II.H.3 Laboratory-Scale High Temperature Electrolysis System

J. Stephen Herring (Primary Contact), James E. O'Brien, Carl M. Stoots, Kevin DeWall, Michael G. McKellar, Edwin Harvego, Manohar Sohal, G.L. Hawkes
Idaho National Laboratory (INL)
2525 N. Fremont Ave.
Idaho Falls, ID 83415-3860
Phone: (208) 526-9497; Fax: (208) 526-2930
E-mail: j.herring@inl.gov

DOE Technology Development Manager:
Carl Sink
Phone: (301) 903-5131; Fax: (301) 903-0180
E-mail: carl.sink@nuclear.energy.gov

DOE High Temperature Electrolysis Manager:
Melissa C. Bates
Phone: (208) 526-4652; Fax: (208) 526-6249
E-mail: batesmc@id.doe.gov

Subcontractor:
Ceramatec, Inc.
Joseph J. Hartvigsen, S. Elangovan, Dennis Larsen, Mark Timper
2425 South 900 West
Salt Lake City, UT

Collaborating National Laboratories:
Argonne National Laboratory (ANL), Argonne, IL
Theodore Krause, Deborah Myers, J. David Carter, Jennifer Mawdsley

Collaborating Universities:
Massachusetts Institute of Technology (MIT), Boston, MA
Bilge Yildiz, Vivek Sharma
University of Nevada Research Foundation (UNRF), Las Vegas, NV
Anthony Hechanova, Clemens Heske

Start Date: January 23, 2003
Projected End Date: Engineering Demo, 1 MW, 2015

Objectives

- By 2012, reduce the cost of central production of hydrogen from high temperature electrolysis to $3.10/gasoline gallon equivalent (gge) at plant gate. By 2017, reduce the cost of central production of hydrogen from high temperature electrolysis electrolysis to <$2.00/gge at plant gate[1].
- Develop energy-efficient, high-temperature, solid-oxide electrolysis cells (SOECs) for hydrogen production from steam.
- Develop and test integrated SOEC stacks operating in the electrolysis mode.
- Develop optimized plant configuration for coupling to Generation IV Reactor.
- Combine components in an Integrated Laboratory-Scale (ILS) experiment.
- Scale-up to a 200 kW pilot plant and a 1 MW engineering demonstration facility.

Technical Barriers

This project addresses the following technical barriers of the Hydrogen Program MYPP 2007 and the Nuclear Hydrogen Initiative:

- Nuclear reactor and central hydrogen production capital costs (Barrier G, MYPP 2007, p.3.1-24).
- Overall system efficiency (Barrier H, MYPP 2007, p.3.1-24).
- The need for high-temperature, corrosion resistant materials, particularly in enriched-oxygen and steam-hydrogen environments.
- Oxygen separation and handling technology.

Technical Targets

- No greenhouse gas releases from industrial-scale H_2 production.
- Energy efficiency: 50% (lower heating value, LHV, of H_2 produced/total thermal output of reactor).
- Cost of hydrogen: $2.50/kg – centralized production only.
- Life of Cells: 20,000 hours in continuous operation.

Contribution to Achievement of DOE Systems Analysis Milestones

This project contributed/will contribute to achievement of the following DOE Systems Analysis milestones from the Systems Analysis section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 2:** Complete baseline economic, energy efficiency and environmental targets for fossil, nuclear and renewable hydrogen production and delivery technologies. (4Q, 2005)

[1] Since there are no objectives specific to the nuclear production of hydrogen, we have adopted those cited from wind water electrolysis (Multi-Year Program Plan (MYPP) 2007, 3.1.1)

- **Milestone 8:** Complete analysis and studies of resource/feedstock, production/delivery and existing infrastructure for technology readiness. (4Q, 2014)
- **Milestone 10:** Complete an analysis of the hydrogen infrastructure and technical target progress for technology readiness. (2Q, 2015)

Accomplishments (FY 2008)

