IV.G.6 Clean Energy Research*

Dr. Ralph E White (Primary Contact),
Drs. John W. Weidner, James A. Ritter,
Michael A. Matthews, John W. Van Zee, and
Jerome Delhommelle
University of South Carolina
College of Engineering and Information Technology
Columbia, SC 29208
Phone: (803)-777-3270; Fax: (803)-777-6769
E-mail: white@engr.sc.edu

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

DOE Project Officer: Paul Bakke
Phone: (303) 275-4916; Fax: (303) 275-4753
E-mail: Paul.Bakke@go.doe.gov

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- Savannah River National Laboratory, Aiken, SC
- South Carolina State University, Orangeburg, SC

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*Congressionally directed project

Objectives

1. J. W. Weidner: To advance thermochemical hydrogen production processes.
2. J. A. Ritter: To develop high capacity complex hydride materials from alanates, boronates, and their mixtures for reversible on-board hydrogen storage.
3. M. A. Matthews: To investigate the gravimetric efficiency and kinetics of steam hydrolysis of sodium borohydride for on-board hydrogen storage and hydrogen production.
4. J. W. Van Zee: To analyze the effect of CO, NH_3, and H_2S on the durability of the fuel cell membrane electrode assembly.
5. R. E. White: To develop mathematical models to characterize the performance and aging of fuel cell cathodes.
6. J. Delhommelle: To develop new insights for hydrogen storage materials via molecular simulation.

Technical Barriers

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

- Objective #1: cost of H_2 production.
- Objective #2: addresses weight and volume, durability, refueling time, hydrogen capacity and reversibility, and lack of understanding of hydrogen physisorption and chemisorption for a viable on-board hydrogen storage system.
- Objective #3: addresses on-board hydrogen storage technical barriers for weight and volume and thermal management.
- Objective #4: addresses the durability barrier for fuel cells.
- Objective #5: addresses the durability barrier and the cost barrier associated with fuel cells.
- Objective #6: identifies suitable materials for hydrogen storage using molecular simulations.

Technical Targets

- Objective 1: These studies will be applied toward meeting the cost target for production of hydrogen from high-temperature thermochemical cycles of $3/gge.
- Objectives 2 and 3: Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets: cost: $4/kWh net; specific energy: 2 kWh/kg; energy density: 1.5 kWh/L.
- Objectives 4 and 5: Insights gained from these studies will be applied towards the design and synthesis of the proton exchange membrane (PEM) fuel cell that meets the following DOE 2010 targets listed in Table 3.4.4 of the Multi-Year Research, Development and Demonstration Plan: cost: $30/kW; durability: 5,000 hours.
- Objective 6: Insights gained from the molecular simulations will be used to develop new hydrogen storage materials.

Accomplishments

Objective #1: Low Temperature Electrolytic Hydrogen Production

- Gained an understanding of the effects of catalyst loading, membrane thickness and temperature on the electrolyzer performance.
- Generated hydrogen from a PEM electrolyzer by feeding gaseous HBr.
- Developed a model to predict water transport.
- Identified best candidates by cyclic voltammetry.

Objective #2: Development of Complex Metal Hydride Hydrogen Storage Materials

- Disclosed the reversible hydrogen storage properties of scandium-doped $NaAlH_4$.
- Developed a novel synthesis technique for $NaAlH_4$ and $LiAlH_4$.
- Prepared a novel *in situ* Ti catalyst for improved dehydrogenation and hydrogenation kinetics of sodium aluminum hydride.
- Revealed that hydrogen desorption from metal-doped $LiBH_4$ might be facilitated through the use of multiwall carbon nanotubes via a hydrogen spillover mechanism.
- Studyied the hydrogenation and rehydrogenation of a Ti-doped lithium borohydride modified with aluminum.
- Revealed the reversible hydrogen storage properties of a Ti-doped lithium borohydride modified with aluminum.
- Measured the hydrogen storage capacity of a destabilized and sintered Ti-doped lithium borohydride modified with aluminum.

Objective #3: Hydrogen Storage Using Chemical Hydrides

- Modified the primary experimental apparatus to improve the performance of the system and hold pressures up to 4 psi.
- Developed different prototype hydrogen generation reactors and compared their performance.
- Disclosed proprietary details of the reactors to the University of South Carolina Research Foundation.
- Verified hydrogen generation using a residual gas analyzer (RGA); H_2 was the only gaseous species detected.
- Designed a reactor to allow visual observation of the phase behavior of the steam hydrolysis reaction.
- Carried out visualization experiments that revealed water being absorbed by $NaBH_4$ and subsequently forming a liquid phase before the reaction started.

