
<th></th>
<th>batch #1</th>
<th>stdev</th>
<th>batch #1</th>
<th>stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>84</td>
<td>14</td>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>600C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Seal Failure Data and Analysis

Higher strength samples show fracture that crosses the thickness of the glass seal indicating an interface strength higher than the seal material.

At low sealing pressures, seals show evidence of interface debonding during high temp testing. Most of the glass is left on one side of the test specimen.

16 Mpa at 750 C
Room temperature shear strength of glass sealed assembly varies from 10 to 25 Mpa depending on fabrication process.
Data currently being generated for Modeling

**SOFC Materials**

- Fundamental Properties of G18 and other glasses
- Fundamental Properties of braze metals, Cu-Ag and Ni based

**Seal Failure Subtask**

- **Glass seal** (ferritic stainless to ferritic stainless)
  - Pure Tension and Shear stress at failure (Room temp and 720 C)
  - Biaxial Tension Torsion (Room temp and 720 C)
  - Thermal cycling (720 C tension and shear after cycling)

- **Braze seal** (ferritic stainless to ferritic stainless, and SS to YSZ)
  - Pure Tension and Shear stress at failure (Room temp and 720 C)
  - Biaxial Tension Torsion (Room temp and 720 C)
  - Thermal cycling (Room temp and 720 C tension and shear after cycling)

- **Bonded Compliant seal** (ferritic stainless to YSZ)
  - Pure Tension and Shear elastic response (Room temp and 720 C)
  - Failure (tension) in annular configuration (Room temp and 720C)
  - Elastic and failure response in square (frame) configuration
  - Thermal cycling (Room temp and 720 C tension and shear after cycling)

- **Compressive Mica seal**
  - Axial load to shear strength response (hot biaxial tension torsion)
  - Leak rate with axial load in air and in fuel gas
Adapco has created an Expert System Modeling Tool named ES-SOFC based upon the PNNL CFD-Electrochemistry Calculation Methodology.

The GUI takes an SOFC model from Concept, to Mesh Creation, to Post-processing.

PNNL Validation Case
ES-SOFC: Modeling Tool

ES-SOFC is capable of creating and performing simulations of a number of flow configurations (soon to include tubular designs).

Users can easily create cells of their own dimensioning and flow configurations for parametric simulations.

Built-In Templates for custom cross-, co-, and counter-flow configurations make parametric studies easy for the user.
ES-SOFC: Modeling Tool

ES-SOFC has capability to create multiple-cell stack models for simulation

Adapco will be demonstrating the tool during this SECA workshop.

ES-SOFC Status
• Development is complete
• Validation is nearly complete
• Reviewing and testing.
• Public release at end of May, 2004
SOFC Modeling Tools from MSC Software in Collaboration with PNNL

Technical approach

- **Commercial software:** provide the shortest path to well developed, multi-function tools that are widely accessible. MARC is used for its multi-physics capability, numerical stability and efficiency due to its implicit algorithm.

- **EC module:** in-house developed. 
  a) Electrochemistry based on continuum level I-V relations: two models; 
  b) Chemical reaction (water-gas shift, CH₄ internal reforming) based on equilibrium theory; 
  c) Flow solution based upon assumption of laminar flow, taking conservation law into consideration; 
  d) Distributed heat flux calculated according to respective mechanisms.

- **GUI:**
  a) effective way of generating stack model; 
  b) flexibility in adjusting (geometry & operational) model parameters; 
  c) user friendliness.

- **PNNL worked with MSC on the development of GUI. GUI details will be presented by MSC.**
On-Cell Steam-Methane Reforming (SMR)

Motivation:
- Create an SOFC system that is:
  - More compact,
  - More efficient, and
  - More energetic
  than an SOFC operating without steam-methane reformation
- The possibility for this exists because:
  - SMR is an endothermic reaction
  - Electrochemical reactions are exothermic
  - When these reactions take place simultaneously, the possibility exists for auto-thermal cell operation
- Results of this would include:
  - Decreased size of External Reformer
  - & decreased cooling air demand (more compact)
  - Improved fuel delivery system (more efficient)
  - Fuel (H2, and CO) enriched in process boosts power (more energetic & efficient)
On-Cell Steam-Methane Reforming (SMR)

Experimental Testing to Determine:
- Catalytic activity of the anode material (relative to other catalysts)
- Dependence of methane conversion rate on CH4, H2O, and CO2.
- Tests with “flow-by” and “plug flow” differential reactors to determine:
  - The intrinsic kinetics of the methane conversion and
  - The final form of the model used in the codes
- The ongoing tests will also provide knowledge of fuel recycling effects on the SMR kinetics.

“flow-by” - like actual cell w/ flow gap

“plug flow” – pore scale diffusion length

methane conversion and CO selectivity data from “flow-by” reactor tests at PNNL

Pacific Northwest National Laboratory
On-Cell Steam-Methane Reforming (SMR)

Kinetics model Presently Implemented: (Subject to Modification by Experiment)

- Described by Langmuir-Hinshelwood surface reaction mechanism
- The constants (Ki) are equilibrium constants for the gas species adsorbed on the catalyst surface (anode):

\[ r_{CH_4} \text{ (mol/s - m}^2) = \frac{K_1 K_2 K_3 P_{CH_4} P_{H_2O}}{(1 + K_2 P_{CH_4} + K_3 P_{H_2O})^2} \]

\[ K_i = A_i \exp\left(-\frac{E_i}{RT}\right) \]

Equilibrium constants have Arrenhius temperature dependence

K1 is the overall rate constant for methane conversion
K2 is the equilibrium constant for CH4
K3 is the equilibrium constant for H2O

<table>
<thead>
<tr>
<th>i</th>
<th>( A_i )</th>
<th>( E_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400-612, mol/s-m2</td>
<td>49</td>
</tr>
<tr>
<td>2</td>
<td>3e-4 to 5e-4, 1/kPa</td>
<td>-45</td>
</tr>
<tr>
<td>3</td>
<td>0.18 to 0.28, 1/kPa</td>
<td>7</td>
</tr>
</tbody>
</table>

SMR involves two Reactions:

**Steam Reformation**

\[ CH_4 + H_2O \rightarrow CO + 3H_2 \]

**Gas-Water Shift**

\[ CO + H_2O \rightarrow H_2 + CO_2 \]
Steam-Methane Reforming (SMR) EXAMPLE Cross-Flow Case

Effect of Steam-Methane Reformation:
- Maximum Cell Temperature Decreased
- Location of Tmax moved toward mid-cell
- Fuel Enriched by H2 and CO released
- Current/Power Density Increased by 50%

Problem Setup:
- Mole fractions of inflow fuel: H2=0.3, H2O=0.1, CH4=0.05 (ie. S:C=2.0), CO, CO2=0.01, 0.01
- Cell Voltage: 0.7 Volts
- Average cell temperature: 750°C

Temperature **without** SMR (Range: 729-795°C)

Temperature **with** SMR (Range: 714-788°C)

I = 0.18 A/cm²

I = 0.27 A/cm²
Degradation report was completed.

Fracture & leaks of PEN & seals is 1st priority.

Flow diversion caused by I/C deformation is 2nd priority.

Chemical degradation of electrical circuits & electrochemical interfaces is 3rd priority.
I-V Degradation Model

- A section of anode (500 µm), electrolyte (8 µm) and cathode (50 µm) is subdivided into nodes ranging in size from 1-20 µm.
- Averaged transport properties are used to describe gas diffusion, electrical conductivity, vacancy transport, etc.
- A voltage is applied at the electrode surfaces and the integrated current is calculated.
- Defects may be introduced, such as fractures, oxygen leaks and degraded transport properties due to sintering or changes in material composition.
- We look at the effect of fracture location on I-V performance.
I-V Degradation Model

Provides a detailed distribution of the following fields:

- Gas concentrations (O₂, H₂, H₂O, CO, CO₂, CH₄)
- Surface concentrations (O₂, H₂, H₂O)
- Electron electrochemical potential (\(\eta_e\))
- Temperature

Fracture Simulation Features

- Boundary conditions at electrode surfaces include specified voltage and gas composition.
- Kinetics for anode and cathode interfaces modeled using local Butler-Volmer expressions.
- Circular thumbnail fractures are introduced which disrupt the electric current but have little effect on gas diffusion.
Fractures at Various Cathode Locations

- Fractures that have minimal effect on performance (I-V Curve) are those that do not significantly destroy the current path:
  - At cathode center and parallel to electrolyte plane
  - Vertical fracture through cathode effectively bisecting the cathode

- Example of fracture having substantial effect:
  - The fracture located at electrolyte interface
  - The fracture starves the triple-phase region of current and significantly degrades cell performance
To realize the efficiency and reliability goals set out by SECA, SOFCs must be effectively controlled.

To design good control strategies, the dynamic or transient response of the SOFC must be known.

For example, the transient voltage response to changing loads affects the control of fuel flow, load management and the control algorithms in the power conversion electronics.

As a first step, we have investigated the transient voltage-current (V-I) relationship of an SOFC through experimental validation of a theoretical model.
Stack Dynamic V-I Validation Experimental Setup

Fuel Cell Test Bed with Furnace, Fuel Source and Test Circuit

Close-up of test circuit

Cell with hearth plate

Cell before assembly

Experimental Circuit Schematic

Power Supply

Fuel Cell

V_{out}

R R R

Pacific Northwest National Laboratory
Graph shows SOFC voltage versus time. The three load transitions are easily seen.
Dynamic V-I Relationship

Theoretical Model

\[ V_{oc} = \text{open circuit voltage} \]
\[ R_{ohm} = \text{ohmic resistance through cell} \]
\[ R_a = \text{activation loss, caused by slowness of reaction} \]
\[ C_{cdl} = \text{charge double layer effect capacitance} \]
\[ I = \text{electrical current} \]
\[ s = \text{Laplace variable} \]

Transfer Function

\[ \frac{V_{oc} - V_{out}(s)}{I(s)} = \frac{R_a R_{ohm} C_{cdl} \cdot s + R_a + R_{ohm}}{R_a C_{cdl} \cdot s + 1} \]
Future Modeling

- Validation of SOFC-ES and MSC-SOFC
- Further development of the SMR model including the incorporation of experimentation observations.
- Parametric studies to characterize effect of fracture on I-V relations using microstructural calculations.
- Degradation workshop and development of methodology for modeling degradation (combined with experiments)
- Seal property development
- Material data base development in collaboration with ORNL
- Release of dynamic system control software
- Incorporation of power electronic models in collaboration with University of Illinois.
- Thermal cycling of stacks and leak predictions.
Reduction of Carbon Formation From Nickel Catalysts Using Nickel-Gold Surface Alloys

David King, Yong Wang, Bob Rozmiarek, Ya-Huei (Cathy) Chin, John Hu
Pacific Northwest National Laboratory
SECA Annual Workshop and Core Technology Program Peer Review
May 12, 2004
Project Objectives

- Evaluate ability of gold modification of nickel catalysts to minimize carbon formation during hydrocarbon reformation.
- Quantify effect of gold addition to nickel catalyst surface on catalyst activity.
- Develop characterization techniques to clarify the effect of gold on nickel surface properties.
- Extend catalyst modification concepts to Ni anodes, enabling partial on-anode reforming of natural gas.
What is Known

- Carbon can form during reforming with nickel catalysts even under conditions not predicted by thermodynamics.
- Small crystallite nickel particles (<10nm) have been shown to be more resistant to carbon formation:
  - Maintenance of small crystallites under reforming conditions is challenging due to sintering and compound formation.
  - Plausible approach for pre-reforming.
- Addition of gold to nickel catalysts retards deposition of carbon and consequent deactivation.
Relevant Theories

**Step site model**
- The most active catalytic sites on nickel (step and edge sites) are also nucleation points for carbon formation
- Deactivation of these most active sites (by sulfur, gold, other) results in reducing carbon formation at some loss of catalytic activity

**Ensemble model**
- Groups of contiguous nickel atoms (ensembles) have high tendency to deposit carbon during reforming
- An impurity atom that breaks up ensemble size may retard carbon formation more than reforming activity
- Electronic properties of nickel atoms can also be altered by an ad-atom (ligand effect)
Project Tasks

- Baseline supported nickel catalyst (Ni/MgAl$_2$O$_4$) performance in reforming methane and butane
- Quantify effect of gold addition on carbon formation and reforming activity with supported Ni catalyst
- Develop analytical methodology to characterize nickel surface
- Verify methane reforming kinetics with Ni/YSZ anode
  - Provide to modeling effort
- Quantify effect of gold addition on carbon formation and reforming activity with nickel anode catalyst
TGA Studies Show Gold Addition Reduces Carbon Deposition From Supported Ni Catalysts

Total Carbon Deposition n-Butane Reforming S/C = 0.25
8 hours Isothermal Operation

% Mass

Temperature (C)

Ni 15.8%
Ni 15.8% Au 0.5%
Ni 8%
Ni 8% Au 0.5%
Particle Counting by TEM Shows Difference in Crystallite Size

700°C Reduction

8.8 % Ni/MgO-Al2O3

15.8 % Ni/MgO-Al2O3
Catalyst Preparation and Pretreatment

- **Ni/MgAl₂O₄**
  - Preparation
    - MgAl₂O₄ acquired from supplier, surface area 271 m²/g
    - Incipient wetness impregnation using Ni(NO₃)₂
    - Calcination: 500°C
  - Testing
    - Reduction: 700°C in H₂ (2h)
    - Begin flow H₂ and steam, then butane or methane

- **Ni-Au/MgAl₂O₄**
  - Preparation
    - Reduce (700°C) and passivate (1%O₂/He, ambient, 12h) Ni/MgAl₂O₄ catalyst
    - Add Au by incipient wetness impregnation of HAuCl₄
    - Dry at 200°C under inert atmosphere
  - Testing
    - Same as above
Test Reactor
Supported Nickel Catalyst Shows Rapid Deactivation in Butane Reforming

n-C4 Reforming Ni Small Particle
247,500 GHSV; 485°C; Varying Steam to Carbon

- C4 Conversion
- CO Selectivity
- CH4 Selectivity
- Change to 3:1 Steam to Carbon
- Change to 6:1 Steam to Carbon

Time (hrs)
0.4% Gold Addition Eliminates Nickel Catalyst Deactivation

Ni/Au Small Particle n-C4 Reforming
247,500 GHSV; 485°C; Varying Steam to Carbon

Conversion and Selectivity (%)

Time (hours)
Effect of Gold Addition on n-Butane Reforming with Supported Nickel Catalyst

![Graph showing the effect of gold addition on n-butane reforming conversion over time. The graph compares 8.8% Ni, 8.8% Ni 0.2% Au, and 8.8% Ni 0.4% Au catalysts. The conversion percentage is plotted against time on stream (hours).]
## Gold Addition to Achieve Theoretical Monolayer Coverage

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% Ni dispersion</th>
<th>Wt.% Au for monolayer coverage (1Au/3Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.8% Ni/MgAl2O4</td>
<td>4</td>
<td>0.61</td>
</tr>
<tr>
<td>8.8% Ni/MgAl2O4</td>
<td>4</td>
<td>0.36</td>
</tr>
<tr>
<td>50%Ni-50%YSZ anode</td>
<td>0.02</td>
<td>0.011</td>
</tr>
</tbody>
</table>
Suppression of Ni 2p peak observed with increasing Au loadings.
Comparison of XPS and Hydrogen Chemisorption on Au Promoted 15.8%Ni/MgAl2O4 Catalyst

XPS represents possible method to determine the fraction of Ni covered by Au
- Attenuation of Ni signal consistent with Au adsorbed on Ni surface
- Addition of 0.5% Au estimated to provide approximately 8-9% of a monolayer
- Not all Au is associated with Ni

Decrease in H₂ chemisorption upon Au addition is far greater than estimated monolayer coverage by XPS
- Consistent with effect of Au addition extending beyond simple site blocking
## Summary of H₂ Chemisorption Data

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pretreatment</th>
<th>H₂ Uptake, cc/g</th>
<th>Dispersion, %</th>
<th>Xtal size (H₂)</th>
<th>Xtal size (other)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.8%Ni/MgAl₂O₄</td>
<td>H₂, 900C</td>
<td>0.967</td>
<td>3.1</td>
<td>40</td>
<td>14 (TEM)</td>
</tr>
<tr>
<td>15.8%Ni-0.3%Au/MgAl₂O₄</td>
<td>H₂, 900C</td>
<td>0.771</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.8%Ni-0.5%Au/MgAl₂O₄</td>
<td>H₂, 900C</td>
<td>0.206</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.8%Ni/MgAl₂O₄</td>
<td>H₂, 900C</td>
<td>0.642</td>
<td>4.5</td>
<td>25</td>
<td>6 (SEM); 10 (TEM)</td>
</tr>
<tr>
<td>8.8%Ni/MgAl₂O₄</td>
<td>H₂, 700C</td>
<td>0.856</td>
<td>6.0</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>8.8%Ni-0.2%Au/MgAl₂O₄</td>
<td>H₂, 900C</td>
<td>0.196</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.8%Ni-0.4%Au/MgAl₂O₄</td>
<td>H₂, 900C</td>
<td>0.10</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Effect of Gold on Steam Reforming of Methane Over Supported Nickel Catalyst

247,500 GHSV; 485°C; 3:1 Steam to Carbon
Effect of Gold Addition on Hydrocarbon Conversion

- Butane Initial Conversion
- Methane Initial Conversion
- Hydrogen Uptake
N₂O Temperature Programmed Desorption

Mass 28 N₂

Mass 46 N₂O

Area under the peak

<table>
<thead>
<tr>
<th></th>
<th>N₂O</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>9583</td>
<td>3500</td>
</tr>
<tr>
<td>N-Au</td>
<td>3430</td>
<td>366</td>
</tr>
</tbody>
</table>
Summary of Probe Molecule Results

- **H₂ chemisorption**
  - Best method to quantify available surface sites, dispersion
  - H₂ uptake less than expected from XRD line broadening or TEM
  - Uptake significantly decreased with Au addition
  - H₂ uptake correlates with observed activity

- **N₂ chemisorption**
  - Proposed (in literature) as method to titrate step sites ("B5" sites)
  - Does not correlate with catalyst activity, carbon formation, or gold effects

- **H₂S titration of Ni surface sites**
  - Ambient temperature H₂S adsorption is significantly greater than H₂ chemisorption—suggests formation of bulk plus surface sulfides

- **N₂O TPD**
  - Two types of sites observed:
    - “A” sites--desorb N₂ (form NiO) at low temperature
    - “B” sites--desorb N₂O at higher temperature
  - Addition of Au reduces “A” sites more than “B” sites
  - Evaluating approach as method to distinguish step from planar sites
Nickel Anode Steam Methane Reforming

Potential benefits
- Use endothermic reforming reaction to consume heat generated in fuel cell operation
- Reduce cathode cooling by excess air
- Reduce or eliminate external reformer

Challenges
- Carbon formation catalyzed by Ni
- Temperature gradients near fuel inlet due to strong endotherm may lead to failure
- Need to spread out conversion over broader area of anode to achieve thermal balance
Nickel Anode Steam Methane Reforming

Approach

- Obtain kinetic data on methane reforming to support modeling effort
- Identify operating parameters leading to deactivation by carbon formation
- Quantify effect of Au addition on activity and activity maintenance under carbon forming conditions
- Develop methods for reliable, reproducible introduction of Au to anode
Ni YSZ Anode

- Composition: 60% ZrO₂-40% NiO₂ by volume; 50% NiO₂ by weight
- Particle size: 0.5-5 µm agglomerates
- BET: 0.43 m²/g
- H₂ adsorption: 0.0221 cc/g; 0.023% Ni dispersion

Testing method—anode substrate
- Two test strips 0.5x1” against opposite walls of channel
- Strips have YSZ on back side—only one active surface

Gold doping procedure
- Incipient wetness impregnation not viable method
- Pore fill anode material with solution of appropriate concentration HAuCl₄
- Procedure tends to give poorer dispersion of metals onto substrate
SEM of Ni/YSZ Anode (Reduced)

5000 X back-scattered image

10,000 X
Ni/YSZ Anode Shows Significant Deactivation in Butane Reforming

n-C4H10 Conversion (%)

Time on Stream (hours)

S/C = 6
S/C = 3
Anode Catalyst
Post Reaction with n-Butane

Carbon readily wipes off surface of anode
SEM of Deactivated Ni-Anode Following Butane Steam Reforming
SEM of Ni/YSZ Anode (Spent)

30,000 X

10,000 X

Back Scattered Image + SE image  50,000 X
## Ni Anode vs. Supported Nickel Catalyst Activity

<table>
<thead>
<tr>
<th></th>
<th>8.8%Ni/MgAl₂O₄</th>
<th>Ni/YSZ Anode</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mols C₄ converted/g catalyst-min</td>
<td>0.00721</td>
<td>0.000232</td>
<td>31.1</td>
</tr>
<tr>
<td>Mols C₄ converted/g Ni-min</td>
<td>0.08190</td>
<td>0.000463</td>
<td>176.9</td>
</tr>
<tr>
<td>Mols C₄ converted/ (cc H₂ uptake-min)</td>
<td>0.015499</td>
<td>0.011349</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Ni/YSZ Shows Small Effect of Au Addition

3:1 Steam to Carbon; 10:1 CH$_4$ to H$_2$, 700°C

0.02%Au on anode is equivalent to 0.8%Au on supported Ni catalyst

No deactivation observed with either material

Conversion (%)

0% 10% 20% 30% 40% 50% 60% 70% 80% 90% 100%

WHSV (sccm inlet/g cat)

0 100 200 300 400 500 600 700 800

Ni Anode

Ni Anode + 0.02% Au
Anode SEM After CH₄ Reforming
Summary and Conclusions

- Addition of gold to supported nickel catalyst at sub-monolayer coverage significantly retards carbon formation.
- Sufficient gold to retard carbon formation nickel results in decrease in catalyst activity by factor ~65-85%:
  - Methane conversion more affected by Au addition than butane conversion.
- \( \text{H}_2 \) chemisorption provides best method to correlate Ni availability with catalyst activity.
- \( \text{N}_2\text{O} \) chemisorption may provide method to measure step sites.
Summary and Conclusions

- Step site poisoning model does not fully explain results
  - Addition of gold affects many nearest neighbor Ni sites
  - Anode activity on surface Ni basis (H₂ chemisorption) comparable to supported Ni despite expected differences in step sites between two catalysts

- Reforming studies have been initiated over Ni/YSZ anode
  - Butane reforming at even 6:1 S:C observed
    - Filamentous carbon identified
    - Carbon filament diameter smaller than Ni/YSZ crystal size (by XRD)
  - Carbonizing effect not observed with CH₄ feed at 3:1 S:C and short reaction times
  - Addition of gold to Ni/YSZ shows small activity decrease compared to supported Ni case, based on current preparation method
Future Work

- Obtain kinetic data for on-anode reforming to support model development
- Evaluate effect of gold addition to Ni/YSZ for methane steam reforming
  - Carbon tolerance at reduced S/C ratios
  - Au concentration-reforming activity correlation
  - Identify best methods for Au introduction onto Ni/YSZ
- Evaluate effect of other additives to improve nickel anode performance (alkaline earth, Sn, Ce)
- Evaluate efficacy of natural gas pre-reforming with modified Ni catalysts
- Initiate studies of doped strontium titanate as sulfur-tolerant pre-reforming catalyst
Development of advanced SOFC anodes

Olga A. Marina
Pacific Northwest National Laboratory, Richland WA
Olga.Marina@pnl.gov

SECA Core Technology Program Peer Review
Boston, MA, May 11-13, 2004
Existing Technology: Nickel-YSZ Anode

**Pros**
- High electronic conductivity
- Excellent activity for clean reformed fuels
- Chemically and physically compatible with YSZ electrolyte
- Relatively inexpensive

**Cons**
- Sintering / agglomeration during operation
- Sensitive to oxygen
- Too high activity towards steam reforming
- Coking in hydrocarbons
- Easy poisoning by sulfur
- Toxic

**Objective:** Develop a high-performance anode that offers higher tolerance to oxidizing, hydrocarbon-containing and sulfur-containing environments.
Composite Sr(La)TiO$_3$ – Ce(La)O$_{2-\delta}$ anodes

**Pros**
- Excellent activity for H$_2$ oxidation - comparable to that of Ni-YSZ
- Dimensional, chemical and electro-chemical stability under multiple red-ox cycling
- Tolerance to sulfur impurities
- Resistance to carbon formation in hydrocarbon fuels
- Good TEC compatibility with other cell components
- Good adhesion to YSZ at relatively low temperatures

**Cons**
- Low electrical conductivity for use as self-support
- Potential reactivity with the YSZ electrolyte at high processing temperatures (above 1300°C)
- Loss of electrocatalytic activity following high processing temperatures
Approach

- Synthesis and characterization of oxides
  - Glycine-nitrite synthesis
    - Simultaneously co-synthesized
    - Separately synthesized and mixed
  - Calcination at 1200°C
  - XRD analysis
  - Attrition milling
  - Electrode ink
  - Screen printing on YSZ
  - Sintering at 900-1000°C
- 2- and 3-electrode cell tests
- Evaluation of the electrical, thermal and thermo-mechanical properties

2-electrode and 3-electrode configuration

<table>
<thead>
<tr>
<th>2-electrode and 3-electrode configuration</th>
</tr>
</thead>
</table>

- Anode seals: Pt or Au current collector
- Working electrode (Anode): Pt reference
- Cathode: Pt counter electrode
- Air: 2- and 3-electrode configuration
- H₂: Pt or Au current collector
Recent Highlights

- Evaluated different anode compositions
- Investigated properties of alternative dopants in the ceria phase
- Alternative dopants led to the improved activity for hydrogen oxidation
- Evaluated effects of sulfur (H₂S) on anode performance
- Implemented a deconvolution method to facilitate impedance data analysis
Optimization of anode compositions

- Evaluated different mixtures of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3 + \text{Ce}_{1-y}\text{La}_y\text{O}_{2-0.5y}$ to identify the most electrochemically active composition.

- Activity for hydrogen oxidation is mainly determined by the composition and amount of the ceria phase rather than the titanate phase; samples containing $\text{Sr}_{0.75}\text{La}_{0.25}\text{TiO}_3$-doped ceria and $\text{Sr}_{0.65}\text{La}_{0.35}\text{TiO}_3$-doped ceria showed similar activity.

- Increasing La content in the ceria phase ($\text{Ce}_{0.7}\text{La}_{0.3}\text{O}_{1.85}$, $\text{Ce}_{0.6}\text{La}_{0.4}\text{O}_{1.8}$ and $\text{Ce}_{0.5}\text{La}_{0.5}\text{O}_{1.75}$) led to an electrocatalytic activity increase.
Doped ceria phase optimization

Alternative dopants appear to give slightly better performance compared to La$_2$O$_3$ and Gd$_2$O$_3$ dopants.

Impedance spectra of doped ceria in H$_2$/H$_2$O=97/3 vs. Pt/air
Effect of gaseous sulfur additives (280 ppm H$_2$S) on cell performance

Experimental conditions
160 µm YSZ electrolyte-supported cell; (La)SrTiO$_3$ - Ce(La)O$_2$ (Ti/Ce=4) anode; LSF20 cathode with SDC interlayer; T=850°C; Cell voltage =0.3 Volt

Results
- 7% initial performance drop in the presence of 280 ppm H$_2$S
- Further 12% drop over 370 hours
- Anode full self-recovery after shutting H$_2$S down
- Visually, no sulfur deposits found on the anode after cooling in H$_2$
- Further degradation in H$_2$
- Anode degrading with time was not observed in half-cell measurements
**Effect of gaseous sulfur additives (950 ppm $H_2S$) on cell performance**

**Results**
- After initial 160 hours of operating in wet hydrogen, the cell ran for 500 hours on 90% hydrogen with 950 ppm $H_2S$.
- Performance dropped by 30% in the presence of $H_2S$.
- Self-recovered after turning $H_2S$ off (repeated twice).
- No air required to the anode for sulfur removal.

**Experimental conditions**
- 160 $\mu$m YSZ electrolyte-supported cell;
- $La_{0.35}Sr_{0.65}TiO_3 - Ce_{0.7}La_{0.3}O_2$ (7:3 mol%);
- LSF20 cathode with SDC interlayer; $T=850^\circ C$; Cell voltage =0.3 Volt.

---

**Graph Description**
- Current density (A/cm²) vs. time (hours).
- Graph showing the performance of the cell under different conditions:
  - 97% $H_2$
  - 90% $H_2 + 950$ ppm $H_2S$
  - 90% $H_2 + 10% N_2$
  - 90% $H_2 + 950$ ppm $H_2S$

**Legend**
- $\Delta 30\%$
Effect of gaseous sulfur additives (1000 ppm $H_2S$) on cell performance

Results
- 40% performance drop in the presence of 1000 ppm $H_2S$
- Anode self-recovery after shutting $H_2S$ down (repeated twice)
- No air or hot steam required for sulfur removal
- Visually, no sulfur deposits found on the anode after cooling in $H_2$
- Sulfur found on the alumina sample holder
- Final performance decrease of 18% may be related to (i) anode degradation in the presence of $H_2S$; (ii) cathode degradation with time; (iii) observed Pt current collector delamination from the anode; (iv) Pt poisoning by sulfur.

Experimental conditions
160 $\mu$m YSZ electrolyte-supported cell; (La)SrTiO$_3$- Ce(La)O$_2$ (Ti/Ce=4) anode; LSF20 cathode with SDC interlayer; $T=850^\circ C$; Cell voltage =0.7 Volt
Effect of $H_2S$ on the anode polarization resistance

Experimental conditions
Half-cell measurements
La$_{0.35}$Sr$_{0.65}$TiO$_3$ - Ce$_{0.7}$La$_{0.3}$O$_2$ (7:3 mol%)
T=850°C
12-24 hours at each pH$_2$S to reach steady-state
Predominance diagrams for Ce-S-O system

$S_2$ partial pressure is 10 and 1000 ppm;
Variables are $T$ and $pO_2$
XPS photoemission spectra of the S 2p region

- Control sample was tested in H₂ only and showed no sulfides.
- Samples #1 and 2 tested in H₂-H₂S contained surface sulfates. It is likely due to sulfides converted to sulfates in air. No bulk sulfides or elemental sulfur was found.
- Sample #3 contained surface sulfides and sulfates as well as bulk sulfides.

Red – as it is
Blue - after 4 kV Ar+ ion sputter ~100 nm
Deconvolution of impedance spectra for the identification of the electrode reaction mechanism

Impedance spectra can be described by the equivalent circuit series
\[ LR_s(RQ)_1(RQ)_2 \ldots (RQ)_n. \]

Due to the high complexity of the system it is difficult to separate the individual processes by conventional semi-empirical equivalent circuit models.

A deconvolution method is being implemented to calculate the relaxation distributions related to the physical processes [Schichlein et al., University of Karlsruhe]. With that it should be possible to recognize the different processes without \textit{a priori} knowledge.

Each peak on the distribution of relaxation times will correspond to a process.

Estimating \( R_n \) and calculating \( C_n \) one can find all \( (R_nC_n) \), suggest an equivalent circuit and using the nonlinear least square algorithm fit the experimental impedance spectrum.
Example of the relaxation time distribution
Anode composition was being optimized by

- Varying the La dopant in the titanate phase to increase the electronic conductivity;
- Varying the La dopant amount in the ceria phase to increase the catalytic activity;
- Using alternative dopants in the ceria phase to improve the activity.

Cell performance was evaluated in fuels containing potential impurities (sulfur).

Long-term performance test revealed relative tolerance of ceramic composites to H$_2$S:

- No performance loss was seen in fuels with H$_2$S lower than 30 ppm.
- Degradation in 50-1000 ppm of H$_2$S was reversible.
- XPS analysis of anodes operated in H$_2$-H$_2$S did not show the bulk sulfide formation.

Electrode reaction mechanisms are being elucidated using a deconvolution of impedance spectra approach.
Future work

- Long-term anode testing for carbon tolerance
- Anode tests in a variety of hydrocarbon fuels
- Scale-up testing to include larger dimension cells
- Further optimization of anode materials and microstructures
- Improvement of mechanistic understanding of effects of sulfur and carbon on anode performance
Acknowledgements

Financial support from the SECA Core Technology Program, U.S. Department of Energy, National Energy Technology Laboratory (NETL).

Contributors
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Cathode-Chromia Interactions

Steve Simner and Jeff Stevenson

May 13th, 2004

Funded as part of the Solid-State Energy Conversion Alliance (SECA) Core Technology Program by the U.S. Department of Energy’s National Energy Technology Laboratory (NETL).
Technical Issues

- Recent studies at PNNL have shifted from enhancing cathode electrochemical activity to understanding the effects of Cr containing alloys on cathode degradation.

- Generally agreed that there are at least two degradation mechanisms associated with Cr poisoning.
  
  • Solid state reaction of cathode and alloy oxide scales (typically Cr$_2$O$_3$ and MnCr$_2$O$_4$) $\Rightarrow$ poorly conducting interfacial phases.

  • Cr volatilization $\Rightarrow$ predominantly CrO$_3$ (g) and CrO$_2$(OH)$_2$ (g) evaporation, and subsequent re-condensation/reaction within the cathode, and at cathode-electrolyte interface.
R&D Objectives and Approach

- Principal objective is understanding the level of Cr interaction with established cathodes such as La(Sr)FeO$_3$, La(Sr)MnO$_3$ and La(Sr)Fe(Co)O$_3$.

- Modified button cell testing utilizing an alloy mesh compressed directly onto cathode → assessment of solid-state and vapor interactions.

- Conventional button cell testing utilizing a sintered Pt current collector with physical separation between the cathode and various Cr containing compounds (Cr$_2$O$_3$, LaCrO$_3$ and MnCr$_2$O$_4$) → relative vapor effects of different Cr sources.

- In-situ reactivity of aforementioned cathodes on alloy foil using HTXRD → technique enables direct assessment of phase formation at the cathode-alloy interface.
Compressive Button Cell Fixture

- Fixture enables compressive loading of alloy mesh onto cathode negating the need for sintered Pt/Ag contacts.
Experimental Details

- All cells consisted of anode-supported thin film YSZ configuration, and incorporated an Sm-doped ceria (SDC-20) protective interlayer.

- 3 cathodes considered: LSM-20 (sintered at 1150°C/2h), LSF-20 (1150°C/2h), LSCF-6428 (1050°C/2h).

- Preliminary data utilized a Crofer 22 APU mesh embedded in cathode contact paste and fired on cell at 800°C (temperature required for sealing). Contact pastes were the same composition as the bulk cathode.

- Typical operating conditions:
  - Cell temperature – 750°C
  - Cell voltage – 0.7V
  - Anode gas – 100 sccm H₂ – 100 sccm N₂ (3% H₂O)
  - Cathode gas – 300 sccm air (~25-35% relative humidity)
  - Test duration – ~100-120 hours
All 3 cathodes indicate significant degradation. LSM and LSF appear most susceptible to short-term Cr poisoning (50% or greater power loss in 110 hours).
SEM/EDX Analysis of Post-Tested Cathode-Crofer Samples

- EDX area and spot analysis conducted at 2-20 µm intervals from SDC interlayer to Crofer wire to establish Cr distribution.
LSF-Crofer (SEM/EDX Analysis)

- SDC interlayer and LSF cathode (fired at 1150°C) contain ~1 at.% Cr.

- LSF contact paste (fired at 800°C) contains ~3 at.% Cr – very defined boundary between the high and low Cr content regions – finer particles in contact paste presumably getter more Cr.

- LSF close to Crofer wire ~4-5 at.% Cr.

- A separate Cr rich phase is not readily discernible → Cr probably forms a solid solution with the LSF perovskite.
No discernible SrCrO$_4$ in agreement with SEM/EDX data. A high Fe/Sr ratio compound is formed again possibly implying that Cr is occupying Fe cation sites in the LSF perovskite.
LSCF-Crofer (SEM/EDX Analysis)

- No Cr detected in SDC layer or LSCF cathode layer.

- Contact paste (particularly close to Crofer wire) contains as much as 5 at.% Cr. Distinct high Sr-Cr phases detected \( \Rightarrow \) SrCrO\(_4\).

- At cathode-air interface a dense layer of SrCrO\(_4\) appears to form.
LSCF-6428 indicates substantial SrCrO$_4$ formation at 800$^\circ$C (due to higher Sr content). A high Fe/Sr ratio compound is also observed.
LSM-Crofer (SEM/EDX Analysis)

- SDC interlayer contains ~4-5 at.% Cr. No Cr detected in the LSM cathode (fired at 1150°C) – even adjacent to SDC layer. No Cr detected in bulk of 800°C fired LSM contact paste layer.

- LSM close (10-20 µm) to Crofer wire ~1-2 at.% Cr.

- 2 distinct phases discernible – one with zero Cr (likely pure LSM) and one with elevated Sr and Cr contents (possibly indicating SrCrO₄).
HTXRD – LSM-20 on Crofer Foil – 800ºC/72h

- LSM-20/Crofer interaction does not indicate SrCrO₄ formation – possibly amount formed below XRD detection limit. However, HTXRD analysis of an LSM/Cr₂O₃ powder mixture does suggest trace SrCrO₄ formation.
Summary of Crofer-Cathode Cell and XRD Data

- Solid state reactivity of cathodes with Crofer.
  - LSCF > LSF > LSM

- Short term (110 hours) cell degradation.
  - LSM > LSF > LSCF

- In the short term LSCF and LSF may getter more Cr and prevent Cr vapor migration to the cathode-electrolyte interface.

- LSM more susceptible to Cr evaporation due to low solid state reactivity.

- Implication is perhaps that Cr volatility and re-condensation adjacent to the electrolyte is more detrimental than cathode-Cr solid state reactivity.
Effect of Variable Chromia Sources on Cell Performance (750°C/0.7V)

- The chromia sources were physically separated from the cathodes via a fine porosity Pt layer to study the relative effects of Cr vapor species.

- \( \text{Cr}_2\text{O}_3 \) – initially the majority oxide scale component on Cr-containing alloys
- \( \text{MnCr}_2\text{O}_4 \) – can form a continuous layer above \( \text{Cr}_2\text{O}_3 \) scale on certain alloys
- \( \text{La(Sr)CrO}_3 \) – potential coating for alloy interconnects to reduce Cr volatility
LSF Cells with Variable Chromia Sources

- Only the presence of Cr$_2$O$_3$ initiates rapid degradation.
LSM Cells with Variable Chromia Sources

- SEM/EDX indicates significant Cr deposition at the LSM-electrolyte interface when Cr$_2$O$_3$ used as Cr source – other samples not yet analyzed.
LSCF Cells with Variable Chromia Sources

- LSCF cells indicate their own intrinsic degradation ➔ difficult to discern increased degradation rates with any of the Cr sources.
Approximately 0.3 µm LSCr-30 and LSM-20 sputtered onto Crofer foil prior to LSCF application.
Summary

- Different Cr related degradation mechanisms may predominate for each cathode.

  - **LSM** – indicates little solid state reaction but significant Cr deposition at cathode-electrolyte interface ➔ Cr vapor phase transport probably predominates.

  - **LSF** – Cr observed throughout cathode and at electrolyte interface ➔ possibly indicates degradation due to solid state and vapor phase interactions.

  - **LSCF** – highly reactive due to high Sr content ➔ LSCF very effective Cr getter – in the short term reduces effects of Cr volatility.

- As expected using Cr$_2$O$_3$ as a Cr vapor source causes severe degradation. La(Sr)CrO$_3$ and MnCr$_2$O$_4$ sources do not result in significant short-term poisoning.
Future Work

- All cell data presented is preliminary ➔ needs repeat sample verification.

- Longer-term testing (1000+ hours) of cells incorporating Crofer (and alternative alloy interconnects) ➔ Do the cells ever stabilize within this time-frame?

- Assess the effects of pre-oxidizing the Crofer ➔ after several hundred hours at 750-800°C Crofer should form a continuous MnCr₂O₄ layer – does this scale really suppress Cr volatilization?

- Establish effectiveness of various coatings (LSCr, LSM, LSCo, Ag) on Crofer foils with respect to solid state reaction and Cr evaporation suppression ➔ cell testing and HTXRD.

- May be possible to modify cathode chemistry or utilize graded cathodes incorporating different compositions to tolerate Cr interactions (with minimal degradation) until a protective spinel scale is formed.
After 100 hours of testing with ambient air, the air source was humidified to 100% RH → no discernible change in degradation rate.
LSM Cells with $\text{Cr}_2\text{O}_3$ Source at Various Operating Temperatures
Advanced Metallic Interconnect Development

Z. Gary Yang, Gordon Xia, Prabhakar Singh, Jeff Stevenson

SECA Annual Workshop and Core Technology Program Peer Review

Boston, May 11-13, 2004
**Interconnect Development**

**Objectives:**
- Develop cost-effective, optimized materials and coatings for intermediate temperature SOFC interconnect and interconnect/electrode interface applications.
- Identify and understand degradation processes in interconnects and at their interfaces.

**Approaches:**
- Evaluation of conventional and newly developed alloys (chemical, electrical, mechanical properties, cost).
- Investigation and understanding of degradations in bulk alloy interconnects and at their interfaces under SOFC operating conditions.
- Materials development
  - Surface modification
  - Bulk modification or alloy development
  - Cathode/interconnect interfaces
Focus Areas & Progress

- Study of Ni-based alloys.
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions.
- Development of cathode-side functional interfaces.
Focus Areas & Progress

- Study of Ni-based alloys
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions
- Development of cathode-side functional interfaces
Ferritic Stainless Steels: Status and Issues

Crofer22 APU

In-situ X-Ray Diffraction Analysis

- Scale volatility;
- Long term oxidation resistance under SOFC operating conditions;
- Life time scale electrical properties;
- Mechanical/thermomechanical stability.

Battelle
Study and Evaluation of Ni-Based Alloys

Why Ni-based Alloys?

- Excellent oxidation resistance, super high temperature strength, and good manufacturability.
- Formation of NiO top scale as potential Cr stopping layer.
- CTE can be modified through alloying.
- Scale can be potentially engineered for improved electrical conductivity.

Questions

- Can the required combination of properties be found in a single alloy composition?
- Cost?

Haynes242, C, S, and 230 were developed by Haynes International; LTES700 by Mitsubishi Heavy Industries.

### Alloys

<table>
<thead>
<tr>
<th>Alloysa</th>
<th>Nominal composition, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>Haynes242</td>
<td>Bal</td>
</tr>
<tr>
<td>LTES700</td>
<td>Bal</td>
</tr>
<tr>
<td>Hastelloy C-4</td>
<td>Bal</td>
</tr>
<tr>
<td>Hastelloy S</td>
<td>Bal</td>
</tr>
<tr>
<td>Haynes230</td>
<td>Bal</td>
</tr>
</tbody>
</table>

---

Haynes242, C, S, and 230 were developed by Haynes International; LTES700 by Mitsubishi Heavy Industries.
Low CTE Ni-Based Alloys

- Traditional Ni-based alloys have a CTE of 15.0~19.0 $\mu$m/m.K$^{-1}$ (RT~800°C). A relatively low CTE of 13.0~14.5 $\mu$m/m.K$^{-1}$ (RT~800°C) can be achieved via alloying.
- Mo, W, Ti and Al reduce CTE of Ni-based alloys; while Cr, Ta+Nb and Co increase it;
- Cr concentration has to be relatively low in these alloys.

\[
\alpha = 13.87 + 7.28 \times 10^{-2} \text{Cr} + 3.75 \times 10^{-2} (\text{Ta} + 1.95 \text{Nb}) + 1.98 \times 10^{-2} \text{Co} - 1.84 \times 10^{-2} \text{Al} - 7.95 \times 10^{-2} \text{W} - 8.24 \times 10^{-2} \text{Mo} - 1.63 \times 10^{-1} \text{Ti}
\]

Yamamoto, et al.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>TEC×10$^{-6}$ K$^{-1}$ (from manufacturers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crofer22 APU</td>
<td>12.2 RT-760°C</td>
</tr>
<tr>
<td>Haynes242</td>
<td>12.2-13.9 20-540-760°C</td>
</tr>
<tr>
<td>LTES700</td>
<td>13.6 RT-760°C</td>
</tr>
<tr>
<td>Hastelloy C-4</td>
<td>13.3-14.4 20-540-760°C</td>
</tr>
<tr>
<td>Hastelloy S</td>
<td>13.3-14.4 20-540-760°C</td>
</tr>
<tr>
<td>Haynes 230</td>
<td>15.2 25-800°C</td>
</tr>
</tbody>
</table>

From in-house measurement

Haynes230: 14.9 (25-800°C)
Hastelloy S: 14.8 (25-800°C)
Haynes242: 13.1 (25-800°C)
After oxidation at 800°C for 300 hours in moist AIR.

M: alloy substrate
G-γ’ precipitates
S: M₃O₄ (spinel)
C: Cr₂O₃
N: NiO

1. Haynes242
2. Hastelloy S
3. Haynes230
After oxidation at 800°C for 300 hours in moist HYDROGEN.

M: alloy substrate
G-γ’ precipitates
S: M₃O₄ (spinel)
C: Cr₂O₃

Intensity (a.u.)

2θ
Scale ASR

The measurement was carried out at 800°C in moist air.
Summary

**Ferritic Stainless Steels**

- The newly developed FSS demonstrates reduced scale volatility, good CTE matching, reduced scaled resistance, and improved surface compatibility with sealing glasses.
- There is however a need for further improvement in long term scale chemical, electrical, and mechanical stability (for temperatures >700°C).

**Ni-Based Alloys**

- CTE of Ni-based alloys can be adjusted to a relatively low value via lowering Cr% and adding metal elements such as W, Mo, etc.
- The decreased Cr% may however raises concerns over the oxidation resistance of an alloy in cathode environment; The heavy alloying also creates nonlinearity in the CTE curve.
- A scale with a NiO outer-layer can be formed on low Cr% Ni-alloys in cathode-side environment, but its suitability as an electrically conductive protective layer is questionable.
Focus Areas & Progress

- Study of Ni-based alloys
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions
- Development of cathode-side functional interfaces
Oxidation Behavior of Alloys under Interconnect Dual Exposures

Motivation:
- Oxidation study has been a common area of interest, but typically under single atmosphere exposure.
- Dual exposures are commonly found in SOFC stacks and BOP, as well as other systems.
- Understanding helps develop robust materials.

Materials studied:

- NiBS
  - Haynes 230-22%Cr
  - Hastelloy S-17%Cr
  - FeSS
  - Haynes 242-8%Cr

- Crofer22-22%Cr
- AISI430-17%Cr
- E-brite-27%Cr

Variables:
- Alloy composition
- Isothermal vs. cycling
- Moisture
Anomalous Oxidation of FSS under Interconnect Dual Exposures: A Summary

The DUAL exposures lead to an anomalous oxidation behavior of ferritic stainless steels under the SOFC interconnect dual exposure conditions;

The anomalous oxidation behavior appears to be caused by hydrogen diffusion from the fuel side to the airside of alloy interconnects.

- For 430 with 17% Cr, dual exposures enhanced the iron transport in the scale on the airside, leading to hematite formation and localized attack;
- For Crofer22 (22% Cr), Fe enrichment was found in the spinel layer after isothermal oxidation; thermal cycling resulted in the hematite nodule formation and localized attack;
- For ferritic stainless steels with enough chromium, e.g. E-brite (27% Cr), the accelerated iron transport and iron oxide formation are inhibited, though differences in scale microstructure and morphology are observed.

Airside of Crofer22 APU

Isothermal: 800°C, 300h

Thermal cycling: 800°C, 3x100h
Crofer22 APU: Effects of Moisture

Grown on the coupon in moist (3%H₂O) air only and on the airside of the coupon that was ISOTHERMALLY heat-treated at 800°C, 300 hours.

Presence of moisture accelerated the anomalous oxidation.
**Haynes230: Oxidation Behavior**

Grown on the coupon in **air only** (ambient air) and on the **airside** of the coupon that was **isothermally** heat-treated at 800°C, 300 hours.
Hastelloy S: Oxidation Behavior

Grown on the coupon in **air only** and on the **airside** of the coupon that was **isothermally** heat-treated at 800°C, 300 hours.

- **M**-metal substrate
- **G**-γ' precipitation
- **C**-Cr$_2$O$_3$
- **S**-(Mn,Ni,Cr)$_3$O$_4$
- **N**-NiO

---

**Air exposure at both sides**

**Airside of dual exposures**
Haynes242: Oxidation Behavior

Grown on the coupon in **air only** and on the **airside** of the coupon that was **isothermally** heat-treated at 800°C, 300 hours.

![Air exposure at both sides](image1)

![Airside of dual exposures](image2)
Summary

- For **ferritic stainless steels** with relatively low chromium levels (22% or less), dual exposure enhances the iron transport in scale on the airside, leading to hematite formation and localized attack.

- The presence of moisture enhances the anomalous oxidation, leading to localized attack.

- For **Ni-based alloys**, dual atmosphere exposure tends to reduce NiO formation, and to facilitate the formation of a uniform chromia/spinel dominated scale.
Focus Areas & Progress

- Study of Ni-based alloys
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions
- Development of cathode-side functional interfaces
Cathode-Side Functional Interfaces

Before assembly

- Cathode
  - Contact layer
  - Protection layer
    - Chromia forming alloy interconnects

During operation

- Cathode
  - Contact layer
  - Protection layer
    - $\text{Cr}_2\text{O}_3$
      - Chromia forming alloy interconnects

- Protection layer acts as a mass barrier to mitigate or prevent Cr migration via both gas transport and solid state reactions, as well as to decrease electrical contact resistance. The subsequently grown chromia sub-scale serves as cation and anion transport barrier, protecting the alloy interconnect.

- Contact layer promotes contact between cathodes and interconnects, and helps minimize interfacial resistance and power loss.
The provskite coatings decrease electrical resistance and mitigate or prevent Cr migration;

The growth rate of the chromia beneath the coatings and the eventual scale depends on the ionic conductivity of coatings.

Long term stability needs to be further studied.

Both bare and coated samples were pre-oxidized in air at 800°C for 100h before carrying out tests in air at 800°C.
Thermal Grown Spinel Protection Layer

**Concept**

- **As prepared**
  - Ms$_3$O$_4$ spinel
  - Chromia forming alloy interconnects

- **During operation**
  - Ms$_3$O$_4$ spinel
  - Cr$_2$O$_3$
  - Chromia forming alloy interconnects

**Approach**

- Solution coating, PVD, CVD or EC plating of spinel formation metals.
- Growth of a thin spinel layer via reactions during a heat treatment in an optimized environment.
- Formation of a spinel-chromia functional scale on interconnects during subsequent oxidation or SOFC operations.

The protection layer is intended to be thermally grown.
Growth of \((\text{Mn,Co})_3\text{O}_4\) on Crofer22 APU

Current focus is on thermally grown spinels which contain no Cr and/or are more stable than \((\text{Cr,Mn})_3\text{O}_4\).

\begin{align*}
\text{MnCO}_3 + \text{Co}_3\text{O}_4 \\
\text{Slurry coating} \\
\text{Heat treating in 2.75H}_2 + \text{Ar at 950°C for 24 hours.} \\
\text{Oxidation in oxidizing environment}
\end{align*}

\textbf{Graph:}
- \textbf{S: Spinel Ms}_3\text{O}_4
- \textbf{Co: Cobalt}
- \textbf{M: Crofer22 APU}

\textbf{Legend:}
- \text{Mn0.1Co0.9}
- \text{Mn0.3Co0.7}
- \text{Mn0.5Co0.5}
- \text{Mn0.7Co0.3}
Interfacial ASR of Crofer22 APU Grown with Spinel Protection Layers

The (Mn,Co)$_3$O$_4$ spinel protection layer on Crofer22 APU minimizes the interfacial resistance when (La$_{0.8}$Sr$_{0.2}$)Co$_{0.5}$Mn$_{0.5}$O$_3$ used as a electrical contact.

\[
\text{ASR}_{\text{cathode/interconnect}} = \Phi(\text{scale, contacts, reactions})
\]
Continuous, thin spinel protection layer can be thermally grown on chromia forming alloys during optimized pre-heat treating; the spinel protection layer is intended to help minimize volatilization of Cr vapor species and the interfacial electrical resistance.

Preliminary work on Co/Mn spinel layers indicates low interfacial electrical resistance.

Mitigation of Cr volatility to be verified experimentally.
Future Work:

Study oxidation behavior under dual exposures

- Mechanistic understanding: Interaction and transport of H/H⁺ at the metal/oxide interface and in the oxide scale; their effects on defect structure, transport properties, scale growth.
- Study effects of dual exposure on scale electrical conductivity.
- Oxidation behavior of alloys under the reforming gas/air dual exposures.

Investigate and develop cathode-side functional interfaces

- Spinel protection layers: Continue to screen and search for spinels that compatible to candidate alloys and more thermochemically stable than (Mn,Cr)₃O₄; optimize processing and materials composition.
- Electrical contact layers: Continue to study the interactions between conductive oxides and candidate alloys; investigate the interfacial ASR and optimize the composition for a minimized interfacial resistance.

Develop and investigate cladded composite-structure interconnects

- Continue to the proof of concept investigation.
- Study interdiffusion and predict life via modeling.
- Optimize structure and compositions.
The authors wish to thank Wayne Surdoval, Lane Wilson, and Don Collins (NETL) for their helpful discussions regarding this work. This work was funded by the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.
Compressive Seal Development for Solid Oxide Fuel Cells

Y-S Matt Chou, Jeffry W. Stevenson
and Prabhakar Singh

Pacific Northwest National Laboratory
Richland, WA 99352

Funded under the SECA Core Technology Program
through US Department of Energy’s
National Energy Technology Laboratory (NETL)

April 17-21, 2005, Asilomar, CA
Outline

- Status of mica-seal development
- Current work objective
- Results of long-term ageing and thermal cycling
  - Problem of degradation/reaction of mica/G18
  - Solutions to reactive interlayer glasses
  - Ageing and thermal cycling with metallic interlayer
  - Issue of long-term Ag volatilization
  - Reproducibility with Ag interlayers
  - Isothermal ageing in 30v% H₂O fuels
  - Fractography
  - Issue of long-term mica volatilization in 30v% H₂O
- Summary and conclusion
- Future work
**Status of compressive mica seal**

- Final goals:
  - >40,000 hrs stability
  - >$10^2$ or $10^3$ cycle
  - No degradation to mating mat’l
  - Low stresses
  - Low cost in SOFC stack
  - Vibrational stability?

