

IV.A.3 A Reversible Planar Solid Oxide Fuel-Fed Electrolysis Cell and Solid Oxide Fuel Cell for Hydrogen and Electricity Production Operating on Natural Gas/Biogas

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Objectives

- Develop the concept of a solid oxide fuel-fed electrolysis cell (SOFEC) for hydrogen production.
- Identify and develop SOFEC cathode materials that are electrocatalytically and chemically stable in both reducing and oxidizing atmospheres.
- Develop a novel concept of a composite/hybrid planar SOFEC-solid oxide fuel cell (SOFC) stack to co-generate hydrogen and electricity.
- Demonstrate a 1-kW composite stack co-generating hydrogen and electricity either from distributed natural gas or biogas fuel.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- G. Capital Cost (Cost of high-temperature materials)

Technical Targets

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

This project targets development of a high-temperature solid oxide-based system to co-produce hydrogen and electricity at a 1-kW scale from distributed natural gas. Technologies to be developed will be applied towards

the design and construction of distributed hydrogen production systems to achieve the following DOE 2010 hydrogen production target:

- Cost: \$1.50/gge

Approach

- Identify and develop cathode materials possessing electrocatalytic and chemical stability in both reducing and oxidizing atmospheres.
- Evaluate and optimize cathode materials to reduce the area-specific resistance (ASR).
- Optimize anode-support substrate to reduce overpotentials.
- Prove the concept of the SOFEC-SOFC hybrid co-producing hydrogen and electricity.
- Construct and test the SOFEC-SOFC hybrid capable of generating 1 kW worth of hydrogen and electricity from natural gas.

Accomplishments

- Identified and developed cathode materials for the SOFEC-SOFC.
- Designed and built a single-cell test rig capable of operating in both the SOFC and the SOFEC modes.
- Fabricated defect-free anode-supported solid oxide cells.
- Investigated and optimized anode substrate porosity and microstructure.
- Tested button cells with newly developed cathodes, operating in both the SOFC and SOFEC modes.

Future Directions

- Optimize the cathode materials to minimize ASR.
- Design and fabricate SOFEC-SOFC composite stack.
- Test short composite SOFEC-SOFC stack to prove the concept of co-generation.
- Build and test a 1-kW composite stack to co-generate hydrogen and electricity from natural gas.

Introduction

There are many processes to produce hydrogen, such as electrolysis and steam reforming on an industrial scale, and thermochemical water splitting, photo-electrochemical processes and biological processes on a small scale. These technologies are not sufficient to meet the needs of a hydrogen-based economy due to large electricity costs and/or low system efficiency. Additionally, the capital requirements of establishing an infrastructure for hydrogen storage, distribution pipeline build-up, supply chain, and transportation from a central hydrogen production facility to the end user will add significant cost for small-scale applications, such as an automobile refueling station. An attractive alternative is to apply a reversible solid oxide fuel-fed electrolysis cell (SOFEC) to produce clean hydrogen for onsite application, such as refueling

stations for hydrogen-powered vehicles, and for delivering electricity to power parks directly from either natural gas (which has well-established distribution infrastructure nationwide) or from locally available renewable resources.

A SOFEC is an electrochemical cell similar in structure to a solid oxide fuel cell (SOFC), except that the oxidant on the cathode side of the cell is steam rather than air. As a fuel is fed to the anode side of the cell, the steam dissociates into hydrogen and oxygen. Along with residual steam, the dissociated hydrogen exhausts from the SOFEC cathode; the exhaust stream is then separated by condensation of the steam, forming a pure hydrogen gas. In this approach, the fuel provides a chemical potential to substitute for the electrical potential conventionally used to drive electrolysis. The fuel may be distributed natural gas or locally available

biogas. Since the energy cost of these fuels is less than that of electricity, this results in higher overall system efficiency than that of traditional high-temperature steam electrolysis. The hydrogen produced is extremely pure relative to that from steam reformation, which makes the SOFEC technology ideal for use in distributed refueling stations to supply proton exchange membrane-based fuel cell vehicles. The system is versatile, allowing it to be operated in several modes to accommodate the dynamics of energy supply and demand. In addition to the production of hydrogen, the system may be operated reversibly as a solid oxide fuel cell to produce electricity from hydrocarbon fuels, or it may be operated as a direct electrolysis cell to produce hydrogen from an intermittent electricity source such as wind turbines.

Approach

This project is directed toward the development of a planar solid oxide composite device to co-produce hydrogen and electricity from distributed natural gas or biogas fuels. The research and development efforts have been conducted by a team led by Materials and Systems Research, Inc. (MSRI), including Aker Industries, Inc. and the University of Missouri-Rolla.

Reversible planar solid oxide fuel-fed electrolysis cells will be developed and validated first in a button-cell level in both the SOFEC and SOFC modes. Anode-supported cell fabrication techniques that have been developed for SOFC stacks at MSRI will be applied to the SOFEC development. A SOFEC differs from a SOFC in that the cathode materials must be stable in a reducing gas atmosphere in addition to possessing good electronic and ionic conductivity and good electrocatalytic properties. Additionally, there is a more rigorous requirement for a defect-free electrolyte layer. A fixture for testing 1" button cells in both the SOFC mode and the SOFEC mode has been designed and built, as shown in Figure 1. A gas chromatograph (GC) is attached to analyze the gas stream composition to quantify the hydrogen production. On the second stage, lab-level cells will be scaled up to either 2"x2" (with 32 cm² active area) or 4"x4" (with 100 cm² active area) planar stacks. Multiple-cell short stacks will be developed and tested in both modes.



