

II.C.5 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 chemically and electrocatalytically stable cathode materials under both reducing and oxidizing environments.
- Fabricate anode-supported solid oxide fuel cells (SOFCs) and solid oxide fuel-assisted electrolysis cells (SOFECS), comprised of Ni-YSZ (yttria-stabilized zirconia) anode supports, thin film YSZ electrolytes, and optimized composite cathodes.
- Investigate thermo-mechanical properties of anode substrates, including strength, creep behavior, toughness, thermal shock resistance, coefficient of thermal expansion (CTE), and redox affection.
- Develop glass seal compositions and demonstrate hermeticity and materials compatibility for glass-ceramic seals under SOFC-SOFEC operational conditions.

- Demonstrate the concept of SOFC-SOFEC hybrid co-generating hydrogen and electricity directly from hydrocarbon fuels at temperatures between 750 and 800°C.
- Design, construct, and test a 5 kW module-based SOFC-SOFEC co-generation system with improved thermal and fluid management.
- Develop a cost analysis model for hydrogen production using the hybrid SOFC-SOFEC technology.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Generation by Water Electrolysis section 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 to develop a high temperature solid oxide-based hybrid system to co-produce hydrogen and electricity directly from coal-derived fuels at a 5 kW scale. Technologies to be developed will be applied toward the design and construction of hydrogen refueling stations to achieve the following DOE 2012 target set for the distributed electrolysis hydrogen production:

- Cost: \$3.7/gge
- Efficiency: 69%

Accomplishments

- Synthesized new cathode materials using a water-based polymeric precursor technology.
- Demonstrated a new composite material performing as an n-type conductor in reducing atmospheres and a p-type conductor in oxidizing atmospheres.
- Investigated and optimized the anode substrate porosity and microstructure using various pore-formers.
- Fabricated defect-free anode-supported SOFCs and SOFECS with the optimized anode porosity and microstructure.
- Investigated the hardness of the NiO-8YSZ anode supports and dependence on the microstructure and pore-formers.

- Studied the effects of the reducing atmosphere on the microstructure and elastic properties of anode substrates.
- Developed the finite element modeling (FEM) to complement experimental studies of fracture toughness using the indentation method.
- Identified alkaline earth silicate glass composition with requisite thermal properties, including sealing temperatures at or below 900°C and CTE in the range $11\text{-}12 \times 10^{-6}/^\circ\text{C}$.
- Demonstrated the stability of the seal materials under SOFC-SOFEC operational conditions: e.g. stable CTE and low material volatility at temperatures up to 800°C, for up to 100 days in air and in wet forming gas.
- Produced hermetic seals between 430 stainless steel interconnect alloys and SOFC components, including 8YSZ electrolytes and Ni-8YSZ anode substrates, that passed room temperature helium-leak tests after over 30 thermal cycles between 800°C and room temperature.
- Evaluated particle-size effects on the densification of commercially-supplied glass.
- Designed, constructed, and demonstrated 1 kW class hybrid stacks, comprised of SOFCs and SOFECs, to co-generate hydrogen and electricity directly from hydrocarbon fuels.
- Designed a 5 kW hybrid system for co-generation of hydrogen and/or electricity.
- Designed and fabricated balance-of-plant (BOP) components for the 5 kW hybrid system.



Introduction

The development of safe, reliable, cost-effective, and efficient hydrogen-electricity co-generation systems is of paramount importance from the standpoint of national energy security and minimizing reliance on foreign oil. This project is directed toward the materials research and development of a novel planar solid-oxide hybrid for hydrogen and electricity co-generation directly from coal-derived fuels, or other type of fuels, such as distributed natural gas. This innovative hybrid system under development is comprised of reversible SOFECs integrated with SOFCs. Both SOFECs and SOFCs 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 coal-derived syngas or natural gas. Hydrogen is produced by SOFECs, while electricity is generated by SOFCs from the same hybrid system.