**Hybrid micas**
- Survived ~4000 hr, 47+30+10 cycles @12 psi, 0.02-0.04 sccm/cm @0.2psi
- Showed reproducibility
- Survived 88 cycles@12.5 psi
- Showed low leakage @ 6 psi and Nernst OCV

**Hybrid Ag micas**
- Aged 1000hrs and 39 cycles in 70%H$_2$/30%H$_2$O, 0.02-0.03 sccm/cm

**Glass-mica composites**
- Infiltrated micas
- Hybrid micas

**Plain mica paper**
- Plain Muscovite mica (monolithic)

*3 solutions* to minimize materials degradation

*Pacific Northwest National Laboratory*
*U.S. Department of Energy*
1st and 2nd (FY05) quarters:
The objective was to evaluate the combined isothermal ageing and thermal cycling effect on hybrid mica seals of metallic interlayers with respect to materials and interfacial degradations in a simulated and high water content (30 v%) SOFC environment.
Hybrid Phlogopite mica

Phlogopite is more thermally stable (~960°C) than Muscovite (~600°C)
Isothermal ageing and short-term thermal cycling

800°C ageing
- 850°C/1h
- 800°C/1000h
- 750/4h
- 10h

Thermal cycling
- 800°C/2h
- 800°C/1000h
- ~100°C
- 2h
- 4h
Combined ageing and thermal cycling of hybrid mica with G18 glass interlayers

Inc/G18/PH-A or PH-B/G18/8YSZ @ 6psi with flowing ~2.7%H₂/Ar+~3% H₂O

800°C ageing

PH-A: Cogebi, cogemica, PH-B: McMaster Carr

800°C ageing thermal cycling
Cross-section of aged and cycled hybrid mica with G18 glass

Pressed @6psi after 1036 hrs ageing and 21 cycles

- Fracture occurred along with the G18 glass near the Inconel600 side
- Thick G18 glass showed undesirable porous microstructure
Solutions to minimize mica degradation

- Promote rapid crystallization of G18 by adding nucleation agent (e.g., TiO$_2$)
- Use less reactive (more “refractory”) glass G-M (less B$_2$O$_3$)
- Use of non-reactive metallic materials (Ag, Cu, etc)
No degradation of mica with glass G-M

**Graphs:**

1. **Inconel/GM/PH8/GM/SS430 (AR or CT), 6 psi**
   - X-axis: hrs @ 800°C
   - Y-axis: sccm/cm @ 800°C
   - Data points for #1 and #2

2. **After ageing @800°C for 1000 hrs**
   - X-axis: # thermal cycles
   - Y-axis: sccm/cm @ 800°C
   - Data points for #1 and #2

**Text:**

- Inconel/GM/PH8/GM/CT SS430 @ 6 psi after 1000 hrs 800°C and 34 cycles
Hybrid mica with metallic interlayers

- Non-reactive with Mica
- Volatilization issue
- Oxidation issue
- Poison issue
- High water content fuels
- Easily deformed
- Adhere or bonding to metal of high CTE
- Ag, Cu, and brazes
Ageing and thermal cycling of hybrid mica with Ag interlayers (0-4000 hrs)

Inconel/Ag/Phlogopite/Ag/8YSZ @12psi

**Isothermal ageing**

**Thermal cycling after ageing**

fuel loss = 0.2% @0.03 sccm/cm, 0.2 psid, 0.7V, 0.5 W/cm², 800°C, 80% fuel utilization of pure hydrogen of a 6”x6” SOFC cell

SECA target: fuel loss <1% @ 0.1 psid after 10 thermal cycles for 6”x6”
Good reproducibility for hybrid mica with Ag interlayers

Inconel/Ag/Ph-mica/Ag/SS430 @12psi, 2.7%H₂/Ar+~3% H₂O

Isothermal ageing @12psi hybrid Ag mica in flowing ~2.7% H₂/Ar + ~3% H₂O

Thermal cycling after isothermal ageing in a flowing ~2.7% H₂/Ar + ~3% H₂O

Battelle

Pacific Northwest National Laboratory
U.S. Department of Energy
Fracture surface of aged and cycled hybrid mica with Ag interlayers

12 psi, 800°C/1000 hr 45 cycles
Issue of vaporization loss of Ag


- 690°C/air: 0.094 μg/cm²/h, 2.16% @40,000hrs
- 790°C/air: 1.29 μg/cm²/h, 28.7% @40,000 hrs
- 800°C/Ar/H₂/H₂O: 0.161 μg/cm²/h, 2.33% @40,000 hrs
~1 wt% loss of Ag in hybrid mica over 40,000 hrs @ 790-800°C

For a width (W) = 0.5 cm
\[ \rho(\text{Ag}) = 10.5 \text{ g/cc} \]

Ag loss on fuel side
= \[40,000(aTL)/(\rho TWL) = 0.12\% \]
Ag loss on air side
= \[40,000(bTL)/(\rho TWL) = 0.98\% \]

- Loss from exposed edges only
- No diffusion loss to metals
- Electrical shorting?
- Degradation of electrochemical performance unknown; however, possible solutions are available.
Ageing and thermal cycling of hybrid mica in high humidity (30v%) fuel gas

Inconel/Ag/Phlogopite/Ag/8YSZ @12psi

 Isothermal ageing

 Thermal cycling after ageing
Fracture surface of aged hybrid mica in 70% H₂/30% H₂O @800°C

Inconel/Ag/Phlogopite/Ag/8YSZ @12psi, 1000hrs and 39 cycles

Majority fracture between mica flakes, one spot of mica/Ag interface
Issue of vaporization loss of Phlogopite mica, KMg$_3$(AlSi$_3$O$_{10}$)(F,OH)$_2$

- Silicate glass material loss by Si(OH)$_4$ g
- 1”x1” mica exposed in 2.7% H$_2$/bal. Ar + ~30v% H$_2$O @ 100 sccm, 800°C

slope =
~1.2x10$^{-4}$mg/cm$^2$/h
~1.6x10$^{-4}$mg/cm$^2$/h

Incomplete binder
Burnout <200 hrs
No degradation to mica exposed to 30 v% H₂O @ 800°C/1400hrs

1”x1” mica in 2.7% H₂/bal. Ar + ~30v% H₂O @ 100 sccm, 800°C/1400 hrs

before ageing

after ageing
No degradation to mica exposed to 30 v% H₂O @ 800°C/1400 hrs

1”x1” mica in 2.7% H₂/bal. Ar + ~30v% H₂O @ 100 sccm, 800°C/1400 hrs

<table>
<thead>
<tr>
<th>Element</th>
<th>before</th>
<th>after</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>46.3</td>
<td>48.1</td>
</tr>
<tr>
<td>F K</td>
<td>4.34</td>
<td>4.1</td>
</tr>
<tr>
<td>Mg K</td>
<td>14.97</td>
<td>14.44</td>
</tr>
<tr>
<td>Al K</td>
<td>6.69</td>
<td>6.56</td>
</tr>
<tr>
<td>Si K</td>
<td>20.15</td>
<td>19.51</td>
</tr>
<tr>
<td>K K</td>
<td>6.09</td>
<td>5.75</td>
</tr>
<tr>
<td>Ti K</td>
<td>0.25</td>
<td>0.23</td>
</tr>
<tr>
<td>Fe K</td>
<td>1.22</td>
<td>1.32</td>
</tr>
</tbody>
</table>
Minute loss (<0.5 wt%) of Phlogopite @ 800°C and 30 v% H₂O fuel gas

For a width (W) = 0.5 cm
ρ(mica) = ~2.82 g/cc
a=1.2-1.6 mg/cm²/hr

mica loss on fuel side
= 40,000(aTL)/(ρTWL)
= ~0.34-0.45 wt%

• mica loss from free exposed edges at fuel side only
Engineering control the leak rate

\[
\text{total leak} = K_{\text{eff}} A \frac{dP}{dx} + D_{\text{eff}} A \frac{dC}{dx}
\]

Reduce leak by increasing seal width and/or reducing mica thickness

- Inconel/G6/PP80/G6/SS430, 12psi, 2.64% H2/Ar+ ~3%H2O @ 64 sccm

![Graph showing leak rate sccm/cm @ 800C over hours at 800C](image)
Conclusion

Hybrid Phlogopite mica demonstrated desirable properties as a strong candidate for SOFC sealing:

- Long-term thermal cycle stability over 1026 cycles.
- Long-term ageing stability with constant leak rates (~0.02 sccm/cm) over 4,000 hrs.
- Constant leakage during combined ageing and thermal cycling.
- Low leakage (~0.01-0.02 sccm/cm) at minimal stress of 6 psi.
- Good thermal stability in high water content fuels (30 v%), lean and rich in hydrogen.
- Calculated minute materials loss due to volatilization over 40,000 hrs.
- Identified the effect of mica thickness and compressive stresses.
- Identified cause for mica degradations and 3 solutions demonstrated.
- Good reproducibility and scale-up from 2”x2” to 3.5”x3.5”.
- No effect of temperature gradients on leakage during thermal cycling.
- Low leakage (~0.02 sccm/cm) satisfied SECA’s target of <1% fuel loss.
- Low cost, easy processing, and engineering.
Future work

- Development of durable low-cost glass (glass-ceramics) seals with minimal materials/interfacial interaction/degradation and engineered interface for optimal shear strength at various sealing temperatures.

- Study interfacial reaction/degradation of G/M and G/C at various stages of operation, temperatures, and environments.

- Understand and model engineered interface for optimal interfacial strength: to prevent Mode II and III fracture.

- Evaluate “refractory” glass compositional effect on basic thermal properties (T<sub>g</sub>, T<sub>s</sub>, T<sub>c</sub>, CTE, sealing temperatures, 850-1100°C).

- Identify the microstructural effect due to crystallization on basic thermal and mechanical properties.

- Candidate metals: Crofer22 and FeCrAl and surface treatment.

- Candidate ceramics: 8YSZ/NiO-YSZ anode bilayers.

- Candidate glasses: alkaline earth-Al-Ca-Silicates.
Weakest link is at the metal/glass interface

Oxidation scale or reaction/corrosion products at the metal/glass interfaces often have mismatched CTE.

- Oxidation
- Interfacial reaction BaCrO₄
- Inter-diffusion precipitation and reaction
- Cr, Fe
- molten glass corrosion
- SiO₂ loss in humid environment
- sub-critical crack growth with H₂O
- grain growth of phases with low CTE
- phases anisotropy
- minor reaction YSZ with glass: BaZrO₃, SrZrO₃
proposed fracture of a rigid glass (glass-ceramic) seal at various stages

Short-term, 96 h

Intermediate stage, 1000 h

metal

8YSZ

short-term (through glass)

intermediate-Term (mixed)

long-term Metal/glass Interfacial failure
Finite Element SOFC Analysis with SOFC-MP and MSC.Marc/Mentat-FC

Ken Johnson,
Speaker
Pacific Northwest National Laboratory

SECA 6th Annual Workshop,
April 18-21, 2005
**Solution Flow**

- **Mentat-FC:**
  Graphical User Interface for flexible finite element model generation.

- **SOFC-MP:**
  Finite element based electrochemistry, flow and heat transfer solution.

- **MSC.Marc:**
  Finite element stress analysis with temperatures from SOFC-MP.
Mentat-FC: Parametric and CAD based Models

Parametric
- Fixed SOFC designs
- Meshed from dimensional parameters
- Used for parametric design studies

CAD Based
- Meshed from user CAD files
- Accepts existing FE meshes
- Quick generation of very complex models
Mentat-FC: Model Generation from CAD Geometries

- Finite element grid meshed from CAD volumes.
- Generic ACIS file format used.
- Layers identified by name.
- Material properties assigned to components from the database.
- Contact and boundary conditions are defined.
Mesh Generated from CAD

67,919 Nodes
30,629 elements
Generic Model Regions are Defined for Meshing

- **Required Regions** - define bounds of the electrochemical and flow calculations:
  - PEN layers = Anode, Electrolyte, Cathode.
  - Fuel = Inlet, Outlet, Anode flow channel.
  - Air = Inlet, Outlet, Cathode flow channel.
  - Separator plates.

- **Additional Regions** – define the PEN Support Structure = components making up the manifolds, seals, and structure around the PEN.
  - Anode and Cathode spacers.
  - PEN support frame.
  - Seals.
Material Data and Electrochemical Parameters

Material data base for thermal, electrical, and structural properties is included for:

- Metallic interlayers and support plates
- Seals,
- Anode, electrolyte, and cathode layers

Electrochemistry parameters

- I-V relationships
- Fuel and Air composition and flow rates.
- Startup conditions
Features of SOFC-MP

- **Generic fuel and oxidants** can be simulated. NASA’s CEA code used for chemical equilibrium and species calculations.

- **Finite element based** flow, temperature and electrochemistry calculations. Thermal and structural solutions use the same mesh.

- **Reduced dimensional analysis** for fast flow solution.

- **Contact algorithms** treat incompatible meshes for contacting solids with different surface profiles.
Reduced Dimensional Approach for Fast Approximate Solutions

Reduced Analysis

- Electrochemistry – 1D through thickness of the PEN
- Flow
  - Manifolds – Use an analytical pipe flow approximation
  - Channels across Cell – 2D with hydraulic approximation for varying channel height.
- Temperature – 3D for solids, 2D in flow domains.

Full 3D Analysis

- Stress and Distortion – 3D in solids.
Solution Performance

- Algorithms are efficient for rapid analysis and extension to transient thermal-mechanical analysis.
- Single cell examples on a single processor (Memory~1.5 Gb)
  - Mentat-FC Mesh generation ~ 15 min.
  - SOFC-MP solution ~20 min.
  - MSC.Marc stress solution ~ 3 min.
- Coarse stack models with up to 3 cells have been run on the PC.
- Significant multi-cell analysis requires parallel processing for:
  - Increased memory
  - Reduced compute time.
### Generating a Model from CAD files

<table>
<thead>
<tr>
<th>Required Components</th>
<th>Additional Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Separator Plate – Blank</td>
<td>Anode Seal</td>
</tr>
<tr>
<td>Fuel Flow</td>
<td>Anode Spacer</td>
</tr>
<tr>
<td>Anode</td>
<td>Picture Frame</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Pen Seal</td>
</tr>
<tr>
<td>Cathode</td>
<td>Cathode Seal</td>
</tr>
<tr>
<td>Air Flow</td>
<td>Cathode Spacer</td>
</tr>
<tr>
<td>Separator Plate</td>
<td></td>
</tr>
<tr>
<td>Fuel In</td>
<td></td>
</tr>
<tr>
<td>Fuel Out</td>
<td></td>
</tr>
<tr>
<td>Air In</td>
<td></td>
</tr>
<tr>
<td>Air Out</td>
<td></td>
</tr>
</tbody>
</table>

**Diagram:**

[Diagram showing components of a fuel cell model]
Importing Existing FE Meshes

- User provides meshes identified for individual components.
- Can mix and match with CAD generated components.
- Fuel and Air cavities must also be meshed.
- Incompatible meshes are allowed through contact.
- Hex v.s. tetrahedral elements
  - Hex and wedge elements give smaller mesh and more accurate stresses in solid layers.
  - Tetrahedral mesh is sufficient for mapping temperatures in fuel and air.

Example ANSYS mesh read into Marc
Starting Mentat-FC

Mentat-FC Solid Oxide Fuel Cell Analysis Program

A cooperative effort between:

MSC Software

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

- Parametric SOFC
  Allows for input of parametric dimensions for SOFC
- CAD Input SOFC
  Allows for input of generic CAD/FEA files

Cancel
The CAD Opening Menu

- **Model Generation**
  - Number of cell stacks
  - Model refinement (Coarse)

- **EC Cell Performance**
  - Model refinement selection (Coarse, Medium, Fine)
  - OK button

No. of cells in stack
CAD file specification

Required

Specify scale factor to convert input geometry to m units (default = 1.0):

OK

Additional
Extruded = surface mesh extruded through thickness

Non-extruded = Tetrahedral meshing of air and fuel solids
Material properties are from the SECA database:
- PNNL and ORNL data on cell materials.
- PNNL data on seal materials.
Finite Element Model Generation

Four ‘action’ buttons to provide for complete fuel cell model generation

1. Mesh solids
2. Define exterior surfaces
3. for radiation and convection.
4. Duplicate cells for stack mesh
5. Apply structural boundary conditions
Parametric Based Model Input
Defining Cell Performance

- **IV Relation**: Tafel-Volkov
- **EC Operation**: None
- **Ohmic Polarization**: None
- **Activation Polarization**: None
- **Concentration Polarization**: None
- **Fuel and Oxidant Definition**: None
- **Boundary Conditions**: None
- **Process Summary**: None
- **Update Analysis Model**: None

**Total Voltage Operation**
- Total Voltage = Voltage \times \text{no. of cells in stack}
- Voltage (V): 0.7
- No of Cells: 1
- Total Voltage (V): 0.7

**Total Current Operation**
- Total Current = \text{current} \times \text{active PEN area}
- Current (A/cm^2): 1.0
- Active PEN area: 0
- Total Current (A): 0

**Fuel Utilization Operation**
- Fuel Utilization (%): 0.50
Ohmic Polarization

For TAFEL-VIRKAR Relation

Electrolyte Conductivity \( k = AT^3 + BT^2 + CT + D \):

- A
- B
- C
- D

Effective Activation Energy: 0.007355
Prefactor: 6.97e-7

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Anode Parameters</th>
<th>Cathode Parameters</th>
<th>Interconnect Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td>1273</td>
<td>1273</td>
<td>1273</td>
</tr>
<tr>
<td>Ohmic Resistance</td>
<td>3.33e-5</td>
<td>7.69e-5</td>
<td>4.0e-5</td>
</tr>
</tbody>
</table>

For BUTLER-VOLMER Relation

Activation Energy
Pre-factor
Porosity
Conductivity
### Activation Polarization

#### For TAFEL-VIPKAR Relation

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Exchange Current (A/</th>
<th></th>
<th>Tafel Prefactor</th>
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</thead>
<tbody>
<tr>
<td>923</td>
<td>0.051e-4</td>
<td></td>
<td>0.031</td>
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<tr>
<td>973</td>
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<tr>
<td>1073</td>
<td>0.132e-4</td>
<td></td>
<td>0.0247</td>
</tr>
</tbody>
</table>

#### For BUTLER-VOLMER Relation

Exchange Current ($i=\text{prefactor} \cdot \exp(-\text{act. energy/RT})$:

- **Activation Energy**
- **Prefactor**
- **Symmetry Factor**

**OK**
Concentration Polarization

For TAFEL-VIRKAR Relation

Testing Fuel Pressure (atm):

<table>
<thead>
<tr>
<th>Gas</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.96</td>
</tr>
<tr>
<td>H2O</td>
<td>0.04</td>
</tr>
<tr>
<td>CO</td>
<td>0.0</td>
</tr>
<tr>
<td>CO2</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Temperature (K): Anode Current Density ($A$)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Current Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>923</td>
<td>3.134e-4</td>
</tr>
<tr>
<td>973</td>
<td>4.74e-4</td>
</tr>
<tr>
<td>1023</td>
<td>4.953e-4</td>
</tr>
<tr>
<td>1073</td>
<td>5.85e-4</td>
</tr>
</tbody>
</table>

For BUTLER-VOLMER Relation

Concentration Polarization Parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tortuosity</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

OK
Fuel and Oxidant Definition

Stack Flow Rate

Fuel Composition

Oxidant Composition
Stack Boundary Conditions

Boundary conditions defined on top, sides, and bottom of stack.
Stack Boundary Conditions
Write EC parameter file

Submit Analyses
The Post Processing Menus
Fuel Species
(Inlet Fuel: 0.6 H₂, 0.1 H₂O, 0.3 CO, 0.1 CO₂)

Hydrogen

Water

CO

CO₂
Fuel and Oxidant Temperature

Fuel Temperature

Air Temperature

Pacific Northwest National Laboratory
U.S. Department of Energy
Temperatures Imported to Marc
Marc Stress Results

Pen Seal

Electrolyte
3-Cell Model directly from CAD

- Fuel
- Air
Mentat-FC: Original Parametric GUI

Analysis Procedure

Geometry Creation  FEA Model Construction  EC Solution  Structural Solution

Parametric  Mentat-FC  MARC  MARC

EC Results  Steady State

Steady State  EC Results
Mentat-FC: Present Modeling Tool

Analysis Procedure

Geometry Creation
- Parametric

FEA Model Construction
- Mentat-FC
- SOFC-MP

EC Solution
- EC Results

Structural Solution
- MARC

Structural Results
- Steady State
- Transient Creep

EC Results
- Steady State
Completed Modeling Suite

Analysis Procedure

Geometry Creation
- Parametric
- CAD
- FEA Mesh

FEA Model Construction
- Mentat-FC

EC Solution
- SOFC-MP

Structural Solution
- MARC

Structural Results
- Steady State
- Transient Creep
- Coarse Design Methodology
- Thermal Cycling
- Seal Damage
- Thermal Fatigue
- User Supplied

Coupled Behaviors
- Steady State
- On-Cell Reforming
- User Supplied

User Supplied

EC Results

Pacific Northwest National Laboratory
U.S. Department of Energy
How to get this software and more training

- MSC Evaluation Licenses
- PNNL Summer Workshop
Questions?

5-minute break before starting

the live demo of

SOFC-MP and MSC.Marc/Mentat-FC
Test Problems

- 1-Cell course model from CAD
- 3-Cell model from existing ANSYS mesh files.
- 1-Cell cross-flow parametric model
- 1-Cell co-flow parametric model
- 1-Cell counter-flow parametric model
Fuel Species

Hydrogen

Water
SECA Core Technology Program - PNNL: Cell Materials Development

Jeff Stevenson
Cathode Development: Steve Simner, Mike Anderson
Anode Development: Olga Marina, Axel Mueller

Pacific Northwest National Laboratory
Richland, WA 99352

Presented at the 6th Annual SECA Workshop
Pacific Grove, CA, April 21, 2005
Outline

■ Cathodes
  • LSF-based Cathodes
    – Current Collector Effects
    – Performance Degradation
  • LSM-based Cathodes
    – Optimization of Performance
    – Joint GE-PNNL-ANL Cr Degradation Study

■ Anodes
  • Current Collector/Contact Materials Development
Button Cell Experimental Set-Up

- Cathode Pt I-V Wires
- Anode Substrate
- Ni current collector
- Pt current collector
- V lead
- I lead
- YSZ
- Alumina tube
- Alumina sealing cement
- Pt Grid
- Pt Mesh
- Cathode Pt I-V Wires
- Anode Pt I-V Wires
- Ni Mesh
- Alumina tube
Effect of Current Collector on LSF Performance

Anode supported cells tested on 50/50 H₂/N₂; 750°C; 0.7 V
Pt migrates from the current collector to the LSF-SDC interface.

- Increased ohmic resistance possibly associated with removal of Pt from the Pt-cathode interface and increased contact resistance.
LSF - Platinum *(Possible Scenario)*

- PtO₂ evaporates and deposits as Pt metal at reduction sites at the LSF-SDC interface

\[ PtO_{2(g)} + 4e' + 2V_{O}^{\bullet\bullet} \rightarrow Pt_{(s)} + 2O_{O}^{x} \]

- Pt deposition may catalyze the oxygen reduction reaction, and enhance cell performance.

- Consistent with other studies detailing enhanced catalytic activity of SOFC cathodes by purposefully adding Pt or Pd at the cathode-electrolyte interface.
Silver deposition different to Pt → Ag not limited to interface – may indicate a different mechanism.

Ag (and possibly AgO) vaporize and deposit at the LSF-SDC interface and within the SDC pores.
Volatility of Noble Metal Species

![Graph showing the volatility of noble metal species as a function of temperature and partial pressure. The graph includes lines for Ag(g), AgO(g), Ag2(g), Pt02(g), PtO(g), Pt(g), Au(g), AuO(g), and Au2(g). The x-axis represents temperature (°C) ranging from 500 to 1100, and the y-axis represents partial pressure (atm) ranging from 1.E-26 to 1.E-00.]
No detectable gold migration to the LSF-SDC interface or within the bulk cathode.

Cell indicates continued degradation during 500 hour test.

Only slight increase in ohmic resistance – Au-cathode contact maintained due to lack of Au volatility
Effect of Current Collector on LSF Performance

Anode supported cells tested on 50/50 H₂/N₂; 750°C; 0.7 V
LSF Degradation – Role of Ni?

- Is the degradation of LSF (with inert Au current collector) intrinsic to LSF or due to the combination of LSF with an anode-supported cell geometry → Ni migration.

- Pt at LSF-SDC interface (for cells that show conditioning/stability) contains higher Ni levels than surrounding materials → Pt may act as a Ni getter.

- Potential degradation mechanism involving Ni has not been established.
LSM-20 Optimization

- Variables include:
  - A/B ratio – 0.99 and 0.95
  - Cells prepared with and without a ceria interlayer
  - Additions of ceria or YSZ to form a composite active cathode layer.
  - Microstructure: Sintering temperature, pore former addition, starting particle size.
  - B-site dopant additions.

LSM-SDC mixed cathode with SDC interlayer. Au mesh/paste current collector.
Cr Degradation Study

- Collaboration between GE, PNNL, & ANL
- Objectives
  - Determine under what conditions, if any, chromium transport has a detrimental effect on LSM-based cathodes
  - Determine if the observed Cr transport is predominantly vapor phase, solid state or both
  - Determine Cr compounds formed at cathode/electrolyte interface and cathode/interconnect interface regions
  - Correlate Cr observed at interfaces vs. observed performance degradation (if any)

- Test Conditions
  - InDEC cells w/ LSM-YSZ cathodes; 700, 800ºC; 1000 hours
  - Cr sources evaluated:
    - E-brite flow field (ANL, GE)
    - Vapor phase from outside fixture (PNNL)
    - Transpiration experiments (PNNL)
Fixture for Cr Degradation Tests
Anode Development - Introduction

- Ni-based anodes offer excellent performance in clean hydrogen or reformed hydrocarbon fuels
  - Challenges include redox stability, hydrocarbon tolerance (coking, thermal gradients), sulfur tolerance
- Ceramic anodes (doped SrTiO$_3$/CeO$_2$ mixtures) combine high electrocatalytic activity for fuel oxidation with redox stability, tolerance of hydrocarbons, and tolerance of sulfur
  - Electronic conductivity, redox stability provided by titanate, activity for fuel oxidation provided by ceria
  - Challenges include relatively low electronic conductivity (compared to Ni-based anodes), processing temperature limitations (reactivity and microstructure coarsening at high processing temps).
  - Need to develop current collector / contact materials for ceramic anode / alloy interconnect interfaces
“Traditional” Anode / Interconnect Interface

- Need to establish stable, conductive interface between anode and alloy interconnect
- Ni-based anodes allow establishment of metallurgical bond between anode and interconnect
- Typical approach: Bond Ni Mesh to alloy interconnect; Apply NiO contact paste between cell and mesh/interconnect during stack fabrication (850-950ºC)
Ceramic Anode / Interconnect Interface

• Need to establish stable, conductive interface between thin active ceramic anode and alloy interconnect

• Pt too expensive

• One option: Ni based contact material - high conductivity - may retain S tolerance (not concerned with S poisoning away from active anode) - probably lose redox, hydrocarbon tolerance

• Graduated approach to improve bonding between Ni and anode
Electrolyte-supported cell operation with Pt/Pt and Ni-LST/Ni current collector/contact paste

160 µm YSZ electrolyte-supported cell (La, Sr)TiO$_3$-Ce(La)O$_2$ anode and LSF20 cathode with SDC interlayer; Fuel: H$_2$/H$_2$O=97/3; Oxidant=air
SEM image of a tested titanate/ceria ceramic anode w/ Ni-titanate (60/40 v%) current collecting layer

Bonding between Ni/titanate cc layer and Ni contact paste requires improvement
Summary

- **LSF-based cathodes**
  - Considerable performance disparity depending on the type of noble metal current collector used.
  - The LSF-Au configuration is most representative of true LSF performance, and reveals LSF instability.
  - Impact of Ni migration (from the anode into YSZ, SDC and LSF layers) on cathode degradation is being examined.

- **LSM-based cathodes**
  - Encouraging long-term stability data but modest power densities.
  - Cr Degradation study in progress – GE, PNNL, ANL

- **Ceramic anodes**
  - Optimization of Ni-based current collection / contact layers in progress
Future work

- **Cathode:**
  - Evaluate LSF degradation mechanisms, including role of Ni
  - Optimize LSM-based cathodes
  - Joint GE-PNNL-ANL Cr poisoning study

- **Anode:**
  - Develop/optimize current collector/contact materials for the ceramic anode
    - Improve bonding, performance of Ni based current collection
    - Develop alternative current collectors/contact materials to maintain HC, redox tolerance
  - Evaluate anode performance in reformates
Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.
- The authors wish to thank Wayne Surdoval, Lane Wilson, Travis Shultz, and Don Collins (NETL) for their helpful discussions regarding this work.
- Metallographic preparation and SEM: Jim Coleman, Shelley Carlson, Nat Saenz.
Advanced Interconnect Development

Z. Gary Yang, Gary Maupin, Steve Simner, Prabhakar Singh, Jeff Stevenson, Gordon Xia

6th SECA Annual Workshop

Pacific Grove, CA
April 18-21, 2005
Objectives

- Develop cost-effective, optimized materials for intermediate temperature SOFC interconnects and interconnect/electrode interface applications.

- Identify and understand degradation processes in interconnects and at their interfaces with electrodes and seals.
Approach

Oxidation resistant alloys:

- Alumina–forming alloys
- Chromia-forming alloys

- Body-centered–cubic (BCC) e.g. ferritic steels
- Face-centered-cubic (FCC) e.g. austenitic Fe-Cr, Ni-Cr-base alloys


Screening-studies of conventional and newly developed alloys
Investigation and understanding of degradation in metallic interconnects and at their interfaces under SOFC operating conditions.

Materials development

- Surface modification
- Bulk alloy development
- Electrode/interconnect interfaces
### Focus Areas & Accomplishments

<table>
<thead>
<tr>
<th>Focus Area</th>
<th>Accomplishments</th>
</tr>
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<tbody>
<tr>
<td><strong>Ferritic stainless steel interconnects with spinel protection layer</strong></td>
<td>- Thermally grown (Mn,Co)$_3$O$_4$ spinel protection layers on FSS;</td>
</tr>
<tr>
<td></td>
<td>- Characterized thermally, electrically, and electrochemically.</td>
</tr>
<tr>
<td><strong>Austenitic-base alloys and laminated, composite interconnect structures</strong></td>
<td>- Developed Ni-base alloys for improved scale properties.</td>
</tr>
<tr>
<td></td>
<td>- Investigated the feasibility of cladding approach for fabrication of laminated, composite metallic interconnects.</td>
</tr>
<tr>
<td><strong>Interactions and contact layer b/w cathode and interconnect</strong></td>
<td>- Screening-studied perovskites as an electrical contact layer and interactions b/w metallic interconnects and the perovskites;</td>
</tr>
<tr>
<td></td>
<td>- Developed new electrical contacts and methods of making them.</td>
</tr>
<tr>
<td><strong>Degradation of metallic interconnects under SOFC operating conditions</strong></td>
<td>- Investigated oxidation behavior of metals and oxidation resistant alloys under dual exposures;</td>
</tr>
<tr>
<td></td>
<td>- Carried out advanced analyses to gain fundamental understanding.</td>
</tr>
</tbody>
</table>
Focus Areas

- Ferritic stainless steel interconnect with spinel protection layer
- Austenitic-base alloys, and laminated, composite interconnect structures
- Interactions and contact layer b/w cathode and interconnect
- Degradation of metallic interconnects under SOFC operating conditions
Protection Layer: The Need

To improve long term scale structural and electrical stability.

Yang, Stevenson, Meinhardt, Solid State Ionics, 160, 213 (2003)).
Protection Layer: The Need

To mitigate or prevent Cr migration and potential poisoning.

Crofer22 APU, 800°C, in air

In-situ X-Ray Diffraction Analysis

M: Fe-Cr substrate
C: Cr₂O₃
S: (Mn,Cr)₃O₄ spinel


Development of (Mn,Co)$_3$O$_4$ Spinel Protection Layer

Why (Mn,Co)$_3$O$_4$ spinel?
- Electrical conductivity:
  \[ \sigma_{(Mn,Co)_3O_4} = 10^{3-4} \sigma_{Cr_2O_3} = 10^{2-3} \sigma_{MnCr_2O_4} \]
- Appropriate CTE:
  \[ CTE_{Mn_3Co_1O_4} = 11.5 \times 10^{-6} K^{-1} , 20 - 800^\circ C \]
- Non-Cr containing: Cr-containing oxides will release Cr
- Flexibility of fabrication: THERMAL GROWTH

Why thermal growth?
- Strong adherence to the substrate;
- Introduction of porosity for strain tolerance;
- Improved thermomechanical stability;
- Cost effectiveness.

Approach

Preparation of (Mn,Co)$_3$O$_4$: SS or GNP

Solution based coating

Heat-treated in reducing environments

Thermally grown during heating in oxidizing environments or during first SOFC stack heating

Thermal Growth of Mn$_{1.5}$Co$_{1.5}$O$_4$ on FSSs

**Reduction**
In H$_2$/Ar+3% H$_2$O, 800$^\circ$C, 24h

\[
[MnCo_2O_4]_{\text{cubic}} + 3H_2 \rightarrow 2Co + MnO + 3H_2O \\
[Mn_2CoO_4]_{\text{tet}} + 2H_2 \rightarrow Co + 2MnO + 2H_2O \\
\]

\[4Mn_{1.5}Co_{1.5}O_4 + 5H_2 \rightarrow 6Co + 6MnO + 5H_2O \]

**Oxidation**
Air+3% H$_2$O, 800$^\circ$C, 100h

\[4Co + 2MnO + 3O_2 \rightarrow 2[MnCo_2O_4]_{\text{cubic}} \]
\[2Co + 4MnO + 2O_2 \rightarrow 2[Mn_2CoO_4]_{\text{tet}} \]

\[6Co + 6MnO + 5O_2 \rightarrow 4Mn_{1.5}Co_{1.5}O_4 \]
Contact ASR w & w/o Protection Layers

\[ \text{ASR}_{\text{cathode/interconnect}} = \Phi(\text{scale, contacts, reactions}) \]

- **Crofer22 APU without spinel protection layer**
- **AISI430 with spinel protection layer**
- **Crofer22 APU with spinel protection layer**

**Graph**

- **Time (h)**
- **ASR (mohm.cm\(^2\))**

**Diagram**

- **Interconnect**
- **Screen-printed cathode**
- **Sintered, dense LSF**
- **Electrical contact**
- **LSCM electrical contact, 800\(^\circ\)C, air**

**Text**

- **Contact ASR w & w/o Protection Layers**
- **6.5 PSI Load**
- **500mA.cm\(^2\)**

**Technical Details**

- Crofer22 APU with spinel protection layer
- Crofer22 APU without spinel protection layer
- AISI430 with spinel protection layer

**Date**

*Pacific Northwest National Laboratory*
*U.S. Department of Energy*
Six Month Thermal Cycling Test

IRU test: 800°C, air, cycling from 80-800°C, 125 cycles plus 4 times of power failure.

Test was started in an isothermal mode on May 24, 2004; cycling began 300 h later on June 6, 2004.

As of Nov. 24, 2004, ASR slowly dropped to 14.3 mohm.cm² after enduring four months testing and three power failures.
Improved Surface Stability

- LSF substrate
- LSF cathode
- Contact layer
- Crofer22 APU
- Protection layer
Effective Cr-Barrier

No Cr migration across the spinel protection layer after six months of heating and cycling.

<table>
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<tr>
<th>Element</th>
<th>App Conc.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
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<tr>
<td>Sr K</td>
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<td>La L</td>
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<td>18.79</td>
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<td>Mn K</td>
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<td>1.1185</td>
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<tr>
<td>Cr K</td>
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<td>LSF cathode</td>
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</tr>
<tr>
<td>LSF substrate</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Contact layer</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Crofer22 APU</td>
<td></td>
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</table>

Summary

- Mn$_{1.5}$Co$_{1.5}$O$_4$ spinel protection layers can be thermally grown on ferritic stainless steel interconnects.
- The thermally grown Mn$_{1.5}$Co$_{1.5}$O$_4$ spinel protection layer:
  - improved surface stability
  - minimized contact resistance
  - prevented Cr migration
- The spinel protection layer demonstrated excellent long-term stability.
Focus Areas

• Ferritic stainless steel interconnect with spinel protection layer
• Austenitic-base alloys, and laminated, composite interconnect structures
• Interactions and contact layer b/w cathode and interconnect
• Degradation of metallic interconnects under SOFC operating conditions
Modification of Haynes 230

**Evaluation:**
- Oxidation and scale growth in moist air as well as under dual environments
- Scale constitution and structure
- Scale electrical conductivity
- Thermal expansion

*Alloys were made at Haynes International Inc.*

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>M1</th>
<th>M2</th>
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<tbody>
<tr>
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<td>1% Mn EN1304-4-812</td>
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<td>Al</td>
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<td>B</td>
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<td>C</td>
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<td>Cu</td>
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<tr>
<td>Mn</td>
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<tr>
<td>Mo</td>
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<td>2.02</td>
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<tr>
<td>P</td>
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<td>0.005</td>
</tr>
<tr>
<td>S</td>
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<td>0.003</td>
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<tr>
<td>Si</td>
<td>0.38</td>
<td>0.42</td>
</tr>
<tr>
<td>Ta</td>
<td>&lt;0.100</td>
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</tr>
<tr>
<td>Ti</td>
<td>&lt;0.01</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>W</td>
<td>14.23</td>
<td>13.62</td>
</tr>
</tbody>
</table>
Scale structure similar to Crofer, i.e. (Mn,Cr)$_3$O$_4$+Cr$_2$O$_3$;
Mn addition increased scale growth, but still better than Crofer;
Superior oxidation resistance under dual environments.
Properties of M Alloys

- (Mn, Cr)₃O₄ spinel help improved scale conductivity,
- Mn addition increased scale growth rate and thus the scale electrical resistance.

CTE of M alloys is comparable to Haynes230 and higher than that of ceramic cells,
- Mn addition slightly increased CTE.
Laminated, Composite Interconnect Structures via Cladding*

- **Clad Metal:**
  - A layered, composite metallic material
  - Cost-effective and widely used in Industries as well as in our daily life

- **Clad Metal for interconnect applications**
  - Integrate advantages of different alloys, while avoiding disadvantages.
  - Solve the issue of thermal expansion mismatch;
  - Optimize the interconnect mechanical and structural stability;
  - Make more cost-effective.
  - Allow to address cathode- and anode-side issues separately;
  - Mass production and very cost effective.

*Collaboration with Leigh Chen, Engineered Materials Solutions Inc.*
Proof-of-Concept: Haynes230||AL453||Haynes230

The proof of concept work proved the viability of cladding FSS with Ni-based alloys and another piece of FSS; the cladded structures were stable during a subsequent heat treatment.
Thermal expansion of clad metals, compared to Haynes 230 and Al453

CTE* of the clad metal in comparison with that of Haynes230 and AL453

The cladding is a viable approach to modify the thermal expansion of metallic interconnect and help improve its cost-effectiveness.

Chen, Yang, Jha, Xia, Stevenson, J. Power Sources, in press (2005).
Summary

- The austenitic Ni-Cr-base alloys can be modified for improved properties for SOFC applications.

- The initial work demonstrated that cladding is a viable approach to fabricate laminated, composite interconnect structures that integrate the advantages of different alloys, while avoiding their disadvantages.
Focus Areas

- Ferritic stainless steel interconnect with spinel protection layer
- Austenitic-base alloys, and laminated, composite interconnect structures
- Interactions and contact layer b/w cathode and interconnect
- Degradation of metallic interconnects under SOFC operating conditions
Contact Layers

Functions

- Promote electrical contact
- Facilitate stack assembling
- Act as a buffer zone to trap Cr

Materials requirements

- High electrical conductivity
- Chemical compatibility
- Thermal expansion matching
- Thermochemical stability
- Low cost
Contact Resistance

\[
\text{ASR}_{\text{contact}} = \Phi \left[ \text{Scale : conductivity, growth – rate; contact : area, conductivity; reactions : scale | contact | electrodes} \right]
\]

- SrCrO\textsubscript{4} can be formed via both solid-solid and solid–gas reactions.
- LSM and LSCM facilitate (Mn,Cr)\textsubscript{3}O\textsubscript{4} spinel formation.

Yang, Xia, Singh, Stevenson, J. power Sources, accepted (2005).
Performance of Newly Developed Contacts

- Combination of the spinel protection layer and a newly developed contact led to a significantly minimized contact ASR.

**IRU test: LSF cathode; Temperature: 800°C**

**Graphs:**
- LSF cathode and bare Crofer22 APU as interconnect
- Crofer22 APU with thermally grown spinel protection layer

**Graph Details:**
- **Time (h)**
- **ASR (mOhm.cm²)**
- **ASR (Ohm.cm²)**

- **Newly developed contact**
- **La0.8Sr0.2Co0.6Mn0.4O3**
- **La0.8Sr0.2Co0.6Mn0.4O4**
- **Newly developed contact**
Summary

- It is desirable to have an electrical contact layer to minimize the contact resistance between oxide cathodes and metallic interconnects.

- Screening study on perovskite contacts indicated that the contact ASR depends on scale conductivity, contact area, and conductivity of contact materials, as well as interactions between interconnects and electrical contacts.

- The combination of spinel protection layer and the newly developed contact materials demonstrated a very low contact ASR.
Focus Areas

- Ferritic stainless steel interconnect with spinel protection layer
- Austenitic-base alloys, and laminated, composite interconnect structures
- Interactions and contact layer b/w cathode and interconnect
- Degradation of metallic interconnects under SOFC operating conditions
Oxidation Behavior of Alloys under Interconnect Dual Exposures

- Oxidation study has been a common area of interest, but typically in a single exposure.
- Oxidation behavior under interconnect dual exposures can be very different from that in a single exposure.
- Understanding helps develop robust materials.

Materials studied:

NiBS
- Haynes 230-22%Cr
- Hastelloy S-17%Cr
- Haynes 242-9%Cr
- Pure Ni, Ag, etc.

FeSS
- E-brite-27%Cr
- Crofer22-22%Cr
- AISI430-17%Cr

Variables:
- Alloy composition
- Thermal history: isothermal vs. cycling
- Fuels: Hydrogen & Reformates

Anomalous Oxidation of Alloys under Dual Exposures: A Summary

Ferritic stainless steels (FSS):
FSS demonstrate anomalous oxidation behavior under dual exposures. Depending on alloy composition, thermal history, and surrounding environment, the anomalous oxidation can lead to a localized attack by formation of hematite nodules.

Ni-Cr-base alloys (NCA):
NCA also demonstrate anomalous oxidation behavior under dual exposures. The anomalous oxidation usually leads to less defects and a better scale adherence.
The anomalous oxidation of metals or alloys under dual exposures is due to the hydrogen transport from the fuel side to the airside.

Both a hydrogen and a water vapor gradient can contribute to the hydrogen flux and affect the scale growth at the airside.

Mechanistic understanding is an ongoing work: how the hydrogen/proton interacts with scale oxides and affects the scale composition, structure and its properties.
Future Work:

Surface modification of metallic interconnects
- Study spinel materials to optimize protection layers for best performance;
- Explore different approaches and search more economic ways for mass production.

Development of electrical contact layers
- Continue to study interfacial interactions and ASR;
- Develop and optimize contact layer materials for further improved performance.

Alloy development and optimization of clad interconnect structures
- Continue to develop and optimize bulk alloys for improved scale properties.
- Optimize laminate, composite interconnect structure and compositions.
- Study interdiffusion and predict life via modeling.

Study of oxidation behavior and scale properties under dual exposures
- Mechanistic understanding: Interaction and transport of H/H⁺ at the metal/oxide interface and in the oxide scale; their effects on defect structure, transport properties, scale growth.
- Oxidation behavior of alloys under the reforming gas/air dual exposures.
- Study effects of dual exposure and electrical field on scale properties.
Acknowledgements

The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.

The authors wish to thank Wayne Surdoval, Lane Wilson, Travis Shultz and Don Collins (NETL) for their helpful discussions regarding this work.

Metallographic preparation and SEM: Jim Coleman, Shelley Carlson, Nat Saenz.
SECA Core Program—Recent Development of Modeling Activities at PNNL

MA Khaleel
Email: moe.khaleel@pnl.gov  Phone: (509) 375-2438

KP Recknagle, X Sun, BJ Koeppel, EV Stephens, BN Nguyen, KI Johnson, VN Korolev, JS Vetrano* and P Singh

Pacific Northwest National Laboratory
Richland, WA 99352

Travis Shultz, Wayne Surdoval, Don Collins
National Energy Technology Laboratory

SECA Core Technology Program Peer Review
Philadelphia, PA
September 12-14, 2006
Objective: Develop integrated modeling tools to:
- Evaluate the tightly coupled multi-physical phenomena in SOFCs
- Aid SOFC manufacturers with materials development
- Allow SOFC manufacturers to numerically test changes in stack design to meet DOE technical targets

Approach: Finite element-based analysis tools:
- Mentat-FC: Easy-to-use pre- and post-processor to construct a complete analytical model from generic geometry or templates
- SOFC-MP: A multi-physics solver that quickly computes the coupled flow-thermal-electrochemical response for multi-cell SOFC stacks
- Targeted evaluation tools for eminent engineering challenges:
  - Interface and coating durability
  - Reliable sealing
  - On-cell reformation for thermal management
  - Scale up
  - Time dependent material degradation
Technical Issues Addressed

- Provide a flexible, multi-physics SOFC stack design tool capable of importing SOFC manufacturer designs (planar & tubular) for electrochemical/thermal/structural analyses.
- Provide a coarse design methodology by which SOFC manufacturers can develop a stack design.
- Provide analysis tools for evaluating the effects of on-cell steam-methane reformation in stacks for optimal thermal management.
- Address the challenging reliability issues of glass-ceramic seals, interfaces, and scales due to steady operation and thermal cycling of stacks.
- Experimentally gather necessary physical and mechanical property data to support model development.
Accomplishments

► **Commercially Available SOFC Stack Design Tool**: PNNL and MSC-Software combined efforts to develop and release a user-friendly electrochemical-thermal-structural stack design software package. Design tool capability includes import of planar and non-planar SOFC stack designs.

► **Tools and Methods for Optimization of Internal Reforming**: Methodology developed in which control of the reaction rate via custom anode and/or control of the percentage of reformation to occur on-cell is used to optimize the thermal management of a proposed stack design.

► **Glass-Ceramic Sealant Damage Model**: Developed a viscoelastic continuum damage mechanics model based on experimental characterization of G18 glass-ceramic to evaluate sealants in SOFC stack models to prevent failure/delamination.

► **Interconnect Creep and Degradation**: Developed a modeling methodology to predict interconnect integrity at different stages of oxide scale growth. Examined influence of interconnect creep on the possible stack geometry change and stress redistribution.

► **Experiments Provide Critical Properties**: Testing has provided fundamental material properties enabling model development.
Publications

► SECA Presentations

► Topical Reports
  • Sun X, WN Liu, P Singh, and MA Khaleel, “Effects of Oxide Thickness on Scale and Interface Stresses under Isothermal Cooling and Micro-Indentation.” PNNL-15794.

► Conference Papers & Presentations
  • Koeppel BJ, JS Vetrano, BN Nguyen, X Sun, and MA Khaleel, “Mechanical Property Characterizations and Performance Modeling of SOFC Seals,” 30th International Conference & Exposition Advanced Ceramics, January 24, 2006, Cocoa Beach, FL.

► Journal Articles
Teaming & Collaborations

Industry
- Modeling and Software Training
  - GE
  - Delphi
  - Acumentrics
  - Siemens
  - FCE

University & National Labs
- Modeling
  - U of Illinois, Chicago
  - Georgia Tech
- Materials
  - ORNL
  - Carnegie Mellon University
  - Penn State
- Software Training
  - U of Connecticut
Results

SOFC Analysis Overview
SOFC-MP/Mentat-FC
On-Cell Reformation & Thermal Management
Seal Property & Time Dependent Behavior
Interconnect-Coating Interface & Interconnect Creep
Experimental Property Measurement
Developed tools to build/analyze SOFC cells and stacks

- Mentat-FC: GUI to build models from templates, CAD files, or FEA meshes
- SOFC-MP: Coupled thermal, flow, and electrochemistry solver
- MSC.Marc: Structural finite element analysis using SOFC-MP temperatures
SOFC-MP/Mentat-FC

- Mentat-FC GUI
  - Guides user through entire analysis
  - Builds geometry from CAD files, FEA meshes, or templates (planar co-, counter-, cross-flow)
  - SOFC operating parameters (I-V, fuel/oxidant inputs, polarizations)
  - Exterior thermal boundary conditions
  - Material properties database
  - Has tubular capability

- SOFC-MP Solver
  - Finite element based
  - Generic fuel and oxidants (CEA)
  - Efficient reduced order dimensional analyses for electrochemistry and gas flows
  - Contact algorithms treat incompatible meshes

- Post-processing of electrical output, species, thermal distribution, deformations, and stresses
On-Cell Reforming & Thermal Management:
Optimization of Percent On-Cell Reformation

At 0% OCR temperature reached maximum at air exit

40% OCR heat load was decreased with cooling at fuel inflow

80% OCR heat load was minimum but air temperature was high

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<th>% OCR</th>
<th>∆T</th>
<th>T_max</th>
<th>Anode S1_max</th>
<th>Seal S1_max</th>
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SUMMARY:
- To maintain 750°C, inflow temperature increased to offset decreased heat load due to reforming (all configurations and sizes)
- Seal stresses, anode stresses, and ∆T had minimums at 40-50% OCR for this configuration and cell size
Seal Property & Time Dependent Behavior: Glass-Ceramic Seals

1. Test the glass-ceramic strength and creep behavior
2. Test the weaker interface strength
3. Obtain coefficient of thermal expansion (CTE) and elastic modulus
Seal Property & Time Dependent Behavior: Creep of Glass-Ceramics

- Evaluated short-term creep behavior of G18
  - Glassy matrix above its Tg at cell operating temperatures
  - Creep rate increased with applied stress and temperature

- Estimated G18 viscosity
  - Assume Maxwell material model
  \[ E = E^0 (1 - D) \]
  - Derived viscosity is very high (5-65e6 MPa-s) but still important for assessing steady state seal stresses in the stack
Seal Property & Time Dependent Behavior: Glass-Ceramic Constitutive Model

- Stress-strain response of G18 glass-ceramic shows strong rate dependence
  - Due to viscoelastic response of residual glass
  - Processing/microstructure variations noted

- Viscoelastic damage model predictions compare reasonably well to experimental data
  - Failure strain prediction good
  - Stress prediction possibly affected by heterogeneous structure

![Stress-strain graph](image)
Seal Property & Time Dependent Behavior: Stack Modeling Results

Seal Damage Distribution

Anode Principal Stress Distribution

Seal Failure After 2 Thermal Cycles

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>Elastic Model: Anode Maximum Principal Stress (MPa)</th>
<th>Viscoelastic Model: Anode Maximum Principal Stress (MPa)</th>
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<tr>
<td>Cycle 1 Shut-Down</td>
<td>65.6</td>
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<td>4.4%</td>
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<tr>
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<td>Cycle 2 Shut-Down</td>
<td>74.4</td>
<td>67.4</td>
<td>9.4%</td>
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Interconnect Life Prediction

- Sources of interconnect stress studied:
  - Thermal stress
  - Growth stress
- Predicted interfacial stress compared with interface strength 
  \( \rightarrow \) scale delamination
- Predicted scale stress compared with critical buckling stress 
  \( \rightarrow \) scale spallation

Residual stresses measurements in Cr2O3 films

Pacific Northwest National Laboratory
U.S. Department of Energy
Interconnect Life Prediction

- Using indentation test to quantify strength of oxide/interconnect interface:
  - Effect of scale growth on interfacial shear stress
  - Effects of thermal stress on indentation stress

- Conclusions:
  - Shear stress on the interface caused by indenter contact is high enough to lead to delamination
  - Shear stress dominates the fracture mode of the interface
  - The thinner the thickness of oxide scale is, the bigger the interfacial shear stress is, at the small indentation depth
  - Effect of thermal stress on the interfacial shear stress may be neglected
Interconnect Scale Growth Kinetics and Growth Stress Prediction

- Diffusion potential used to govern stress-diffusion interaction

- Predicting:
  - Oxidation kinetics
  - Diffusion and concentration evolution of species
  - Stress distribution in scale and substrate

Interconnect Creep and Stress Redistribution

Creep law used for IC

\[
\sigma < 100 \text{MPa} \quad \dot{\varepsilon}_c = \begin{cases} 
1.72 \sigma^{5.5} e^{-277400/RT} & \text{for } T \geq 725^\circ \text{C} \\
1.65 \times 10^{11} \sigma^{5.8} e^{-488700/RT} & \text{for } T \leq 710^\circ \text{C}
\end{cases}
\]

\[
\sigma > 100 \text{MPa} \quad \dot{\varepsilon}_c = \begin{cases} 
> 10^{-3} & \text{for } T \geq 725^\circ \text{C} \\
2.82 \times 10^{-5} \sigma^{0.5} e^{-488700/RT} & \text{for } T \leq 710^\circ \text{C}
\end{cases}
\]

Test temperature (°C)

- Q = 292.5 KJ mol\(^{-1}\)
- \(\dot{\varepsilon}_A = 786 \text{ MN m}^{-2}\)
- Q = 262.3 KJ mol\(^{-1}\)
- Q = 466.9 KJ mol\(^{-1}\)
- Q = 510.4 KJ mol\(^{-1}\)
- Curie temperature for Fe-15% Cr

Time = 0.01 h
Time = 70 h
Experimental Support of Modeling

Providing input data to the material models and validating the models through experimental testing. In addition, contributing to the materials database maintained by NETL.

- Creep testing of G18 glass to measure long-term deformation behavior
- Torsion testing of thin glass-seal analogs to determine failure stress and fracture behavior
- 4-pt bend bar testing of G18 glass to capture constitutive and failure behavior of the material
Experimental Property Measurement

Seal Property & Time – Dependent Behavior

- Creep tests of the G-18 glass performed to support damage models in predicting the long-term stack performance

Interfacial Degradation and Failure Mechanisms

- Investigating failure locations and mechanisms to incorporate into seal and coating development models

Creep specimen

Comparison of a non-tested creep sample and a sample tested at 800°C and loaded at 129lb. Forty-three percent strain observed.

Creep strain results of samples tested at 800°C under three different loadings

SEM cross-section of a torsion sample that failed at 800°C
Experimental Property Measurements

Interconnect-Scale/Coating Interface Properties

- Indentation tests performed to support interface models in establishing a stress-based criteria for interfacial strength and fracture toughness

SEM image of the cross-section of a crofer plate oxidized at 800°C for 12hr

Top view of the indent test. Spallation of the oxide observed under 150kg load
Activities for the Next 6 Months

- Mentat-FC/SOFC-MP: Deploy at the 6 industry sites and provide training and support.
- Scale-up: Examine planar SOFC design limitations considering electrochemistry, flow, and structural
- Parametric studies on the effects of creep of various SOFC components on long-term behavior of multiple cell stacks
- Continue interconnect degradation and life prediction work
- Development of structure-property relationships for glass-ceramic sealants; improvement via microstructural design
- Effect of high pressure on electrochemistry and stack performance
- Measurement of Oxide-Crofer and Spinel-Crofer interfacial properties
Looking Forward- Phase II

Design Limitations for Scale-up of SOFC Stacks
- Virtual feasibility study on:
  - Stack EC performance and thermal management
  - Stack structural reliability

Degradation modeling and life prediction
- Creep considerations on the structural stability of stacks
- Seal and seal interfaces
- Interconnect scale and coatings
- Cell and cell interfaces
- Current collector interfaces

System integration
- Stack thermal management and cell thermal profiles
- System integration, power electronics and control

Validation
SOFC Interconnects & Coatings


Pacific Northwest National Laboratory
Richland, WA 99352

7th Annual SECA Workshop and Peer Review
Philadelphia, PA, September 14, 2006
Objectives and Approach

Objectives

- Develop cost-effective, optimized materials and fabrication approaches for intermediate temperature SOFC interconnect and interconnect/electrode interface applications
- Identify and understand degradation processes in interconnects and interconnect/electrode interfaces

Approach

- Materials and process development
  - Surface modification (Focus of today’s presentation)
  - Interconnect/electrode contact materials
  - Alloy development
- Characterization of candidate materials
  - Oxidation tests (including dual atmospheres – air vs. moist hydrogen; air vs. simulated reformate), ASR tests, CTE, alloy and scale chemistry via XRD, SEM, EDS, TEM, etc.
Spinel Protective Coatings: Background

Goal: Cost-effective protective coatings which improve alloy oxidation resistance, mitigate Cr volatility, and minimize contact resistance

Previous Accomplishments:
- Studied structure and properties of compositions in (Mn,Co)\textsubscript{3}O\textsubscript{4} system; selected (Mn\textsubscript{1.5}Co\textsubscript{1.5})\textsubscript{3}O\textsubscript{4}
- Developed slurry-based fabrication process for fabricating (Mn,Cr)\textsubscript{3}O\textsubscript{4} spinel coatings onto FSS interconnects
- Evaluated performance of coated alloys: oxidation, ASR, coating/alloy interactions

FY06 Accomplishments:
- Investigated performance/stability of spinel-coated alloys under SOFC exposure conditions (dual atmosphere)
- Performed long-term (> 1 year) oxidation tests on coated/uncoated FSS
- Optimized slurry-based fabrication approach
Conclusions

- $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ spinel protective coatings are effective in reducing oxide scale growth kinetics and Cr volatility of Cr-containing ferritic stainless steels
- Spinel-coated Crofer22APU (22-23% Cr, low Si) demonstrates long-term (>1 year) structural, thermo-mechanical, and electrical stability
- No iron oxide nodule formation or other localized attack observed in coated Crofer22APU under dual exposure conditions
- Spinel-coated AISI 430 (17% Cr, 0.5% Si) exhibits significant Fe diffusion into coating, and high ASR due to silica subscale formation
- Slurry-based fabrication method has been improved; better control of microstructure and thickness
- Alternative electroplating-based approaches under investigation
Properties of \((\text{Mn}_{1.5}\text{Co}_{1.5})_3\text{O}_4\) Spinel

- High electrical conductivity
  \(~60\ \text{S/cm at 800}^\circ\text{C}\)
  \[\sigma_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} = 10^{3.4} \sigma_{\text{Cr}_2\text{O}_3}\]
- Good CTE match to FSS and anode-supported cells
  \[\text{CTE}_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} = 11.5 \times 10^{-6}\ \text{K}^{-1}, 20 - 800^\circ\text{C}\]
- Chemically compatible with contact pastes, cathodes
- Cr-free composition
Fabrication of (Mn,Co)$_3$O$_4$ Spinel Protection Layers

Slurry-Based Process

- Preparation of materials and slurry
- Spray- or dip-coating
- Heat treatment in reducing environment (4 hr, 800°C)
- Oxidation in air (800°C - Pre-oxidation or in-stack)

Mathematical Equations:

\[ 4Mn_{1.5}Co_{1.5}O_4 \Rightarrow 6Co + 6MnO + 5O_2 \]

\[ 6Co + 6MnO + 5O_2 \Rightarrow 4Mn_{1.5}Co_{1.5}O_4 \]
Effect of Coating on Scale Growth

800°C in air
Long-Term Test of AISI 430

**Coated**

800°C - 9,200 h - air

Note ~10% Fe in coating

**Uncoated**

800°C – 8,850 h - air
Effect of Coating on Crofer22APU Scale Growth

\[ T (\text{microns}) = 0.0277t^{0.5} + 0.751 \]

\[ R^2 = 0.9961 \]

Scale thickness (microns)

125 cycles, 12 hrs at 800°C in air

Bare Crofer 22APU:
8,850 hrs, 800°C, air

Bare Crofer 22APU:
after thermal cycling

T (microns) = 0.0277t^{0.5} + 0.751
R^2 = 0.9961
Long-Term Oxidation Behavior of Crofer22 APU

Coated

~ 4 µm scale

Uncoated

~ 14 µm scale

800°C - 9,200 h - air

800°C – 8,850 h - air
Electrical Resistance after Long-Term Oxidation Test

- MC Coated Crofer
- Bare Crofer22

Graph showing ASR (mOhm-cm²) over time (h) for MC Coated Crofer and Bare Crofer22.
Electrical Resistance of Spinel-Coated AISI 430

Results demonstrate need for low Si content in alloy; AISI 430 has ~0.5wt% Si

AISI 430 has ~0.5wt% Si
Cr Volatility Experiments

Cr release of coated Crofer22APU was <4% of Cr release of uncoated Crofer22APU

Transpiration measurements were carried out at 800°C in air with ~3%H₂O
Performance & Stability under Dual Atmosphere Exposure: *Isothermal Test*

- Mn$_{1.5}$Co$_{1.5}$MnO$_4$ coating on Crofer22APU; pre-reduced at $800^\circ$C for 4 hours
- **Tested isothermally at 800°C / 1000 hours**
- Air (~3%H$_2$O) vs. Hydrogen (~3%H$_2$O)
- SEM/EDS: ~2 wt%Fe in coating; no Fe$_2$O$_3$ nodule formation or other localized attack
Performance & Stability under Dual Atmosphere Exposure: *Thermal Cyclic Test*

- **60 microns thick**
  Mn$_{1.5}$Co$_{1.5}$MnO$_4$ coating on Crofer22APU; pre-reduced at 800ºC for 4 hours; pre-oxidized at 800ºC for 24 hours

- **110 thermal cycles: 8 hours at 800ºC, 5ºC/min**

- Total test duration: 2100 hours

- Air (~3%H$_2$O) vs. hydrogen (~3%H$_2$O)

- SEM/EDS: ~2 wt%Fe in coating; no Fe$_2$O$_3$ nodule formation or other localized attack
Optimization of Spinel Coating Process

- Transitioning from Solvent-based to Aqueous Slurry System
  - Environmentally friendly; compatible with spray-coating, dip-coating process
- Improved control of coating thickness
  - ~2-20 microns via optimization of slurry viscosity and spray parameters
- Reducing atmosphere heat treatment
  - Typically 800°C, but XRD indicates ~650°C is sufficient
  - Typically 4 hours, but TGA, XRD indicate 1 hour is sufficient
- Investigating elimination of reducing heat treatment via combined slurry/solution-infiltration approach
Growth of Spinel Protection Layers via Oxidation of Co layer on Crofer

Possible Fabrication Route: Electroplating of Co (or Co+Mn) followed by oxidative heat treatment

Proof-of-concept via sputtering of Co

EDS/XRD indicate Mn-Co spinel above chromia layer

Thickness: ~2 microns (thinner than slurry-based coatings)

Electroplated samples received and under evaluation

800°C; 100 hours; air
Future Work

- Final optimization of slurry-based coating process
  - Elimination of reducing heat treatment?
- Evaluate viability of electroplating approaches
  - Composition, microstructure, performance
- Investigate alternative coating compositions
  - Eliminate Co?
- Assess effects of air/reformed fuel dual atmospheres on performance of interconnect alloys
- Develop improved interconnect/electrode interfaces
  - Reaction-sintered interconnect/cathode contact materials for improved conductivity and strength
Conclusions

- \( \text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4 \) spinel protective coatings are effective in reducing oxide scale growth kinetics and Cr volatility of Cr-containing ferritic stainless steels.
- Spinel-coated Crofer22APU (22-23% Cr, low Si) demonstrates long-term (>1 year) structural, thermo-mechanical, and electrical stability.
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Acknowledgements

The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.

