II.J.6 Laboratory-Scale High Temperature Electrolysis System

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Start Date: January 23, 2003
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- 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 Nuclear Hydrogen Initiative:

- Nuclear reactor and central hydrogen production facility costs
- The need for high-temperature, corrosion resistant materials, particularly in steam-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: 40,000 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)
- **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 (July 2006 through June 2007)

- Tested the initial dual-stack (2 x 60 cells) half-module for the Integrated Laboratory Scale experiment for 2,040 hours at Ceramatec facility with an initial output of 1.2 Nm^3 H_2/hour and final output of 0.65 Nm^3 H_2/hour, 9/22/06.
- Completed assessment of degradation in long-duration test cells, ANL, 11/29/06.

- Completed analysis of SOEC stack and cell configurations to optimize hydrogen production, ANL, 6/15/07.
- Demonstrated improved electrode materials for high-temperature steam electrolysis, ANL, 6/15/07.
- Completed ILS fabrication drawings, INL, 12/22/06.
- Completed documentation of ILS Safety Analyses, INL, 11/30/2006.
- Completed report describing reactor/high temperature electrolysis (HTE) models and hydrogen production efficiencies, INL, 10/27/06.
- Completed Corrosion Test Series #1, INL, 4/27/07.
- Delivered report on initial corrosion test series, INL, 6/25/07.
- Delivered initial four-stack ILS module to INL, (Ceramatec), 3/21/07.

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Introduction

A research project is under way at the Idaho National Laboratory 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 900°C. The research project 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. Experimental results were obtained from a dual stack (2 x 60 cells) half-module, fabricated by Ceramatec, Inc. The half-module is a prototype for one of the three four-stack modules that will be installed in the ILS experiment. The first of the full-modules was delivered to the INL in March 2007. A range of static and dynamic operating parameters were explored.

A three-dimensional computational fluid dynamics (CFD) model was also created to model high-temperature steam electrolysis in a planar SOEC. A solid-oxide fuel cell (SOFC) model 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 are shown to compare favorably with the experimental results obtained from the 10-cell, 22-cell and 25-cell stacks tested at INL, as well as with the half-module test at Ceramatec.

Approach

A schematic of the 15 kW High Temperature Electrolysis ILS experiment is provided in Figure 1. A photo of the half-module test during the summer of 2006 is shown in Figure 2. A three-dimensional illustration of the ILS experiment is shown in Figure 3, with the power supplies and instrumentation in the racks on the left and the hot zone containing the electrolytic modules on the right. The ILS experiment will use three 4-stack modules and produce about 6 Nm^3 of H_2 per hour. The ILS facility has been designed such that later insertion of heat recuperation and hydrogen separation equipment will be simplified. The construction status of the ILS on June 4, 2007 is shown in Figure 4. A photo of a four-stack module is shown in Figure 5.

Results

The most recent large-scale test of HTE was performed from June 28 through September 22, 2006 at the Ceramatec plant in Salt Lake City. The test apparatus, shown in Figure 2, consists of two stacks of 60 cells each in a configuration that will be used in the ILS experiment during FY 2007. The ILS will contain three modules of four stacks each. The "half-module," which is about 30 cm wide and high and 15 cm deep,