- Tested the initial single module (4 x 60 cells) for the ILS experiment for 420 hours in Idaho Falls with a maximum output of 2.0 N m^3 H_2/hour and an average output of 0.8 N m^3 H_2/hour, Oct. 12, 2007.
- Developed an optimized flowsheet as reference case for high temperature electrolysis (HTE) comparisons with other methods with complete parameter description for economic analysis and comparison with other cycles, Nov. 15, 2007.
- Completed a set of as-built drawings of the initial ILS configuration, the configuration in which it was tested in Sept-Oct 2007, Dec. 10, 2007.
- Completed a characterization of the transient response of the ILS with one module installed to heat-up changes in power level and cool-down, Dec. 14, 2007.
- Completed test plan for ILS operations with three modules, May 15, 2008.
- Completed report on oxygen handling and cooling options based on collaboration with the Atomic Energy of Canada Limited, July 2, 2008.
- Completed construction of the ILS experiment, capable of testing three HTE modules simultaneously, August 2008.
- Began three module test in the ILS at 15 kW input power, Sept. 15, 2008.
- Issued analysis report on corrosion testing of the second series of balance-of-plant materials, Sept. 30, 2008.
- Demonstrated improved performance of oxygen and steam hydrogen electrodes through the deposition of electrocatalytic materials by the atomic layer deposition (ALD) or other infiltration processes, Sept. 30, 2008.

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Introduction

A research project is under way at the INL and collaborating laboratories to assess the performance of solid-oxide cells operating in the steam electrolysis mode for hydrogen production over a temperature range of 800 to 900ºC. The research program includes both experimental and modeling activities. The electrolysis cells are electrolyte-supported, with scandia-stabilized zirconia electrolytes (~140 µm thick), nickel-cermet steam/hydrogen electrodes, and manganite oxygen electrodes. The metallic interconnect plates are fabricated from ferritic stainless steel. During Fiscal Year 2008, experimental results were obtained from a four-stack module (4 x 60 cells), fabricated by Ceramatec, Inc. Additional experiments at ANL, MIT, UNRF and INL investigated the performance of ALD cells and the performance of a variety of materials being considered for use in the balance-of-plant for HTE hydrogen production plants.

Approach

High-temperature electrolysis testing of single button cells and stacks has been in progress at the INL and the subcontractor Ceramatec Inc. since 2003. The scales of testing accomplished to date at the INL are pictured in Figure 1. The ILS facility has been designed for a nominal hydrogen production rate of 14.1 kW based on LHV, or 4735 Normal (273°K, 1 atm) l/hr. The initial ILS single module implementation was designed for ~5 kW of hydrogen production and was tested Sept. 24-Oct. 11, 2007. The full, three-module ILS will be tested beginning about Sept. 15, 2008.

After each of the tests, the stacks have been disassembled and the cells have been destructively examined to determine elemental migration during the test and to detect changes in the morphology of the electrolyte and electrodes. These examinations will also be conducting following the test of the three-module ILS.

Results

Our results for FY 2008 are divided into three areas: The operation of the single-module ILS, results of post-test examination of ILS and earlier stacks and numerical analysis of stacks and other SOEC configurations.

ILS Experiment

The ILS began experimental operations in Bay 9 of the Bonneville County Technology Center, Idaho Falls, on August 22, 2007. Initial operation included the following.

This initial operations test was performed without an electrolysis module installed. Following the shakedown test, a four-stack initial HTE module was installed. Heat-up of the first ILS electrolysis module commenced at 4:10 PM on September 24, 2007. The ILS first began producing hydrogen at 8:32 AM on September 25, 2007. The primary objective for this test was to ensure proper design, scaling, fabrication, and operation of all ILS components prior to committing the funding and man-hours necessary for installation

