



PNNL- 17745

Prepared for the U.S. Department of Energy  
under Contract DE-AC05-76RL01830

# SECA Coal-Based Systems Core Research: Anode Reactions in Coal- Derived Fuels

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September 2008



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UNITED STATES DEPARTMENT OF ENERGY  
*under Contract DE-AC05-76RL01830*

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## III.B.4 SECA Coal-Based Systems Core Research: Anode Reactions in Coal-Derived Fuels

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- Montana State University, Bozeman, MT
- University of Florida, Gainesville, FL

Contract Number: 44036

Start Date: October 1, 2006

Project End Date: September 30, 2008

### Objectives

- Determine how contaminants found in coal gas affect the performance of nickel-based solid oxide fuel cell (SOFC) anodes, with an emphasis on those contaminants expected to form secondary solid phases with nickel.
- Establish maximum concentrations of contaminants and contaminant combinations in coal gas that would allow SOFCs operating on that fuel to meet long-term degradation standards.

### Accomplishments

- Irreversible losses in SOFC performance up to 10 percent per 100 hours were observed when exposed to low, 1-10 ppm, concentrations of phosphine ( $\text{PH}_3$ ) in simulated coal gas. Lower, but still irreversible SOFC degradation was observed in the presence of similar concentrations of arsine ( $\text{AsH}_3$ ). Both phosphine and arsine interact strongly with Ni in the upper part of the anode to form stable secondary phases such as  $\text{Ni}_3\text{P}$ ,  $\text{Ni}_5\text{P}_2$  and  $\text{Ni}_5\text{As}_2$ . No interactions of phosphorus- or arsenic-containing species with either zirconia or ceria were observed.
- In the presence of multiple contaminants such as phosphorus, arsenic and sulfur present in similar

low, 1-2 ppm, concentrations, sulfur is the most rapid to attack the nickel and is responsible for a 15-30%, depending on the temperature, performance drop. Cell performance losses due to sulfur exposure were reversible and independent of the presence of other impurities. Sulfur-nickel interactions were limited to the surface and no secondary phases were formed. Following slow second stage degradation is attributed to the presence of phosphorus and arsenic.

### Introduction

The coupling of coal gasification with SOFCs is being considered by the U.S. Department of Energy as a highly efficient means of electricity production [1]. Gasified coal contains high concentrations of hydrogen and carbon monoxide, which can be utilized by an SOFC to produce electricity. Gasified coal also contains many other minor and trace components that could have an impact on SOFC performance. A recent modeling study by Trembly et al. [2] identified Sb, As, Cd, Hg, Pb, P, and Se as coal gas contaminants that are most likely to affect the performance of an SOFC, some of which are predicted to form secondary bulk phases with nickel in the SOFC anode. Experimental verification of modeling calculations was identified as a critical need.

The effect of phosphorus, arsenic and sulfur impurities in the simulated coal gas on the SOFC performance was investigated under typical SOFC operation conditions. Cells tested were standard nickel/yttria-stabilized zirconia (YSZ) – supported cell with a thin YSZ electrolyte and 20 at% strontium-doped lanthanum manganese cathode. Electrodes were exposed to single and multiple contaminants at concentrations appropriate to their presence in gasified coal, and the cell electrochemical performance was evaluated.

### Approach

The ultimate goal of this project is to establish maximum acceptable concentrations of coal gas contaminants and contaminant combinations that would permit SOFCs to meet long-term standards for degradation. In the current year, the principal focus was on the effect of phosphorus, arsenic and sulfur on the standard nickel/YSZ SOFC anode when present as a single contaminant or in combination in the coal gas. Phosphorus and arsenic at parts per million