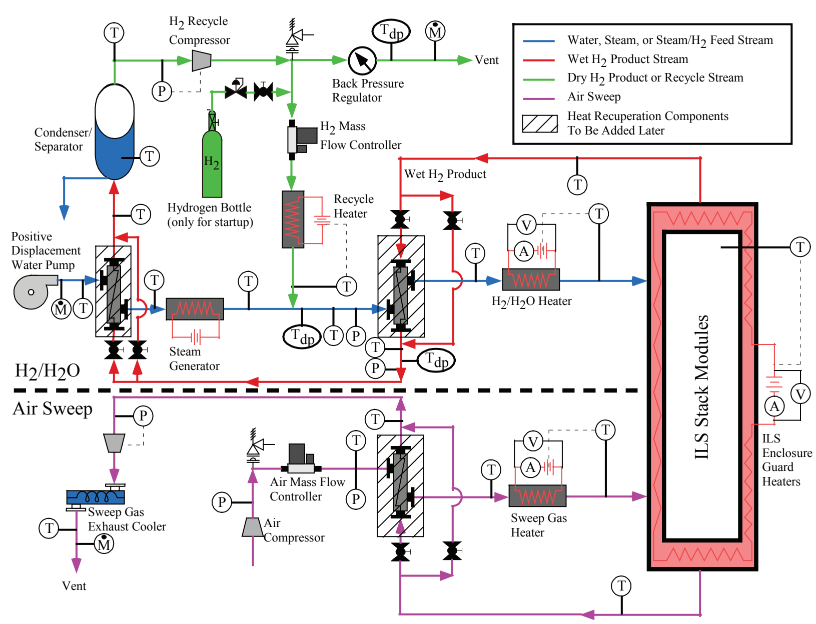

FIGURE 1. High Temperature Electrolysis Integrated Laboratory Scale Experiment Schematic for Initial Operation

initially produced 1.2 Nm^3 of H_2/hour and 0.65 Nm^3/hr at the end of the 2,040-hour continuous test. The steam/hydrogen mixture enters the two stacks from either side and flows through the cells to the center manifold, exiting at the top as about 75% hydrogen, 25% steam. Heated air is supplied to a plenum on the opposite side of the two stacks and a mixture of air and oxygen exits through the opening visible in the front.

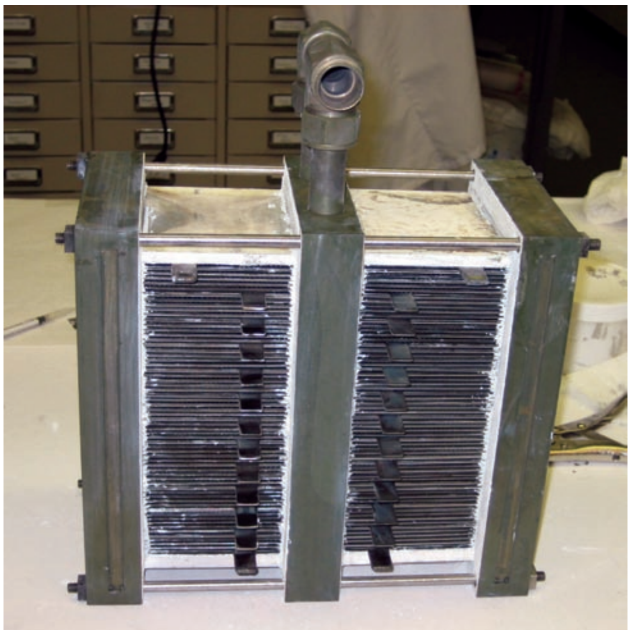

FIGURE 2. Dual stack (2 x 60-Cell) ILS Half-Module, Tested June 28 through September 22, 2007