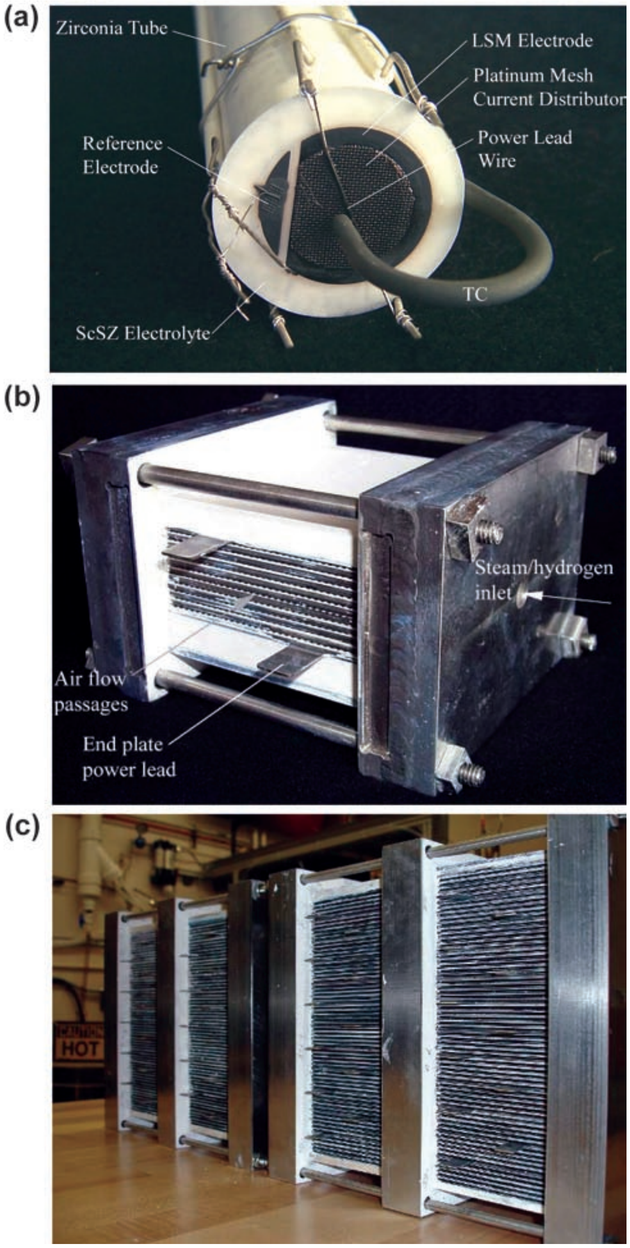

FIGURE 1. (a) A typical high temperature electrolysis button cell (~1.5 W, 2003), (b) A planar 10-cell stack (~500 W (~0.015 kg H_2/hr), 2004), and (c) The two halves (4 x 60 cells) of a single ILS module (~5 kW (~0.150 kg H_2/hr), 2007).

and operation of three modules. It was also of interest to quantify large stack performance. Finally, the test was the largest high-temperature steam electrolysis demonstration to date.

Initial Sweep

On September 25, 2007, the ILS module performance was tested by sweeping the module power supply voltage over the range of 50 to 79 V (0.83 V/cell to 1.32 V/cell). This range corresponds to operation from the open-cell voltage to slightly above the thermal neutral voltage. The corresponding voltage/current (VI) or polarization curve is displayed in Figure 2. The average area specific resistance for the initial ILS module, represented by the average slope of the VI curve, was measured to be 2.38 Ωcm^2. This value was significantly higher than the design value of 1.5 Ωcm^2, but was not unexpected. Ceramatec Inc, the manufacturer of the ILS module, had forewarned INL to expect lower performance from this particular module due to manufacturing difficulties they had encountered.

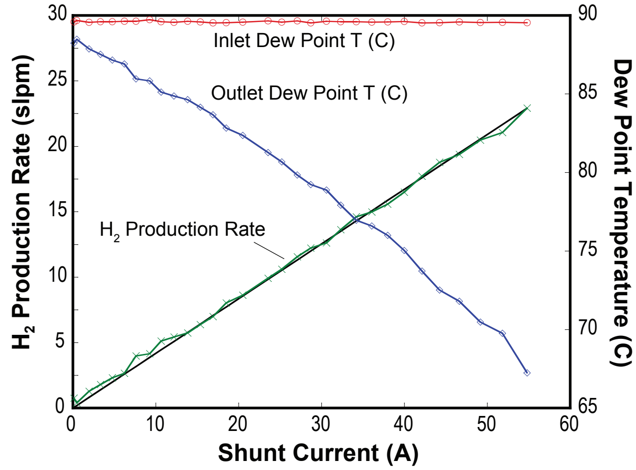

FIGURE 2. ILS Module Voltage Sweep Hydrogen Production Rates and Dew Points

Stack internal temperatures initially decreased during the voltage sweep, due to the endothermic heat of reaction for water splitting. Once the operating voltage exceeded the thermal neutral voltage (77 V for 60 cells), outlet gas temperatures exceeded inlet values.

