II.C.3 Development of a Novel Efficient Solid-Oxide Hybrid for Co-Generation of Hydrogen and Electricity Using Nearby Resources for Local Application

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Objectives

- Develop and optimize composite cathodes for solid oxide fuel-assisted electrolysis cells (SOFECs).
- Fabricate anode-supported solid oxide fuel cells (SOFCs) and SOFECs with Ni-YSZ anode supports, thin film YSZ electrolytes, and composite cathodes.
- Quantify the issues affecting the mechanical stability (particularly the strength) of the anode supports, followed by characterization of the anodes.
- Develop glass seals.
- Demonstrate SOFC-SOFEC hybrids co-generating hydrogen and electricity directly from hydrocarbon fuels at temperatures between 750 and 800°C.
- Design, construct, and evaluate a 5 kW module-based SOFC-SOFEC system for co-generation of hydrogen and electricity directly from natural gas.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Generation by Water Electrolysis section (3.1.4.2.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(G) Capital Cost

(H) System Efficiency

Technical Targets

This project is conducting the research and development of an advanced technology that cogenerates hydrogen and electricity directly from distributed natural gas using hybrid SOFECs and SOFCs. Insights gained from this project will be applied toward the future design and construction of hydrogen and/or electricity cogeneration systems that meet the following DOE 2012 distributed hydrogen production targets:

- Hydrogen cost: $3.7/gasoline gallon equivalent
- Energy efficiency: 69% (lower heating value)

Accomplishments

- Synthesized (La,Sr)(Cr,Mn)O_3 (LSCM) as a p-type material and Sm-doped CeO_2 (SDC) as a n-type material and fabricated a composite that has p-type and n-type conductivity at the same time.
- Demonstrated redox stability of the LSCM-based composite cathode.
- Fabricated defect-free anode supports for SOFCs and SOFECs with optimized anode porosities and microstructure.
- Identified alkaline earth silicate-based glass compositions with requisite thermal properties.
- Demonstrated stability and hermeticity of the glass seal materials for up to 100 days in air and in a wet reducing atmosphere, and over 30 thermal cycles.
- Refined interconnect manifold designs for the SOFC-SOFEC hybrid stack with features of heat transfer-enhancement and in-stack pressure drop reduction.
- Constructed and evaluated stacks operating in SOFEC mode for hydrogen production directly from syngas.
- Demonstrated long-term stability of SOFEC operation for up to 360 hours with no significant degradation observed.

- Constructed and demonstrated hybrid stack modules comprised of SOFECs and SOFECs co-generating hydrogen and electricity directly from hydrocarbon fuels, including syngas and methane.
- Completed the design of a stand-alone 5 kW co-generation system. Construction and evaluation of balance-of-plant (BOP) components are underway.

Introduction

Developing safe, reliable, cost-effective, and efficient hydrogen-electricity co-generation systems is an important step in the quest for national energy security and minimized reliance on foreign oil. This project focuses on materials research and the development of a novel planar solid-oxide hybrid for hydrogen and electricity co-generation directly from fuels such as distributed natural gas and/or coal-derived fuels. The innovative hybrid system under development uses reversible SOFECs integrated with SOFCs, both of which are anode-supported solid oxide electrochemical cells. The SOFECs and SOFCs are manifolded in a stack such that the anodes of both the SOFCs and the SOFECs are fed the same fuel, such as natural gas or syngas. Hydrogen is produced by SOFECs and electricity is generated by SOFCs within the same hybrid system.

A redox stable cathode for the reversible SOFECs has been developed, using composite cathodes comprised of p-type and n-type materials. The performance of each composite has been carefully evaluated as a cathode and suitable materials have been selected and optimized. Although the main factors influencing the design are electro-chemical in nature, the requirement to operate the components at elevated temperatures and the need for thermal cycling between room and operation temperature has made thermomechanical aspects of the components extremely important. In order to achieve the high power densities possible for SOFC-SOFEC hybrid stacks, reliable hermetic sealing technologies have been developed and are undergoing continuous refinement.

Approach

This project is developing a 5 kW planar solid-oxide hybrid system to co-generate hydrogen and electricity directly from natural gas, coal-derived syngas, and other type of fuels. The research and development efforts have been conducted by a team led by Materials and Systems Research, Inc. (MSRI), including University of Alaska Fairbanks, Missouri University of Science and Technology (MST), and University of Utah.

