IV.A.5k Metal Hydride Center of Excellence Work Performed at Savannah River National Laboratory

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Project End Date: September 30, 2010

Objectives

- Quantify and optimize the efficiency of alane production synthesized through electrochemical charging.
- Develop optimized operating conditions for a high pressure electrolytic cell specifically designed for the electrolytic charging of alane.
- Lead the Metal Hydride Center of Excellence (MHCoE) Task E, Engineering, Analysis, Design and Test.
- Quantify the system mass penalties associated with various advanced heat exchange methodologies.
- Quantify the system mass and volume efficiencies of the hybrid storage system approach.

Technical Barriers

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

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(F) Codes and Standards
(G) Materials of Construction
(H) Balance of Plant Components
(J) Thermal Management

Technical Targets

Solid State Hydride System Engineering

This project is conducting engineering studies of the *in situ* rechargeable hydrogen storage systems. Insights gained from these studies will be applied toward the design of hydrogen storage systems which would meet the following DOE 2010 hydrogen storage targets:

- System gravimetric density: 6% kgH_2/kg system.
- System volumetric density: 0.045 kg H_2/liter system.
- System fill time: 3 min.
- Minimum full flow rate: 0.02 g/sec.

Electrolytic Charging of Alane

This project is conducting fundamental studies of the electrolytic charging of Al to AlH_3 (alane). Insights gained from these studies will be applied toward the design of alane regeneration systems which would meet the following DOE 2010 hydrogen storage targets:

- System gravimetric density (SGD): 6% kgH_2/kg
- System volumetric density (SVD): 0.045 kg H_2/liter

Accomplishments

- Quantified optimum hydrogen pressure for an idealized graphite reinforced epoxy composite hybrid storage tank to be 300-400 bar, maximizing both gravimetric and volumetric storage density.
- Conclusively identified AlH_3 formation through electrolytic charging at ambient pressure and temperature.

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Solid State Hydride System Engineering

Approach

The objective of this effort is to quantify the advantages of the hybrid tank, which utilizes combined high pressure and solid state hydrides, in both volumetric and gravimetric density.

The hybrid storage tank concept has been identified as a candidate design for a solid state hydrogen storage system. This concept utilizes both the high pressure tank concept, operating at pressures of 200 to 500 bar along with a powdered solid state hydride. The solid state hydride holds hydrogen in a much more

volumetrically dense manner, while the void space between the particles is also used to store hydrogen at high pressures, which both increases total hydrogen storage capacity of the system and allows for a reservoir of hydrogen gas available immediately for use by the fuel cell without requiring heat. The theoretical drawback is the real gas behavior of hydrogen, which deviates from ideality by 10% at 200 bar and increases in non-ideality at increasing pressures. This study will determine the optimum pressure for a hybrid storage system for various tank materials, media hydrogen storage densities and media void fractions.

The independent variables of the analysis assume the tank to be cylindrical with a 0.5 m radius and 1 m length and having hemispherical ends. This yields an internal volume of 261.8 liters. The pressure vessel is designed to meet ASME Schedule 8 Pressure Vessel Code. The calculations were performed for hydrogen storage media void fractions of 40% and 60% of theoretical density and a density of 1.3 g/cc (that of $NaAlH_4$). All calculations were performed assuming a 20°C operating temperature.

The dependant variables included tank material, solid state hydride weight capacity for hydrogen, and vessel maximum operating pressure. The operating pressure was varied from 50 to 800 bar and media gravimetric density from 2 to 8 wt%. The materials for tank construction were either 316 stainless steel (SS), A92014-T76 high strength aluminum, **Al**, or IM6 continuously wound graphite carbon reinforced epoxy composite (GREC).

The non ideal gas behavior of compressed hydrogen was assumed to follow the Redlich-Kwong equation of state, which predicts 48% deviation from ideality at 1,000 bar pressure.