Additional PNNL contributors: J. Coleman, S. Carlson, N. Saenz
Rigid Seals for SOFC

J.W. Stevenson, Y.S. Chou (Task Leader), and P. Singh

Pacific Northwest National Laboratory
Richland, WA 99352

7th Annual SECA Workshop and Peer Review
Philadelphia, PA, September 14, 2006
“Refractory” Glass-Ceramic Seals for SOFC

Objective
- To develop reliable, CTE-matched “refractory” sealing glasses (with higher sealing temperatures than typical SOFC sealing glasses) to minimize seal reactivity and increase seal stability. Higher sealing temperatures may also electrical contact and bonding of cathode/interconnect interfaces.

Approach
- Glasses are fabricated in-house by melting of raw materials.
- Evaluation includes sealing temperature, crystallization behavior, CTE, chemical compatibility, leak testing, isothermal and thermal cycle stability.
- Standardized tests allow for meaningful comparison between different sealing materials (PNNL or other SECA participants).
Background

General Issues:
- Matching CTE (~12.5x10^{-6}/°C)
- Minimal interfacial reaction (metal and ceramics)
- Long-term thermal stability (crystallization rate and products)
- Wetting properties
- Volatility in dual atmosphere, moist environments
- Mechanical integrity during thermal cycling
- Electrically insulating

State-of-art glass: G18 (Ba-Ca-Al-B-Si-O)
- Sealing temperature ≤ 850°C
- Decrease in CTE from ~12.5 ppm/°C to ~11.0 ppm/°C after 750°C/1000h aging, due to phase transformation: hexagonal celsian (BaAl₂Si₂O₈ CTE~8 ppm/°C) to monoclinic celsian (CTE ~3 ppm/°C)
- Reaction with interconnect alloys to form BaCrO₄
Conclusions

- New “refractory” sealing glasses have been developed. Optimized glasses exhibit stable, matching CTE in the as-cast glass, short-term crystallized samples, and aged samples.
- Studies of weight loss, XRD, and microstructure showed good stability of candidate glasses after aging for 1000-2000 h at 800-900°C.
- For several candidate glasses, sealed alloy/bilayer coupons tested in dual environment retained hermetic sealing after 1000 h at 800-850°C.
- No interfacial reactions observed at glass/YSZ interface. However, SrCrO$_4$ was found at the glass/alloy interface when sealed at 900-950°C.
- To prevent undesirable interactions during long-term operation, protective coatings may be required.
- Preliminary results for aluminized Crofer22APU showed no chromate formation at glass/alloy interface after aging at 800°C/1000h in air.
- Larger (11cm x 11cm) samples showed hermetic behavior in some cases; however, they failed after 10 thermal cycles in dual atmosphere environment. Recent improvements in sealing process are expected to improve future results.
Approach: Development of glass compositions

- Starting composition: G-18: Ba-Ca-Al-B-Si-O glass
- YS series:
  - Replaced Ba with Sr, decreased B, added Y
  - Higher sealing temps, but unstable CTE (decreased over time)
- YSO series:
  - Removed Al from YS series to avoid possible formation of Sr-based celsian phase
  - Improved CTE stability (in ~11.5 ppm/°C range)
  - Sealing temperature ~950°C
- YSP series:
  - Included some Ba to raise CTE
  - Improved CTE stability (in ~12.5 ppm/°C range)
  - Sealing temperature ~1000°C
Properties of YSO-1 Glass

Composition (mol%):
42.5% SrO, 10% CaO, 6% Y2O3, 7.5% B2O3, 34% SiO2

CTE (ppm/°C):
Glass: 12.1; Crystallized: 11.7; 1000 hrs: 11.5; 2000 hrs: 11.6

YSO-1 900°C/2000h air aged
Thermal stability of YSO-1: Crystallization Products

1: SrSiO$_3$, 2: Ca$_3$SiO$_5$, 3: Ca$_2$SiO$_4$, 4: SrB$_2$O$_4$, 5: Y$_2$SiO$_5$
Thermal stability of YSO glass: weight loss in wet reducing environment

1. 2 stages of weight loss
2. Estimated loss rate to be $3.1 \times 10^{-8} \text{g/(cm}^2\text{.h)}$
3. Total material loss in 40,000 hrs \(\text{@}800\text{C} \ < 0.1 \text{ wt\%}
Glass/alloy interfacial stability

2SrO + Cr₂O₃ + 1.5O₂ = 2SrCrO₄ \[ \Delta G = -156 \text{ kJ/mole} \]
2SrSiO₃ + Cr₂O₃ + 1.5O₂ = 2SrCrO₄ + SiO₂ \[ \Delta G = -24 \text{ kJ/mole} \]

YSO-1: Cr₂O₃ = 2:1 mixed powder fired at 1000°C/1h and 800°C/4h

1: SrSiO₃, 2: Ca₃SiO₅, 3: Ca₂SiO₄, 4: SrB₂O₄, 5: Y₂SiO₅,
6: Cr₂O₃, 7: SrCrO₄, 8: CaSiO₃

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U.S. Department of Energy
Glass/alloy interfacial reaction

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900°C/1h 800°C/4h

YSO-1 Crofer22APU

#2: SrCrO₄

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U.S. Department of Energy
Dual atmosphere test: air side

YSO-75 850°C/500hr in dual environments (30%H₂O/70%H₂ vs. air)

SrCrO₄

Near seal edge

Interior of seal

3.8 cm x 3.8 cm anode-supported bilayer sealed onto 5 cm x 5 cm Crofer22APU; Aged at 850°C for 500 hrs
Thermal Expansion of BaCrO$_4$, SrCrO$_4$

BaCrO$_4$ (98%) $1150^\circ$C

\[ y = 2.113 \times 10^{-5}x - 1.503 \times 10^{-3} \]

\[ R^2 = 9.941 \times 10^{-1} \]

SrCrO$_4$ (95%) $1150^\circ$C

\[ y = 2.338 \times 10^{-5}x - 9.820 \times 10^{-4} \]

\[ R^2 = 9.986 \times 10^{-1} \]
Protective coating to prevent seal / alloy interaction

► Aluminizing of alloy
  - Established commercial process
  - Possible formation of low CTE celsian-like phase (similar to $\text{BaAl}_2\text{Si}_2\text{O}_8$), as observed in Al-containing glasses such as G18?

► Mn-Co spinel
  - Potential to use one coating for both active and seal areas of interconnect
  - Chemical compatibility with glass?
  - Unstable in reducing fuel environment
Aluminized Crofer22APU
Aluminized Crofer22APU/Glass Interface

- YSO75 sealed at 950°C/2h followed by 800°C/4h in air; aged in air 800°C for 1000 h
- Preliminary room temperature leak tests showed good hermeticity after 1000 hours and 10 thermal cycles (800°C; air or reducing atmosphere)
- Alumina layer effectively blocked the diffusion of Cr, Mn, Fe into glass-ceramic
- No SrCrO₄ formation at alloy/glass interface (edge or interior)
- Possible dissolution of Al into glass-ceramic seal
Reactivity with $\text{Al}_2\text{O}_3$

1: SrSiO$_3$, 2: Ca$_3$SiO$_5$, 3: Ca$_2$SiO$_4$, 4: SrB$_2$O$_4$, 5: Y$_2$SiO$_5$, 6: Sr$_2$Al$_2$SiO$_7$, 7: Al$_2$O$_3$

YSO-1: Al$_2$O$_3$ = 2:1 mixed powder fired at 1000°C/1h and 800°C/4h
Scale-up of seal testing

• 11cm x 11cm Crofer22APU with 9.5cm x 9.5cm ceramic bilayer sealed in air
• Only 2 out of 8 specimens hermetic after sealing
• Recently improved sealing process (furnace issues resolved, improved seal fabrication)
Future work

- Evaluate the interfacial chemical compatibility and mechanical integrity of aluminized Crofer22APU with candidate sealing glasses.
- Evaluate the interfacial chemical compatibility and mechanical integrity of (Mn,Co)$_3$O$_4$ spinel-coated Crofer22APU with candidate sealing glasses.
- Implement scaled-up seal testing
- Study the behavior of coated alloys with candidate sealing glass in a simulated SOFC environment with DC electrical loading.
- To investigate effect of transition element additions on chromate formation reaction.
Conclusions

- New “refractory” sealing glasses have been developed. Optimized glasses exhibit stable, matching CTE in the as-cast glass, short-term crystallized samples, and aged samples.
- Studies of weight loss, XRD, and microstructure showed good stability of candidate glasses after aging for 1000-2000 h at 800-900°C.
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- Preliminary results for aluminized Crofer22APU showed no chromate formation at glass/alloy interface after aging at 800°C/1000h in air.
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Additional PNNL contributors: J. Coleman, S. Carlson, N. Saenz
Brazed Seals
Alternative Sealing Technology for Solid Oxide Fuel Cells

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Richland, WA 99352
USA
What is Brazing?

Definition: A filler metal is heated to melting and under capillary action fills the gap between the sealing surfaces. When cooled, a solid joint forms.
Brazing Ceramics to Metals

Active Metal Brazing: A specialized technique that employs a reactive element such as titanium to facilitate wetting between the filler metal and a ceramic substrate.

Typical Filler Metals: Au-Ni-Ti, Au-Ni-V-Mo, Ag-Cu-Ti, Pd-Ni-V

Process Conditions: Vacuum or inert gas environment, 850°C or higher

3.2Ni, 0.7Ti, Au-bal

8YSZ

Reaction zone
Issues with Active Metal Brazing

Joint Oxidation

(Cr,Fe)$_2$O$_3$ scale formation after 200hrs air exposure at 700°C


Cathode Decomposition

Under vacuum at $T > 700^\circ$C:

$$\text{LaFeO}_3 \rightarrow \frac{1}{2} \text{La}_2\text{O}_3 + \frac{1}{2} \text{Fe}_2\text{O}_3$$
New Approach: Air Brazing

- A new method of ceramic-to-ceramic and ceramic-to-metal joining
- Uses a unique filler metal system: a soluble metal oxide dissolved in a noble metal – e.g. CuO in Ag
  - Is conducted in open air (i.e. in a simple muffle or continuous belt furnace)
  - Does not require fluxing or the use of inert cover gas
  - Confers oxidation resistance and ductility to the joint

Air Brazing: Aging & Cycling Tests

Thermal Cycling (75°C/min, RT → 750°C):

KS Weil, CA Coyle, JT Darsell, GG Xia, and JS Hardy, *J. Power Sources*, 152 (2005) 97
Preliminary testing with full-scale components is very encouraging:

Seal remains hermetic after testing through five thermal cycles
Potential Concerns

- High-temperature degradation in a dual atmosphere environment

Pure Silver


- Process consistency

Pore formation due to poor wetting and/or cooling upon shrinkage and “Squeeze-out”
Summary of Findings to Date

- Dual atmosphere degradation
  - Observed three different types of pore defects – all of which we suspect can be mitigated
  - Phenomenon is not significant with respect to short-term use (up to 2000hrs) – no loss in hermeticity, but a measurable loss of strength
  - Could potentially be problematic over longer periods of operation

- Al-Ag-CuO air braze filler metals are being investigated to eliminate long-term dual atmosphere degradation
  - Initial alloy compositions have been successfully synthesized, but require further optimization with respect to joint strength
  - Observe improved joint strength upon H$_2$ exposure
  - Dual atmosphere testing currently in progress

- New composite filler metal composition (containing Al$_2$O$_3$ particulate) looks very promising
  - Joint strength equal to that of the base material (Al$_2$O$_3$)
  - Can combine with the Al-alloyed material to develop a very durable air braze filler metal
Dual Atmosphere Degradation: Experiments

- Tube testing – 200 - 2000hr aging tests conducted at 800°C with flowing $H_2$ inside and flowing air outside
- Examined the following variables: exposure time (200, 1000, and 2000hrs), filler metal composition (Ag$_2$CuO and Ag$_8$CuO), and braze temperature (980°C and 1100°C)
Dual Atmosphere Degradation: Results

- Three types of pores were found:
  - Air pockets formed during processing (Type 1) - large (mm in size) and often found near the center of the joint
  - Pores (Type 2) formed within 5hrs of exposure due to CuO reduction:
    \[ \text{CuO} + 2\text{H}_{\text{diss}}\text{Ag} \rightarrow \text{Cu}_{\text{diss}}\text{Ag} + \text{H}_2\text{O} \uparrow \]
    - >5\(\mu\)m in size, found first along the boundary exposed to \(\text{H}_2\)
  - Pores (Type 3) formed around ~2000hrs due to \(\text{H}_{\text{diss}} + \text{O}_{\text{diss}} \rightarrow \text{H}_2\text{O} \uparrow\) - sub-micron to micron in size and only found after “extensive” dual atmosphere exposure (within the center of the joint)

- In all cases, the porosity remains isolated (not interconnected)
- In all cases, the tubes are hermetic at the end of testing
- Progression of Type 2 pore front appears to scale with \(\sqrt{t}\) fit, which suggests a means of estimating the lifetime of an Ag-CuO seal based on dual atmosphere degradation
Ag₈CuO brazed at 980°C; dual atm exposure at 800°C for 1000hrs
Dual Atmosphere Degradation: Hermeticity

Seal hermeticity:

Progression of the Type 2 pore front appears to scale with $\sqrt{t}$.
Based on this, we can roughly extrapolate the lifetime of the seal:

$$t_{95\% \, \text{Degradation}} \sim 5,200\,\text{hrs at } 800^\circ\text{C and } 12,600\,\text{hrs at } 750^\circ\text{C}$$

∴ standard filler metal needs to be modified for longer-term use
Aluminum Alloying Additions

Concept: develop a passivation layer that inhibits H and O diffusion and eliminates pore Types 2 & 3

Prior work on $\text{Al}_2\text{O}_3$/Al/$\text{Al}_2\text{O}_3$ joining:

1000°C, 10hr, Air:

Forms an adherent $\text{Al}_2\text{O}_3$ scale that protects the underlying metal

Ag-Al-(CuO) Filler Metal Alloys

- Started by fabricating Ag-Al binary compositions
- Observed adequate joining, but found poor joint strength
- Turned to the Ag-Al-CuO system
Observe improved strength after H₂ exposure

Ag-Al-2CuO

- as-brazed
- air (100h, Foil)
- H₂ (100h, Foil)

Al Content (mol%)

Bend Strength (MPa)

Ag-CuO
(H₂, 100h)
Al₂O₃-modified Ag-CuO Filler Metal

- Alumina addition to high CuO content filler metals leads to a dramatic increase in bend strength. *The joints are as strong as the ceramic substrate!*

- For no or low CuO, the alumina addition did not improve bend strength.
No squeeze out or porosity observed in the \( \text{Al}_2\text{O}_3 \)-modified filler metals.
Al$_2$O$_3$-modified Ag-CuO Filler Metal

Ag$_8$CuO

0 vol% Al$_2$O$_3$

Air Pockets

Brittle fracture through alumina substrate

5 vol% Al$_2$O$_3$

Ductile fracture in the filler metal
Summary

- Have identified three types of pores that can form in Ag-CuO air brazed joints exposed to a high-temperature, dual atmosphere environment
  - Type 1 – air pockets formed during joining
  - Type 2 – micron-sized pores formed due to reduction of CuO ppts
  - Type 3 – pores formed along the matrix grain boundaries due to reaction between dissolved H and O (observed at ~2000hrs of exposure)

- The pores do not appear to be problematic in short-term testing (2000hrs or less)

- Can eliminate Type 1 pores using filler metals containing Al₂O₃ particulate and a high CuO content

- Preliminary testing indicates that Type 2 and possibly Type 3 pores can be eliminated by adding Al as an alloying agent
Next Steps

- Investigate the use of $\text{Al}_2\text{O}_3$ in combination with high CuO-containing Ag-Al-CuO filler metals as a means of achieving high strengths and mitigating dual atmosphere degradation.

- Examine the mechanical properties of Ag-Al-CuO-$\text{Al}_2\text{O}_3$ brazed joints after single atmosphere exposure for $t_{\text{exposure}} < 1000\text{hrs}$ and compare with prior results obtained on bend specimens joined using the Ag-CuO, Ag-Al, and Ag-Al-CuO filler metals.

- Conduct 1000+hr dual atmosphere exposure testing on tube specimens sealed using the Ag-Al-CuO-$\text{Al}_2\text{O}_3$ filler metals.

- Conduct post-exposure hermeticity testing and metallographic analysis.

- Carry out preliminary joining studies using prototypic SOFC materials.
Acknowledgements

- John Hardy, Joe Rice, Jim Coleman, Nat Saenz, and Shelly Carlson
- Support: U. S. DOE, Office of Fossil Energy, SECA program

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High Temperature Glass Seal

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K2-44, Materials Division
Pacific Northwest National Laboratory

Funded under the SECA Core Technology Program
through US Department of Energy’s
National Energy Technology Laboratory

August 7-9, 2007, San Antonio, Texas
Outline

- Accomplishment of FY07
- Mechanical strength evaluation: plain crofer, aluminized, spinel-coated
- Electrical stability evaluation: aging under DC loading
- Summary
- Future work
Completed seal strength evaluation of high-temperature glass. Evaluated pre-oxidation, aging, coating, and environmental effects on strength.

Without coating, strength would degrade if a thick Cr$_2$O$_3$ oxide layer present or aged in air. No strength reduction if aged in reducing gas. Cause for strength degradation was SrCrO$_4$ formation.

Alumina coating is effective in blocking Cr; however, the deposition process needs to be optimized to minimize overdose.

Spinel coating showed best results with minimum strength reduction even aging in air.

Tested conventional and high-temperature sealing glasses in SOFC environment and 0.7 V DC loading. Conventional glass showed severe Fe diffusion and rapid increase in conductivity (830°C/~80hr), while high-temperature glass showed excellent electrical stability over ~1200hr at 850°C.
High-temperature sealing glass

1. Increase contact bonding strength
2. Increase thermal stability
3. Decrease interfacial reactions
Mechanical strength evaluation

1. Effect of pre-oxidation: Cr$_2$O$_3$ layer thickness
2. Effect of different protective coating: Al$_2$O$_3$, (Mn,Co)$_3$O$_4$
3. Effect of environment: oxidizing, reducing
4. Accelerated condition:
   ◆ 850°C/500h in air
   ◆ 850°C/250h in 30%H$_2$O, 70%(2.7%H$_2$/Ar)
Interfacial tensile testing

- R. T.
- 0.5 mm/min cross-head speed
- 5-7 samples tested for each condition
- Self-aligned grip fixture
- ½”x½” sample size
Pre-oxidized crofer

To mimic long-term oxidation
1200°C resulted in pores underneath
Outside discrete and non-uniform (Mn,Cr) oxide, inside dense and continuous Cr$_2$O$_3$-rich oxide
T<0.5μm (800°C/2h)
Effect of pre-oxidation on tensile strength

crofer/YSO75, pst/crofer, 1/2"x1/2" at RT

average tensile strength, MPa

<0.5 μm  
~1-2 μm  
~6-10 μm

pre-oxidation conditions:
- none
- 800C/2h
- 1000C/2h
- 1200C/2h
Load-displacement curve showed typical brittle failure

All showed brittle failure: coating, aging, oxide layer thickness, environment
Mixed fracture

As-received

1000°C/2h
Pre-oxidized
Fracture initiated mostly from edge flaws
Effect of aging and environment

Air: 850°C/500h
Wet and reducing: 30%H₂O, 70%(2.7H₂/Ar) 850°C/250h

![Bar chart showing the effect of aging on strength, crofer/YSO75/crofer, 1/2"x1/2" with average tensile strength in MPa. The chart compares no aging, 850°C/500h air aged, and 850°C/250h red.aged conditions.]
Fracture surface of aged sample

850°C/500h air
850°C/250h reducing gas

Presence of substantial amount of SrCrO$_4$
Aluminized crofer showed no chromate formation

Plain crofer  Aluminized crofer

SrCrO₄
Tensile strength of aluminized crofer from pack cementation

Pack cementation, followed by heat-treatment in air

RT average strength, MPa

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<th>Oxidation Condition</th>
<th>Average Strength, MPa</th>
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<td>1000°C/2h</td>
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<tr>
<td>1200°C/2h</td>
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</table>
Sealing with aluminized crofer from vapor phase deposition

Vapor phase deposition followed by heat-treatment at 1000°C/2h air
As-sealed coupons all fractured through glass.
Glass bonded well to aluminized crofer coupons.
Appreciable amount of Al diffusion
Issue of overdosing Al

Aluminizing by vapor phase deposition followed by heat-treatment at 1000-1100°C/2h air
RT seal strength of spinel-coated crofer/YSO75 glass

(Mn,Co)$_3$O$_4$ coated crofer22APU
Fracture surface of as-sealed \( \text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4 \)-coated crofer22APU

Fracture through glass, not at the interface. YSO75 not fully coverage. All 8 samples showed edge flaw.
Fracture surface of air aged $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$-coated crofer22APU

850°C/500 h air

Suggest 5 $\mu$m coating was not enough
Setup for resistivity measurement

- compressive loading
- hybrid mica seal
- Inconel pressing fixture
- crofer
- glass
- crofer
- air side
- alumina support pipe
- Power supply
- resistor
- + sense
- + out
- - out
- - sense
Good electrical stability for HT glass on plain crofer22APU

Crofer(as-received)/glass/crofer(as-received) @ 0.7V

YSO75 @ 0.7V & 20%H2O, 2.7%H2/Ar (t<432hrs), 80%H2 (t>432hrs)
power outage @ ~700 h

YSO75 @ 850°C

G18 @ 830°C
EDS showed substantial Fe diffusion

G18 near air side after electrical stability test

<table>
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<tr>
<th>point</th>
<th>O%</th>
<th>Al%</th>
<th>Si%</th>
<th>Ca%</th>
<th>Cr%</th>
<th>Fe%</th>
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</table>
Good electrical stability for HT glass on (Mn,Co)$_3$O$_4$-coated crofer22APU
Materials set evaluation in 2”x2” single cell test @ 800°C

INDEC cell, SS441, spinel coating, LSM contact paste, aluminizing

![Graph showing power density at various hours at 800°C.](image)

SS441, YSO77x1, spinel, LSM, H-micax4, 97%H2 450 sccm, air 900 sccm

Timespan: 0 to 200 hours at 800°C

Power density: 0 to 0.6 W/cm²
Mechanical strength tests of M/G/M coupons showed strength degradation for uncoated crofer22APU only if aged in air or started with thick Cr$_2$O$_3$ surface layer.

Aluminizing is effective in blocking Cr; however, overdosing would increase CTE for thin samples and leads to seal failure.

(Mn,Co)$_3$O$_4$-coated crofer showed similar initial seal strength as plain crofer or aluminized ones. Minimal strength degradation when aged in air.

HT glass showed very good electrical stability in SOFC and DC loading at 850°C up to ~1200h.

Successful demonstration of 2”x2” single cell test at 800°C with candidate materials set: HT glass, spinel coating, SS441, and LSM contact paste.
Future work

Materials set validation with single cell (2”x2”) stack testing and standardize the design:

1. Sealing glass: high-temperature, self-healing and composite.
2. Metallic interconnect: SS441 (standard or low Si), crofer22APU
3. Protective coating: (Mn,Co)$_3$O$_4$, alumina

- Short-term (200-500h) performance test at 800-850°C
- Short-term thermal cycling test (800°C/24h, cool to RT)x10

- Collaboration with modeling work
- Strengthening of candidate high-temperature glass with reinforcement
SECA Core Program: Recent Development of Modeling Activities at PNNL

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Pacific Northwest National Laboratory
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Travis Shultz, Lane Wilson and Wayne Surdoval
National Energy Technology Laboratory

8th Annual SECA Workshop
San Antonio, TX
August 8, 2007
R&D Objectives & Approach

**Objectives:**
- Develop integrated modeling tools to:
  - Evaluate the tightly coupled multi-physical phenomena in SOFCs
  - Aid SOFC manufacturers with materials development
  - Allow SOFC manufacturers to numerically test changes in stack design to meet DOE technical targets
- Provide technical basis for stack design

**Approach:** Finite element-based analysis tools coupled with experimental validation:
- **SOFC-MP:** A multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks
- Targeted evaluation tools for cell design challenges:
  - Interface and coating durability
  - Reliable sealing
  - Time dependent material performance
- Collaborate with ORNL and ASME to establish and document the stack design approach.
Accomplishments

- Distributed the SOFC-MP and Mentat-FC software packages to multiple industry teams and CTP university researchers for modeling and development of SOFC stacks.

- Established a methodology to assess glass-ceramic seal failure. The damage model was implemented in MSC MARC and used for SOFC stack stress analysis to predict accumulated damage and failure of the seals under thermal-mechanical loading. The methodology was extended to predict seal damage accumulation in stacks due to thermal cycling processes.

- Developed an integrated modeling/experimental framework to predict the life of SOFC interconnect materials. Oxide scale properties were evaluated experimentally and the effects of interconnect oxide growth on interfacial structural integrity during isothermal cooling was studied.

- Initiated a design basis document in collaboration with ASME and ORNL to provide industry teams with technical guidance on materials characterization, constitutive models, modeling techniques, failure analyses, and software usage to support SOFC design and development efforts.
Accomplishments

- Developed modeling methodologies and constitutive models based on experimental characterizations to evaluate the time-dependent mechanical response of stack components. The models can quantify the effect of creep in metallic components and glass-ceramic seals on stack deformations and cell component stresses during operation and shutdown. A homogenization model to predict glass-ceramic seal properties as a function of composition was developed and implemented.

- Established a methodology to assess interconnect scale growth and effect of the associated electrical resistance increase on stack performance. The capability enables evaluation of the long term behavior of prospective interconnect materials with respect to thermal and electrical stack performance.

- Supported development of a standardized SOFC cell geometry for use in the SECA program to evaluate materials and technologies within a common testing platform.
Selected Publications

Collaborations

Industry
- Modeling and Software Training
  - GE
  - Delphi
  - Acumentrics
  - Siemens
  - FCE

University & National Labs
- Modeling
  - U of Illinois, Chicago
  - Georgia Tech
- Materials
  - ORNL
  - Carnegie Mellon University
  - Penn State
- Software Training
  - U of Connecticut

Vendors
- MSC Software
Results

- Support of SECA teams and core program participants
- Advancements for SOFC-MP stack modeling tool
- Metal interconnect
- Glass-ceramic sealants
- SECA Test Cell
- Activities in Progress
Support of SECA teams and core participants

- Sub-models being added to SOFC-MP
- SOFC-MP used in collaborative efforts for modeling seal creep
Developed tools to build/analyze SOFC cells and stacks

- **Mentat-FC**: GUI to build models from templates, CAD files, or FEA meshes
- **SOFC-MP**: Coupled thermal, flow, and electrochemistry solver
- **MSC.Marc**: Structural finite element analysis using SOFC-MP temperatures
SOFC-MP/Mentat-FC

Mentat-FC GUI
- Guides user through entire analysis
- Builds geometry from CAD files, FEA meshes, or templates (planar co-, counter-, cross-flow)
- SOFC operating parameters (I-V, fuel/oxidant inputs, polarizations)
- Exterior thermal boundary conditions
- Material properties database
- Has tubular capability

SOFC-MP Solver
- Finite element based
- Generic fuel and oxidants (CEA)
- Efficient reduced order dimensional analyses for electrochemistry and gas flows
- Contact algorithms treat incompatible meshes

Post-processing of electrical output, species, thermal distribution, deformations, and stresses
Support of SECA Teams and Core Program Participants

- Model improvements for SOFC-MP:
  - Distributed resistance within active area flow region
    - $\Delta P/L = -\beta u$, $\beta = f(\text{density, channel height, viscosity, temp})$
    - Implementation in 3D code in progress

- SOFC-MP used for collaboration with the University of Cincinnati to study the performance of their glass sealant in a realistic SOFC cell.
  - Nirmal Govindaraju

- Other university participants from West Virginia University, Carnegie Mellon University, Georgia Tech, and University of Idaho will participate in summer internships to learn about SOFC modeling.
  - Said Ahzi, Iqbal Gulfam, Emily Ryan, Jackie Milhans, Matt Hinkelman
Advancements for SOFC-MP stack modeling tool

- On-cell reformation
- Pressurized SOFC operation
On-Cell Reformation: Variable Methane Concentration in anode feed

Objectives:
- Predict the cooling benefit of on-cell reformation within stacks of various flow configurations and size as the methane concentration of the anode feed is varied
- Evaluate the thermal and electrical performance of the stacks
- Optimize the anode feed composition for minimum thermal gradients and anode stress

Technical Approach:
- Apply the validated thermal-electrochemistry-reforming calculation methodology within generic models of co-flow, counter-flow, and cross-flow stacks of 10x10 cm and 20x20 cm cell size
- Anode feed varied to represent the partially pre-reformed compositions
- Compare results of the simulation matrix for thermal and electrical performance
On-Cell Reformation: Variable Methane Concentration in anode feed - Results

- Temperature difference and anode stress was minimized with 40-50% of reaction occurring on-cell (counter, cross flow 10x10)
- Co-flow benefited most by largest % on-cell reformation (80%) for both 10x10 and 20x20 cell size
- Larger (20x20cm) stacks benefited similarly to the smaller stacks and also benefited from increased air flows

<table>
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<th>Cell Size / Air Use</th>
<th>Flow Configuration</th>
<th>% OCR</th>
<th>Temperature, °C</th>
<th>Anode Stress S1max, MPa</th>
<th>Power, W/cm²</th>
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<td>Maximum</td>
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</table>
Pressurized SOFC

Objective:
- Predict electrochemical performance in pressurized SOFC systems

Background:
- Increased pressure on both anode and cathode sides has three effects:
  - Nernst Potential is increased
  - Activation and concentration polarizations are decreased
  - Increased electrical power results in decreased net heat load
Pressurized SOFC

Technical Approach:
- Activation polarization $\eta_{Act}^*$
  
  \[ \eta_{Act} = \frac{RT}{2F} \sinh^{-1}\left( i \frac{4F}{RTS^c} \right) \]

  - Cathode side - dependent upon absolute pressure
    
    \[ S^c = P_{exp} \exp\left( -\frac{E_{act}}{RT} \right) \left( P_{O_2cath} \right)^{0.5} \]

  - Anode side - independent of absolute pressure

- Concentration polarization in the cathode:
  - Limiting current is pressure dependent
    
    \[ V_{ca} = \frac{RT}{4F} \ln\left( \frac{1-i}{i_{cs}} \right) \]
    
    \[ i_{cs} = \frac{4FPD_{eff}}{RT\delta} \ln\left( \frac{P}{P - P_{O_2}} \right) \]

Pressurized SOFC

Effect of Pressure on Planar SOFC*

Metal Interconnect

- Indentation testing of scale on Crofer and 441
- Numerical analysis of scale/coating strength
Interfacial Strength Quantification and IC Life Prediction

Overall goal and objective:
- Predict interconnect life with and without spinel coating under isothermal cooling and thermal cycling
- Evaluate life of different candidate IC materials by proposed methodology
- Optimize spinel coating thickness to ensure IC life satisfies SECA life requirement

Technical approach:
- Quantify interfacial strength by integrated experimental/analytical approach
- Predict interfacial stress generated during isothermal cooling and thermal cycling
- Predict interconnect life by comparing stress and strength at the interfaces
Interfacial Strength Quantification and IC Life Prediction

Accomplishments:

- Identify the driving force for interfacial delamination – Interfacial shear stress
- Finished experimental indentation tests on Crofer22 and SS441 with and without spinel coating
- Quantified the strength of oxide/Crofer22 interface
- Predicted Crofer22 life under isothermal cooling without spinel coating
- Quantify the strength of oxide/SS441 interface
Accomplishment - Identify the driving force for interfacial delamination

KII dominant interfacial crack growth → Shear stress at the interface identified as the driving force for interfacial delamination

FEM fracture analyses

Scale Thickness: 5 microns
L = 50 microns

- $a=5$ micron; L-tip
- $a=5$ micron; R-tip

Indentation Depth (micron)

Pacific Northwest National Laboratory
U.S. Department of Energy
Accomplishment - Interfacial Strength
Quantification and Life Prediction for Uncoated Crofer22

Determine interfacial strength using critical indentation force and corresponding finite element indentation analysis: 455MPa

=>

Determine critical scale thickness at which interfacial shear stress of 455MPa will be created during cooling

1/16" Rockwell indentor

Determine IC life using the scale growth kinetics results and the critical scale thickness for delamination

=>

7570 hour <=

PNNL report - 16610

T (m) = 0.0277t^{0.5} + 0.751
R^2 = 0.9961

Bare Crofer 22APU after thermal cycling

Bare Crofer 22APU: 8,850 hrs, 800°C, air

Spinel coated Crofer 22
Accomplishment - Interfacial Strength Quantification for Uncoated SS441

Oxide/SS441 interfacial strength: 344MPa

=> strength of oxide/Crofer22 interface > strength of oxide/SS441 interface

=> consistent with observations from experimental indentation tests

Crofer22: 1.5micron scale thickness, 1/16" indenter

SS441: 1.13micron scale thickness, 1/16" indenter
Accomplishment – Experimental Indentation
Tests on Coated Crofer22 and SS441 Tri-layer Systems

Spinel-coated Crofer illustrating failure occurring at spinel/oxide interface. Failure load was 60kgf utilizing 1/16” ball indenter.

Shear-driven failure in the spinel coating has been observed during indentation tests. Consistent failure zone size and shape have been predicted by finite element indentation simulations.

Spinel-coated SS441 illustrating failure occurring at oxide/substrate interface. Failure load was 150kgf utilizing 1/8” ball indenter.
Current and Future Research Activities on Metallic Interconnect Modeling

**Current activities**
- Identify the weakest interface of spinel/oxide/Crofer22, validate with integrated analytical/experimental approach
- Identify the weakest interface of spinel/oxide/SS441, validate with integrated analytical/experimental approach
- Incorporate statistical nature of the interfacial into distribution of interfacial strength

**Future activities**
- Predict life for SS441 without spinel coating
- Predict life for Crofer22 and SS441 with spinel coating
- Optimize spinel coating thickness by considering growth stress, thermal stress and interfacial strength
- Predict reliability of IC at different operating time based on interfacial strength distribution
Seals

- Creep testing and initial creep model
- Improved creep model
- Thermal & mechanical property predictions
Seal Modeling and Design

**Objectives**
- Derivation of accurate constitutive relations for refractory glass-ceramic
- Optimization of seal properties for desired stack performance
- Design of processing methodology for seal material with desired properties

**Methodology**
- Experimental characterization: elastic properties, thermal properties and creep behavior
- Micromechanical modeling and statistical homogenization
- Correlation of microstructure to physical/mechanical properties and creep flow behavior
- Validation
Accomplishment - A Homogenization Approach to Modeling of Glass-Ceramic Seals

**Assumptions**
- Elastic ceramic crystallites and viscoelastic glassy phase
- Glassy matrix obeys Maxwell’s model
- Ellipsoidal and 3-D random orientation crystallites
- Perfect crystallite/matrix interface

**Approach**
- An incremental homogenization method has been developed to model the viscoelastic response
- This is an incremental procedure that involves the computation of the instantaneous stiffness tensor of the glassy matrix
- Orientation of crystallites is accounted for using the orientation averaging technique developed for random fiber composites

A microstructure of glass-ceramic considered in modeling

Orientation is depicted by means of orientation tensors

A rheological model for glass-ceramic: spring $E_1$ represents the crystallites while spring $E_2$ in series with dashpot $\eta$ describes the viscoelastic behavior of the glassy phase

Relaxation response of a glass-ceramic seal for 0.5 % uniaxial applied strain at 700°C
Accomplishment - Mechanical Property of Fresh and Aged G18 Glass/Ceramic

- Dynamic resonance technique (ASTM C1198) was used to measure the elastic moduli of G18

- Fresh Glass
  - Modulus dramatically drops when T is higher than Tg

- Aged Glass/Ceramic:
  - Presence of crystals
  - No Tg
  - Modulus varies slightly with temperature
  - Ageing induced micro-damage

- Modeling using continuum damage mechanics

---

Young's Modulus (Pa)

Temperature (oK)

0 20 40 60 80

0 300 600 900 1200

Fresh G18
G18 - 1000h aged by Green
G18 - Un-aged by Green

Young's Modulus (Pa)

T (K)

0 200 400 600 800 1000

Damaged G-C: Aged 1000h
Exp: Aged 1000h
Exp: 4h Aged
Seal Property & Time Dependent Behavior: Stack Modeling Results

Seal Damage Distribution

Anode Principal Stress Distribution

Temperature (C) | Elastic Model: Anode Maximum Principal Stress (MPa) | Viscoelastic Model: Anode Maximum Principal Stress (MPa) | Change
--- | --- | --- | ---
Cycle 1 Operation | 38.4 | 36 | 6.3%
Cycle 1 Shut-Down | 65.6 | 62.7 | 4.4%
Cycle 2 Operation | 40.2 | 40 | 0.5%
Cycle 2 Shut-Down | 74.4 | 67.4 | 9.4%

Seal Failure After 2 Thermal Cycles
Accomplishment – Microstructure Characterization for G18

- Multi-phase microstructure of the glass-ceramic seal by SEM
- Preliminary nanoindentation test results

<table>
<thead>
<tr>
<th>Amorphous Matrix</th>
<th>Modulus, $E_r$ (GPa)</th>
<th>Hardness, $H$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>119.5996</td>
<td>7.989734</td>
</tr>
<tr>
<td>Sample 2</td>
<td>100.0175</td>
<td>7.984434</td>
</tr>
<tr>
<td>Sample 3</td>
<td>113.7207</td>
<td>7.727709</td>
</tr>
<tr>
<td>Sample 4</td>
<td>95.39279</td>
<td>7.897548</td>
</tr>
<tr>
<td>Sample 5</td>
<td>93.50994</td>
<td>7.883003</td>
</tr>
</tbody>
</table>

Room Temperature Nanoindentation results for G18 aged for 4 hours at 750°C.

SEM backscatter images of G18 at different magnifications are shown. The white phases represent the barium silicate needles, while the dark phase is the amorphous matrix. The darker needles are hexacelsian.
Case Study: modeling results for the effective elastic properties and CTEs for a glass-ceramic seal material with elastic moduli ratio Ec/Ea=10.

These results depict how the effective elastic moduli and CTE evolve with the microstructure (such as the volume fraction of the ceramic phase). The modeling accounts for the interaction between the phases.

This type of analysis will be used to design the microstructure leading the desired properties.
SECA Test Cell

- Thermal and structural modeling
- Design guidance
SECA Test Cell

Objectives:
- Examine proposed initial designs for test cell suitability
- Long-term: Assist in design of next generation test cell

Technical Approach:
- Apply modeling tools to evaluate thermal and structural performance of designs
- Predict the reliability of the proposed designs using elastic-plastic and creep behaviors of the materials
- Examine influence of geometry, preload, and seal type
- Evaluate the initial designs for structural performance and reliability
Baseline Test Cell Geometry

- Serpentine flow channels
- Thick plate construction with integral ribs
- Separator plate added to facilitate glass-ceramic seal fabrication
Alternate Test Cell Geometries

- **Same general construction**
- **Cross-flow ribs**
  - Improved pressure drop for large cells
- **Hybrid design**
  - Fuel: porous mesh
  - Oxidant: rib channels
Test Cell Model Description

Stack model
- 1 cell model
- Compressive preload
- Operating and shutdown conditions

Components
- Interconnects: SS441
- Picture frame: SS441
- Seals: glass-ceramic
- Anode contact paste: Ni
- Cathode contact paste: LSM
- Anode: Ni:8YSZ
- Cathode: LSM
- Electrolyte: 8YSZ

Geometry
- 50x50 mm cell with edge seal
- 40x40 mm active area
- 80x83 mm stack
- 1.8 mm rib/channel width
- 1.0 mm channel height

MSC MARC FE code

Evaluations
- Effect of geometry
- Effect of material models
- Effect of preload
- Effect of sealing temperature
- Effect of sliding seal
Pressure drop analysis showed:

- Serpentine geometry cell had small $\Delta P (< 0.3 \text{ psi (10" H}_2\text{O)})$ for 4 cm test cells.
- Cross-flow channel design had very small $\Delta P$ for 4 cm size, and could be used for up to a 30 cm cell with similar $\Delta P$ showing promise for use in next generation test cell ($< 0.2 \text{ psi (6" H}_2\text{O)})$.

Thermal analyses of both the serpentine and cross-flow design showed that the entire structure was nearly isothermal (within 5°C).

Structural analysis was subsequently performed assuming isothermal conditions.

$$\Delta p = \frac{1}{2} \frac{fl}{D_h} \rho u^2$$
Test Cell Structural Analysis
Material Properties

- **Plasticity**
  - SS441 interconnect
  - Ni anode contact paste
  - Bilinear stress-strain curve

- **Creep**
  - All materials
  - Experiment & literature data
  - Secondary creep only
  - Temperature & stress dependence included

---

**Creep Rate (s⁻¹)**

- Steel
- 8YSZ
- Ni:8YSZ
- LSM
- G18
- LSM paste
- Ni paste
- Ag

**Strength (MPa)**

- SS441 YS
- SS441 TS
- Nickel YS
- Nickel TS
- Silver YS
- Silver TS

---

**Temperature (°C)**

0 200 400 600 800 1000

**Creep Rate (s⁻¹)**

0 1E-20 1E-19 1E-18 1E-17 1E-16 1E-15

0.0001 0.001 0.01 0.1

---

**Temperature (°C)**

0 200 400 600 800 1000

**Strength (MPa)**

0 100 200 300 400 500 600

---

**Temperature (°C)**

0 200 400 600 800 1000

**Creep Rate (s⁻¹)**

0 1E-20 1E-19 1E-18 1E-17 1E-16 1E-15

0.0001 0.001 0.01 0.1

---

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0 200 400 600 800 1000

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---

**Temperature (°C)**

0 200 400 600 800 1000

**Creep Rate (s⁻¹)**

0 1E-20 1E-19 1E-18 1E-17 1E-16 1E-15

0.0001 0.001 0.01 0.1
Test Cell Structural Analysis Loading

- Electrochemistry analyses showed less than 5°C variation across the stack for furnace operation
  - Use isothermal temperature loading for analysis

- Evaluate stresses at operation and shutdown
  - Begin at stress-free temperature 800°C
  - 1 hr operation 750°C
  - 1 hr uniform cooling to room temperature

- Assume stack has compressive preload applied uniformly to top
  - 0.2 MPa (~30 psi)

- Bottom of stack allowed to slide on rigid plane

![Graph showing temperature and time relationship](image-url)
Test Cell Structural Analysis
Reliability Post-Processing

- Computed reliability from Weibull data sources
  - ORNL: 8YSZ, Ni:8YSZ
  - PNNL: G18 bend bar
  - Literature: LSM

- Assumptions
  - 2 parameter Weibull model
  - Weakest link theory
  - Volumetric flaws
  - PIA model for multiaxial stresses

\[
\sigma_{OV} \left( \text{MPa} \cdot m^{3/m_V} \right) \quad \sigma_{OS} \left( \text{MPa} \cdot m^{2/m_S} \right)
\]
Test Cell Structural Analysis
Solution Procedure

Build Stack Model (Mentat)

Solve Stack Model (MARC)

Convert Results to Neutral File (WeibPar)

Specimen FEA Model

Extract Weibull Scale Parameter (WeibPar/CARES)

Component Reliability Analysis (CARES)

Known Specimen Stress Distribution

Experimental Weibull Strength

STRESS ANALYSIS

RELIABILITY ANALYSIS

EXPERIMENT

Component Reliability Analysis (CARES)
Test Cell Structural Analysis
Results: Effect of Geometry

- Serpentine and cross-flow ribbed geometries similar results
  - Reliability good at operating temperature
  - Glass-ceramic seal failure rate of 27-32% at room temperature
  - Remaining components acceptable

- Anode mesh material with low stiffness presents challenges
  - High stresses in anode, cathode, and seals at shutdown
  - Bending of anode due to high preload and low stiffness of mesh
  - Choice of stiffer mesh material can address the challenges

Serpentine
Cross-Flow
Anode Mesh

CAUTION
Potentially sensitive to other material development efforts
Test Cell Structural Analysis
Results: Effect of Preload

- Stack preload had only small effect on reliability
  - Nominal value 0.2 MPa
  - Decrease to 0.083 MPa caused only minor increase in failure rate from 32% to 33%
  - Increase to 2.0 MPa caused moderate reduction in failure rate from 32% to 23%

- Effect of maldistribution of preload on stresses and contact will be of interest

- Initial test cell design fairly insensitive to preload
Test Cell Structural Analysis
Results: Effect of Seal Technology

Evaluated the influence of having a “sliding” seal surface in stack to mitigate thermal strain mismatches

- Used same mechanical properties of glass-ceramic, and...
- Allowed frictional contact between seal and interconnect with Coulomb friction coefficient of 0.1
- Significantly reduced shutdown seal failure rate from 32% to 2.6%

“Sliding” seal could benefit the test stack during shutdown
Test Cell Structural Analysis
Summary

- Reliability predicted for proposed test cell designs
- Stack elastic, plastic, and creep behaviors characterized
- Influence of geometry, preload, and seal type characterized

Conclusions

- Reliability issues only on shutdown
- Dual rib design good with only potential seal problem on shutdown
- Sliding seal reduces shutdown stresses further

Next Steps

- Multi-cell effects
- Cathode contact sintering stresses
- Validation with experimental tests
Activities in Progress

- Improvements for the SOFC-MP modeling tool
- Cathode contact modeling and experiments to determine required strength (collaboration with ORNL)
- Continued modeling support for test cell development
- Stack performance simulation considering creep of multiple components
- Scale-up modeling for prediction of thermal and electrochemical performance of large stacks
- Coated interconnect life prediction: Crofer and SS441
- Development of methodology for correlating seal microstructure to properties
- Sealant material creep testing
Proposed SOFC-MP Improvements

- Distributed resistance model with thermal property effects
- Interface with user-provided electrochemistry subroutine
- Post-processing of all species variables
- Symmetry plane capability
- Coal-based fuels capability
- Stack performance data summary
- Shell element capability
- Compressive preload
- Sliding contact surfaces
Cathode Contact

Objectives:
- Provide “target” contact layer strength to material development activities
- Establish a predictive methodology for stack assembly stresses
- Develop modeling and analysis tools (aided by material experiments to characterize constitutive and failure behaviors) to evaluate and improve durability of cathode-side mechanical interfaces

Approach
- Combined numerical and experimental approach to develop needed models and validate experimentally

Tension test schematic of coated IC/ceramic paste interface
Conclusions and Future Directions

In the last year, the modeling tools had greater usage and additional capabilities to address durability issues have been developed. Future modeling activities will continue to focus on reliability, degradation, time-dependent response, and scale-up issues:

- Continue to add new capabilities to the modeling tools to meet the needs of the SECA program.
- Continue to increase the usage of the tools by the industry and academic teams.
- Continue to add improved material models and numerical procedures to the modeling tools for simulation of time-dependent response and reliability.
- Continue modeling to improve bond strengths of the oxide and protective coating layers for ferritic stainless steel interconnects.
- Evaluate thermal management needs, influence of high pressure electrochemistry, and reliability of seal/cell structures during cell scale-up.
Conclusions and Future Directions

… continued

► Continue to support development of a robust test cell design.

► Evaluate the mechanical requirements for successful fabrication using refractory glass sealants and low-temperature sintering of cathode contact materials for reliable interconnection during operation and shutdown.

► Continue to develop seal property predictions via homogenization methods to identify reliable composite seal structures and compositions for stacks.

► Develop analytical methods to evaluate the time-dependent mechanical behavior (creep, thermal fatigue, loss of interconnect contact) of fuel cell stacks/components and corresponding influence on electrochemical performance.
Development of ASME Design Guide for Reliable SOFC

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Edgar Lara-Curzio
Oak Ridge National Laboratory

Rick Swayne, Jim Ramirez, Raj Manchanda, Brandy Smith
ASME

Travis Shultz
National Energy Technology Laboratory

San Antonio, TX
August 9, 2007
**R&D Objectives & Approach**

**Objectives of the guidelines are to provide recommended:**
- Rules and practices for design of SOFCs stacks
- Associated SOFC modeling and analyses procedures

**Guidelines may serve as a repository for state-of-the-art knowledge and experience gained in SOFC designs**

**Technical approaches:**
- Documenting design and experimental practices following ASME past and similar experiences.
- Providing technical basis by:
  - Quantifying the electro-chemistry activities and the associated thermal-mechanical behaviors of various SOFC design configurations
  - Quantifying the variability in material properties and design parameters of all elements in the SOFC structure
  - Evaluating the reliability of various SOFC components
  - Providing methodology for deriving possible design improvements
Status

- NETL Kick-off meeting
- Weekly/Bi-weekly teleconferences
  - PNNL, ORNL, and ASME participation
  - Using C&S Connect online repository
  - Hosted visit by technical consultant Rick Swayne’s visit to PNNL
  - Developed document outline
  - Obtained consensus on the document outline
  - Assigned authorship for various sections
- Writing of document
  - Finished first draft version of the document on July 30, 2007
  - Sent to ASME external review committee for first round of review
Collaborations

Internal collaborators:
- Jeff Stevenson, Prabhakar Singh
- Gary Yang
- Matt Chou
- Dave King

External collaborators:
- Rick Swayne - Reedy Engineering
- Edgar Lara-Curzio - ORNL
- Jim Ramirez, Raj Manchanda, Brandy Smith - ASME
- Travis Shultz - NETL
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- 9.4. Creep Behavior of Current Collector Mesh
SOFC Design Basis: Next Steps

- Review written sections
  - Complete technical input for section components
  - Ensure technical accuracy and completeness
  - Obtain NETL content approval

- Final document assembly
  - Ensure content and flow sufficient to convey design basis
  - Assemble ancillary information (material properties, examples, references)

- Peer review
SOFC Operation on Hydrogen and Coal Gas in the Presence of Phosphorus, Arsenic and Sulfur Impurities

Olga A Marina, Larry R Pederson, Danny J Edwards, Chris W Coyle, Jared Templeton, Mark Engelhard, Z Zhu

Contract Manager: Heather Quedenfeld

8th Annual SECA Workshop, San Antonio, TX, August 9, 2007
Outline

- Objective
- Experimental Results
- Post-mortem cell investigations using SEM/EDS, TEM, EBSD, XPS, ToF-SIMS, and XRD
- Summary
Objective and Approach

- Evaluate performance of SOFCs operating on coal gas assuming warm gas clean-up

- Phosphorus, arsenic, and antimony are potentially the most harmful to the Ni/YSZ anode because of possible second phase formation with Ni

- Studies also were performed with key contaminants in hydrogen to aid in poisoning mechanism understanding

- Adsorption studies on small Ni, Ni/YSZ, Ni/SDC coupons were performed to determine the interactions between Ni and P or As as a function of exposure time
Schematic of Button Cell Test Stands

Test Conditions:
- 700 and 800°C
- Fuel (at equilibrium): H₂/H₂O = 97/3 or H₂/CO/CO₂/H₂O = 30/23/21/26
- Initially preconditioned in H₂ at 0.7 V for 24-30 hours followed by 0.5 A/cm² in H₂ or coal gas for ~100 hours
- All impurities were added after water bubbler
- Tested at a current of 0.5 A/cm²

Standard Ni/YSZ anode:
- 50 vol% Ni (solids) active anode (~ 8 µm)
- 40 vol% Ni (solids) bulk anode ~ 800 µm thick
SOFC Performance at 800°C in Coal Gas with 2 ppm of PH₃

PH₃ exposure leads to cell degradation, ~0.13-0.2%/hr increase in ASR. This degradation is irreversible. Cells continue to degrade after PH₃ removal from the fuel.
Effect of Phosphorus on Cell Performance

- Power loss onset occurs more rapidly at 700°C.
- After onset, degradation rates do not appear to be significantly different at 700 and 800°C.

% Power retention calculated after the impurity introduction over power before impurity introduction.
More Rapid ASR Increase in Coal Gas

![Graph showing ASR increase over time for different conditions: coal 800°, coal 700°, 0.3 A/cm², and H₂ 700°, H₂ 800°. The y-axis represents ASR increase (%) and the x-axis represents time (hours).]
Effect of Arsenic on Cell Performance

Slow degradation (~1%/100 hr) in the presence of 1 ppm of As in both H₂ and coal gas.
Effect of P and As on Cell Resistance

- $R_{\text{Ohmic}}$ and $R_{\text{electrolytic}}$ increase with time of exposure to PH$_3$
- Change in $R_{\text{ohmic}}$ is more significant for AsH$_3$ exposure

800°C
coal gas+2 ppm of PH$_3$
$I_{\text{bias}} = 0.5$ A/cm$^2$

800°C
coal gas+1 ppm of AsH$_3$
$I_{\text{bias}} = 0.5$ A/cm$^2$
Effect of Sulfur on Cell Performance: Baseline for Tests with Contaminants

- Rapid initial degradation (ca. 15%) during first 30 hours in both H₂ and coal gas
- 2nd stage degradation rate (0.06%/hr in H₂ and 0.26%/hr in coal gas)
Synergistic Effect of P+As+S Contaminants in Coal Gas

In the presence of S, initial drop is ca. 15% and appears to be independent of other impurities.

- Effect of S is predominant over first 30 hours
- S-related 2nd stage degradation is suppressed by the presence of P and As
- 2nd stage degradation is similar to that in P

1 ppm of AsH₃, 1 ppm of H₂S, 2 ppm of PH₃
All surface Ni under the fuel inlet is converted into Ni$_3$P. Surface Ni away from the fuel channel is present as the metal.

381 hr test in H$_2$/H$_2$O=97/3 with 2 ppm of PH$_3$ at 800°C

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>P (at%)</th>
<th>Ni (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>31.00</td>
<td>69.00</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>30.89</td>
<td>69.11</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>32.67</td>
<td>67.33</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>24.69</td>
<td>75.31</td>
</tr>
</tbody>
</table>

Ni$_3$P (TEM & XRD confirmed)
381 hr test in H₂/H₂O=97/3 with 2 ppm of PH₃ at 800°C

Based on intensity maps, Ni is coarsened and converted into Ni₃P within the top 60 μm.
Current Collecting Wire after 381 hr Test with 2 ppm of PH$_3$

Outer layer of the wire is converted into phosphides
EBSD Reveals $\text{Ni}_5\text{As}_2$ Formation after 70 hr Test with 1 ppm of AsH$_3$

70 hr test in $H_2/H_2O=97/3$ with 1 ppm of AsH$_3$ at 800°C
Ni has two phase regions, one rich in As (ca. 45 μm) and the other rich in P (150 μm).
Surface Layer after 700 hr Test in Coal Gas with $PH_3 + H_2S + AsH_3$

Ni is converted into a mix of $Ni_5As_2$ and $Ni_3P$
Ni Grain Surfaces Uniformly Covered with P Throughout Ni/YSZ

This is likely an adsorption layer undetectable by SEM/EDS

ToF-SIMS line-scan of the cross-section of button SOFC after test at 800°C in coal gas with H₂S, PH₃ and AsH₃.

