PNNL-37579

FCET Solid Oxide Fuel Cell Testing and Development (CRADA 526) Final Report

March 2025

Brent W Kirby

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

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CRADA Final Report Certification Memo

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Responsible Technical Contact at DOE Lab (PNNL):

Brent W Kirby

Provide a list of publications, conference papers, or other public releases of results, developed under this CRADA:

None

Provide a detailed list of all subject inventions, to include patent applications, copyrights, and trademarks:

No subject inventions were generated under this CRADA

Executive Summary of CRADA Work

Pacific Northwest National Laboratory (PNNL) tested electrolyte coatings from Fuel Cell Enabling Technologies, Inc. (FCET) for use in solid oxide fuel cells (SOFCs). The key technology held by FCET is a process to deposit thin layers of oxide materials, less than 1 μm in thickness. The range of possible materials that can be deposited with their method is broad, but this project focused on the gadolinium-doped ceria (GDC) and yttria-stabilized zirconia (YSZ) electrolytes for SOFCs. Thin, gas tight electrolyte membranes have been a long-sought target in SOFC research. The thinner the electrolyte, the lower the cell resistance, and the higher performance of the cell (or the lower the operating temperature). A YSZ thickness of 1 μm would be a step change from the state-of-the-art, tape-cast electrolytes (~10 μm).

An in-house prototype SOFC stack from FCET was first tested. The sealing geometry of the prototype stack was determined to be problematic, and testing shifted to button cells. Anode-supported solid oxide electrolysis cell (SOEC) button cells without an electrolyte layer were produced at PNNL and sent to FCET for coating with electrolyte. Three cells were tested with a gadolinium-doped ceria (GDC) electrolyte applied via spin coating. GDC was chosen for its conductivity at lower temperatures than YSZ. All three cells failed during initial reduction under hydrogen at 600°C.

Testing then shifted to YSZ, which is the standard SOFC electrolyte. Several button cells were coated with YSZ and examined with scanning electron microscopy (SEM). A promising coating of ~1 mm thickness was observed under SEM. A similarly coated button cell was tested and failed similarly to previous tests during reduction at 600°C.

The YSZ coating appeared dense and uniform in SEM analysis. The roughness of the underlying Ni/YSZ anode is on the order of 1 μm, and that may have compromised the gas-tightness of the coating. Further development is warranted to understand and refine the coating process. Thin YSZ applied via this spin-coating technique could be used as a low-cost, drop-in replacement in large-scale SOFC manufacturing processes, improving cell performance and lowering the cost per watt of SOFCs.

Summary of Research Results

Pacific Northwest National Laboratory (PNNL) tested electrolyte coatings from Fuel Cell Enabling Technologies, Inc. (FCET) for use in solid oxide cells (SOCs), either solid oxide fuel cells (SOFCs) or solid oxide electrolysis cells (SOECs). The key technology held by FCET is a process to deposit thin layers of oxide materials, less than 1 μm in thickness. The range of possible materials that can be deposited with their method is broad, but this project focused on the gadolinium-doped ceria (GDC) and yttria-stabilized zirconia (YSZ) electrolytes for SOECs. Thin, gas tight electrolyte membranes have been a long-sought target in SOC research. The thinner the electrolyte, the lower the cell resistance, and the higher performance of the cell (or the lower the operating temperature).

The original statement of work called for PNNL to test a prototype solid oxide fuel cell from FCET on PNNL test equipment. That prototype cell was found to be leaking from anode to cathode, and it was decided the geometry of the stack would not allow for proper sealing at high temperature. This led to a change in strategy to focus on coating button cells, small, one-inch diameter circular cells used for developmental work.

PNNL has existing projects to produce anode-supported button cells for solid oxide electrolysis cell (SOEC) testing, and surplus materials were utilized for the FCET work. Standard button cells are produced by tape casting and lamination of several layers. The anode support is a Ni/YSZ cermet, with a finer-grained NiO/YSZ active anode layer adjacent to the electrolyte. The electrolyte is dense YSZ, with a thickness of ~10 μm. Upon reduction when exposed to hydrogen at high temperature, the NiO portion of the cermet is reduced to nickel metal, which also creates some empty void space. Under SOC operation, electrons are conducted through the nickel metal, O^{2-} ions are conducted through the YSZ, and gas is transported through the void space.