Results

Gravimetric Density

The SGD of the hybrid tank described above is given in Figure 1 as system gravimetric density vs. system operating pressure at media void fractions of 40 and 60%. The 2, 4, 6, and 8 wt% media are represented by red, green, blue, and pink symbols, respectively. The GREC tank material is given in open symbols with the stainless steel tank in solid symbols. The empty tank configuration is also given representing a high pressure tank alone.

The SS tank material is seen to be inferior in to the GREC tank at all pressures but becomes increasingly inferior with rising pressure. Analysis of the aluminum tank resulted in nearly identical densities to the SS tank owing to the similar specific strength of these two materials. For reasons of clarity and brevity, only the SS tank materials are given here. The two tank materials, SS and GREC, do converge at lower pressures, which would give the SS tank a cost advantage at pressures lower than 50 bar.

It is interesting to observe that for the GREC tank, SGD increases significantly with pressure, finally coming to a maximum before the non-ideality of hydrogen compression defeats further gas compression. This maximum occurs at approximately 550 bar (8,085 psi) for the 4 wt% media and 400 bar (5,720 psi) for the 6 wt% media. It is also apparent that a 6 wt% media can yield optimally, a 6 wt% system density utilizing the free

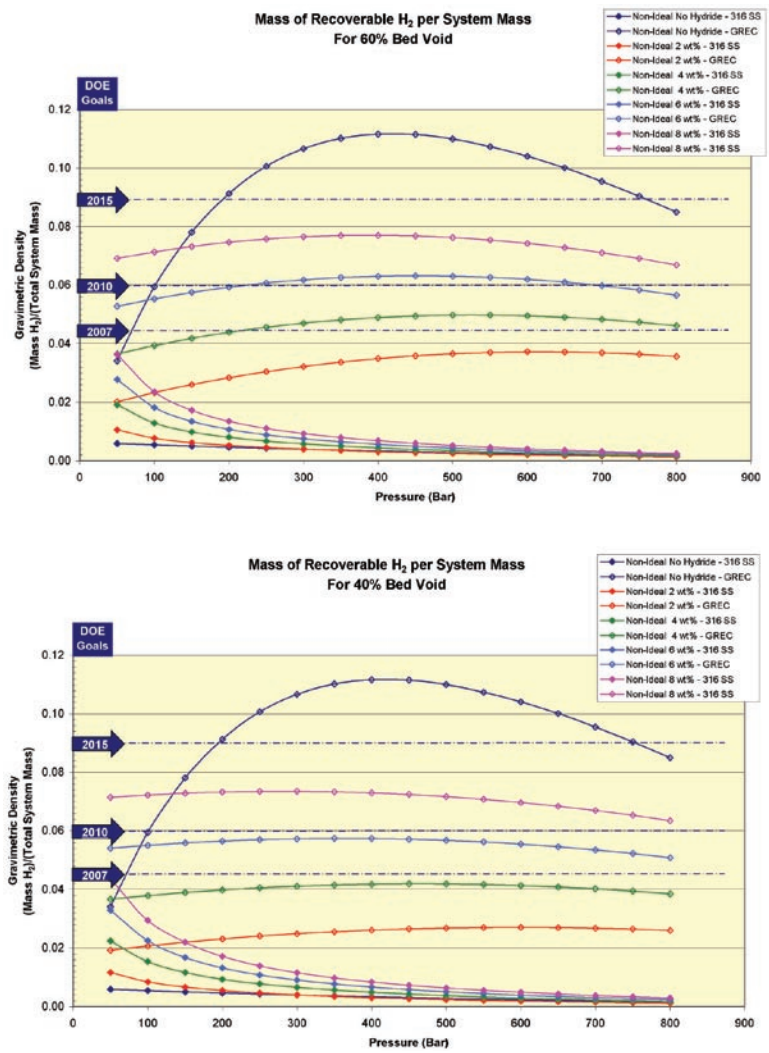

FIGURE 1. Gravimetric Density of Hybrid Tanks as a Function of Operating Pressure for Void Fractions of 40% and 60%

space between the media particles. Similarly, a 4 wt% media can yield a 4.5 wt% system, albeit at significantly higher operating pressures. These pressures are both within the region of current compressed tank designs and should be achievable. The empty high pressure tank has superior gravimetric density to the solid state tanks at only 150 bar and maintains this advantage at higher pressures.

