II.A.2 A Reversible Planar Solid Oxide Fuel-Assisted Electrolysis Cell and Solid Oxide Fuel Cell for Hydrogen and Electricity Production Operating on Natural Gas/Biogas

Greg Tao (Primary Contact) and Anil Virkar
Materials and Systems Research, Inc.
5395 West 700 South
Salt Lake City, UT 84104
Phone: (801) 530-4987; Fax: (801) 530-4820
E-mail: gtao@msrihome.com

DOE Technology Development Manager:
Roxanne Garland
Phone: (202) 586-7260; Fax: (202) 586-9811
E-mail: Roxanne.Garland@ee.doe.gov

DOE Project Officer: David Peterson
Phone: (303) 275-4956; Fax: (303) 275-4788; E-mail:
David.Peterson@go.doe.gov

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Objectives

- Develop the concept of a solid oxide fuel-assisted electrolysis cell (SOFEC) for hydrogen production.
- Identify and develop low-cost, reversible SOFEC cathode materials, which are electrocatalytically and chemically stable in both reducing and oxidizing atmospheres.
- Develop the concept of a planar solid oxide fuel cell (SOFC)-SOFEC hybrid stack to co-generate hydrogen and electricity directly from fuels.
- Develop and demonstrate a 1 kW hybrid stack cogenerating hydrogen and electricity.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production 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
(K) Electricity Costs

Technical Targets

High Efficient and Cost Effective Hydrogen Generation System Based on Solid Oxide Technology:

This project is developing a high-temperature solid oxide-based system to co-produce hydrogen and electricity on a 1 kW scale directly from natural gas. Technologies to be developed will be applied toward the design and construction of hydrogen refueling stations to achieve the following DOE 2010 hydrogen production targets:

- Cost: $2.85/gge
- Efficiency: 75%

Accomplishments

- Identified and developed perovskite-type cathode materials, possessing electrocatalytical and chemical stability over a wide range of oxygen activity from 1 to 10^{-23} atm.
- Developed a process to synthesize nanosize powder to increase electrode efficiency.
- Evaluated and optimized cathode materials to reduce the area specific resistance (ASR).
- Fabricated defect-free anode-supported SOFCs-SOFECs with optimized anode porosity and microstructures.
- Completed the design of a hybrid stack, comprising SOFCs and SOFECs.
- Designed and built an automated test station for the 1 kW stack testing in SOFC-SOFEC hybrid mode for co-generation of hydrogen and electricity directly from hydrocarbon fuels.
- Constructed multiple-cell short stacks with optimized cathodes, and evaluated in the reversible fuel cell/electrolysis cell mode, and in the fuel assisted electrolysis cell mode.
- Performed a 4,200-hour long-term test in SOFC mode, and demonstrated a degradation rate less than 1% per 1,000 hours.
- Initiated cost analysis model for hydrogen production based on the hybrid SOFC-SOFEC technology.

Introduction

Currently, Materials and Systems Research Inc. (MSRI) teamed with the University of Missouri-Rolla and Aker Industries Inc. is conducting research and development efforts to develop a planar solid oxide hybrid device for hydrogen and electricity cogeneration directly from natural gas or biogas fuels. This hybrid electrochemical device comprises solid oxide fuel cells (SOFCs) and solid oxide fuel-assisted electrolysis cells (SOFECs). Steam is dissociated at the SOFEC cathode to produce oxygen (which is transported across the cell to oxidize the anode fuel) and hydrogen (which is separated from the effluent stream by condensation of the residual steam). The chemical potential from the fuel significantly reduces the electrical input required for hydrogen production relative to traditional electrolysis processes, resulting in high overall system efficiency and reduced energy costs. The hydrogen produced is extremely pure, relative to that from steam reformation, that makes the SOFEC technology ideal for use in distributed refueling stations for hydrogen fuel cell vehicles. The SOFCs provide an additional driving force to increase the H_2 production rate and to produce electricity, as needed.