Objective #4: Diagnostic Tools for Understanding Chemical Stresses and Membrane Electrode Assembly (MEA) Durability Resulting from Hydrogen Impurities

- Completed experiments to understand the effect of ionomer wt% in the catalysts layer on the rates of NH_3 poisoning of anode.
- Completed kinetic analysis that suggested the reaction of NH_3 with the ionomer sites obeyed a pseudo-first order reaction with a reaction rate constant of 1.2 h^{-1}.
- Developed a methodology for 3-D predictions of degrading effects.
- Completed analyses of similarities and differences in concentration and dosage effects between data for CO for NH_3 and H_2S.
- Formulated model equations for NH_3 and H_2S.
- Determined that the degradation with NH_3 did not follow the same mechanism of competitive adsorption that was apparent with CO in H_2 mixtures.

Objective #5: Developing Mathematical Models to Characterize the Performance and Aging of Fuel Cell Cathodes

- Studied the peroxide generation in the oxygen reduction reaction (ORR) in different acidic electrolytes such as sulfuric, perchloric, hydrochloric, and organic acid solutions using a rotating disk ring electrode (RRDE) experiment.
- Developed a two dimensional mathematic model based on Nernst Plank equations to simulate the ORR at the RRDE in an acidic electrolyte.
- Performed parameter estimation based on the experimental data to quantify the processes occurring during the ORR mechanism.

Objective #6: Molecular Simulation of Hydrogen Storage Materials

- Studied hydrogen storage in clathrate hydrates.
- Studied hydrogen storage in metal-organic frameworks.
- Studied hydrogen storage in doped single and multi-metal hydrides.

FY 2007 Publications

1. P. Sivasubramanian, R. P. Ramasamy, F. J. Freire, C. E. Holland and J. W. Weidner, "Electrochemical Hydrogen Production from Thermochemical Cycles using a Proton Exchange Membrane Electrolyzer," *Int. J. Hydr. Engery*, 32, 463-468 (2007).

2. R. P. Ramasamy, P. Sivasubramanian, J. Staser, and J. W. Weidner, "Effect of Water on the Electrochemical Oxidation of SO_2 in a PEM Electrolyzer for H_2 Production," *Electrochem. Solid-State Lett.*, in press (2007).

3. T. Wang, J. Wang, A. D. Ebner and J. A. Ritter, "Reversible Hydrogen Storage Properties of NaAlH4 Catalyzed with Scandium," *J. Alloys and Compounds*, on line in press (2007).

4. J. Wang, A. D. Ebner and J. A. Ritter, "Synthesis of Complex Hydrides for Hydrogen Storage," *J. Physical Chemistry C*, accepted (2007).

5. J. Wang, A. D. Ebner, and J. A. Ritter, "Novel in situ Preparation of Ti Catalyst for Improved Dehydrogenation and Hydrogenation Kinetics of Sodium Aluminum Hydride," in preparation (2007).

6. T. Wang, A. D. Ebner, and J. A. Ritter, "Enhanced Hydrogen Desorption from Metal-Doped LiBH4 via Hydrogen Spillover through MWNTs," in preparation (2007).

7. M. A. Nicholson, B. Bangasser, A. D. Ebner and J. A. Ritter, "Reversible Hydrogen Storage Properties of Ti Catalyzed Lithium Borohydride and Aluminum," in preparation (2007).

8. E. Y. Marrero-Alfonso, J. R. Gray, T. A. Davis, and M. A. Matthews, "Hydrolysis of Sodium Borohydride with Steam," *International Journal of Hydrogen Energy*, in Press (2007).

9. Marrero-Alfonso, E.Y., Gray, J.R., Davis, T.A. and Matthews, M.A., "Minimizing Water Utilization in Hydrolysis of Sodium Borohydride: The Role of Sodium Metaborate Hydrates," *International Journal of Hydrogen Energy*, Accepted, (2007).

10. Q. Dong, S. Santhanagopalan, and R. E. White, "Simulation of Polarization Curves for Oxygen Reduction Reaction in 0.5 M H_2SO_4 at a Rotating Ring Disk Electrode," *Journal of the Electrochemical Society*, 154, A816-A825 (2007).