Volumetric Density

The graph of the SVD vs. operating pressure is given in Figure 2. Again, the 2, 4, 6, and 8 wt% media are represented by red, green, blue, and pink symbols respectively. The GREC tank material is given in open symbols with the SS tank in solid symbols. The high pressure tank is again given by the black symbols.

The volumetric densities of the two tank materials are much closer at low pressures than was observed for the gravimetric densities. Again, however, increasing pressure caused the GREC tank to increase in hydrogen density while the SS tank decreases.

A maximum in volumetric density was not identified in the pressure range of this analysis for the GREC tank, which continually increased with increasing pressure. The 6 wt% media yielded a volumetric density of 0.046 kg H_2/liter at 400 bar, the pressure yielding the optimum gravimetric density. This meets the DOE 2010 goal for volumetric storage density.

The high pressure tank is clearly observed to have a very great volumetric density disadvantage to the GREC and SS tanks. Only at very high pressures exceeding 400 bar does the high pressure tank exceed the volumetric density of the SS tank and never does it approach the density of in the GREC tank.

Conclusions & Future Directions

Given that any solid state hydrogen storage material will be in powder form and pack to approximately 50% of its theoretical density, a hybrid tank approach will be required to utilize the 50% void space in the system. This void space can be optimally utilized at a 400 bar (5,720 psi) operating pressure, well within the current bounds of compression technology and tank design, if a GREC tank material is employed. At operating pressures below 50 bar, SS tank materials are feasible for cost and manufacturing considerations. Overall, the DOE 2010 goals for system gravimetric and volumetric density can be met utilizing a hybrid tank design operating at 400 bar utilizing media having 6 wt% hydrogen storage capacity at media density 1.3g/cc (equivalent to $NaAlH_4$).

Three heat exchange designs have been identified. These designs will be analyzed to determine if significant reductions in the heat exchange masses can be obtained to lower the overall system mass and increase system gravimetric densities.