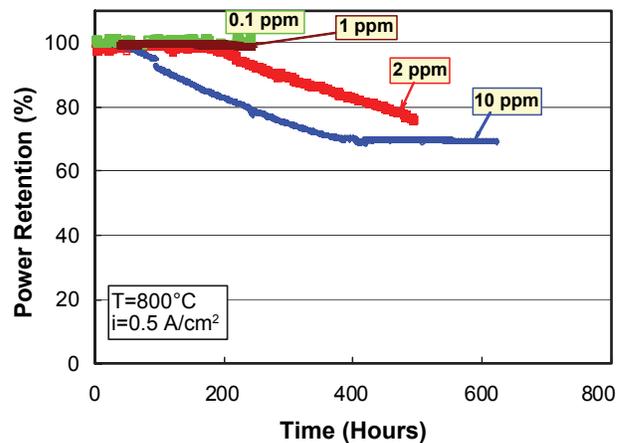
concentrations are expected from thermochemical calculations to form secondary bulk phases with nickel, whereas sulfur is not. Though extensive studies of sulfur compound interaction with SOFC anodes have been conducted previously, little information is available with regard to sulfur in combination with other coal gas contaminants.

The long-term performances of the anode-supported button cells were evaluated as functions of contaminant concentration, temperature, fuel utilization, current density and time of the exposure. In addition, screening tests were conducted where Ni/YSZ anode support coupons were exposed to coal gas contaminants in a flow-by and flow-through arrangement. Post-test analyses were conducted with analytical scanning and transmission electron microscopies (SEM and TEM), X-ray diffraction (XRD), electron back-scatter diffraction (EBSD), X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) to establish the extent and form of contaminant/anode interactions. Surface analytical probes, ToF-SIMS and XPS, are sufficiently sensitive to reveal sub-monolayer adsorption, including competitive adsorption effects, whereas electron microscopy and diffraction techniques revealed the formation of bulk or surface phases.

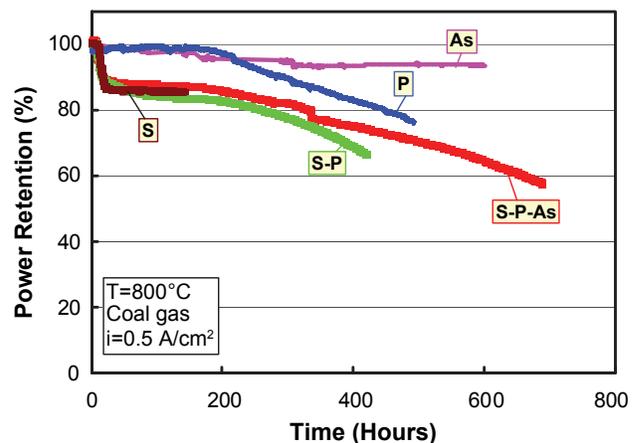
## Results

SOFC operation on simulated coal gas was evaluated in the presence of phosphorus, arsenic and sulfur at low (0.1 to 20 ppm) concentrations. For phosphorus exposure, introduced as  $\text{PH}_3$  in concentrations of 10 ppm or less into coal gas, no immediate change in the cell area specific resistance (ASR) was observed. After 40-250 hours, depending on the  $\text{PH}_3$  concentration and temperature, the ASR began to increase rapidly, as is shown in Figure 1. During this period of rapid change, degradation rates of 0.1-0.2% per hour were observed. With continued exposure, degradation abated and a new steady-state level of performance was reached, typically at power retention level of 70% of the initial value. This degradation appeared to be irreversible: when  $\text{PH}_3$  exposure was ended and the cell was left running under otherwise identical conditions in pure coal gas, no recovery in performance occurred.

Similar to phosphorus, when arsenic was introduced into the coal gas fuel at concentrations of 10 ppm or less, the SOFC performance did not change immediately. A period of slow (~1 percent per 100 hours) ensued, as shown in Figure 2, followed by steady-state performance at a power retention level greater than 90 percent. Figure 2 also shows results for sulfur and phosphorus exposure either alone or in combination with arsenic. Upon exposure to 1 ppm of  $\text{H}_2\text{S}$ , independent of whether  $\text{PH}_3$  or  $\text{AsH}_3$  were present, the SOFC showed



**FIGURE 1.** Effect of phosphine concentration in the coal gas on SOFC performance at 800°C and current density of 0.5 A/cm<sup>2</sup>.  $\text{H}_2/\text{CO}/\text{CO}_2/\text{H}_2\text{O} = 30/23/21/26$ .