A redox stable cathode for the reversible SOFECs will be developed. The cathode materials must have

high efficiencies in the low oxygen activity range of 10^{-20} – 10^{-15} atm as well as under oxidizing conditions (air). Composite cathodes comprised of p-type and n-type materials are to be developed. The performance of each composite will be carefully evaluated as a cathode and the most suitable materials will be selected and further optimized. Due to the nature of the hybrid system operating at elevated temperatures, material constraints and integrity issues, such as temperatures and residual stresses causing creep, and long-term performance will be investigated. 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 makes thermomechanical aspects of the components extremely important. In order to achieve the high power densities possible for SOFC-SOFEC stacks, reliable hermetic sealing technologies must be developed. Compositions with the requisite thermal properties for seals have been developed, but questions about long-term property stability, deleterious interfacial reactivity, and component volatility make the development of new, reliable sealing materials a priority.

Approach

This project is aimed towards the materials research and development of a 5 kW planar solid-oxide hybrid system to co-generate hydrogen and electricity directly from coal-derived syngas, natural gas, or other types of fuels. The research and development efforts are being conducted by a team led by Materials and Systems Research, Inc. (MSRI), including the University of Alaska Fairbanks (UAF), the University of Missouri-Rolla (UMR), and the University of Utah (UU).

Redox stable composite cathodes, mixtures of n-type and p-type materials, will be fabricated. Candidate materials, such as (La, Sr)TiO₃ (LST) or doped ceria (Gd or Sm) as the n-type and (La, Sr)MnO₃ (LSM), (La, Sr)(Co, Fe)O₃ (LSCF) or (La, Sr)(Cr, Mn)O₃ (LSCM) as the p-type, are selected to make composite materials and are investigated in both reducing and oxidizing conditions. Factors affecting the electro-mechanical and thermo-mechanical integrity of the SOFC-SOFEC anode supports are assessed experimentally and numerically. Glass-ceramic seals with low silica contents will be developed. The glass possesses molecular-level structures that are much less connected than conventional silicate glasses. Meanwhile, depolymerized structures contribute to desirably low viscosities at the sealing temperatures (~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. Proof-of-concept of the SOFEC-SOFC hybrid co-generating hydrogen and electricity will be carried out in kW stacks implemented

with the cathodes and seals developed. A 5 kW system based on multiple modules will be designed. BOP components will be fabricated and integrated into the 5 kW hybrid system.

Results

Important results and accomplishments are summarized in the following.

Cathode Materials Development: Electrical conductivities of LST/LSCM composites were studied as a function of oxygen activity at 900°C. The measured conductivity of the composite was about 0.1 S/cm and 0.25 S/cm at the oxygen activity of 10^{-1} and 10^{-20} atm, respectively, indicating that LST should be replaced by other cathode materials. Samarium doped ceria (SDC) was thus investigated as a potential candidate. Calculations of the electrical conductivity of SDC were performed based on impedance spectroscopy data as a function of temperature. Results are shown in Figure 1, indicating that to increase the conductivity of SDC cells at all temperatures, the volume of the grain boundary should be minimized for operating temperatures below 400°C and maximized for those above 400°C.

Anode Substrate Thermo-Mechanical Properties Investigation: The as-received planar SOFECs from MSRI were characterized using X-ray diffraction, thermo-gravimetric/differential thermal analyzer (TG-DTA) and optical microscopy. The porosity and density of the as-received anode substrates were estimated. The maximum Vickers hardness values of the anode and electrolyte were 9.1 GPa and 14.7 GPa, respectively. The fracture toughness of the as-received samples was estimated as $1.95 \text{ MPa}\cdot\text{m}^{1/2}$. The microstructure analysis using scanning electron microscopy (SEM)