Some button cells were produced without any electrolyte layer for use in other research into electrolyte deposition techniques. Several of these bare anode supports were sent to FCET to be coated with electrolyte layers via FCET's proprietary, solution-based process. The first target electrolyte was gadolinium-doped ceria, chosen for its high O^{2-} conductivity at relatively low temperatures, and because it does not require a barrier layer between the cathode and electrolyte. FCET explored both dip coating and spin coating single layers and multiple layers of GDC precursor. FCET chose to target lower operating temperature enabled by their thin electrolytes, and the chosen operating temperature was 600°C.

<u>GDC Cell Testing</u>

The first round of testing included three cells coated via spin coated with two, four, and six layers of GDC precursor, with drying steps in between coats. The four- and six-layer cells were processed into finished SOECs and tested at PNNL. The as-received cells were fired at PNNL at 600°C to burnout the GDC electrolyte layer. An LSCF cathode was screen-printed and sintered at 1005°C [LSCF 6428, 5% A-site deficient, $(La_{0.6}Sr_{0.40})_{0.95}(Co_{0.2}Fe_{0.8})O_3$, Trans-Tech Ceramics, SO#396947-10-2, Batch 13609, Surface Area: 15 m2/g, Date: 5/12/2020]. The active area was 1.5 cm^2. This active area is smaller than a full-size button cell to limit current due to test channel current constraints. The cathode (air side) current collector was Ag mesh with Pt wire attached with Ag paste (see Figure 1). The anode (fuel side) current collector was Ni mesh with Pt wire attached with Ni paste (see Figure 2).

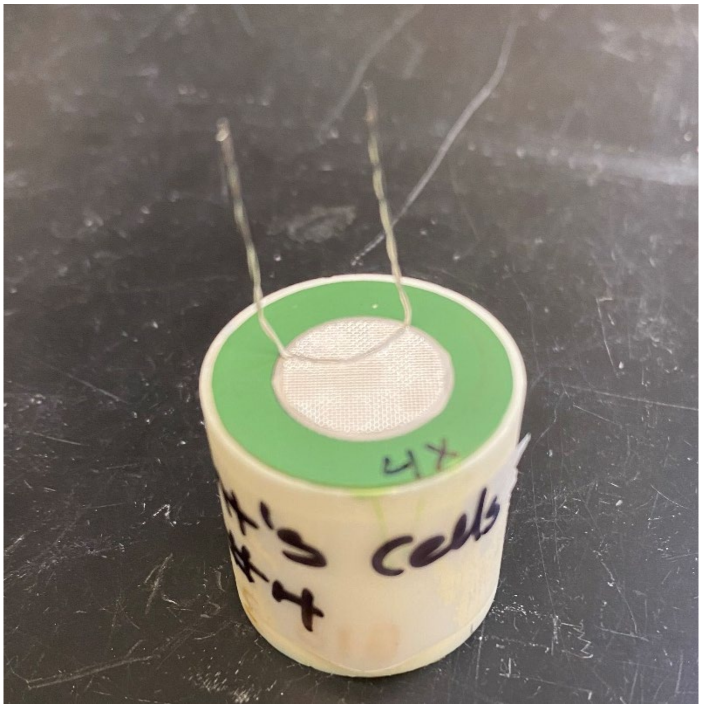

Figure 1: Cathode side, untested (shown for 4x cell)

