SOLID OXIDE FUEL CELL DEVELOPMENT AT PNNL

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ABSTRACT

Through a variety of programs, Pacific Northwest National Laboratory is working with government agencies and private industries to help bring SOFC-based technology to the commercial marketplace. These activities include the development of advanced materials and fabrication techniques for SOFC stack components, the development and utilization of modeling tools for optimization of cell and stack designs, and the development and application of advanced characterization techniques to increase the understanding of fundamental electrochemical processes occurring in SOFCs.

INTRODUCTION

Pacific Northwest National Laboratory (PNNL), in collaboration with government agencies and private industries, is developing advanced solid oxide fuel cell (SOFC) power generation systems for a wide variety of applications ranging from stationary power production to automotive auxiliary power applications. The technology development at PNNL, which consists of both experimental and computational activities, covers many R&D areas, including optimized materials for cell/stack components, cost-effective fabrication procedures, and advanced stack designs offering high performance and reliability.

Much of the effort at PNNL is directed towards the development of inexpensive, high power density SOFC stacks operating at intermediate temperatures, e.g. 650-800°C. Advantages of operation in the intermediate temperature range include the possibility of using inexpensive alloys as interconnect components, reduced thermal stability demands on other “hot box” components (manifolds, pipes, etc.), thermal compatibility with fuel reformers, and simplified system thermal management (i.e., smaller ΔT from room temperature to operating temperature reduces challenges related to cathode air preheating and thermal cycling). However, reducing the stack operating temperature to the intermediate temperature range presents challenges in regard to obtaining high power density from the cells, as both electrode polarizations and ohmic resistances within the cells tend to increase with decreasing temperature. Specific efforts related to intermediate temperature stacks include optimization of compositions, microstructures,
and fabrication techniques for anode-supported cells, improved electrode materials, inexpensive alloy-based interconnect materials, and thermally cyclable seals.

In addition to its in-house research activities, PNNL acts as a co-leader (along with the National Energy Technology Laboratory (NETL)) of the Department of Energy’s Solid-State Energy Conversion Alliance (SECA) initiative. The goal of the SECA initiative is to accelerate the development of modular 3 to 10 kW size SOFC power systems offering fuel flexibility and low system cost (~$400/kW).

SOFC DEVELOPMENT PROGRAMS AT PNNL

PNNL has several programs pursuing SOFC technology development. These include: SECA Core Technology Program (funded by DOE-Fossil Energy (FE)), SOFC auxiliary power unit (APU) Development (Delphi Corporation/Battelle Memorial Institute (BMI)/DOE-FE), Advanced SOFC Component Materials Development (Cummins Power Generation/McDermott Technologies/DOE-FE), Palm Power SOFC Advanced Cathode Development (DARPA), and the High Temperature Electrochemistry Center (DOE-FE). Technology development highlights for some of these programs are summarized below.

SECA Core Technology Program (DOE-FE)

The SECA Core Technology Program (CTP) funds work at universities, national laboratories, and industries intended to support the SECA industry teams in their efforts to develop commercially successful SOFC power systems. SECA-CTP development activities at PNNL are focused on advanced cell/stack component materials (cathode, anode, interconnect, and seals), and the development of computational models which simulate cell and stack performance in both transient and steady-state modes.

Cathode Development. Sr-doped lanthanum ferrite, $La_{0.8}Sr_{0.2}FeO_3$ (LSF-20), cathodes exhibit low cathodic polarization in cells tested in the 650 – 850°C temperature range (1-3). 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 “button” cells using this cathode material (including a Sm-doped ceria ($Ce_0.8Sm_{0.2}O_2$) layer between the cathode and YSZ membrane) are ~1.2 W/cm² at 800°C and ~0.8 W/cm² at 750°C (measured at 0.7 V; fuel: 97%H₂/3%H₂O; oxidant: air; low fuel and air utilization; see Figure 1). In addition, LSF-20 has shown very promising long-term behavior. Figure 2 illustrates recent performance data of an anode-supported YSZ cell utilizing a LSF-20 cathode. After initial data acquisition at 850°C and 800°C, the cell was held at 0.7 V and 750°C, and achieved a power density of 770 mW/cm² with no discernible degradation over a 500 hour period. (The vertical lines on the graph are the result of periodic I-V sweeps).