Figure 1. Picture of the SOFEC-SOFC Test Rig, Capable of Operating in Both SOFC and SOFEC Modes

In order to increase specific hydrogen output (g H₂/sec-cm² of cell area) and thereby reduce stack volume, capital cost and electricity consumption, SOFCs will be stacked in series with the SOFECs to form a composite/hybrid. The SOFC anodes will be fed the same fuel as the SOFECs, while the SOFC cathodes are air-fed. The hybrid operating conditions can be controlled so that it operates adiabatically and produces electrical output to deliver electricity. At zero electrical load, only hydrogen is produced. The electrical output can be increased, as needed, by switching the cathode feed gas to the SOFECs from steam to air. In this way, both hydrogen and electricity can be co-produced to meet market demand.

Results

Cathode Materials Development

The cathode materials used in both SOFEC and SOFC modes must possess good electronic and ionic conductivity, exhibit good electrocatalytic properties, and must be chemically stable in both oxidizing (SOFC mode) and reducing (SOFEC mode) gas atmospheres. Therefore, manganites or ferrites, typical cathodes for SOFCs, may not be suitable for use as SOFEC cathodes since they are not chemically stable and they exhibit thermal expansions that are too large. Chromites, such as (La,Ca)CrO₃, have been proven to possess a good electronic conductivity and to be stable in oxidizing and

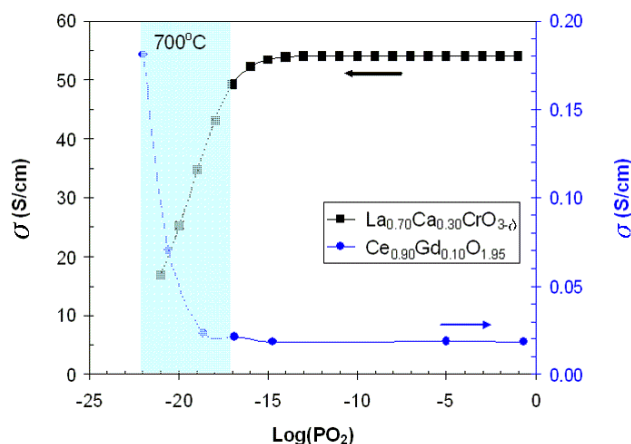


Figure 2. Plot of the conductivities as a function of oxygen activity for $\text{La}_{0.70}\text{Ca}_{0.30}\text{CrO}_{3-\delta}$ and $\text{Ce}_{0.90}\text{Gd}_{0.10}\text{O}_{1.95}$. Conductivity data of $\text{La}_{0.70}\text{Ca}_{0.30}\text{CrO}_{3-\delta}$ were simulated from a defect chemistry model.

reducing environments. Because of this, these materials have had utility as interconnects or other components in the SOFC electrode. With the addition of a second phase—for instance, ceria-based materials—as an electrocatalytic component to assist electrochemical reaction, the material is a promising candidate for the SOFEC cathode. $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_{3-\delta}$ (LCC) and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) have been characterized. The conductivities for these two materials as a function of oxygen activity are shown in Figure 2. At 700°C, the conductivity of CGO drops sharply as oxygen partial pressure increases between 10^{-22} and 10^{-17} atm, corresponding to a steam concentration between 5% and 90%, respectively. When the oxygen partial pressure increases further, the conductivity of CGO becomes level. The response of LCC is quite different, increasing drastically as oxygen partial pressure increases from 10^{-22} to saturation at 10^{-17} atm. In the case of a composite cathode comprising LCC and CGO each working in reducing atmosphere, LCC functions as the electronic conductor providing a mechanism for charge transfer, while CGO functions as the catalyst at a three-phase boundary region at the electrolyte.

Button-cell Tests in SOFC and SOFEC Modes

Electrochemical properties of composite cathodes have been evaluated on anode-supported

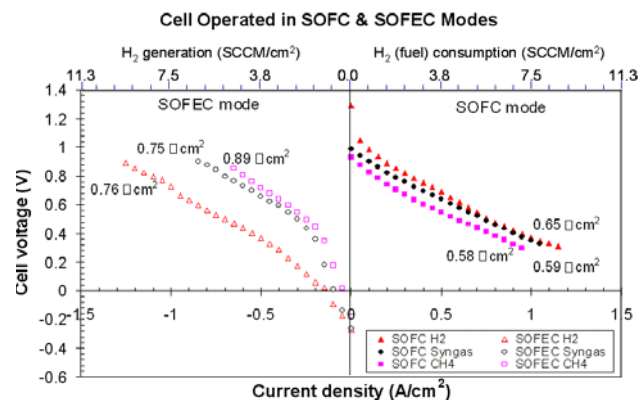


Figure 3. Performance characteristics of cells operated at 800°C in the SOFC and SOFEC modes. Mixtures of steam (10%) with hydrogen, steam (27%) with syngas, or steam (50%) with methane were used as the fuel. Dry air was used as the oxidant in the SOFC mode. A mixture of steam (90%) with hydrogen was used as the oxidant in the SOFEC mode.