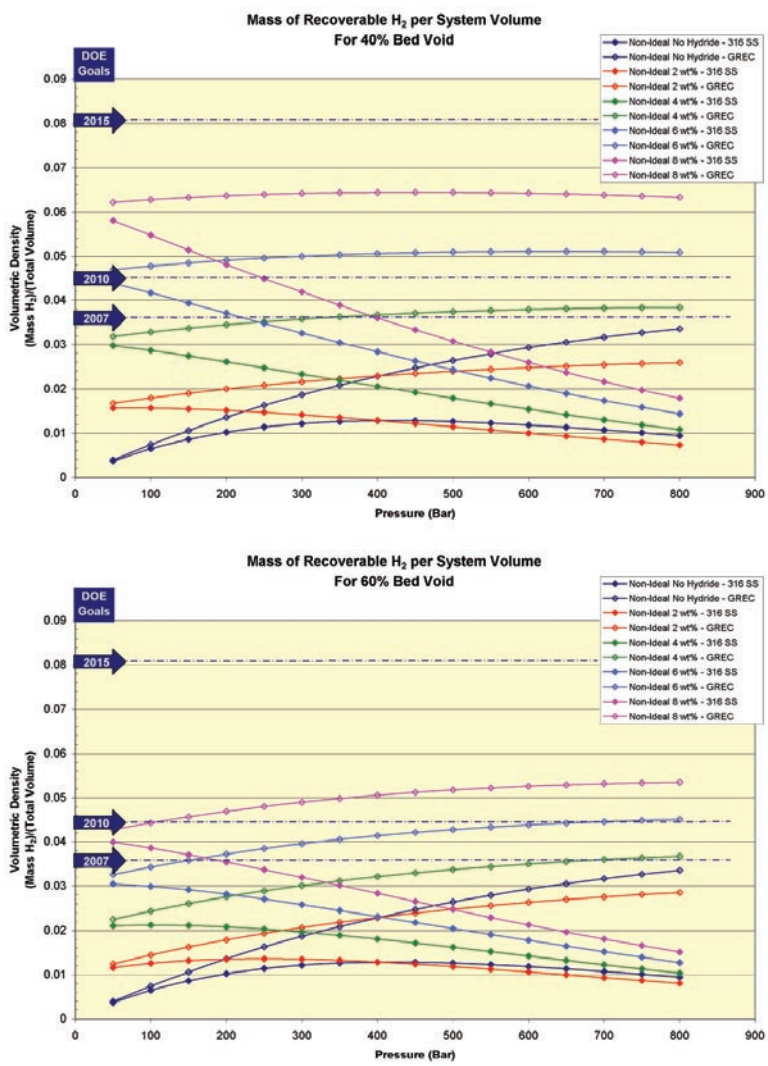

FIGURE 2. Volumetric Density of Hybrid Tanks as a Function of Operating Pressure for Void Fractions of 40% and 60%

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Electrochemical Charging of Alane

Approach

The objective of this effort is to achieve efficient charging of Al to AlH_3 through the incorporation of electrolytic charging methods.

Due to the large gravimetric and volumetric hydrogen storage densities of AlH_3 (10 wt% and 149 g/liter, respectively), this compound has reemerged as a potential H_2 storage material and is ideally suited for many proposed applications, such as automobile fuels. The re-hydrogenation of AlH_3 (10^5 bars at room temperature) has proven to be a serious obstacle in its development. Recently, the idea of electrochemically charging aluminum has been proposed as a method to produce the large hydrogen chemical potentials needed to form AlH_3. Utilizing this idea, investigations have been conducted validating this hypothesis at ambient pressure and room temperature.

The approach is to utilize the high chemical potentials present in electrochemical cells to generate AlH_3. This is achieved through the use of two experimental electrolytic cells: an ambient pressure electrochemical cell (APC) and an elevated pressure electrochemical cell (EPC). These cells were used in conjunction with varying electrode materials to determine the most appropriate path for the formation AlH_3 and also to determine the underlying mechanism of its formation. The choice of the electrolyte plays a very important role in the experimental setup and its selection must also be made carefully.

Results

A literature review of electrolytic charging of hydride materials was completed and is in preparation for publication. This review concentrated on electrode construction and properties of metal hydride storage materials. The development of a test matrix for the APC was formulated, and the experiments completed to validate the approach and to serve as a foundation for continuation of this effort. As a result of these efforts, the electrochemical cells designed and fabricated in the first year of the program were redesigned (Figure 3 - top) to improve reproducibility and efficiency. Evidence for AlH_3 has been shown with this technique (Figure 3 - bottom) and further work is in progress to improve upon this finding.

Furthermore, the thermodynamics necessary to understand electrolytic charging was more deeply investigated to show the feasibility of the proposed project. Essentially, the Gibbs Free Energy is given as:

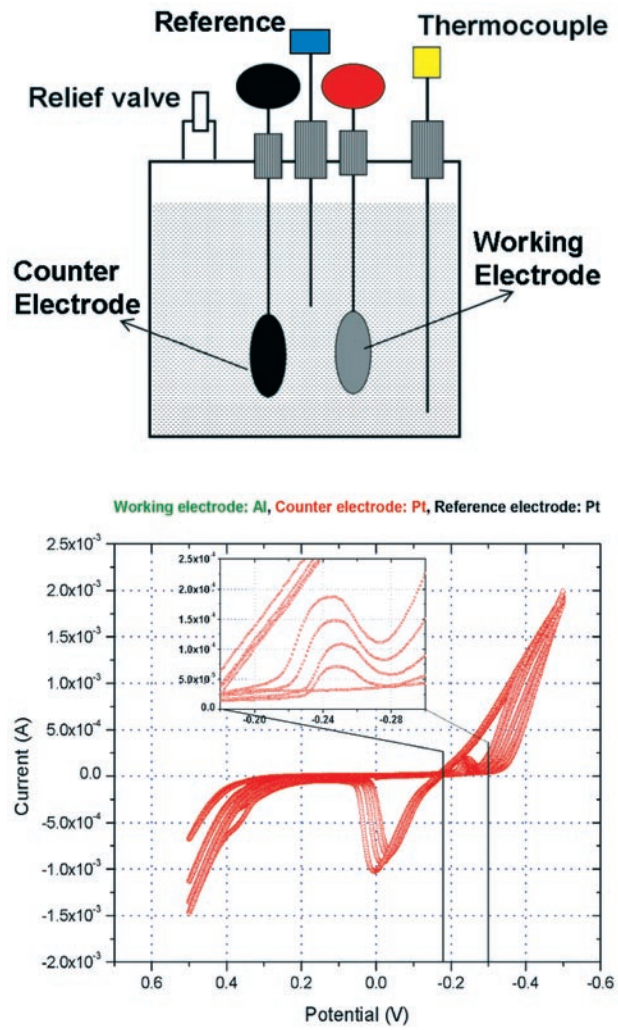

FIGURE 3. Schematic of the New APC Designed to Improve the Production of the Formation of AlH_3 (Top) and Cyclic Voltammetry (CV) Experiment Using Al Working Electrode, Pt Counter Electrode, and Pt Reference Electrode with Sweeps from -0.5 V to 0.5 V (Bottom)

$$\Delta G = RT \ln\left[\frac{f(H_2)}{f_0}\right] \quad (1)$$

where f is the fugacity, R is the gas constant, and T is the temperature. The fugacity is equal to gas pressure when working in the limit of low pressure (i.e. <100 atm). Equation 1 provides a means by which it is possible to relate the hydrogen pressure necessary to charge metal hydrides to the electric potential required for charging, when used in conjunction with Faraday's equation:

$$E = -\frac{RT}{2\Im} \ln\left(P_{H_2}\right) \quad (2)$$

where E is the electrical potential, $\Im$ represents Faraday's constant, and R and T have the usual meanings. By varying the voltage applied to the electrolyte, the hydrogen fugacity (or its effective "pressure") is increased and it is, thus, possible to access different pressure induced phases of these materials. The literature review covers these topics in detail.

Originally, the APC consisted of a two-cell apparatus with a glass frit in between the cells. To improve conduction through the electrolyte, the cell was decreased in size to approximately 2 cm in diameter, bringing the working and counter electrodes into closer proximity to one another. A reference electrode was also added to more accurately monitor voltage across the working electrodes. Thus, the head of the cell contains five ports; three for electrodes, one for a thermocouple, and one for pressure relief. Future cell designs will more precisely control the geometry of the electrodes and will isolate the electrodes. This will allow for an increase in the reproducibility and efficiency of the cell itself. Also, electrode geometry, i.e., mesh plates versus wire, will be investigated.

Initial experimental work was conducted to determining the optimum electrode materials combination for cyclic CV experiments. Electrode materials including graphite, Pt, Pd, PdH, AlH_3 pellets, and Al were investigated. The majority of experiments relied on Pt for the reference and counter electrode while the working electrode was varied. The criteria used to establish the optimum electrodes were two fold: (1) find the electrode pair that produces the largest amount of AlH_3; and (2) establish which electrode pair is most suitable for the discovery of the correct reaction mechanism. The latter being a concern because electrodes that do not interact with the electrolyte will make it easier to differentiate the effects that arise strictly from the chemistry of the electrolyte in the presence of an applied potential and the chemistry the interactions with the electrode.