High resolution photoemission spectra of the P 2p region
Surface Probe Shows Presence of Adsorbed Sulfur on Ni

- Ni/YSZ anodes tested in coal gas with H₂S have higher S concentrations than the reference.
- No second Ni-S phase found

PH₃+H₂S+AsH₃
700 hrs

1 ppm H₂S
850 hrs

No impurities (Reference)
Post Test Analysis Summary: Ni Interactions with P, S, and As

- S, P, and As adsorb on the Ni surface
- Affinity for Ni increases in the order $S < P < As$
  - Phosphorus displaces absorbed sulfur
  - Arsenic displaces adsorbed phosphorus
- Unlike sulfur, P and As form secondary phases, nickel phosphides and nickel arsenides. This transformation is irreversible.
Ni/YSZ anodes were tested in simulated coal gas with 1 ppm of H$_2$S, 2 ppm of PH$_3$ and 1 ppm of AsH$_3$ in various combinations at 700-800$^\circ$C for up to 800 hours.

Initial cell degradation, $\sim$ 15 % of the power density, is attributed to the presence of sulfur (effect on the anode resistance).

Second stage degradation, 0.01-0.07%/hr, is P and As related and is due to the increase in the ohmic resistance and electrode resistance.

- Ni contact paste, wires and Ni in the top Ni/YSZ later under the fuel inlet were severely affected by the presence of 2 ppm of PH$_3$. Surface and bulk ($\sim$ 150 μm) Ni$_3$P was formed during 700 hours test at 800$^\circ$C.
- Ni$_3$P showed extensive agglomeration and self-crystallization followed by the densification of the upper Ni layer. Similar grain orientation of Ni$_3$P suggests partial liquefaction and re-solidification as a single, continues grain.
- A nickel deficient layer was formed in the upper part of the Ni/YSZ affecting the Ni percolation.
- Surface Ni$_5$As$_2$ was formed after exposures to 1 ppm of AsH$_3$ at 800$^\circ$C. Arsenide formation alone had insignificant degradation over 700 hour test because of strong Ni-As interaction near the surface (and not at the active interface).
Support for this work is provided by the US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory through the SECA Program.

We would like to acknowledge NETL management team for helpful discussions.

Pacific Northwest National Laboratory is operated for the US Department of Energy by Battelle.
Advanced Interconnect and Interconnect/Electrode Interfaces Development at PNNL


Pacific Northwest National Laboratory
Richland, WA 99352

8th Annual SECA Workshop and Peer Review
San Antonio, TX, August 6-9, 2007
Objectives and Approach

♦ Objectives
  • Develop cost-effective, optimized materials and fabrication approaches for SOFC interconnect and interconnect/electrode interface (i.e. contacts) applications
  • Identify and understand degradation processes in interconnects and interconnect/electrode interfaces

♦ Approach
  • Materials and process development
    ■ Cost-effective oxidation resistant alloys
    ■ Surface modification via coatings
    ■ Interconnect/electrode contact materials
  • Materials evaluation and degradation study
    ■ Screening study of alloys and ceramics for interconnect and interface applications, respectively
    ■ Investigation and understanding of oxidation/corrosion and interfacial reactions and stability under SOFC operating conditions.
Accomplishments in FY07

- Investigation and development of cost-effective ferritic stainless steels (In collaboration with Allegheny Ludlum Corp.)
  - Systematically investigated 430
  - Identified and evaluated 439 and 441, two modified versions of 430
  - Applied protection layers onto candidate alloys and evaluated their performance

- Development of protection layers and fabrication approaches
  - Completed long-term thermal stability and electrical performance evaluation
  - Initiated optimization of materials and fabrication for further cost-reduction

- Investigation and development of contact layers between metallic interconnects and electrodes
  - Screening-studied more than a dozen materials systems via different fabrication approaches
  - Identified two promising material groups and three approaches
  - Evaluated electrical performance of selected candidates
Investigation and Development of Novel Interconnect Alloys

♦ **Goal**: Identify/develop a novel ferritic stainless steel (FSS) with an optimized alloy chemistry that offers comparable or improved performance relative to the state-of-the-art compositions such as Crofer 22 APU, while being more cost-effective.

♦ **Approach**: To achieve the desired alloy chemistry or control residual alloy elements of Si, C, N, etc., via alloying, instead of extra refining that adds cost.

♦ **Accomplishments**
  - Investigated properties of 430 relevant to interconnect applications
  - Identified potential candidates 441 and 439, two modified versions of 430
  - Evaluated their properties relative to interconnect requirements
  - Surface-modified the potential candidates with spinel protection layers and investigated their stability and electrical performance
Oxidation Kinetics of Bare and Coated 430

Why 430: cost reduction
- 430: 17% Cr, via conventional melting – more cost-effective
- Crofer 22 APU: 23%Cr, extra refining (e.g. vacuum refining) for cleaning residual elements, Si, C, N, etc.

- Bare 430 demonstrated a fairly low scale growth rate at early stages
- Leveling off of the weight gain indicated likely spallation
- Mn$_{1.5}$Co$_{1.5}$O$_4$ (MC) spinel protection layers drastically mitigated the scale growth beneath the coating
Surface Stability of 430

- Unlike bare 430, no spallation observed on MC 430
- Fe transported through the coating, BUT not Cr
- No solubility of SiO₂ in Cr₂O₃
- Formation of continuous, insulating SiO₂ layer b/w scale and Fe-Cr substrate

Bare 430

1,200 hrs, air, 800°C

MC coated 430

10 μm
Long-Term Performance of MC Coated430

- The formation of a continuous insulating SiO₂ layer at the scale/metal interface led to a high ASR.
- The ASR became unstable after about 4,000 hours, likely due to detachment of scale from the metal substrate.

Area specific resistance (ASR) measurement:
IC//contact//cathode/LSM pellete/cathode//contact//IC
800°C, air

Cathode: La₁₀Sr₀₂MnO₃
IC: Mn₁₁Co₁₅O₄ coated 430
Contact: La₀₈Sr₀₂Co₀₅Mn₀₅O₄

MC protection layer||scale||Fe-Cr

FeCr
Si
Mn Co
20 μm

Electron Image 1

Pacific Northwest National Laboratory
U.S. Department of Energy
Metallurgy of 441 and 439

<table>
<thead>
<tr>
<th>Designation</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Nb</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-441</td>
<td>17.8</td>
<td>0.33</td>
<td>0.20</td>
<td>0.010</td>
<td>0.045</td>
<td>0.47</td>
<td>0.024</td>
<td>0.001</td>
<td>0.18</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>439 HP</td>
<td>17.5</td>
<td>0.44</td>
<td>0.20</td>
<td>0.012</td>
<td>0.040</td>
<td>0.73</td>
<td>0.016</td>
<td>0.0004</td>
<td>0.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL 430</td>
<td>17.0</td>
<td>≤1.0</td>
<td>≤0.75</td>
<td>≤0.12</td>
<td>≤1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crofer 22 APU</td>
<td>23.0</td>
<td>0.4-0.8</td>
<td>0.030</td>
<td>≤0.50</td>
<td>≤0.50</td>
<td>0.020</td>
<td>0.050</td>
<td>≤0.2</td>
<td>0.04-0.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Fractional % of Ti and Ti/Nb were added into Fe-17%Cr substrate for 439 and 441, respectively.
- Nb leads to laves phase (Fe₂Nb) precipitation along grain boundaries that significantly improves high temperature strength and creep resistance of the Fe-Cr substrate (double yield strength at 800ºC).
- As strong carbide/nitride formation elements, Ti and Nd lower interstitial elements C and N in the substrate.
- Can Nb (or Ti) tie up Si to prevent SiO₂ layer?
Electrical Evaluation of 441 and 439

La$_{0.8}$Sr$_{0.2}$MnO$_3$ cathode and contact, air, 800°C

- **Chipping**
- Crofer 22 APU (LSCM contact)
- **441**
- **439**

**ASR (mOhm-cm²)**

**Time (hours)**

500 mA.cm$^2$

FSS IC

LSM contact

LSM cathode

MC layer

500 mA.cm$^2$

439 HP

Scale

Pacific Northwest National Laboratory
U.S. Department of Energy
Effects of Minor Alloying Elements in 441

- There was Si buildup or silica layer formation between scale/metal interface, in spite of about 0.5% residual Si in the metal substrate.
- Nb tied up Si, preventing formation of SiO₂ layer at the scale/metal interface.

Atomic%: 21.9Nb, 8.4Si, 2.8Ti, 10.0Cr, 56.9Fe
Scale Structure and Compositions of 441

- Scale grown on 441 is mainly comprised of \((\text{Mn}, \text{Cr})_3\text{O}_4\) and \(\text{Cr}_2\text{O}_3\), similar to that of Crofer 22 APU
- Negligible Fe or iron oxides in the scale, different from that of 430

300 hours, 800°C, air
Kinetics of Scale Growth on 441

- Scale growth rate comparable to Crofer 22 APU, but with inferior scale adherence
  (Local spallation found occasionally after extensive oxidation)
- 2–3 times lower for MC coated specimens; no spallation

After 900 hours
Electrical Performance of Surface-Modified 441

- $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ spinel protection layers minimized area specific electrical resistance (ASR)
- ASR of coated sample increased little, if any, over the course of the test

Graph:
- Bare T-441
- T-441 with $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ protection

Conditions:
- Cathode: LSM
- Contact: LSM
- IC: bare 441 or MC coated 441
- Current: 500 mA.cm$^{-2}$
- Temperature: 800°C, air
SEM Cross-Sections of ASR Samples

- Improved surface stability: no spallation or detachment observed
- No penetration of Cr through the protection layer, though there appeared Fe migration into the coating (similar to 430).

MC coated 441

BS image

10 μm
Summary

- 441 exhibited promising alloy chemistry: addition of a small amount of Nb helps avoid formation of a continuous silica layer and promote desirable second phase precipitation, thus leading to a lower scale resistance and higher mechanical strength.

- The alloying approach eliminates the costly refining process that is currently employed for making Crofer 22 APU and other super-grade ferritic stainless steels for IC applications.

- Protection layers are required to further improve alloy surface stability and electrical performance, and seal off Cr.

Future Work

- Evaluate long-term thermal stability and electrical performance of bare and surface modified 441

- Further understand the alloy chemistry via advanced diagnostic study

- Investigate and optimize bulk alloy chemistry and surface modification for satisfactory long-term stability and performance. (In collaboration with Allegheny Ludlum Corp.)
Protection Layer Development and Investigation

**Goal**: develop cost-effective, optimized protection layers that are effective barriers to both oxygen inward and chromium outward diffusion, while being stable over lifetime of SOFC operation.

**Previous work:**
- Developed spinel protection layers with a nominal composition $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$
- Systematically studied $(\text{Mn,Co})_3\text{O}_4$ spinel materials
- Developed slurry-based approaches for fabrication of the spinel protection layers
- Evaluated kinetics of scale growth, stability under thermal cycling, electrical and electrochemical performance, chromia volatility, etc., of coated Crofer 22 APU
- Completed one year thermal stability evaluation of coated Crofer 22 APU

**Recent Accomplishments:**
- Completed half year electrical evaluation of MC coated Crofer 22 APU and 430 (with LSM cathode & contact paste)
- Investigated suitability and performance of the spinel protection layers on 430 and 441 (see previous slides)
- Started developing alternative fabrication approaches, e.g. electrochemical deposition
Summary and Future Work

- Spinel protection layers with a nominal composition Mn$_{1.5}$Co$_{1.5}$O$_4$ and fabricated with slurry coating approaches are an effective oxygen inward and chromium outward diffusion barrier, mitigating scale growth and sealing off chromium.

- Interconnect FSS, e.g. Crofer 22 APU, with the spinel protection layers demonstrated excellent long-term stability and electrical performance.

- Developing cost-effective approaches compatible with mass production and practical shapes of interconnect:
  - Electroplating, electrophoresis, etc., in addition to spray process.
Contact Layer Investigation and Development

**Goal**: develop cost-effective, optimized contact layers between metallic interconnects and electrodes.

- **Functions**
  - Promote electrical contact
  - Facilitate stack assembling
  - Act as a potential buffer zone to prevent unwanted reactions and transport, such as Cr volatility

- **Challenges**
  - A metallurgical bond can be built between a metallic interconnect and Ni-YSZ anode, providing a low resistance path for electrons.
  - Oxide-metal interfaces are present between metallic interconnects and cathodes, increasing electrical resistance and thus causing power loss.
Challenges of current materials

- Precious metals demonstrate suitable properties, but too expensive (Ag, a possible exception).
- Conductive oxides of high sintering activity, e.g. superconductors, usually too reactive, negatively affecting the stack and interface stability.
- Conductive oxides, e.g. LSM, that are typically used as cathode compositions demonstrated good compatibility, but need improvement in sintering activity at 800-900°C and thus better electrical contact.

**Approach:** improve sintering activity via reaction sintering, addition of sintering agents or chemical modification.
Fabrication of Contact Layers via Reaction Sintering

- Paste of metals and/or oxides mixture
- During first stack heating or sealing
- Conductive oxide contact layer
- Reactions assisted sintering

Conductive oxides → MC layer → Crofer 22 APU

- After reaction sintering
- Without sintering

5 μm

Electron Image 1
Contac Layers via Adding Sintering Agents

- Among studied, CuO and Bi$_2$O$_3$ more effective for LSM
- To be effective needs 4~5%
Electrical Performance and Stability Evaluation

Interfacial resistance evaluation unit (IRU)

ASR, mOhm.cm²

Time (hours)

0 100 200 300 400 500

0 100 200 300 400 500

0 500 mA.cm²

500 mA.cm²

FSS IC

contact
cathode

MC layer

LSM

500 mA.cm²

LSM+1%CuO

LSM+2%CuO

LSM+4%Bi₂O₃

Temperature (°C)

Temperature

500 mA.cm²

25.0

20.0

15.0

10.0

5.0

500 mA.cm²
Enhanced Sintering via Chemical Modifications

% Shrinkage vs Temperature, °C

- LSM
- Modified LSM
Summary

- Reaction sintering appears to be a promising approach to fabricate contact layers between perovskite cathodes and metallic interconnects.
- Addition of sintering aids and chemistry modifications also help improve sintering activity of conductive oxides.

Future work

- Continue to search and optimize contact materials and processing approaches
- Systematically evaluate candidate systems: dilatometry, IRU (ASR), SEM, XRD.
- Evaluate long term electrical performance and interface stability under isothermal and thermal cycling
Acknowledgements

The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.

The authors wish to thank the SECA management team at NETL for their helpful discussions regarding this work.

Metallographic preparation and SEM: Jim Coleman, Shelley Carlson, Nat Saenz
Modeling Tools for Solid Oxide Fuel Cell Analysis

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BJ Koeppel, VN Korolev, W Liu, KP Recknagle, EV Stephens, X Sun
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9th Annual SECA Workshop
Pittsburgh, PA
August 5-7, 2008
Motivation

The SOFC is a complex system:
- Multiple physical phenomena including fluid flow, electrochemistry, electric fields, thermal field, mechanical deformations, materials compatibility
- Physical phenomena are tightly coupled (i.e. not independent)
- High operating temperature range

SOFC testing is very expensive:
- Characterization of material properties, stability, and performance required
- Stack fabrication, assembly, monitoring, and testing are time intensive
- Only a minimal number of experimental tests can be done to validate long term technical performance targets (e.g. 10,000 hr)

Modeling can be used for numerical design experiments:
- Can simulate the multiple physical phenomena
- Can be used repetitively to quickly evaluate the effects of design changes or explore the viable design space
- Can be used in conjunction with testing to optimize performance
- Can investigate long term behaviors
Objectives & Approach

Objectives

- Develop integrated modeling tools to:
  - Evaluate the tightly coupled multi-physical phenomena in SOFCs
  - Aid SOFC manufacturers with materials development
  - Allow SOFC manufacturers to numerically test changes in stack design to meet DOE technical targets
  - Support industry teams use of modeling for SOFC development
  - Provide technical basis for SOFC stack design

Approach

- Multiphysics-based analysis tools coupled with experimental validation:
  - SOFC-MP: A multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks

- Targeted modeling tools for specific cell design challenges:
  - Reliable sealing
  - Interface and coating durability
  - Thermal management of large stacks
  - Cathode contact paste durability

- Collaboration with ORNL and ASME to establish a stack design approach based on modeling and experiments
SOFC-MP: Capabilities and Features

- **SOFC-MP Capabilities**
  - Coupled flow, EC, and thermal solutions
  - Reduced order models for computational efficiency
  - Contact of incompatible meshes
  - Single or multi-cell models
  - Generic fuel and oxidants
  - Operation at assigned voltage, current, or fuel utilization
  - Thermal and electrochemical results output for visualization

- **Recent Improvements**
  - Improved solution speed with use of AMG solver on PC
    - ~5hr for 8-cell stack model w/ 100k nodes and 200 solution iterations
  - Elimination of memory restrictions to solver larger problem sizes
    - Models w/ 100k nodes and 55k elements on PC w/ 4Gb memory
    - Port to Linux to take advantage of large shared memory
  - Improved energy balances with non-conformal meshes
  - Internal code restructuring to facilitate requested enhancements
SOFC-MP: Capabilities and Features (cont’d)

- SOFC-MP has the ability to compile and utilize subroutines to customize the solution
- User subroutines can be defined to include proprietary EC models
  - Generic I-V relationship can be coded to compute voltage as a function of partial pressures, temperature, current, etc.
- User subroutines can be used to control the flow resistance
  - Different interconnect media can be simulated
  - \( \frac{dP}{dL} = RV \)
SOFC-MP: Stack Modeling Examples

- Multi-cell 3D stacks using SOFC-MP
  - 6-cell: 360min for 76k nodes and 200 iterations
    - Stack $\Delta T$: 160°C, Cell $\Delta T$: 73-127°C
  - 7-cell: 18min for 88k nodes and 60 iterations
    - Faster due to low UF & different EC model
  - AMG solver: time/memory scales with # of cells

- 2D vertical stack slice model
  - Useful for co/counter-flow
  - Can be adjusted for cross-flow
  - Can handle internal reforming
  - Example: temperature profiles for various cells in 24-cell stack

![6 Cell Stack Temperature](image1)

![Cell 1/7](image2)

![Cell 7/7](image3)

![24-Cell Vertical Slice Model](image4)
Thermal Management: Internal Reforming

Previous work demonstrated possible performance improvement by manipulation of the percent of reformation on-cell
- Stack $\Delta T$ and component stress could be decreased depending upon methane content in fuel

Separate work manipulated heat transfer and heat distribution within stack to optimize the operating condition and performance
- Both the improved conduction, and decreased air (and fuel) utilizations decreased the stack $\Delta T$

Present study is a continuation of the manipulated heat transfer work to further optimize stack performance including:
- Internal reforming
- Pressurization
Optimization of stack performance will also include the effect of pressurization:

- The Nernst Potential correctly captures the pressure effect and requires no further examination.
- The Butler-Volmer equation describes the activation polarization $\eta_{act}$ related to the current ($j$) and the exchange current density ($j_0$). For the SOFC it can be written as:

$$\eta_{act,e} = \frac{RT}{\alpha F} \sinh^{-1} \left( \frac{j}{2j_0} \right)$$

- Pederson’s tests showed $j_o = j_0(\text{PO}_2)^{1/2}$
- The exchange current density model was improved by adding the pressure dependence, and applied to both electrodes as:

$$j_0 = \beta \exp \left( \frac{-E_{act,e}}{RT} \right) \text{PO}_2^\gamma$$
Thermal Management: Pressurization (cont’d)

- Performance improvements:
  - Increased Nernst potential
  - Decreased activation polarization
  - Increased cell voltage and electrical power -> decreased heat load
  - Decreased Heat load leads to improved thermal performance

- Electrochemistry model with improved activation polarization properly characterizes the performance improvements for planar and tubular cells operating at elevated pressures.

### Tubular SOFC data (Siemens), 89% H₂, 3% H₂O, running at 1, 3, and 10 atm at constant 85% UF

### Planar SOFC data (GE), 25% H₂, 3% H₂O, 72%

N₂ running at 1, 3, and 10 atm
Seal Property Characterization

- Performed shear tests of refractory glass sealants at room and elevated temperatures
  - Compared to G18 glass-ceramic

- Results
  - Room temperature strength of refractory glass about 2/3 less
  - Elevated temperature strength comparable (~7% less)

![Graph showing shear tests at 25°C and 800°C](image)
Perform creep experiments to quantify effect of aging on time-dependent response

Creep rate an order of magnitude less after 1000hr devitrification

Short-term seal creep expected to accommodate high stresses initially, but much slower creep after aging
Modeling of Different Seal Glasses

Greatly different creep rates at 30 MPa applied stress
- UC glass: $1.0 \times 10^{-3}$/s at 1000°C
- G18 glass-ceramic: $1.0 \times 10^{-6}$/s at 973°C (700°C)
Modeling of Different Seal Glasses (cont’d)

- For G18 glass-ceramic sealant, maximum equivalent total strain and creep strain keep constant after the initial creep stage:
  - no overflow of the glass ceramic seal materials will occur during the operation of SOFC stacks
- For UC self-healing glass seal, maximum equivalent total strain and creep strain keeps increasing after one hour operation:
  - Overflow of seal glass will occur, control block of total creep deformation is necessary during the desired SOFC operating duration
Modeling of Different Seal Glasses (cont’d)

- Maximum equivalent von Mises stress, maximum $\sigma_{11}$, and $\sigma_{33}$, for the PEN seal with the different glass sealants, respectively
- Stress results for both sealants possess similar trends
  - von Mises stress is released rapidly, and
  - normal stress $\sigma_{11}$, and $\sigma_{33}$ are constant after a small drop
- Time to release the shear/deviatoric stress for G18 is much longer than UC seal healing glass
Aging/Self-Healing Behavior of G18

- Evolution of crystalline phase is time dependent

After sintering

- Glass/ceramic displays possible self-healing behavior at high temperature

After 1000 h aging

- Aging induced micro-voids in glass-ceramic

Typical Vickers impression at 750°C for half an hour
This model includes:

- Aging-time-dependent crystalline content model for volume evolution of crystalline phases
- Temperature dependency
- Degradation of modulus of glass/ceramic due to aging induced micro-damage
- Mechanical property restore due to self-healing performance at high temperature

This model was applicable to general glass/ceramic materials
Contact Paste: Introduction

The cathode contact layer is a highly challenging interface:

- Must make bond between ceramic cathode and metallic interconnect (likely with oxide scale and coatings)
- Must survive oxidizing environment
- Must likely be formed at temperatures lower than that of the conventional range for sintering of ceramics

Modeling can aid understanding of load requirements and guide design improvements

Areas of interest for modeling and experiments:

- Quantification of expected interface stress levels
- Characterization of paste mechanical/strength properties
- Evaluation of the contact layer as a load carrying interface to reduce seal loads
- Evaluation of contact layer stresses and reliability due to low temperature processing methods
Contact Paste: Stress Levels

- Evaluated continuous paste support
  - High peeling stresses (35 MPa) and shear stresses (17 MPa) concentrated near the sealed edge of the cell at operating temperature
  - Even higher local peeling and shear stresses at shutdown
  - Cell scale-up from 10-30cm showed only moderate changes in peak stresses- dominated by edge effects
  - Sliding seals were more beneficial than rigid seals
  - Consideration of stack creep effects was beneficial for relaxing stresses
  - Higher stack sealing temperatures with rigid seals increased stresses in all the cell components
Contact Paste: Property Characterization

- Joint collaboration between PNNL and ORNL
  - Yanli Wang from ORNL visited PNNL to work on specimens fabrication
  - Continued PNNL support to ORNL for fabrication of specimens

- Experimental work in progress
  - ORNL conducting notched specimen bend tests to determine interfacial toughness of fabricated analogs
  - PNNL conducting tensile tests to determine interfacial strength of fabricated analogs
  - Beginning with spinel-coated Crofer interconnect substrate material and LSM-10 contact paste; next step to test Ce-spinel coated 441SS and LSM-10 contact paste

- Preliminary interfacial tensile strengths at test temperatures ranging from RT to 850°C indicate 1-6 MPa
Q: Can a load-carrying cathode contact layer benefit the seals?

Load transfer between cell and manifold (due to CTE mismatch) carried potentially by three parallel paths:

- Edge seals
- Anode interconnect
- Cathode interconnect

\[ \alpha_{\text{manifold}} \, 5\% > \alpha_{\text{cell}} \]

\[ \alpha_{\text{manifold}} \, 5\% < \alpha_{\text{cell}} \]

Can seal load be reduced?

Depends on relative stiffness of components
Contact Paste: Load Transfer (cont’d)

- Seal load dependence on contact paste design was simulated
  - Co- versus cross-flow
  - Bonded versus sliding contact
  - Variation of paste modulus as a function of cathode modulus
  - Ribbed and continuous ICs

- Results
  - Bonded paste reduced seal shear load up to 10-20% compared to sliding interface
  - Paste modulus for bonded layer had only small effect (<5%) on seal load
    - Implies low modulus sensitivity good for processing the porosity
  - Seal load varied greatly (~40%) with orientation relative to rib direction
  - Continuous IC evaluations still in progress

- Conclusion: load sharing concept is viable, but not fully characterized yet
Contact Paste: Sintering

Modeling Goal

- Material and process for strong, reliable cathode contact
- Develop a model to predict the properties and stress state of the cathode contact layer including effects of:
  - Initial state/stresses due to the sintering/processing step
  - Mechanical stresses induced by any volumetric changes of the anode during reduction
  - Typical thermal stresses due to cell operation and shutdown

Technical Approach

- Implement constitutive model to predict the sintering strains and developed stresses
  - Evolution of relative density and grain size
  - Changes in elastic and strength properties as a function of relative density
- Extend the model to include the enhanced densification due to $pO_2$ cycling
- Test in spreadsheet model and then implement in stack models
- Evaluate structural reliability in realistic geometry
Contact Paste: Sintering (cont’d)

- Model captures densification behavior of LSM10 paste
  - Effect of pO\textsubscript{2} cycling and temperature changed observed in experimental tests is simulated
  - Model computes free densification strains, grain growth, and elastic property changes at different stages of sintering
  - Next implement spreadsheet model into 3D FEA tool for actual IC geometries

Densification from atmospheric cycling

Impacts of pO\textsubscript{2} cycling and temperature on dimensional change of LSM10 paste.

Collaborations

- PNNL modeling staff are currently collaborating with SOFC researchers on several technical issues
  - ASME design document
    - ORNL: E Lara-Curzio, Y Wang
    - ASME: J Powers, R Swayne
  - Contact paste characterization
    - ORNL: E Lara-Curzio, Y Wang
    - PNNL: L Pederson, B McCarthy
  - Interconnect coatings
    - PNNL: Z Yang
  - SECA test cell
    - PNNL: J Stevenson, M Chou
  - Modeling tool support
    - Delphi
  - Seal characterization & modeling
    - U of Cincinnati: R Singh
    - GaTech: H Garmestani
    - PNNL: M Chou
  - Chrome Migration
    - Carnegie Mellon: E Ryan
  - Pressurized EC
    - PNNL: L Pederson
Conclusions & Ongoing Work

Conclusions

- Speed and capabilities of SOFC-MP were improved
- Cathode contact paste stresses were evaluated and a sintering model was developed
- An EC model to simulate pressurized SOFC was developed
- Seal mechanical properties continue to be characterized and modeling was used to evaluate novel sealants

Ongoing Work

- Completion of the SOFC design document
- Release of SOFC-MP v1.1
- Thermal management using coal-based fuels w/ methane and pressurization
- Characterization of contact paste mechanical strengths
- Simulation of contact paste development and cell load paths
- Improved interconnect coating systems
Interactions of Ni/YSZ Anodes with Coal Gas Contaminants

OA Marina, LR Pederson, CA Coyle, EC Thomsen, DJ Edwards, CD Nguyen, GW Coffey

9th Annual SECA Workshop, August 7, 2008, Pittsburgh, PA
Goal: Establish Maximum Acceptable Coal Gas Contaminant Concentrations

Part of a coordinated study involving:

- Randy Gemmen, Kirk Gerdes, NETL
- Gopala Krishnan, SRI International
- Stephen Sofie, MSU
- Jason Trembly, RTI
- PNNL team
Approach

- Thermodynamic assessment of coal gas contaminant - Ni phase equilibria
- Button cell testing of Ni interactions with coal gas contaminants. Parameters addressed included contaminant concentration, temperature, reaction time, fuel utilization, and current density
- Post-test analyses to determine the composition and extent of nickel modification
- Coupon tests in flow-through and flow-by arrangements to determine penetration rate and nature of contaminant/Ni interactions – companion to button cell tests
Phosphorus and arsenic interact strongly with Ni and are nearly completely captured by the anode.

One degradation mode involves loss of electronic percolation due to nickel phosphide and nickel arsenide formation, grain growth, and inducement of micro-fractures within the anode support.

Electrochemical degradation may be very low if an electrical pathway to the active interface is maintained (“shadowing effect” for strongly interacting contaminants).

Nickel conversion to the active interface by P and As results in significant degradation.

Selenium poisoning occurs quickly, similar to but slower than sulfur, and reaches steady state performance.
Phosphorus and Arsenic: Very Strong Interactions with Nickel

- $\text{Ni}_3\text{P}_2$ stable
- $\text{Ni}_3\text{P}$ stable
- Ni-P solid solution stable
  - 0.32 at% at 870°C

- $\text{Ni}_5\text{P}_2$ stable
- Ni-P solid solution (ss) stable
- Maximum solubility = 0.32 at% at 870°C

- $\text{Ni}_5\text{As}_2$ stable
- Ni-As solid solution stable
  - 4.5 at% at 897°C
Schematic of Button Cell Test Stands

- Ni/YSZ anode-supported cells
- Electrolyte supported cells with 30 μm Ni/YSZ anode (from Fuel Cell Materials, NexTech)

Eight button cells installed per box furnace, with individual gas flow controls
Current Contact Method Important in Degradation Studies

Glass Coated Contact

- Fuel Gas
- Glass seal
- Ni mesh
- Screen-printed Ni grid
- Glass coated Pt wire

Single Point Contact

- Fuel Gas
- Ni wire
- Ni mesh
- Glass seal

Pt and Ni wire instability affected some earlier results
Anode after Exposure to 5 ppm of PH₃ in Coal Gas for 790 hours at 700°C
Glass Coated Contacts:
Minimal Effect of PH₃ or AsH₃ on Cell Performance

Contaminants Started at 25.4 Hours

Voltage Loss (V)

i=0.25A/cm² at 800°C

Time (Hours)
Low Degradation Rates at Different Fuel Utilizations* at 700°C with 1 ppm of AsH₃

* Fuel utilizations were adjusted by adding oxygen to the coal gas mix
Single Point Contact Tests with PH$_3$: Electrical Percolation Losses More Visible

![Graph showing cell voltage over time with different contaminant levels and temperatures.](image)

- Contaminants Started at 75 Hours
- $T = 750^\circ C$
- Cell Voltage (V)
- Time (Hours)
- Power bump
- Adjusted el. contacts
- Baseline
- 2 ppm
- 5 ppm
- 10 ppm
Ohmic and electrodic resistances double after 1000 hours of exposure

- New process appears at around 50-100 Hz
Single Point Contact: Ohmic Losses Increase More Rapidly with Exposure than Electrodic Losses

![Graph showing resistance increase in 1000 hr (%) for PH₃ pressures (ppm) at 750°C. The graph compares Ohmic and Electrodic losses.]
Ohmic and electrodic resistances calculated from the impedance spectra obtained at 750°C at a bias current of 0.1A/cm² in coal gas with 1, 2, 5 and 10 ppm of PH₃. Single point contact test configuration.
Extensive Re-crystallization in the Upper Part of the Cell

800°C, 770 hours with 5 ppm PH₃
Anode Current Collector Surface after 357 Hour Test in Coal Gas with 2 ppm of PH$_3$, 1 ppm of AsH$_3$, and 1 ppm of H$_2$S at 800°C

Ni$_3$P - Ni$_5$As$_2$
No Ni-S (by SEM/EDS)

Ni mesh corroded to form Ni$_3$P and Ni$_5$P$_2$
Anode-Supported Cells after 990 Hour Test at 700°C with 1, 2, 5 and 10 ppm of PH₃ in Coal Gas

Ni₃P, Ni₅P₂, Ni₂P

Ni₃P/YSZ

Ni/YSZ

YSZ

P penetration depth per hour (um/h)

100 um

YSZ is here

1 ppm

2 ppm

5 ppm

10 ppm

1 ppm

2 ppm

5 ppm

10 ppm

1000/T (K⁻¹)

0.9

0.95

1

1.05

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Active Interface of an Anode-Supported Cell after 1000 h Test at 700°C with 10 ppm of PH₃

Unreacted interface

Complete conversion of nickel to Ni-P showing extensive coarsening
Elemental Maps of Bulk Ni/YSZ after 1000 hour Test at 700°C with 5 ppm of PH₃

Ni-P agglomerates

Ni/YSZ

ZrLa1

Ni Ka1

Ni/YSZ

P Ka1

Zr Lb1

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Electrolyte-Supported Cell

Anode-Supported Cell

The same configuration for both cell types
Electrolyte Supported Cell
Voltage Losses in Coal Gas with PH₃ at 800°C

Contaminants Started at 0 Hours

- Contaminants at 0.5 ppm PH₃
- Contaminants at 1 ppm PH₃
- Contaminants at 2 ppm PH₃
- Contaminants at 5 ppm PH₃
- Contaminants at 10 ppm PH₃

Graph showing voltage loss over time for different concentrations of PH₃ in coal gas.
Higher degradation rate at higher $\rho$PH$_3$

No clear temperature dependence in this range
Ni/YSZ after 100 Hour Test in Coal Gas at 800°C (Ni – Red, YSZ – Green, Ni-P – Blue)

No contaminants

0.5 ppm PH₃

1 ppm PH₃

2 ppm PH₃

5 ppm PH₃

10 ppm PH₃
Time Dependence for the YSZ Supported Cells after Exposure to 1 ppm of PH₃ at 800°C (Ni-Red, Ni-P – Blue, YSZ – Green)

Moved towards higher order Ni-P phases with increased exposure
Time Dependence for the YSZ Supported Cells after Exposure to 2 ppm of PH$_3$ at 800$^\circ$C (Ni-Red, Ni-P – Blue, YSZ – Green)

At highest exposures, observed mixture of Ni$_2$P and Ni$_5$P$_4$
Anode-Support Coupon Test in Flow Through Configuration Shows Ni Redistribution (no current collector)

Ni is red, Ni-P is magenta, YSZ is green
How Long Does It Take to Consume Nickel?

- Assume 0.5 watts at 0.7 volts

Graph showing the time to complete Ni conversion for anode-supported (550 micron) and electrolyte-supported (10 micron) cells at different phosphine concentrations in coal gas (ppm).
Much Higher Se Concentration Needed to Form Nickel Alteration Phase
Effect of 1 ppm of Hydrogen Sulfide or Hydrogen Selenide on Anode Supported SOFC at 800°C
Phosphorus and arsenic interact strongly with Ni and are nearly completely captured by the anode.

One degradation mode involves loss of electronic percolation due to nickel phosphide and nickel arsenide formation, grain growth, and inducement of micro-fractures within the anode support.

Electrochemical degradation may be very low if an electrical pathway to the active interface is maintained (“shadowing effect” for strongly interacting contaminants).

Nickel conversion to the active interface by P and As results in significant degradation.

Selenium poisoning occurs quickly, similar to but slower than sulfur, and reaches steady state performance.
Acknowledgements

Support for this work is provided by the DOE-NETL’s Solid State Energy Conversion Alliance (SECA) Coal Based Systems Core Research Program - Briggs White, NETL program manager.

Helpful discussions with Briggs White, Wayne Surdoval and other members of the coordinated team are gratefully acknowledged.

J Templeton, J Bonnet, B McCarthy contributed to cell fabrication.

Pacific Northwest National Laboratory is operated for the US Department of Energy by Battelle under Contract AC06 76RLO 1830.
Advanced Interconnect Development at PNNL


Pacific Northwest National Laboratory
Richland, WA 99352

August 6, 2008
9th Annual SECA Workshop
Pittsburgh, PA
Presentation Outline

- Conclusions
- Objectives/Approach
- Background
- Results:
  - Oxidation behavior of AISI 441
  - Performance of Spinel-coated 441
- Future Work
- Conclusions
- Acknowledgements
Conclusions/Accomplishments

- **AISI 441 exhibits promising alloy chemistry**
  - Expensive refining processes not required, so cost is reduced
  - Nb/Ti additions promote desirable Laves phase precipitation, leading to lower electrical resistance (and higher mechanical strength)

- **Limitations identified through oxidation testing:**
  - Poor scale adherence due to lack of rare earth additions
  - As with other FSS, protective coating is required due to inadequate intrinsic oxidation resistance, and Cr volatility

- **Ce-modified MnCo spinel coatings exhibit the benefits of original MnCo coatings**, but also result in improved scale adherence, presumably due to the rare earth (RE) effect (usually achieved through RE additions to base alloy)
Objectives and Approach

► Objectives
- Develop cost-effective, optimized materials and fabrication approaches for intermediate temperature alloy-based SOFC interconnects
- Identify, understand, and mitigate degradation processes in alloy-based interconnects

► Approach
- Materials and process development
  - Collaboration with Allegheny Technologies, Inc. and NETL
  - Emphasis on AISI 441 as alloy substrate
    - Modified alloys also being evaluated
  - Mn-Co spinel coatings for cathode-side protection
- Characterization of candidate materials
  - Oxidation tests (including dual atmospheres – air vs. fuel)
  - ASR tests
  - CTE
  - Alloy, scale, and coatings chemistry via XRD, SEM, EDS, TEM, etc.
Alloy-based Interconnects: Background

Emphasis on “Chromia-forming” Ferritic Stainless Steels, because:

- CTE match
- Conductive, protective oxide scale
- Low cost
- Ease of fabrication

Also: Co-base superalloys

[Diagram showing the alloy system with Fe, Ni, and Cr as axes, showing areas for Fe-Ni-base superalloys, Ni-Fe-base superalloys, and ferritic stainless steels.]

[Note: The diagram includes phases such as BCC, FCC, BCC + FCC, FeBSA, NiBSA, and FeNiBSA, with emphasis on specific areas related to alloy systems and their properties.]
Candidate Interconnect Alloy: AISI 441

- Manufactured via conventional (inexpensive) melt metallurgy
  - No vacuum processing required
- Similar to AISI 430, but additions of Nb and Ti improve high temperature strength and prevent formation of insulating SiO$_2$ layer at alloy/scale interface
- Similar to all other FSS, relatively high oxidation rate at SOFC operating temperatures (and volatility of Cr) indicates need for protective coating

Typical Analysis:

<table>
<thead>
<tr>
<th>Designation</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Nb</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 441</td>
<td>18</td>
<td>0.35</td>
<td>0.30</td>
<td>0.01</td>
<td>0.05</td>
<td>0.34</td>
<td>0.023</td>
<td>0.002</td>
<td>0.22</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>AISI 430</td>
<td>16-18</td>
<td>≤1.0</td>
<td>≤0.12</td>
<td>≤1.0</td>
<td>≤0.04</td>
<td>≤0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crofer 22 APU</td>
<td>23.0</td>
<td>0.4-0.8</td>
<td>0.030</td>
<td>≤0.02</td>
<td>0.02</td>
<td>0.050</td>
<td>≤0.2</td>
<td>0.04-0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sources: Allegheny Technologies, Inc.; Thyssen Krupp
Microstructural Evolution in 441

- Second phase (Laves phase) randomly distributed in the alloy grains
- Intergranular precipitates decorate grain boundaries after oxidation
- No obvious grain growth during oxidation
TEM Analysis of 441

- As received: clean grain boundaries
- After oxidation, Laves phase precipitated along grain boundaries
  - Laves phase enriched in Ti, Nb, and Si

As received: clean grain boundaries

After 300 hrs oxidation in air at 800°C
Oxidation Kinetics of AISI 441

Approximately parabolic growth:

\[ K(800) \sim 5 \times 10^{-14} \text{ g}^2/\text{cm}^4\text{-sec} \]
Issue: Weak Scale Adherence

Oxidized at 800°C in air

After 300 hours

After 900 hours

Note secondary scale growth after 600 hours.
Properties of \((\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4\) Spinel

- High electrical conductivity
  \(~60\text{ S/cm at 800°C}\)
  \[
  \sigma_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} = 10^{3-4} \sigma_{\text{Cr}_2\text{O}_3}
  \]

- Good CTE match to FSS and anode-supported cells
  \[
  CTE_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} = 11.5 \times 10^{-6} \text{ K}^{-1}, 20 - 800°C
  \]

- Chemically compatible with contact pastes, cathodes
- Cr-free composition
- Tested with several FSS (Crofer22APU, 430, Ebrite, 441)

- 6 month thermal cycle test (800°C)
- Negligible Cr transport into coating
- Reduced oxidation rate of alloy
MC Spinel-Coated AISI 441

- **ASR Test:** 1000 hours at 800°C in air.
- Note Fe migration into the spinel protection layers, presumably due to lower Cr (18%), but no Cr transport into coating. Fe migration not observed for Crofer22APU.
- No silica layer formation at alloySCALE interface, as observed with AISI 430.

Probably La overlap rather than Cr
Oxidation Kinetics of AISI 441: Bare and MC Spinel Coated

The graph shows the oxidation kinetics of AISI 441 for bare and MC spinel-coated samples at different temperatures. The x-axis represents time in hours, ranging from 0 to 1400, and the y-axis represents the oxidation rate in units of meters per second. The graph includes data points for temperatures of 800 and 850 degrees Celsius for both bare and MC spinel-coated samples.
Poor adhesion of scale under MC spinel coating

700 h, 850°C ASR measurement
Ce-modified Mn-Co Spinel

**Motivation:**

- Rare earth (RE) additions (e.g., Ce, La) to alloys - well-established means of improving scale adherence
  - Crofer22APU has La addition; AISI 441 has no RE additions
- NETL-Albany: Ce surface treatment leads to improved oxidation resistance, lower ASR
- PNNL: Ce-modified Mn-Co spinel ($\text{Ce}_{0.05}\text{Mn}_{1.475}\text{Co}_{1.475}\text{O}_4$) coatings appear promising for improving scale adherence
  - Simple modification – Ce nitrate included in glycine/nitrate precursor
  - May provide
    - Established benefits of MC spinel coating (improved oxidation resistance, lower ASR, Cr volatility mitigation)
    - Benefits of rare earth effect without need for RE additions to alloy
Oxidation Kinetics of AISI 441: Bare, MC Spinel Coated, and Ce-MC Spinel Coated
Improved Scale Adherence with Ce-MC Coatings

After 1,000 h, 800°C ASR measurement
Improved Scale Adherence with Ce-MC Coatings

After 700 h, 850°C ASR measurement (similar results at 800°C)

Ce-MC coated 441

Ce-MC coating:
$\text{Ce}_{0.05}\text{Mn}_{1.475}\text{Co}_{1.475}\text{O}_4$
Electrical Testing of 441

- **FSS**
- **LSM contact**
- **MC layer**

Graph showing:
- Time vs. some electrical parameter (AR?, mOhm)
- Power breaks indicated
- Data points for different conditions or materials

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No detachment along scale/steel interfaces; Spallation was observed on bare 441 surface (not shown).

Scale growth rates: Bare > MC > Ce-MC

Ce altered interface morphology: smooth scale/metal interface for MC 441, rough interface for Ce-MC 441 (also for bare, possibly due to the La in contact material)
SEM Analysis on 1 year ASR Test

- No Cr-penetration into MC or Ce-MC protection layers, as confirmed by EDS point and area analyses.
- Some Fe transport into the MC or Ce-Mc protection layers.
- EDS analyses found neither Cr nor Fe in LSM contact (apparent increase in Cr profile in contact is due to spectra overlap of Cr and La).
Dual Exposure Testing of Ce-MC Spinel-Coated AISI 441

- Moist air vs. moist hydrogen, 1000 hours, 800°C
- Air only exposure: Effective barrier only to Cr, but not Fe.
- Air side of dual exposure: Inhibited Fe transport may have caused reduced sintering activity of the Ce-MC coating on the airside; no nodule formation; good scale adherence

Airside of the sample that was exposed to air at one side and moisture hydrogen at the other

The sample that was exposed to air at both sides
Conclusions

- **AISI 441 exhibits promising alloy chemistry**
  - Expensive refining processes not required, so cost is reduced
  - Nb/Ti additions promote desirable Laves phase precipitation, leading to lower electrical resistance (and higher mechanical strength)

- **Limitations identified through oxidation testing:**
  - Poor scale adherence due to lack of rare earth additions
  - As with other FSS, protective coating is required due to inadequate intrinsic oxidation resistance, and Cr volatility

- **Ce-modified MnCo spinel coatings exhibit the benefits of original MnCo coatings, but also result in improved scale adherence, presumably due to the rare earth (RE) effect (usually achieved through RE additions to base alloy)**
Future Work

► Evaluate long-term stability and electrical performance of Ce-MC spinel-coated 441 under dual atmosphere (w/ simulated coal gas fuel) and thermal cyclic conditions.

► Optimize RE-modified MC coatings (composition, fabrication procedures) on Fe-Cr-Nb-Ti steels.
  - Composition: La as alternative to Ce, reduction in Co content
  - Fabrication: Optimize heat treatment conditions (reducing, oxidizing) for improved density; Develop automated spray process for larger, shaped parts.

► Investigate oxidation and corrosion at anode-side, in particular in a coal gas environment, and, if required, develop protective solutions for long-term stability.
Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.
- The authors wish to thank Wayne Surdoval, Ayyakkannu Manivannan, Briggs White, and Paul Jablonski at the National Energy Technology Laboratory (NETL) for helpful discussions regarding the initiation and implementation of this study.
- The authors wish to thank Jim Rakowski at ATI Allegheny Ludlum for providing the AISI 441 alloy samples and for helpful discussions.
- Metallographic preparation: Shelley Carlson, Nat Saenz
SECA Stack Test Fixture Development and Implementation


Pacific Northwest National Laboratory
Richland, WA 99352

August 7, 2008
9th Annual SECA Workshop
Pittsburgh, PA
Presentation Outline

- Conclusions
- Background
- Objectives
- Approach
- Test Fixture Design & Assembly
- Implementation: Test Results
- Future Work
- Conclusions
- Acknowledgements
Conclusions/Accomplishments

- A stack test fixture based on 50mm x 50mm cells (40mm x 40mm cathode) has been developed for evaluation/validation of new materials, fabrication processes, and design concepts.

- **Implementation:**
  - Performance of refractory glass seals has been validated.
    - Seals exhibited excellent performance during 25 deep thermal cycles
  - Current emphasis is on evaluation/validation of low-cost interconnect alloys and cathode-side interconnect modifications:
    - AISI 441 ferritic stainless steel
    - Ce-MnCo spinel coatings for exposed interconnect surfaces
    - Aluminization of sealing surfaces

- **Working to improve performance and reproducibility**
  - Minimize “hand-crafted” aspects of assembly; replace with “automated” assembly processes

- **Developing revised fixture design**
  - Consistent with future available thicknesses of AISI 441 (coil purchased from ATI Allegheny Ludlum by SECA program)
  - Multiple cell capability (3 cells or more)

- **Transferring test capability to NETL**
Background

▶ SECA Core Program Testing at Sub-stack Level
  ■ Materials Characterization
    ▪ XRD, SEM, EDS, TEM, XPS, TGA, DSC, PSA, dilatometry, electrical conductivity, single & dual atmosphere oxidation
  ■ Multiple Component Tests
    ▪ Button cell testing
    ▪ ASR testing of interconnect/cathode contact/cathode structures
    ▪ Electrical testing and leak testing of seal/interconnect and cell/seal/interconnect structures

▶ Next Step: Testing under realistic “stack-like” conditions
  ■ Advantage: Higher degree of relevance to SECA Industry Team cells/stacks
  ■ Challenges:
    ▪ Multiple components & phenomena, so results more difficult to interpret
    ▪ Increased complexity of assembly, co-fabrication of seals and electrical contact materials
Objectives

► Develop SOFC stack test fixture for SECA Core Technology Program (CTP)
► Evaluate/validate new materials and fabrication processes under realistic stack conditions
  ■ Larger cell size (≥50mm x ≥50mm)
  ■ Complete stack functionality (cell, cell frame, seals, interconnects, electrical contact materials)
► Share fixture design with other SECA participants
  ■ Easy to assemble and test; Minimal fabrication cost
► Accelerate technology transfer from SECA CTP to SECA Industry Teams
  ■ Bridge the gap between small-scale CTP tests (e.g., button cells) and SECA industry team stacks
Approach

► Design

- Initial fixture design provided by LBNL and NETL
- Design modified by PNNL to incorporate cell-in-frame design concept, both cell-to-frame and perimeter seals, alternative flow path geometries. Iterative design approach – i.e., results from previous tests used to identify design limitations

► Current Implementation

- Parts
  - Cells purchased from H.C. Starck (InDEC)
    - 50 mm x 50 mm ASC3 anode-supported cells; LSM/YSZ cathode; ~$200 each
  - Other components (interconnects, cell frame, seals, contact pastes) fabricated at PNNL
    - AISI 441 stainless steel provided by Allegheny Technologies, Inc.
- Assembly and testing at PNNL
  - Electrochemical performance evaluation via I-V and EIS analysis
  - Post-test analysis via optical microscopy, XRD, SEM, EDS, TEM, XPS, etc
  - Compare stack results with results from tests on individual materials and sub-stack structures, as well as modeled results
Schematic Illustration of Stack Test Fixture

Stack Test Cross-Section (Not to Scale)
Scale Drawing of Counter-Flow Test Fixture
Stack Test Fixture Components

- Anode interconnect plate (SS441)
- Cell sealed in “window frame” (SS441) w/ refractory glass
- Air heat exchanger (Inconel 600)
Implementation of Stack Fixture Tests

- Selected Test Results
  - Seal validation
    - Refractory glass seals tested under thermal cyclic conditions
  - Evaluation of low-cost steel interconnects with protective coatings
    - Simultaneous testing of spinel-coated and aluminized alloy surfaces
SECA CTP Stack Test Fixture: Refractory Glass Seal Evaluation

- Refractory sealing glasses --- Compositional modifications to G18 glass have resulted in:
  - Excellent wetting/sealing behavior to YSZ and interconnect alloys at 950-1000°C
    - Potentially improves electrical conductivity and strength of cathode/interconnect contacts
  - Rapid de-vitrification and stabilization of polycrystalline phases
  - Stable, matching CTE (11.5-12.5 ppm/°C; stable CTE up to 2,000 hours testing)
  - Improved chemical stability at operating temperatures
  - Stable, high electrical resistance in contact with steel interconnect (up to 1,200 hours testing)
SECA CTP Stack Test Fixture: Refractory Glass Seal Evaluation

Cell with refractory glass seal demonstrated stable OCV during 25 deep thermal cycles (RT – 750°C)
SECA CTP Stack Test Fixture: Refractory Glass Seal Evaluation - Post-test Analysis

- Cell-to-frame glass seal remained intact (no dye penetration)
- Refractory glass selected as baseline seal composition for stack fixture testing
Evaluation of Low-Cost Steel Interconnects with Protective Surface Coatings

Interconnect Components:
- **AISI 441 stainless steel**
  - Pros: Inexpensive, matching CTE, easy to fabricate, conductive Cr-based scale, no SiO₂ subscale layer
  - Cons: Oxidation leads to increased electrical resistance, poor scale adherence, Cr volatility, reaction with glass seals
- **Ce-modified MnCo Spinel Coating**
  - Reduces oxidation rate, improves scale adherence, mitigates Cr volatility
- **Aluminization**
  - Mitigates reaction with glass seals
Evaluation of Low-Cost Steel Interconnects with Protective Surface Coatings

- Aluminization of alloy surface
  - Mitigates chromate formation, which degrades strength of seal
Evaluation of Low-Cost Steel Interconnects with Protective Surface Coatings

- Anode plate: 441 Steel
- Cathode plate: 441 Steel w/ Dual Coatings
- 441Frame
- Nickel Mesh
- Cell-to-Frame Seal: Refractory Glass
- Aluminization
- Ce-MC Spinel
- LSM-20 Contact Paste
- Nickel Oxide Contact Paste
Evaluation of Low-Cost Steel Interconnects with Protective Surface Coatings

**Dual Coatings**
- Ce-MnCo spinel application to surfaces exposed to air
- Aluminization of sealing surfaces

**Aluminization**
- Commercial processes also available from vendors, but challenging when dealing with small quantities of parts
- New aluminization process under development at PNNL
Evaluation of Low-Cost Steel Interconnects with Protective Surface Coatings - Results

First test
- Good OCV, but poor electrical performance
- Test was held at 800ºC for 400 hours under OCV conditions
- Post-test structural/chemical analysis performed by SEM/EDS

Second test
- Off to good start, but aborted by building power failure

Third test
- In progress
- Plan to run for 1000 hours, then perform post-test analysis
Aluminized 441/Glass Seal Interface

- Aluminized SS441 frame / glass seal after 404h @ 800°C
- Cr transport from the alloy observed, possibly due to non-uniform aluminized interface
- Uniform coatings have been obtained in previous work with oxidizing treatment only
- May be consequence of double heat treatment required for dual coating of parts
- Optimization of dual coating process in progress

<table>
<thead>
<tr>
<th>point</th>
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<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>35.0</td>
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<tr>
<td>Al</td>
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<td>5.0</td>
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<tr>
<td>Si</td>
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<tr>
<td>Ba</td>
<td>2.9</td>
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</table>
Ce-modified spinel-coated section of SS441 interconnect after 404h @ 800°C
Results similar to substack testing (ASR tests)
Effective blocking of Cr by spinel coating
Changes in alloy availability

- Current design is based on 0.175” and 0.060” thick 441 sheet
  - 0.175” no longer available
- SECA program is acquiring large stock of 441 for use by SECA participants
  - 0.133”, 0.040”, 0.020”, and 0.010” sheet
- Developing new fixture design consistent with available sheet thicknesses
  - Lower mass design – closer replica of real stacks under development
  - Simpler component shapes (less machining, lower fabrication cost)
  - Multi-cell stack capability (3-cell stack tests planned)
Scale Drawing of Revised Design: 3 Cell Stack
Modeling of Flow Distribution in 3-cell Stack

- Similar oxidant and fuel flows through three cells
- Flow distribution summary:

<table>
<thead>
<tr>
<th>Cell</th>
<th>Fuel</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell 3</td>
<td>99.7</td>
<td>99.72</td>
</tr>
<tr>
<td>Cell 2</td>
<td>99.93</td>
<td>99.92</td>
</tr>
<tr>
<td>Cell 1</td>
<td>100.37</td>
<td>100.36</td>
</tr>
</tbody>
</table>

- Small ΔP in manifolds (slots)
- Larger ΔP over cell
- Flow on both anode and cathode sides within +- 0.4% of mean
Future Work

► Design
  ■ Transition to revised, reduced-mass stack fixture
    ● Single cell tests
    ● Multi-cell tests
  ■ Continue to improve performance and reproducibility
    ● Issues related to simultaneous fabrication of stack seals & contact materials
    ● Minimize “hand-crafted” aspects; replace with “automated” processes
  ■ Transfer stack test capability to NETL

► Implementation
  ■ Complete initial evaluation of interconnect materials system: 441 steel with Ce-modified MnCo spinel and alumina coatings
  ■ Continue to evaluate/validate new materials/processes/design concepts. Candidates include:
    ● Contact materials
      ◆ Novel processing approaches (atmospheric cycling)
      ◆ Novel materials (sintering aids, reaction sintering approaches)
      ◆ Examine role of high temperature sealing on contact structure and load distribution (validation of modeling results)
    ● New cathode materials
    ● New interconnect alloys/coatings
    ● Commercial cells
Conclusions/Accomplishments

- A stack test fixture based on 50mm x 50mm cells (40mm x 40mm cathode) has been developed for evaluation/validation of new materials, fabrication processes, and design concepts.