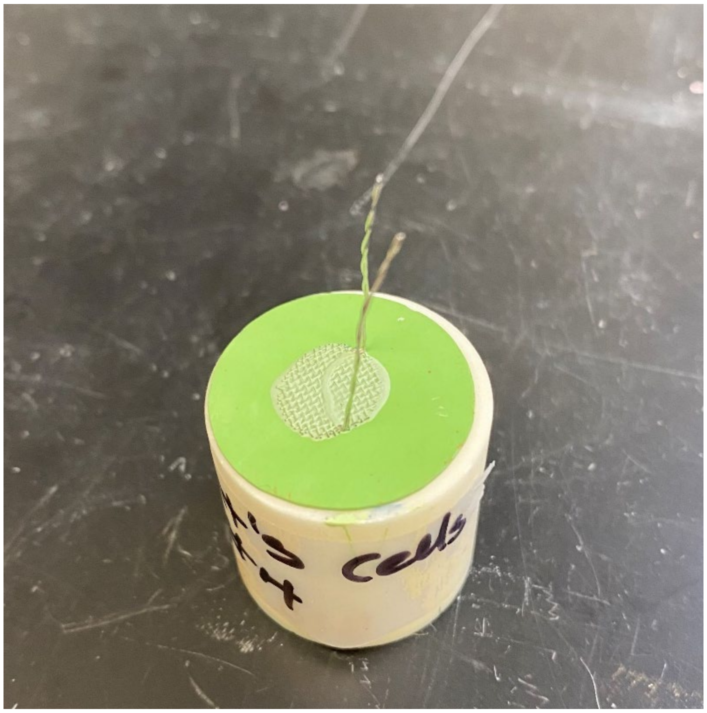

Figure 2. Anode side, untested (shown for 4x cell)

The cell was sealed to the end of an alumina tube as part of the test fixture. A glass paste was applied by hand on the mating surfaces and around the edge of the cell (Schott glass #GM31107). This glass was chosen for its sealing temperature to allow operation down to 600C and below.

A spring-loaded alumina top cap applied pressure to the cell for sealing, and directed the air flow into the cathode current collector mesh. The cell was sealed at 700°C with a ramp rate of 1C/min. ~200cc/min of air was supplied to the cathode top cap. The anode was left open to ambient air during sealing. Temperature was then lowered to 600°C for testing. Temperature was monitored by a thermocouple situated to the side of the cell. The furnace control thermocouple was placed somewhat higher in the furnace and read ~15C higher than the cell thermocouple (see Figure 3).

