

IV.A.3 High Density Hydrogen Storage System Demonstration Using NaAlH₄ Based Complex Compound Hydrides

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Subcontractors:

- Hydrogen Components Inc., Littleton, CO
- QuesTek, LLC, Evanston, IL
- Spencer Composites, LLC, Sacramento, CA
- Lyons Tool & Die, Meriden, CT

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End Date: March 31, 2007

Objectives

- Identify and address key engineering technologies for complex hydride storage systems.
- Model, design, fabricate and demonstrate two solid state hydrogen storage systems to determine realistic performance for NaAlH₄-based systems and to project performance of systems containing other hydride materials.
- Supporting objectives include:
 - Enhance NaAlH₄ charge/discharge rates through alternate catalysis and processing.
 - Determine the safety and risk factors associated with enhanced compositions.
 - Develop experimental and modeling capabilities for heat exchanger optimization.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage Technical Challenges section 3.3.4 of the Hydrogen, Fuel Cells

and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (H) Balance of Plant (BOP) Components
- (J) Thermal Management

Technical Targets

Results based on Prototype 2 for the most relevant technical targets are listed in Table 1. Comparison of Prototype 1 to Prototype 2 and comparison of as-fabricated to projected values for the gravimetric and volumetric targets are given in Table 2. Hydrogen pressure during the absorption was 100 bar and temperature during desorption was 150°C. From this information, we can see that significant improvements were made from Prototype 1 to Prototype 2, but the performance of a NaAlH₄-based complex hydride system is roughly 1/2 to 1/4 of what is desired for the 2007 targets.

TABLE 1. Technical Targets

Storage Parameter	Units	2007 Target	Prototype 2
System Gravimetric Capacity	kg H ₂ /kg system	0.045	0.020
System Volumetric Capacity	kg H ₂ /L system	0.036	0.020
System Fill Time	min	10	60
Minimum Full Flow Rate	(g/s)/kW	0.02	0.005
Safety		Meets codes & standards	Reactive material

TABLE 2. Comparison of Technical Targets for Prototype 1 versus 2 and for As-Fabricated versus Projected

Metric	Units	As-Fabricated		Projected	
		Prototype 1	Prototype 2	Prototype 1	Prototype 2
Gravimetric efficiency	kg H ₂ /kg system	0.14	0.515	0.48	0.60-0.63
Gravimetric density	% kg H ₂ /kg system	0.4%	2.0%	1.7%	2.3%
Powder density	g/cc	0.44	0.72	0.60	0.85
Volumetric density	Wh/L	200	700	600	800

Accomplishments

- Fabricated finned-tube heat exchanger and carbon fiber composite pressure vessel for Prototype 2. The design facilitated advanced powder loading methods, produced a lightweight pressure vessel and resulted in compact manifolding for the heat exchanger fluid.
- Developed system assembly hardware to conduct biaxial vibratory powder loading within a controlled atmosphere glove box.
- Achieved an average NaAlH_4 powder density within the finned heat exchanger for Prototype 2 of 0.72 g/cc compared with an average of 0.44 g/cc for Prototype 1. Identified ball milling procedures which result in improved powder densification up to 0.85 g/cc with enhanced vibratory methods.
- Tested and modeled operation of Prototype 2, which demonstrated that 60% gravimetric efficiency (improved from 48% with Prototype 1) and 75% volumetric efficiency are reasonable projections for a full scale system. Model comparisons indicated that hydrogen mass transfer may be restricted due to the high level of powder densification.
- Developed a procedure for neutralization of NaAlH_4 within a prototype vessel and applied this to the 19 kg of hydride within Prototype 1.



Introduction

As an early effort to accelerate the development of on-board rechargeable complex hydride-based hydrogen storage systems, this project has designed, fabricated and evaluated two prototype systems. During this development, new or reprioritized engineering hurdles differing from those of conventional metal hydride systems were identified, addressed and implemented. These include safety evaluation, materials catalysis, component optimization and system assembly. The storage material used in these demonstrations was NaAlH_4 , which was selected at the beginning of this effort as being the highest performing reversible complex hydride, having a theoretical hydrogen capacity of 5.5 wt% and a proven reversible capacity of over 3.5 wt% within anticipated operating conditions. Kinetics have been routinely measured within an order of magnitude of those required to meet charging and discharging goals. However, the design process and system hardware were sufficiently general for modification to accommodate other endothermically discharging hydrides with similar thermodynamics developed in the DOE Hydrogen Storage Program.

