V.I.8 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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- Missouri University of Science and Technology, Rolla, MO
- University of Utah, Salt Lake City, UT

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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 + yttria-stabilized zirconia (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 SOFEC-SOFC hybrids co-generating hydrogen and electricity directly using hydrocarbon fuels at 800°C.
- Design, construct, and evaluate a 5 kW module-based SOFEC-SOFC system for co-generation of hydrogen and electricity directly using 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 using the distributed natural gas based on a hybrid SOFEC-SOFC. 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/gallon of gasoline equivalent (gge)
- Energy efficiency: 69% (lower heating value)

Accomplishments

- Completed the design of a stand-alone 5 kW co-generation system.
- Defined specifications and purchased off-the-shelf hardware for the hybrid system.
- Fabricated and pre-tested major balance-of-plant (BOP) components.
- Developed an interconnect brazing system featuring significant cost-savings in materials and machining.
- Completed fabrication of anode-supported cells necessary for module-based 5 kW hybrid stacks.
- Completed fabrication of non-cell repeat stack units.
- Conducted and demonstrated long-term stability tests of SOFEC stacks operation for up to 360 hours, no significant degradation was observed.
- Constructed and evaluated a kW SOFC stack with refined manifold designs featuring thermal and fluid flow management enhancements.
- Assembly and burn-in cycle tests of SOFEC-SOFC hybrid modules are underway.

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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 development of a novel planar solid-oxide hybrid for hydrogen and electricity co-generation directly using 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 SOFECs and the SOFCs 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.

Redox stable cathodes for the reversible SOFECs have been developed, using composite cathodes comprising 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 SOFEC-SOFC hybrid stacks, reliable hermetic sealing technologies have been developed. Hydrogen and electricity cogeneration concept has been proofed at a 1 kW stack level, but questions about complexity of hybrid stacks integration and concept demonstration at a system level make the development of a complete hybrid system a priority.

Approach

This project is to develop and demonstrate a 5 kW hybrid system based on advanced solid-oxide electrochemical cells to cogenerate hydrogen and electricity directly using 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, and University of Utah.

In order to achieve the project objectives, project efforts have been shifted from focusing on electrodes and sealing materials research and development, to developing SOFEC-SOFC hybrid stacks and dedicated SOFC stacks design and fabrication, to proof-of-concept demonstration of cogeneration at cell and stack levels, and finally to system design, manufacture and experimental verification. Perovskite-type (La,Sr)(Cr,Mn)O_3-based composite cathodes have been developed and the materials' redox stability has been demonstrated in both reducing and oxidizing atmospheres. Elastic properties, as well as equibiaxial flexural strength of Ni+YSZ-based anode substrates were evaluated in both air and reducing environments simulating the actual operating conditions of the SOFEC-SOFC hybrid stacks. The influence of glass particle sizes on glass-ceramic crystallization behavior was characterized using a hot-stage microscopic technique. SOFECs and stacks were fabricated and long-term stability tests of the stacks were performed for hydrogen production. Once the proof-of-concept of cogeneration was demonstrated at a stack level and sufficient know-how and understanding had been obtained, the research efforts were carried to the development and demonstration of hydrogen and electricity cogeneration at a system level. A stand-alone 5 kW system comprising module-based SOFEC-SOFC hybrid and dedicated SOFC stacks, BOP components, and electronic controls was designed. Major BOP components have been fabricated and off-the-shelf hardware was purchased, followed by evaluation under the forecasted operating conditions. Meanwhile, the system design will be refined and assembled for final evaluation.

Results

Stack Design and Fabrication: In the past year, a great amount of efforts has been made to complete design and fabrication of anode-supported solid oxide electrochemical-cells and stacks necessary for a 5 kW system. This 5 kW system consists of six modular stacks, including three hybrid SOFEC-SOFC stacks with hexagonal design for hydrogen and power coproduction, and three dedicated SOFC stacks with square design for power generation. Figure 1 is a picture of the completed 360 cells to be assembled into six modules. Stack manifolds were designed and refined for providing a unique flow pattern such that both gas flow and temperature distributions are uniform, leading to minimized stack pressure drop and enhanced thermal management. A process to braze interconnect was developed in-house by acquiring and engineering a spray system to precisely control the uniformity of coating layers with optimum thickness. With this process, high yield and high quality interconnect assembles were fabricated without creep-flattening at a significant cost-saving in materials and machining. The electronic resistance of brazed interconnect assembly was low, even after extended operation at 800°C.

