Low-Cost Modular Solid Oxide Fuel Cell Development

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Objectives

- Develop optimized cathode materials and microstructures for intermediate temperature SOFCs.
- Develop anode compositions that will satisfy advanced anode requirements, including redox tolerance, sulfur tolerance, and carbon tolerance.
- Develop optimized materials for intermediate temperature SOFC interconnects.
- Develop advanced seals for intermediate temperature SOFCs.
- Develop computational tools to further the understanding of thermal, mechanical, chemical, and electrical processes occurring in solid oxide fuel cells and stacks.

Key Milestones

- Achieved high power density in anode-supported cells with LSF cathode (~1.2 W/cm^2 at 800ºC and ~0.8 W/cm^2 at 750ºC); measured at 0.7 V; fuel is 97%H_2/3%H_2O; oxidant is air; low fuel and air utilization.
- Developed 2 phase anode materials in the Sr-La-Ti-Ce-O system that exhibit low anodic polarization resistance as well as excellent dimensional and chemical stability under thermal and red-ox cycling.
- Compiled a database containing the compositions and properties of over 300 high-temperature alloys; screen tested selected alloys to determine their oxidation resistance; oxide scale electrical conductivity, and compatibility with sealing glasses are in progress.
- Developed an advanced mica-based "hybrid" compressive seal concept that exhibits leak rates as low as 0.0001-0.001 sccm per cm of seal length under moderate compressive loads.
- Developed a thermo-fluid-electrochemical model which predicts the fuel utilization, electrical power, and temperature distributions in cells and planar SOFC stacks with various three-dimensional geometries.

Approach

Cathode Development: Doped lanthanum ferrite shows considerable promise as a cathode material for intermediate temperature SOFCs. Sr-doped lanthanum ferrite (LSF) and $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC-20) powders were synthesized using the glycine-nitrate combustion technique. The synthesized powders were typically calcined from 1000°-1200°C for 1 hour, and then attrition milled for 10-30 minutes depending on the desired particle size distribution. SDC-20 interlayers (~5 mm post-sintered thickness) were applied to anode-supported YSZ bilayers via screen-printing, and sintered from 1100-1300°C for 2 hours. The cathodes were also applied by screen-printing (25-40 µm post-sintered thickness). Cathode compositions were typically sintered from 1100-1250°C. The diameter of the bilayers was 25 mm, and that of the screen-printed cathode 22.0 mm. Screen-printed Pt grids with embedded Pt gauze, and screen-printed NiO grids with embedded Ni gauze, were used as current collectors for the cathode and anode, respectively. The cells were sealed to alumina test fixtures using Aremco cements, and current-voltage data recorded from 700°-850°C using an Arbin BT2000 potentiostat-galvanostat electrochemical testing system. The cells were held at 0.7 V and periodically subjected to current sweeps from 0-7 A. Ninety-seven percent H_2-3% H_2O was flowed to the anode at 200 sccm, and air to the cathode at 300 sccm.

Anode Development: Two phase composites consisting of a mixture of doped strontium titanate and doped ceria exhibit promising behavior as redox- and sulfur-tolerant anode materials. Candidate oxide powders in the Sr-La-Ti-Ce-O system were prepared by glycine/nitrate combustion synthesis. The powders were calcined and then attrition-milled to reduce the average particle size to less than 0.5 μm. The compositions were characterized by dilatometry, XRD, EDS, SEM, and TEM. Electrode inks were prepared by mixing the powder with a commercial binder in a 3-roll mill, and then screen-printed in a circular pattern onto YSZ pellets or membranes. The screen printed electrodes were sintered in air at 900-1200ºC.

The cells were mounted between two vertical alumina tubes and isolated from the environment by sealing with gold rings when heated to 900ºC in air. After that, fuel was introduced into the anode compartment to reduce the anode. The opposite side of the cell was supplied with air. Experiments were performed at atmospheric pressure in the 550-900ºC temperature range. Electrochemical measurements were carried out using a Solartron 1280 frequency response analyzer in combination with a Solartron 1286 potentiostat or an Arbin BT4 potentiostat.