button cells operated in both the SOFC and SOFEC modes at 800°C. Three kinds of fuels—hydrogen, methane, and syngas comprising 77% H_2 , 15% CO , and 8% CO_2 —have been used to either generate power or to assist in steam electrolysis to produce hydrogen. In order to prevent carbon deposition, both methane and syngas fuels were humidified to a desired steam concentration. Button cells were first tested in the SOFC mode to produce electricity from the fuel. Typical performance characteristics are shown in the first quadrant of Figure 3. ASRs of 0.58 Wcm^2 , 0.59 Wcm^2 and 0.65 Wcm^2 are observed for CH_4 , syngas and H_2 fuel, respectively. The same button cells were also operated in the SOFEC mode using the same fuels as in the SOFC mode, except that a mixture of 90% steam with balance of hydrogen was used as the oxidant. The experimental results are illustrated in the second quadrant in Figure 3 for comparison. In the SOFEC mode, the open circuit voltage (OCV), V_{OCV} or minimum electrical energy required to decompose water vapor, is observed to be -0.18 V and -0.26 V for CH_4 -assisted electrolysis and for H_2 -assisted electrolysis, respectively. Therefore, with the anode depolarized by the fuel, the electrical energy input, which is 0.97 V (based on Gibbs free energy calculation) for a traditional solid oxide electrolysis cell, is substantially reduced, leading to an economical approach to producing hydrogen. When the

electrical circuit was connected, cells started to operate in a self-driven dissociation mode, with the cell functioning as a fuel cell with steam as the oxidant, instead of air. Hydrogen is thus produced without extra electricity input. In order to drive the disassociation of water vapor to further increase the H₂ production rate (electrolysis current density), an external power supply was applied to the electrodes. As shown in Figure 3, at an equal hydrogen production rate of 3 SCCM/cm² or 432 liter (std. T.P.) per day over a 100 cm² active area, the external electrical energy needed to split steam is only 0.28 V (or 0.11 W/cm²) for the H₂-assisted SOFEC, compared to 0.64 V (or 0.26 W/cm²) for the CH₄-assisted SOFEC. The ASRs of 0.76 Wcm², 0.75 Wcm² and 0.89 Wcm² are observed for H₂-assisted, syngas-assisted, and CH₄-assisted electrolyzer modes, respectively. Further investigations and improvements are underway to reduce the cell ASR, thereby further increasing the system efficiency.

Anode Substrate Improvement

Extensive experimental investigations conducted at MSRI have shown that significant concentration overpotentials and ohmic losses are introduced within the anode for anode-supported solid oxide cells, especially for high-performance cells. Therefore, anode substrate composition and microstructure have been studied and optimized. The quantity of pore former in the anode was adjusted, increasing the anode substrate porosity. Cells were constructed using various anode substrates, to which the same cathode material was applied. The anode improvements have been evaluated in the SOFC mode; a comparison of results is presented in Figure 4. As shown, thin high-porosity anodes can greatly improve cell performance. The extent to which this can be implemented is limited only by the mechanical strength requirements of the system.

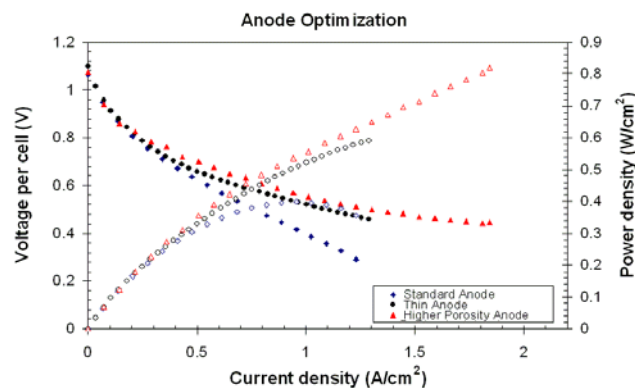


Figure 4. Anode Substrate Improvements

Conclusions

- The objectives defined by the project have been met on time and within the specified budget.
- Electrocatalytically and chemically stable cathode materials have been developed and evaluated in the button-cell scale.
- SOFEC test results show that with a fuel-assisted solid oxide electrolyzer, the external electricity input can be significantly reduced, directly substituting chemical energy. Thus, a hydrogen generation system with high electrical efficiency can be made based on the SOFEC technology.
- In the remainder of FY 2005, the stack repeat unit, including the interconnect, flow channels and seals, will be designed and fabricated. A short composite SOFEC-SOFC stack comprising either 2"x2" or 4"x4" cells will be tested to prove the concept of co-generation of hydrogen and electricity.

FY 2005 Publications/Presentations

1. 2005 DOE Hydrogen Program Annual Merit Review Meeting, Arlington, VA, May 23-26, 2005.