Anode Development. Oxide anode materials offer several potential advantages over conventional Ni-based anodes, including sulfur tolerance and stability under red-ox cycling (4-6). In particular, stability towards red-ox cycling would simplify system requirements by eliminating the need to provide a protective inert or reducing atmosphere for the anode during stack heatup and cooldown. Anode compositions in the
Sr-La-Ti-Ce-O system have demonstrated excellent dimensional and chemical stability under thermal and red-ox cycling. The thermal expansion behavior is similar to that of other SOFC components, and the electrical conductivity, while lower than that of Ni-based anodes, may be adequate. These materials, which contain two phases (La-doped strontium titanate and doped ceria), exhibit low anodic polarization resistances in hydrogen fuel at intermediate temperatures. For example, electrolyte supported cells using these anodes have yielded power densities of approx. 0.5 W/cm² at 800°C measured at 0.7 V (fuel: 97%H₂/3%H₂O; oxidant: air; low fuel and air utilization). The cells exhibited no degradation during 200 hours of continuous testing. Operation on fuels other than hydrogen (methane and carbon monoxide) was also investigated and the results are given in Table 1. While utilization of both carbon-containing fuels typically led to lower performance than that in hydrogen, no carbon deposition (coking) was observed at steam-to-carbon ratios as low as 0.06-0.12. Preliminary testing also indicates that this novel anode material is unaffected by the presence of 1-26 ppm H₂S in the fuel stream.

**Compressive Seal Development.** A novel mica-based compressive seal concept has demonstrated very low leak rates (in coupon testing in air). The seal is comprised of a mica “gasket” with compliant interlayers (glass or metal) inserted in the interfaces between the mica and adjacent SOFC stack components (7-9). Leak rates on the order of 0.0001-0.001 sccm per cm of seal length have been measured; these leak rates are several orders of magnitude lower than leak rates measured with plain mica compressive seals (without the interlayers). During thermal cycling, leak rates tended to increase abruptly during the first few cycles, with modest increases in leak rate occurring during subsequent thermal cycling. Development efforts are focused on modifications to the seals to minimize the observed degradation in performance during thermal cycling.

**Metallic Interconnect Development.** PNNL has performed an in-depth study evaluating the suitability of a variety of stainless steels and other alloys for the SOFC interconnect/current collector application. A database of compositions and properties of over 300 alloys was compiled, and several of the most promising alloys have been evaluated in screening tests which evaluated oxidation resistance, oxide scale electrical conductivity, thermal expansion, and compatibility with sealing glasses (10-13). At present, screen testing efforts are focused on evaluation of high temperature oxidation behavior of candidate ferritic stainless steels. Interconnect materials development efforts are focusing on the development/optimization of conductive oxide coatings intended to minimize scale resistance and Cr-species volatilization of commercially available ferritic stainless steels.

**Computational Modeling and Simulation.** A key feature of the SECA core technology program is the development of modeling and simulation tools that are applicable to a wide range of SOFC designs (14-17). Efforts at PNNL have been focused on the development of new analytical and computational techniques for modeling of thermal cycling, steady state operation, life prediction, and system-level thermal and electric modeling. The SOFC stack modeling capability at PNNL has developed to a level at which planar stack designs can be compared and optimized for startup performance. New tools include routines for simulating rapid start-up which are based on a methodology for applying the thermal results from computational fluid...
dynamics analysis to finite element models for determining an optimal thermal controller. PNNL developed electrochemical models to be used for stack design and optimizing material properties. The stack electrochemistry model calculates the electrical current density, cell voltage, and heat production in solid oxide fuel cell stacks with H₂ or other fuels, taking into account as inputs local values of the gas partial pressures and temperatures. This approach is based on an existing current-voltage (I-V) relation. The model includes the heat generation from both Joule heating and chemical reactions. It also accounts for species production and destruction via mass balance. The model is linked to the finite element analysis code MARC and computational fluid dynamics code Star-CD to allow evaluations of temperatures and stresses during steady state operations. A three-dimensional model geometry, including internal manifolds, was created to simulate a cross-flow stack design. Similar three-dimensional geometries were created for simulation of co-flow and counter-flow stack designs. This tool and others are being used to assist in design optimization of cells and stacks for optimum performance. Parameters being optimized include cell performance at high fuel utilization, uniformity of gas flows, and thermal and mechanical stress profiles during stack operation and startup/shutdown. As an example, calculated thermal profiles for counter-flow, co-flow, and cross-flow cases are shown in Figure 3. PNNL also has developed detailed micro-structural electrochemistry models for cell design and optimizing of material properties. The models are capable of simulating the performance of porous electrode materials by based on the microstructure of the material, the distribution of reaction surfaces, and the transport of oxygen ions through the material. Lattice Boltzmann simulations on the detailed local micro-structural geometry are performed using the CHEMKIN and SURFACE-CHEMKIN simulation packages to describe the chemical kinetics.