Approach

This project aims to develop and validate the hybrid SOFC-SOFEC technology for co-production of hydrogen and electricity directly from distributed natural gas or alternative fuels. Anode-supported planar SOFECs were fabricated first in 1 inch button-cells with 2 cm^2 active area per cell, then in multiple-cell short stacks having either 30 cm^2 or 100 cm^2 per-cell active area. These stacks were tested in the SOFC and SOFEC modes. To quantify electricity savings relative to the traditional water electrolysis, the same cells/stacks were also tested in the solid oxide electrolysis cell (SOEC) mode. Anode-supported SOFC cell-fabrication techniques developed at MSRI have been applied to SOFEC development. Unlike SOFCs, cathode materials used for SOFECs must be stable in a reducing atmosphere, as well as possessing good electronic and ionic conductivity. Low-cost perovskite-type cathodes have been identified and developed, and MSRI's patented infiltration technique was applied to increase the cathodes electrocatalytic properties.

In order to increase specific hydrogen output (g H_2/sec-cm^2 of cell active area) and thereby reduce stack volume, capital cost and electricity consumption, SOFCs will be stacked with the SOFECs to form a hybrid. The SOFC anodes are fed the same fuel as the SOFECs, while their cathodes are air-fed. By switching the cathode feed gas between air and steam, the output of the hybrid can be operated for either complete hydrogen production or electricity generation. An automated test station was constructed for co-production testing. The hydrogen production rate is quantified by two parallel approaches: (I) measuring the SOFEC cathode exhaust flow rate after condensing steam out, and (II) calculating flux from the stack current. A gas chromatograph (GC) is equipped to the test station for analyzing the gas stream composition.

Results

Cathode Materials Development: The cathode materials for SOFC and SOFEC modes are operated over a wide range of oxygen activity. The conventional cathode materials developed for SOFC, such as (La, Sr)CoO_3 (LSC), cannot be used due to the decomposition of cathodes under a reducing atmosphere. Three mixed-conducting perovskite-type oxide systems, (La, Sr)MnO_3 (LSM), (La, Sr)CrO_3 (LSCr), and (La, Sr)(Cr, Mn)O_3 (LSCM), were identified as potential candidates for SOFEC cathodes, and stability tests have been performed for these materials over an oxygen activity varying from 1 to 10^{-23} atm. Figure 1 shows the results of the electrical conductivity measurement at 800°C. The LSM is found to dissociate at oxygen activity around 10^{-20} atm. However, LSCr and LSCM remain as a single phase as low as 10^{-23} atm, suggesting that the addition of Cr to LSM may give the electrode sufficient stability to operate in the oxygen activity range of 10^{-15}-10^{-20} atm, which is required for SOFEC operation. New LSCM samples prepared at 1,500°C show a higher conductivity than LSCr, as shown in the Figure 1. This result has led to the development of LSCM as the SOFEC cathode. Glycine-nitrate, sucrose-nitrate, and ethylene glycol-nitrate methods were adopted to fabricate LSCM nano-size powder, which was mixed with a binder to prepare the LSCM ink for electrochemical properties characterization.

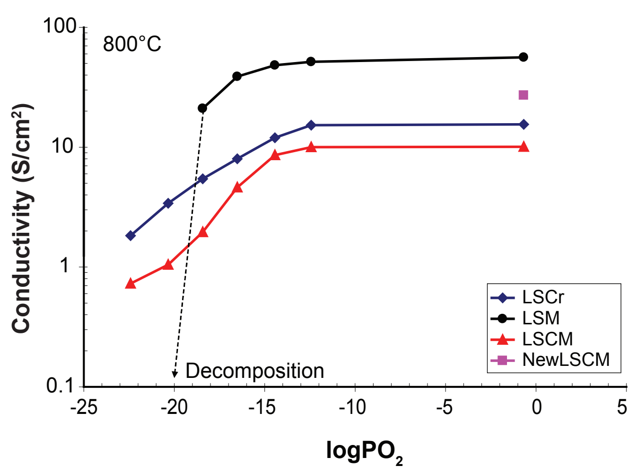

FIGURE 1. Electrical Conductivity of LSCr, LSM and LSCM as a Function of Oxygen Activity at 800°C