11. Q. Dong, S. Santhanagopalan, and R. E. White, "Simulation of the Oxygen Reduction Reaction at a Rotating Ring Disk Electrode in 0.5 M H_2SO_4 including an Adsorption Mechanism," *Journal of the Electrochemical Society*, accepted May 2007, Manuscript #: JES-07-0250R.

12. Q. Dong, S. Santhanagopalan, and R. E. White, "A Comparison of the Solutions to the Fluid Motion Generated by a Rotating Disk," *Journal of the Electrochemical Society*, to be submitted.

FY 2007 Conference Presentations

1. J. W. Weidner, P. Sivasubramanian, J. Staser, C. E. Holland, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," Grove Fuel Cells Conference, Turin, Italy, September 2006.

2. J. W. Weidner, J. Staser, P. Sivasubramanian, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," The American Institute of Chemical Engineers Fall Meeting, San Francisco, CA, November 2006.

3. J. A. Staser and J.W. Weidner, "Electrocatalysts for the Production of Hydrogen via the Hybrid Sulfur Process," The Electrochemical Society, Chicago, IL, May 2007.

4. T. Wang, J. Wang, M. A. Nicholson, A. D. Ebner and J. A. Ritter, "Reversible Hydrogen Storage in High Temperature Complex Hydrides," Fundamentals of Adsorption FOA9, Giardini Naxos, Italy, May 2007.

5. J. Wang, T. Wang, M. A. Nicholson, A. D. Ebner and J. A. Ritter, "High Capacity and High Temperature Complex Hydrides for Reversible Hydrogen Storage," 2nd Annual Korean-USA Joint Symposium on Hydrogen and Fuel Cell Technologies, Columbia, SC, May 2007.

6. J. Wang, A. D. Ebner and J. A. Ritter, "New Synthesis Route for Complex Hydride Hydrogen Storage Materials," AIChE 2007 Spring National Meeting, Houston, TX, April 2007.

7. J. Wang, T. Wang, M. A. Nicholson, A. D. Ebner and J. A. Ritter, "High Capacity Reversible Hydrogen Storage Materials," AIChE 2006 Annual Meeting, San Francisco, CA, November 2006, contributed.

8. J. Wang, T. Wang, M. A. Nicholson, A. D. Ebner and J. A. Ritter, "Synthesis of Metal Complex Hydride Reversible Hydrogen Storage Materials," AIChE 2006 Annual Meeting, San Francisco, CA, November 2006, contributed.

9. J. R. Gray, E. Y. Marrero-Alfonso, A. M. Beaird, C. Campbell, T. A. Davis and M. A. Matthews, "The Application of Steam Hydrolysis of Chemical Hydrides to Facilitate Hydrogen Storage and Generation," AIChE 2006 Annual Meeting, San Francisco, November 2006.

10. E. Y. Marrero-Alfonso, J. R. Gray, A. M. Beaird, T. A. Davis and M. A. Matthews, "Reaction Pathways in the Gas/Solid Hydrolysis of Chemical Hydrides as a Novel Approach to Hydrogen Storage and Generation," AIChE 2006 Annual Meeting, San Francisco, November 2006.

11. A. M. Beaird, J. R. Gray, E. Y. Marrero-Alfonso, M. A. Matthews and T. A. Davis, "Characterization of the Gas Phase Hydrolysis of Sodium Borohydride," AIChE 2006 Annual Meeting, San Francisco, November 2006.

12. Q. Dong and R. E. White, "Parameter Evaluation of the ORR at a RRDE," *Journal of the Electrochemical Society Transactions*, 211th Meeting in Chicago, submitted (2007).

13. Q. Dong and R. E. White, "Parameter Evaluation of the ORR at a RRDE", presentation made in 211th ECS meeting in Chicago, IL, May 2007.

14. Q. Dong and R. E. White, "Simulation of Polarization Curves for Oxygen Reduction Reaction in 0.5 M H2SO4 at a Rotating Ring Disk Electrode," presentation made in 2nd MEA Manufacturing Symposium, Dayton, OH, August 2006.

FY 2007 Patent Application

1. J. A. Ritter, T. Wang, A. D. Ebner J. Wang, and C. E. Holland, "Reversible Hydrogen Storage Material," US Patent Application, filed November (2006).