IV.A.4k Development of Reversible Hydrogen Storage Alane

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Introduction

Alane has a usable hydrogen weight fraction of 10% and a low enthalpy of reaction. The latter will require minimal heat exchange for both charge and discharge cycles. This material is thermodynamically unstable at near ambient conditions, requiring 10^5 bar of hydrogen pressure to achieve charging at temperatures from ambient to 150°C. It is, however, kinetically stable, having a proven shelf life well over twenty years. This project will utilize electrochemical potential to replace chemical fugacity as the thermodynamic driver to charge alane materials, allowing for its economical regeneration.

The Metal Hydride Center of Excellence, MHCoE, has the objective of developing a hydrogen storage system meeting DOE and commercial goals for powering either a fuel cell or internal combustion engine powered automobile. The solid state hydride engineering task will develop and utilize thermal, chemical and mass flow models to predict system operational performance. Performance parameters for various media will be used to design and predict system performance metrics. These metrics will be used to optimize system designs in preparation for the building, and testing of a prototype hydrogen storage system to validate system projections.

Approach

AlH_3 Charging

The objective of the alane project is to enable a low-cost rechargeable hydrogen storage material based on aluminum hydride, AlH_3, having a capacity of 10 wt%, cyclic stability and favorable thermodynamics and kinetics fulfilling the DOE onboard hydrogen transportation goals. The theoretical pressure required to regenerate spent alane is on the order of 10^5 bar, far in excess of what is readily achievable commercially. Hydrogen charging of metals has readily been accomplished through the utilization of electrical potential. The relatively low potential required to achieve high hydrogen potentials is illustrated in Faraday's equation as:

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

where E is the electrical potential, $\mathfrak{F}$, Faraday's constant and R & T have the usual meanings. From this calculation is can be clearly observed that the driving potential is only proportional to the logarithm of the hydrogen pressure, resulting in modest driving potential requirements.

This effort will demonstrate the electrolytic charging of alane and thus open the use of this material as an on-board hydrogen storage media. To do this, novel electrolytic cells will be designed and fabricated. The first of these is a moderate pressure cell operating at <100 bar and the second ambient pressure device. Following cell design and fabrication, a search for useful electrodes and solvents will be made. These are critical components which must transport both hydrogen ions and electrons between the electrodes in adequate supplies to prove commercially acceptable and not break down under the applied electrical potential. Once adequate electrode and electrolytes have been identified, operational windows will be established. Electrolyte concentrations and electrode deposition products will be analyzed utilizing x-ray diffraction and scanning electron microscopy (SEM) techniques. Optimized experimental conditions will be identified and projections made as to the commercial feasibility of this approach.

System Engineering

SRNL is leading the MHCoE task on Engineering Analysis, Design and Test. Coordination of the efforts of other MHCoE participants with engineering efforts is included in this effort. Specific SRNL technical activities include the development and use of modeling methods, both at the chemical, component and system level. Development of these models will be used to design optimized heat exchange systems and predict system performance. Other, non-media specific tasks include media scale-up development. These tools and techniques will be used to design, build and evaluate the next generation hydrogen storage system prototype based on new metal hydride compositions developed in the CoE.

Modeling tasks have included development of heat and mass transfer methods and models to design ultra-high gravimetric and volumetric density storage systems, development and utilization of both static and dynamic system models to design efficient proton exchange membrane fuel cells and internal combustion engine hydrogen fueled power generation systems, and development of media process techniques to achieve large batch kinetic and capacity goals.

Results

AlH_3 Charging

The design and fabrication of a high pressure electrolytic cell capable of 200 bar operation was completed. Electrode design and materials are under evaluation. Electrolyte solution and composition need to be selected to avoid electrolytic or thermal breakdown during operation. The initial run of the system led to very encouraging results with the deposition of aluminum dendrite on the cathode, see Figure 1. This is the result of reduction of aluminum from solution in the electrolyte. Safety and chemical handling procedures were established for the safe and efficient use of electrolytic devised with these materials.

Two ambient pressure electrolytic cell designs have been completed utilizing different electrolyte and electrode designs. Construction of one cell has been completed (see Figure 2) and the other is currently in process. Various electrode designs and materials are under evaluation. Electrolyte solution and composition will be selected to avoid electrolytic or thermal breakdown during operation. Safety and chemical handling procedures were established.

System Engineering

Baseline system models have been developed using ASPEN with conventional 5 & 10 ksi pressurized hydrogen tanks. These models will be compared with those including metal hydride tanks having various characteristics such as enthalpy of reaction, heat capacity, chemical kinetics etc. to evaluate the system level effects of these variables. With an understanding of the system dynamics, optimized systems configurations can be made to determine PEMFC system trade-off and gains afforded by solid state hydride system in comparison to gaseous and liquid systems.