1 Inch Button-Cell Tests in Reversible SOFC/SOEC, and SOFEC Modes: The electro-chemical properties of the LSCM+SDC-based composite cathode have been evaluated at 800°C on anode-supported 1 inch button-cells made from MSRI standard tape. First, baseline tests were conducted in the reversible SOFC/SOEC modes, and then the cells were tested in the SOFEC mode for hydrogen production. Optimizations of the composite cathode were performed to reduce overpotentials by adjusting the porosity, microstructure, compositions, and catalyst infiltration. Three kinds of fuels, hydrogen, methane, and syngas (77% H_2, 15% CO, and 8% CO_2) have been used either to generate power or to assist in steam electrolysis for hydrogen production. In order to prevent carbon deposition, both methane and syngas fuels were humidified at a desired steam to carbon ratio. The reactant composition effects on the cell performance were investigated by varying the anode feed of the fuel/steam composition from 10% to 90% in the SOFC/SOEC modes, and the cathode feed of the steam/hydrogen composition from 10% to 90% in the SOFEC mode. Figure 2 shows the typical performance characteristics tested in three modes. The button cell was made from MSRI standard tape and deposited with the LSCM-based composite. In the SOFC mode, wet H_2 (50% steam), wet syngas (27% steam), or wet CH_4 (50% steam) was supplied to the anode, and air was supplied to the cathode. In the SOEC mode, a mixture of steam (50%) with H_2 as the carry gas was fed to the anode, and air was fed to the cathode. In the SOFEC mode, wet H_2 (50% steam), wet syngas (27% steam), or wet CH_4 (50% steam) was fed to the anode, and a mixture of steam (90%) with H_2 as the carry gas was fed to the cathode. The four quadrants identify the cell operation modes. The first quadrant represents the SOFC mode, which consumes a fuel (H_2, syngas, or CH_4) to generate the electricity. The second quadrant represents cells operating in the traditional electrolyzer mode (SOEC) without a fuel assist to produce hydrogen from steam. In this quadrant, the cell current flows in the opposite direction relative to the SOFC mode. The SOFEC mode is located across the first and fourth quadrants where the current flows in the same direction as the SOFC mode. As shown in the figure, in the SOFEC mode, the cell can cogenerate both hydrogen and electricity as the current density is smaller than 0.3 A/cm^2. However, an external power supply, or negative voltage in the fourth quadrant, is required to increase the hydrogen production rate. An ASR of 0.29 Ωcm^2, 0.29 Ωcm^2, and 0.37 Ωcm^2 is observed for the H_2-assisted, syngas-assisted, and CH_4-assisted electrolyzer, respectively. These values are significantly lower than what were reported last year. In order to compare the fuel-assisted electrolysis with the traditional electrolysis, the SOFEC performance is redrawn along the negative current direction, which is in the same direction as the SOEC in the quadrant I. At a current density 0.6 A/cm^2, or equivalent to 4.5 cc/min-cm^2 hydrogen production rate, the energy required to electrolyze steam is 1.58 V and 0.087 V for the SOEC and SOFEC, respectively. This directly results in a significant amount of electricity saving by the use of the SOFEC technology to generate hydrogen.

Long-term Stability Testing: In order to evaluate both the anode and cathode stability and to determine the amount of degradation over time, a long-term test has been conducted. Figure 3 shows a four thousand hour continuous test in the SOFC mode at 800°C. The cell was constructed from an MSRI standard anode with a 2 cm^2 active area with LSCM+SDC composite cathode. In the test, a constant load was applied at a current density 0.7 A/cm^2. As shown in the figure, the cell voltage shows negligible degradation in the first 2,500 hours, and less than 1.5% per 1,000 hours degradation afterwards. Periodically, throughout the long-term test, cell polarization curves were measured

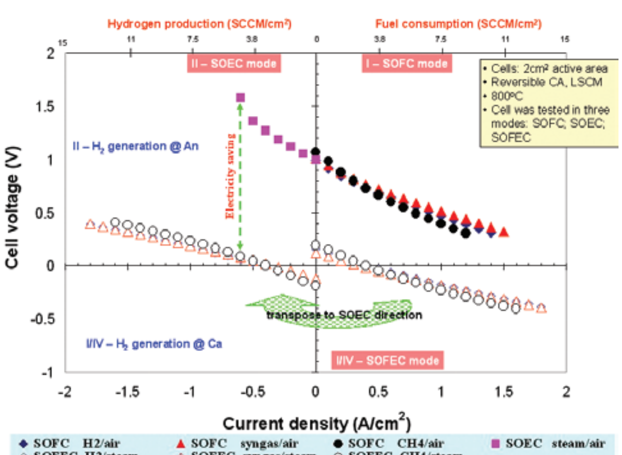

FIGURE 2. Typical Performance Characteristics of a Button-Cell Operated in the Reversible SOFC, SOEC, and SOFEC Modes at 800°C