**FIGURE 2.** Effect of 1 ppm of  $\text{H}_2\text{S}$ , 1 ppm of  $\text{AsH}_3$  and 2 ppm of  $\text{PH}_3$  as well as mix of  $\text{H}_2\text{S}$  with  $\text{PH}_3$  or  $\text{PH}_3$  and  $\text{AsH}_3$  at the same concentrations on SOFC performance at 800°C.

an immediate drop in performance. After 30 hours of exposure, ASR reached a new steady-state with a power retention of 85-70% of the initial value, depending on the temperature. When phosphorus or phosphorus and arsenic were also present, slow second stage degradation was observed. Thus, if sulfur is present in the gas mixture, it dominates the cell performance over the first 30 hours. Later changes in performance are attributed to the presence of phosphorus and/or arsenic, which are independent of changes due to sulfur.

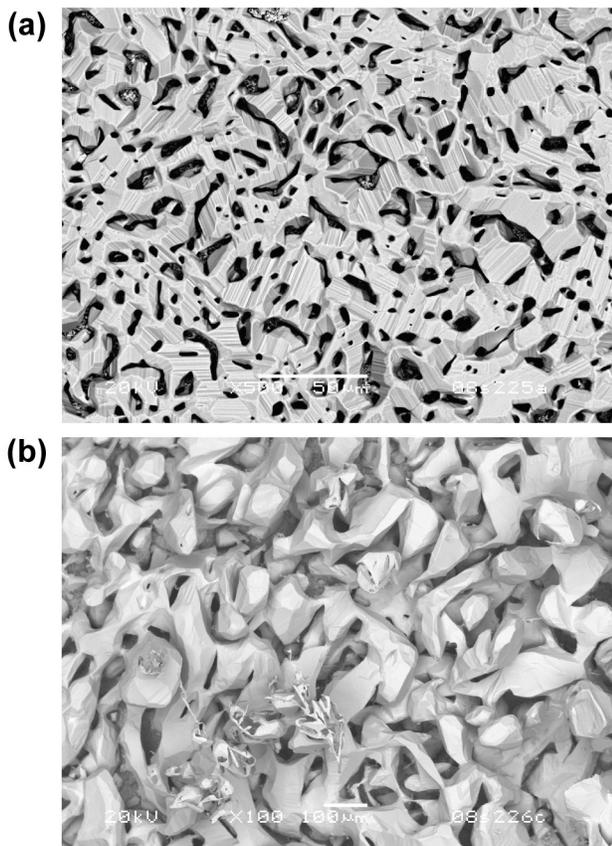
Post-mortem microstructural and surface analyses were conducted on cells following extended testing in coal gas containing contaminants, which revealed secondary nickel phase formation both in the nickel current collecting grid and the Ni/YSZ anode. Depending on the time of exposure, Ni was partially or entirely converted either into nickel phosphides or nickel arsenide. SEM/EDS identified the presence of

only one form of the arsenide,  $\text{Ni}_5\text{As}_2$ , while several forms of nickel phosphides,  $\text{Ni}_3\text{P}$ ,  $\text{Ni}_5\text{P}_2$  and  $\text{Ni}_2\text{P}$ , were found depending on the  $\text{PH}_3$  concentration. In contrast, no secondary phases containing nickel and sulfur were ever observed. Although nickel arsenide and nickel phosphide phases are electrically conductive [3], electronic percolation in the outer portion of the anode support is believed to be compromised through extensive recrystallization of alteration phases. A loss of porosity can also occur. Micrographs showing extensive grain growth following phosphorus and arsenic exposure are given in Figure 3. The phases  $\text{Ni}_3\text{P}$  and  $\text{Ni}_5\text{P}_2$  are formed by eutectic reactions at 870 and 897°C, respectively [4], which are sufficiently close to test temperatures to promote high solid state diffusivities and thus substantial grain growth of alteration phases.