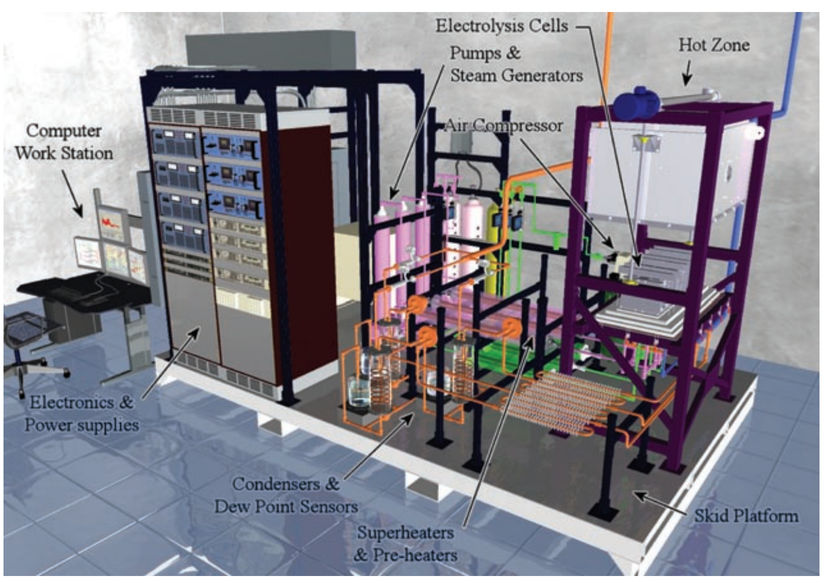

FIGURE 3. Integrated Laboratory Scale Experiment – Designer's Illustration

Electrode Development

The overall goal of the Electrode Materials Development task at the Argonne National Laboratory is to develop SOEC oxygen electrodes and steam electrodes that will lead to improved performance, reduced cost, and improved durability. The majority of voltage efficiency loss in an electrolyte-supported high-temperature steam electrolysis cell, such as those produced by Ceramatec, arises from ohmic losses due to the high resistance of the thick electrolyte layer (~150 μm) and activation losses due to the sluggish kinetics of the oxygen evolution reaction. These electrolyte and oxygen electrode losses are comparable and constitute 80% of the total cell (anode/electrolyte/cathode) voltage efficiency loss.

Durability of the SOEC system is an important requirement to lower the amortized cost of the hydrogen production system. For high efficiency operation, the SOEC hydrogen electrode inlet must operate with high steam content to reduce the need for recycling of the product hydrogen. In addition, the hydrogen electrode must be stable under high steam concentrations at the cell inlet and high hydrogen concentrations at the outlet. The currently-used SOEC hydrogen electrode is a cermet made of nickel, for electronic conductivity and catalytic activity, and yttria- or scandia-stabilized zirconia (YSZ or ScSZ) to provide oxygen ion conductivity. Past high-temperature steam electrolysis work has shown that the polarization of a nickel-based electrode is high at high steam concentrations, which has been attributed to surface oxidation of the nickel and loss of catalytic activity. Furthermore, mechanical deterioration of the electrode is observed as the nickel undergoes repeated oxidation-reduction cycles that may be encountered under varying cell operating conditions.

The objective of this year's work was to develop improved oxygen and steam electrodes for the SOEC, and demonstrate improved durability. In the last 8½ months, increased effort was spent developing steam/hydrogen electrodes based on perovskite ceramics, finding compositions that have better stability and maintain the good electrode activity found in the standard Ni-cermet. In addition, we worked to improve the electrode activity and demonstrate long-term durability of Pr_2NiO_4. Finally, to further prove the electrodes, testing of complete cells was begun. From this effort the following progress is highlighted:

FIGURE 4. Integrated Laboratory Scale Experiment, June 4, 2007

FIGURE 5. Integrated Laboratory Scale Four-Stack Module

- A new family of perovskite materials based on (La,Sr)(Mn,Al)O_3 and (Pr,Sr)(Mn,Al)O_3 has been made and tested, which shows electrode area specific resistance (ASR) as low as 0.34 ohm-cm^2 at 830°C in H_2O:N_2:H_2 = 5.9:3.9:1 (85% N_2-free steam) and good stability in higher steam concentrations.
- Improved Pr_2NiO_4 electrodes in half-cell tests showed low electrode ASRs of 0.06-0.08 ohm-cm^2 during galvanostatic tests at 200-mA/cm^2 and 800°C. Durability tests showed that this electrode maintained this performance up to 350 hours.
- Long term testing of the Ceramatec oxygen electrode with a cobaltite bond layer showed that a large part of degradation can be attributed to the bond layer.
- Initial full-cell electrolytic tests were made using a sparger-type humidifier and later with an improved tube and shell steam generator. Difficulty was encountered with the sparger in controlling the flow of steam and needed to improve the efficiency of testing cells long term, so the setup was remodeled to test three cells at a time.

Numerical Modeling

INL and ANL researchers are analyzing the electrochemical and thermal-fluid behavior of SOECs for high temperature steam electrolysis using CFD techniques. The major challenges facing commercialization of steam electrolysis technology are related to efficiency, cost, and durability of the SOECs. The goal of this effort is to guide the design and optimization of performance for HTE systems.

An SOEC module developed by FLUENT Inc. as part of their general CFD code was used for the SOEC analysis by INL. ANL has developed an independent SOEC model that combines the governing electrochemical mechanisms based on first principals to the heat transfer and fluid dynamics in the operation of SOECs. The ANL model was embedded into the commercial STAR-CD CFD software, and is being used for the analysis of SOECs by ANL.