Figure 2 presents inlet and outlet dewpoint temperatures and hydrogen production rate for the ILS initial single-module sweep. The inlet gas dew point remained essentially constant at 89.6°C throughout the duration of the sweep. The outlet stream dew point temperature decreased continuously through the sweep as the operating voltage and stack current increased. The straight black line in Figure 2 represents the hydrogen production rate based on electrolysis current, while the green trace is the hydrogen production rate based on the difference between inlet and outlet dew points. Agreement between the two independent measurements of hydrogen production was generally excellent. At the highest current levels, H_2 production rates exceeded 1.5 Nm^3/hr (25 slpm or 0.134 kg H_2/hr) during the sweep.

TABLE 1. Long Duration Operating Conditions for the ILS Module

Hot zone temperature	810-820°C
Inlet water mass flow rate	34 ml/min
Inlet H_2 flow rate	5.4 Nl/min
Inlet N_2 flow rate	5.4 Nl/min
Inlet air flow rate	25 Nl/min
Measured inlet dew point	91.3°C
Module operating voltage	78 V

Long Duration Test

After performing a voltage sweep, the ILS operating parameters were set to the conditions listed in Table 1. Figure 3 presents the complete time history of module voltage, current, and H_2 production rate. The test was concluded after 420 hours duration. This was not due to any equipment failure. It was the opinion of the researchers that since the stack performance degradation had essentially stopped after about 250 hours, there was little more to be learned from the test.

Over the period of the test, the H_2 production rate dropped from over 1.5 Nm^3/hr (0.134 kg H_2/hr) to a steady value of 0.7 Nm^3/hr (0.0625 kg H_2/hr). Early on in the test, the module underwent a temperature excursion.

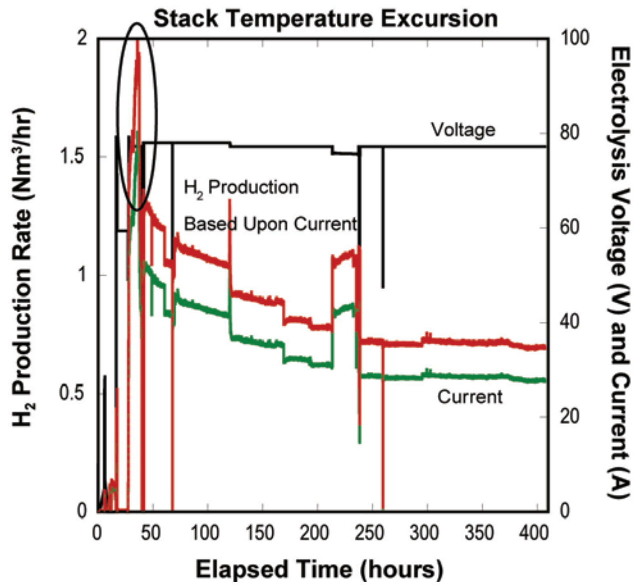

FIGURE 3. Complete Electrical History of the ILS Single-Module Test

Post-Test Examination

The objectives of this project are to evaluate ILS stack components to find causes of degradation in stack materials. As part of this work we analyzed components taken from the ILS test, stack 3, which was completed in September 2007. Argonne also worked with Ceramatec to continue making improvements on the oxygen electrode materials and fabrication. As part of the study, we evaluated the deposition of electrocatalytic platinum into the oxygen electrode by the ALD infiltration process.

Summary of Results

Stack Degradation Analysis

- X-ray absorption near-edge spectroscopy analysis of the Ni-cermet in the steam-hydrogen electrode showed that the nickel had oxidized to 60 vol% NiO. This illustrates the vulnerability of the Ni-cermet electrode.
- Elemental maps of the oxygen electrode of the cell show that Mn has diffused into or otherwise mixed with the bond layer preferentially along the air inlet edge of the stack. The effect of this diffusion is uncertain at this point.
- Chromium elemental maps show Cr abundance at the interconnect coating is greater near the center of the stack.
- Resistance maps show an increase in resistance in the oxygen bond layers of the cells and interconnects at the hydrogen exit of the stack. This effect is most prevalent near the bottom of the stack.