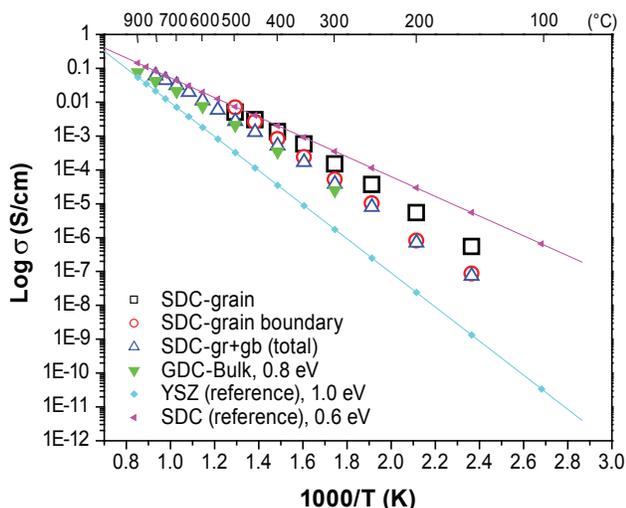


FIGURE 1. Grain and Grain Boundary Contribution to the Total Electrical Conductivity of SDC Button Cells as a Function of Temperature

and energy dispersive X-ray (EDX) was carried out for the anode-supports. The thermal expansion behavior of the unreduced NiO-8YSZ cell was studied and CTE was calculated as $13.1 \times 10^{-6} \text{ } 1/^{\circ}\text{C}$. The anode substrate reduction kinetics were studied at 800°C, and results are shown in Figure 2. The development of crystalline phases is also shown in the same figure. A three dimensional (3D) Vickers indentation process was modeled using a commercial finite element package, ABAQUS, in order to complement experimental studies of fracture toughness using the indentation method. The numerical modeling helps to understand the deformation and failure behaviors of the anode substrate during indentation, and post failure behavior after.

Hermetic Seals Development: A glass-ceramic seal, comprised of low silica content Ca-Sr-Zn-silicate composition, was developed. The glass, called glass #50, showed promising characteristics of possessing the requisite thermal properties for SOFC-SOFEC seals. After four months of testing at 800°C, the CTE of the glass #50 remained unchanged at $11.5 \times 10^{-6} /^{\circ}\text{C}$. The influence of glass particle size on the crystallization behavior was investigated. Figure 3 shows DTA of different particle sizes of a commercially-provided glass #50, collected at $10^{\circ}\text{C}/\text{min}$. The glass transition temperature (T_g), the temperature of the onset of crystallization (T_x), and the crystallization peak temperature (T_p), are indicated in the figure for particle size of 2.3 μm . Studies show that larger particle sizes have greater values of ΔT_x , suggesting a greater resistance to immediate crystallization. The effect of particle size on crystallization behavior was also characterized using a hot-stage microscopic (HSM) technique. The investigation on the competition between the sintering

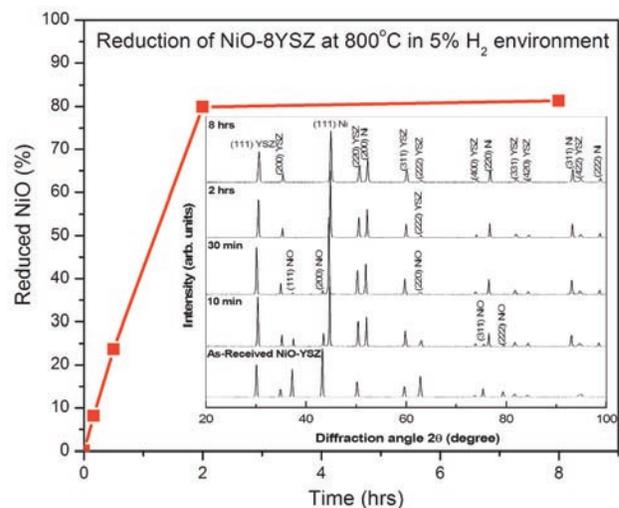


FIGURE 2. Reduction Kinetics of NiO-8YSZ at 800°C in 5% H_2 Environment (Data points represent results obtained from interrupted reduction tests. The development of crystalline phases is shown in the same plot.)