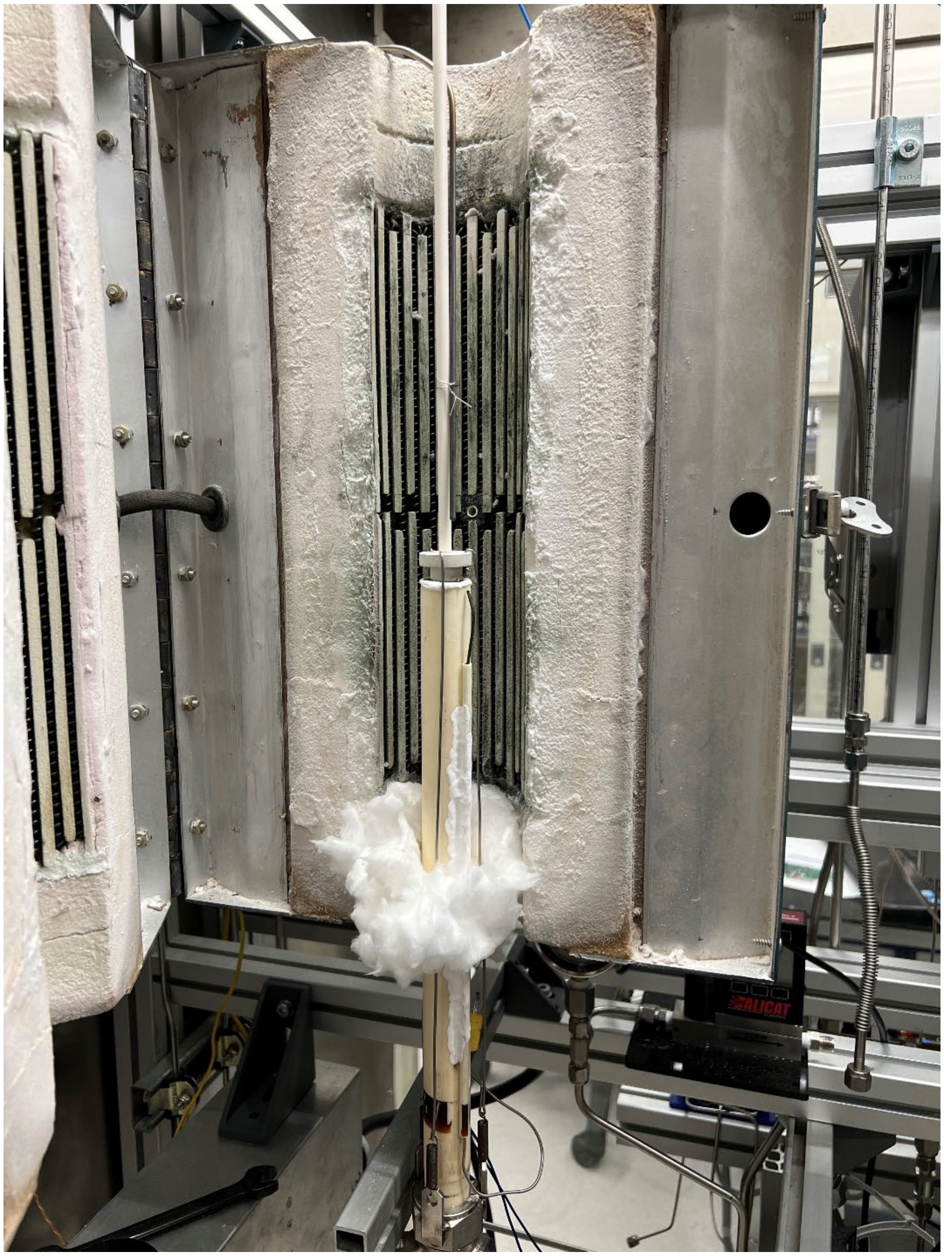

Figure 3. Vertical tube furnace with test fixture

Once the cell temperature was reduced to 600°C, the anode gas line was connected and 100 cc/min of nitrogen was supplied to purge air from the anode side. The anode gas was then switched to 100 cc/min of hydrogen. The open circuit voltage (OCV) of the six-layer cell rose to ~0.9V before declining slowly and then falling to zero after ~2 minutes under hydrogen. This indicates failure of the cell and a total loss of electrical contact. A slow transition from nitrogen to hydrogen was used during testing of the four-layer cell to lessen the material stresses during cell reduction. The four-layer cell reached an OCV of 0.95V on 20% hydrogen with 80% nitrogen. After raising the hydrogen content to 30% the OCV began to fall and the cell eventually failed.

The cells were cooled at 3C/min under 50cc/min of hydrogen to keep them reduced during cooling. The test fixture was removed and photographs were taken. For the six-layer cell, the cathode was found to be completely detached in the active area. The GDC coating appeared to be intact outside of the active area. (see Figure 4). The NiO across the entire button cell anode had been reduced to nickel metal under the 100% hydrogen flow (even where the anode was covered by the glass seal). For the four-layer cell, the cathode remained attached to the cell. Under the lower hydrogen flow, the NiO was only reduced to nickel metal in the area left open within the glass seal (see Figure 5 and Figure 6).

Figure 4. Six-layer GDC cell after testing. The entire cathode was detached.

Figure 5. Four-layer GDC cell after testing.

Figure 6. Four-layer cell after disassembly. Note how the glass seal on the anode side defines where the anode has been reduced from NiO (green color) to nickel metal (gray color).

These cell failures prompted a process change for the GDC-coated cells. The failed cells had only been fired up to 600°C before the cathode was applied and fired at 1005°C. An additional six-layer GDC cell was pre-sintered at 1250°C to improve bonding between the GDC and the anode and to increase the density of the GDC layers. Cell testing proceeded as before with a slow transition from nitrogen to hydrogen. The pre-sintered cell OCV rose to a maximum of 0.93V while on 5% hydrogen before beginning to decline. Raising the hydrogen level to 10%, then 20%, did not stop the OCV decline and the test was ended. The cathode remained attached.

YSZ Cell Testing

The next process change was to use YSZ as the electrolyte. PNNL has the most experience with YSZ electrolytes, and the bare anodes already contain YSZ, which could improve bonding of the electrolyte to the anode. FCET applied two layers of YSZ electrolyte to bare anodes, and PNNL sintered them to 1300°C. One cell was cross-sectioned and mounted for scanning electron microscopy (SEM) analysis. Those results are presented below.

Figure 7 shows a 3,000x SEM image of the active anode region, with the coarser bulk anode at the bottom of the image. The YSZ electrolyte coating is at the top of the image. The bright white regions are YSZ, the gray regions are NiO, and the black areas are voids. Zooming in to 7,500x magnification in Figure 8, a layer of dense YSZ can be seen on top of the active anode. Some roughness and porosity was observed, but the coating was very dense overall and followed the rough contours of the active anode surface, covering both YSZ and NiO particles on the active anode surface. This was confirmed by an elemental map using energy dispersive spectroscopy (EDS) in the microscope. Figure 9 shows an uncoated bare anode for comparison. Figure 10 and Figure 11 show the elemental map of yttrium and zirconium, respectively, confirming that the electrolyte layer is continuous YSZ.