Mass flow models in packed hydride beds have been analyzed leading to new bed design concepts.

Heat and mass transfer models have been created including chemical kinetics models to aid in heat transfer design. Alternative solid state hydride system designs have been conceptualized and are currently being modeled for both volumetric and gravimetric efficiency.

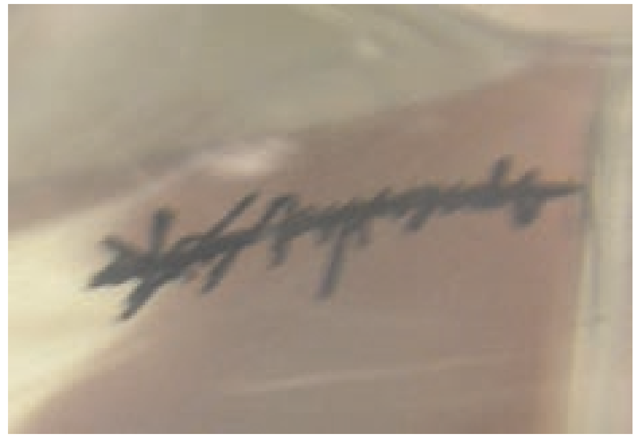

FIGURE 1. Preliminary Tests Resulted In Anode Dendrite Formation

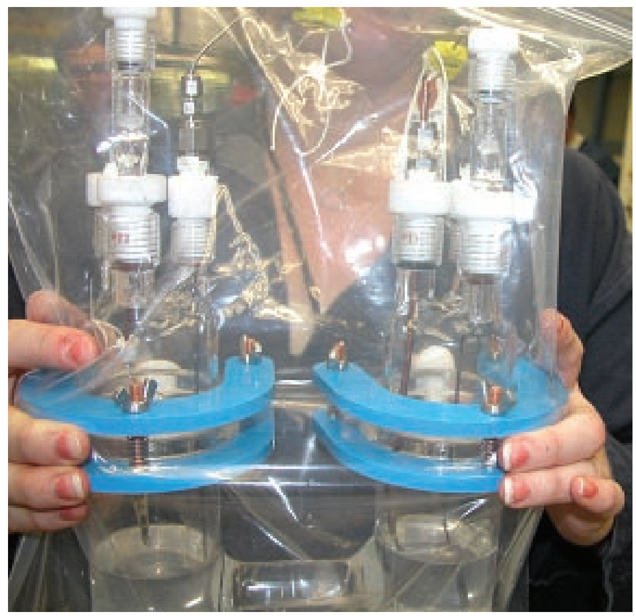

FIGURE 2. Ambient Pressure Electrolytic Cell Has Been Designed and Fabricated

To aid in system scale-up tasks which will be required if demonstration programs are to be initiated, large scale batch methods have been developed for the mechanico-chemical synthesis of catalyzed complex compound hydrides in 0.5 to 1 kg batches as shown in Figure 3. Kinetics have shown $TiCl_3$ catalyzed $NaAlH_4$ compositions to be comparable to those achieved in 1 to 2 gram batches via SPEX milling. Temperature control of the large-scale batches has been identified as a key variable in high energy processing and is required to achieve kinetically active media.

FIGURE 3. Attrition Mill Used to Synthesize 0.5 kg Batches of Complex Hydrides

Conclusions and Future Directions

AlH_3 Charging

Conclusions

Electrolytic charging of alane is still promising, but direct evidence of alane synthesis by this method has yet to be achieved. Numerous routes have been identified to achieve this demanding task, and multiple systems have been designed. Only very preliminary results have been achieved thus far.

Future Work

- Perform high-pressure cell testing utilizing various electrolytes and compositions to achieve electrolytic charging will be performed.
- Initiate ambient pressure cell testing utilizing various electrolytes and compositions to achieve electrolytic charging will be performed.
- Structural characterization and physical property analyses of both anode and cathode products to identify material purity and yield.
- Optimize cell performance to achieve efficient AlH_3 yield.
- Modify electrolytic charging parameters to yield alane having discharge kinetics sufficient to meet DOE 2010 targets.

System Engineering

Conclusions

The system engineering work is necessary, independent of media development. Methods and techniques need to be developed, and refined to predict system performance prior to subscale prototype development. This will minimize program cost and schedule delays in determination of optimum component and system design.

Future Work

Novel heat and mass transfer approaches will be modeled to minimize system mass and volume.

- Solid state hydrogen storage systems incorporating leading media candidates will be modeled and subscale units will be evaluated to determine system performance.
- New concepts in storage system design around regenerable AlH_3 will be developed and modeled to take advantage if its specific attributes.
- Hydrogen storage-internal combustion engine systems will be modeled to determine these system specific requirements.
- Initial automobile/fueling station models will be developed to account for the large heat load requirement during fueling.