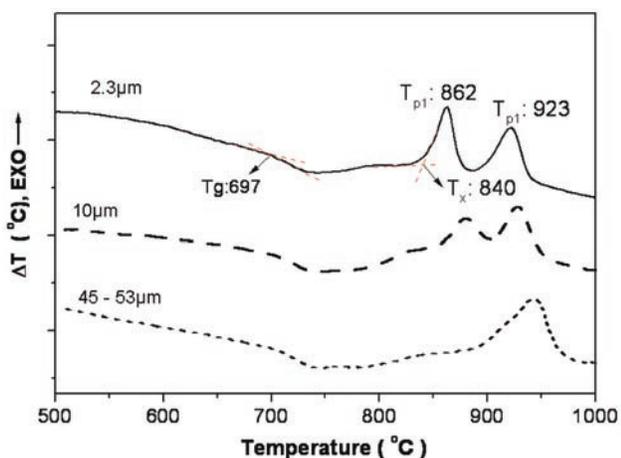


FIGURE 3. Differential Thermal Analyses of Glass #50 Powders with Different Average Particle Sizes, at a Heating Rate of 10°C/min

and crystallization of glass powders of three different particle sizes (2.3, 10, and 45~53 μm) showed that crystallization of 2.3 and 10 μm powders could impede the sintering process, leading to poorly sintered and porous seals.

Proof-of-Concept of SOFC-SOFEC Hybrid Stack Co-Generating H₂ and Electricity: Proof-of-concept tests of the SOFC-SOFEC hybrid have been carried out to co-generate hydrogen and electricity directly from the coal-derived syngas. Hybrid stacks, comprised of both SOFCs and SOFECs, were constructed and tested in the SOFC mode first as the baseline for power generation and the hybrid mode for co-generation of hydrogen and electricity. The ratio of SOFECs per SOFC was studied based on the experimental results to maximize the hydrogen production capacity under an electrically self-sustaining condition. Figure 4 shows hybrid stack performance characteristics obtained at the furnace temperature of 770°C. The hybrid stack had 20 anode-supported SOFECs and 13 anode-supported SOFCs connected in series. The active area of each SOFECs and SOFCs was 100 cm². A glass-ceramic seal was used to ensure the cells were capable of switching between the SOFC and SOFEC modes. Wet syngas was fed to the anode sides of the SOFECs and SOFCs simultaneously. Air and steam were fed to the cathode sides of the SOFCs and SOFECs, respectively. Utilization of fuel, air and steam were fixed at 40%. The power generated from the SOFCs was applied directly to the SOFECs for driving hydrogen production from steam. As shown in the figure, at 35 A, the 13 SOFCs generated 350 W electrical power, of which 125 W power was used to drive the 20 SOFECs for hydrogen production, and of which 225 W power was used as output from the hybrid. Simultaneously, this hybrid produced 5.4 SLPM hydrogen, equivalent to 325 SLPH hydrogen from the 20 SOFECs. It can be projected from the plot that the hybrid can make the maximum