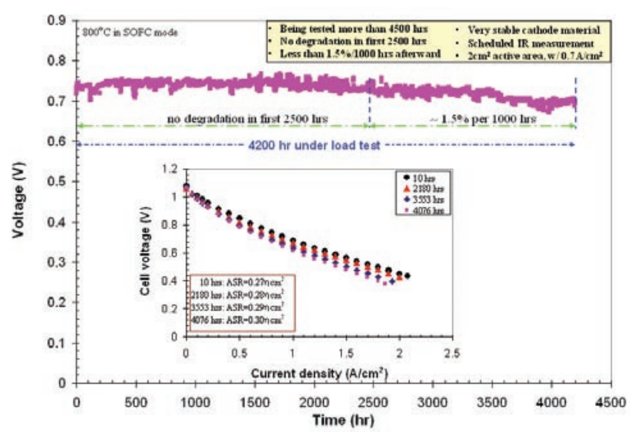

FIGURE 3. 4,200 Hour Long-Term Test (The cell, constructed from a MSRI standard anode tape and deposited with LSCM+SDC-based cathode, was operated in the SOFC mode with a constant load at 800°C. Hydrogen was the fuel and air was the oxidant.)

along with IR losses (via the current-interruption method) to investigate the degradation mechanisms. These results are inset in Figure 3. The cell performance at 2,180 hours of operation time is almost identical to its initial performance. However, slight performance drops are observed at 3,553 and 4,076 hours.

Multiple-Cell Short Stack Tests in Reversible SOFC/SOEC, and SOFEC Modes: Multiple-cell short stacks, varying from two to five cells per stack, have been developed and tested in three modes: SOFC, SOEC and SOFEC, at 800°C. Each stack tested has a per-cell active area of either 30 cm^2 (2"x 2" cell) or 100 cm^2 (4"x 4" cell) with a screen printed LSCM+SDC composite cathode. Figure 4 shows the test results of a 5-cell 4"x 4" stack operated in the SOFC mode as a baseline, and in the SOFEC mode for hydrogen production. Fuels used in both tests are hydrogen, wet syngas, and wet methane. In the SOFC mode, this stack generates 100 W at 45 A current, while in the SOFEC mode, the stack produces over 100 standard liters hydrogen per hour while consuming just 80 W of electrical power.

Hydrogen Production Cost Analysis: A cost analysis model of the hybrid SOFC-SOFEC system has been initiated to evaluate forecourt hydrogen production from distributed natural gas. The total cost of hydrogen production includes both fixed and variable costs, but neglects the costs of the system operation, hydrogen storage and delivery. Stack performance criteria (such as utilization and ASR) and cost factors (such as feedstock consumption, cost, and required stack size) have been integrated in the model. A preliminary cost analysis result is illustrated in Figure 5, showing the effect of SOFC-SOFEC ratio on the hydrogen production cost (in solid lines). Under the current stack performance with ASR 0.5 Ωcm^2 and 1.0 Ωcm^2

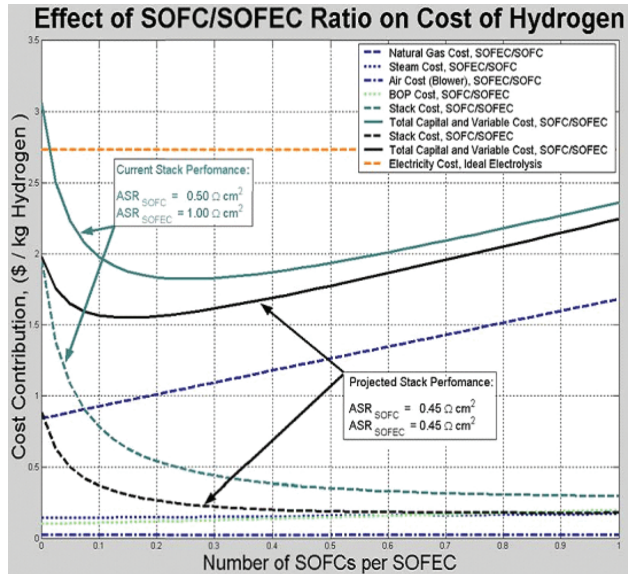

FIGURE 5. Preliminary Cost Analysis Result for Hydrogen Production Based on Hybrid SOFC-SOFEC Technology