- Implementation:
  - Performance of refractory glass seals has been validated.
    - Seals exhibited excellent performance during 25 deep thermal cycles
  - Current emphasis is on evaluation/validation of low-cost interconnect alloys and cathode-side interconnect modifications:
    - AISI 441 ferritic stainless steel
    - Ce-MnCo spinel coatings for exposed interconnect surfaces
    - Aluminization of sealing surfaces

- Working to improve performance and reproducibility
  - Minimize “hand-crafted” aspects of assembly; replace with “automated” assembly processes

- Developing revised fixture design
  - Consistent with future available thicknesses of AISI 441 (coil purchased from ATI Allegheny Ludlum by SECA program)
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Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.
- The authors wish to thank Wayne Surdoval, Ayyakkannu Manivannan, Briggs White, and Travis Schultz at the National Energy Technology Laboratory (NETL) for helpful discussions regarding the initiation and implementation of this study.
- Initial fixture design provided by LBNL & NETL
- 441 steel provided by Jim Rakowski at Allegheny Technologies, Inc.
- Additional PNNL contributors: Gary Maupin, Jared Templeton, Kerry Meinhardt, Jim Coleman, Shelley Carlson, Nat Saenz
SOFC test fixture development and materials evaluation at PNNL

Y-S Chou, J. W. Stevenson, J-P Choi, C-M Wang, Z.G. Yang, G.G. Xia, K.S. Weil, J.D. Templeton,

Energy Materials Department
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Presented at 10th Annual SECA Workshop, Pittsburgh, July 14-16, 2009
Outline

- Conclusions
- Objectives
- Test Fixture: Materials, Design, and Assembly
- Cell Testing Results and Materials Characterization
- Future Work
- Conclusions
- Acknowledgements
Conclusions/Accomplishments

- Two stack test vehicles based on 50mm x 50mm cells (40mm x 40mm cathode) have been developed for evaluation/validation of new materials, fabrication processes, design concepts.
- Candidate materials have been validated in a single cell testing for ~2300 h:
  1. Refractory sealing glass showed hermeticity, minimal reaction with YSZ and aluminized SS441.
  2. (Mn,Co)-spinel coating was effective in blocking Cr at cathode IC.
  3. Aluminization was able to minimize (Ba,Sr)-chromate formation.
- A novel double-seal concept was developed and demonstrated successfully for 25 deep thermal cycles.
- Developing revised fixture design for multiple cells testing.
- Transferring test capability to NETL.
Objectives

- To develop a SOFC cell/stack test fixture on behalf of Core Technology Program in order to evaluate/validate new materials and fabrication processes under realistic stack conditions.

- To bridge the gap between small-scale tests (e.g., button cells) and SECA industry team stacks.

- To share fixture designs with other SECA participants.
Test fixture: 1st generation design (co-flow or counter-flow)

1. Cell (Stark ASC-3) anode-supported YSZ cell 2”x2” with LSM cathode
2. LSM-20 (Praxair) and NiO (Baker) contact paste
3. Refractory glass seal for PEN/WF seal (950°C/2h)
4. Perimeter seal in double seal geometry
5. (Mn,Co)-spinel coating for cathode IC plate
6. Aluminization for sealing area
7. SS441 for IC (0.170”) and window frame (0.064”) plates
Seal system in cell test

Inconel air heat-exchanger

SS441 cathode IC plate

PEN

WF

SS441 anode IC plate

Ni-mesh

glass

hybrid mica

Inconel fuel heat-exchanger

H₂ in

H₂ out

air
Double seal (mica + glass) concept

1. Glass will creep/flow under stress and lead to large dimensional change.
2. Hybrid mica was proven stable over 28366 hr @ 800°C.
3. The creep/flow of glass may transfer compressive load to fracture PEN/WF seal.
Cell #16: refractory glass seal showed good thermal cycle stability

25 deep cycles with constant OCV of ~1.10 V @ 800°C with, 97%H₂+3%H₂O vs. air RT to 750°C in 3 hr, 750°C/3h, furnace cool to ~RT in 18 hr
Cell test #24: candidate materials validation at constant voltage

- 1st generation V3 design with (Mn,Co)-spinel and aluminization using thick SS441 plates (0.170” and 0.064”)
- Standard LSM and NiO/Ni mesh for contact
- Double seal concept of glass and hybrid mica for perimeter seal

![Graph showing cell test #24 results]

- OCV = 1.0V @ 2325hr
- Large data fluctuation
- Inconel tubing leak

Cell #24: 97% H2, 3% H2O vs air, aluminization and Ce-spinel (two steps process for aluminization)

Cool down to
Add water
Short
Grounding
Post-test analysis of cell #24, optical

PEN plate fractured during dissembling, indicating strong bonding of Ni contact paste. Glass seal remained whitish indicating good seal and minimum reaction with Interconnect due to aluminization.
Cell #24: sealing glass characterization at glass/YSZ interface

Minimal reaction of refractory glass with YSZ after ~2300hr @800°C near fuel side
Needle formation along interface (BaZrO₃, CTE ~10)

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<td>Ni</td>
<td>3.38</td>
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</table>
Cell #24: glass/aluminized SS441 interface of fuel side

No (Ba,Sr)-chromate formation at fuel side; however, alumina appeared to be leached into glass matrix.
Cell #24: glass/aluminized SS441 interface of air side
Post-test analysis of cell #24, cathode top surface

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<tr>
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<th>Weight% Sigma</th>
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Cell #24: characterization of Cr near YSZ electrolyte

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<td>La L</td>
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<tr>
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Cell #24: characterization of Cr near (Mn,Co)-spinel coated SS441

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<td>26.02</td>
<td>27.07</td>
<td>27.32</td>
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Cell #24: LSM grain characterization
Cell #24: LSM grain boundary characterization

LSM grain boundary

200 nm

Pacific Northwest
NATIONAL LABORATORY
Cell #24: LSM/YSZ grain boundary
Cell #24: Ni characterization

1. Cell #24 tested at 800°C for 2325 hr @0.7V with 97%H₂,3%H₂O vs. air
2. Previous SS441 oxidation characterization focused on non-welded section
Cell #24: Ni characterization

<table>
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</table>
Cell #24: Ni/SS441 interface characterization

800°C/~2325h

Ni wire spot-welded

SS441
Test fixture: 2\textsuperscript{nd} generation design

- anode IC plate
- cathode IC plate
- WF plate
- double seal
Cell #33: 2nd G design seal test

No cross-bubbling is consistent with insensitivity of OCV with varying air flow rate, indicating hermetic PEN/WF glass seal.
2nd G design for 3-cells stack test
Two stack test vehicles based on 50mm x 50mm cells (40mm x 40mm cathode) have been developed for evaluation/validation of new materials, fabrication processes, design concepts.

Candidate materials have been validated in a single cell testing for ~2300 h:

1. Refractory sealing glass showed hermeticity, minimal reaction with YSZ and aluminized SS441.
2. (Mn,Co)-spinel coating was effective in blocking Cr at cathode IC.
3. Aluminization was able to minimize (Ba,Sr)-chromate formation.

A novel double-seal concept was developed and demonstrated successfully for 25 deep thermal cycles.

Developing revised fixture design for multiple cells testing.

Transferring test capability to NETL.
Future work

- Candidate materials evaluation in a single cell test using 2nd G design with new SS441 thin stock materials and high moisture content fuel.
- Implement cathode reinforcement in single cell testing.
- Modify current 2nd G designs for short 3-cells stack evaluations.
- Collaboration with ORNL in evaluation of compliant sealing glass with current design.
- Transfer test fixture to NETL.
- Validating other novel materials and processing (e.g., infiltrated cathode) with current test fixture.
Acknowledgements

The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.

The authors wish to thank Wayne Surdoval, Briggs White, and Travis Schultz at the National Energy Technology Laboratory (NETL) for helpful discussions regarding the initiation and implementation of this study.

Initial fixture design provided by LBNL & NETL.

441 steel provided by Jim Rakowski at Allegheny Technologies, Inc.

Additional PNNL contributors: Gary Maupin, Jared Templeton, Kerry Meinhardt, Jim Coleman, Shelley Carlson, Nat Saenz.
Modeling Tools for Solid Oxide Fuel Cell Analysis

Moe A Khaleel
BJ Koeppel, W Liu, K Lai, KP Recknagle, E Ryan, EV Stephens, X Sun
Pacific Northwest National Laboratory
Richland, WA 99352

Wayne Surdoval, Travis Shultz, Briggs White
National Energy Technology Laboratory
Morgantown, WV 26508

10th Annual SECA Workshop
Pittsburgh, PA
July 14-16, 2009
Modeling Project Overview

- Motivation
- Objectives & Approach
- Project Accomplishments
- Collaborations
- Overview of Modeling Tools
- Conclusions & Ongoing Work
Motivation

The SOFC is a complex system:
- Multiple physical phenomena including fluid flow, electrochemistry, electric fields, thermal field, mechanical deformations, materials compatibility
- Physical phenomena are tightly coupled (i.e. not independent)
- High operating temperature range

SOFC testing is very expensive:
- Characterization of material properties, stability, and performance required
- Stack fabrication, assembly, monitoring, and testing are time intensive
- Only a minimal number of experimental tests can be done to validate long term technical performance targets (e.g. 10,000 hr)

Modeling can be used for numerical design experiments:
- Can simulate the multiple physical phenomena
- Can be used repetitively to quickly evaluate the effects of design changes or explore the viable design space
- Can be used in conjunction with testing to optimize performance
- Can investigate long term behaviors
Objectives & Approach

Objectives

- Develop integrated modeling tools to:
  - Evaluate the tightly coupled multi-physical phenomena in SOFCs
  - Aid SOFC manufacturers with materials development
  - Allow SOFC manufacturers to numerically test changes in stack design to meet DOE technical targets
  - Support industry teams use of modeling for SOFC development
  - Provide technical basis for SOFC stack design
  - Disseminate/transfer modeling tools to SECA industry teams and CTP members

Approach

- Multiphysics-based analysis tools coupled with experimental validation:
  - SOFC-MP: A multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks
- Targeted modeling tools for specific cell design challenges:
  - Reliable sealing
  - Durable interfaces
  - Cathode contact paste durability
  - Pressurized operation for large stacks
  - Secondary reactions
- Collaboration with NETL, ORNL, and ASME to establish a stack design approach
Project Accomplishments

- Continued to promote and support the use of SOFC-MP and Mentat-FC software packages with industry teams and CTP university teams
- Enhanced calculation speed and efficiency of SOFC-MP and porting to multiple platforms
- Developed a stack calculator (2D SOFC-MP) that quickly solves the temperature distribution and is suitable for incorporation into a system level model.
- Completed first-of-a-kind design guide for SOFCs
- Implemented time dependent constitutive model for glass seal materials in stack simulations.
- Developed a modeling capability to evaluate densification and strength of cathode contact materials, load path, and residual stresses due to stack assembly processes.
- Investigated the effect of oxide growth and metallic IC surface quality on interfacial strength of oxide scale and substrate.
- Developed a model to include creep of SOFC materials and to examine the effect on stress distribution with the stack components.
- Added elevated pressure capability to the EC and reforming models and examined effects on performance of large stacks.
Collaborations

PNNL modeling staff are currently collaborating with SOFC researchers on several technical issues

- **ASME design document**
  - ORNL: E Lara-Curzio, Y Wang, A Shyam
  - ASME: J Powers, R Swayne

- **Contact paste characterization**
  - ORNL: E Lara-Curzio, Y Wang
  - NDSU: L Pederson

- **Interconnect coatings**
  - PNNL: J Stevenson

- **SECA test cell**
  - PNNL: J Stevenson, M Chou

- **Modeling tool support**
  - Delphi
  - Siemens
  - FCE
  - UCI: J Brower

- **Seal characterization & modeling**
  - PNNL: M Chou, J Stevenson
  - ORNL: E Lara-Curzio
  - GaTech: H Garmestani

- **Secondary reactions**
  - Carnegie Mellon: E Ryan
  - PNNL: O Marina
  - NDSU: L Pederson
SOFC-MP: Capabilities and Features

- SOFC-MP Capabilities
  - 3D coupled flow, EC, and thermal solutions
  - Reduced order models for computational efficiency
  - Contact of incompatible meshes
  - Single or multi-cell models
  - Generic fuel and oxidants
  - Operation at assigned voltage, current, or fuel utilization
  - Thermal and electrochemical results output for visualization

- Recent Improvements
  - 2D version for symmetric stacks adapted from 3D SOFC-MP
  - Slice model computes results along stack centerline
    - Co/counter-flow only
    - Can handle many cells
    - Faster for parametric studies of large stacks
  - Computations
    - Current distribution
    - Voltage distribution
    - Thermal distribution
    - Species distribution
    - Heat losses
2D SOFC-MP- Stack Model Description

- Geometric features
  - Co/Counter flow
  - Number of cells
  - Cell length/width
  - Thicknesses
  - Top/bottom plates
  - External insulation

- Thermal-EC properties
  - I-V curve parameters
  - Conduction, convection, and radiation parameters

- Assumption
  - Distributions are uniform in the lateral direction
Thermal model accounts for the coupled heat transfer modes of the fluid domains, solid components, and insulating enclosure.

Assumptions:
- Temperatures are uniform in the lateral direction.
- Currently, no explicit rib conduction link.
2D SOFC-MP- Example Results

- Example: counter-flow, 10 cm long cell, 30 cells, adiabatic
- Operation: 428 mA/cm², 0.8 V, 65% UF, 15% UA

- 50% OCR Fuel: 0.324 H₂, 0.333 H₂O, 0.049 CO, 0.061 CO₂, 0.110 CH₄, 0.124 N₂, 1 atm
- Air 0.21 O₂, 0.79 N₂, 1 atm

![Current Density Graph]

![Fuel Mole Fraction Graph]
2D SOFC-MP- Example Results

Results

- Cell min/average/max 667/742/802°C
- Fuel in/out: 650/668°C
- Air in/out: 650/753°C

In summary, model is useful for more quickly characterizing large stacks
Modeling the Effect of Pressurization on Electrochemistry and Methane Reforming

Background
- Pressurized operation increases electrochemical efficiency and thus decreases the net heat load
- On-cell steam-methane reforming is used effectively to decrease the heat load and is also affected by pressure

Objectives
- Extend the SECA modeling capabilities to include the pressurization effects on the SOFC electrochemistry and on-cell steam-methane reforming performance
- Incorporate the updated models into stack level tools to enable prediction of thermal and electrical performance of stacks operating at elevated pressure

Approach
- Examine and model the coupled effects of pressurization on the SOFC electrochemistry, fuel gas composition, and reforming rates
- Validate model by parts (no public data for pressurized reforming operation of SOFC)
- Exercise the extended models on an example stack model to examine expected effects on thermal and electrical performance
Effect of Pressure on Electrochemistry and Steam-Methane Reforming Rate

- Advanced SECA Electrochemical model considers activation polarization of both electrodes as described by the Butler-Volmer equation, which depends on the exchange current density ($j_o$)
  - PNNL tests showed: $j_o = j_o(PO_2^{0.5})$ for cathode
  - Others agree and find $j_o = j_o(PO_2^{0.133})$ for the anode

$$ j_o = \beta \exp\left(\frac{-E_{act,e}}{RT}\right)P_{O_2}e^{\gamma} $$

$$ \eta_{act,e} = \frac{RT}{aF} \sinh^{-1}\left(\frac{j}{2j_o}\right) $$

- The recently developed reforming rate expression considers effects of pressure on forward and reverse reaction, and maintains consistency with the literature, being 1st order in methane pressure, and with previous validated PNNL model

$$ R_r = C_K \left(2.09 e + 9\right) \exp\left(\frac{-E_{act,e}}{RT}\right) P_{CH_4} P_{H_2O} - (1.54 e - 4) P_{CO} P_{H_2}^3 $$

$$ C_K = (4.8 e - 7) \exp\left(-1.45 e 4 \frac{RT}{RT}\right) $$

Activation Polarization

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<th>Beta</th>
<th>Eact</th>
<th>Gamma</th>
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<tr>
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<td>1.10e+05</td>
<td>0.133</td>
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</table>

Effective $j_o$ and Eta:

| Eta(fuel) > | 3.3276 | 0.008657 |
| Eta(air) >  | 0.3264 | 0.030660 | 0.048207 | 0.133 |

Equilibrium CH$_4$ concentrations

$$ CH_4 + H_2O \rightleftharpoons 3H_2 + CO $$

$ CH_4$
Effect of Pressurization on Performance: Simulations of 20x20 cm Cross-Flow Stack

- Reforming rate near fuel inflow increased with pressure to a maximum at 7.5 atmospheres limited by available CH$_4$
  - Low fuel utilization would support further rate increase
  - CH$_4$ concentration mirrored the reforming rate being decreased when the local rate was high
- Reforming rates varied downstream, as effected by the electrochemistry, depending on concentration and temperature
- Maximum temperature and ΔT decreased for operating pressures above 2.5 atmospheres
- Electrical performance increased steadily with increased operating pressure
Modeling of Contact Paste and Load Path

Technical Drivers

- How does the interconnect geometry and contact paste layer affect load path and stresses in the stack?
- How does in-stack densification affect the load path and stresses in the stack?
- What are the mechanical properties of the contact paste?
- How much in-stack densification of the contact paste can be achieved to increase its strength?

Technical Approach

- Stack simulations to evaluate seal loads and stresses due to contact layer and interconnect features
- Stack simulations with densification strains for the contact paste layer
- Experimental testing at PNNL/ORNL and literature
- Combined materials model development and modeling effort
1. Stack Load Path
Concept of Seal Load Reduction

Previously, the potential for the cathode contact bond to beneficially reduce edge seal forces by I.C. load transfer was shown.

No mechanical support from interconnects

With mechanical support from interconnects
1. Stack Load Path
Results: Effect of IC Thickness/Creep

Thicker interconnects with good cathode contact bonding were demonstrated to beneficially decrease the stresses in the perimeter glass-ceramic seal.

- Seal interface shear stresses less than experimental strengths, but localized seal and interface normal stresses predicted to be too large.
- Creep deformations of IC’s also caused seal stress increase.

PEN seal stresses decrease with IC thickness

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<th>$s_{VM}$</th>
<th>$s_{11}$</th>
<th>$s_{22}$</th>
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<th>$s_{12}$</th>
<th>$s_{23}$</th>
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PEN seal interface stresses decrease with IC thickness

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<td>H=1.5</td>
<td>326</td>
<td>294</td>
<td>240</td>
<td>368</td>
</tr>
<tr>
<td>R (%)</td>
<td>9.2</td>
<td>7.2</td>
<td>13.3</td>
<td>6.0</td>
</tr>
</tbody>
</table>
2. Cathode Contact Paste Modeling
Impacts of Densification on SOFC

- Densification is necessary to improve the mechanical properties of contact pastes
  - Higher density provides a higher elastic modulus
  - Higher density provides a higher strength and fracture toughness

- Densification in the cell causes volumetric changes that may be important for good contact
  - In-plane constraint causes higher out-of-plane strains
  - Glass-ceramic seals also experience volumetric changes due to devitrification
  - Will the contact paste/seals form correctly for strong bonds?

- Continuum constitutive model implemented for FEA evaluations

\[
\sigma_{ij} = \frac{\sigma(W)}{W} \left[ \varphi \dot{\varepsilon}_{ij} + \left( \Psi - \frac{1}{3} \varphi \right) \dot{\delta}_{ij} \right] + P_L \delta_{ij}
\]
2. Cathode Contact Paste Modeling Results: Paste Densification

- Greatest volumetric shrinkage in the out-of-plane direction
  - Strains ~50X greater than in-plane directions due to lateral constraint of the cathode/IC rib
  - Same behavior as during electrolyte formation during co-firing
- Higher preload through the center cause enhanced sintering leading to relative density increase to 0.618
- The reduced sintering on the corners causes less densification to 0.604
- The corner region actually experiences tensile stresses during heat treatment that reverses the densification

*Preload distribution during paste formation determines final properties*
2. Cathode Contact Paste Modeling Results: Loads and Stresses

- Models were evaluated with and without consideration of the densification strains in the contact paste layer.
- With inclusion of densification strains:
  - Contact paste stresses increased slightly, but the maximum value was still less than the experimental strength (~1-14 MPa).
  - For the seal, in-plane shear loads decreased and out-of-plane normal loads were more compressive (to beneficially hinder delamination).
  - For the seal, in-plane peak stresses were not affected significantly while out-of-plane stresses were beneficially lower at operating temperature but unchanged at shutdown.
  - Principal stresses in the anode/cathode/electrolyte layers were not significantly impacted by the contact paste densification at operating temperature or shutdown.
3. Contact Paste Property Characterization

- Strength testing (PNNL, ORNL)
  - 1-14 MPa for spinel coated Crofer substrate/LSM-10
  - 2-8 MPa for Ce-spinel coated 441SS substrate/LSM-10
  - Average energy release rate of 1.47 Jm\(^{-2}\) for spinel coated Crofer substrate/LSM-10

- Material challenges for inks and processing
  - Must ensure ink is calcined and attrition milled for good sintering
  - Must be cognizant of binder burn out rates to prevent void formation

- Currently, fabrication of 441SS specimens with the updated Ce-spinel coating is in progress
  - PNNL: Evaluate high versus low temp interfacial tensile specimens and compare to literature observations
  - ORNL: Evaluate the effect of porosity and thickness on interfacial fracture toughness. Evaluate thermal cycling and thermal aging.
Lifetime Quantification of Coated Metallic Interconnects

Current activities:

- Quantifying adhesion strength between oxide and substrate for shot peened specimens
  - Bare shot peened 441 SS specimens are being oxidized in air at 850°C for 600, 900, and 1200 hours
- Quantifying effects of shot peening on substrate surface:
  - Texture
  - Chemistry on grain boundary
- Quantifying delamination driving force with a shot peened surface
- Preparing Ce-doped spinel coated shot peened specimens

Future activities:

- Quantify interfacial strength of SS441/oxide for shot peened samples:
  - Surface finish
  - Residual stress
  - Surface chemistry/Grain boundary modification
- Quantify interfacial strength of Ce doped MC spinel/oxide for coated SS441 samples
- Life prediction for coated SS441
- Integrate ORNL measured growth stress in IC life prediction
- Optimization of coating thickness for SS441
Accomplishment: Quantified Effects of Batch and Surface Quality on Oxide Adhesion upon Cooling

2007: First batch (left: as received, right: polished)

2008: Second batch (left: as received, right: polished)

- Different batches of as-received materials have different level of spallation tendency upon removal from furnace
  - Different batches of as-received materials have different oxide adhesion strength

- Polished surfaces have less spallation for both batches:
  - Surface quality influences adhesion strength

- Further work in quantifying IC life should consider:
  - Substrate thickness
  - Substrate chemistry composition/thermal mechanical processing parameters
  - Substrate surface quality

<table>
<thead>
<tr>
<th></th>
<th>First Batch</th>
<th>Second Batch</th>
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<tbody>
<tr>
<td>Surface Condition</td>
<td>As-received</td>
<td>Polished</td>
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<td>Roughness</td>
<td>0.7</td>
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<tr>
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<td>0.02</td>
</tr>
<tr>
<td>Total Number of Specimens</td>
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<td>4</td>
</tr>
<tr>
<td>Number that Spalled</td>
<td>3</td>
<td>0</td>
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Accomplishment: Examined Effects of Shot Peening on Oxide Adhesion upon Cooling for SS441

Surface roughness measurements of shot-peened samples

<table>
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<tr>
<th>Profile</th>
<th>Ra (µm)</th>
<th>Rq (µm)</th>
<th>Rz (µm)</th>
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<tr>
<td>1</td>
<td>2.79</td>
<td>3.49</td>
<td>24.23</td>
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<td>2</td>
<td>2.95</td>
<td>3.67</td>
<td>21.03</td>
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<td>3</td>
<td>3.00</td>
<td>3.80</td>
<td>24.88</td>
</tr>
<tr>
<td>Mean</td>
<td>2.91</td>
<td>3.65</td>
<td>23.38</td>
</tr>
<tr>
<td>Std Dev</td>
<td>0.11</td>
<td>0.16</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Surface modification through mechanical shot peening *dramatically* reduces the tendency for oxide scale spallation during cooling:

- Surface modification through cold work/mechanical work
- Higher surface roughness  
  - 10 times rougher than a polished surface
- Surface residual stress
- Removal of edge spallation:
  - Reduced free-standing length of oxide layer
  - Increased critical buckling load
  - Decreased cooling induced interfacial shear stress
Conclusions & Ongoing Work

Conclusions

► Speed and capabilities of SOFC-MP were improved
► Cathode contact paste stresses were evaluated and a sintering model was developed
► An EC model to simulate pressurized SOFC was developed
► Seal mechanical properties continue to be characterized and modeling was used to evaluate novel sealants
► SOFC design document is completed

Ongoing Work

► Release of the SOFC design document
► Release of 2D SOFC-MP
► Develop a modeling framework to examine cell electrochemistry and secondary reactions
► Characterization of contact paste mechanical strengths
► Simulation of contact paste development and cell load paths in SECA test cell geometry
► Develop modeling capabilities and supporting experiments to evaluate feasibility of advanced sealing concepts
Ni/YSZ Anode Interactions with Antimony, Arsenic, Chlorine, Phosphorus, Selenium, and Sulfur in Coal Gas

OA Marina, LR Pederson, CA Coyle, EC Thomsen, DJ Edwards, GW Coffey, CN Cramer, BW Arey, YS Chou

10th Annual SECA Workshop, Pittsburgh
July 14-16, 2009
Objective: Establish Maximum Acceptable Coal Gas Contaminant Concentrations

- **Button cell testing:**
  - Anode-supported cells – typical of architectures used by SECA industrial SOFC development teams
  - Electrolyte-supported cells – more rapid response to coal gas contaminants
  - Test parameters include contaminant concentration, temperature, reaction time, fuel utilization, and current density

- **Coupon tests in flow-through and flow-by arrangements**
  - To determine penetration rate and nature of contaminant/Ni interactions

- **Post-test analyses by SEM/EDS, EBSD, TEM, FIB-SEM, AES, XPS, Tof-SIMS**

- **Thermochemical modeling of Ni/contaminant interactions in coal gas**
Schematic of Button Cell Test Stands

- Ni/YSZ anode-supported cells
- Electrolyte supported cells (NexTech Materials, Inc) with 30 μm Ni/YSZ anode
Selenium and Sulfur – degradation processes affected by local conditions at the active anode/electrolyte interface

Hydrogen Chloride – minor reversible degradation, without formation of new solid phases

Arsenic – strong interactions with nickel, resulting in solid phase formation and structural rearrangement

Phosphorus – also strong interactions with nickel, both solid phase formation and phosphorus surface diffusion to the interface

Antimony – rapid surface adsorption followed by solid phase formation
Three Levels of Ni-Se Interactions

Anode-supported cells
800°C; 0.25 A/cm²

- 0.5 ppm Se
- 1 ppm Se
- 2 ppm Se
- 0.5 ppm S
- 1 ppm S
- 2 ppm S
- Se off
- S off

1st level: relatively rapid but modest decrease in performance to a new steady state, very similar to effects of sulfur but slower kinetics and less reversible
Ni-Se Interactions: Effect of Overpotential

2nd level: at higher polarization losses, oscillatory behavior observed in constant current mode, where cell performance falls rapidly and then regains activity. Oscillations cease if current density is decreased.
More Degradation at Lower Temperature, Higher Current Density, higher H₂Se Concentration

3rd level: at even higher polarization losses, irreversible cell failure occurs
Microstructural Changes at the Interface after Exposure to $\text{H}_2\text{Se}$

Ni/YSZ – YSZ interface after 160 hour exposure to 1 ppm of $\text{H}_2\text{S}$ in coal gas at 700°C

Ni/YSZ – YSZ interface after 160 hour exposure to 1 ppm of $\text{H}_2\text{Se}$ in coal gas at 700°C
Nickel Selenide Observed at the Anode/Electrolyte Interface: 650°C, 0.5 ppm H$_2$Se
Comparison of Experimental Phase Observations to Calculated Phase Boundary for Ni-Se System in Coal Gas

Second phase is easier formed at the active interface (with a current load) than anywhere else in the cell.
Antimony: Two Levels of Degradation

1st level: rapid modest decrease in performance to a new steady state, similar to effects of S and Se
Antimony Strongly Interacts with Nickel

- 2nd level: second phase formation, loss of electrical percolation in the anode support
Antimony Strongly Reacts with Nickel to Form new $\text{Ni}_x\text{Sb}_y$ Solid Phases

Anode-supported cell after test with 1 ppm Sb at 800°C for 600 hours
Electrolyte-Supported Cell after Test with 1 ppm Sb at 800°C for 440 hours
Strong Antimony Interactions with Nickel Results in Non-Uniform Uptake

1 ppm Sb is captured at the gas inlet forming Ni-Sb secondary phases; 800°C, 100 hours
Nickel-Chlorine Interactions

- Small cell performance degradation due to HCl exposure, primarily due to increases in electrodic resistance; reversible
- Solid nickel chloride phase formation should not occur in coal gas at realistic HCl concentrations
No Changes in Anode Microstructure after Testing in Coal Gas with HCl

Control cell with no HCl, 800°C

800°C, 450 hrs, 50 ppm HCl
HCl Removes Impurities in YSZ Electrolyte; Grain Boundaries Likely Most Affected

Visible decreases in ohmic resistance (as determined by EIS) at low temperatures, 700°C or below

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Al</th>
<th>Mn</th>
<th>Y</th>
<th>Zr</th>
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<tr>
<td>GB #1-1</td>
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<td>2.74</td>
<td>12.12</td>
<td>70.82</td>
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<td>GB #1-2</td>
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<tr>
<td>YSZ Matrix #2</td>
<td>0.00</td>
<td>0.00</td>
<td>10.27</td>
<td>75.92</td>
</tr>
</tbody>
</table>

STEM analysis of YSZ electrolyte
Nickel-Arsenic Interactions

- Forms bulk nickel arsenide phases at arsenic concentrations below 1 ppb in coal gas
- For anode-supported cells, cell failure occurs well before arsenic reaches the active anode/electrolyte; failure is attributed to loss of electrical percolation in the anode support
- For electrolyte-supported cells with a relatively thin anode, poisoning of the active interface was observed
Abrupt cell failure for anode-supported cells in coal gas with arsenic

Cell failure occurs well before any evidence of arsenic reaching the active anode/electrolyte interface

Coyle, Marina, Thomsen, Edwards, Coffey, Cramer, Pederson, *J. Power Sources*, 193 (2009) 730
Impedance Spectra Reveal no Electrochemical Degradation Prior to Complete Failure
Calculated and Observed Phase Boundaries in the Ni-As System in Coal Gas

Experimental observations consistent with thermochemical modeling

Coyle, Marina, Thomsen, Edwards, Coffey, Cramer, Pederson, *J. Power Sources*, 193 (2009) 730
Progressively greater Ni reaction with time, arsenic concentration

480 hour exposure to coal gas with AsH₃ at 800°C.
Reaction progression for electrolyte-supported cells following 50 h at 700°C

Red: Ni  Light Green: YSZ  Dark Green: Ni(As) solid solution
Blue: Ni₅As₂  Magenta: Ni₁₁As₈
Morphology of Ni/YSZ anode following reaction with As in coal gas
Ni/YSZ Coupon Exposed to Coal Gas with As in Flow-by Arrangement: As Captured within Short Distance of Fuel Gas Inlet

0.5 ppm AsH\textsubscript{3}
500 hours
700\degree C
Time to Failure Linearly Related to As Concentration for Electrolyte-Supported Cells

Square root dependence for anode-supported cells is attributed to diffusional processes (coalescence of grains, which disrupt electrical connectivity). At long times and low concentrations, expect both anode and electrolyte-supported cells to show log log slope of 1, where degradation is limited by rate of As delivery.

Coyle, Marina, Thomsen, Edwards, Coffey, Cramer, Pederson, *J. Power Sources*, 193 (2009) 730
Nickel-Phosphorus Interactions

- Like arsenic, nickel reacts strongly to form bulk nickel phosphides at concentrations less than ~1 ppb in coal gas.
- For anode-supported cells, loss of electrical percolation in the anode support was the principal mode of failure; coalescence of nickel phosphide crystals and the appearance of microcracks in the zirconia support contributed.
- For electrolyte-supported cells, migration of phosphorus to the active interface led to poisoning.
Anode-Supported Cell Tests in Coal Gas with Phosphorus: Degradation Onset More Gradual Than with Arsenic

Marina, Coyle, Thomsen et al, submitted to SSI
Impedance Spectra Show Increases in both Ohmic and Electrodic Contributions to Cell Resistance

- New process appears at around 50-100 Hz
- Ohmic and electrodic resistances double after 1000 hours of exposure
SEM Analysis of Anode-Supported Cells after 1000 hour Tests at 700°C with PH₃ in Coal Gas

NiₓPᵧ

Ni/YSZ

Electrolyte

1 ppm  2 ppm  5 ppm  10 ppm

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

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100 μm

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100 μm

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Electrolyte

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Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

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Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ

Ni - YSZ

100 μm

1 ppm  2 ppm  5 ppm  10 ppm

Electrolyte

Ni/YSZ

Ni/YSZ
Electrolyte Supported Cells in Coal Gas with PH₃ at 700°C

The graphs show the change in cell resistance over time for different concentrations of PH₃. The x-axis represents time in hours, ranging from -20 to 120, and the y-axis represents the change in cell resistance in Ohm cm², ranging from 0 to 14.

The left graph indicates the baseline and the changes at 0.5 ppm, 1 ppm, 2 ppm, 5 ppm, and 10 ppm of PH₃. The right graph demonstrates similar changes in resistance for ohmic and electrodic mechanisms at concentrations of 1 ppm, 2 ppm, 5 ppm, and 10 ppm.

The graphs highlight the impact of PH₃ concentration on cell resistance, with higher concentrations leading to more significant resistance changes over time.

Source: Pacific Northwest National Laboratory

Proudly Operated by Battelle Since 1965
Time Dependence for Electrolyte-Supported Cells after Exposure to 2 ppm PH$_3$ at 800°C (Ni-red, Ni-P – blue, YSZ – green)
Effect of Phosphorus on SOFC Anode

Coalesced Ni$_x$P$_y$

Nickel in Ni/YSZ support converted to Ni$_x$P$_y$

Diffusion of P to active interface

Electrolyte
Ni/YSZ Coupon after 500 Hour Exposure to 0.5 ppm PH₃ and 0.5 ppm AsH₃ at 800°C
Phosphorus and Antimony
Strongly react with Ni to form a series of Ni-P or Ni-Sb solid phases. Performance losses due to surface adsorption at the active interface and to loss of electrical percolation in the anode support.

Arsenic:
Strongly reacts with Ni to form a series of nickel arsenide solid phases. Performance losses primarily due to loss of electrical percolation in the anode support.

Sulfur:
Reversible performance degradation due to surface adsorption at the active interface. No solid phase formation with nickel at expected concentrations.

Selenium:
Partially reversible performance degradation due to surface adsorption at the active interface at low overpotentials. Cell failure because of nickel selenide formation at high overpotentials and/or high fuel utilizations is likely.

Chlorine:
Minimal reversible degradation.
Support for this work is provided by the US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory through the SECA Program.

We would like to acknowledge NETL management team for stimulating and helpful discussions.

Pacific Northwest National Laboratory is operated for the US Department of Energy by Battelle.
Advanced Interconnect Development at PNNL


Pacific Northwest National Laboratory
Richland, WA 99352

July 15, 2009
10th Annual SECA Workshop
Pittsburgh, PA
Presentation Outline

- Objectives/Approach
- Background
  - AISI 441
  - Spinel coatings for steel interconnects
- Results:
  - Performance of MnCo spinel-coated 441
  - Optimization of MnCo spinel coatings
  - Alternative coating compositions
- Conclusions
- Future Work
- Acknowledgements
Objectives and Approach

► Objectives
  ■ Develop cost-effective, optimized materials and fabrication approaches for intermediate temperature alloy-based SOFC interconnects
  ■ Identify, understand, and mitigate degradation processes in alloy-based interconnects

► Approach
  ■ Materials and process development
    ◆ Collaboration with ATI Allegheny Ludlum and NETL
    ◆ Emphasis on AISI 441 as alloy substrate
      ◆ Modified alloys also being evaluated
    ◆ Mn-Co spinel and other coatings for cathode-side protection
  ■ Synthesis of coating materials, Fabrication of coatings
  ■ Characterization of candidate materials
    ◆ Oxidation tests (including dual atmospheres – air vs. fuel)
    ◆ Area-specific resistance (ASR) tests
    ◆ CTE
    ◆ Alloy, scale, and coatings chemistry via XRD, SEM, EDS, TEM, etc.
Candidate Interconnect Alloy: AISI 441

- Ferritic stainless steel: Good CTE match to other components; Electrically conductive Cr-based oxide scale
- Inexpensive - Manufactured via conventional melt metallurgy
  - No vacuum processing required
- Similar to AISI 430, but additions of Nb and Ti improve high temperature strength and prevent formation of insulating SiO₂ layer at alloy/scale interface
- Similar to all other FSS, relatively high oxidation rate at SOFC operating temperatures (and volatility of Cr) indicates need for protective coating
- Also, relatively weak scale adherence (no RE in alloy)

Typical Analysis:

<table>
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<tr>
<th>Designation</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Nb</th>
<th>La</th>
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<tr>
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<td>0.30</td>
<td>0.01</td>
<td>0.05</td>
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<td>0.002</td>
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<td>AISI 430</td>
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<td>0.050</td>
<td>≤0.2</td>
<td>0.04-0.20</td>
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</table>

Sources: Allegheny Technologies, Inc.; Thyssen Krupp
Properties of \((\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4\) Spinel

- High electrical conductivity
  \(~60\ \text{S/cm at 800}^\circ\text{C}\)

\[
\sigma_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} = 10^{3-4}\ \sigma_{\text{Cr}_2\text{O}_3}
\]

- Good CTE match to FSS and anode-supported cells

\[
\text{CTE}_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} = 11.5 \times 10^{-6} \ \text{K}^{-1}, 20 - 800^\circ\text{C}
\]

- Chemically compatible with contact pastes, cathodes

- Cr-free composition

- Tested with several FSS (Crofer22APU, 430, Ebrite, 441)

- 6 month thermal cycle test (800°C)
- Negligible Cr transport into coating
- Reduced oxidation rate of alloy
Ce-modified Mn-Co Spinel

- Rare earth (RE) additions (e.g., Ce, La) to alloys is well-established means of improving scale adherence
- NETL-Albany: Ce surface treatment leads to improved oxidation resistance, lower ASR
- PNNL: Ce-modified Mn-Co spinel coatings improve scale adherence on AISI 441
  - Simple modification – Ce nitrate included in glycine/nitrate precursor
  - Provides
    - Previously established benefits of MnCo spinel coating (improved oxidation resistance, lower ASR, Cr volatility mitigation)
    - Benefits of rare earth effect without need for RE additions to alloy
Improved Scale Adherence with Ce-MC Coatings

After 700 h, 850°C ASR measurement (similar results at 800°C)

Ce-MC coating:
$\text{Ce}_{0.05}\text{Mn}_{1.475}\text{Co}_{1.475}\text{O}_4$
Oxidation Kinetics of AISI 441: Bare vs. Ce-MnCo Spinel Coated

![Graph showing oxidation kinetics]

- Bare 800 C
- Bare 850 C
- Ce-MC 800 C
- Ce-MC 850 C

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Δm² (g²/cm⁴)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>200</td>
<td>2.0e-7</td>
</tr>
<tr>
<td>400</td>
<td>4.0e-7</td>
</tr>
<tr>
<td>600</td>
<td>6.0e-7</td>
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<tr>
<td>800</td>
<td>8.0e-7</td>
</tr>
<tr>
<td>1000</td>
<td>1.0e-6</td>
</tr>
<tr>
<td>1200</td>
<td>1.2e-6</td>
</tr>
<tr>
<td>1400</td>
<td>1.2e-6</td>
</tr>
</tbody>
</table>
Electrical Testing of 441

- Scale growth rates: Bare > MC coated > Ce-MC coated
- Ce altered interface morphology: smooth scale/metal interface for MC 441, rough interface for Ce-MC 441
SEM/EDS/EBSD Analysis

Ti-doped Chromia
Hexagonal Corundum structure
Cr-Mn spinel Cubic
Effect of Ti doping on Conductivity of Cr$_2$O$_3$

\[ TiO_2 = Ti^{\bullet}_{Cr} + \frac{3}{2} O_o + e^+ + \frac{1}{4} O_2(g) \]

For conductivity of 0.1 S/cm and scale thickness of 6 microns, calculated ASR = 6 mOhm-cm$^2$

ASR testing of AISI 441:
0.02Ce-MnCo spinel, NETL-Albany Ce surface treatment

![Graph showing ASR testing results for different samples: Bare NETL Ce-441, Ce0.02MC coated 441, and Ce0.02MC coated on NETL Ce-441.](image-url)
## Optimization of Ce-MnCo spinel coatings

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination Temp.</td>
<td>900°C</td>
<td>key parameter</td>
</tr>
<tr>
<td>Particle Size</td>
<td>&lt;1mm</td>
<td>attrition -milled</td>
</tr>
<tr>
<td>Binder to Powder Ratio</td>
<td>0.6:1</td>
<td>may vary with binder type</td>
</tr>
<tr>
<td>Coating Drying Temp.</td>
<td>&lt;60°C</td>
<td>better results with slow drying</td>
</tr>
<tr>
<td>Reducing atmosphere</td>
<td>2.7% H₂, wet</td>
<td>gas passing through a water bubbler</td>
</tr>
<tr>
<td>Reducing Temp. and Time</td>
<td>850°C, 4h</td>
<td>at least 650°C</td>
</tr>
<tr>
<td>Pre-oxidation Temp.</td>
<td>950°C, 0.5h</td>
<td>match with sealing temperature</td>
</tr>
</tbody>
</table>
Ultrasonic spray-based fabrication of Ce-MnCo spinel coatings: Preliminary Results

- Coating speed: 80mm/sec
- Head height: 35mm
- Coating mode: Wide mode
- Ink feeding rate: 1.5ml/sec
- Air flow rate: 50ml/sec
Ultrasonic spray-based fabrication: Process Optimization

Design Of Experiment (DOE) Optimization
Taguchi, Grey-Taguchi method and ANOVA (Analysis of Variance)

Points of reference: Coating thickness, pore area per unit area and the amount of material used

Two different mode: 1. Wide mode
2. Narrow mode

<table>
<thead>
<tr>
<th>Factors</th>
<th>level1</th>
<th>level2</th>
<th>level3</th>
<th>level4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>37 cP</td>
<td>17 cP</td>
<td>9 cP</td>
<td>5 cP</td>
</tr>
<tr>
<td>Coating speed</td>
<td>40mm/sec</td>
<td>60mm/sec</td>
<td>80mm/sec</td>
<td>100mm/sec</td>
</tr>
<tr>
<td>Head height</td>
<td>15mm</td>
<td>25mm</td>
<td>35mm</td>
<td>45mm</td>
</tr>
<tr>
<td>Ink feeding rate</td>
<td>0.5ml/sec</td>
<td>1ml/sec</td>
<td>1.5ml/sec</td>
<td>2ml/sec</td>
</tr>
<tr>
<td>Air flow rate</td>
<td>30ml/sec</td>
<td>40ml/sec</td>
<td>50ml/sec</td>
<td>60ml/sec</td>
</tr>
</tbody>
</table>
Elimination of Reducing Atmosphere Heat Treatment for MnCo Spinel Coatings

- Standard fabrication approach requires heat treatment in reducing atmosphere followed by oxidative heat treatment.
- Use of metallic precursor powders (Mn, Co) eliminates reducing heat treatment, and thus reduces coating cost.
- Compatible with reactive air aluminization (RAA) of sealing surfaces of the interconnect
- Preliminary results:
Solid-State Sintering

**Conventional Sintering**

- **Thermodynamics**
  - Driving Force: Decrease in surface free energy, $E_S$
  - $S_A = 4\pi r^2 N = 3V_m/r$; \(E_S = 3\gamma V_m/r\)
  - Assume $\gamma = 1$ J/m$^2$, $r = 1$ $\mu$m, $V_m = 2.5 \times 10^{-5}$ m$^3$: $E_S = 75$ J/mole. (Rahaman, “Ceramic Processing and Sintering,” Dekker)

- **Kinetics**
  - Diffusion-based process, so thermally activated: $D \propto \text{Exp}(-E_a/kT)$
  - Thermal Energy obtained from furnace
  - Assuming $E_a = 1.5$ eV, $D_{1400^\circ C}/D_{900^\circ C} \approx 80$

**Pressure Sintering**

- Driving Force: Externally applied pressure, $P_a$, during heating
- Assume 30 MPa pressure: $W = P_a V_m = 750$ J/mole

**Reaction Sintering**

- Driving Force provided by decrease in energy accompanying chemical reaction
- Challenges in controlling microstructure due to simultaneous processes (chemical reaction/sintering)
Reaction-Assisted Sintering of Spinels

- Reaction-Assisted Sintering
  - Both Thermal and Chemical Energy available to enhance densification rate
  - Example (data for MnCo spinel not available):
    - \( \text{Co(s) + 2 FeO(s) + O}_2(\text{g}) = \text{CoFe}_2\text{O}_4 \)
    - \( \Delta H_r(900^\circ\text{C}) = -547 \text{ kJ/mol} \)
    - Adiabatic Temperature: \( \sim 3600^\circ\text{C} \)

- Less advantage with all-oxide precursors:
  - \( \text{CoO(s) + 2 FeO(s) + 0.5O}_2(\text{g}) = \text{CoFe}_2\text{O}_4 \)
  - \( \Delta H_r(900^\circ\text{C}) = -314 \text{ kJ/mol} \)

- Greater advantage with all-metallic precursors:
  - \( \text{Co(s) + 2 Fe(s) + 2O}_2(\text{g}) = \text{CoFe}_2\text{O}_4 \)
  - \( \Delta H_r(900^\circ\text{C}) = -1077 \text{ kJ/mol} \)
Alternative Interconnect Coating Compositions

Emphasis on reduction / elimination of Co, to reduce coating cost

MnCo with reduced Co content

MnCo with reduced Co content

Mn4Co1

Mn3Co1

800°C in air, 24 hours
Alternative Interconnect Coating Compositions

- Mn only precursor (Cobalt-free)
- Mn oxide coating prepared from Mn powder:

Heat treatment: 800ºC in air for 24 hours
ASR of Mn Coated 441 at 800°C

- Post-test analysis will be performed to determine cause of ASR increase
- Other compositions are under investigation
Conclusions

► AISI 441 exhibits promising alloy chemistry for SOFC interconnect applications
  ■ Expensive refining processes not required, so cost is reduced

► Ce-modified MnCo spinel coatings exhibit the benefits of original MnCo coatings, and also provide improved scale adherence and lower scale growth rate

► Ultrasonic spray-based fabrication process appears promising
  ■ DOE matrix of optimization trials in progress

► Cost-reduction approaches are under investigation
  ■ Elimination of need for preliminary reducing atmosphere heat treatment
  ■ Reduction or elimination of Co content
Future Work

- Evaluate long-term stability and electrical performance of Ce-MC spinel-coated 441 steel, including dual atmosphere (w/ simulated coal gas fuel) and thermal cyclic conditions.
- Optimize automated ultrasonic spray process for coating of larger, shaped parts.
- Reduce cost of protective coatings through elimination of reducing heat treatment and/or minimization or elimination of Co content.
Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.
- The authors wish to thank Wayne Surdoval, Briggs White, Travis Shultz, Paul Tortora and Joseph Stoffa at the National Energy Technology Laboratory (NETL) for helpful discussions regarding the initiation and implementation of this study.
- The authors wish to thank Paul Jablonski at the National Energy Technology Laboratory (NETL) for helpful discussions and Ce-treatment of AISI 441 samples.
- The authors wish to thank Jim Rakowski at ATI Allegheny Ludlum for providing the AISI 441 alloy samples and for helpful discussions.
- Metallographic preparation: Shelley Carlson, Nat Saenz, Clyde Chamberlin
Compliant glass seal development

Y-S Matt Chou, E. Thomsen, E. Mast, J-P Choi, W. Voldrich, and J. W. Stevenson

- Introduction and objectives
- Q1: Effect of differential pressure on thermal cycle stability
  1. experimental
  2. leak rates versus cycling (700-850°C/1000h)
- Q2: thermal stability study in a duel environment
  1. leak rates versus time (750-800°C/1000h)
  2. microstructure and interface characterization
- Q3: assess YSZ coating and other mat’l for spacer rings
- Summary
- Future work

Solid-State Energy Conversion Alliance Core Technology Programs Review
July 27-29, 2010, Pittsburgh, PA
Compliant versus refractory sealing glass

\[ \sigma = E \Delta \alpha \Delta T \]

Compliant sealing glass

Data provided by ORNL 850h aged

- Advantage:
  - Low stress or relaxation, healing?
  - Wetting,

- Disadvantage:
  - metal-stable, narrow T window, volatile, reactive/corrosive?
Objectives

➢ To conduct a comprehensive study of a commercial compliant sealing glass in terms of thermal, chemical, physical, electrical, and mechanical stability in SOFC environments

SCN-1 glass: Si, K, Na, Mg, Ba, Ca, Al
Experimental: sample preparation

1. Thickness of spacer rings ~220 µm
2. SCN-1 glass mixed with ESL450 binder to form paste

1.4” φ bilayer
Sealing condition screening

- Sealing profile: RT to 550°C/2h, T/2h, then cooled to RT with a contact load
- Leakage tested with ultra-pure helium @ 0.2 psi & iso-propanol

<table>
<thead>
<tr>
<th>RT Hermeticity</th>
<th>700°C/2h</th>
<th>750°C/2h</th>
<th>800°C/2h</th>
<th>850°C/1h</th>
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</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Sample 2</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Experimental: high-temp leakage test

- Inconel600 load block (2”x2”) with incoming and outgoing tubing
- Load (~12 psi)
- He/H₂ in
- He/H₂ out or to pressure sensor
- Corrugated Ni-mesh to mimic some contact load
- PEN cell or bilayer (1.4”φ)
- Al-SS441 (2”x2”x0.06” with a central hole)
- ZrO₂ or mica ring spacer
- porous Al₂O₃ support
- Compliant glass
- Al₂O₃ pipe
- SCN-1 or Ag/mica hybrid seal with known leak rate or plain Ag foils
Thermal cycle stability at 850°C in air

SCN-1 glass @ 850°C Helium @ various pressures

Aluminized AISI441 with YSZ spacer rings
Samples was tested with iso-propanol after cycling test and showed hermetic.
Thermal cycle stability at 800°C in air

The measured leak rate is from mica seal not from (SCN-1) glass seal since the fracture of monolithic glass seal would contributed leakage an order of magnitude higher.
Thermal cycle stability at 750°C in air

The leakage suggested the SCN-1 glass was hermetic that the measured leakage was from perimeter mica seals. Post-mortem leak test with iso-propanol also showed hermetic.

Test #13  8YSZ rings SCN-1 sealed at 800°C/2hr cycled to 750°C
Thermal cycle stability at 750°C in air

Test #16 12mil mica rings SCN-1 sealed at 800°C/2hr cycled to 750°C

Found a broken fitting prior to cycle 7 testing.

Mica as spacer rings
Samples was tested with iso-propanol after cycling test and showed hermetic.
Leakage versus thermal cycling at 700°C in air with aluminized SS441 and 8YSZ rings

Samples were tested with iso-propanol after cycling test and showed hermetic.
Characterization of 850°C/20 cycled sample: SCN-1 glass/8YSZ bilayer interface

Exposed in air and 850°C/3h per cycle
With aluminized SS441 plate, bilayer, and 8YSZ narrow rings (0.1”)

SCN-1

Al-SS441
8YSZ ring
YSZ/anode bilayer
8YSZ bilayer
Characterization of 850°C/20 cycled sample: SCN-1 glass/8YSZ bilayer interface
Characterization of 850°C/20 cycled sample: SCN-1 glass/aluminized SS441 interface
Q2: thermal stability in dual environment
800°C/1000h then 5 thermal cycles

Very stable during isothermal ageing test
Sample failed after 4 deep thermal cycles
Post-mortem analysis: 800°C/1000h+4 cycles

As-sealed

After 1000h and 4 cycles
Glass/aluminized SS441 interface (800°C 1000h)

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<th>Element</th>
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<th>#3</th>
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<tbody>
<tr>
<td>O K</td>
<td>63.0</td>
<td>61.9</td>
<td>63.9</td>
</tr>
<tr>
<td>Na K</td>
<td>3.0</td>
<td>6.0</td>
<td>0.9</td>
</tr>
<tr>
<td>Mg K</td>
<td>0.9</td>
<td>6.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Al K</td>
<td>1.3</td>
<td>0.3</td>
<td>5.5</td>
</tr>
<tr>
<td>Si K</td>
<td>25.9</td>
<td>22.2</td>
<td>23.4</td>
</tr>
<tr>
<td>K K</td>
<td>3.2</td>
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<td>5.7</td>
</tr>
<tr>
<td>Ca K</td>
<td>1.4</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>Ba L</td>
<td>1.4</td>
<td>1.2</td>
<td>0.3</td>
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Glass/YSZ electrolyte interface (800°C-1000h)

<table>
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<td>O K</td>
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<td>62.9</td>
</tr>
<tr>
<td>Na K</td>
<td>0.6</td>
<td>3.2</td>
</tr>
<tr>
<td>Mg K</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Al K</td>
<td>1.7</td>
<td>1.5</td>
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<tr>
<td>Si K</td>
<td>29.0</td>
<td>25.9</td>
</tr>
<tr>
<td>K K</td>
<td>1.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Ca K</td>
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<td></td>
</tr>
<tr>
<td>Ba L</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Ti K</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Zr L</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>
Q2: thermal stability in dual environment
750°C/1000h then 5 thermal cycles

Very stable during isothermal ageing test
Sample failed after 1 cycle and more damages after 5 cycles

Test #24 Sealed at 800°C/2hr with YSZ rings, @ 750°C in 5% H2/N2

Leak Rate (sccm/cm)

0.000 0.020 0.040 0.060 0.080 0.100
0 200 400 600 800 1000
Time at 750°C (Hours)

Leak Rate (sccm/cm)

0.000 0.020 0.040 0.060 0.080 0.100 0.120
0 200 400 600 800 1000
# thermal Cycle after 750°C/1000h

0.2psi 0.5psi 1psi

0.2psi 0.5psi 1psi
Post-mortem analysis: 750°C/1000h+5 cycles

Consistent radial fractures of bi-layers as previous (800°C/1000h) sample

**Cause for fracture**
- High stress from thick YSZ spacer rings
- Lower strength after reduced (~60 MPa from as-sealed of ~240 MPa).
- Lower modulus after reduced (~45 GPa from ~80 GPa as-sealed)
- Increased flaw size and distribution
Other containment geometry

- PEN
- AISI441
- YSZ spacer rings
- Glass
- Spacer ring design
- Machined groove design
YSZ coating on SS441

- Vapor deposition at PNNL showed poor adhesion on plain SS441
- Double coating: YSZ coating (15-20 μm) by ultrasonic sprayer on aluminized SS441
- Single coating by high velocity cold spray on plain SS441 without heat treatment (S. Dakota School of Mines)
Low leak rates suggest no bi-layer fracture

SS441 was aluminized then coated with YSZ with ultrasonic sprayer

Test continued for 1000h stability
Thermal cycle stability of YSZ-coated SS441

SS441 substrate was coated with high velocity cold spray in collaboration with S. Dakota School of Mines
Poor adhesion of YSZ coating on plain SS441
Summary and conclusion

- SCN-1 glass showed good thermal cycle stability between RT and T=700-850°C when sealed between a ceramic bi-layer and an aluminized SS441 substrate.
- SCN-1 glass was able to stand back pressure to 1.0 psi and remained hermetic after thermal cycling.
- Current spacer ring design resulted in bi-layer fracture after anode reduction. Using groove design low leak rates were obtained suggesting no bi-layer fracture.
- SCN-1 glass appeared thermally stable for 1000h at 750-800°C in dual environment and 1psi.
- Microstructure analysis showed more precipitates along YSZ/glass interface than glass/aluminized SS41 interface. There were also two types of precipitates/crystallites observed in glass matrix.
- The adhesion of direct coating of YSZ on SS441 was poor.
Future work

1. Incorporate compliant glass into stack fixture testing.
2. Continue stability test (750-800°C/1000h) in dual environment for aluminized+YSZ coated SS441. Conduct post-mortem interfacial characterization and optimize YSZ coating and process.
3. Conduct volatility (K+Na ~13 at%) and electrical stability study in dual environments with high water content to assess long-term durability.
5. Optimize compliant glass-based seal designs for long-term and thermal cycle stability.
6. Evaluate other compliant glasses developed under SECA programs with PNNL leak test fixtures.
Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program
- NETL: Briggs White, Travis Shultz, and Wayne Surdoval
- ORNL: Edgar Lara-Curzio, Amit Shyam
- South Dakota School of Mines: Prof. West
- PNNL: Jim Coleman, Shelley Carlson, Nat Saenz
Will the glass be pushed out by back pressure

\[ \eta = 10^5 \text{ Pa s (800}^\circ\text{C)}, \ 10^{5.5} \text{ Pa s (750}^\circ\text{C)} \]
\[ \gamma = 250-350 \text{ mN/m as liquid, } ?750-800^\circ\text{C} \]

Force to push-out = area x \( \Delta P \)

Force to resist push-out = length x \( \gamma \)
Crack healing

- Commonly observed in glass at elevated temperatures.
- 3 mechanisms proposed: diffusion-driven thermal healing, adhesion from intermolecular forces, and chemical reaction at crack-tip.

G18 indented 2 kg
Fired at 750°C
Modeling Tools for Solid Oxide Fuel Cell Design and Analysis

Moe A Khaleel
BJ Koeppel, W Liu, K Lai, KP Recknagle, EM Ryan, EV Stephens, X Sun

Pacific Northwest National Laboratory
Richland, WA 99352

11th Annual SECA Workshop
Pittsburgh, PA
July 27-29, 2009
PNNL SOFC Modeling Tools

- SOFC-MP
  - Stack level model for fast analysis of co/counter-flow SOFC stack performance
- Detailed electrochemistry model
  - Cell level model for the investigation of secondary reactions (degradation/contamination) mechanisms within the tri-layer
- Component-based design and performance modeling
  - Contact material
  - Interconnect
  - Glass seal
SOFC-MP Stack Simulation Code
Recent Accomplishments

- Major memory improvements of 3D model to accommodate 50-cell stacks on LINUX platform.