SOFC APU Development (Delphi Corporation/BMI/DOE-FE)

A SECA industry team, comprised of Delphi Corporation and Battelle Memorial Institute, is jointly developing an SOFC-based on-board auxiliary power unit (APU) for the automotive industry (18). Research and development activities at PNNL are focused on SOFC stack development, and include:

- Development of optimized electrode materials and cost-effective fabrication techniques for high-performance anode-supported cells. A combination of tape-casting and screen-printing techniques are used for fabricating the cells. Anode-supported YSZ membranes are prepared by laminating several layers of NiO/YSZ tape (40vol% final Ni content) with a single layer of “active” anode tape and a single layer of 8YSZ electrolyte tape. After co-sintering of the laminated tapes, a ceria interlayer and the cathode are applied to the supported electrolyte via screen printing, followed by lower temperature heat treatments. Typical cell geometries are ~12 cm x ~12 cm. Typical thicknesses of the anode substrate, active anode, YSZ membrane, and cathode are ~500 μm, 10 μm, 7 μm, and 30 μm, respectively.

- Optimization of SOFC stack interconnects and seals for long-term stability, thermal cyclability, and high power densities (volumetric and mass basis).
- Modeling (using CFD and FEA simulation tools) to optimize stack design parameters for uniform gas flow distributions and minimal mechanical stresses during system startup and operation.

- Thermomechanical measurements to characterize bulk and interfacial properties of cell/stack components during fabrication, operation, and system startup and shutdown.

- Testing of stacks to validate improvements in materials and component design.

**Advanced SOFC Component Materials Development (Cummins Power Generation/McDermott Technologies/DOE-FE)**

PNNL is working with another SECA industry team, Cummins Power Generation and McDermott Technologies, to develop improved cell component materials that enhance the cell performance and performance stability. Advanced electrochemical and analytical techniques are used to characterize and understand anodic and cathodic electrode processes. This study is targeted at developing electrode materials formulations and processing conditions that lead to electrical performance enhancement and bulk and interfacial stability during cell fabrication and operation.

**Palm Power Cathode Development (DARPA)**

Under a DARPA-sponsored “Palm Power” program, PNNL is developing advanced cathode materials and architectures to optimize the activation and mass transport limitations in the cathode. Through computational modeling, PNNL has developed an engineered electrode microstructure that allows for increased three phase boundary (TPB) length near the electrode/electrolyte interface and desired porosity at the electrode/gas interface for gas phase diffusion without compromising the current collection ability. A- and B-site doped perovskite materials have been developed and tested.

**High Temperature Electrochemistry Center (DOE-FE)**

Recently, PNNL has teamed with the Department of Energy’s Fossil Energy and Montana State University to form the High Temperature Electrochemistry Center. The purpose of this center is to further the understanding of the fundamental electrochemical and microstructural processes occurring in high temperature electrochemical systems such as fuel cells, electrolyzers, thermoelectric devices, and sensors. Specific areas of study include cathode and anode electrodics and degradation mechanisms of metallic interconnect materials in the SOFC environment.

**SUMMARY**

PNNL is developing advanced cell/stack component materials, fabrication processes, and computational modeling tools to assist the efforts of SECA industrial teams and other developers in meeting the required cost and performance targets for SOFC power systems to enter the commercial marketplace.
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Table 1. Power densities (W/cm²) obtained from YSZ electrolyte-supported cell with (La, Sr)TiO₃-(La, Ce)O₂ anode and LSF cathode at 800°C at a cell voltage of 0.5 V.

| Gas pressure, kPa | 48.5/48.5/3 | 24.3/72.7/3 |
|-------------------|-------------|-------------|
| H₂/N₂/H₂O        | 0.274       | 0.220       |
| CH₄/N₂/H₂O       | 0.135       | 0.109       |
| CO/N₂/H₂O        | 0.074       | Not tested  |

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1.1 Figure 1. Temperature dependent electrical performance of anode-supported cell (LSF cathode, ceria interlayer, YSZ electrolyte, Ni/YSZ anode). Fuel: 97% H₂/3% H₂O. Oxidant: Air. Low fuel and oxidant utilization.

Figure 2. Performance data for an anode-supported YSZ cell utilizing a LSF-20 cathode. After initial data acquisition at 850°C and 800°C, the cell was held at 0.7V and 750°C, and achieved a power density of ~770 mW/cm² over a 500 hour period. Same test conditions as Figure 1.
Figure 3. Calculated thermal profiles for (a) cross-, (b) co-, and (c) counter-flow cases.

Figure 4. Evolution of cell fabrication and testing at PNNL. Small-, intermediate-, and full-size cells have 12, 34, and 106 cm² of active area, respectively.