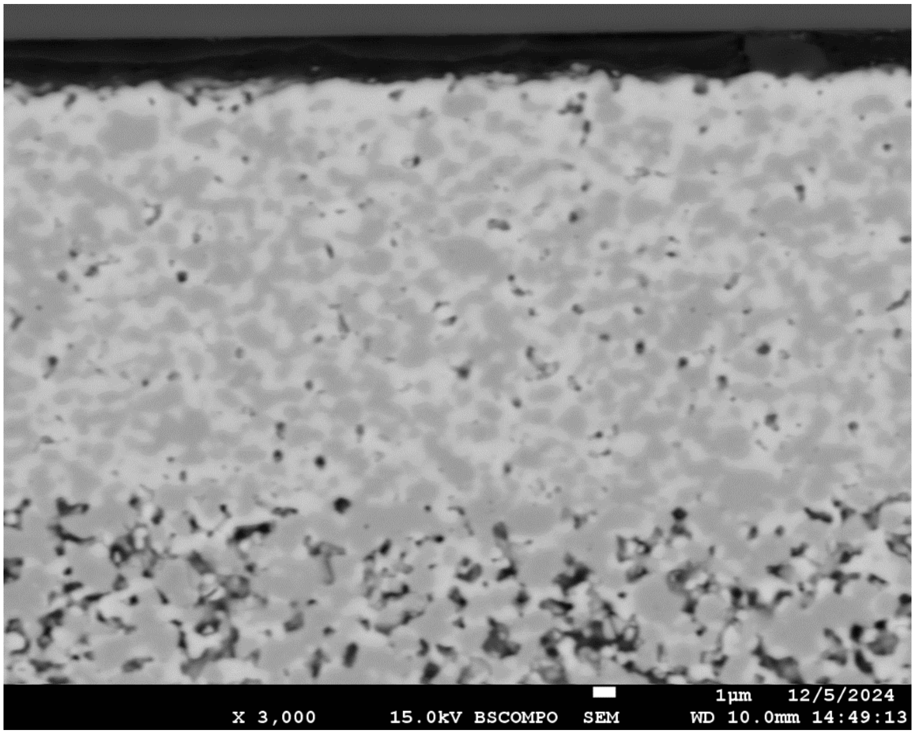

Figure 7. SEM image of two-layer YSZ cell showing the active anode layer with the coarser bulk anode layer at the bottom of the image. The YSZ electrolyte coating is on the top surface.

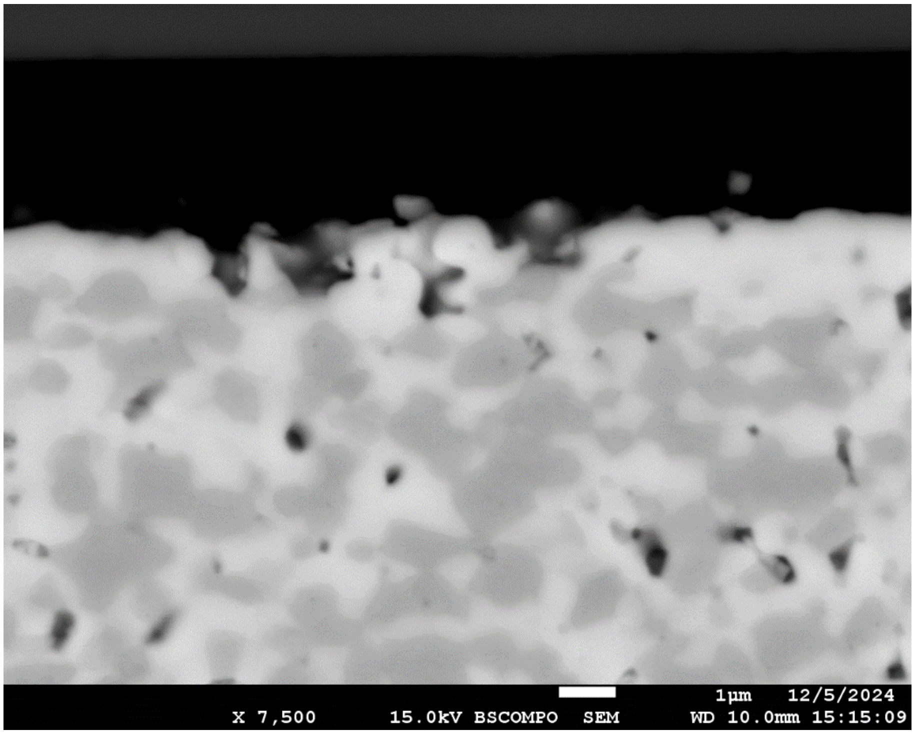

Figure 8. SEM image of two-layer YSZ cell showing ~1 µm layer of dense YSZ (white) electrolyte on top of the active anode.