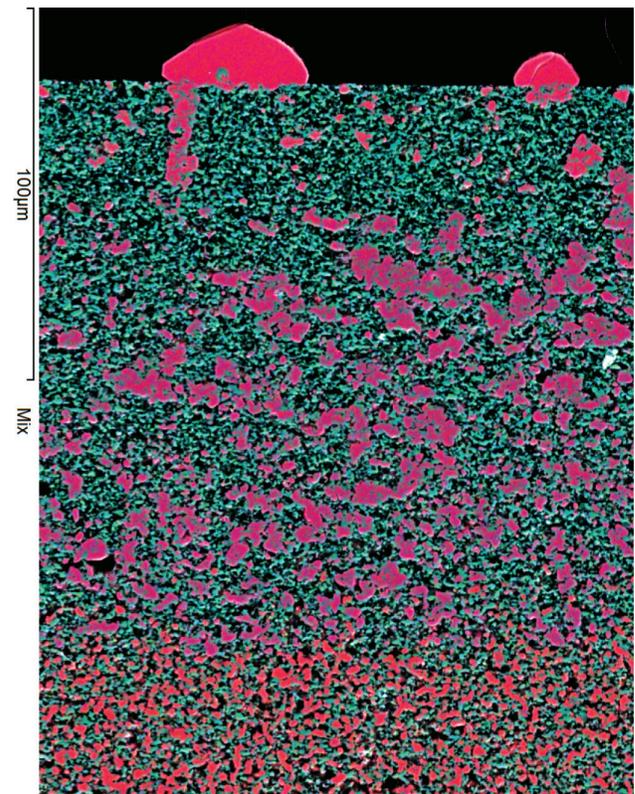
Tests performed with both arsenic and phosphorus added to coal gas revealed distinctive differences in the distribution of alteration phases. While  $\text{Ni}_5\text{As}_2$  was observed only in the very upper part of the anode, up to 30-40  $\mu\text{m}$  from the top,  $\text{Ni}_3\text{P}$  penetrated much deeper into the anode, up to 160  $\mu\text{m}$  following ~700 hours of operation at 800°C, as is shown in Figure 4.

As such, arsenic competes effectively with phosphorus for reaction with nickel. Both phases formed large agglomerates instead of fine nickel particles, which obviously compromised percolating Ni network as well as electronic conductivity in the upper anode later. Further down towards the active interface, only pure nickel in the Ni/YSZ was observed, as expected. No secondary phosphorus-nickel, arsenic-nickel or sulfur-nickel phases were detected in the bulk Ni/YSZ anode away from the upper part.

Surface sensitive techniques, ToF-SIMS and XPS, were engaged to analyze whether coal gas contaminants had migrated to the active anode/electrolyte interface to form an adsorption layer. At monolayer coverage, such surface adsorption layers would not be visible by analytical electron microscopic techniques. For sulfur, surface probes showed the presence of an adsorption layer on all exposed nickel surfaces to the active interface, which is well-known to lead to reversible SOFC performance loss. Adsorbed phosphorus was similarly found on all exposed nickel surfaces by XPS point scans and ToF-SIMS line scans. Unlike sulfur, the presence of a phosphorus surface adsorption layer



**FIGURE 3.** SEM image of the Ni/YSZ anode after 250 hour cell operation in the coal gas with 5 (a) and 20 ppm (b) of  $\text{PH}_3$  at 800°C. EDS revealed ca. 25 at% (a) and 27-30 at% (b) that corresponded to  $\text{Ni}_3\text{P}$  and  $\text{Ni}_5\text{P}_2$ , respectively.