Elastic properties of reduced bi-layer structures comprised of a Ni-8YSZ anode support and a 8YSZ electrolyte were investigated in detail at elevated temperatures in both air and reducing environments simulating the actual operating conditions of the SOFC-SOFEC. Equibiaxial flexural strength of the samples was also evaluated. The influence of glass particle sizes on glass-ceramic crystallization behavior was characterized by using a hot-stage microscopic technique. The long-term stability of the selected glass-ceramic materials' properties was studied by measuring the CTE and electrical conductivity over a period of time. The redox stable composite cathode, a mixture of LSCM and SDC materials, was fabricated and applied to large SOFECs for evaluation in-stack. Long-term stability tests of stacks were performed in the SOFEC mode for hydrogen generation. A stand-alone 5 kW system comprised of module-based SOFC-SOFEC hybrid, BOP components, and electronic controls was designed. Major BOP components were designed, fabricated, and evaluated under the forecast operating conditions.

Results

Anode Substrate Thermo-mechanical Properties Investigation: The as-received planar SOFEC samples from MSRI (with thickness of 600 µm and 900 µm) were cut into pieces and reduced in an autoclave for durations up to 8 hours. Hardness of the samples was measured by Vicker's indentation method with a load of 500 g for 15 seconds. Elastic properties, such as Young's modulus (E) and shear modulus (G), were determined by the impulse excitation technique using the commercially available Buzz-o-sonic nondestructive testing system. The elastic properties of NiO-8YSZ anodes were dependent on several factors, i.e., microstructure, composition, temperature, physical dimension, etc. It was observed that the room temperature elastic moduli and hardness of the NiO-8YSZ anode samples decrease significantly with increasing fraction of reduced NiO. Since the elastic properties of fully dense Ni, NiO and 8YSZ are comparable to each other, the observed colossal decrease in elastic moduli in the two sets of samples (ΔE~38%, ΔG~33% [600 µm] and ΔE~52%, ΔG~54% [900 µm]) after 8 hours of reduction is primarily due to the significant increase in porosity with the reduction of NiO. In addition to the porosity, the high operating temperature significantly influences the elastic moduli of Ni-8YSZ anodes. Figure 1(a) shows the Young's moduli of the as-received and the 8 hours reduced anodes of both batches as a function of temperature in ambient air up to 1,000°C. The high NiO containing as-received samples show the steady value of room temperature Young's modulus up to 150°C. An increase in E was observed over a temperature range of 200-500°C with a maximum value