The SOECs operate with an applied potential to electro-catalytically split steam into H_2(g) and O_2(g). There is limited knowledge about the intermediate reaction steps that define the phenomenological behavior of solid oxide electro-chemistry, especially for the less investigated SOEC mode of operation. The model developed in this work at ANL appropriately combines the governing electrochemical mechanisms based on the first-principals to the heat transfer and fluid dynamics in the operation of SOECs. In this way, it is used to guide the design and optimization of SOEC-based hydrogen production systems, as well as to allow the detailed investigation of the SOEC performance. In addition, this model can be coupled to a complete simulation model of the full-size HTE plant to support the plant thermodynamic analysis.

The model has been developed to simulate a planar 3-dimentional SOEC by using a finite element approach. The model combines an in-house developed electrochemical (EC) module and the commercially available CFD code (STAR-CD). It calculates the local electrochemical kinetics of the SOEC coupled to the mass- and heat-balances of the gaseous flow and the solid medium.

The main coupling between the EC and CFD modules is due to the mutual use of the temperature profile. The CFD module provides the temperature field for the EC module to generate the current density distribution through using the temperature dependent electrochemical parameters. The EC module provides the species and heat generation rates, based on the current density that it calculates, for the CFD module to generate the consistent temperature profile.

Conclusions

- Experimental results from a dual stack (2 x 60-cell) test, conducted at the Ceramatec facility in Salt Lake City showed:
  – Hydrogen production rates in excess of 1.2 Nm^3/hour were achieved initially, and the module operated continuously (with only short-duration electrical and gas flow interruptions) for 2,040 hours.
  – The stack endurance test was terminated due to shorting in the main power leads, though the hydrogen production had fallen at that time to 0.65 N m^3/hour.
- The ILS will produce ~6 Nm^3 of H_2, while incorporating, at reduced scale, all of the components of a commercial plant.
- INL, in collaboration with FLUENT and ANL, using STAR-CD, developed electrochemical CFD models for electrolysis that predict product flow, current density, temperature and ASR distributions within the SOEC.

Future Directions

FY08 Priorities

- Long-term operation of the ILS and corrosion tests
- Additional components
- Diagnosis of long-term degradation of output
- 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

Special Recognitions & Awards/Patents Issued

1. Patent Application (in progress): Stoots, C. M., O'Brien, J. E., Herring, J. S., Lessing, P. A., Hawkes, G. L., and Hartvigsen, J. J., "High temperature H2O/CO2 Co-Electrolysis for Syngas Production," IDR# BA-069, pending US Patent 11/461,337, filed July 31, 2006.

2. Patent Application (in progress): Hawkes, G. L., Herring, J. S., Stoots, C. M., and O'Brien, J. E., "Electrolytic/Fuel Cell Bundles and Systems Including a Current Collector in Communication with an Electrode Thereof, Methods for Generating Electricity and/or Performing Electrolysis Using the Same," BA-133, elected for Patent Application, March 2006.

FY 2007 Publications/Presentations

Journal Papers

1. O'Brien, J. E., Stoots, C. M., Herring, J. S., and Hartvigsen, J. J., "Performance of Planar High-Temperature Electrolysis Stacks for Hydrogen Production from Nuclear Energy," in press, *Nuclear Technology*, Vol. 158, pp. 118 – 131, May, 2007.

2. Hawkes, G. L., O'Brien, J. E., Stoots, C. M., Herring, J. S., "CFD Model of a Planar Solid Oxide Electrolysis Cell from Hydrogen Production from Nuclear Energy," accepted for publication, *Nuclear Technology*, Vol. 158, pp. 132 – 144, May, 2007.

3. Herring, J. S., O'Brien, J. E., Stoots, C. M., and Hawkes, G. L., "Progress in High-Temperature Electrolysis for Hydrogen Production using Planar SOFC Technology," *International Journal of Hydrogen Energy*, Vol. 32, Issue 4, pp. 440–450, March 2007.

4. Harvego, E. A., Reza, S. M. M., Richards, M., and Shenoy, A., "An Evaluation of Reactor Cooling and Coupled Hydrogen Production Processes using the Modular Helium Reactor," *Nuclear Engineering and Design*, Vol. 236, pp. 1481–1489, 2006.