CV runs over the potentials spanning, -0.5 V to +0.5 V, with no prior experiment to higher voltages had been conducted, showed no evidence of redox peaks. By extending the potential range to, -1.0 V to +1.0 V, a redox peak appeared near 0 V (relative to the reference electrode), providing evidence that the salt cations are plating in this region. Lack of a peak in the initial range of -0.5 V to +0.5 V is evidence that a critical voltage is required to activate the low voltage region. This critical voltage required may be necessary to clean off the electrode surface or serve to seed the electrode in a supersaturated solution. Further, it was noticed that the redox peaks were not symmetrical, in the sense that reversing polarization did not mirror the current profile of the previous voltage sweep (see CV graph in Figure 3). This behavior, along with the increase in peak size with each potential sweep cycle, is currently being investigated.

Evidence of proton mobility in solution was first observed in an X-ray spectrum of a Pd electrode previously used in a CV experiment. This spectrum showed small quantities of PdH to be present. Further experiments produced large amounts of H_2 gas at the working electrode. It was found that, regardless of the composition of the electrode present, H_2 gas could be generated with an appropriately applied potential. While the gas at the working electrode was being generated, dendrite formation occurred at the counter electrode. Dendrite production also occurs irrespective of the electrode type.

Large positive voltages ($>$ +0.5 V) were necessary before H_2 gas generation was observed at the working electrode, while large negative voltages ($<$ -0.5 V) were necessary for H_2 gas formation at the counter electrode. Dendrite formation always occurred at the electrode (other than the reference electrode) which is not forming H_2. In fact, the H_2 gas production acted as a scrubber to clean off the electrode surface. The dendrites were quite fragile; stirring would periodically break them from their electrode. For a more quantitative analysis to be performed and to confirm the previous X-ray results, the dendrites were removed from the electrode and reacted/dissolved in distilled water. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on the solution to find a ratio of the metals present in the dendrites. Follow up experiments are in the works, but initial results correspond well with the X-ray data. Understanding the stoichiometry of the dendrites and their concentrations at the counter electrode combined with the determination of the amount of gas produced at the working electrode should provide the necessary information to design a more efficient setup to produce larger quantities of AlH_3.

After performing CV experiments and determining the voltages of high interest (those where high currents were observed), constant voltage runs were carried out. Constant voltage runs allow for the build up of a large amount of material while also helping in the determination of the exact voltage where chemical processes start. This voltage can then be used to determine a corresponding hydrogen fugacity (as indicated from the literature review), aiding in the determination of a reaction mechanism. These experiments are closer in practice to those that will be required to produce AlH_3. Thus, perfecting this technique is one of the highest priorities. Constant voltage runs at +0.2 V and +0.5 V have been completed. No prior experiment was performed before the constant voltage experiments to ensure the same starting point for each attempt. The current flow at +0.2 V dropped to zero in less than one minute, indicating a change in electrode chemistry, the formation of a Helmholtz

layer on the surface of the electrode, or a similar time dependant chemical change at the electrode. At +0.5 V, current flow was significant and lasted for well over three hours. There were unexplained anomalies in the current/time graph (not shown here) for the +0.5 V run, which were attributed to the vigorous stirring of the solution, causing the dendrites to fracture and, in turn, causing the electrode geometry and composition to vary. New experiments are being devised in which the voltage will be stepped with long waiting times in between each step to mitigate these anomalies.

A reaction mechanism for the formation of AlH_3 which corresponds to the experimentally determined compositions of the dendrites observed has yet to be outlined. Without knowledge of the salient electrolytic mechanism, effective production of AlH_3 will be difficult. With these thoughts in mind, two goals appear for future experiments: (1) the production of AlH_3 must be increased; and (2) design and conduct of experiments to elucidate the mechanism of dendrite and AlH_3 formation must be developed such that the most efficient cell setup can be achieved.

The first generation of this work was completed while using the APCs with successful results. From this work, it was established that the Pt/Al electrode pair shows the most potential towards the production of AlH_3 (Figure 4). The second generation of APC experiments will concentrate on perfecting the Pt/Al cell while also trying new electrodes to better understand the mechanism of the system.