Numerical Modeling

INL established a Cooperative Research and Development Agreement (CRADA) with Rolls Royce Fuel Cell Systems (RRFCS) in 2005 to investigate the performance of the RRFCS fuel cells operating in the electrolysis mode. The CRADA has established a framework that has allowed for testing and analysis of the RRFCS design at INL. In terms of analysis, a three-dimensional computational fluid dynamics (CFD) electrochemical model has been created to assess high-temperature electrolysis performance of an integrated planar porous-tube-supported SOEC. The model includes ten integrated planar cells in a segmented-in-series geometry deposited on a flattened ceramic support tube. Mass, momentum, energy, and species conservation and transport are provided via the core features of the commercial CFD code FLUENT. A solid-oxide fuel cell (SOFC) module adds the electrochemical reactions and loss mechanisms and computation of the electric field throughout the cell. The FLUENT SOFC user-defined subroutine was modified for this work to allow for operation in the SOEC mode. Model results provide detailed profiles of temperature, Nernst potential, operating potential, activation over-potential, anode-side gas composition, cathode-side gas composition, current density and hydrogen production over a range of stack operating conditions.

Predicted mean outlet hydrogen and steam concentrations vary linearly with current density, as expected. Contour plots of local electrolyte temperature, current density, and Nernst potential indicate the effects of heat transfer, endothermic reaction, ohmic heating, and change in local gas composition. Discussion of thermal neutral voltage, enthalpy of reaction, hydrogen production is reported herein. CFD results indicate negative gauge pressures in the hydrogen electrode, indicating a possible limit for steam diffusion through the porous ceramic tube. Minimum temperatures occur in the fuel and air downstream corner of the ceramic tube for operating voltages below the thermal neutral value.

Conclusions

- Experimental results from the single-module ILS (4 x 60 cells), conducted on the ILS skid in Idaho Falls, showed:
  - Hydrogen production rates of up to 1.5 Nm^3/hour were achieved initially, and the module operated continuously (with only short-duration electrical and gas flow interruptions) for 420 hours.
  - The single-module endurance test was terminated due to shorting in some of the control diagnostics. Hydrogen production had fallen at that time to 0.70 Nm^3/hour.
- The ILS experiment, with three modules, was constructed. This experiment, due to start operation Sept. 15, 2008, will produce ~6 Nm^3 of H_2, while incorporating, at reduced scale, all of the components of a commercial plant.
- INL is continuing the numerical modeling of various cell geometries, in support of both experimental design and the post-test examination of stack components.
- INL, in collaboration with MIT, UNRF and ANL, is conducting post-test examinations of the cells to determine the causes for cell degradation during long-duration tests.

Future Directions

FY 2009 Priorities

- Operation of the ILS with three modules.
- Diagnosis of long-term degradation of cell performance.
- Larger format cells for better economics.

New Tasks

- Continued testing of alternate geometries at a small scale.
- Long term assessment.
- Goal: commercial viability in 2014.

FY 2008 Journal Articles

1. O'Brien, J.E., McKellar, M.G., Stoots, C.M., Herring, J.S., and Hawkes, G.L., "Parametric Study of Large-Scale Production of Syngas via High Temperature Electrolysis," in review, *International Journal of Hydrogen Energy*, 2008.

2. Hartvigsen, J.J., Elangovan, S., Frost, L., Nickens, A., Stoots, C.M., O'Brien, J.E., and Herring, J.S., "Carbon Dioxide Recycling by High Temperature Co-electrolysis and Hydrocarbon Synthesis," in review, *Electrochemical Society Transactions*, 2008.

3. Stoots, C.M., O'Brien, J.E., "Results of Recent High-Temperature Co-electrolysis Studies at the Idaho National Laboratory," in review, *International Journal of Hydrogen Energy*, 2008.