5. Richards, M., Shenoy, A., Schultz, K., Brown, L., Harvego, E. A., McKellar, M. G., Coupey, J. P., Reza, S. M. M., and Okamoto, F., "H2-MHR Conceptual Designs based on the Sulphur–Iodine Process and High-Temperature Electrolysis," *Int. J. Nuclear Hydrogen Production and Applications,* Vol. 1, No. 1, 2006, pp. 36 – 50.

6. O'Brien, J. E., Stoots, C. M., Herring, J. S., and Hartvigsen, J. J.,"Hydrogen Production Performance of a 10-Cell Planar Solid-Oxide Electrolysis Stack," *Journal of Fuel Cell Science and Technology*, Vol. 3, pp. 213–219, May, 2006.

7. Lessing, P. A., "A Review of Sealing Technologies Applicable to Solid Oxide Electrolysis Cells", accepted for publication, *Journal of Materials Science*, May 2006.

8. Lessing, P. A., "Materials for Hydrogen Generation via Water Electrolysis", accepted for publication, *Journal of Materials Science*, May 2006.

Conference Papers

1. O'Brien, J.E., Stoots, C.M., Hawkes, G.L., Herring, J.S., and Hartvigsen, J., "High-Temperature Coelectrolysis of Steam and Carbon Dioxide for Direct Production of Syngas: Equilibrium Model and Single-Cell Tests," submitted, Fifth International Conference on Fuel Cell Science, Engineering & Technology, June 18–20, 2007, New York, USA.

2. Stoots, C.M., O'Brien, J.E., and Hartvigsen, J., "Syngas Production Via High-Temperature Coelectrolysis of Steam and Carbon Dioxide In A Solid-Oxide Stack," submitted, Fifth International Conference on Fuel Cell Science, Engineering & Technology, June 18–20, 2007, New York, USA.

3. McKellar, M. G., O'Brien, J. E., Hawkes, G. L., and Stoots, C. M., "Development of a One-Dimensional Co-Electrolysis Model for Use in Large-Scale Process Modeling Analysis," submitted, Fifth International Conference on Fuel Cell Science, Engineering & Technology, June 18–20, 2007, New York, USA.

4. Hawkes, G. L., Hawkes, B. D., Sohal, M. S., Torgerson, P. T., Williams, M. C., "Tubular Porous-Metal Supported Solid Oxide Fuel/Electrolysis Cell: Part 1: CFD and Electrochemical Model, submitted, Fifth International Conference on Fuel Cell Science, Engineering & Technology, June 18–20, 2007, New York, USA.

5. Hawkes, B. D., Hawkes, G. L., Sohal, M. S., Torgerson, P. T., Williams, M. C., "Tubular Porous-Metal Supported Solid Oxide Fuel/Electrolysis Cell: Part 2: Thermal-Stress Model," submitted, Fifth International Conference on Fuel Cell Science, Engineering & Technology, June 18–20, 2007, New York, USA.

6. O'Brien, J.E., Stoots, C., Hawkes, G.L, Herring, J.S., and Hartvigsen, J., "High-Temperature Co-electrolysis of Carbon Dioxide and Steam for the Production of Syngas: Equilibrium Model and Single-Cell Tests," ANS Embedded Topical: International Topical Meeting on the Safety and Technology of Nuclear Hydrogen Production, Control, and Management, June 24 – 28, 2007, Boston, MA, USA.

7. Stoots, C.M., O'Brien, J.E., Herring, S.J., and Hartvigsen, J., "Test Results of High Temperature Steam/CO2 Coelectrolysis In A 10-Cell Stack," ANS Embedded Topical: International Topical Meeting on the Safety and Technology of Nuclear Hydrogen Production, Control, and Management, June 24 – 28, 2007, Boston, MA, USA.

8. Hawkes, G.L., O'Brien, J.E., Stoots, C.M., Herring, S.J., and Hartvigsen, J., "3D CFD Model of High Temperature H2O/CO2 Co-Electrolysis," ANS Embedded Topical: International Topical Meeting on the Safety and Technology of Nuclear Hydrogen Production, Control, and Management, June 24 – 28, 2007, Boston, MA, USA.