**FIGURE 4.** Cross section of the upper part of the Ni/YSZ anode after 700 hour test in the coal gas with 1 ppm of  $\text{PH}_3$ , 1 ppm of  $\text{H}_2\text{S}$  and 1 ppm of  $\text{AsH}_3$  at 800°C. According to the elemental maps, zirconia is shown in teal, a mix of  $\text{Ni}_3\text{P}$  and  $\text{Ni}_5\text{As}_2$  in pink,  $\text{Ni}_3\text{P}$  is shown in purple and metal Ni is in red.

did not appear to have electrochemical consequences: phosphorus adsorption layers formed much faster than the onset of degradation in button cell tests. For arsenic, no surface adsorption layer was detectable by surface probes at the active interface, even after hundreds of hours of exposure. Rather, arsenic was restricted to outer portions of the anode, where secondary phases with nickel were found.

### Conclusions and Future Directions

- Exposure of nickel-based SOFC anodes to phosphorus compounds in coal gas at concentrations from 0.1 to 20 ppm resulted in irreversible performance losses. Depending on temperature and phosphorus concentration, no changes in cell performance were observed for periods of 40 to 250 hours. A period of degradation of up to 0.1 to 0.2 percent loss in retained power then occurred, followed by steady output at approximately 70 percent of the initial power. Degradation is attributed to a loss of electrical percolation in the outer portion of the anode support associated with secondary phase formation.
- Arsenic exposure of nickel anodes similarly led to irreversible performance losses, principally attributed to loss of electrical percolation in the anode support associated with secondary phase formation.
- When 1 ppm of sulfur was also present in the coal gas along with phosphorus and arsenic, it dominated cell performance during the first 30 hours of testing. Nickel-sulfur interactions were limited to the surface and no new bulk phases were detected.
- Other critical coal gas contaminants previously identified will be considered in future tests. Both anode-supported and electrolyte-supported cell configurations will be utilized, the former of which provides information on possible reduction of continuity in the anode support, and the latter of which will allow contaminants to reach the active interface more rapidly. Maximum allowable concentrations of contaminants and combinations of contaminants will be established that would permit SOFC stacks operating on coal gas to meet requirements for long-term degradation.

### FY 2008 Publications/Presentations

1. OA Marina, LR Pederson, DJ Edwards, CA Coyle, JW Templeton, MH Engelhard, and Z Zhu, "Effect of Coal Gas Contaminants on Solid Oxide Fuel Cell Operation", ECS Transactions, Volume 11: Solid-State Ionic Devices, in press.
2. OA Marina, LR Pederson, DJ Edwards, CA Coyle, JW Templeton, MH Engelhard, and Z Zhu, "Effect of Coal Gas Contaminants on Solid Oxide Fuel Cell Operation", presented at the 212<sup>th</sup> Electrochemical Society, Washington, D.C., October, 2007.
3. OA Marina, **LR Pederson, CA Coyle, JW Templeton, MH Engelhard, and DJ Edwards**, "Effect of Coal Gas Contaminants on SOFC Anode Performance and Stability," presented at 8<sup>th</sup> Annual SECA Workshop, San Antonio, TX on August 9, 2007.
4. **JW Stevenson, LA Chick, MA Khaleel, P Singh, LR Pederson, GL McVay, OA Marina, ZG Yang, GG Xia, and DL King**, "Solid Oxide Fuel Cell Technology Development at Pacific Northwest National Laboratory," Presented at 2007 Fuel Cell Seminar, San Antonio, TX on October 17, 2007.
5. OA Marina, **LR Pederson, CA Coyle, EC Thomsen, GW Coffey, DJ Edwards, and MH Engelhard**, "Effect of Coal Gas Contaminants on Solid Oxide Fuel Cell Operation," Presented at 213<sup>th</sup> meeting of the Electrochemical Society, Phoenix, AZ on May 21, 2008.

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