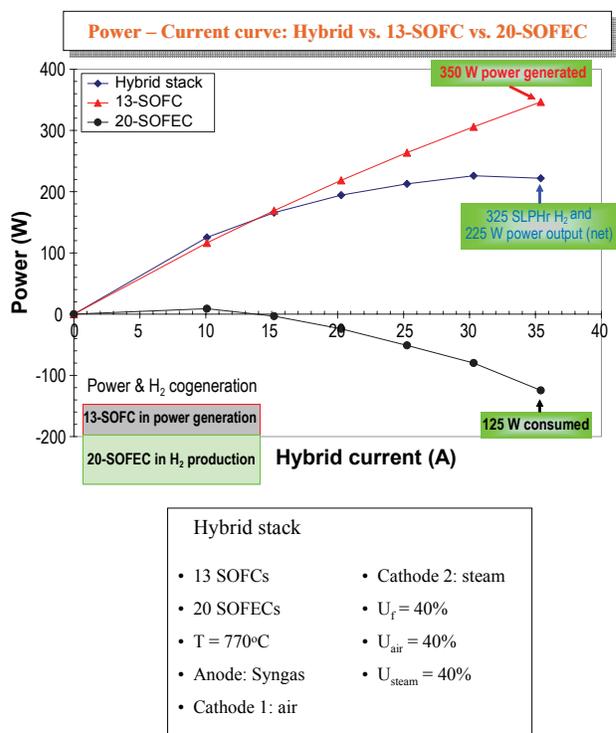


FIGURE 4. Performance Characteristics of a 33-Cell Hybrid Stack for Hydrogen and Electricity Co-Generation

hydrogen production around 60~75 A with zero net power output. Therefore, with the flexibility of the hybrid stack, the cogeneration capacity can be adjusted for maximizing either power generation or hydrogen production, to meet market demand. Meanwhile, the hybrid also provides significant electricity savings over the traditional electrolysis technology, such as a solid oxide electrolysis cell (SOEC), to produce hydrogen. For instance, at the same production rate of 5.4 SLPM (35 A) hydrogen, the required minimum electrical power is about 770 W for a 20-SOEC without counting any losses caused by ohmic losses, concentration and activation overpotentials. By comparison, the power requirement is only 125 W by implementing the SOFEC technology at the same hydrogen production rate.

Conclusions and Future Directions

- The objectives defined by the project have been met on budget and on time.
- Impedance spectroscopy was used to separate the grain and grain boundary contribution to SDC conductivity as a function of temperature. Controlling mechanism studies suggest that grain volume should be minimized and grain boundary should be maximized for the SDC applications. Symmetrical cells will be prepared and tested to evaluate stability and performance as a function of temperature and oxygen activity.

- Kinetic studies of the anode substrate reduction show the significant effects on the phase transformation, density, porosity and microstructure development. The effect of temperature, porosity and fraction of reduced NiO on the strength will be investigated.
- Characterization of the glass particle size effect on crystallization behavior shows that 45-53 μm powders exhibited desirable thermal stability against crystallization. The investigation will be continued and results will be applied to optimize processing conditions for SOFC-SOFEC seals.
- Proof-of-concept tests of kW class 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. In comparison with hydrogen production using the conventional electrolysis technology, the hybrid technology can provide significant electricity savings.
- A 5 kW hybrid system will be constructed and evaluated for hydrogen and electricity co-generation. A cost model will be set up to analyze the cost of hydrogen production using the hybrid technology under development.

FY 2007 Publications/Presentations

1. N. Thangamani, N.T. Saraswathi, S. Biswas, J. Zhang, and S. Bandopadhyay, "The Influence of Reduction on the Microstructure and Elastic Properties of Ni-YSZ Anodes for SOFCs at Ambient and Elevated Temperatures", Materials Science & Technology 2007 Conference & Exhibition to be held in Detroit, Michigan on Sept. 16–20 (2007).
2. N. Thangamani, N.T. Saraswathi, S. Biswas, J. Zhang, and S. Bandopadhyay, "Mechanical Properties of the Nickel Based Anodes for Solid Oxide Fuel Cells at Ambient and Elevated Temperatures", Materials Science & Technology 2007 Conference & Exhibition to be held in Detroit, Michigan on Sept. 16–20 (2007).
3. G. Tao and A. Virkar, "Reversible solid oxide fuel-assisted electrolysis cells for hydrogen generation", 16th International Conference on Solid State Ionics, July 1–6, 2007, Shanghai, China.
4. Y. W. Sin, V. Petrovsky, and H. U. Anderson, "Redox Stable Electrodes for Hydrogen Producing Solid Oxide Electrolyzer," ECS Transactions Volume 2, "Hydrogen Production, Transport, and Storage" (2007).