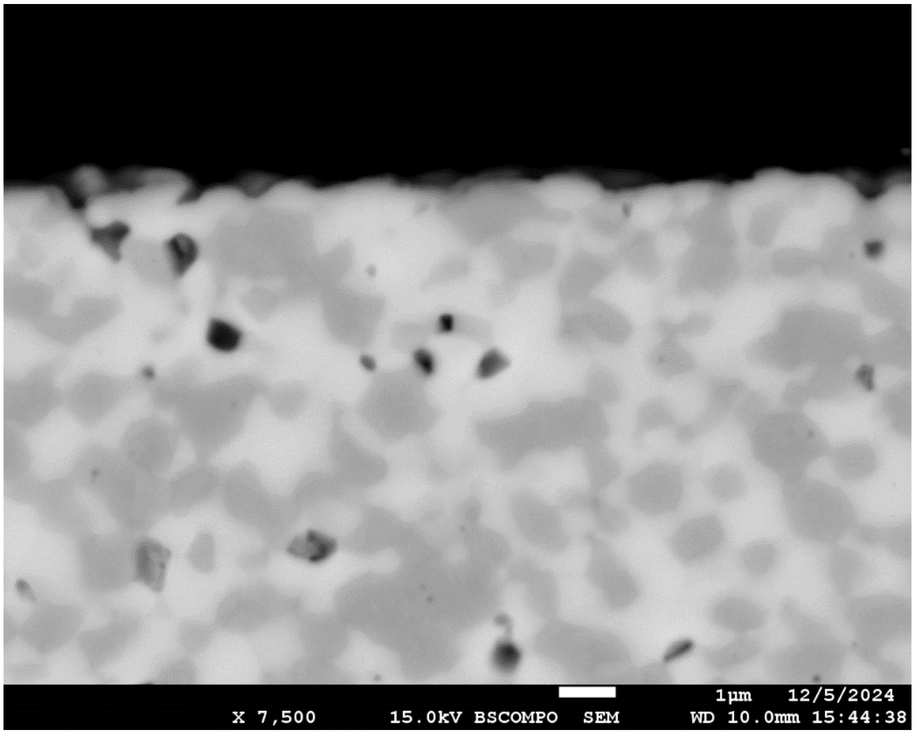

Figure 9. SEM image of an uncoated bare anode showing both YSZ (white) and NiO (gray) particles at the top surface.