Interconnect Development: PNNL is engaged in an in-depth study evaluating the suitability of a variety of stainless steels and other alloys for the SOFC interconnect/current collector application. To begin the study, a database containing the compositions and properties of over 300 high-temperature alloys was compiled. The database was then used as a resource to grade the alloys against intermediate temperature interconnect requirements. The most promising alloys are being evaluated in screening tests to determine their oxidation resistance (via mass gain measurements and microscopy), oxide scale electrical conductivity (via 4 point conductivity measurements), and compatibility with sealing glasses (via SEM and EDS analysis of annealed coupons).

Seal Development: A novel mica-based "hybrid" compressive seal concept is being developed and optimized. The advanced seals consist of mica "gaskets" with compliant interlayers (which can be either glass or metal) inserted at the interfaces between the mica and adjacent stack components. For leak testing, mica samples were cut into 1.5" squares with a 0.5" diameter central hole. Glass or metal interlayers were inserted between the mica and the adjacent test components (a metal tube and an alumina substrate). Samples were heated in a clamshell furnace at a heating rate of ~2ºC/min to 800ºC. Compressive loads were applied using a universal mechanical tester with a constant load control; the leak rate was measured by monitoring the pressure change with time. After leak testing, the seals were disassembled and examined by SEM.

Modeling: Spreadsheet, CFD, and FEA-based computational tools have been developed to further the understanding of thermal, mechanical, chemical, and electrical processes occurring in solid oxide fuel cells and stacks. These tools are being used to assist in design optimization of cells and stacks for improved performance. Parameters being optimized include cell performance at high fuel utilization, uniformity of gas flows, and thermal and mechanical stress profiles during both transient and steady-state operation.

Results

Cathode Development: Sr-doped lanthanum ferrite ($La_{0.8}Sr_{0.2}FeO_3$) cathodes exhibit low cathodic polarization in solid oxide fuel cells tested in the 650 – 850ºC temperature range. The low polarization can be attributed both to optimized microstructure and to the high oxygen ion conductivity and surface exchange kinetics intrinsic to the lanthanum ferrite. Typical power densities for anode-supported cells using this cathode material (including a Sm-doped ceria ($Ce_{0.8}Sm_{0.2}O_2$) layer between the cathode and YSZ membrane) are ~1.2 W/cm^2 at 800ºC and ~0.8 W/cm^2 at 750ºC (measured at 0.7 V; fuel is 97%H_2/3%H_2O; oxidant is air; low fuel and air utilization). Temperature dependent test results are shown in Figure 1.

Anode Development: Oxide anode materials in the Sr-La-Ti-Ce-O system have demonstrated excellent dimensional and chemical stability under thermal and red-ox cycling. The anode materials, which contain 2 phases (La-doped strontium titanate and doped ceria), exhibit low anodic polarization resistances; electrolyte

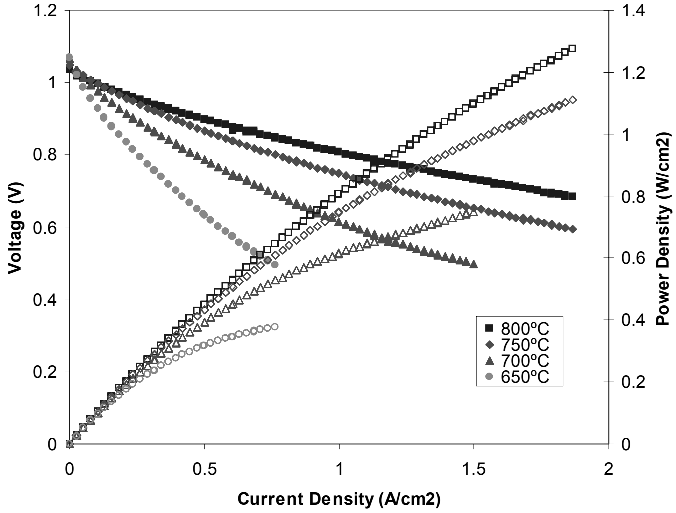

Figure 1. *Temperature dependent electrical performance of anode-supported cell (LSF Cathode, SDC Interlayer, YSZ Electrolyte, Ni/YSZ anode). Fuel: 97%H_2/3%H_2O. Oxidant: Air. Low fuel and oxidant utilization.*