- Previously, developed a 2D (or stacked 1D) model for fast analysis of co/counter-flow SOFC stack performance.
  - Benchmarked with literature cases.

- New features added for design and evaluation of realistic stack experiments,
  - Allows users to maximize understanding of actual experiments where uniform nominal performance is not always achieved.
  - Allows users to implement custom CH$_4$ reforming and I-V relationships.
  - Allows users to quickly evaluate different conditions with automated output of stack performance metrics.

- Capable of modeling cell-to-cell variations, e.g.:
  - Thick measurement plate in middle of stack
  - Different flow rates into cells, e.g. due to blockage, leak, or bypass
  - Different I-V performance of cells
  - Short current in cells
  - Partial contact loss in cells

- Capability to analyze large stacks, e.g., a 96-cell 25 kW stack.
SOFC-MP Stack Simulation Code
Nominal Stack Performance – H₂/CH₄ Fuels

- 96-cell stack, 625 cm², 65% UF, 15% UA

**Electrical Performance**
- Hotter inflow gases cause current consolidation on leading edge of H₂ stack
- 50% OCR fuel resulted in 7.5% less power

**Thermal Performance**
- Cell ΔT for top/bottom cells smaller than middle cells due to heat transfer to environment
- Highest ΔT nearer bottom due to cooler inlet gas
- OCR reduced Tmax by 31°C and ΔT by 20°C

<table>
<thead>
<tr>
<th>Results Comparison</th>
<th>H₂ Fuel</th>
<th>CH₄ Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (kW)</td>
<td>25.5</td>
<td>23.6</td>
</tr>
<tr>
<td>V avg (V)</td>
<td>0.852</td>
<td>0.785</td>
</tr>
<tr>
<td>ΔV (V)</td>
<td>0.015</td>
<td>0.023</td>
</tr>
<tr>
<td>J avg (A/cm²)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>J max (A/cm²)</td>
<td>0.65</td>
<td>0.64</td>
</tr>
<tr>
<td>T avg (C)</td>
<td>793</td>
<td>743</td>
</tr>
<tr>
<td>T max (C)</td>
<td>848</td>
<td>817</td>
</tr>
<tr>
<td>ΔT (C)</td>
<td>139</td>
<td>119</td>
</tr>
</tbody>
</table>

Current Density

Cell Temperature
SOFC-MP Stack Simulation Code
Effect of Thick Plates – H2 Fuel

- ½” measurement plate (e.g. thermocouples) used for cells #32 and #64
  - Observer effect: the measurement itself affects the data
  - Larger thickness plate makes good thermal conductivity path to spread heat better and provides better thermal communication with ambient
- Mean cell temperature about the same, but $\Delta T$ underestimated by 21%
- Power actually increased 0.2% due to hotter leading edge
SOFC-MP Stack Simulation Code
Effect of Flow Maldistribution – H2 Fuel

- Cells may have off-nominal flow rates
  - Flow blockage due to excessive spread of seal materials
  - Fuel by-pass around cell

- Example H2 case
  - 75% fuel flow in cell #32, 50% air flow in cell #64

- Results
  - Min voltage on cell #32 0.81V
  - Higher max current density of 0.74 A/cm²
  - Local utilization on cell #32 increased to 87%
SOFC-MP Stack Simulation Code
Effect of Contact Loss – H2 Fuel

- Case with contact loss at cooler inlet entrance for 10% of active area
- Power loss -0.7%
- Peak current density increased 10% on the top cell with hottest inflow temperature
- Peak cell temperature increased 5°C
- Stack $\Delta T$ increased 7°C

![Current Density Graphs]

**Current Density**

- **100% Contact**
- **90% Contact**

![Composition Graph]

**Composition**
Detailed Electrochemistry Modeling

Objective

► Resolve the local fields (potential, species, thermal) through the thickness of the tri-layer

► Understand the local conditions that contribute to the onset of secondary reactions in the tri-layer to enable prevention
  ■ Secondary Reactions: Any reactions not directly related to the electrochemistry which can cause degradation and damage to the fuel cell

► Investigate the effects of secondary reactions on the operation and performance of the SOFC

Accomplishments

► Developed 2D electrochemistry model which resolves the potential, current density and species through the anode-electrolyte-cathode assembly.

► Implemented chemistry model for the gas reforming reactions within the anode

► Validated the model with previous modeling data from literature.
Effective properties (transport, surface reaction, electrochemistry) model to calculate the species, thermal and electric potential distributions in the tri-layer

Solves for the electrochemistry through the tri-layer which removes the assumption of a zero thickness reaction zone and allows calculation of the physical potential distribution within the electrodes

Resolves the 2-D distributions through the thickness of the tri-layer, with implementation extendable to 3-D

Begins by modeling the physics of the active cell and then overlaying the secondary reaction mechanisms and threshold energies
2D domain made up of the anode, cathode, electrolyte and fuel and air channels

Gas transport in the porous electrodes including the species: \( H_2, H_2O, CO, CO_2, O_2, CH_4 \)

Surface chemistry with adsorption, desorption, reformation, and water-gas-shift, including the surface species: H, O, OH, \( H_2O, CH_4, CH_3, CH_2, CH, CO, CO_2, HCO, O^2-, OH^-, \) and free Ni sites

Modified Butler-Volmer relationship for the electrochemistry in the electrodes
- Based on the electrochemical reactions
- Assumes one of the charge transfer reactions is rate limiting

Within electrolyte and electrode phases
- Solid state conduction of \( O^{2-} \) and \( e^- \)
- Electric potential distribution
Verifying the model for the \( \text{H}_2 \) – \( \text{H}_2\text{O} \) binary fueling system

Further verification and validation ongoing
Detailed Electrochemistry Model: Two-Dimensional Variable Property Model

Variable properties in anode (green sections)

Four cases:
- Baseline
- Electrochemically inactive zones
- Decreased ionic conductivity (decreased YSZ fraction)
- Increased ionic conductivity (decreased YSZ tortuosity)
Contact Materials and Stack Load Path
Recent Accomplishments

- Previously, developed models to study influence of contact layers on load path through the stack
- Recently, evaluated densification behaviors of actual contact materials under development and sensitivity to initial material state, applied loads, and kinematic constraints
  - LSM + 3mol% CuO + BaCuO$_2$
  - LNF + 3mol% Bi$_2$O$_3$
  - LSCF + 3mol% CuO
  - Ni-Co oxides

- Results:
  - Method established to obtain model parameters for low temperature sintering from dilatometric screening test
  - Good densification (>80%) of candidate material systems predicted as possible based on dilatometer testing (e.g. 4 hour treatment at 950°C)
  - If possible, initial grain sizes <1 $\mu$m very beneficial for low temperature sintering
  - Constrained contact layers <1 mm have nearly uniform density but normal and shear stresses vary through the section
  - Expected maximum stress levels in stack structures up to 10-15 MPa
Contact Materials and Stack Load Path
Material Data from Experiments

- Use densification strain data for candidate contact materials from dilatometry under ramped heating
  - LSM + 3mol% CuO + BaCuO₂
  - LNF + 3mol% Bi₂O₃
  - LSCF + 3mol% CuO

- Fit parameters from the material constitutive model
- Include grain growth rate model from literature
- Verify performance of the constitutive model in FEA

\[
\eta_0 = -\frac{P_L}{6\dot{\varepsilon}\psi}
\]

\[
P_L = \frac{3\alpha}{r_0}(1-\theta)^2
\]
Contact Materials and Stack Load Path Free/Pressurized Sintering

- For LSM+aid, much higher densification in 900-1000°C processing range
  - Less benefit for LNF+aid due to flat densification curve
- Great benefit to initial densification with grain sizes less than 1.0 micron
  - 0.1 micron gives 99% relative density; 1.0 micron give 72% relative density
  - Small grain growth rate for this temperature range so sintering is sustained
- Uniaxial pressure will increase the densification rate
  - Preload less than the sintering stress (~5 MPa) shows only small benefit

Effect of Sintering Temperature

<table>
<thead>
<tr>
<th>Sintering Temperature (°C)</th>
<th>Initial Relative Density</th>
<th>4hr Relative Density</th>
<th>Initial Grain Size</th>
<th>4hr Grain Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.2</td>
<td>0.5</td>
<td>0.1</td>
<td>0.8</td>
</tr>
<tr>
<td>900</td>
<td>0.4</td>
<td>0.8</td>
<td>0.3</td>
<td>1</td>
</tr>
<tr>
<td>1000</td>
<td>0.6</td>
<td>0.9</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

Effect of Initial Grain Size

<table>
<thead>
<tr>
<th>Initial Grain Size (micron)</th>
<th>Final Relative Density</th>
<th>4hr Relative Density</th>
<th>2hr Relative Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.9</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>1.0</td>
<td>0.7</td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Effect of Compressive Preload

<table>
<thead>
<tr>
<th>Preload (MPa)</th>
<th>Final Relative Density</th>
<th>2hr Relative Density</th>
<th>Lateral Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9</td>
<td>0.6</td>
<td>-0.8</td>
</tr>
<tr>
<td>2</td>
<td>0.7</td>
<td>0.4</td>
<td>-0.6</td>
</tr>
<tr>
<td>4</td>
<td>0.6</td>
<td>0.2</td>
<td>-0.4</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>0.0</td>
<td>-0.2</td>
</tr>
<tr>
<td>8</td>
<td>0.4</td>
<td>-0.2</td>
<td>-0.0</td>
</tr>
<tr>
<td>10</td>
<td>0.3</td>
<td>-0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Contact Materials and Stack Load Path
Constrained Sintering (LSM + sinter aid)

- For bonded structures, the relative density varies through the part due to the constraint and stress field.
  - Thin contact layers <1.0 mm have more uniform relative density
    - Dominated by constraint of the two bonded surfaces so less variation
- Thin contact layers also showed smaller residual normal stress development
  - In-plane stress remains significant
  - Out-of-plane stress near zero
  - Edge shear stress becoming larger

Effect of Contact Layer Thickness

Extend to stack rib/contact structures
- 100x5 mm strip
- 2mm ceramic
- 0.2mm paste
- 1mm steel
- Hypothetical 4 hour treatment at 950°C
Contact Materials and Stack Load Path
Stack Contact Structures (LSM + sinter aid)

- Densification varies across layer with faster rates at edges
  - In-plane stresses initially high but reduce after densification
  - Out-of-plane stresses increase with time and vary spatially
  - In-plane strains 200-400X greater than out-of-plane

- Final stresses at temperature:
  - Highest shear stresses at the edges (~14 MPa)
  - Highest normal stresses at the center (~7 MPa)

- Bulk layer and interfaces will both need adequate strength
  - Construction of lap shear strength testing system in progress

In-plane Stress History

Out-of-plane Stress History

Peak contact layer stresses from rib in 3D stack models of similar magnitude
- ~2 MPa shear
- ~10 MPa normal
Accomplishments

- Substrate thickness has significant effect on delamination/spallation of oxide scale
- Shot-peening avoids or delays the spallation of oxide scale
- Optimized cooling profile reduces the compressive stress in oxide scale to some degree → reducing driving force for scale spallation
Effect of Substrate Thickness on Cooling Induced Oxide Stresses for Uncoated SS441

- Modeled different substrate and oxide scale thicknesses
  - SS441: 0.25mm, 0.5mm, 1.0mm, 3.0mm
  - Oxide scale thickness: 2um, 4um, 6um, 8um, 10um, 15um

- For a given oxide scale thickness, i.e., oxidation time:
  - Shear stress increases with increasing substrate thickness
  - Compressive stress increases with increasing substrate thickness – more likelihood to spall

- For a given substrate thickness:
  - Shear stress increases with increasing oxide thickness, i.e., oxidation time.
  - Compressive stress decreases with increasing oxide thickness, i.e., oxidation time.
    - The magnitude still remains high, ~2GPa

- Thinnest substrate with the lowest oxidation time will have the least chance to spall.
The thicker the substrate, the higher the driving force for spallation

- Cooling induced interfacial shear stress calculation – PNNL 17781
- Interfacial shear strength: 395MPa*
- Interfacial failure driving force can be reduced by reducing the bulk thickness of SS441.

*Liu et al., *Journal of Power Sources* 189 (2009) 1044–1050

Verified by experimental data from J. Stevenson and PNNL Materials Task
To date, no spallation has been observed on the shot-peened specimens whether un-coated or coated that have been exposed to at least 2000h or more at 850°C.

Need to determine whether to expose shot-peened specimens for additional thermal cycles or to cross-section and evaluate.
Effects of Shot Peening on Scale Spallation

- Increase critical scale buckling strength by reducing critical buckling length (1)

\[ \sigma_{cr} = 1.2235 \frac{E}{1 - \nu^2} \left( \frac{H}{a} \right)^2 \]

- Decrease buckling driving force, i.e., cooling induced compressive stress, by non-uniform oxidation of the shot peened surface:

- Reduce scale spallation/buckling tendency from both directions:
  - Increased strength
  - Decreased driving force

Optimizing Cooling Profile to Minimize Spallation

Objective: Utilize creep/stress relaxation of SS441 at temperature above 500ºC-600ºC to minimize oxide spallation during cooling

Cooling profile examined:

- Temperature drops linearly from 800ºC to 500ºC/600ºC within 10min to 20hr in the first step; then drops to room temperature within 10s in the second step
- Slower cooling rate to intermediate temperature can be helpful in reducing spallation
- The shear stress reduction tapers off after 10h, maximum at 6.7% for 20h

<table>
<thead>
<tr>
<th>Intermediate temperature</th>
<th>500ºC</th>
<th>600ºC</th>
<th>No Creep</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max Shear Stress (Mpa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10min</td>
<td>362</td>
<td>2.1%</td>
<td>370</td>
</tr>
<tr>
<td>1 h</td>
<td>357</td>
<td>3.5%</td>
<td></td>
</tr>
<tr>
<td>10 h</td>
<td>347</td>
<td>5.8%</td>
<td>348 6.1%</td>
</tr>
<tr>
<td>20 h</td>
<td>345</td>
<td>6.7%</td>
<td>345 6.7%</td>
</tr>
</tbody>
</table>
Glass Seal Modeling

Accomplishments

- Studied the effects of ceramic stoppers on the geometric stability of the self-healing seals in a simulated stack environment using creep analysis.
- Studied effects of various interfaces of PEN/Stopper, IC/Stopper, and Stopper/glass on the interfacial stresses upon cooling.
- Modeled the self-healing behavior of glass.

Several topical reports and papers written by PNNL are available on this subject.

- Please see me after the presentation if you are interested in more information.
Conclusions and On-Going Work

Conclusions

- Array of tools to model SOFCs at various scales (stack, cell, component levels)
- Models improve understanding of SOFC operation and performance
- Collaborations with experimentalists can help to design materials, interpret experimental data and understand degradation issues

On-going work

- Benchmarking and enhancement of 3D SOFC-MP
- Validation and verification of detailed electrochemistry model
- Enhancement of the detailed electrochemistry model to include the energy equation and to investigation of secondary reactions
- Continued modeling of interconnects and coatings to validate our assumption on reduction of free buckling length
- Additional modeling of shot peened SS441 for process optimization and lifetime prediction of coatings
- Strength testing and modeling after contact material is selected
SOFC Tolerance Limits for Phosphorus and Arsenic

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July 27-29, 2010
11th Annual SECA Workshop
Pittsburgh, PA
INTRODUCTION

- Different coals, gasification processes, and cleanup processes result in different levels of impurities.
- Different contaminants lead to different types of interactions with SOFC anode.
- Performance degradation due to trace impurities is affected by various factors such as concentration of contaminants, temperature, operation time, cell voltage, and fuel utilization.
- Previous studies at PNNL focused on P, As, Sb, S, Se, Cl at ppm levels.
- Current studies are focused on:
  - Effect of sub-ppm levels of P and As on anode chemistry/microstructure
  - Effect (if any) of electrical potential on reactions between contaminant and anode
ANODE–PHOSPHORUS INTERACTIONS: CONCLUSIONS FROM PREVIOUS WORK

Strong interaction between Ni and P-containing contaminants in coal gas (PH₃, PO₂, etc.)

- Nickel phosphide solid phases: Ni₃P, Ni₅P₂, Ni₁₂P₅, Ni₂P, etc.
- Phosphide formation predicted even at low P concentrations (< 0.01 ppb at 800°C)
- Sharp boundary observed between reacted and un-reacted parts of the anode

Degradation Mechanisms

- Increased Ohmic resistance due to
  - Loss of electrical connectivity in the anode support due to phosphide formation (Ni depletion)
  - Micro-crack formation due to particle coalescence
ANODE–PHOSPHOROUS Interaction

SEM Analysis of anode-supported button cells after exposure

- Sharp Boundary Between Ni and Ni-P
- Considerable Coalescence of Ni-P
- WDS → P is associated only with nickel, not zirconia.
- Micro-cracks in Reacted Area
Degradation Mechanisms (continued)
- Poisoning due to slow migration of phosphorus to the active interface (increased electrodic polarization)
- P adsorbs on surface of Ni grains in unreacted anode (observed by XPS, ToF-SIMS)

Effect of Contaminant Level
- For $[\text{PH}_3] = 1$-10 ppm, both ohmic and electrodic losses in tested cells increased substantially during 1000 hours of testing
ANODE–ARSENIC INTERACTIONS: CONCLUSIONS FROM PREVIOUS WORK

Strong interaction between Ni and As-containing contaminants in coal gas (AsH₃, As₂, etc.)
- Nickel arsenide solid phases: Ni₅As₂, Ni₁₁As₈, etc.
- Arsenide formation predicted even at low As concentrations (<0.1 ppb at 800ºC)
- Sharp boundary observed between reacted and un-reacted parts of the anode

Degradation Mechanisms
- Loss of electrical connectivity in the anode support due to arsenide formation: Ni depletion (increased Ohmic resistance)
  - Abrupt failure after long-term operation upon loss of electrical percolation
- Unlike case for P, poisoning effects due to adsorption of As at active anode interface were not observed

For [AsH₃] = 0.5 – 10 ppm, substantial degradation of performance observed in 1000 hours or less
**ANODE–ARSENIC INTERACTION**

- **SEM Cross-Section Image (800°C, 500 hours)**
  - AsH₃ Concentration ↑ ~ Depth of Reaction ↑, Agglomeration↑

- **Conversion of Nickel to Nickel Arsenide (Ni₅As₂, Ni₁₁As₈)**
  - 700°C, 50 Hours
  - Red: Ni, Dark Yellow: Ni-As Solid Solution, Green: YSZ, Blue: Ni₅As₂, Magenta: Ni₁₁As₈

*Proudly Operated by Battelle Since 1965*
Current Study: Effect of 10 ppb contaminant levels

- Ni Phosphide / Ni Arsenide formation expected to occur even at sub-ppb contaminant levels:

![Graph showing the relationship between temperature and partial pressure of As species.](Image)
Current Study: Effect of 10 ppb contaminant level

- Ni Phosphide / Ni Arsenide formation expected to occur even at sub-ppb contaminant levels
- However, also can expect low rate of reaction due to low contaminant delivery rate

Calculated rates of Ni conversion

Assumptions:
- 50/50 vol% Ni/YSZ anode w/ 40% porosity; 500 microns thick
- 65% fuel utilization, 0.8 A/cm² current density
- Complete capture of contaminant by anode (worst-case scenario)
- Dominant phase formed:
  - P: Ni₃P
  - As: Ni₅As₂
For 10 ppb contaminant level, expect low rate of Ni conversion.
“Flow-by” anode contaminant tests

- Flow rate: 200 sccm, corresponding to ~65% fuel utilization at 0.8 A/cm²
- Gas composition: Simulated coal gas (55% H₂; 45% CO₂)
- Contaminant type and level:
  - 10 ppb AsH₃
  - 10 ppb PH₃
  - 10 ppb AsH₃ + 10 ppb PH₃
- Temperature: 800°C
- Exposure time: 2000 hours +

![Diagram of fuel cell system with Perimeter Seal, YSZ membrane, Ni/YSZ Anode, Fuel Inlet, and Fuel Outlet.]
1 ppm PH$_3$ + 1 ppm AsH$_3$, 800° C, 100h

Inlet: Ni$_5$As$_2$ + Ni$_5$P$_2$

3.8 mm is converted
Surface crystals are Ni-As; Ni-P is. The P penetration at the inlet was \( \sim 70 \).
1 ppm AsH$_3$ at 800°C, 100h

4.5 mm was transformed to Ni$_5$As$_2$ and some As was found up to 6 mm away.
0.5 ppm PH$_3$ at 800$^\circ$C, 100h

Ni$_3$P was found out to 1.7 mm from the inlet.
“Flow-by” anode contaminant tests at 10 ppb

- 2000 hour tests completed
  - Total As supplied: 0.8 mg
  - Total P supplied: 0.3 mg
  - Total contaminant dosage was 40% of dosage in 0.5 ppm, 100 h tests
- Nickel arsenide detected by surface SEM/EDS
  - “Needle in a haystack”; unclear why secondary phase is so hard to find
  - Confirmed that 10 ppb is higher than minimum As concentration for secondary phase formation

- Will follow up with cross-section SEM/EDS
- Longer term are tests in progress
“Flow-by” anode contaminant tests at 10 ppb
“Flow-by” anode contaminant tests at 10 ppb
Arsenic – Nickel Phase Diagram

Note eutectics at 897 and 804ºC

Effect of Electrical Potential on Ni Conversion

- Flow rate: 200 sccm, corresponding to ~65% fuel utilization at 0.8 A/cm²
- Gas composition: Simulated coal gas (55% H₂; 45% CO₂)
- Contaminant type and level:
  - 1 ppm AsH₃
- Temperature: 800°C
- Exposure time: 2000 hours (ending date: 7/29/10)

Case 1: No electric potential/current (baseline)
Case 2: Anode at 0V potential (connected to ground) /1.5 A/cm²
Case 3: Anode at 40V potential / 1.5 A/cm²
SUMMARY

► Strong interactions occur between Ni-based anodes and P and/or As contaminants in coal

► These interactions result in formation of secondary phases
  - Nickel phosphide solid phases: Ni$_3$P, Ni$_5$P$_2$, Ni$_{12}$P$_5$, Ni$_2$P, etc.
  - Nickel arsenide solid phases: Ni$_5$As$_2$, Ni$_{11}$As$_8$, etc.
  - Phosphide/arsenide formation were observed at ppm levels, and are predicted at much lower concentrations (< 1 ppb at 800ºC)
  - Sharp boundaries are observed between reacted and un-reacted parts of the anode

► At ppm levels, interactions result in ohmic (P, As) and non-ohmic degradation (P) of cell performance

► Tests with P and As at 10 ppb are in progress
  - For coal gas fuels cleaned to ppb levels, secondary phase formation is expected, but low rate of contaminant delivery may significantly reduce degradation rates, and also simplify upstream mitigation.
Future Work

- Complete longer term tests at 10 ppb level (P, As, P+As)
- Perform tests at intermediate contaminant levels (between 10 ppb and 0.5 ppm)
  - Equivalent total dosage (concentration x time)
- Correlate dosing level and time with extent of observed Ni conversion
- Complete electric potential tests
Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program
- NETL: Briggs White, Travis Shultz, and Wayne Surdoval
- PNNL: Clyde Chamberlin, and Alan Schemer-Kohrn
Development of Cathode Contact Materials for SOFC

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July 27-29, 2010
11th Annual SECA Workshop
Pittsburgh, PA
Cathode/Interconnect Contact Materials

Current flow

Cathode
Contact layer
Protective Coating
Chromia-forming alloy interconnect
Cathode/Interconnect Contact Materials

Requirements:
- High electrical conductivity to reduce interfacial electrical resistance between cathode and interconnect
- Chemical and structural stability in air at SOFC operating temperature
- Chemical compatibility with adjacent materials (perovskite cathode, interconnect coating)
- Adequate mechanical strength and bonding to adjacent components
- Low cost materials and fabrication

Challenges:
- Low processing temperature during stack fabrication (800-1000ºC)
  - Low density results in low intrinsic strength and bond strength, reduced conductance
- Brittle nature of ceramics; Cost/volatility of noble metals

Goal:
- Develop cathode/interconnect contacts with low electrical resistivity and increased mechanical strength
  - Modeling results suggest strengthening of contacts can relieve stresses on seals
Area Specific Resistance (ASR) Measurements

\[ ASR_{\text{cathode-interconnect}} = \Phi(\text{scale, contact material, coatings}) \]

Contact Layers

Current Density: 0.5A.cm\(^{-2}\)

~12psi

Interconnect (coated)

Simulated cathode with dense body and porous surface layers

ASR Stack (3 sets)
Conventional Contact Pastes: LSM, LSCM, LNF and LSCF

Relatively low ASR (with suitable coating on steel)
Conventional contact layers exhibit low intrinsic strength and/or bonding strength.
Approaches

► **Sintering Aids**
  - Reduce the sintering temperature of contact materials to obtain increased density/conductance/strength

► **Reaction-Sintering**
  - Similar to process used to prepare MnCo spinel coatings for steel interconnects
  - Contact material precursor powder contains multiple phases, which react during stack assembly to form a conductive single phase
  - Enthalpy of reaction provides additional driving force (besides surface energy reduction) for densification

► **Transition Layers**
  - Apply to cathode and/or interconnect coating to enhance bond strength of contact material
  - Used in conjunction with either of above approaches
Approaches

► Sintering Aids
  ■ Reduce the sintering temperature of contact materials to obtain increased density/conductance/strength

► Reaction-Sintering
  ■ Similar to process used to prepare MnCo spinel coatings for steel interconnects
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► Transition Layers
  ■ Apply to cathode and/or interconnect coating to enhance bond strength of contact material
  ■ Used in conjunction with either of above approaches
Effect of Sintering Aids on LNF-60/40: Sintering Activity

Dilatometric measurements: Constant heating rate of 3°C/min
Effect of Sintering Aids on LNF-60/40: Electrical Resistance

![Graph showing the effect of sintering aids on LNF-60/40 electrical resistance over time. The graph includes lines representing LNF, LNF+1%Bi₂O₃, LNF+3%Bi₂O₃, and LNF+5%Bi₂O₃. The x-axis represents time in hours (0 to 1200), and the y-axis represents ASR (mOhm-cm²).]
Minimal improvement in density, bond strength

Cross-section SEM images of the samples after the contact ASR measurements:
(a) LNF only, (b) LNF+1mol% Bi₂O₃, (c) LNF+3mol% Bi₂O₃, and (d) LNF+5mol% Bi₂O₃.
Effect of Sintering Aids on LSM-20: Sintering Activity

Dilatometric measurements: Constant heating rate of 3°C/min
Effect of Sintering Aids on LSM-20: Electrical Resistance

[Graph showing the electrical resistance (ASR) over time for different types of LSM-20 with various sintering aids.]
Minimal improvement in density, bond strength

LSM+$\text{B}_2\text{O}_3$

LSM+$\text{BaCuO}_2$

LSM+$\text{Co}_3\text{O}_4$
Sintering Curves of LSCF-6428 with Various Additives

800 900 1000 1100 1200

Temperature (°C)

-0.25 -0.20 -0.15 -0.10 -0.05 0.00 0.05

Linear Sintering Shrinkage $\Delta L/L_0$

Temperature

LSCF
LSCF-Cu
LSCF-Bi
LSCF-B
LSCF-Co
LSCF-Mo

3 mol% additions
Sintering Curves of LSCF with Various Amounts of CuO Additions

LSCF with infiltrated CuO did not show significant difference of sintering activity with powders prepared by mixing LSCF with CuO.
Contact ASR Results of LSCF with Sintering Aid CuO

(441-0.02MC|LSCF-CuO|LSCF)

Will perform SEM to evaluate densification, bonding
Approaches

➤ **Sintering Aids**
- Reduce the sintering temperature of contact materials to obtain increased density/conductance/strength

➤ **Reaction-Sintering**
- Similar to process used to prepare MnCo spinel coatings for steel interconnects
- Contact material precursor powder contains multiple phases, which react during stack assembly to form a conductive single phase
- Enthalpy of reaction provides additional driving force (besides surface energy reduction) for densification

➤ **Transition Layers**
- Apply to cathode and/or interconnect coating to enhance bond strength of contact material
- Used in conjunction with either of above approaches
Reaction Sintering

- Successfully used in fabricating MnCo spinel coatings

\[ MnO + Co + 3.5O_2 \rightarrow 2(Mn_{0.5}Co_{0.5})O_4 \]

- Driving force for densification:
  - Reduction of surface energy (~75 J/mol)
  - Enthalpy of formation (~500 kJ/mol)

- 2 methods:
  - Oxidation/Reduction
    - Reduction of complex oxide to binary oxides, metals
    - Re-oxidation to simultaneously densify coating and form complex oxide
  - Direct fabrication from precursor oxides and/or metals
    - Single oxidation heat treatment
Primary systems of interest

- Reaction sintered $(\text{Ni,Co})O_x$ with fillers (tailor CTE, reduce cost)

- Reaction sintered $\text{Mn}_{1.5}\text{Co}_{1.5-x}\text{Cu}_x\text{O}_4$
Reaction-Sintered Ni-Co Oxide (Ni:Co=1:2)
Reaction Sintered (Ni,Co)O\textsubscript{x}

► Reduced (Ni, Co) O\textsubscript{x}
  ■ 5 compositions with Ni: Co=1:2, 1.25:1.75, 1.5:1.5, 1.75:1.25 and 2:1

► Characterization
  ■ Phase analysis (XRD)
  ■ CTE (Dilatometry)
  ■ Electrical Conductivity
  ■ ASR
  ■ Microstructure
  ■ Mechanical Strength

► Approach:
  ■ Select optimum (Ni,Co)O\textsubscript{x} composition
  ■ Add alloying elements if needed for higher conductivity
  ■ Add fillers to reduce cost; also can adjust CTE (if needed)
Powders with various Ni:Co ratios were synthesized by GNP process.
Powders were calcined at 850°C for 5h, then attrition-milled for 7h.
The majority of the powder is (Ni,Co)O.
CTE of Ni-Co Oxides

CTE~14.6x10^{-6}

Temperature, °C

Expansion, ΔL/L₀

Ni2Co oxide
Ni1.5Co1.5 oxide
NiCo2 oxide

Will investigate addition of fillers to reduce CTE and cost
Abnormal behaviors for Ni2Co and NiCo oxides were observed, with current density over 0.1A/cm² resulting in oscillating ASRs.
# New Compositions in Mn-Co-Cu System

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Compositions Mn:Co:Cu</th>
<th>Current Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide Powders</td>
<td>1.5:1.41:0.09 (3mol% Cu)</td>
<td>Powder synthesis and reduction</td>
</tr>
<tr>
<td></td>
<td>1.5:1.35:0.15 (5mol%Cu)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5:1.2:0.3 (10mol%Cu)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.5:1.05:0.45 (15mol%Cu)</td>
<td></td>
</tr>
<tr>
<td>Metal Mixtures</td>
<td>Same as oxide powders</td>
<td>Ball milling</td>
</tr>
</tbody>
</table>

Characterization:
- Phase analysis (XRD)
- CTE (Dilatometry)
- Electrical Conductivity
- ASR
- Microstructure
- Mechanical Strength

Approach: Select optimum composition, investigate fillers to reduce cost and adjust CTE (if needed)
XRD of dense bars of $\text{Mn}_{1.5}\text{Co}_{1.5-x}\text{Cu}_x\text{O}_4$ Oxides after sintering shrinkage tests

Green: $\text{Cu}=0.09$
Red: $\text{Cu}=0.3$
Blue: $\text{Cu}=0.45$

* $\text{AB}_2\text{O}_4$ spinel

Non-spinel peaks ($\text{CuO}_x$) appear when $x=0.45$
CTE Curves of Mn$_{1.5}$Co$_{1.5-x}$Cu$_x$O$_4$ Oxides

<table>
<thead>
<tr>
<th>Cu Concentration</th>
<th>Thermal expansion coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.09</td>
<td>1.18E-05</td>
</tr>
<tr>
<td>x=0.3</td>
<td>1.28E-05</td>
</tr>
<tr>
<td>x=0.45</td>
<td>1.33E-05</td>
</tr>
</tbody>
</table>

% Shrinkage vs. Temperature, °C
SEM Images of Reduced Mn$_{1.5}$Co$_{1.5-x}$Cu$_x$O$_4$ Powders as Contact Pastes (800°C for 100hrs)
ASR Test Results for Mn-Co-Cu Contacts
Approaches

► **Sintering Aids**
  - Reduce the sintering temperature of contact materials to obtain increased density/conductance/strength

► **Reaction-Sintering**
  - Similar to process used to prepare MnCo spinel coatings for steel interconnects
  - Contact material precursor powder contains multiple phases, which react during stack assembly to form a conductive single phase
  - Enthalpy of reaction provides additional driving force (besides surface energy reduction) for densification

► **Transition Layers**
  - Apply to cathode and/or interconnect coating to enhance bond strength of contact material
  - Used in conjunction with either of above approaches
Transition Layer to Enhanced Bonding Strength between Cathode and Contact Layer

- Approach: Co-sintered transition layers may help to increase bonding strength between interconnect
- Example: Co-sinter thin layer of contact material on cathode during cathode sintering heat treatment
- Enhanced chemical bonding of like materials may strengthen cathode/contact interface
Measurement of Mechanical Properties of Interconnect/Contact/Cathode Structure
Effect of Cathode Surface Morphology on Cathode/Interconnect Bond Strength

Tensile Strength (lbs)

<table>
<thead>
<tr>
<th>LSM #1</th>
<th>LSM #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6</td>
<td>23.0</td>
</tr>
<tr>
<td>0.0</td>
<td>13.0</td>
</tr>
<tr>
<td>0.7</td>
<td>40.6</td>
</tr>
<tr>
<td>0.0</td>
<td>25.0</td>
</tr>
<tr>
<td>1.1</td>
<td>71.1</td>
</tr>
<tr>
<td>10.6</td>
<td>6.8</td>
</tr>
</tbody>
</table>
LSM-20 layer #1

Image Surface Area Difference: 12.279%
LSM-20 layer #2

Image Surface Area Difference: 18.055%
Summary and Future Work

- Sintering aids can provide some improvement to sintering activity of candidate contact materials at stack fabrication temperatures.
- Reactive sintering approaches are being applied to Ni-Co oxide and Mn-Co-Cu oxide systems.
- Above approaches result in very low cathode-to-interconnect ASRs.
- Transition layers may reduce contact resistance and reinforce bonding strength between cathode and interconnect.
- Tensile testing of cathode/contact/interconnect structures has been initiated.
  - Determine “weak link”: bulk or interfacial bonding
  - Effects of cathode/coating surface morphology
  - Effects of contact materials composition/processing
Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program
- NETL: Briggs White, Travis Shultz, and Wayne Surdoval
- PNNL: Jim Coleman, Shelley Carlson, Nat Saenz, Rick Williford
Development of SOFC Interconnects and Coatings

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Richland, WA 99352

July 27-29, 2010
11th Annual SECA Workshop
Pittsburgh, PA
Presentation Outline

► Objectives
► Background
  ▪ AISI 441
  ▪ Spinel coatings for steel interconnects
► Results:
  ▪ Performance of Ce-modified MnCo spinel-coated AISI 441
  ▪ Effect of alloy surface treatments
  ▪ Optimization of Ce-modified MnCo spinel coatings
  ▪ Alternative coating compositions
► Conclusions
► Future Work
► Acknowledgements
Objectives

► Global Objectives
  ▪ Develop cost-effective, optimized materials and fabrication approaches for intermediate temperature alloy-based SOFC interconnects
  ▪ Identify, understand, and mitigate degradation processes in alloy-based interconnects

► Specific Objectives
  ▪ Improved understanding of performance of Ce-modified (Mn_{0.5}Co_{0.5})_3O_4 spinel coatings on AISI 441 steel
    ◆ ASR, oxidation behavior, scale adhesion at 800 and 850ºC
  ▪ Evaluation of alloy surface treatments
    ◆ Collaborations with Allegheny Ludlum and NETL-Albany
  ▪ Optimization of Ce-modified (Mn_{0.5}Co_{0.5})_3O_4 spinel coatings
    ◆ Ultrasonic spray process; effect of coating thickness
  ▪ Evaluation of cost reduction approaches
    ◆ Reduced Co content to lower coating cost
    ◆ Metallic precursors
Candidate Interconnect Alloy: AISI 441

- Ferritic stainless steel: Good CTE match to other components; Electrically conductive Cr-based oxide scale
- Inexpensive - Manufactured via conventional melt metallurgy
  - No vacuum processing required
- Similar to AISI 430, but additions of Nb and Ti improve high temperature strength and prevent formation of insulating SiO\(_2\) layer at alloy/scale interface
- Similar to all other FSS, relatively high oxidation rate at SOFC operating temperatures (and volatility of Cr) indicates need for protective coating
- Also, relatively weak scale adherence (no RE in alloy)

Typical Analysis:

<table>
<thead>
<tr>
<th>Designation</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Nb</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 441</td>
<td>18</td>
<td>0.35</td>
<td>0.30</td>
<td>0.01</td>
<td>0.05</td>
<td>0.34</td>
<td>0.023</td>
<td>0.002</td>
<td>0.22</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>AISI 430</td>
<td>16-18</td>
<td>≤1.0</td>
<td>≤0.12</td>
<td></td>
<td></td>
<td>≤1.0</td>
<td>≤0.04</td>
<td>≤0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crofer 22 APU</td>
<td>23.0</td>
<td>0.4-0.8</td>
<td>0.030</td>
<td>≤0.02</td>
<td></td>
<td>≤0.02</td>
<td>0.02</td>
<td>0.050</td>
<td>≤0.2</td>
<td></td>
<td>0.04-0.20</td>
</tr>
</tbody>
</table>

Sources: Allegheny Technologies, Inc.; Thyssen Krupp
Ce-modified \((\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4\) Spinel Coatings

- High electrical conductivity
  \(~60\text{ S/cm at } 800^\circ\text{C}\)
  \[
  \sigma_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} = 10^{3\text{ to } 4}\sigma_{\text{Cr}_2\text{O}_3}
  \]
- Good CTE match to FSS and anode-supported cells
  \[
  \text{CTE}_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} \approx 11 \times 10^{-6} \text{ K}^{-1}, 20 - 800^\circ\text{C}
  \]
- Chemically compatible with contact pastes, cathodes
- Cr-free composition
- CeO\(_2\) inclusions improve scale adhesion of alloy substrate (rare earth effect)

Coating Provides:

- Reduced Cr volatility from steel
- Improved scale adhesion

Reduced oxidation rate of alloy:

<table>
<thead>
<tr>
<th>(k_p) ((\text{g}^2/\text{cm}^4\cdot\text{s}))</th>
<th>800(^\circ\text{C})</th>
<th>850(^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-MC coated 441</td>
<td>(2 \times 10^{-14})</td>
<td>(1 \times 10^{-13})</td>
</tr>
<tr>
<td>Bare 441</td>
<td>(5 \times 10^{-14})</td>
<td>(3 \times 10^{-13})</td>
</tr>
</tbody>
</table>
Performance of Ce-modified $(\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4$ spinel coatings on AISI 441 steel
Area Specific Resistance (ASR) Measurements

\[ \text{ASR}_{\text{cathode–interconnect}} = \Phi(\text{scale}, \text{contactmaterial}, \text{coatings}) \]

- Interconnect (coated)
  - Simulated cathode with dense body and porous surface layers

Contact Layers
- Current Density: 0.5A.cm\(^{-2}\)
- ~12psi

ASR Stack (3 sets)
Long-Term ASR measurements: 800 and 850°C

800°C except where noted.
ASR Testing including Thermal Cycling

![Graph showing ASR (mOhm-cm²) over time (Hours) for different materials at 800°C.](image)

- Ce02MC LSM 800C
- Ce05MC LSM 800C
- Ce05MC LSCF 800C
SEM/EDS/EBSD Analysis

Ti-doped Chromia
Hexagonal Corundum structure
Cr-Mn spinel
Cubic

Cr (red) - Mn (green) - Co (blue)

40μm
Effects of Temperature on Scale Growth and Adhesion

Spallation observed (scale/alloy interface) after 1670 hours at 850ºC
No evidence of spallation in long term ASR test (no thermal cycling)
Effect of Surface-Treatment on Oxidation Behavior of Spinel-coated 441

800°C

- **Allegheny Ludlum**: Mill Reference, De-siliconized, Surface blasted, Surface ground, Temper rolled
- **NETL Albany**: Ce surface treatment
- All coated with Ce-MnCo spinel, heat-treated in air at 800°C for up to 10,000 hours
  - As expected, no spallation after 2000 hours

<table>
<thead>
<tr>
<th>Surface Treatment</th>
<th>Ave. Scale Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill Reference (1200 grit)</td>
<td>2.23 ± 0.17</td>
</tr>
<tr>
<td>De-siliconized</td>
<td>1.71 ± 0.14</td>
</tr>
<tr>
<td>Surface ground</td>
<td>3.83 ± 0.97</td>
</tr>
<tr>
<td>Surface blasted</td>
<td>3.27 ± 0.40</td>
</tr>
<tr>
<td>Temper rolled</td>
<td>1.55 ± 0.18</td>
</tr>
<tr>
<td>Ce Treatment</td>
<td>3.27 ± 0.68</td>
</tr>
</tbody>
</table>
Effect of Surface-Treatment on Oxidation Behavior of Spinel-coated 441 (continued)

 ► 850°C
  ▪ As-received 441 w/ Ce-MC spinel coating
    ▪ Typically observe spallation at scale/alloy interface after 1000 - 1500 hours
  ▪ NETL-Albany Ce surface treatment
    ▪ No spallation observed on uncoated, surface treated coupons after 5100 hours, possibly due to enhanced RE effect from higher Ce level at surface
    ▪ Testing of spinel-coated coupons in progress
  ▪ Shot-peened 441 (Metal Improvement Co.)
    ▪ No spallation observed on uncoated coupons after 2500 hours or on coated coupons after 2000 hours
    ▪ Testing of spinel-coated coupons in progress
  ▪ Allegheny Ludlum surface treatments w/ spinel coating
    ▪ To be initiated in near future

► Post-test analysis:
  ▪ Evaluate scale adhesion
    ▪ Visual inspection for spallation
    ▪ Indentation for quantification of interfacial strength to allow for prediction of interconnect lifetime
Optimization of Ce-modified $(\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4$ spinel coatings
Ultrasonic spray coating: Optimization of Spray Parameters

Design Of Experiment Optimization (DOE Optimization) With Taguchi, Grey-Taguchi method and ANOVA (Analysis of Variance)

Wide Mode
- Viscosity: 5cp
- Coating speed: 100mm/sec
- Head height: 35mm
- Ink feeding rate: 1ml/sec
- Air flow rate: 30ml/sec

Narrow Mode
- Viscosity: 5cp
- Coating speed: 100mm/sec
- Head height: 15mm
- Ink feeding rate: 0.5ml/sec
- Air flow rate: 40ml/sec
Ultrasonic spray process currently used for aluminization and spinel coating of interconnects/frames for PNNL's single/multiple stack fixture testing
Optimization of Ce-MC Spinel Coatings

- Adaptation of ultrasonic spray process to Ce-modified spinel powder
  - Extension of previous optimization of fabrication process for unmodified spinel

- Effect of coating thickness on oxidation resistance of AISI 441
  - Two studies in progress: Sprayed coatings, Screen-printed coatings
    - ~5, 10, 20 microns thick
    - Oxidation for 2000 hours
Alternative Interconnect Coating Compositions

- Reduce Co content to reduce coating cost
  - Mn oxide (Cobalt-free)
  - Mn-Co oxide coatings: Reduced Co content relative to \((\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_4\)
Initial Study: ASR of Mn oxide coated 441 at 800°C

ASR of Mn coating on 441

Slope = 4.15 \times 10^{-3} \text{ m\Omega-cm}^2/\text{h}
Oxide scale thickness as f(time)

Rapid scale growth under Mn oxide coating: Intrinsic or bad microstructure?
Optimization of Mn oxide Protective Coatings on AISI 441

- Densification study of Mn oxide coatings prepared from Mn powder
  - Effect of particle size distribution
  - Effect of binder system and binder/solids ratio
- Optimization via SEM analysis
- Evaluation via electrical resistance testing (ASR)
Effect of particle size
SEM of Mn oxide coating on AISI 441

As received powder, <10um
milled powder, <5um
milled powder, <3um

The coatings prepared using Mn powder with smaller particle size showed more uniform surface
ASR Evaluation of Mn Coated 441 Samples

ASR increased linearly with time on oxidation even though the improved Mn oxide coatings appeared to be gas tight.
Cross-section SEM Images of Mn Coated 441 after ASR Measurement

Mn < 5\(\mu m\)

Mn < 10\(\mu m\)

Composition from SEM

Mixed Mn powder (30\% <3\(\mu m\)+70\%10\(\mu m\))
Alternative Mn-Co oxide coatings:

Reduced Co content relative to $(\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4$
SEM Images of Mn-Co Oxide Coated 441
(after ASR measurements at 800°C for ~500hrs)

Prepared from metal precursors according to listed molar ratios
ASR Measurement Data / 800°C

Specific Resistance (mOhms-cm²)

- Mn-only
- Mn20Co1
- Mn10Co1
- Mn6Co1

Time (hours)
Effect of Co Content on Rate of ASR Increase

![Graph showing the effect of Co content on the rate of ASR increase. The graph plots ASR slope (mOhms-cm$^2$/hr x 103) against Co/(Co+Mn). The slope decreases as Co/(Co+Mn) increases.]
Summary

- MnCo spinel coatings on AISI 441 exhibit excellent long-term performance at 800ºC.

- At 850ºC, MnCo spinel coatings exhibit low, stable ASR obtained after 4,000 hours.
  - Scale adhesion issues observed at 850ºC.
  - Additional studies/approaches, including alloy surface treatments, are in progress.

- Ultrasonic spray process for application of MnCo spinel coatings has been optimized.

- MnCo oxide coatings with substantially reduced Co content appear to be promising approach for reducing coating cost.
  - Mn oxide coatings did not provide low, stable ASR.
Future Work

► Continue to evaluate long-term stability and electrical performance of Ce-MC spinel-coated 441 steel
  ■ Evaluate at 800 and 850°C
  ■ Long-term evaluation in stack test fixture

► Evaluate effect of alloy surface treatments on oxidation and spallation resistance of Ce-MC coated 441

► Optimize thickness, and automated ultrasonic spray process, for Ce-modified spinel coatings

► Reduce cost of protective coatings through elimination of reducing heat treatment and/or minimization or elimination of Co content
Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program
- NETL: Briggs White, Travis Shultz, and Wayne Surdoval
- NETL-Albany: Paul Jablonski
- ATI Allegheny Ludlum: Matt Bender
- PNNL: Jim Coleman, Shelley Carlson, Nat Saenz, Dan Edwards, Clyde Chamberlin, and Alan Schemer-Kohrn
Compliant glass seal development at PNNL

Y-S Matt Chou, E. Thomsen, J-P Choi, W. Voldrich, and J. W. Stevenson

- Introduction and objectives
- Experimental: materials and test fixture
- Q1: chemical compatibility study with YSZ coating
- Q2: electrical stability under 0.8V loading
- Q3: volatility evaluation in dual environment
- Q4: validation in stack test fixture

This work is funded by US DOE SECA Core Technology Program
Compliant versus refractory sealing glass

\[ \sigma = E \Delta \alpha \Delta T \]

Compliant sealing glass

Data provided by ORNL 850h aged

Advantage:
Low stress or relaxation, healing?
Wetting,

Disadvantage:
Metal-stable, narrow T window, volatile, reactive/corrosive?
Crack healing

- Commonly observed in glass at elevated temperatures.
- 3 mechanisms proposed: diffusion-driven thermal healing, adhesion from intermolecular forces, and chemical reaction at crack-tip

SCN-1 indented @ 2 kg
Fired to 700°C held for 6min
Objectives

- To conduct a comprehensive study of a commercial compliant sealing glass in terms of thermal, chemical, electrical, physical, and mechanical stability in SOFC environments.
- To apply compliant glass in stack test fixture for validation.
Experimental: sample preparation

1. Thickness of spacer rings ~220 μm
2. SCN-1 glass mixed with ESL450 binder to form paste
Experimental: stability and high-temp leak test

- **Inconel600 load block (2”x2”) with incoming and outgoing tubing**
- **SCN-1 or Ag/mica hybrid seal with known leak rate or plain Ag foils**
- **ZrO₂ or mica ring spacer**
- **Compliant glass**
- **PEN cell or bilayer (1.4”φ)**
- **Al-SS441 (2”x2”x0.06” with a central hole)**
- **porous Al₂O₃ support**
- **Corrugated Ni-mesh to mimic some contact load**
- **Load (~12 psi)**
- **Al₂O₃ pipe**
Microstructure of YSZ and Al$_2$O$_3$ coated SS441
Q1: chemical compatibility with YSZ and Al₂O₃ coated SS441 in dual environment at 750°C

SCN-1 glass showed good thermal and thermal cycle stability at 700, 750, and 800°C.

Leak test during isothermal ageing

Leak test during thermal cycling
Post-mortem analysis: glass/YSZ electrolyte interface near air side
Post-mortem analysis: glass/YSZ coating interface near air side
Minimal crystallization during pure thermal cycling

- **Ceramic bi-layer**
- **Aluminized-441**
  - 800°C 20 cycles
- **Ceramic bi-layer**
- **Aluminized-441**
  - 750°C 20 cycles
More crystallization during isothermal ageing

- 800°C/1000h plus 10 cycles
- 750°C/1000h plus 10 cycles
More crystallization during isothermal ageing

700°C/1000h plus 10 cycles: Ba-silicate and K-Al silicate

Aluminized-441

Ceramic bi-layer

<table>
<thead>
<tr>
<th>oxide</th>
<th>mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>1.84</td>
</tr>
<tr>
<td>BaO</td>
<td>3.57</td>
</tr>
<tr>
<td>CaO</td>
<td>3.96</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>0.09</td>
</tr>
<tr>
<td>K2O</td>
<td>7.07</td>
</tr>
<tr>
<td>MgO</td>
<td>1.03</td>
</tr>
<tr>
<td>Na2O</td>
<td>7.83</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.45</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.01</td>
</tr>
<tr>
<td>ZrO2</td>
<td>0.01</td>
</tr>
<tr>
<td>Li2O</td>
<td>0.05</td>
</tr>
<tr>
<td>B2O3</td>
<td>0.03</td>
</tr>
<tr>
<td>SiO2</td>
<td>74.06</td>
</tr>
</tbody>
</table>
Q2: Electrical stability test

Hybrid mica

SCN glass

SS441

Inconel

5%H₂ in 5%H₂ out

Power supply
And sensor

resistor

+ sense
+ out
-
-out
- sense

load

+ V

- V

V

5%H₂ in

Hybrid mica

SS441

Al2O3

SCN glass
Chemical compositions

Alkali ions (Na\(^+\) and K\(^+\)) are major charge carriers for conductivity in silicate glasses. Two concerns: **liquid glassy phases**, and **alkali** effect.

### SCN-1 glass

<table>
<thead>
<tr>
<th>oxide</th>
<th>mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>1.84</td>
</tr>
<tr>
<td>BaO</td>
<td>3.57</td>
</tr>
<tr>
<td>CaO</td>
<td>3.96</td>
</tr>
<tr>
<td>Fe2O3</td>
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<td>K2O</td>
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</tr>
<tr>
<td>MgO</td>
<td>1.03</td>
</tr>
<tr>
<td>Na2O</td>
<td>7.83</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.45</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.01</td>
</tr>
<tr>
<td>ZrO2</td>
<td>0.01</td>
</tr>
<tr>
<td>Li2O</td>
<td>0.05</td>
</tr>
<tr>
<td>B2O3</td>
<td>0.03</td>
</tr>
<tr>
<td>SiO2</td>
<td>74.06</td>
</tr>
</tbody>
</table>

### Refractory glass YSO77

<table>
<thead>
<tr>
<th>oxide</th>
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</thead>
<tbody>
<tr>
<td>Y2O3</td>
<td>6.00</td>
</tr>
<tr>
<td>BaO</td>
<td>6.00</td>
</tr>
<tr>
<td>SrO</td>
<td>42.50</td>
</tr>
<tr>
<td>B2O3</td>
<td>10.00</td>
</tr>
<tr>
<td>SiO2</td>
<td>35.50</td>
</tr>
</tbody>
</table>
Comparison of crystallized glass (YSO75) and less crystallized glass (G18) with as-received crofer

G18 (less crystallized compared to refractory glass) showed rapid decrease in resistivity, suggesting dissolution/diffusion of metal ions from crofer 22 APU.
Electrical stability with YSZ coated Aluminized SS441

Tested with flowing 5%H$_2$ (≈3%H$_2$O) and a DC load of 0.8V across glass. Stable apparent resistivity (calculated by ohm x area/thickness neglecting coating contribution) indicates coatings remain intact (compatible) with SCN-1 glass.
Microstructure of 800°C/1000h electrically tested sample with YSZ coating
Chemical compatible with YSZ coating

No reaction and segregation of alkalis at interfaces under DC loading
electrical stability with plain SS441

SCN glass with as-received SS441 @0.8V

- 800°C
- 750°C
- 700°C

Apparent resistivity, ohm-m
hrs
### Presence of Fe in SCN-1 glass

<table>
<thead>
<tr>
<th>spot #</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67.09</td>
<td></td>
<td></td>
<td></td>
<td>26.46</td>
<td>0.35</td>
<td>4.90</td>
<td></td>
<td></td>
<td></td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>65.41</td>
<td></td>
<td></td>
<td></td>
<td>13.52</td>
<td>0.84</td>
<td>19.43</td>
<td>0.51</td>
<td>0.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>66.89</td>
<td>0.63</td>
<td>0.25</td>
<td>1.55</td>
<td>27.67</td>
<td>1.92</td>
<td>0.14</td>
<td>0.14</td>
<td>0.53</td>
<td>0.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>64.84</td>
<td>2.24</td>
<td>0.61</td>
<td>1.54</td>
<td>24.90</td>
<td>3.32</td>
<td>0.86</td>
<td></td>
<td>0.70</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>65.83</td>
<td>0.95</td>
<td>0.31</td>
<td>1.28</td>
<td>28.26</td>
<td>2.04</td>
<td>0.37</td>
<td>0.10</td>
<td>0.38</td>
<td>0.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>64.44</td>
<td>2.43</td>
<td>0.69</td>
<td>1.25</td>
<td>24.84</td>
<td>3.17</td>
<td>1.23</td>
<td>0.15</td>
<td>0.50</td>
<td>1.31</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fe at% = 0.06% SCN-1

![Image of TEM analysis showing the presence of Fe in SCN-1 glass with spots labeled and elemental compositions listed.]
Electrical stability with Aluminized SS441

Tested with flowing 5%H₂ (~3%H₂O) and a DC load of 0.8V across glass. Stable apparent resistivity indicates coatings remain intact (compatible) with SCN-1 glass.
**Q3: volatility issue**

Weight loss vs. time data provided by ORNL of SCN-1 pellets at 800°C in stagnant air or flowing steam
Linear volatility rate (R) was averaged for 5000h (steam) or 10000h (air)

<table>
<thead>
<tr>
<th>Test cond.</th>
<th>Avg. volatility (g/mm²-hr)</th>
<th>Total wt. loss (%) in 40,000h</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ-air</td>
<td>6.33x10⁻⁹</td>
<td>1.7</td>
</tr>
<tr>
<td>YSZ-steam</td>
<td>9.90x10⁻¹⁰</td>
<td>0.3</td>
</tr>
<tr>
<td>Al₂O₃-air</td>
<td>8.04x10⁻⁹</td>
<td>2.1</td>
</tr>
<tr>
<td>Al₂O₃-steam</td>
<td>1.08x10⁻⁹</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Total weight loss %

\[
\text{Total weight loss \%} = \frac{(R \cdot L \cdot T \cdot 40,000 \cdot 100)}{(\rho \cdot L \cdot T \cdot W)}
\]
Q4: evaluate glass in stack test fixtures-thermal cycle stability

- Objectives: *thermal cycle stability*, containment/spreading issue, and volatile species interaction in base-line stability for 1000h
- Reasonable consistent OCV at 800°C (1.040 V) theoretical 1.048V over 10 deep thermal cycles (~50°C to 800°C in 3h, 800°C/3h, 18h to ~50°C).
Q4: evaluate glass in stack test fixtures-containment/spreading issue
Compliant SCN-1 glass was evaluated comprehensively in thermal cycles stability, thermal stability, and chemical compatibility with candidate SOFC materials.

The glass demonstrated very good thermal cycle and thermal stability with constant leak rate.

Interfacial characterization showed minimum reaction at YSZ electrolyte and YSZ coating interfaces.

Electrical stability test under DC load indicated insulating nature of the glass and no segregation of alkalis. Crystallization was similar as 1000h stability test without DC loading.

Volatality estimation indicated minimal glass loss in 40,000h operation.