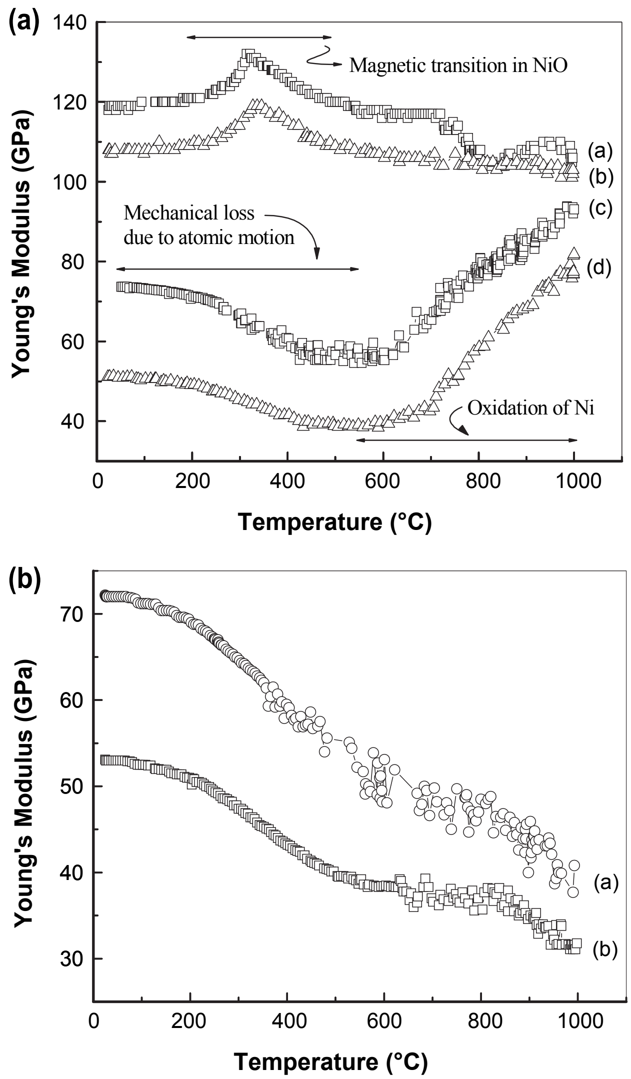

FIGURE 1. (a). Variation of Young's Moduli of As-received (a & b) and 8 hr Reduced Samples (c & d) of 600 μm & 900 μm, Respectively. (b). Young's Moduli of 8 hr Reduced Samples of (a) 600 μm and (b) 900 μm as a Function of Temperature in a Reducing Atmosphere

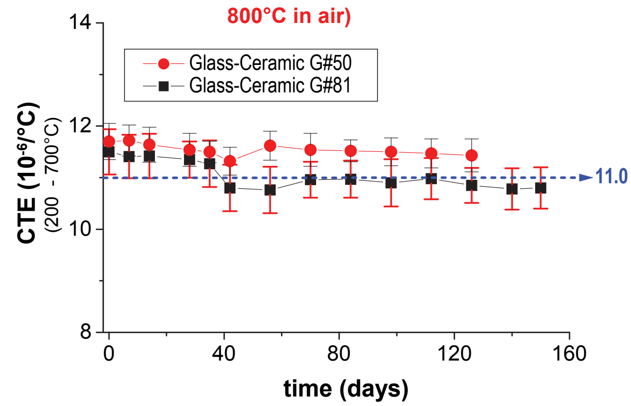

FIGURE 2. Coefficient of Thermal Expansion for Sealing Glass Compositions after Heating to 800°C in Air for Extended Time

at ~325°C (due to magnetic transition in NiO), prior to a broad decline with further increase in temperature. The behavior was rather different in the 8 hours reduced Ni-8YSZ anodes and can be divided into three separate regions. From room temperature to 250°C, *E* decreases slowly, and then decreases more rapidly from 250 to 550°C (mechanical loss due to atomic motion). Finally it increases monotonically with further increase in temperature (due to the oxidation of Ni). In a reducing environment, however, the *E* values decrease monotonically until the temperature reaches to 1,000°C, as shown in Figure 1(b).

Hermetic Seal Development: The glass-ceramic seals developed at MST have relatively low silica content (<45 mole%) and possess molecular-level structures that are much less connected than conventional silicate glasses. These depolymerized structures contribute to desirably low viscosities at the sealing temperatures (850-900°C), and lead to the formation of crystalline phases that possess relatively high CTEs and good thermal stabilities when the seals are crystallized to form glass-ceramics. Two compositions, named as G#50 and G#81, have been developed that possess the requisite thermal properties for SOFC-SOFEC applications forming a $CaSrSiO_4$- and Sr_2SiO_4-based glass-ceramic, respectively. Figure 2 shows that the CTE of two glasses remains around 11-11.5 x 10^{-6}/°C over four months at 800°C. Electrical conductivity studies over 40 hours showed the material stability under both reducing and oxidizing atmospheres. The influence of the glass particle size on crystallization behavior was characterized by the differential thermal analyses (DTA) method for particles varying from 2.3 µm to 75 µm. Tests of thermal cycling effects on hermeticity showed that seals by G#81 passed 60 cycles and 40 cycles in air and reducing atmospheres, respectively, without failure.