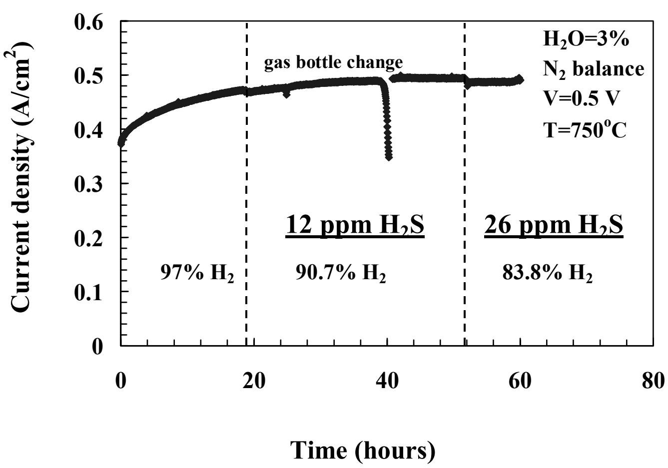

Figure 2. Preliminary test for anode sulfur tolerance on electrolyte supported (160 mm YSZ) cell with doped LSF cathode.

supported cells using these anodes have yielded power densities of ~0.5 W/cm^2 at 800ºC (measured at 0.7 V; fuel is 97%H_2/3%H_2O; oxidant is air; low fuel and air utilization). Preliminary testing also indicates that this novel anode material is unaffected by the presence of H_2S in the fuel stream (Figure 2), and is resistant to carbon deposition/coking in carbon-containing fuels.

Interconnect Development: To function well as a bi-polar plate, the interconnect must offer a low resistance electrical path in order to minimize electrical losses within the SOFC stack. For heat resistant alloys, the bulk electrical resistance is typically quite low, so the electrical resistance of oxide scales formed at the surface will dominate the electrical behavior of heat resistant alloys during SOFC operation. Since a metallurgical bond can be easily developed through elemental interdiffusion between the anode and an adjacent current collector (such as a Ni mesh) and the metal interconnect in the stack, the resistance resulting from the scale growth in air at the cathode side represents the primary challenge. Results from tests on Haynes 230 (a representative superalloy) and E-brite (a representative ferritic stainless steel) are shown in Figure 3, in comparison with properties of 5-mm thick lanthanum chromite, the preferred high-temperature ceramic

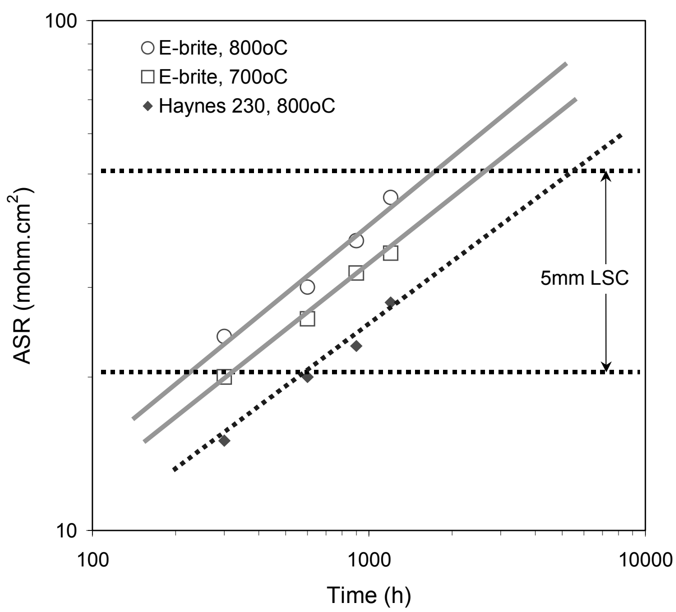

Figure 3. ASR of E-brite and Haynes 230 annealed at the indicated temperatures in air, compared with that of a ceramic lanthanum chromite interconnect.

interconnect material. Extrapolation of the measured data indicates that at some point the scale growth will lead to an ASR higher than the LSC ceramic oxide and eventually to an unacceptably high level. (It should be noted that interactions with adjacent stack materials (such as ceramic contact pastes) may also affect, for better or worse, the properties of the oxide scales.) Our screening study on selected compositions indicates that it will be difficult for the conventional, currently commercially available compositions to satisfy this standard for SOFCs operating at 700ºC or higher. Therefore, bulk- and/or surface-modifications may be required to enable metallic interconnects to provide satisfactory performance during full SOFC stack lifetimes.