The EPC is a more promising route for the production of AlH_3. The benefit of working with the EPC is its greater operating temperature without associated electrolyte boiling or vaporization loss. Higher temperatures will result in an increase in the electrolyte conductivity and concentration of soluble salts. Currently the EPC is being redesigned to include a reference electrode while the EPC matrix is being established based on reviews of the APC tests.

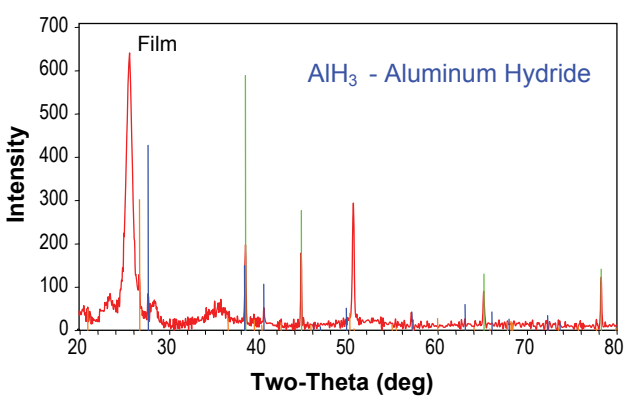

FIGURE 4. X-Ray Plot of Powder Growth on the Working Electrode from a Constant Voltage Experiment (Blue lines indicate the presence of γ-AlH_3.)

Conclusions and Future Directions

It has been established that the Pt/Al electrode pair shows the most potential towards the production of AlH_3. The formation of AlH_3 utilizing the APC has been demonstrated. This serves as validation of the approach and warrants continuation of the project. CV tests have been performed in the range of -1.0 to +1.0 V, elucidating potentials leading to chemical reductions and dendrite formation. The mechanisms of alane and dendrite formation have yet to be fully understood and are the subjects of intense study at this time.

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Special Recognitions & Awards/Patents Issued

Patents

1. "Complex Hydrides for Hydrogen Storage," issued August 23, 2006, U.S. Patent No. 7,094,387 B2.

2. "Electrochemical Process and Production of Novel Complex Hydrides," drafted for submission.

FY 2007 Publications/Presentations

1. "Design Formulas for Hydrogen Storage Vessel of Composite Materials," T. Wu, B. Hardy, D. Anton and J. Gorczyca, *Proceedings of the 2007 ASME Pressure Vessel and Piping Division*.

2. Ragaiy Zidan, Kirk Shanahan, Don Anton, Polly Berseth, and Arthur Jurgensen, "Development of Complex Hydrides using Novel Techniques," Metal Hydrides 2006, Lahina, Hawaii.

3. Polly A. Berseth, Ashley C. Stowe, Ragaiy Zidan, Donald L. Anton, Laura K. Laughlin, and Thomas P. Farrell,"Mixed Metal Complex Hydrides," South East Regional Meeting of the American Chemical Society, 2006 Fall Meeting.

4. Ashley C. Stowe and Ragaiy Zidan, "Potential Hydrogen Storage Materials: Chemical Hydrides vs. Complex Metal Hydrides," South East Regional Meeting of the American Chemical Society, 2006 Fall Meeting.

5. Ragaiy Zidan, "Development and Characterization of Novel Hydrogen Storage Materials," Study of Matter at Extreme Conditions Conference (SMEC), Miami Beach, FL, April, 2007.

6. Ashley C. Stowe1, Monika Hartl, Alice Acatrinci, Luke Daemen, Donald Anton, and Ragaiy Zidan, "The Role of Vibrational Coupling in Understanding the Thermodynamics of Hydride Formation," SMEC, Miami Beach, FL, April, 2007.

7. Polly A. Berseth, Ashley C. Stowe, Donald L. Anton, Ragaiy Zidan, Laura K. Laughlin, and Thomas P. Farrell, "Exploration of Mixed Metal Hydride Materials," SMEC, Miami Beach, FL, April, 2007.

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1. S.M. Wallis, *Phase Equilibrium in Chemical Engineering*, Butterworth-Heinemann, New York, NY (1984), p. 44.