Development of a 5 kW System Co-generating H_2 and Electricity: Design of a stand-alone 5 kW system for co-generating hydrogen and electricity directly from natural gas has been carried out and completed. The specification, sourcing and design of a number of essential BOP components have been completed and fabrication has begun on the stack components, compression systems, and tailgas-fired process heaters. The tailgas-fired steam generator has been made and tested. A preliminary evaluation proved the steam generator meets the system specification. An electronic control algorithm for the system has been designed to enable the hybrid stacks to operate at maximum fuel efficiency and produce hydrogen from excess capacity. Features of multiple stacks in parallel operation increase the reliability and disrupt failure cascades. Stacks comprised of cells with LSCM-based composite cathodes were constructed and tested in the SOFEC mode to evaluate the hydrogen production characteristics. Long-term stability tests of stacks operated in the hydrogen production mode were carried out to investigate the degradation mechanisms. Figure 3 shows typical test results. Over the 360 hours of continuous operation, the stack voltage was nearly unchanged, showing only minimal degradation. The test was interrupted for scheduled SOFC operations, which served as check-points for the functionality of the stack and redox stability of the LSCM-based cathode. As shown in the figure, the LSCM-based cathode material exhibits high redox stability even after six SOFC/SOFEC operating cycles. Hybrid stacks, comprised of multiple SOFCs and SOFECs, were constructed and underwent continuous testing to evaluate hydrogen and electricity co-generation features. Figure 4 shows 48-hour test results of a 10-cell hybrid stack, comprised of six SOFECs and four SOFCs with per-cell active areas of 100 cm^2. It is observed that at the fixed fuel/air/steam utilizations of 60/60/40, at 30 A, the four SOFCs generated ~85 watts of power, of which 25 watts was consumed by the six SOFECs to produce 80 standard liters of hydrogen per hour (SLPH), and simultaneously output 60 watts of net power for other applications. The hydrogen production rate can be increased further by increasing the ratio of SOFECs per SOFC.

Conclusions and Future Directions

- Structures of highly porous Ni-8YSZ anode supports were studied to characterize the effects of porosity, composition, temperature and effect of sample thickness on their hardness, elastic properties and equibiaxial strength. The effect of thermal cycling on the mechanical properties is being investigated.
- Two glass compositions, namely, G#50 and G#81, have been tested under operational conditions. Both glasses tested over 150 days demonstrated compositions that possess the requisite thermal properties for SOFEC/SOFC seals. Electrical conductivity tests of these glass-ceramics shows stable feature over time under operational conditions.

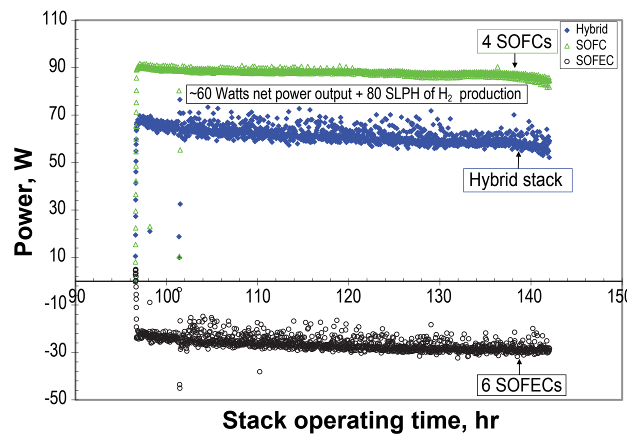

FIGURE 4. Continuous Co-Generation of Hydrogen and Electricity with a 10-cell Hybrid Stack (6-SOFECs and 4-SOFCs). Utilizations of syngas, air, and steam were fixed at 60%, 60%, 40%, respectively. The furnace temperature was set at 800°C.