4. Hawkes, G.L., O'Brien, J.E., and Stoots, C.M., "3D CFD Model of a Multi-Cell High Temperature Electrolysis Stack, in review, *International Journal of Hydrogen Energy*, 2008.

5. Stoots, C.M., O'Brien, J.E., Herring, J.S., and Hartvigsen, J. J., "Syngas Production via High-Temperature Coelectrolysis of Steam and Carbon Dioxide," accepted for publication, *Journal of Fuel Cell Science and Technology*, 2008.

6. Harvego, E.A., McKellar, M.G., O'Brien, J.E., Herring, J.S., "Parametric Evaluation of High-Temperature Electrolysis Hydrogen Production Processes using Different Advanced Nuclear Reactor Heat Sources," *Nuclear Engineering and Design*, in review, November, 2007.

FY 2008 Conference Papers and Presentations

1. Harvego, E.A., McKellar, M.G., Sohal, M.S., O'Brien, J.E., and Herring, J.S., "Economic Analysis of a Nuclear Reactor Powered High Temperature Electrolysis Hydrogen Production Plant," ASME 2nd International Conference on Energy Sustainability, Jacksonville, FL, August 10-14, 2008.

2. Stoots, C.M., O'Brien, J.E., Herring, J.S., and Hartvigsen, J.J., "High Temperature Coelectrolysis For Direct Syngas Production Using Solid-Oxide Cells," 8th European Solid Oxide Fuel Cell Forum, Lucerne, June 30 – July 4, 2008.

3. O'Brien, J.E., Stoots, C.M., McKellar, M.G., and Herring, J.S., "Demonstration and System Analysis of High Temperature Steam Electrolysis for Large-Scale Hydrogen Production using SOFCs," 8th European Solid Oxide Fuel Cell Forum, Lucerne, June 30 – July 4, 2008.

4. Stoots, C.M., O'Brien, J.E., Herring, J.S., and Hartvigsen, J.J., "Design and Initial Operation of a Multi-Kilowatt High Temperature Steam Electrolysis Test Facility at the Idaho National Laboratory," 6th International Fuel Cell Science, Engineering & Technology Conference, June 16-18, 2008, Denver, CO.

5. Hawkes, G.L., O'Brien, J.E., Haberman, B., Marquis, A. J., Martinez Baca, C., Tripepi, D., Costamagna, P., "Numerical Prediction of Performance of Integrated Planar Solid Oxide Fuel Cell, With Comparison of Results from Several Codes," 6th International Fuel Cell Science, Engineering & Technology Conference, June 16-18, 2008, Denver, CO.

6. O'Brien, J.E., McKellar, M.G., and Herring, J.S., "Performance Predictions for Commercial-Scale High-Temperature Electrolysis Plants Coupled to Three Advanced Reactor Types," ANS International Congress on Advances in Nuclear Power Plants (ICAPP08), June 8-12, 2008, Anaheim, CA.

7. Stoots, C.M., O'Brien, J.E., "Initial Operation of the High-Temperature Electrolysis Integrated Laboratory Scale Experiment at INL," 2008 International Congress on Advances in Nuclear Power Plants, June 8-12, 2008, Anaheim, CA.

8. Hawkes, G.L., McKellar, M.G., Stoots, C.M., O'Brien, J.E., and Wood, R.A., "Biomass to Liquid Fuels via High Temperature Electrolysis," Abstract accepted, International Biomass 2008 Conference and Trade Show, Minneapolis, Minnesota, April 15-17, 2008.

9. Hartvigsen, J.J., Elangovan, S., Frost, L., Nickens, A., Stoots, C.M., O'Brien, J.E., Herring, J.S., "Carbon Dioxide Recycling by High Temperature Co-Electrolysis and Hydrocarbon Synthesis," Annual Meeting & Exhibition, The Minerals, Metals & Materials Society, March 9–13, 2008, New Orleans.

10. Sohal, M.S., Herring, J.S., O'Brien, J.E., Stoots, C.M., Hawkes, G.L., and McKellar, M.G., "Nuclear Energy Powered Hydrogen Generation using Solid Oxide Electrolyzer," Workshop on New Horizons in Nuclear Reactor Thermal Hydraulics, Bhabha Atomic Research Centre (BARC), Mumbai, India, Jan. 7-8, 2008.