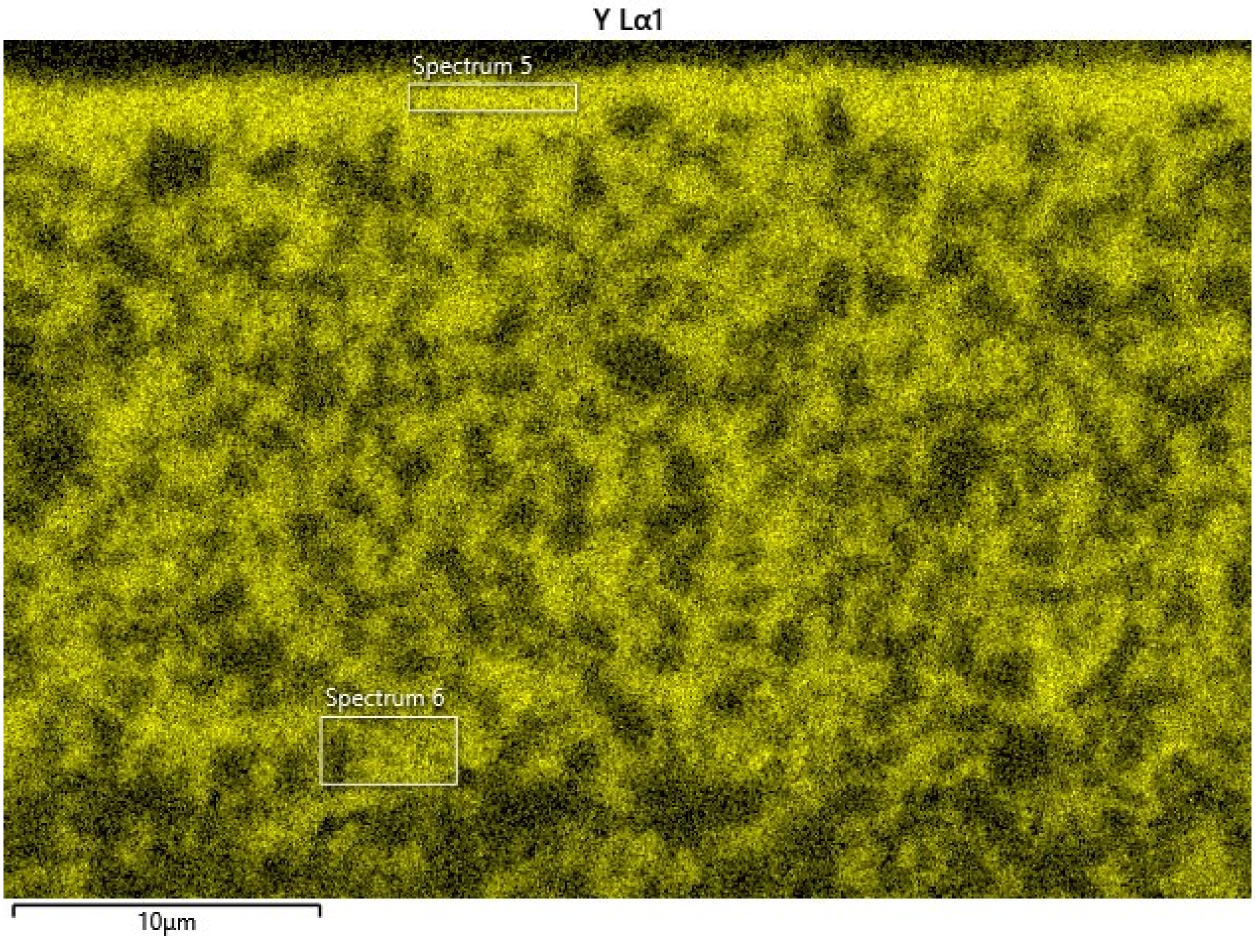

Figure 10. EDS map of yttrium in two-layer YSZ cell, showing dense YSZ layer on top.