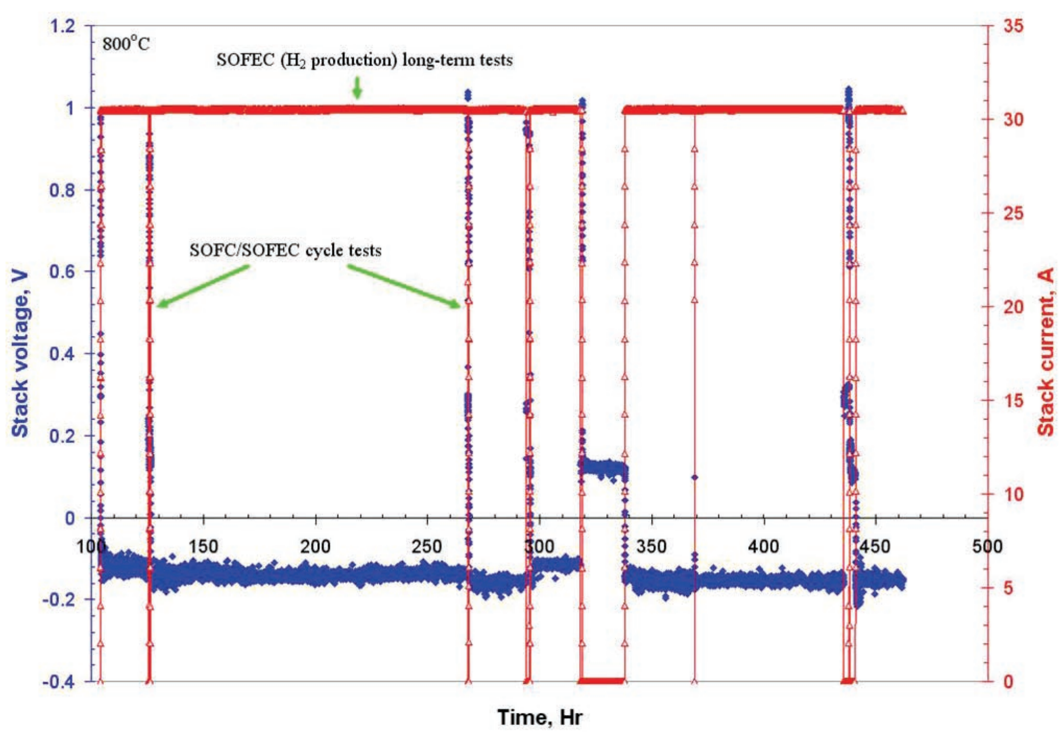

FIGURE 3. Long-Term Test of a 4"x4" Stack in the SOFEC Mode for Hydrogen Production

- Hermetic seal tests of G#50 and G#81 demonstrated that seals survived up to 50 thermal cycles in air and up to 40 thermal cycles in reducing atmosphere.
- Long-term tests of stacks in the hydrogen production mode demonstrated the redox stability of the SOFECs.
- Tests of hybrid stacks, comprised of multiple SOFCs and SOFECs connected in series, showed the versatility of the hybrid for hydrogen production, electricity generation, and co-generation of both hydrogen and electricity.
- A stand-alone 5 kW hybrid system will be constructed and evaluated for hydrogen and electricity co-generation directly using the distributed natural gas.
- A cost model will be set up to analyze the cost of hydrogen production with implementing the experimental results of the 5 kW hybrid system.

FY 2008 Publications/Presentations

1. Thangamani Nithyanantham, N.T. Saraswathi, S. Biswas, S. Bandopadhyay, "Studies on Phase Formation, Microstructure and Mechanical Properties of Reduced Nickel Oxide/Yttria-stabilized Zirconia Anode Precursor for Solid Oxide Fuel Cells", communicated to Journal of Power Sources.

2. Thangamani Nithyanantham, Saraswathi Nambiappan Thangavel, Somnath Biswas, and Sukumar Bandopadhyay, "The Reduction of NiO-YSZ Anode Precursor and Its Effect on the Microstructure and Elastic Properties at Ambient and Elevated Temperatures" 32nd International Conference on Advanced Ceramics and Composites, January 27 – February 1, 2008, Daytona Beach, Florida, USA.

3. J. Zhang, S. Biswas, N. Thangamani, N. T. Saraswathi and S. Bandopadhyay, Presented in the 213th meeting of The Electro-chemical Society (ECS) and accepted for publication in the ECS Transactions (held during May 18–22, 2008 at Phoenix Convention Center, Phoenix, USA).

4. S. Biswas, Thangamani Nithyanantham, N. T. Saraswathi, J. Zhang and S. Bandopadhyay, "Structural and Mechanical Stability of Reduced Nickel Oxide/Yttria-stabilized Zirconia Anode/Electrolyte Structures for Solid Oxide Fuel Cell Applications" MRS Spring Meeting, March 25–27, 2008, San Francisco, CA, USA.

5. Thangamani Nithyanantham, Saraswathi Nambiappan Thangavel, Somnath Biswas, and Sukumar Bandopadhyay, "Thermo-elastic Properties of Ni-8YSZ Anode Supported Half-cells in Air and Reducing Environments" The 6th International Fuel Cell Science, Engineering & Technology Conference, June 16-18, 2008, Denver, Colorado, USA.