Stack Evaluation: The initial conditioning and testing of each stack module will be conducted in a separate test station before being assembled into the 5 kW hybrid system. Figure 2 shows the performance

FIGURE 1. Picture of 360 Cells to be Assembled into Six Modules

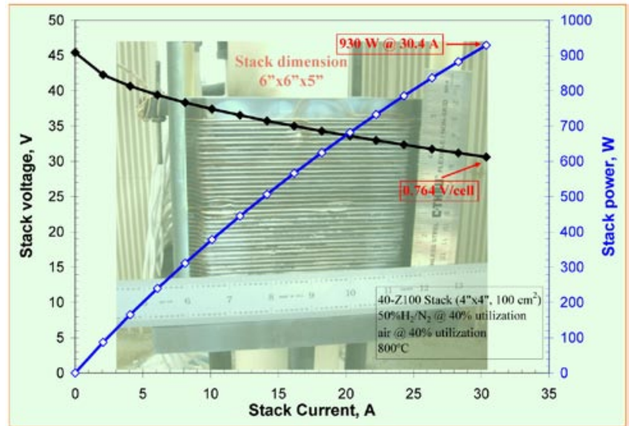

FIGURE 2. Performance Characteristics of a kW Stack Tested in SOFC Mode

characteristics of a forty-cell stack operated in the SOFC mode for power generation. At 800ºC and fixed utilizations of 40% for both fuel and air, the stack generated 930 watts of electric power at 30.4 A. The average per-cell voltage was 0.764 V. The background of Figure 2 is a picture of the stack post-test, with the stack dimension of 6”x6”x5”.

5 kW Hybrid System Development: The hybrid system design and component integration for cogenerating hydrogen and electricity directly using natural gas is preceded by solid modeling of the various BOP components and creation of an assembly of these component models. In the past year, the system design has undergone several revisions in order to reduce the system cost and improve the flexibility of the control system. The final system will be constructed with assembly of a hot-zone comprising six modular stacks, a BOP components zone, and an electronic control zone. Figure 3 is a rendering of the system configuration showing the major sub-systems, inlet and outlet streams. In the hot-zone, a spring-plate compression device will be used for each individual stack with insulated tension rods and load plates that allows the springs to remain relatively cool while minimizing thermal losses from the stack enclosure. Six pairs of the compression devices were manufactured. The individual stack modules will then be assembled to an electrically insulating support plate that separates the stack hot-zone enclosure from the BOP components. Gas feed pipes, welded to each manifold/compression plate, will pass through the support plate and be sealed in compression fittings to the BOP piping. If it is necessary to remove an individual stack for maintenance or replacement, this can be done without removing the compression force from the other stack modules. The major hot BOP components, including the tailgas-fired combustors and reformers, were designed and manufactured with improved catalytic combustion features for stable flame and heat transfer enhancement. Additional features were also

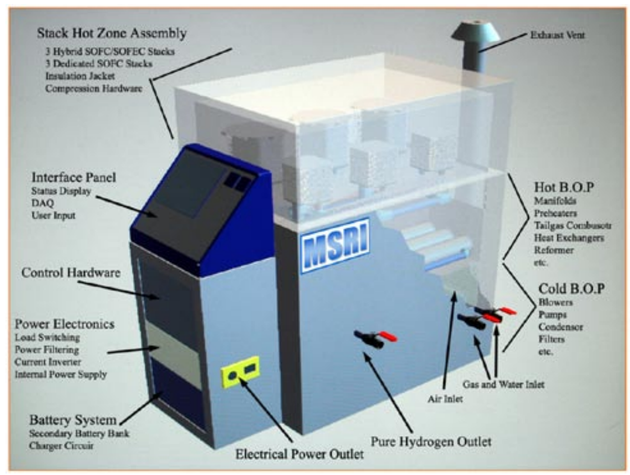

FIGURE 3. Rendering of the 5 kW Hybrid System Configuration

considered for allowing for disassembly and replacement of individual BOP components, as well as access to the catalyst beds. Compact heat exchangers were purchased for recuperating heat from cathode gases to combustion air. A central tailgas-fired boiler supplies steam to the reformers and SOFEC cathodes with separate control mechanisms. The boiler with a shell-and-tube configuration loaded with catalyst on diffuser screens was constructed and tested for providing 130 standard liters of steam per minute under steady state operation. The commercially available multi-module C-DAQ hardware was purchased to build the control system with a user interface operating National Instrument’s LabView software.

Conclusions and Future Directions

A significant amount of effort have been made at MSRI to research and develop the advanced technology that cogenerates hydrogen and electricity directly using chemical energy of fuels to replace the electricity necessary for conventional water/steam electrolysis. MSRI has developed redox stable electrodes and demonstrated stability for more than 5,000 hours. MSRI also developed state-of-the-art planar, SOFEC-SOFC hybrid stack technology, and demonstrated the best and highest performance reported yet at 1 kW stack level.

- Extensive experimental studies conducted at MSRI show that hydrogen production using the advanced SOFEC technology is a viable pathway to reduce the cost of hydrogen.
- Long-term tests of SOFECs at both single-cell level and stack level proved that materials developed at MSRI are applicable to the reversible SOFECs/SOFCs.
- Strong collaboration between the industry and academia encouraged material research and development.
- Test of the 1 kW SOFC stack showed the features of newly designed stack architecture of thermal and fluid flow management enhancement.
- Modular characteristics of SOFEC-SOFC hybrid impart a great flexibility to a system design for hydrogen production that fits various needs.

For the remainder of the project, a hybrid system will be constructed and tested to demonstrate co-generation of hydrogen and electricity directly using natural gas. Cost analysis of hydrogen production using the hybrid SOFEC-SOFC technology will be performed for future system optimization. Important technical findings and results will be prepared for journal publication and conference presentations.