9. Hartvigsen, J., Elangovan, S., Stoots, C.M., O'Brien, J.E., and Herring, J.S., "Pre-ILS Demonstration Of Planar Solid Oxide Fuel Cell Technology Readiness For Application In Nuclear Hydrogen Production," ANS Embedded Topical: International Topical Meeting on the Safety and Technology of Nuclear Hydrogen Production, Control, and Management, June 24 – 28, 2007, Boston, MA, USA.

10. Housley, G., Condie, K., O'Brien, J.E., Stoots, C.M., "Design of an Integrated Laboratory Scale Experiment for Hydrogen," ANS Embedded Topical: International Topical Meeting on the Safety and Technology of Nuclear Hydrogen Production, Control, and Management, June 24 – 28, 2007, Boston, MA, USA.

11. Herring, J.S., O'Brien, J.E., Stoots, C.M., Hartvigsen, J., Petri, M.C., Carter, J.D., and Bischoff, B.L., "Overview of High-Temperature Electrolysis for Hydrogen Production," ANS Embedded Topical: International Topical Meeting on the Safety and Technology of Nuclear Hydrogen Production, Control, and Management, June 24 – 28, 2007, Boston, MA, USA.

12. Hartvigsen, J. J., Elangovan, S., Stoots, C. M., O'Brien, J. E., Herring, J. S., "Pre-ILS Demonstration of Planar Solid Oxide Fuel Cell Technology Readiness for Application in Nuclear Hydrogen Production," ANS Embedded Topical: International Topical Meeting on the Safety and Technology of Nuclear Hydrogen Production, Control, and Management, June 24 – 28, 2007, Boston, MA, USA.

13. Schultz, K., Sink, C. Herring, J. S., O'Brien, J. E., Buckingham, R., Summers, W., and Michele Lewis, M., "Status of the US Nuclear Hydrogen Initiative," Proceedings of ICAPP 2007, Paper 7530, Nice, France, May 13 – 18, 2007.

14. Hawkes, G. L., O'Brien, J. E., Stoots, C. M., Jones, R., "Three Dimensional CFD Model of a Planar Solid Oxide Electrolysis Cell for Co-Electrolysis of Steam and Carbon-Dioxide," 2006 Fuel Cell Seminar, paper no. 298, Nov. 13 – 17, 2006, Honolulu.

15. Stoots, C. M., O'Brien, J. E., Hawkes, G. L., Herring, J. S., and Hartvigsen, J. J., "High Temperature Co-Electrolysis of H2O and CO2 for Syngas Production," 2006 Fuel Cell Seminar, paper no. 418, Nov. 13 – 17, 2006, Honolulu.

16. O'Brien, J. E., Stoots, C. M., Herring, J. S., Hawkes, G. L., and Hartvigsen, J. J., "Thermal and Electrochemical Performance of a High-Temperature Steam Electrolysis Stack," 2006 Fuel Cell Seminar, paper no. 417, Nov. 13 – 17, 2006, Honolulu.

17. McKellar, M. G., Harvego, E. A., Richards, M., and Shenoy, A., "A Process Model for the Production of Hydrogen using High Temperature Electrolysis," paper no. 89694, 14th International Conference on Nuclear Energy (ICONE), Miami, July 17 – 20, 2006.

18. J. E. O'Brien, M. G. McKellar, C. M. Stoots, G. L. Hawkes, J. S. Herring, "Analysis of Commercial-Scale Implementation of HTE to Oil Sands Recovery," September 15, 2006.

19. C. M. Stoots, K. G. Condie, J. E. O'Brien, G. K. Housley, J. S. Herring, "Integral Laboratory Scale Stack Specification Mechanical Design Report," August 15, 2006.

20. J. E. O'Brien, C. M. Stoots, J. S. Herring, "Documentation of INL High-Temperature Electrolysis Milestone: Operation of HTE Stack at 100 NL/hr Hydrogen Production Rate for 1000 Hours, April 15, 2006.

Internal Project Milestone Reports

1. Harvego, E. A., "Implementation of Lead-Bismuth Properties into Unisim," May 2006.

2. Harvego, E. A., "Implementation of Molten Salt Properties into Unisim," May 2006.

3. E. A. Harvego, M. G. McKellar and J. E. O'Brien, "Summary of Reactor-Coupled HTE Modeling Sensitivity Studies," October, 2006.