Preliminary evaluation in stack test fixture showed good thermal cycle stability without containment/spreading issue.
Future work

- Optimize YSZ coating in terms of thickness with collaboration with modeling to stress minimization.
- Evaluate stability (1000h) in stack test fixtures at various temperatures with emphasis on interaction of volatile species with active SOFC components.
- Modify processing and sealing conditions to eliminate large pore formation.
- Collaborate with modeling to predict microstructure evolution effect on compliance, thermal and physical properties.
- Continue evaluating the spreading/containment issue, and predict the life-time flow under differential pressure.
- Design new window frame for robust sealing.
Modeling Tools for SOFC Design and Analysis

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Brian Koeppel, Kurt Recknagle, Xin Sun, Elizabeth Stephens, Kevin Lai, Emily Ryan
Pacific Northwest National Laboratory
Richland, WA 99352

12th Annual SECA Workshop
Pittsburgh, PA
July 28, 2011
PNNL Modeling Activities: Objectives & Approach

► Objectives

■ Develop integrated modeling tools to:
  ■ Evaluate the tightly coupled multi-physical phenomena in SOFCs
  ■ Allow SOFC designers to perform numerical experiments for evaluation of stack electrochemical, thermal, and mechanical performance
  ■ Aid understanding of materials degradation issues
  ■ Provide wide applicability for industry teams’ to solve their challenging design problems
  ■ Provide technical basis for stack design

► Approach: Multiphysics-based analysis tools

■ SOFC-MP: A multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks
■ Distributed Electrochemistry (DEC) model – Cell level multi-physics model for considering the effects of local properties and conditions on global SOFC performance
■ Targeted evaluation tools for specific cell design challenges
■ Experimental support to provide material property data
PNNL Modeling Tools: Overview

► SOFC-MP
  ■ 2D and 3D multi-physics stack model
  ■ 2D model benchmarked with literature data
► Distributed Electrochemistry (DEC) Model
  ■ 3D multi-physics model of the SOFC electrodes and electrolyte for the investigation of SOFC performance and degradation issues
  ■ Degradation modeling framework
► Cathode Contact Paste Modeling
  ■ FEA model for the simulation of densification behavior in cathode contact materials
► Glass Seal Modeling
  ■ Investigate the behavior of glass seal materials and designs at operating temperatures
► Interconnect Modeling
  ■ Integrated modeling and experimental approach for prediction on interconnect lifetime
SOFC-MP: Multi-Physics Stack Modeling Tool

3D Model

Usage
- Detailed 3D distribution for follow-up structural analysis
- All planar flow configuration including cross-flow

Computes distributions in entire 3D domain
- All planar configurations: Co-flow, counter-flow, and Cross-flow
- Multi-cell configuration (up to 50 cells)

Computations
- Current distribution
- Voltage distribution
- Thermal distribution
  - Used for FEA stress analysis
- Species distribution
- Heat losses

2D Model

Usage
- Tall cell stack
- Fast computation
- Can be integrated to system tools

Computes distributions along the symmetric centerline of the stack
- Co-flow and counter-flow
- Multi-cell configuration (up to 1000 cells)

Computations
- Current distribution
- Voltage distribution
- Thermal distribution
- Species distribution
- Heat losses
2D SOFC-MP Software Release

► Official 2D model released
  ■ NETL can distribute

► User manual for 2D model completed
  ■ Step-by-step instructions on installation, model simulations, solution, and post-processing procedures
  ■ Detailed descriptions of sample cases, including in depth explanation of parameters in the input files

► Includes feedback from users
  ■ Newer version with more robust and faster iteration scheme made available because of request from PNNL users providing vertical team modeling support

► Code usage demonstrated in parametric study on stack temperature uniformity

► * More information available at the poster session
SOFC-MP Rich Features in 2D Model

The module can simulate different flow orientations, cell counts, cell sizes, boundary conditions, fuels, user-defined electrochemistry, reforming, and cell-to-cell variations

- Effect of amount of on-cell reforming
- Effect of on-cell reforming rate on temperature
- Effect of interconnect thickness on temperature
- Effect of local 25% fuel blockage on single cell (#32) current density
- Effect of 2 instrumented measurement plates
  - -21% cell ΔT error from measurement plate
Distributed Electrochemistry (DEC) Model: Modeling SOFC Performance

Technology Challenges

▸ Understand degradation in the electrodes
  ▼ Resolve local conditions in the cell resulting from various operating conditions
  ▼ Investigate the effect of microstructure on cell performance
  ▼ Confidently predict global cell performance for a range of conditions

▸ Increase performance by advanced electrode design

Objectives

▸ Develop a model to predict cell performance based on operating conditions and microstructure
  ▼ Base the performance model on coupled electric potential, charge transfer, and reactive transport
  ▼ Use a modeling approach that enables varying structural parameters
  ▼ Validate the model by comparison with experimental data
  ▼ Simulate microstructural and operational effects on cell performance
DEC Model: Recent Accomplishments

- Developed a 3D multi-physics model of the SOFC electrodes and electrolyte
  - Resolves the electrochemistry throughout the electrode thickness
  - Predicts the global SOFC performance based on local conditions within the electrodes
  - Includes electrode microstructures via an effective properties model
  - Allows for spatially varying microstructural and electrochemical properties
- Validated the DEC model with experimental button cell data at various fuel compositions and operating voltages
- Demonstrated the DEC model’s capabilities to investigate the effects of electrode microstructure on SOFC performance
- Developed a degradation modeling framework for considering the effects of local degradation within the electrodes on the overall SOFC performance

* More information available at poster session
Validation of DEC Model by Comparison with Experimental Button Cell Data

- Experimental data set for binary fuel [Jiang and Virkar 2003]
  - DEC Model shows good agreement with He-H₂ and N₂-H₂ systems
- Highlights model sensitivity to gas diffusion in electrodes
- Good predictions of limiting currents and peak power

<table>
<thead>
<tr>
<th>Binary Fuel</th>
<th>Maximum Difference: DEC model to Experimental Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak Power</td>
</tr>
<tr>
<td>He-H₂</td>
<td>7%</td>
</tr>
<tr>
<td>N₂-H₂</td>
<td>12%</td>
</tr>
</tbody>
</table>

---

He-H₂ fueling

N₂-H₂ fueling
Degradation and Life Prediction of Coated Metallic Interconnects Summary

Motivation: Ensure IC life meets the SECA life time requirement

Goal: Use modeling to predict interconnect life with and without spinel coating under isothermal cooling and thermal cycling

Technical Approach: Develop a combined modeling/experimental approach to enhance spallation resistance; use finite element based modeling tools to evaluate various design issues on spallation driving forces and determine the main factors influencing IC degradation in terms of spallation; and evaluate IC candidate materials

Accomplishments:
- Developed an integrated modeling and experimental approach for IC life prediction:
  - Identified and quantified spallation driving forces
  - Quantified interfacial strength
  - IC life prediction for coated and uncoated Crofer 22
  - Interfacial strength quantification for as-received and surface modified SS441
Doping Coating with Rare Earth Improves Spallation Resistance

- Model determined increase in interfacial strength between oxide scale and substrate when spinel coating was doped with Ce
- Improvement of adhesion also observed experimentally (SECA CTP Materials team)

<table>
<thead>
<tr>
<th></th>
<th>Crofer 22 (0.5 mm thick)</th>
<th>441 Substrate (1.5 mm thick)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bare</td>
<td>Bare</td>
</tr>
<tr>
<td>Coating thickness (µm)</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Scale thickness (µm)</td>
<td>2.41</td>
<td>3.82</td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>395</td>
<td>324</td>
</tr>
</tbody>
</table>
Surface Modification Increases Adhesion Strength – Mechanical Polishing

Initial surface modification studies began with the effects of mechanical polishing on scale spallation of bare specimens.

Model determined that surface quality influenced the interfacial strength.

Bear in mind: this technique increases both interfacial strength and spallation driving force.

Polishing substrate surface became a common practice prior to applying coating on specimens for experimental studies.

<table>
<thead>
<tr>
<th>441 Substrate (1.5 mm thick)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Surface Roughness (Ra)</td>
</tr>
<tr>
<td>Scale thickness (µm)</td>
</tr>
<tr>
<td>Strength (MPa)</td>
</tr>
</tbody>
</table>
Optimizing Cooling Profile to Reduce Spallation Driving Force

- Optimization of cooling profile helps to reduce the interfacial stress, only to a certain extent
- Benefit plateaus to about 6.8% stress reduction

<table>
<thead>
<tr>
<th>Time</th>
<th>Max Shear Stress (MPa)</th>
<th>500°C</th>
<th>600°C</th>
<th>No Creep</th>
</tr>
</thead>
<tbody>
<tr>
<td>10min</td>
<td>362</td>
<td>2.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 h</td>
<td>357</td>
<td>3.5%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 h</td>
<td>348.3</td>
<td>5.8%</td>
<td>347.9</td>
<td>6.1%</td>
</tr>
<tr>
<td>20 h</td>
<td>345.3</td>
<td>6.7%</td>
<td>345.2</td>
<td>6.7%</td>
</tr>
</tbody>
</table>

Temperature ºC

Cooling profile schematic
Reducing IC Substrate Thickness to Reduce Driving Force

Interfacial failure driving force can be reduced by reducing the bulk thickness of SS441. The thicker the substrate, the higher the driving force for spallation.

<table>
<thead>
<tr>
<th>Model Predictions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate thickness</td>
</tr>
<tr>
<td>Coating thickness</td>
</tr>
<tr>
<td>Scale (um)</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>15</td>
</tr>
</tbody>
</table>

*Liu et al., Journal of Power Sources 189 (2009) 1044–1050*

Experimental Validation

Results provided by Materials team
Contact Modeling Task Summary

**Motivation:** Cathode contact layer is weak and must meet multiple design criteria

**Goal:** Use modeling to understand *in situ* low temperature formation of the cathode contact layer and its influence on the stack’s mechanical reliability

**Technical Approach:** Develop FEA modeling approach to simulate the densification behavior of cathode contact materials and determine their influence on the stack thermal-mechanical stress state during formation

**Task Accomplishments:**
- Determined expected stress levels for contact layer in the cell
- Verified reduced seal loads by load path modification
- Implemented constitutive model for constrained sintering
- Supported test cell development
- Developed method to extract model input parameters from Task 1 material experiments
- Simulated contact materials and effects of design parameters on densification in stacks
Contact Modeling: Realistic Multi-Cell Stack Geometry

2-hr Free Sintering

- LSCF-based contact material
- Heat treatment schedule modeled:
  - 2 hr @ 930°C
  - Operating temperature distribution
  - Shutdown to 25°C

- Stack operating conditions:
  - 400 mA/cm²
  - 97% H₂ fuel
  - 80% UF
  - 12% UA
  - 700°C furnace

- Stack temperature 703°C to 823°C with 120°C ΔT

Contact Material Locations
Symmetric Half-cell Geometry
Operating Temperature

Sintering Temperature (C) vs Final Relative Density

Initial Relative Density
LSM + 3mol% Cu)+BaCuO₂
LSCF + 3mol% CuO
LNF + 3mol% Bi₂O₃

800 900 1000
Final Relative Density

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965
Contact Modeling: Smaller Initial Grain Size Improves Density

- Densification with nominal 0.4 μm grain inadequate
  - Maximum density only 72%
  - Distribution non-uniform across the cell
    - Corners and edges restricted by stiff surrounding frame; relative spring stiffness between frame and active area will be critical design parameter
- Grain size < 0.5 μm substantially improved density but geometry influence remained

![Contact Interface Stress](chart)

<table>
<thead>
<tr>
<th>Initial Grain Size (μm)</th>
<th>Max Final Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>59%</td>
</tr>
<tr>
<td>0.7</td>
<td>63%</td>
</tr>
<tr>
<td>0.4</td>
<td>72%</td>
</tr>
<tr>
<td>0.2</td>
<td>91%</td>
</tr>
<tr>
<td>0.1</td>
<td>98%</td>
</tr>
</tbody>
</table>
Seal Materials Modeling: Task Summary

**Motivation:** To explore the behavior of seal materials at operating temperatures and better understand the interplay of material microstructure and properties on stresses and degradation.

**Goal:** Use modeling to assist the development of a reliable sealing system to achieve the stack-level design requirements.

**Technical Approach:** Develop time and temperature dependent seal models to use as building blocks in stack-level seal performance simulations and investigate the effects of various design parameters on multi-cell stacks.
Seal Modeling: Predicted In-Stack Behavior of Pure Glass Sealants

- Pure glass sealant will flow out without stopper.
- The stress in the glass and its interface with IC and PEN are very small at the working temperature.
- Cooling-induced stress in the glass and its interface with IC and PEN are relatively large, and potential interfacial damage will occur.
- Gap between ceramic stopper and glass will reduce the stress in the glass and interface of glass and IC/PEN.
- Scale up of cell will increase the stress level in glass as well as its interfaces with IC and PEN.
Studied the effects of ceramic stoppers on the geometric stability of the self-healing seals in a simulated stack environment using creep analysis:

- Stoppers will help the glass seal to maintain geometry during operation.

Studied effects of various interfaces of PEN/Stopper, IC/Stopper, and Stopper/glass on the interfacial stresses upon cooling:

- Weak interfaces between stopper and glass always lead to lower stresses on glass/PEN and glass/IC interfaces.
- In most cases, localized high stress regions are predicted for the edge of the glass seal: possible localized failure.
PNNL Modeling Summary

- **SOFC-MP**: 2D and 3D multi-physics stack models
  - 2D Software and manual released
- **DEC Model**: 3D multi-physics cell model
  - Resolves the local conditions within the cell and predicts SOFC global performance from cell level electrochemistry
- **Contact Modeling**: Continuum sintering model suitable for stack modeling
  - Good free sintering densification of candidate materials possible for T<1000°C
  - Reduced initial grain size improved densification with only a small negative impact on predicted stresses at operation and shutdown
- **Interconnect Modeling and Experimentation**: Integrated modeling and experimental approach for IC life prediction
  - Spallation resistance can be improved by increasing the interfacial strength between the oxide scale and substrate
  - Spallation driving force can be reduced through cooling profile optimization and by reducing IC thickness
- **Seal Modeling**:
  - Predicted the outflow pattern for pure glass seal with different initial glass height (volume) in PNNL leak test setup
  - Studied the possible self-healing mechanisms/driving forces for glass seal:
    - Role of pressure on crack healing rate
    - Role of gravity on healing rate for thin glass seal
Current/Future Modeling Activities

➤ Simulation of long-term and transient degradation behaviors
  ▪ DEC Model: Implement secondary reactions (degradation)
  ▪ SOFC-MP: Include transient degradation of state variables & coupling to DEC model

➤ Improved accessibility to software tools
  ▪ Transfer DEC model to open source tool (e.g. OpenFoam)
  ▪ Transfer SOFC-MP to a more flexible framework for interface with FEA solvers beyond MSC MARC

➤ Contact Modeling:
  ▪ Identify/test a specimen configuration for validation of constrained sintering simulations
  ▪ Adapt model to other volumetric behaviors in the stack (e.g. anode reduction, seal formation, re-oxidation tolerance)

➤ Interconnect Modeling:
  ▪ Quantification of interfacial strength for varying surface modified SS441
  ▪ Life prediction for coated and surface modified SS441

➤ Seal Modeling:
  ▪ Continue to quantify the self-healing mechanisms for SCN glass and develop temperature dependent constitutive models for SCN glass considering aging/crystallization
  ▪ Use modeling tools to virtually examine the various concepts of engineering seal design with glass/stopper sealing system in multi-cell stack
Development of Cathode-Interconnect Contact Materials for SOFC


Pacific Northwest National Laboratory
Richland, WA 99352

July 26-28, 2011
12th Annual SECA Workshop
Pittsburgh, PA
Cathode-Interconnect Contact Materials

Current flow

Interconnect
Anode
Electrolyte
Cathode
Interconnect
Anode

Contact layer
Protective Coating
Chromia-forming alloy interconnect

Cathode
Contact Layer
Protective Coating Scale
Interconnect
Cathode/Interconnect Contact Materials

**Requirements:**
- High electrical conductivity to reduce interfacial electrical resistance between cathode and interconnect
- Chemical and structural stability in air at SOFC operating temperature
- Chemical compatibility with adjacent materials (perovskite cathode, interconnect coating)
- Adequate mechanical strength and bonding to adjacent components
- Low cost materials and fabrication

**Challenges:**
- Low processing temperature during stack fabrication (800-1000ºC)
  - Low density results in low intrinsic strength and bond strength, reduced conductance
- Brittle nature of ceramics; Cost/volatility of noble metals

**Goal:**
- Develop cathode/interconnect contacts with low electrical resistivity and increased mechanical strength
  - Modeling results suggest strengthening of contacts can relieve stresses on seals
Key Characterization Methods

ASR

Tensile Bond Strength

XRD

SEM

TGA/DSC

Dilatometer
Area Specific Resistance (ASR) Measurements

\[ ASR_{\text{cathode-interconnect}} = \Phi(cathode, contactmaterial, coatings) \]

Simulated cathode with dense body and porous surface layers

Current Density: 0.5A.cm\(^{-2}\)

ASR Stack (3 sets)
Conventional Contact Pastes: LSM, LSCM, LNF and LSCF

Relatively low ASR (with suitable coating on steel)
Conventional contact layers exhibit low ASR but also low intrinsic strength and bond strength
Approaches to Improve Contact Strength

► Sintering Aids
  ■ Goal: Reduce the sintering temperature of contact materials (LSM, LNF, LSCF) to obtain increased density/conductance/strength

► Reaction-Sintering
  ■ Similar to process used to prepare MnCo spinel coatings for steel interconnects
  ■ Contact material precursor powder contains multiple phases, which react during stack assembly to form a conductive single phase
  ■ Enthalpy of reaction provides additional driving force (besides surface energy reduction) for densification
Approaches to Improve Contact Strength

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Sintering Curves of LSCF with Various Additives

LSCF with CuO exhibited the highest sintering activity.
Sintering Curves of LSCF with Various Amounts of CuO Additions

LSCF with infiltrated CuO did not show significant difference of sintering activity with powders prepared by mixing LSCF with CuO.
Contact ASR of LSCF with CuO Sintering Aid

\[(441\text{-Ce}_{0.02}\text{MC}|\text{LSCF-CuO}|\text{LSCF})\]

Low ASR, but tensile stress measurements showed very weak bonding strength between contact layer and cathode or interconnect coating.
SEM Images of LSCF-x%CuO Contact Materials after ASR Measurements

LSCF only  LSCF+3mol% CuO  LSCF+5mol% CuO
Approaches to Improve Contact Strength

Sintering Aids
- Goal: Reduce the sintering temperature of contact materials (LSM, LNF, LSCF) to obtain increased density/conductance/strength

Reaction-Sintering
- Similar to process used to prepare MnCo spinel coatings for steel interconnects
- Contact material precursor powder contains multiple phases, which react during stack assembly to form a conductive single phase
- Enthalpy of reaction provides additional driving force (besides surface energy reduction) for densification
Contact material precursor powder contains multiple phases, which react during stack assembly to form a conductive single phase. Similar to the process used in fabricating MnCo spinel coatings.

\[
\text{MnO} + \text{Co} + 3.5\text{O}_2 \rightarrow 2(\text{Mn}_{0.5}\text{Co}_{0.5})\text{O}_4
\]

Driving forces for densification:
- Reduction of surface energy (~75 J/mol)
- Enthalpy of formation (~500 kJ/mol)

Systems of primary interest
- \((\text{Ni,Co})\text{O}_x\)
- \((\text{Mn,Co,Cu})_3\text{O}_4\)
- Numerous compositions evaluated (CTE, conductivity, microstructure, strength); down-selected to \(\text{Ni}_{0.33}\text{Co}_{0.67}\text{O}_x\) and \(\text{Mn}_{2.7-x}\text{Co}_x\text{Cu}_{0.3}\text{O}_4\)
- Potential to include fillers and fugitive phases (tailor CTE and porosity, reduce cost)
Ni$_{0.33}$Co$_{0.67}$O as cathode-interconnect contact material

- Prepared from mixture of Ni and Co powder
- Paste prepared using binder vehicle and 3 roll mill
- Primary phase is (Ni,Co)O; secondary phase is NiCo$_2$O$_4$
- CTE ~14.6 ppm/K
  - Possible inclusion of filler to reduce cost and CTE

Cross-section SEM image of (Ni$_{0.33}$Co$_{0.67}$)O$_x$ contact heat treated at 950°C for 30 min in air
ASR test results for Ni$_{0.33}$Co$_{0.67}$O as cathode-interconnect contact material: 800ºC

ASR increased from ~4 to ~9 during initial 1000 h of isothermal testing (with 1 unscheduled thermal cycle at ~500 h)

Thermal cycling every 24h, ~60-800ºC
Mn$_{1.5}$Co$_{1.2}$Cu$_{0.3}$O$_4$ as cathode-interconnect contact material

- Prepared from mixture of Mn, Co, and Cu powder
- Paste prepared using binder vehicle and 3 roll mill
- Single phase MCC spinel
- CTE $\sim$12.8 ppm/K

Cross-section SEM image of Mn$_{1.5}$Co$_{1.2}$Cu$_{0.3}$O$_4$ heat treated at 950ºC for 30 min in air, 800ºC for 100 h
Isothermal and cyclic ASR test results for Mn$_{1.5}$Co$_{1.2}$Cu$_{0.3}$ as cathode-interconnect contact material: 800$^\circ$C
Mechanical Bond Strength Measurement

Cathode or Coated 441
Contact Layer
Cathode or Coated 441

Aluminum grip fixture
Force
Epoxy
Contact paste
Cathode or interconnect
Cathode or interconnect
Force
Strong bonds can be obtained for both coated 441 and cathode using Mn$_{1.5}$Co$_{1.2}$Cu$_{0.3}$ and NiCo$_2$ as contact pastes; bonds on cathode are stronger.
Stronger bonds can be obtained for both coated 441 and cathodes using Mn$_{1.5}$Co$_{1.2}$Cu$_{0.3}$ and NiCo$_2$ as contact paste; bonds on cathode are stronger.
SEM Images of Specimens after Mechanical Bond Strength Measurement (950°C treated)
Tensile strength results for Mn-Co-Cu contact materials with varying Co content

![Bar chart showing tensile strength](chart.png)
ASR of Mn$_{2.7-x}$Co$_x$Cu$_{0.3}$O$_4$ Contact Materials

![Graph showing ASR values for different compositions over time.]

- Mn$_{1.5}$Co$_{1.2}$Cu$_{0.3}$
- Mn$_{1.9}$Co$_{0.8}$Cu$_{0.3}$
- Mn$_{2.3}$Co$_{0.4}$Cu$_{0.3}$
- Mn$_{2.7}$Cu$_{0.3}$

Temperature: 800°C
Alternative Fabrication Approach: Tape-casting

Application of cathode - interconnect contact material in tape form instead of paste form
ASR of $\text{Mn}_{2.7-x}\text{Co}_x\text{Cu}_{0.3}\text{O}_4$ Contact Materials

![Graph showing ASR values over time for Mn1.5Co1.2Cu0.3 paste and MnCoCu0.3 Metal Tape ~30um.](image-url)
Summary and Future Work

- Reactive sintering has been demonstrated as a means of preparing cathode/interconnect Ni-Co oxide and Mn-Co-Cu oxide contact materials from precursor mixtures of metallic powders.
- The reactive sintering approach resulted in very low cathode-to-interconnect ASR, and high bond strength (compared to conventional contact materials).
- Clearly, the high density of reaction-sintered contacts will restrict gas phase transport through the contact material.
  - Possible solutions:
    - Application of contact material to selected regions only (e.g., lands of ribs of interconnects)
    - Inclusion of controlled porosity through use of fugitive phases
      - Reactive sintering may result in stronger bulk and interfacial bonding compared to conventional contacts prepared from complex oxides with minimal sintering activity at stack fabrication temperatures

Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program
- NETL: Shailesh Vora, Briggs White, Rin Burke, Travis Shultz, and Joe Stoffa
- PNNL: Jim Coleman, Shelley Carlson, Nat Saenz
Development of SOFC Interconnects and Coatings

J.W. Stevenson, G.G. Xia, J.P. Choi, Y.S. Chou, E.C. Thomsen, K.J. Yoon, R.C. Scott, X. Li, and Z. Nie

Pacific Northwest National Laboratory
Richland, WA 99352

July 26-28, 2011
12th Annual SECA Workshop
Pittsburgh, PA
Presentation Outline

- Objectives
- Background
  - AISI 441
  - Spinel coatings for steel interconnects
- Results:
  - Performance of Ce-modified MnCo spinel-coated AISI 441
  - Effect of alloy surface treatments
  - Optimization of Ce-modified MnCo spinel coatings
  - Alternative coating compositions
  - Ceramic interconnect materials
- Summary
- Future Work
- Acknowledgements
Objectives

► Global Objectives

■ Develop cost-effective, optimized materials and fabrication approaches for SOFC interconnects

■ Identify, understand, and mitigate degradation processes in SOFC interconnects

► Specific Objectives

■ Improved understanding of performance and long-term stability of AISI 441 steel coated with Ce-modified \((Mn_{0.5}Co_{0.5})_3O_4\) spinel coating
  - ASR, oxidation behavior, scale adhesion at 800 and 850°C
  - Stack fixture testing

■ Evaluation of alloy surface treatments
  - Collaborations with Allegheny Ludlum and NETL-Albany

■ Optimization of Ce-modified \((Mn_{0.5}Co_{0.5})_3O_4\) spinel coatings
  - Ultrasonic spray process; effect of coating thickness

■ Evaluation of cost reduction approaches
  - Reduced Co content to lower coating cost
Candidate Interconnect Alloy: AISI 441

- Ferritic stainless steel: Good CTE match to other components; Electrically conductive Cr-based oxide scale
- Inexpensive - Manufactured via conventional melt metallurgy
  - No vacuum processing required
- Similar to AISI 430, but additions of Nb and Ti improve high temperature strength and prevent formation of insulating SiO$_2$ layer at alloy/scale interface
- Similar to all other FSS, relatively high oxidation rate at SOFC operating temperatures (and volatility of Cr) indicates need for protective coating
- Also, relatively weak scale adherence (no RE in alloy)

Typical Analysis:

<table>
<thead>
<tr>
<th>Designation</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Nb</th>
<th>La</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 441</td>
<td>18</td>
<td>0.35</td>
<td>0.30</td>
<td>0.01</td>
<td>0.05</td>
<td>0.34</td>
<td>0.023</td>
<td>0.002</td>
<td>0.22</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>AISI 430</td>
<td>16-18</td>
<td>≤1.0</td>
<td>≤0.12</td>
<td>≤1.0</td>
<td>≤0.04</td>
<td>≤0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crofer 22 APU</td>
<td>23.0</td>
<td>0.4-0.8</td>
<td>0.030</td>
<td>≤0.02</td>
<td>≤0.02</td>
<td>0.02</td>
<td>0.050</td>
<td>≤0.2</td>
<td></td>
<td></td>
<td>0.04-0.20</td>
</tr>
</tbody>
</table>

Sources: Allegheny Technologies, Inc.; Thyssen Krupp
Ce-modified \((\text{Mn}_{0.5}\text{Co}_{0.5})_{3}\text{O}_4\) Spinel Coatings

- High electrical conductivity
  - \(\sim 60\ \text{S/cm at 800}^\circ\text{C}\)
  - \(\sigma_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} = 10^{3-4} \sigma_{\text{Cr}_2\text{O}_3}\)
- Good CTE match to FSS and anode-supported cells
  - \(\text{CTE}_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} \approx 11 \times 10^{-6}\text{K}^{-1}, 20 – 800^\circ\text{C}\)
- Chemically compatible with contact pastes, cathodes
- Cr-free composition
- Ce\(_2\text{O}_2\) inclusions improve scale adhesion of alloy substrate (rare earth effect)
- Reaction-sintering process developed at PNNL increases coating density at low processing temperatures

Coating provides:
- Reduced Cr volatility from steel
- Improved scale adhesion
- Reduced oxidation rate of alloy:

<table>
<thead>
<tr>
<th>(k_p) ((\text{g}^2/\text{cm}^4\text{-s}))</th>
<th>800(^\circ\text{C})</th>
<th>850(^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-MC coated 441</td>
<td>(2 \times 10^{-14})</td>
<td>(1 \times 10^{-13})</td>
</tr>
<tr>
<td>Bare 441</td>
<td>(5 \times 10^{-14})</td>
<td>(3 \times 10^{-13})</td>
</tr>
</tbody>
</table>
Performance of Ce-modified \((\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4\) spinel coatings on AISI 441 steel
Area Specific Resistance (ASR) Measurements

\[ ASR_{cathode\text{-}interconnect} = \Phi(scale, contactmaterial, coatings) \]

Simulated cathode with dense body and porous surface layers

Current Density: \( 0.5 \text{A.cm}^{-2} \)

Interconnect (coated)

Contact Layers

~12psi

ASR Stack (3 sets)
Long-Term ASR measurements: 800ºC
Long-Term ASR measurements: 850° C
Long-term testing at 800°C w/ deep thermal cycle every ~1000 hours
Surface Modifications to AISI 441

- Goal: Improve long-term scale adhesion under spinel coating
- Provided by Allegheny Ludlum:
  1. Mill reference (as would be provided to a customer without any additional modifications)
  2. Desiliconized (treatment to sequester silicon from the near surface of the sheet; an alternative to decreasing Si content of alloy)
  3. Surface blasted (abrasion/peening resulting in surface deformation)
  4. Surface ground (rough surface abrasion resulting in surface deformation)
  5. Temper rolled (cold rolling process resulting in through-thickness deformation)
- 0.020” thick coupons coated with Ce-MnCo spinel, heat-treated in air at 800 or 850ºC; 16 coupons for each condition
- Study is in progress
  - Interim report was sent to SECA industry representatives in February, 2011
Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441 (800°C)

- 2000 hours
  - No spallation

- 4000 hours
  - Spallation observed on 1 mill reference coupon

- 6000 hours
  - Spallation on all except 1 one of the mill reference coupons, also 1 desiliconized coupon
  - De-bonding at scale/alloy interface observed in mounted temper-rolled coupon

- 8000 hours
  - Last of the mill reference coupons spalled, others were OK

- 10000 hours
  - No further spallation
6000 h, 800°C in air

Surface Blast
Surface Grind
Desiliconized

Mill Reference (note: most of scale spalled after cooling)
Cold Rolled (note: scale debonded during mounting)
NETL-Albany Ce treatment
6000 h, 800ºC in Air

- Surface Blast
- Surface Ground
- De-siliconized
- 50% Cold Rolled
- NETL-Albany Ce treatment
8000 h, 800°C in air

Surface Blast

Surface Grind

Desiliconized

Cold Rolled (note: scale debonded during mounting)

NETL-Albany Ce treatment
8000 h, 800°C in Air

- Surface Blast
- Surface Ground
- De-siliconized
- 50% Cold Rolled
- NETL-Albany Ce treatment
Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 8,000 hours, 800ºC, air

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ce</th>
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<td>0.97</td>
<td>33.21</td>
<td>0.28</td>
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<td></td>
<td></td>
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<tr>
<td>2</td>
<td>62.01</td>
<td>0.57</td>
<td>11.04</td>
<td>11.68</td>
<td>2.01</td>
<td>12.69</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>60.52</td>
<td>0.89</td>
<td>1.69</td>
<td>18.83</td>
<td>2.97</td>
<td>15.11</td>
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<tr>
<td>4</td>
<td>58.62</td>
<td>0.75</td>
<td>1.38</td>
<td>19.96</td>
<td>3.18</td>
<td>15.78</td>
<td>0.34</td>
</tr>
<tr>
<td>5</td>
<td>61.77</td>
<td>0.69</td>
<td>1.18</td>
<td>18.32</td>
<td>3.06</td>
<td>14.66</td>
<td>0.32</td>
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<tr>
<td>6</td>
<td>60.39</td>
<td>0.65</td>
<td>1.27</td>
<td>19.31</td>
<td>3.07</td>
<td>15.04</td>
<td>0.26</td>
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<tr>
<td>7</td>
<td>62.33</td>
<td>0.60</td>
<td>1.60</td>
<td>17.80</td>
<td>2.98</td>
<td>14.69</td>
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</tbody>
</table>

Max. 65.53 0.97 33.21 19.96 3.18 15.78 0.34
Min. 58.62 0.57 1.18 11.68 0.28 12.69 0.26
Surface Treated 441 w/coating; 800ºC

Time^0.5 (Hours^0.5)

Scale Thickness (microns)

Mill reference
Temper rolled
Surface ground
Surface blast
Desiliconized
Albany Ce
Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441 (850°C)

- 2000 hours
  - No spallation

- 4000 hours
  - No spallation

- Reached 6000 hours on July 20

![Graph showing scale thickness in microns vs. time to the power of 0.5 (hours to the power of 0.5)]
4000 h, 850°C in air

Surface Blast

Surface Grind

Desiliconized

Mill Reference

Cold Rolled – higher mag
4000 h, 850ºC in Air

- Surface Blast
- Surface Ground
- De-siliconized
- 50% Cold Rolled
- Mill Reference
Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 4,000 hours, 850°C, air

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>Si</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ce</th>
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<tr>
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<td>0.28</td>
<td>0.36</td>
<td>31.71</td>
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<tr>
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<td>60.64</td>
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<td>0.21</td>
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<td>17.44</td>
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<td>15.54</td>
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<tr>
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<td>0.23</td>
<td>1.33</td>
<td>18.88</td>
<td>1.81</td>
<td>15.88</td>
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<tr>
<td>4</td>
<td>59.31</td>
<td>0.30</td>
<td>0.18</td>
<td>1.30</td>
<td>20.22</td>
<td>1.68</td>
<td>16.68</td>
<td>0.33</td>
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<tr>
<td>5</td>
<td>60.74</td>
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<td>19.71</td>
<td>1.76</td>
<td>16.46</td>
<td>0.31</td>
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<tr>
<td>6</td>
<td>57.96</td>
<td>1.17</td>
<td></td>
<td>21.16</td>
<td>1.67</td>
<td>17.61</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>60.30</td>
<td>0.28</td>
<td></td>
<td>1.14</td>
<td>19.59</td>
<td>1.57</td>
<td>16.83</td>
<td>0.29</td>
</tr>
<tr>
<td>Max.</td>
<td>65.18</td>
<td>0.43</td>
<td>0.36</td>
<td>31.71</td>
<td>21.16</td>
<td>1.81</td>
<td>17.61</td>
<td>0.43</td>
</tr>
<tr>
<td>Min.</td>
<td>57.96</td>
<td>0.22</td>
<td>0.18</td>
<td>1.02</td>
<td>1.67</td>
<td>0.60</td>
<td>0.20</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Atomic%
Optimization of Ce-MC Spinel Coatings

- Adaptation of ultrasonic spray process to Ce-modified spinel powder
  - Extension of previous optimization of fabrication process for unmodified spinel
  - Reference J.P. Choi et al., Poster Presentation, 2011 SECA Workshop

- Effect of coating thickness on oxidation resistance of AISI 441
  - Two studies in progress: Sprayed coatings, Screen-printed coatings
    - ~5, 10, 20 microns thick
    - Oxidation for 2000 hours
ASR Results for Reduced Co Content in Mn-Co Oxides on AISI441

ASR Measurement Data

Area Specific Resistance (mOhms-cm²)

Time (hours)

Mn-only
5 wt% Co
10 wt% Co
15 wt% Co
21 wt% Co
35 wt% Co
Alternative Coating Compositions

- **Goal:** Reduce Co content to reduce coating cost
  - Current preferred composition: \((\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4\)
  
- \((\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4 ; 0.0 \leq x \leq 0.5\)
  - \(x = 0\) (Mn oxide)
    - Even after optimization of coating density, did not obtain stable ASR
  - \(0.05 \leq x \leq 0.5\)
    - Strong dependence of ASR rate of increase on Co content

<table>
<thead>
<tr>
<th>[Co]</th>
<th>ASR Slope* (mΩ-cm²/1000hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt%</td>
<td>5.0</td>
</tr>
<tr>
<td>5 wt%</td>
<td>3.5</td>
</tr>
<tr>
<td>10 wt%</td>
<td>1.9</td>
</tr>
<tr>
<td>15 wt%</td>
<td>0.9</td>
</tr>
<tr>
<td>21 wt%</td>
<td>0.2</td>
</tr>
<tr>
<td>35 wt%</td>
<td>0.3</td>
</tr>
<tr>
<td>52 wt%</td>
<td>0.03</td>
</tr>
</tbody>
</table>

\[\text{Co}/(\text{Co}+\text{Mn})\]
SEM Images of Mn$_{3-x}$Co$_x$O$_4$ Protection Coatings on AISI441 after ASR Tests
Reactive Air Aluminization

• Reaction between alkaline earths in glass seals and Cr in interconnect steel can form high CTE chromate phases (e.g., SrCrO$_4$), which degrade interfacial strength

• Cr volatility from alloys can poison cathodes

• Reactive Air Aluminization (RAA) offers a simple alternative to controlled atmosphere aluminization of interconnects
  - Aluminum powder slurry-based process, 1000°C heat treatment in air
Reactive Air Aluminization

Cross sectional SEM analysis: 1000 C, 1 h oxidative heat treatment
Ceramic Interconnects for SOFC

Doped yttrium chromite is being optimized for SOFC with operating temperature >850ºC

- Ca on A-site; Co, Ni, and/or Cu on B-site
- Electrical conductivity, CTE, ionic transference number comparable to standard material (doped lanthanum chromite)
- Improved sinterability, reduced chemical expansion, and lower reactivity (e.g., zirconate formation) relative to lanthanum chromite

- Electrical Conductivity
  - Electronic, Ionic
- Sintering Behavior
- Stability toward Reduction
  - Chemical Expansion
- Thermal Expansion
- Chemical Reactivity

Current emphasis on improving densification under constrained sintering and co-sintering conditions

- A-Site: 20% Ca
- B-site: 10% Co, 4% Ni, 1% Cu
Increased density through infiltration process

- No Infiltration
- 50 vol.% Ethanol 1300°C after S.P. 1300°C after Infiltration
- 50 vol.% Ethanol 1200°C after Screen Printing 1300°C after Infiltration

• Reference: K.J. Yoon et al., Poster Presentation, 2011 SECA Workshop
Summary

▸ AISI 441 w/ Ce-modified MnCo spinel coatings exhibits low, stable ASR in long-term testing
  ■ Less than 12 mΩ-cm² after ~ 2 years at 800ºC in air

▸ Surface-modified AISI 441 w/ Ce-modified MnCo spinel coatings exhibit improved long-term spallation resistance
  ■ 10,000 hours at 800ºC (tests in progress)
  ■ 4,000 hours at 850ºC (tests in progress)

▸ Based on ASR tests, effectiveness of Mn-Co spinel coatings decreases with decreasing Co content, especially for Co/(Co+Mn) < 0.20

▸ Optimization of ultrasonic spray process for application of Ce-modified MnCo spinel coatings is in progress
Future Work

- Continue to evaluate long-term stability and electrical performance of surface modified Ce-MC spinel-coated 441 steel
  - Parametric investigation of surface treatment options
  - Evaluation at 800 and 850°C
  - Long-term evaluation in stack test fixture
- Optimize thickness, and automated ultrasonic spray fabrication process, for Ce-modified spinel coatings
- Reduce cost of protective coatings through minimization or elimination of Co content
- Develop fabrication approaches for sintering of Cr-based perovskite interconnects under constrained/co-sintered conditions.
Acknowledgements

- The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program

- NETL: Shailesh Vora, Briggs White, Rin Burke, Travis Shultz, and Joe Stoffa

- NETL-Albany: Paul Jablonski

- ATI Allegheny Ludlum: Matt Bender

- PNNL: Jim Coleman, Shelley Carlson, Nat Saenz, Dan Edwards, Clyde Chamberlin, and Alan Schemer-Kohrn
Modeling Tools for SOFC Design and Analysis

MOE A. KHALEEL
BRIAN KOEPPEL, KURT RECKNAGLE, ELIZABETH STEPHENS, KEVIN LAI, EMILY RYAN, WEI XU, HUSSEIN ZBĪB, KHUSHBU AGARWAL, WENXIAO PAN
Pacific Northwest National Laboratory
Richland, WA

13th Annual SECA Workshop
Pittsburgh, PA
July 24-25, 2012
PNNL Modeling Activities: Objectives & Approach

► Objectives: Develop integrated modeling tools to:
   - Evaluate the tightly coupled multi-physical phenomena in SOFCs
   - Allow SOFC designers to perform numerical experiments for evaluation of stack electrochemical, thermal, and mechanical performance
   - Aid understanding of materials degradation issues
   - Provide wide applicability for industry teams’ to solve key design problems
   - Provide a technical basis for stack design

► Approach: Multiphysics-based analysis tools
   - SOFC-MP: A multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks
   - Distributed Electrochemistry (DEC): Cell level multiphysics model to study effects of local properties/conditions on global SOFC performance
   - Reduced Order Models (ROM) to interface with system-level models
   - Micro/meso-scale models to study electrode degradation mechanisms
   - Experimental support to provide necessary material data for the models
PNNL Modeling Tools: Task Overview

- **SOFC-MP Stack Modeling**
  - 2D and 3D multi-physics stack model SOFC-MP
  - 2D model benchmarked with literature and experimental data
  - Framework created for high fidelity Reduced Order Model (ROM)

- **Electrochemistry & Degradation Modeling**
  - Validated 3D multi-physics model of the SOFC electrodes and electrolyte for the investigation of SOFC performance and degradation issues
  - Models for electrode degradation and long term performance

- **Interconnect Modeling & Experiments**
  - Integrated modeling and experimental approach for prediction of interconnect lifetime

- **Seal Modeling & Experiments**
  - Investigate the behavior of glass seal material technologies and designs at operating temperatures
BENCHMARKING SOFC-MP 2D TO EXPERIMENTAL RESULTS

- Model temperature predictions were benchmarked against experimentally measured data:
  - SOFC-MP 2D model
  - 30-cell co-flow stack
  - Instrumented 100 cm² cells with multiple thermocouples along the flow field
    - @ ¼, ½, ¾ of stack height
  - Ten different cases
  - 30A or 60A current
  - H₂ or CH₄ fuel mixtures
  - Different gas inlet temperatures

- Analyses showed that accurate model predictions of the cell temperature distribution required:
  - Accounting for all relevant structures that affect the lateral heat conduction of the cells
    - Load frame, heat spreading, and measurement plates in the stack
    - Flow channel media geometry
  - Methane steam reformation rate based on the anode used
  - Precise known location of the thermocouples
  - Calculation of realistic convection coefficients
SOFC-MP Benchmarking: Effect of Methane Concentration

- SOFC-MP 2D model captures the steam-methane reformation effects on the cell temperature distribution for 60A current
  - With no CH₄, heating of the cell along the flow direction
  - With added CH₄, strong endothermic cooling at the inlet

Flow Direction

No CH₄

12.0% CH₄

17.0% CH₄

Model

Experiment

= ¼ stack height thermocouples
= ½ stack height thermocouples
= ¾ stack height thermocouples
SOFC-MP Benchmarking: Effect of Current and Inlet Temperature

- Reduced current density and reformation for 30A cases make the endothermic cooling at the inlet relatively weaker even with 12.5% CH₄.
  - Results in a more uniform cell temperature distribution that is influenced more by the inherent cell heat transfer characteristics.

- Higher inlet gas temperatures primarily caused an upward shift of the temperature profile with little change to its shape.

---

**Nominal Tfuel/Tair Inlet**

**Tfuel/Tair +25°C Inlet**

**Tfuel/Tair + 50°C Inlet**
The instrumented stack has less temperature variation overall due to better heat spreading.

- Better heat transfer mechanisms in vicinity of non-standard cells are critical for temperature field benchmarking.

The model can predict temperature fields of actual stacks with CH$_4$ fuel.
Ability to simulate long term degradation processes added to SOFC-MP 2D

- E.g., oxide scale growth on metallic interconnect causes added ohmic loss for the stack
- The additional heat generation requires reduced air utilization rate to maintain maximum cell temperature
  - Additional BOP losses

\[
\frac{\partial \xi^2}{\partial t} = k_p = k_p^0 e^{(-E_{ox}/RT)}
\]
\[
\sigma_{ox} T = \sigma_{ox}^0 e^{(-E_{el}/RT)}
\]

Air Required

Power Loss

Average Stack Temperature
Reduced Order Modeling (ROM): Overview

- **‘N’ Input Variables and Ranges**
  - Sampling of N-Dimension Space
  - Cases to Run
  - `Stack Model`
  - Slow
  - Stack Results
  - ‘M’ Output Variables
  - Regression
  - Matrices for ‘M’ Response Surfaces
  - Creation of reduced order model

- **Response surface used for system studies**
  - ‘N’ Input Values
  - System Module
  - ‘M’ Output Values
  - Fast
Design of the ROM Framework

Base Fuel Cell Model

Identify Design Parameters:
Stack Voltage
Fuel temperature

Export ROM
-Plugins in ‘larger scale’ simulations

Generic Parser

ROM Analysis Tools
- Visualization
- Error Estimation
- Predictive Analysis

Regression
- Kriging
- FANN
- SVM

ROM Content Manager

Sampling

Job Execution Infrastructure

Model

• Automated Post processing
• Data Management - Velo
Advanced Mathematics for ROM Efficiency and Accuracy

- Check applicability and sensitivity of sampling/regression methods for the nonlinear SOFC model
  - 16-cell co-flow stack w/ H₂ fuel

- Input parameters
  - Air/fuel temperature
  - Air/fuel flow rate
  - Air/fuel composition
  - Stack voltage

- Output variables
  - Air/fuel species
  - Air/fuel outlet temperature
  - Cell maximum temperature
  - Stack current

Uniform Sampling in 4-D Space using QMC
ROM Parameter Sensitivity and Applicability of Regression Method

Sensitivity of Output to Input Parameters

Assessment of Regression Method

Stack Current

Outlet Fuel Temperature

MARS Stack Current

<table>
<thead>
<tr>
<th>Actual Value</th>
<th>Predicted Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>300</td>
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<tr>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>600</td>
<td>700</td>
</tr>
</tbody>
</table>

Probability

Error
Response surfaces computed and visualized by 3D contours
- E.g., 128 samples sufficient to reduce stack current error to less than 1% (maximum of 4% on extremities of the chosen design space)
- Response surface relationships implemented into a calculator
- Multi-Element Probabilistic Collocation Method used to identify regions of highest sensitivity that can be augmented with additional samples to achieve high accuracy
- Principal Component Analysis-based mapping has also been investigated to reduce the number of required regressions for prediction of stack temperature distributions
Benefits of the ROM Framework

- Provides an automated system to build Reduced Order Models for SOFC stacks
  - Generic: Configurable for any domain
  - Portable: Windows, Linux
  - Extensible: Multiple sampling, regression, and analysis tools
  - Cost Efficient: Open source packages
  - Time Efficient: Automated job submission, post-processing, error analysis, augmented sampling, and data management tools
- Data Sharing
- Metadata Management
- Rich client on desktop
  - Wiki interface through web can be available
Electrochemistry and Electrode Degradation Modeling

Technology Challenges

► Investigate degradation issues in the electrodes of the SOFC
► Understand degradation processes in electrodes
  ▪ Investigate the effect of microstructure and local conditions within the electrodes on cell performance
  ▪ Confidently predict global cell performance for a range of conditions

Objectives

► Develop models to predict cell performance and to investigate degradation
  ▪ Calculations based on operating conditions and microstructure within the electrodes
  ▪ Dependent on coupled electric potential, charge transfer, and reactive transport
  ▪ Use different modeling approaches for specific problems
  ▪ Validate the models by comparison with experimental data
  ▪ Simulate microstructural and operational effects on cell performance
Humidity in the Cathode

- Two stage degradation
  - Immediate decrease in performance
  - Slower, steady degradation over long term operation

- Reactions with LSM
  - Testing with LSCF shows little to no degradation
  - LSM-YSZ and LSM-CGO show similar degradation
    - Not YSZ reactions → LSM reactions
  - Theories
    - Formation of $\text{La}_2\text{O}_3$
      - Nano-particles on surface
    - Reaction of $\text{H}_2\text{O}$ with $\text{Mn}^{2+}$ ions
    - Reduction of active interface
Current Work: Development of Micro- and Meso-Scale Cathode Models

Note: Not to scale
Meso-Scale Cathode Model

► Smoothed particle hydrodynamics model of the cathode microstructure
  ■ Includes the reactive transport in the gas (O₂, H₂O, etc.) and solid (O²⁻), charge transfer reactions

► Considers possible reaction mechanisms of H₂O with LSM
  ■ Nanoparticle formation (precipitation)
  ■ Mn²⁺ removal

► Experimentally it is difficult to know what is happening during operation vs. shut down
  ■ Model will help to narrow down possible physical phenomena of H₂O in the cathode
Micro-scale modeling of the Cathode

- Molecular modeling of Sr-doped LSM in presence of H$_2$O.
- What are the possible interactions between LSM and water and how do they interfere with cathode operation?
  - Use molecular modeling techniques to simulate and compare possible reaction mechanisms

- Approach:
  - Adsorption and diffusion simulations using classical molecular dynamics
  - Formation thermodynamics of manganese oxides and hydroxides using density functional theory
  - H$_2$O, O$_2$ dissociation thermodynamics on LSM surface using density functional theory

![Diagram showing dissociation, adsorption, surface diffusion, surface Mn reactions, and bulk diffusion.]
Micro-scale modeling of the Cathode

Current research:
- Build La$_x$Sr$_{1-x}$MnO$_3$ atomistic slab structure
- Develop and test classical potential energy function describing slab structure, motion and intermolecular interactions at any temperature or pressure
- Adsorption, surface and bulk diffusion simulations based on atomistic structure and inter-atomic potentials

Preliminary Results:
- Created 4x4 rhombohedral La$_{0.8}$Sr$_{0.2}$MnO$_3$ slab structure
- Developed and tested initial classical potential energy function
  - PE function correctly reproduces experimental structural parameters
- Adsorption, surface diffusion simulations of O$_2$, H$_2$O, OH- are underway
Next Steps and Future Work

- Continue implementation of degradation models
  - Validation with experimental data
- Couple micro- and meso-scale cathode models
  - Use fundamental reaction information gained from micro-scale modeling to develop reaction parameters of meso-scale modeling.
- Investigate mitigation strategies for humidity in the cathode
Motivation: To quantify the healing capability of the self-healing seal materials under various thermo-mechanical operating conditions

Goal: To assist the development of the reliable stack-level SOFC design integrated with the self-healing glass sealing system

Technical Approach: Develop time and temperature dependent mechanistic based healing models as building blocks in stack-level seal performance simulations to predict the healing behaviors under different conditions
Mechanistic Based Crack Healing Model

A two-stage diffusion driven self-healing mechanism

1\textsuperscript{st}: Creep-driven crack closure

\[ \dot{\varepsilon} = \frac{1}{\eta} \sigma \quad \eta = \eta_0 \exp\left( \frac{Q_v}{RT} \right) \]

2\textsuperscript{nd}: Interdiffusion-driven bond formation - a characteristic dwelling time \( \tau \) is needed for molecular transportation to establish sufficient links on contact area

\[ \tau = \tau(T) = \alpha \exp\left( \frac{\beta}{T} \right) \]

Performed multi-scale simulation, using both Kinetic Monte Carlo and Finite Element Method, to investigate the stress and temperature dependent healing behavior from different scales

The healing path and temperature dependence is fully driven by the proposed mechanism without any prerequisites
Simulation of the Self-healing Process

**kMC simulation**

\[ P = w_h \times \exp\left(-\frac{E_h}{kT}\right) \]
\[ w_h = 6.02 \times 10^9 Hz \quad E_h = 2.555 eV \quad (k: \text{Boltzmann constant}) \]

**Finite Element Analysis**

\[ \tau_0 = \alpha \exp\left(\frac{\beta}{T}\right) \]
\[ \alpha = 2.4082E-9 \quad \beta = 24890 \quad T \text{ is in Kelvin, } \tau_0 \text{ is in minute.} \]
Experimental Calibration of the Characteristic Dwell Time

- Controlled experiments were performed to mimic the healing process. The measured flexural strength recovery was used to calibrate the healing probability function of the kMC model.

Flexural test results summary for specimens exposed to elevated test temperatures with no gap at the interface and no load.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Test Temperature (°C)</th>
<th>Time at Test Temperature (min.)</th>
<th>RT Flexural Strength (MPa)</th>
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<tbody>
<tr>
<td>700-6</td>
<td>700</td>
<td>40</td>
<td>23.0</td>
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<tr>
<td>700-7</td>
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</tr>
<tr>
<td>800-6</td>
<td>800</td>
<td>20</td>
<td>75.5</td>
</tr>
</tbody>
</table>

Pre-test specimen illustrating no gap between glass bars.

Location of original interface

Post-test specimen exposed to 700°C for 60 minutes.

Four-point bend test fixture.
Effects of Operating Conditions

Effects of temperature

Dwelling time only counts the time for the interdiffusion-driven healing stage.

Effects of confining pressure

Stress factor: the total healing time under a pressure of 5MPa divided by the total healing time under 10MPa.
Effects of Crack Morphology

Crack Orientation:
Orientation factor: the total healing time of a crack with arbitrary orientation of $\theta$ divided by the total healing time of the specimen with a crack of $\theta=90^\circ$.

Crack Interaction:
Crack-Crack Interaction Factor: the total healing time divided by the healing time of the specimen with a single crack.

Dimensionless crack-crack distance: $D$ divided by the crack length $L$. 
Stack Modeling
- SOFC-MP 2D successfully benchmarked against experimental temperature data
- Capability added to SOFC-MP 2D to simulate generic degradation behaviors over time and maintain suitable stack operating temperature
- Framework developed to generate reduced order models (ROM) for stacks

Electrochemistry & Degradation Modeling
- Simulated anode Ni volatilization rate for high humidity/fuel utilization case
- Began construction of micro/meso-scale models to predict cathode and anode degradation mechanisms under high humidity conditions

Interconnect Modeling & Experiments
- Modeling tools are being extended to implement new experimental methodologies and quantitative measurements to quantify and predict IC life
- Interfacial analysis of surface modified IC specimens in-process

Seal Modeling & Experiments
- Developed a two-step, mechanistic-based self-healing model to quantitatively capture and predict the crack healing behavior of SCN-1 glass
Future PNNL Modeling Activities

- Simulation of long-term and transient performance behaviors of stacks
  - Evaluation of high humidity conditions on long-term anode/cathode performance
  - Evaluation of high fuel utilization on long-term anode performance
  - Implement micro/meso-scale performance results into higher-level stack models
- Improved accessibility to software tools
  - Release ROM and apply approach to fuel cell-based power system models
  - Transfer SOFC-MP to a more flexible framework for integration with other FEA solvers and a license-free user interface
- Interconnect Modeling & Experiments
  - Quantification of interfacial strength for varying surface modified SS441
  - Life prediction for coated and surface modified SS441
- Seal Modeling & Experiments
  - Develop a continuum damage-healing model to accommodate stack-level simulations
  - Comparative prediction and optimization of seal designs: compliant seal vs. rigid seal
SECA Core Technology Program
R&D at PNNL


Pacific Northwest National Laboratory
Richland, WA 99352

July 24, 2012
13th Annual SECA Workshop
Pittsburgh, PA
Objective

► Provide R&D support to SECA program
  - Development/evaluation of improved materials and fabrication processes for SOFC cells and stacks
  - Improved understanding of performance degradation mechanisms
  - Development/implementation of modeling tools to facilitate cell and stack design and optimization
  - Technology transfer to industry teams
Technology Transfer Process

► **First step:** Testing and characterization at sub-stack level

- Materials Characterization
  - XRD, SEM, EDS, TEM, XPS, TGA, DSC, PSA, dilatometry, electrical conductivity, single & dual atmosphere oxidation

- Multiple Component Tests
  - Button cell testing
  - ASR testing of interconnect/cathode contact/cathode structures
  - Electrical testing and leak testing of seal/interconnect and cell/seal/interconnect structures

► **Second step:** Testing under realistic “stack-like” conditions to bridge the gap between small-scale tests (e.g., button cells) and SECA industry team stacks
Technology Transfer Process

► SECA CTP Stack Test Fixture

■ Advantages:
  - Can evaluate/validate new materials and fabrication processes under more realistic conditions
  - Larger cell size than button cells (50mm x 50mm)
  - Complete stack functionality (cell, cell frame, seals, interconnects, electrical contact materials)

■ Challenges:
  - Increased complexity (and cost) of assembly, co-fabrication of seals and electrical contact materials
  - Multiple components & phenomena, so results can be more difficult to interpret

■ Note: PNNL has transferred fixture design and test protocols to other SECA CTP participants (NETL, U. Conn.)