for SOFCs and SOFECs, respectively, the total cost in concave shape decreases from \$3.1/gge (gallon of gasoline equivalent) to \$1.8/gge when the number of SOFCs per SOFEC increases from 0 to 0.25. Afterwards, the cost of hydrogen production increases with increasing the number of SOFCs per SOFEC. The effect of hybrid stack performance on the hydrogen production cost is also plotted in the figure. Based upon an assumption that the stack ASR can be reduced from the current value of 1.0 Ωcm^2 to 0.45 Ωcm^2 via optimization of the stacks, the cost of hydrogen can be reduced to \$1.55/gge. As a comparison, the electricity cost for traditional water electrolysis, the dashed orange line shown in Figure 5, is \$2.75/gge for a forecourt refuel station with 1,500 kg daily production.

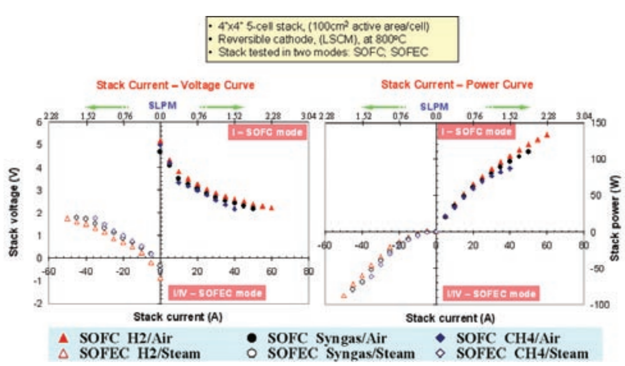

FIGURE 4. Performance of a 5-cell 4"x 4" Stack Operated at 800°C in the SOFC and SOFEC modes. (In the SOFC mode for electricity generation, H_2, wet syngas with 27% steam, or wet CH_4 with 50% steam was fed to the anode, and air was fed to the cathode. In the SOFEC mode for hydrogen production, H_2, wet syngas with 27% steam, or wet CH_4 with 50% steam was fed to the anode, and mixture of 70% steam with H_2 as the carry gas was fed to the cathode.)

Conclusions and Future Directions

- On budget and on time, the objectives defined by the project have been met.
- Electrocatalytically and chemically stable cathode materials have been identified and developed. The electrochemical properties of the cathode materials were evaluated.
- Composite cathodes were deposited and tested in both button-cells and multiple-cell short stacks operated in three modes: SOFC, SOEC and SOFEC.
- SOFEC test results show that with a fuel-assisted electrolyzer, the external electricity required to split water can be significantly reduced by the fuel chemical energy, thus a high electrically-efficient hydrogen generation system can be made based on the SOFEC technology.

- One 4,200 hour long-term test in SOFC mode demonstrated the high stability of the composite cathode material.
- One 5-cell stack with 100 cm^2 per-cell active area demonstrated a hydrogen production rate over 100 standard liters per hour using 80 W of electricity.
- Optimization of the composite cathode has significantly reduced cell resistances.
- A hydrogen cost model has made preliminary results to direct the design and construction of hybrid stacks with optimized SOFCs/SOFECs ratio at a minimum cost of hydrogen production. The economic merits of hydrogen and electricity co-production will be further investigated in an advanced cost model.
- Hybrid stacks comprising SOFCs/SOFECs will be constructed and tested to prove the concept of co-generating hydrogen and electricity.

FY 2006 Publications/Presentations

1. A. V. Virkar and G. Tao, Chemically Assisted Electrolysis using Reversible Solid Oxide Fuel Cells, 209th ECS meeting, May 7-12, 2006, Denver, CO.

2. Y. Sin, V. Petrovsky, and H. Anderson, Redox Stable Electrodes for Hydrogen Producing Solid Oxide Electrolizer, 209th ECS meeting, May 7-12, 2006, Denver, CO.

3. G. Tao and A. Virkar, 2006 DOE Hydrogen Program Annual Merit Review Meeting, Arlington, VA, May 16-19, 2006.