Seal Development: A novel mica-based "hybrid" compressive seal concept has demonstrated leak rates (in coupon testing in air) as low as 0.0001-0.001 sccm per cm of seal length under moderate compressive loads; these leak rates are several orders of magnitude lower than leak rates measured with plain mica compressive seals. The seals consist of mica "gaskets" with compliant interlayers (which can be either glass or metal) inserted at the interfaces between the mica and adjacent stack components. In thermal cycle tests, the seals exhibit increased leak rates (due to localized damage in the mica sublayers in close proximity to the interlayers), but the rate of increase in leak rate decreases after the first few cycles.

Modeling: One of the primary computational tools developed in this task is a thermo-fluid-electrochemical model, which predicts the fuel utilization, electrical power, and temperature distributions in planar SOFC stacks with various three-dimensional geometries. This modeling tool is used to the flow and distribution of anode and cathode gases, temperature and electric current distributions, and fuel utilization. A "generic" single-cell stack model, including internal manifolds, was created to simulate three-dimensional steady state behavior of cross-flow, co-flow, and counter-flow stack designs. The three designs show that, for a given average cell temperature, similar fuel utilizations can result irrespective of the flow configuration. Temperature distributions, which largely determine thermal stresses during operation, are dependent on the chosen geometry/flow configuration. The co-flow design exhibited advantages for control of temperature and stress distributions.

The modeling tool couples a validated electrochemistry calculation model (also available separately in an Excel spreadsheet version) with the commercial computational fluid dynamics code STAR-CD (Computational Dynamics Ltd.). In the calculations, STAR-CD solves the finite-volume Navier-Stokes (conservation of mass and momentum) and transport equations to obtain the flow, species concentrations, and temperature at each location in the cell/stack. This information is passed to the electrochemistry module (subroutine). Here the local current density is calculated, based on the temperature, cell voltage, and pressures. The current is then used to calculate the hydrogen combustion rate. The water-gas shift reaction rate is assumed to maintain equilibrium conditions. Heat generation rates and species source (fuel/air) rates are supplied to the thermo-fluids code based on the hydrogen combustion and shift reaction rates. Gas species concentrations and temperature distributions are then calculated for the next iteration, and so on, until equilibrium is achieved for the shift reaction. Typical results from a multi-cell stack calculation are shown in Figure 4.

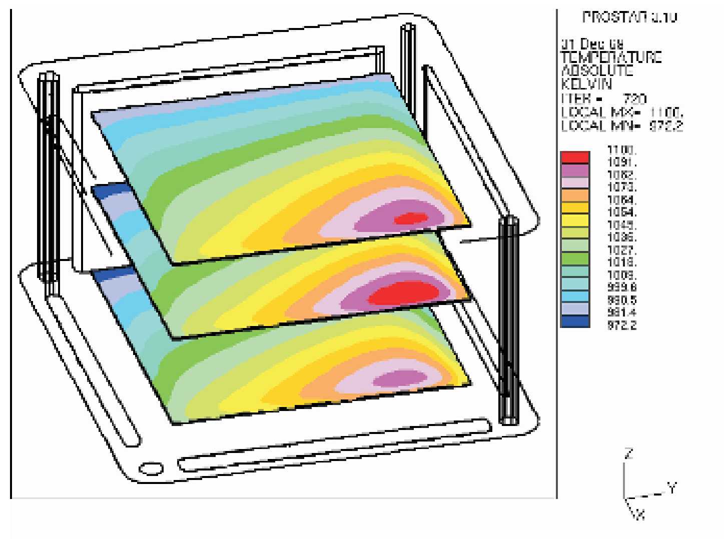

Figure 4. *Predicted temperature distributions on cells #1, 8, and 16 of a 16-cell SOFC stack delivering 0.30 W/cm² at 0.7 Volts and 750°C*

Conclusions

Advanced cell component materials, fabrication processes, and computational modeling tools being developed at PNNL are contributing to the efforts of SECA industrial teams and other industries in meeting the required cost and performance targets for SOFC power systems to enter the commercial marketplace.