► Final step:

■ Delivery of topical reports
■ Delivery of materials to SECA industry teams for in-house evaluation
Scope of Work

- Determined through consultation with NETL program management and SECA industry teams
  - Increased communication with industry teams in past year

- Current areas of emphasis
  - SOFC interconnects
    - Alloys and coatings for IT-SOFC, Ceramic interconnects
  - Seals for SOFC stacks
    - Devitrifying glass seals, Compliant glass seals
  - Cathode materials and interactions
    - In-situ XRD characterization, Effects of humidity
  - Anode materials and interactions
    - Effects of high fuel utilization, Mitigation of sulfur poisoning
  - Modeling
    - 2D and 3D modeling tools to assist in cell/stack design
    - Modeling of cell/stack degradation processes
Seal Development

- **Devitrifying Glass Seals**
  - A series of devitrifying glass seals with sealing temperatures between 825 and 1000ºC have been developed.
    - Good CTE match to other components
    - Rapid stabilization of dimensions and microstructure due to devitrification
    - Good bonding to YSZ and interconnects (with aluminization of steel surface)
      - Reactive air aluminization process developed at PNNL
  - Current work focused on improved wetting/flow behavior at sealing temperatures ≥ 950ºC

- **“Compliant” glass seals also under development**
  - Collaboration with ORNL
  - Potential advantages: reduction of thermal stresses, self-healing behavior
  - Potential challenges: crystallization, reactivity, and containment

- **Poster Presentation**
  - Glass Seal Development at Pacific Northwest National Laboratory
Cathodes

Current Priorities:

- Investigating degradation mechanisms
  - *In-situ* high temperature XRD of operating LSCF cathodes
  - 700, 750, and 800°C

- Effects of air humidity on cell performance
  - LSCF and LSM/YSZ cathodes
  - Dry air vs. 3%H₂O

Poster Presentations

- Effects of Humidity in Cathode Air on LSM-YSZ Cathodes
- Extended Duration (1000 h) *In-situ* XRD of Operating LSCF Cathodes
Anodes

Effects of high steam content (high fuel utilization) on Ni-YSZ anodes
- Test anode-supported button cells with Ni/YSZ anodes and LSM/YSZ cathodes
- Test conditions
  - 700ºC, 800ºC, 900ºC
  - Constant current corresponding to 0.7 or 0.8 V
  - Fuel is a simulated coal gas
  - Fuel humidity corresponding to various fuel utilizations achieved by adding oxygen
  - Include “control” cells held at low fuel utilization
- Ac and dc electrochemical measurements of each cell
- Monitor temperature of each individual cell
- Post-test characterization using SEM/EDS, TEM, and EBSD

Poster Presentation
- Durability of Nickel/Zirconia Anodes in SOFCs at High Fuel Utilization
Alloy Interconnects and Protective Coatings

- Primary emphasis is on AISI 441 w/ Ce-modified MnCo spinel (MC) protective coating. Current activities:
  - Long-term evaluation of oxidation resistance and electrical performance
  - Effects of alloy surface treatments on oxidation behavior, spallation resistance are under investigation (collaboration with Allegheny Ludlum)
  - Optimization of ultrasonic spray fabrication process: coating uniformity and thickness
    - Poster presentation
      - The Effect of Spinel Coating Thickness on SOFC Interconnect Resistance
- Investigation of alternative coating compositions (e.g., oxides with reduced Co content, aluminization)
Low-cost Alloy-based Interconnects

**Interconnect Alloy: AISI 441**
- Ferritic stainless steel: Good CTE match to other components; Electrically conductive Cr-based oxide scale
- Inexpensive - Manufactured via conventional melt metallurgy
- Similar to AISI 430, but additions of Nb and Ti improve high temperature strength and prevent formation of insulating SiO₂ layer at alloy/scale interface
- Similar to all other FSS, relatively high oxidation rate at SOFC operating temperatures (and volatility of Cr) indicates need for protective coating
- Also, relatively weak scale adherence (no RE in alloy)

**Interconnect Coating: Ce-modified (Mn₀.₅Co₀.₅)₃O₄ Spinel**
- High electrical conductivity (~60 S/cm), good CTE match (~11 ppm/K)
- Ceria inclusions improve oxide scale adherence
- Coating improves oxidation resistance and mitigates Cr volatility

<table>
<thead>
<tr>
<th></th>
<th>800°C</th>
<th>850°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-MC coated 441</td>
<td>2 x 10⁻¹⁴</td>
<td>1 x 10⁻¹³</td>
</tr>
<tr>
<td>Bare 441</td>
<td>5 x 10⁻¹⁴</td>
<td>3 x 10⁻¹³</td>
</tr>
</tbody>
</table>
Area Specific Resistance (ASR) Measurements

\[ ASR_{\text{cathode-interconnect}} = \Phi \left( \text{scale, contact material, coatings} \right) \]
Long-Term ASR measurements: 800ºC

![Graph showing long-term ASR measurements at 800ºC. The x-axis represents time in hours, ranging from 0 to 30,000, and the y-axis represents ASR in mOhm-cm², ranging from 0 to 200. The graph includes data points for six different samples: Bare441-2008, MC441-2008, 0.5CeMC441-2008, Bare441, .02CeMC441, and .02CeMC/NETL-Ce441. Each sample has distinct markers and trends over time.]
Long-term testing of Ce-MC spinel-coated AISI 441

- 6,000 hour test under stack-like conditions (SECA CTP stack test fixture)
- 800ºC; air vs. moist H₂/N₂

Poster Presentation: “Recent Progress in SOFC Stack Test Fixture Development and Materials Validation at PNNL”
Spinel-coated cathode IC and LSM contact interface
Spinel-coated cathode IC and LSM contact interface
Spinel-coated cathode IC and LSM contact interface
Surface Modifications to AISI 441

- Goal: Improve long-term scale adhesion under spinel coating
- Provided by Allegheny Ludlum:
  - 1. Mill reference (as would be provided to a customer without any additional modifications)
  - 2. Desiliconized (treatment to sequester silicon from the near surface of the sheet; an alternative to decreasing Si content of alloy)
  - 3. Surface blasted (abrasion/peening resulting in surface deformation)
  - 4. Surface ground (rough surface abrasion resulting in surface deformation)
  - 5. Temper rolled (cold rolling process resulting in through-thickness deformation)

- 0.020” thick coupons coated with Ce-MnCo spinel, heat-treated in air at 800 or 850°C; 16 coupons for each condition
## Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441: 800°C

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Mill Reference (1200 grit)</th>
<th>Temper Rolled</th>
<th>De-siliconized</th>
<th>Surface Grind</th>
<th>Surface Blast</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Macroscopic Spallation</td>
<td>Microscopic De-bonding</td>
<td>Macroscopic Spallation</td>
<td>Microscopic De-bonding</td>
<td>Macroscopic Spallation</td>
</tr>
<tr>
<td>2000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>4000</td>
<td>X</td>
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<tr>
<td>18000</td>
<td>XX</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

- **X** - spallation on at least one coupon
- **XX** - no unspalled coupons left in study
- **C** - complete de-bonding of scale of SEM/EDS sample
- **L** - localized de-bonding of scale of SEM/EDS sample
18000 h, 800°C in Air

- Surface Blast
- Surface Ground
- De-siliconized
- 50% Cold Rolled
Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 18,000 hours, 800°C, air

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>Si</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
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<td>12.15</td>
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<tr>
<td>3</td>
<td>57.78</td>
<td>0.47</td>
<td>5.55</td>
<td>18.04</td>
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<tr>
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<td>13.82</td>
<td>0.41</td>
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<td>60.12</td>
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<td>17.51</td>
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<td>19.27</td>
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<td>10</td>
<td>59.12</td>
<td></td>
<td>3.26</td>
<td>19.26</td>
<td>4.40</td>
<td>13.96</td>
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<td>4.06</td>
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<td>12</td>
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<td>18.74</td>
<td>4.28</td>
<td>14.04</td>
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</table>

Atomic%
Surface Treated AISI 441 w/ Ce-modified MnCo spinel coating; 800°C
ASR Results for Surface Treated AISI441
(LSCF cathode and contact, Ce-MC 441)
**Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441: 850°C**

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Mill Reference (1200 grit)</th>
<th>Temper Rolled</th>
<th>De-siliconized</th>
<th>Surface Grind</th>
<th>Surface Blast</th>
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<td>X</td>
<td>X</td>
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X - spallation on at least one coupon  
XX - no unspalled coupons left in study  
C - complete de-bonding of scale of SEM/EDS sample  
L - localized de-bonding of scale of SEM/EDS sample  
# - coupon not removed for analysis due to limited # of coupons
10000 h, 850°C in Air

- Surface Blast
- Surface Ground
- De-siliconized
- 50% Cold Rolled
- Mill Reference (1200 grit)
Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 10,000 hours, 850°C, air

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<th>Si</th>
<th>Ti</th>
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<td>19.48</td>
<td>2.27</td>
<td>14.95</td>
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Max.       64.99 | 1.01 | 0.78 | 33.58 | 19.48 | 2.27 | 14.95 | 0.50 |
Min.       58.86 | 0.49 | 0.22 | 3.49 | 7.61 | 0.16 | 9.77 | 0.24 |
Reactive Air Aluminization (RAA)

- Reaction between alkaline earths in glass seals and Cr in interconnect steel can form high CTE chromate phases (e.g., SrCrO$_4$), which degrade interfacial strength.
- Cr volatility from alloys can poison cathodes.
- Reactive Air Aluminization (RAA) offers a simple alternative to controlled atmosphere aluminization of interconnects and BOP components.

Report on RAA distributed to industry teams in October, 2011

Samples aluminized and delivered to industry teams for evaluation.
Reactive Air Aluminizing

- Aluminum powder slurry-based process
- Heat treatment in air
  - 3°C/min to 1000°C
  - 1 hour dwell at 1000°C
  - 3°C/min cooldown

1. Application & Drying
2. Heat treatment in Air
3. Removal of loose material (leaving behind an adherent, protective coating)

Brush off
Perovskite Interconnects

► Candidate Compositions
  ■ Yttrium chromite
    ● More stable towards water and YSZ than lanthanum chromite
    ● \( \text{Y}_0.8\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_3 \)
      ◆ CTE = 11 ppm/K
      ◆ Conductivity in reducing atm: \(~5\) S/cm
      ◆ Low chemical expansion: 0.06 at 900ºC
  ■ Lanthanum chromite
    ● \( \text{La}_{0.78}\text{Sr}_{0.2}\text{CrO}_3 \)
      ◆ CTE = 11.1 ppm/K
      ◆ Low chemical expansion: 0.07 at 900ºC
      ◆ More stable towards reduction (no Ni, Co, or Cu)?

► Previously demonstrated densification under constrained conditions
  ■ Multiple liquid infiltrations/heat treatments required
► Two current approaches to enhance sintering under constrained conditions
  ■ Both involve formation of final perovskite phase during sintering process
    ● Reaction sintering approach (enthalpy of reaction)
    ● Sintering aid approach (liquid phase assistance + enthalpy of reaction)
Summary

- AISI 441 w/ Ce-modified MnCo spinel coatings exhibits low, stable ASR in long-term testing
  - Less than 20 mΩ-cm² after 25,000 hours at 800°C in air

- Surface-modified AISI 441 w/ Ce-modified MnCo spinel coatings exhibits improved long-term spallation resistance
  - 18,000 hours at 800°C (tests in progress)
  - 12,000 hours at 850°C (tests in progress)

Future work:
- Continue long-term testing of surface-modified AISI 441
- Quantify relationship between surface morphology and oxidation resistance/scale adhesion
  - Prediction/Extension of IC lifetime
Acknowledgements

- The work summarized in this paper was funded by the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program

- NETL: Dan Driscoll, Briggs White, Rin Burke, Joe Stoffa, and Travis Shultz
- ATI Allegheny Ludlum: Matt Bender
- ORNL: Edgar Lara-Curzio
- PNNL: Jim Coleman, Shelley Carlson, Nat Saenz, Dan Edwards, Clyde Chamberlin, and Alan Schemer-Kohrn
Modeling Tools for SOFC Design and Analysis: Recent PNNL Progress

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E.V. STEPHENS, K. LAI, W. XU, K. AGARWAL, Z. XU, P. SHARMA, W. PAN, D. SMITH, E. RYAN*

Pacific Northwest National Laboratory, Richland, WA
*Boston University, Boston, MA

14th Annual SECA Workshop, Pittsburgh, PA
Objectives: Develop stack modeling tools to:
- Evaluate the tightly coupled multi-physical phenomena in SOFCs
- Aid understanding of materials degradation issues
- Allow SOFC designers to perform numerical experiments for evaluation of electrochemical, thermal, and mechanical stack performance
- Provide wide applicability for industry teams to solve key design problems

Approach:
- SOFC-MP 2D/3D: Multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks
- Stack reduced order model (ROM) creation for system-level studies
- Component and material models to improve stack mechanical reliability
- Micro/meso-scale models to evaluate electrode degradation mechanisms
- Experimental support to provide necessary material data for the models
Recent Progress

- **SOFC-MP Tools**
  - Modifications to the 3D tool for use in a more generic graphical user interface (GUI)
  - Development of the reduced order modeling (ROM) tool

- **Compliant Seals**
  - Constitutive model development and behavior of compliant seal materials in SOFC stacks

- **Metallic Interconnects**
  - Experimental and modeling approach for scale strength and prediction of interconnect lifetime using interfacial indentation tests

- **Electrochemical Degradation**
  - Models for cathode degradation under high humidity
Modeling Tools for SOFC Stack Analysis

**Challenge:**
- SOFC stacks must be designed for high electrochemical performance and mechanical reliability

**Goal:**
- Develop numerical modeling tools to aid the industry teams’ design and engineering efforts

**Technical Approach:**
- **SOFC-MP 3D** - Evaluates detailed 3D multi-cell stack structures for electrochemical, thermal, and mechanical stress analyses
- **SOFC-MP 2D** – Rapid engineering analysis of electrochemical and thermal performance of tall symmetric stacks
- **SOFC-ROM** – Creates reduced order models (ROMs) of SOFC stacks using response surface techniques for use in system modeling analyses
SOFC-MP 3D Recent Progress

- Construction of generic framework for SOFC-MP initiated
  - Replaces existing MSC MARC GUI for pre- and post-processing
  - Eliminates costly commercial license requirement
  - Unifies 3D and 2D packages under a common GUI for ease of use
- Pre- and post-processing for 2D tool completed
- Pre-processing for 3D model creation completed
  - Alternate model creation route beyond legacy Mentat-FC GUI
  - Implemented translators for ANSYS and ABAQUS FEA meshes
  - Fully integrated to the common GUI including assignment of operation and control parameters
Results post-processing for 3D tool started

- Linear plotting of distributions along the flow field for all physics properties completed:
  - Air and fuel temperature
  - Pressure
  - Current density
  - Species concentrations

- Multi-cell plotting and 3D contour plots using open-source software in progress

- Improved multi-physics solver performance for high methane (+20%) fuel compositions
SOFC-ROM Motivation

- More studies being performed for SOFC stack block integration and performance in large-scale demonstration systems
  - Understand performance and issues with BOP versus stand-alone testing
- Need a model to represent the stack in system models
  - Thermodynamic or 0-D models have no information about stack internal parameters such as temperature gradients, but such parameters may be critical for safe operation (e.g., maximum cell temperature)
  - Existing high fidelity SOFC-MP models have necessary information, but are too computationally expensive to run in system analyses
- Reduced order models (ROMs) provide approximate representations of such detailed models in O(1) time
- SOFC-ROM leveraged from the REVEAL framework at PNNL
  - REVEAL: a generic, automated framework for building ROMs for scientific simulations
SOFC-ROM Workflow

**Base Fuel Cell Model**

Identify Design Parameters:
- Stack Voltage,
- Fuel temperature, etc.

Sampling:
- LHS,
- Norm, QMC

**Job Execution Infrastructure**
- Automated Post processing
- Data Management

**Export ROM Plug-in for power system simulations**

**Sampling Method**
- Parameter Ranges
- Number of Samples

**ROM Analysis Tools**
- Visualization
- Error Estimation
- Predictive Analysis

**Regression**
- Kriging
- ANN
- SVM

**Sensitivity Analysis**
- ANOVA
- SRC

**SOFC-ROM User Environment**

August 2, 2013
SOFC-ROM workflow completed

- SOFC-MP 2D tool integrated as stack input
- Multiple sampling methods implemented (LHS, QMC, Gaussian)
- Multiple methods for regression (Kriging, ANN, MARS, SVM) and sensitivity analysis (ANOVA, SRC, MARS) implemented
- ROM output in ACM or CAPE-Open format added
- Fuel/air composition added to parameter set
- Constraints on fuel/air compositions and parameter dependencies added
- Error handling added to trap and discard invalid or unconverged cases from the solution set
- Installation and user manuals prepared
Ongoing and Future Work

- **SOFC-MP 3D**
  - Implement post-processing visualization of SOFC-MP 3D results contours in the common GUI
  - Implement FEA stress analysis routines

- **SOFC-ROM**
  - Evaluate ROM export capabilities and integration with commercial system modeling tools (e.g. ASPEN) for study of SOFC-based power generation systems.
  - Release ROM version with documentation and examples
Challenge:
- SOFC stacks must have reliable hermetic seals under operating and thermal cycling loads

Goal:
- Develop constitutive and damage models to design and simulate robust compliant seal materials and concepts for stacks

Technical Approach:
- Understand the healing and damage mechanisms
- Combine different length-scale modeling approaches to establish quantitative relationships between material structure and its measured physical properties
- Perform stack-level thermo-mechanical simulations to determine the effects of material properties and operating conditions
- Validate the models through comparisons with experimental data
Constitutive Damage/Healing Model

- Continuum thermo-inelastic model for dynamic damage and healing of self-healing glass
  - Includes the crack evolution and internal pore propagation

\[
\dot{\sigma}_{ij}^M = (1 - \xi) \left( C_{ij}^{eq} \dot{\varepsilon}_{ij}^M + C_{ij}^{neq} \dot{\varepsilon}_{ij}^e \right)
\]

\[
\dot{\xi} = \dot{\xi}_c + \dot{\xi}_p
\]

- Consider different underpinning mechanisms
  - Pressure driven crack nucleation
  - Deformation energy driven crack growth
  - Thermal diffusional crack healing
  - Homogeneous and heterogeneous pore nucleation
  - Inelastic flow induced pore growth

\[
\dot{\xi}_c = \dot{\xi}_{cn} + \dot{\xi}_{cg} + \dot{\xi}_{ch}
\]

\[
\dot{\xi}_p = \dot{\xi}_{pn} + \dot{\xi}_{pg}
\]
SOFC single cell simulation predicts the seal mechanical response during rapid thermal cycling

- Realistic temperature profile from SOFC-MP analysis

- Cracking damage fully recovered during 30 min high temperature operation
- Pore damage not recovered (based on experimental observations to date)
Can simulate multiple cycles

Overall damage within the glass seal is still kept within tolerance (<2%)

Periodic maximum crack damage increases with loading cycles due to porosity accumulation and its effect on the elastic properties.
Effect of Temperature Uniformity

- Effects of temperature uniformity in the cell
  - Uniform temperature takes the mean of the non-uniform temperature field
  - Very similar stress distributions in the seal
  - Slightly different damage evolution profiles
  - Temperature variation leads to more non-uniform damage distribution and low temperature regions show slower healing
Effect of Dominant Damage Sources

Depending on which damage sources are dominant, the effects of viscosity on seal glass material behavior may be different.

**pore dominates**

- Damage versus Viscosity

**crack dominates**

- Viscosity \(\uparrow\) Leak Rate \(\downarrow\)

[Chou, PNNL]

Viscosity \(\uparrow\) Leak Rate \(\uparrow\)

**Effect of Material Heterogeneity**

- Reinforcement phases (fibers, particles) can introduce heterogeneity
  - Normal distribution is assumed for the viscosity within the seal geometry
  - Heterogeneous viscosity field greatly reduces the damages
  - Low viscosity regions provide local compliance and stress relief

![Crack Evolution](image1)

![Pore Propagation](image2)
Effect of Material Properties

- Material mechanical response in terms of characteristic material properties, i.e. elastic modulus and viscosity
- 25 cases to establish the response surface: $\log(\eta/\eta_0)$: -2:1:2, $\log(E/E_0)$:-2:1:2
- Cracking damage is highly sensitive to stiffness but less affected by viscosity
- Pore growth is strongly influenced by both properties
- High viscosity together with low stiffness would lead to the least damage
Ongoing and Future Work

- Evaluate the seal performance within multi-cell SOFC stacks
- Continue model development by including effects such as stress dependent viscosity and material stochastic behavior
- Examine different engineering seal designs to support the seal material development effort
Mechanical Reliability and Life Prediction of Coated Metallic Interconnects

- **Challenge:**
  - IC must meet SECA lifetime requirement

- **Goal:**
  - Use experiments and modeling to predict interconnect life for spinel-coated surface-modified specimens under isothermal cooling and thermal cycling

- **Technical Approach:**
  - Vickers pyramidal nano/micro-indentation performed at the substrate/oxide scale interface to assess apparent fracture toughness and spallation resistance of surface modifications
  - Fracture mechanics and FEA modeling tools to evaluate driving force and energy release rate for spallation to determine the main factors influencing IC degradation
  - Evaluation of IC candidate materials
Interfacial Indentation Testing

- Apparent interface fracture toughness ($K_I$) of bimaterial interface may be estimated as [1, 2]:

$$K_{in} = 0.015 \frac{P_c}{a_c^{3/2}} \left(\frac{E}{H}\right)^{1/2}_I$$

- Nano/micro indentation performed to propagate crack between substrate and scale to determine the critical load $P_c$ and critical crack length $a_c$

- Intersection of the indentation data linear fit and the apparent hardness defines the critical load (adaptation of methodology)

Surface ground, 10,000 h, 800 °C

Interfacial Indentation Testing Results

- Data collection time intensive
- Initial results indicate indentation tests follow the expected response
- Average stress intensity factor:
  - 441 SB: $\sim 2.5 \text{ MPa} \cdot \text{m}^{0.5}$
  - 441 SG: $\sim 2.0 \text{ MPa} \cdot \text{m}^{0.5}$
Failure Modes for Coatings

Shear stress distribution

\[
\sigma_{13}(x, 0)
\]

\[
\sigma_{Rh} = \int_{0}^{\infty} \sigma_{13}(x, 0) dx
\]

Edge delamination (Mode II dominant)

Compressive stress distribution

\[
(\sigma_{11})_{ave} = \frac{1}{h} \int_{0}^{h} \sigma_{11} dx_3
\]

\[
\sigma_R = \frac{E \Delta \alpha \Delta T}{1 - \nu}
\]

Buckling delamination (Mixed mode I and II)
Failure Criteria for Critical Thickness $h_c$

**Energy release rate:**

$$G = \frac{(1 - \nu^2)h\sigma^2}{2E} \left(1 - \frac{\sigma_c}{\sigma}\right) \left(1 + 3\frac{\sigma_c}{\sigma}\right)$$

**Thermal stress:**

$$\sigma = \frac{E\Delta\alpha\Delta T}{1 - \nu}$$

**Critical buckling stress:**

$$\sigma_c = \frac{\pi^2}{12} \frac{E}{1 - \nu^2} \left(\frac{h}{b}\right)^2$$

**Fracture toughness:**

$$\Gamma(\Psi) = \Gamma_I \left(1 + \tan^2\left[(1 - \lambda)\Psi\right]\right)$$

$$\Gamma_I = \frac{1 - \nu^2}{E} K_I^2$$

From interface indentation experiment

**Failure Criterion:**

$$G(h, \sigma, b) > \Gamma(\Psi(h))$$

**Toughness of Interface**

**Critical Thickness**

**Energy Release Rate**

If $h > h_c$: coating will fail under cooling
If $h < h_c$: coating will survive cooling
Failure Analysis Results

Based on the measured stress intensity factor, a threshold blister size is predicted for which no buckling delamination failure is expected:

- $K_I = 1.8 \text{ MPa-m}^{0.5}$, $b=60 \ \mu\text{m}$, $h_c \sim 4.4 \ \mu\text{m}$
- $K_I = 2.9 \text{ MPa-m}^{0.5}$, $b=120 \ \mu\text{m}$, $h_c \sim 9.2 \ \mu\text{m}$
For range of stress intensity factor of ~2-3 MPa-m^{0.5}, a critical thickness of 4-9 µm is predicted for SB/SG materials.

Present long-term experiments with average thickness of almost 8 µm for SB/SG materials are still running.
Proposed Predictive Methodology

- Use short duration oxidized specimens for long-term predictions
- Validate on modified and unmodified specimens
- Identify possible standard materials

\[ \text{Oxidize Specimen for Short Duration} \rightarrow \text{Perform Indentation on Cross-Section} \rightarrow \text{Calculate } K_{IC} \rightarrow \text{Calculate Minimum Thickness} \rightarrow \text{Projected Time to Initial Spall Failure} \]

Theory of Interfacial Toughness

Bi-Layer Fracture Mechanics and Isothermal Cooling

Materials Testing

Modeling

Oxide Growth Kinetics
Ongoing and Future Work

- Indentation measurements on 850°C specimens
- Evaluation of experimental/analytical methodology as screening method for life-prediction
  - Life predictions of surface modified specimens exposed to 800°C
  - Determine $K_{in}$ for 2000 h, 800°C, unmodified, coated 441 specimens
  - Benchmarking of methodology with known standards if available
  - Effect of surface roughness on methodology and data scatter
Electrochemical Degradation Under High Cathode Humidity Conditions

**Challenge:**
- Long-term electrochemical performance degradation must be low

**Goal:**
- Use modeling to identify cathode degradation mechanisms and characterize electrochemical impact for high humidity conditions

**Technical Approach:**
- **Micro-scale** – Investigate the surface level kinetics and thermodynamics of H$_2$O with LSM using molecular dynamics modeling of H$_2$O, O$_2$ and LSM in the presence of an applied field
- **Meso-scale** – Resolve the reactive transport in the cathode and at the cathode-electrolyte interface using SPH porous media model
- **Macro-scale** – Cell and stack level modeling of the effects of degradation on stack performance using SOFC-MP
Micro-Scale Modeling Results

- Want to evaluate O\textsubscript{2} and H\textsubscript{2}O competitive adsorption and diffusion on LSM
- La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3} periodic solid structure model built (density, cohesion energy, and O\textsubscript{2} adsorption activation energy) consistent with experiment
- H\textsubscript{2}O adsorption activation energy predicted and passed up to the meso-scale model

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<td>cohesion energy at 1000 K (eV)</td>
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<td>O\textsubscript{2} adsorption activation energy (eV)</td>
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<td>H\textsubscript{2}O adsorption activation energy (eV)</td>
<td>1.32±0.07</td>
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Meso/Macro-Scale Modeling Results

► SPH model for 2D porous cathode structure created
► Langmuir model for competitive adsorption
► Simulated accelerated testing with higher humidity levels (10%, 20%, 40%) for 100 hr to accelerate rate of degradation
  ■ Adsorption site competition alone cannot explain the degradation results of PNNL or Nielsen (2011)
► Electrochemical degradation captured as damage factor and applied to the cathode exchange current density in the macro-scale I-V curve

August 2, 2013
Ongoing and Future Work

- Expand micro-scale model to consider possible reactions with Mn or Sr
- Evaluation of PNNL long-term test data for identification of possible mechanisms at low humidity
Acknowledgements

- The work summarized in this presentation was funded by the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program

- The authors wish to thank Shailesh Vora, Briggs White, Rin Burke, Joe Stoffa, and Travis Shultz for their valuable technical discussions and guidance.
SECA Core Technology Program
R&D at PNNL: Overview


Pacific Northwest National Laboratory
Richland, WA 99354

July 23, 2013
14th Annual SECA Workshop
Pittsburgh, PA
Objective

Provide R&D support to SECA program

- From SECA Program Mission statement: “Increase reliability, robustness, and durability of cell and stack technology”
- Development/evaluation of improved materials and fabrication processes for SOFC cells and stacks
- Improved understanding of performance degradation mechanisms
- Development/implementation of modeling tools to facilitate cell and stack design and optimization

Technology transfer to industry teams

- Stack test fixture validation
- Topical reports, journal articles
- Semi-annual one-on-one reviews, SECA Workshop
- Provide materials, software for evaluation/implementation by industry teams
Scope of Work

Determined through consultation with NETL program management and SECA industry teams
  - Increased communication with industry teams in recent years

Current areas of emphasis (combined experimental/modeling approach)
  - SOFC interconnects
    - Alloys and coatings for IT-SOFC interconnects
  - Seals for SOFC stacks
    - Compliant glass-based seals
  - Cathode materials and interactions
    - Effects of humidity; In-situ XRD characterization
  - Anode materials and interactions
    - Effects of high fuel utilization; Mitigation of sulfur poisoning
  - Cell/stack design
    - 2D and 3D modeling tools to assist in cell/stack design
    - Poster Presentation: ROM Tool for SOFC Modeling (Brian Koeppel)
    - Oral Presentation: Modeling Tools for SOFC Design and Analysis (Brian Koeppel)
Seals for SOFC Stacks

▶ Primary Challenge
- Reliability during thermal cycling (high residual stresses)

▶ Approach (collaboration with ORNL)
- “Compliant glass” based seals: Glass exhibits low Tg and relatively low viscosity at operating temperature, resulting in mitigation of mechanical stresses during operation and thermal cycling. Potential for self-healing of cycling-related damage.

- ORNL is primarily responsible for materials properties characterization, while PNNL has primary responsibility for modeling and seal test activities.
  - Evaluate thermal, mechanical, and chemical sealing glass properties (including glass-based composites).
  - Design and test compliant glass-based seals to evaluate seal performance in terms of leakage, mechanical stability, and reactivity (e.g., interactions with adjacent materials, electrode poisoning due to volatilization and deposition of glass constituents).
  - Develop compliant glass constitutive models to simulate thermal stresses, seal damage evolution, and healing behavior during stack operation.
Compliant Glass-based Seals

Status (completed work)

- Measurement of thermo-physical and mechanical properties (viscosity, CTE, elastic constants, crystallization rate; 15,000 hours)
- Assessment of electrical, microstructural, and chemical stability
  - High electrical resistance maintained with aluminized steel components
  - Some de-vitrification observed; controlled by limited amount of Ba and Al in glass
  - Minimal volatilization over stack lifetime
  - Potential issues associated with pore coarsening/void formation

Glass only

15 vol% Zirconia fiber

Aged 800°C, 250 hours
Compliant Glass-based Seals

- **Ongoing/Future work**
  - Inclusion of fillers (zirconia fibers, particles) to modify viscosity, control porosity and displacement
  - Optimization of seal design and fabrication techniques
  - Long-term evaluation of seals in seal test fixture and stack test fixture
  - Modeling of microstructural, thermophysical, and mechanical behavior
    - Self-healing behavior
    - Simulation of seal performance in stacks

- **Preliminary assessment in seal test fixture:**
  - 12 deep thermal cycles (RT to 800°C)
Preliminary evaluation of compliant glass seal: ~1300h, 800°C, 3 thermal cycles

- No cross-bubbling at room temperature
- No discoloration on either cathode and anode side
- No iso-propanol penetration along sealing edges or through cell

- Long-term evaluation in stack test fixture is in progress

  • Poster:
    Compliant Glass Seal Development at Pacific Northwest National Laboratory (Matt Chou; collaboration with ORNL)
Cathodes

Primary Challenges
- Long-term stability
- Effects of contaminants

Approach
- Emphasis on effects of humidity in cathode air stream on cell performance
  - Button cell tests (including high temperature XRD) at varying temperatures and humidity levels
  - Modeling to develop improved understanding of cathode reactions and degradation mechanisms
- Leveraging activities/results with other SECA Core Program cathode researchers

Status
- 1000 hour cell tests completed on LSCF and LSM-20/YSZ; performance trends identified

Ongoing / Future activities
- Tests in progress on LSM-0 (LM) and LSM-5
- High temperature XRD on working cathodes: Effect of humidity on LSM/YSZ cathodes
- Modeling of kinetics, thermodynamics, and possible reactions with LSM-20

Posters:
- LSM-20/YSZ Cathode Response to Elevated Steam Content in 500-1000 h Tests (John Hardy; collaboration with NETL)
- In-Operando XRD of Anode-Supported LSCF Cathodes at 700 – 800°C for 1000 h (John Hardy)
Anodes

Primary Challenges
- Long-term microstructural stability in high water environments
- Effects of contaminants

Approach
- Emphasis on effects of high fuel utilization (high water content) on Ni-YSZ anode performance
  - Cell and coupon tests at varying temperatures and water levels
  - Fuel is simulated clean coal gas
- Mitigation of sulfur poisoning

Ongoing / Future activities
- Microstructural changes (Ni coarsening) observed at 900 and 1000°C at high fuel water contents; tests and analysis in progress
- Attempting to correlate anode electrochemical performance with microstructural changes

Poster:
- Stability of Nickel in Ni/Zirconia Electrodes at High Steam Concentrations (Olga Marina)
SOFC Interconnects & Coatings

► Primary Challenges
  ■ Cr volatility (cathode poisoning)
  ■ Increasing electrical resistance
  ■ Scale de-bonding/spallation

► Approach
  ■ Low cost ferritic stainless steel interconnects with protective coatings (MnCo spinel, aluminization)
  ■ Experimental: Oxidation testing, ASR testing, stack fixture testing, micro/nano indentation
  ■ Modeling: Finite element-based modeling tools utilizing experimentally obtained strength data to determine spallation mechanisms and predict interconnect lifetime

► Posters
  ■ Recent Progress of SOFC Materials Validation in a Generic Stack Fixture at Pacific Northwest National Laboratory (Matt Chou)
  ■ Novel Interconnect Spinel Coating Process for Planar SOFC Stacks (Jung Pyung Choi)
  ■ Interconnect Lifetime Prediction from Interfacial Indentation (Brian Koeppel)
Low-cost Alloy-based Interconnects

**Interconnect Alloy: AISI 441**
- Ferritic stainless steel: Good CTE match to other components; Electrically conductive Cr-based oxide scale
- Inexpensive - Manufactured via conventional melt metallurgy
- Similar to AISI 430, but additions of Nb and Ti improve high temperature strength and prevent formation of insulating SiO₂ layer at alloy/scale interface
- Similar to all other FSS, relatively high oxidation rate at SOFC operating temperatures (and volatility of Cr) indicates need for protective coating
- Also, relatively weak scale adherence (no RE in alloy)

**Interconnect Coating: Ce-modified (Mn₀.₅Co₀.₅)₃O₄ Spinel**
- High electrical conductivity (~60 S/cm), good CTE match (~11 ppm/K)
- Ceria inclusions improve oxide scale adherence
- Coating improves oxidation resistance and mitigates Cr volatility

<table>
<thead>
<tr>
<th>k_p (g²/cm⁴-s)</th>
<th>800°C</th>
<th>850°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-MC coated 441</td>
<td>2 x 10⁻¹⁴</td>
<td>1 x 10⁻¹³</td>
</tr>
<tr>
<td>Bare 441</td>
<td>5 x 10⁻¹⁴</td>
<td>3 x 10⁻¹³</td>
</tr>
</tbody>
</table>
Surface Modifications to AISI 441

- Goal: Improve long-term scale adhesion under spinel coating

- Provided by Allegheny Ludlum:
  1. Mill reference (as would be provided to a customer without any additional modifications)
  2. Desiliconized (treatment to sequester silicon from the near surface of the sheet; an alternative to decreasing Si content of alloy)
  3. Surface blasted (abrasion/peening resulting in surface deformation)
  4. Surface ground (rough surface abrasion resulting in surface deformation)
  5. Temper rolled (cold rolling process resulting in through-thickness deformation)

- Oxidation testing of 0.02” thick, MnCo spinel-coated coupons at 800 and 850°C
## Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441: 800°C

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Mill Reference (1200 grit)</th>
<th>Temper Rolled</th>
<th>De-siliconized</th>
<th>Surface Grind</th>
<th>Surface Blast</th>
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<td></td>
<td></td>
<td>Macroscopic Spallation</td>
<td>Macroscopic De-bonding</td>
<td>Macroscopic Spallation</td>
<td>Macroscopic De-bonding</td>
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</tbody>
</table>

- X - spallation on at least one coupon
- XX - no unspalled coupons left in study
- C - complete de-bonding of scale of SEM/EDS sample
- L - localized de-bonding of scale of SEM/EDS sample
- # - coupon not removed for analysis due to limited # of coupons remaining
20000 h, 800°C in Air

- Surface Blast
- Surface Ground
- De-siliconized
- 50% Cold Rolled
20000 h, 800°C in air

Surface Blast

Desiliconized

Surface Grind

Cold Rolled
Surface Blasted AISI 441 w/ Ce-modified MnCo Spinel coating: 20,000 hours, 800ºC, air

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>O</th>
<th>Si</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
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<th>Ce</th>
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<tr>
<td>9</td>
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<td>0.42</td>
<td>0.43</td>
<td><strong>4.61</strong></td>
<td>17.30</td>
<td>2.67</td>
<td>12.50</td>
<td>0.24</td>
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</tbody>
</table>

Atomic%
Surface Treated 441 w/coating; 800°C
## Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441: 850°C

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Mill Reference (1200 grit)</th>
<th>Temper Rolled</th>
<th>De-siliconized</th>
<th>Surface Grind</th>
<th>Surface Blast</th>
</tr>
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<tbody>
<tr>
<td></td>
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<td>Macroscopic De-bonding</td>
<td>Macroscopic Spallation</td>
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<td>XX</td>
<td>#</td>
<td>XX</td>
<td>XX</td>
</tr>
</tbody>
</table>

- **X** - spallation on at least one coupon
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- **#** - coupon not removed for analysis due to limited # of coupons remaining
Effect of Surface Condition on Oxidation/Spallation Behavior of Spinel-coated 441: 850°C

- Mill reference
- Temper rolled
- Surface ground
- Surface blast
- Desiliconized

Scale Thickness (microns)

Time (hours)
20000 h, 850ºC in Air

- Surface Blast
- Surface Ground
- 50% Cold Rolled
20,000 h; 850°C in air

Surface Blast

Surface Grind

Cold Rolled

Desiliconized
Surface Blast AISI 441 w/ Ce-modified MnCo Spinel coating: 20,000 hours, 850°C, air

<table>
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<tr>
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<th>Mn</th>
<th>Fe</th>
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<th>Ce</th>
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<tbody>
<tr>
<td>Spectrum 1</td>
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</tr>
</tbody>
</table>
Spinel composition (metals basis)

Surface blast coupons, except 850C, 12000 and 14000h are surface grind
Effect of Cr on spinel electrical conductivity and CTE

Optimization of Surface Blast Surface Modification

- 441 samples (0.5 mm) were prepared via surface grit blasting to further quantify and understand the effects of surface morphology on oxidation/spallation behavior
  - Grit size was varied to evaluate two distinctively different processed surfaces (G80 vs. G40)
  - Long-term oxidation testing in progress

Grit size: G80 (0.125-0.425 mm)  
Grit size: G40 (0.300-1.00 mm)
Summary

- PNNL is using experimental and computational methodologies to support SECA Industry Team SOFC development.

- Interconnects
  - Spinel-coated, surface-modified AISI 441 exhibits improved long-term scale spallation resistance compared to coated, unmodified AISI 441.
    - Surface blast appears to be most promising surface treatment
      - 26,000 hours at 800°C (tests in progress)
      - 22,000 hours at 850°C (tests in progress)
      - Topical Report delivered to SECA Industry Teams (January 2013)

- Cathodes
  - Cell test results indicate that effects of moisture (3% water) on degradation rate become more severe with decreasing temperature for both LSCF and LSM/YSZ cathodes.

- Anodes
  - Microstructural changes (Ni coarsening) observed at 900 and 1000°C at high fuel water contents.

- Compliant Seals
  - Preliminary results indicate excellent isothermal performance (>1000 hours) and stability towards thermal cycling.
Acknowledgements

- The work summarized in this paper was funded by the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program

- NETL: Shailesh Vora, Briggs White, Rin Burke, Joe Stoffa, and Travis Shultz
- ATI Allegheny Ludlum: Matt Bender
- ORNL: Edgar Lara-Curzio
- PNNL: Shelley Carlson, Nat Saenz, Dan Edwards, Clyde Chamberlin, and Alan Schemer-Kohrn
Modeling Tools for SOFC Design and Analysis: Recent PNNL Progress

BRIAN J. KOEPPEL
K. LAI, W. XU, K. AGARWAL, E.V. STEPHENS, Z. XU

Pacific Northwest National Laboratory, Richland, WA
15th Annual SECA Workshop, Pittsburgh, PA
1. Develop stack modeling tools
   - **SOFC-MP 2D/3D**: Multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks
   - **SOFC-ROM**: Creation of high fidelity reduced order model (ROM) for use in system-level studies
   - **User Interface**: Make these tools accessible to stack designers

2. Develop models to improve component durability
   - **Compliant Seals**: Damage-healing constitutive model for study of seal designs
   - **Interconnects**: Model to evaluate effects of surface modifications and coatings on durability and lifetime
Summary of Accomplishments

- **Stack Modeling Tools**
  - Coupled 3D SOFC-MP tool with ANSYS and ABAQUS finite element codes for structural analysis
  - Created a graphical user interface (GUI) for pre- and post-processing of 2D and 3D SOFC-MP models
  - Completed reduced order modeling (ROM) tool

- **Compliant Seals**
  - Evaluated compliant seal performance and damage-healing evolution in multi-cell stack simulations under thermal cycling

- **Metallic Interconnects**
  - Developed an experimental-modeling approach for prediction of interconnect lifetime using interfacial indentation tests of surface-modified, coated interconnects
SOFC-MP 3D Integration with FEM Software

- Integration with ABAQUS and ANSYS FEM models implemented
  - Models created in the FEM environment per guidelines and exported
  - Mesh is read by SOFC-MP and the electrochemical model is solved
  - Thermal distributions from the 3D simulation exported
  - Structural analysis run in the commercial FEM code using the exported temperature field data

3D SOFC-MP Analysis

FEM Geometry/Mesh

Temperature Field

Thermal Stress Distribution
Example: SOFC-MP/ANSYS FEA Model

- 50-cell ANSYS co-flow stack w/ H₂ fuel
SOFC-MP GUI

- Graphical user interface replaces legacy MSC-MARC tool
- Tabular menu structure provides pre-processing, job submission, job monitoring, and post-processing capabilities for both 2D and 3D SOFC-MP simulations

3D SOFC-MP planar contours for cells
Cross-section plot of fuel temperature for 20-cell 2D model

- Effect of different fuel utilizations for cells #5 and #15 show higher peak temperature and gradient

2D SOFC-MP cross-section contours for stack

- Top of stack
- Bottom of stack
- Nominal flow
- Fuel maldistribution
- Fuel/Air Flow Direction
System Design Challenge

- Ultimately, need design/engineering at several scales for successful SOFC commercialization
- Modeling is practically limited by required computation times
  - Lower scales require smaller spatial resolution
  - Higher scales sacrifice detail or accuracy
- Utilizing more details from the cell/stack level models to inform the system level model will allow more insight necessary for optimizing the BOP components and control strategies
Reduced Order Model (ROM) Approach for SOFC Stacks

- ‘N’ Input Variables and Ranges
- Sampling of N-Dimension Space
  - Slow
  - Cases to Run
  - Stack Results
- ‘M’ Output Variables
- Regression
- Matrices for ‘M’ Response Surfaces

SOFC-ROM build

- Fast
  - Aspen Plus use
  - ‘N’ Input Values
  - Stack ROM
  - ‘M’ Output Values

August 19, 2014
SOFC-ROM: Visual Analysis Tools

- Rich menu-driven plotting capabilities to aid understanding
  - visualize 2D-3D response surfaces
  - plot sampling space
  - actual vs. predicted values

- output vs. input values
- output vs. output values
- sensitivity charts
- error histograms
- results as a function of S/C ratio

[Image showing a 3D response surface visualization]

August 19, 2014
Example: Amount of On-Cell Reforming

Region with high current density and reduced temperature identified
Example: Stack Peak Temperature Control

- Evaluate stack maximum temperature as the stack size increases
- E.g., identify required inlet temperature to ensure $T_{\text{max}} < 850^\circ\text{C}$

Use exported ROM

![Graph showing the relationship between number of cells and inlet temperature](image)

- Number of Cells
- Inlet Temperature
- Maximum Temperature

August 19, 2014
Summary for SOFC-ROM

- Implemented data validation tools
  - Checks predicted values from a created ROM against actual values to ensure ROM is suitable

- Implemented scalable error estimation
  - Previous 1-off estimation unsuitable for large number of sampled cases and replaced with 20/80 cross validation approach to test multiple parameter simultaneously

- Implemented scalable visualization
  - Pre-computation of data for rapid plotting replaced with dynamic generation for 2D or 3D graphs

- Planned initial implementation is complete

- Have initiated collaborative testing with BAH systems modelers to demonstrate utility for modeling of SOTA SOFC-based power systems
Seal Modeling Task Overview

**Challenge:**
- Seals must remain hermetic for stack operating lifetime

**Goal:**
- Develop quantitative models to capture the thermo-mechanical behaviors of the sealant glass materials and examine the durability of the compliant sealants under SOFC stack operation conditions

**Technical Approach:**
- Develop constitutive models to resolve the thermo-visco-elastic-damage-healing material behaviors of the sealant glass
- Use multi-scale modeling approaches to bridge the intrinsic material characteristics of the glass and its thermo-mechanical properties

**Accomplishment:**
- Completed model development and stack simulations to evaluate sealing performance under different operating conditions including thermal cycling
Modeling of the compliant SCN-1 glass

**Constitutive thermo-visco-elastic-damage-healing model**

![Diagram of constitutive model](image)

“damage” is considered to be the fractional reduction in elastic modulus and formulated as \( \phi = \phi_c + \phi_p \)

**Physically-driven damage and healing kinetics determined through lower-length scale simulations and experiments:**

- Pressure driven crack nucleation
- Energy driven crack growth
- Thermal diffusional crack healing
- Hydrostatic-stress induced pore nucleation
- Inelastic flow induced pore growth

Finite Element Model of SOFC stack

- PNNL’s SECA Core Technology Program stack test fixture

  - Finite element analyses performed using ABAQUS
  - Compliant seal bonds the cell to the metallic frame
  - Compliant glass material model implemented in the stack simulation through subroutines

- Similar finite element models have also been created for larger planar designs that more closely resemble full-sized SECA cells and stacks.
Reliability of Multi-Cell SOFC Stack During Multiple Thermal Cycles

- Mechanical integrity of the glass seal is minimally impacted by 10 deep and rapid thermal cycles.

- Stress and damage distributions within the three seals (from top to bottom) are almost the same; crack initiation is increased by accumulated pore-related damage which appears to saturate over time.
Compliant SCN-1 glass accumulates much less damage because of timely stress relaxation and its healing capability upon heating.

σ_{\text{max}} = 1.9 \text{ MPa}

SCN-1

σ_{\text{max}} = 21 \text{ MPa}

G18: A state-of-the-art devitrifying glass (Nguyen et al., 2006 and Stephens et al., 2009)
Effects of Ceramic Fillers on Healing (Stack Simulation)

- Healing time will increase with fiber volume fraction

\[ \dot{\varphi}_h = -h_1 \exp(-h_2 f) \left( \frac{T}{T_g} \right)^{h_3} \varphi_h \]

- Required cooling/heating rates and durations during thermal cycling to sufficiently heal cracking damage can be determined

Note: here the existence of ceramic fillers is effectively considered through the activation energy of the healing probability function. In order to explicitly resolve the interaction between the reinforcement phase and the glass matrix as well as to establish a more generic description/prediction of the influence of the fillers, high resolution lower-length scale model is needed.
Simulation of the compliant seal material suggests that it a viable design option to consider for stack sealing
- Cracking damage from thermal-cycling can be completely healed
- Pore damage occurs but is small and can be mitigated with fillers

Description and capabilities of the model developed in this task are described in a recent summary report and journal article
Mechanical Reliability and Life Prediction of Coated Metallic Interconnects

- **Challenge:**
  - IC must meet SECA lifetime requirement

- **Goal:**
  - Use modeling to predict interconnect life under isothermal cooling and quantitatively estimate the effect of materials and geometry parameters on the interconnect life

- **Technical Approach:**
  - Develop a combined analytical/numerical approach based on the theory of bucking driven blistering to relate the interface strength to the life prediction

- **Accomplishment:**
  - Evaluated the predicted statistical lifetime as a function of scatter in the strength measurements
Contributions to Long IC Lifetime

- Different design features contribute jointly to mitigate degradation mechanisms and ensure long lifetime of the IC protection system.

Coating **restricts** $O_2$ diffusion to reduce scale growth rate.

Coating **compatibility** provides very strong coating-scale interface bond.

Coating **CTE matched** with substrate to minimize thermal stresses.

Substrate surface modifications increase **interfacial strength** and **crack resistance** to prevent scale-substrate delamination.

Substrate surface modifications increase scale adhesion post-delamination by **mechanical interlocking**.

Coating stiffness provides **mechanical support** to hinder blister buckling.
Developed technical approach using experiments and modeling

- Uncertainty analysis to capture scatter in the experimental data
1) Indentation Experiments

- Specimen Conditions
  - 800-850°C
  - 2k, 10k, 14k, 20k, 26k, 30k hours
  - Surface blast (SB) and surface grind (SG)

- Plot crack size versus load
2) Uncertainty in Critical Indentation Load

- For the indent where a valid crack propagates along the interface, the log of the average crack size is plotted versus the log of the applied load.
- For all indents with or without a crack, the log of the indent diagonal is plotted versus the log of the applied load (i.e., hardness).
- Linear regression is then used for each set of data.

\[
HV = 1.8544 \frac{P}{a^2}
\]
3) Uncertainty in $K_I$

- Using the mean and standard deviation statistics from the linear fits, determine the distribution for the interface toughness.
- Perform 1000 Monte Carlo simulations.
- Determine the probability distribution function (PDF) of $\ln(P_c)$, $\ln(a_c)$, and $K_I$.

\[ K_{in} = 0.015 \frac{P_c}{a_c^{3/2}} \left(\frac{E}{H}\right)^{1/2} \]

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4) Uncertainty in $h_c$

Assume linear elastic materials with constant thermal expansion for three layers.

Next, evaluate the critical thickness $h_c$ and its uncertainty with derived distribution information on $K_I$.

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Mechanical Properties
$E, \nu, \alpha$

Thicknesses $h$

Interface Toughness $K_I$
Temperature Change $\Delta T$
5) IC Life from Oxidation Kinetic Curves

- From $h_c$, IC life can be identified from the oxidation kinetic curves.
  - Long term oxidation found to better correlate with linear fit than parabolic fit
- By this way, IC life can be quantitatively predicted, and the effect of interface toughness, coating property, etc. can be systematically investigated.

Scale Growth History at 800°C

Scale Growth History at 850°C
Using the experimentally determined oxide growth rate and the $K_{IC}$ distribution, the predicted probability density function for the expected lifetime is obtained. This is integrated to determine the cumulative distribution function.
Initial Lifetime Estimates

- Data scatter
- Still evaluating whether this is due to the methodology or the intrinsic variability of the specimens themselves
- SB is generally better than SG, but SG has much wider range of estimated strength
  - Observations of cross-sections suggest that the grinding is non-uniform
- Assuming the coupon results are representative of the entire IC, mean lifetimes of 34-57k hr at 800°C for SB specimens
Sensitivity of Critical Scale Thickness

- Evaluated effect of various parameters on critical oxide thickness $h_c$
- Mild compressive stress on the interconnect increases the $h_c$
  - Areas under stack preload will be more resistant to delamination
- The coating itself acts a mechanical support for the scale to resist buckling, so thicker coating is beneficial to resist this failure mode

Effect of Compressive Stress

Effect of Coating Thickness
The uncertainty in the IC life prediction was quantitatively derived from the variability in the indentation experiments.

The sensitivity of the critical oxide thickness to various other design parameters were evaluated.

Trends in the IC lifetime evaluations are still being investigated, but the SB surface modification is more uniform than SG which showed wide variability in strength.
Ongoing/Proposed Modeling Activities

- Complete IC analysis
- Continue work with BAH/NETL modelers to implement and test a reduced order model made by the SOFC-ROM tool in IGFC/NGFC Aspen system models
- Perform mechanical reliability study of realistic state-of-art planar stack components and interfaces for different operating conditions and amount of on-cell reforming using SOFC-MP and FEM tools
- Simulate new contact material fabrication methods and engineered surface textures to improve contact layer bulk and interfacial strength
- Evaluate effects of residual stresses from contact layer fabrication on overall stack mechanical reliability
The work summarized in this presentation was funded by the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.

The authors wish to thank Shailesh Vora, Heather Quedenfeld, Briggs White, Rin Burke, Joe Stoffa, and Travis Shultz for their valuable guidance and technical discussions.
Compliant Glass Seal Development

Yeong-Shyung Chou, Jung-Pyung Choi, Wei Xu, Elizabeth Stephens, Brian Koeppel, and Jeff Stevenson
Pacific Northwest National Laboratory, Richland, WA

Edgar Lara-Curzio
Oak Ridge National Laboratory, Oak Ridge, TN

15th Annual SECA Workshop, Pittsburgh, PA
July 22, 2014
Outline

- Optimization of seal composition (glass/zirconia composites) and microstructure
- Results of preliminary seal tests
- Results of long-term tests in stack test fixture
- Conclusions
- Acknowledgments

Note: Modeling of compliant glass seals will be reported tomorrow by Brian Koeppel
Microstructural Optimization

Optimization of sealing heat treatment schedule improves microstructure, but considerable residual porosity is still present (result of pore expansion at higher temperatures where glass viscosity is reduced)
Glass/zirconia composites

- Approach: Inclusion of fillers (zirconia fibers or particles) to modify glass viscosity, limit pore size, and control displacement

- ORNL: Glass/fiber and glass/particle tapes (3:1, 4:1, and 5:1 ratios)
- PNNL: Glass/fiber pastes (5, 10, and 15 vol% fibers)

- 10YSZ fiber: ZYBF-5 (Zircar)

- CaSZ hollow spheres: ZHB (Zircar)
  - 0.2 – 3 mm diameter
Simulated seals: 800°C/4000h

As-sealed (850°C/2h)

SCN-1&ZrO₂ hollow spheres (5:1)

Plain SCN-1

SCN-1&ZrO₂ fibers (15%)
Seal Text Fixture:
Screening tests including thermal cycling

- SCN-1 glass with ZrO₂ hollow spheres at 3:1, 4:1, and 5:1 ratios (from ORNL)
- SCN-1 glass with ZrO₂-YSZ fibers at 0% and 15v%
Sample preparation for screening test

- Aluminized AISI441 (2”x2”) plate and bilayers (1”x1”) were sealed with candidate glass in paste or tape form.
- Heated to 850°C/2h in air and tested with iso-propanol for hermeticity before thermal cycling test
Thermal cycling of SCN-1 glass with YSZ fibers

- ~40°C to 800°C in 3h, held for 3h at 800°C then furnace cooled to ~40°C in ambient air, 1 cycle/day.
- Constant leak rates suggested hermetic seal (observed leakage was consistent with perimeter mica seal)
- Post-test check with iso-propanol showed no penetration through seal
Post-test analysis of SCN-1 glass with 15V% YSZ fibers after 12 thermal cycles

- No iso-propanol penetration along sealing edges or through bilayer
- No cracks in sealing glass
Post-mortem analysis of SCN-1 glass with hollow zirconia spheres (5:1) after 12 thermal cycles

- No iso-propanol penetration along sealing edges or through bilayer
- No cracks in sealing glass
SECA Core Technology Program Stack Test Fixture

Stack Test Cross-Section (Not to Scale)
Validation tests of compliant glass seals in stack fixture

- LSM cell, sealed at 850°C/4h
- Tested at 800°C, constant current mode, 50% H₂ fuel, one deep thermal cycle to RT every 400-500h
- Plain SCN-1 glass, SCN-1 with 15 vol% zirconia fiber or crushed zirconia hollow spheres (5 to 1 volume ratio)

- No evidence of seal damage or failure during post-test analysis
- Test with zirconia fibers was continued for long term testing (Less tendency for pore coarsening)
SCN-1 with zirconia spheres (5:1) after 1500h/800°C & 3 deep thermal cycles

- Stable OCV
- No iso-propanol penetration after ~1500h and 3 thermal cycles
- No discoloration observed on anode
- No discoloration of seal
Power outage and loss of air and compressive loading at ~1500h.
LSM-based cell with LSM20 cathode contact
Comparable degradation rates during last 3000 hours
EIS analysis of cell with SCN/15% YSZ fibers

- Loss of electrical power and air (facility outage) at ~1750h resulted in an abrupt decrease in power (loss of cathode contact?)
- OCV remained fairly constant at 1.040 to 1.030 V
Post-test analysis after stack fixture test

- Hermetic seal?
- Glass spreading?
- Interfacial microstructure and reactions?
- Glass microstructure evolution?
- Alkali deposition/poisoning?
Post-test analysis after 5830h, 800°C

- Homogeneous color, consistent with iso-propanol penetration tests and cross-bubbling tests showing hermetic behavior.
- No glass spreading or penetration into porous anode observed.
Post-test analysis after 5830h, 800°C

- No discoloration of cathode and along sealing edges
Microstructure analysis: YSZ interface

- No precipitates along YSZ/glass interface.
- No dissolution of YSZ or glass leaching.

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Microstructure analysis: aluminized interface

- No distinct reaction/precipitates of along Al₂O₃ interface.
- Al₂O₃ protection layer appeared intact.
- No dissolution of species from AISI441 into glass matrix.

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![Microstructure image with element analysis]
Microstructure analysis after 800°C 5830h

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Small amount of Na detected, while K and Si are below detection limit.
Glass microstructure after 800°C 5830h

- Pore coarsening minimized by ZrO₂ short fibers (size & morphology).

800°C/5830h SCN-1+15% ZrO₂(f) 800°C/1324h plain SCN-1
Conclusions

- Experimental and modeling studies performed for SECA Core Technology Program indicate that compliant glass-based seals offer a number of potential advantages over conventional seals based on de-vitrifying glasses.
  - Reduced stresses during stack operation and thermal cycling
  - Ability to heal micro-damage induced during thermal cycling

- A comprehensive understanding of the thermal, chemical, and mechanical properties of a variety of candidate sealing glasses was developed.

- Multiple tests (up to 5800 hours) on compliant glass seals (with and without modifying fillers) under SOFC stack-like conditions demonstrated viability of the approach.
  - High, stable open circuit voltage (OCV)
  - No spreading of glass or penetration into porous anode supports
  - Chemically compatible with YSZ electrolyte and aluminized AISI 441 interconnects
  - Negligible deposition of alkalis in electrodes
  - Addition of zirconia fillers helps minimize pore coalescence

- June 2014: Final report delivered to SECA Industry Teams
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