11. McKellar, M.G., O'Brien, J.E., Stoots, C.M., and Hawkes, G.L., "A Process Model for the Production of Syngas Via High Temperature Co-Electrolysis," Proceedings, 2007 ASME International Congress and Exposition, Seattle, Nov., 2007.

12. Stoots, C.M., O'Brien, J.E., and Hartvigsen, J., "Carbon-Neutral Production of Syngas Via High Temperature Electrolytic Reduction of Steam And CO2," Proceedings, 2007 ASME International Congress and Exposition, Seattle, Nov., 2007.

13. Stoots, C.M., O'Brien, J.E., "Results of Recent High-Temperature Co-electrolysis Studies at the Idaho National Laboratory," paper 412b, Proceedings, 2007 AIChE Annual Meeting, Salt Lake City, November 4 – 9, 2007.

14. Herring, J.S., Stoots, C.M., O'Brien, J.E., and Hartvigsen, J.J., "Recent Progress in High Temperature Electrolysis," paper 412a, Proceedings, 2007 AIChE Annual Meeting, Salt Lake City, November 4 – 9, 2007.

15. Hawkes, G.L., O'Brien, J.E., and Stoots, C.M., "3D CFD Model of a Multi-Cell High Temperature Electrolysis Stack, paper 412e, Proceedings, 2007 AIChE Annual Meeting, Salt Lake City, November 4 – 9, 2007.

16. O'Brien, J.E., McKellar, M.G., Stoots, C.M., Herring, J.S., and Hawkes, G.L., "Parametric Study of Large-Scale Production of Syngas via High Temperature Electrolysis," paper 412c, Proceedings, 2007 AIChE Annual Meeting, Salt Lake City, November 4 – 9, 2007.

17. Stoots, C.M., O'Brien, J.E., Herring, Condie, K.G., Housley, G., Hawkes, G.L., and Hartvigsen, J.J., "Progress in High-Temperature Electrolysis at the Idaho National Laboratory, paper no. 390, 2007 Fuel Cell Seminar, San Antonio, Texas, Oct 15-19, 2007.

18. Hawkes, G.L., Hawkes, B.D., Sohal, M.S., Torgerson, P.T., Armstrong, T.R., and Williams, M.C., "3D CFD/Stress Model of a Tubular Porous-Metal Supported Solid Oxide Fuel/Electrolysis Cell," paper no. 119, 2007 Fuel Cell Seminar, San Antonio, Texas, Oct 15-19, 2007.

19. Hawkes, GL., O'Brien, J.E., Stoots, C.M., and Herring, J.S., "3D CFD Modeling of Solid Oxide Electrolysis Cells and Stacks," 8th European Solid Oxide Fuel Cell Forum, Lucerne, June 30 – July 4, 2008.

DOE Milestone Reports

1. McKellar, M.G., O'Brien, J.E., Harvego, E.A., and Herring, J.S., "Optimized Flow Sheet for a Reference Commercial-scale Nuclear-driven High-Temperature Electrolysis Hydrogen Production Plant," INL/EXT-07-13573, November 14, 2007.

2. Condie, K.G., Stoots, C.M., O'Brien, J.E., and Herring, J.S., "Characterization of the Transient Response of the ILS with One Module Installed to Heatup Changes in Power Level and Cooldown," INL/EXT-07-13626, December 24, 2007.

3. Harvego, E.A., McKellar, M.G., Sohal, M.S. O'Brien, J.E., and Herring, J.S., "Economic Analysis of the Reference Design for a Nuclear-Driven High-Temperature-Electrolysis Hydrogen Production Plant," INL/EXT-08-13799, January 30, 2008.

4. Herring, J. Stephen, Stoots, Carl M., Condie, Keith and O'Brien, James E., "Test Plan for Three-Module Operation of the High Temperature Electrolysis Integrated Laboratory Scale Experiment," INL/EXT-08-14303, May 15, 2008.

5. Sohal, Manohar S., and Herring, J. Stephen, "Oxygen Handling and Cooling Options in High Temperature Electrolysis Plants," INL/EXT-08-14483, July 2008.