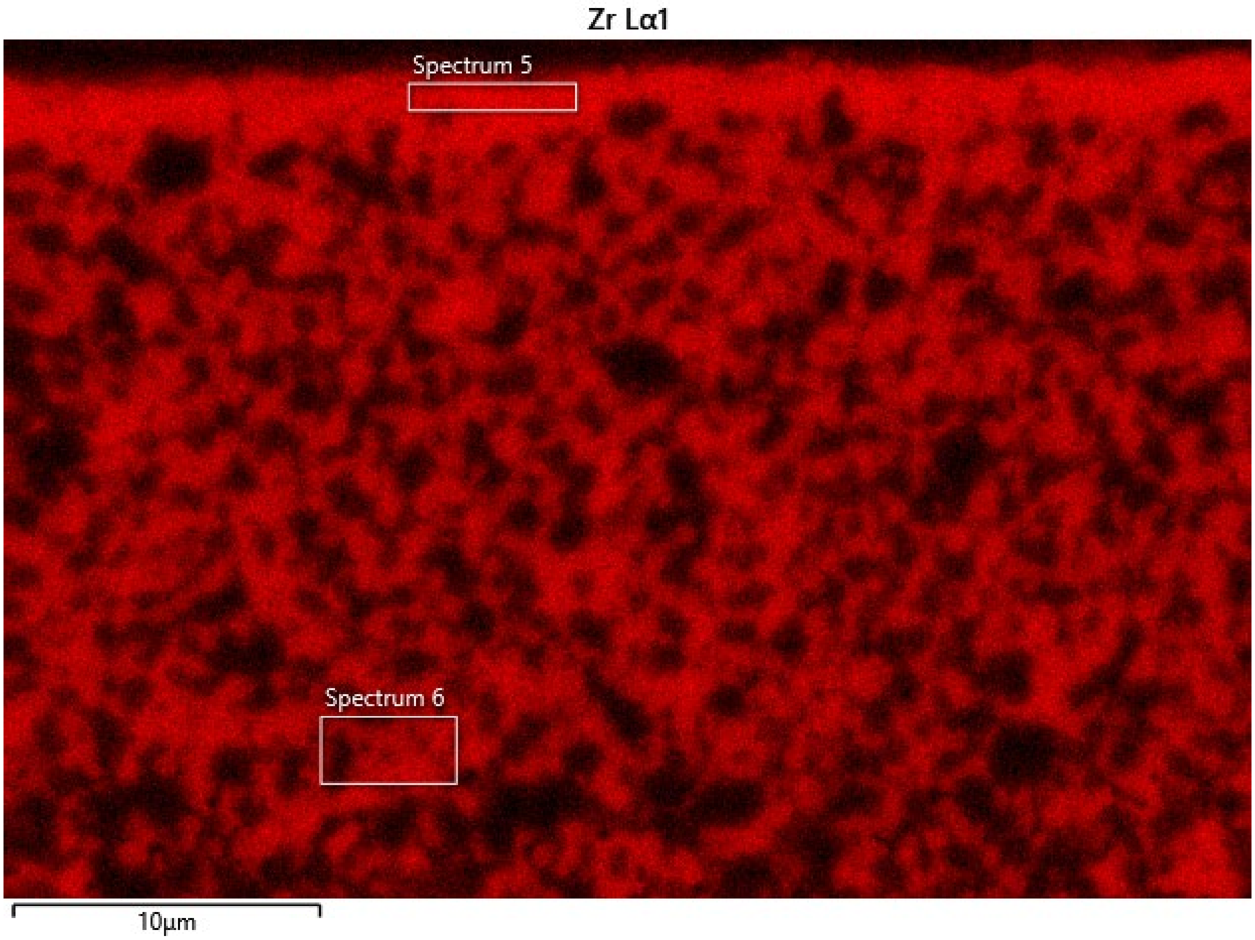

Figure 11. EDS map of zirconium in two-layer YSZ cell, showing dense YSZ layer on top.

The confirmed presence of a continuous YSZ electrolyte warranted a cell test of a similarly coated two-layer YSZ button cell. The as-received cell with YSZ coating was sintered at 1300°C. Then a GDC barrier layer was applied and fired at 1250°C. The rest of the cell was prepared as before. The cell was reduced with a slow transition from nitrogen to hydrogen at 600°C. The OCV reached a maximum of 0.95V before falling. Hydrogen was increase to 50%, but the OCV never recovered and the test was stopped.

Discussion

While a functional SOC was not produced during this project, the coating process went through several iterations and improvements. The SEM results on the YSZ cells show a uniform ~1 μm coating of dense YSZ. Other techniques, such as magnetron sputtering, have been used to produce YSZ layers of ~1 μm thickness, but these are generally slower and more costly than the standard tape casting process. The FCET solution-based process holds promise to produce thin coatings over a wide range of size scales and can be adapted to integrate into various SOC manufacturing processes. Applications beyond electrolytes could include GDC barrier layers, which are notoriously difficult to make thin and dense.

The current CRADA project was an exploratory effort with limited funding of $61,000 over a period from November 2021 through December 2024. These early efforts at applying FCET coatings to SOC button cells have illustrated issues that would benefit from further research in a more robust project. The roughness of the NiO/YSZ cermet in the active anode is on the order of the coating thickness, making the electrolyte layer uneven. Reduced particle size in the active anode or an intermediate polishing step would create a smoother surface for electrolyte application. The coating process is tunable, and coating thicknesses less than 1 μm are possible. The failure of the SOCs during reduction under hydrogen indicates either poor adhesion of the electrolyte coating to the anode support, or porosity in the electrolyte coating allowing leakage across the cell. Adhesion can be evaluated by stress testing the coating followed by systematic SEM analysis. Porosity can be evaluated with helium leak testing and SEM or scanning probe microscopy. Coating parameters and firing schedules can be optimized to produce well-adhered and hermetic coatings. Development of the coatings could be performed at the button cell level, then scaled up to sizes such as the 100-200 cm^2 SOCs produced at PNNL.

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