Approach

In order to design and build prototype systems, both materials and system level initiatives were conducted. The material efforts were performed in order to enable production and incorporation of active catalyzed media into the storage system and included: combined atomistic/thermodynamic modeling, standardized media kinetics test methodology development, evaluation of novel catalyst compositions, cyclic testing of the materials utilizing commercial purity hydrogen to assess degradation rates, large scale media synthesis to produce kilogram scale quantities of material for prototype fabrication and high density media packing to achieve improved volumetric performance.

System level efforts involved the design, fabrication and evaluation of two prototype systems and included: systematic safety studies performed to quantify the risks in large scale synthesis efforts and prototype operation, thermochemical finite element models developed to predict system performance under static and transient conditions, heat exchanger design optimization at both low length scales and for the full vessel cross section, system assembly methods developed to safely load and transport a 1 kg H_2 storage system and construction of a testing facility in order to evaluate full scale solid state hydrogen storage system performance.

Results

The second NaAlH_4 prototype was designed at nominally $(1/2)^3 = 1/8^{\text{th}}$ scale (or $1/8^{\text{th}}$ kg hydrogen) to reduce the level of resources needed for unique fabrication hardware while retaining the ability to demonstrate the technology and perform only moderate extrapolations for full scale system projections. The system was fabricated by first assembling the optimized finned tube heat exchanger constructed from 0.004" thick aluminum that is commonly used in low-cost systems such as residential air conditioners. With a spacing of 0.200", this produced a relative density of 2% aluminum compared with 4% for the aluminum foam used in Prototype 1. The reduction was possible due to the nominal factor of three improvement in long range heat conduction efficiency of fins compared with foam. As discussed below, this heat exchanger design was adequate to produce a tolerable temperature increase of 30°C during rehydriding. The fins were 4.5" in diameter and were formed with collars at the tubing interfaces to reduce thermal contact resistance and with corrugations in increase stiffness and strength. After testing for cyclic chemical compatibility, a coupling agent was applied to the prototype fin collar/tubing interface to secure the fin and reduce thermal contact resistance. The assembled heat exchanger is shown in Figure 1. Optimal locations for the eight heat exchanger tubes and the presence of a central filter for hydrogen exchange are shown in



FIGURE 1. Prototype 2 Optimized Finned Tube Heat Exchanger

Figure 3a. A filament wound carbon fiber composite pressure vessel was then constructed by Spencer Composites Corporation around the heat exchanger and proof tested at 1.5 times the working pressure of 103 bars (1,500 psi) or at 155 bars (2,250 psi).

Previously, powder densification methods were developed with smaller scale experiments involving 5 to 150 g of hydride. These methods were then increased in size to a biaxial shaker system for prototype loading as sketched in Figure 2. This shaker system was located within a 5' by 5' by 4' acrylic glove box which maintained an environment of better than 5 ppm oxygen during the powder loading operation. By applying the densification enhancement methods developed at the smaller scale, a total of 3.5 kg of hydride was loaded into the pre-constructed heat exchanger/vessel system with an average powder density of 0.72 g/cc. As listed in Table 2, this is a significant improvement over the 0.44 g/cc for Prototype 1.

The loaded system was transported to a testing facility that included a steel, secondary containment pressure vessel with a removable, flat cover to which the prototype was mounted. The system was then tested for absorption performance at 100 bars of hydrogen pressure and desorption at nominally 1 bar and 150°C. During testing, the hydrogen was introduced and removed in doses to facilitate accurate measurement. Temperatures were measured for four internal thermocouples, located in the vessel cross-section as

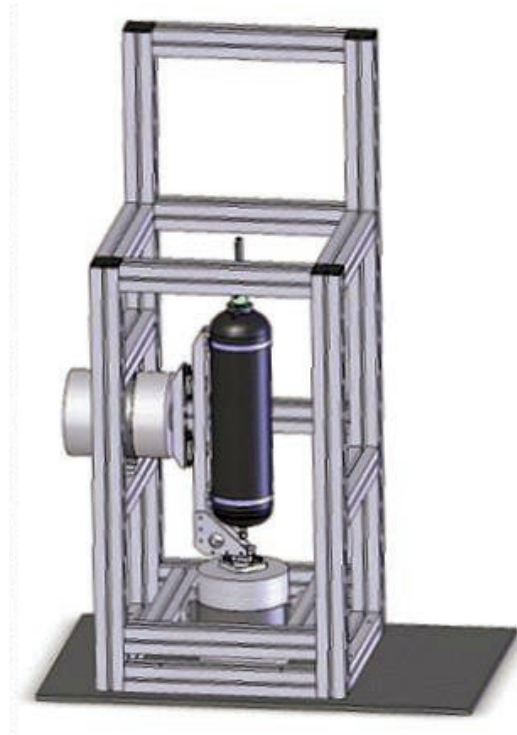


FIGURE 2. Apparatus for Biaxial Vibratory Loading of Hydride Powder

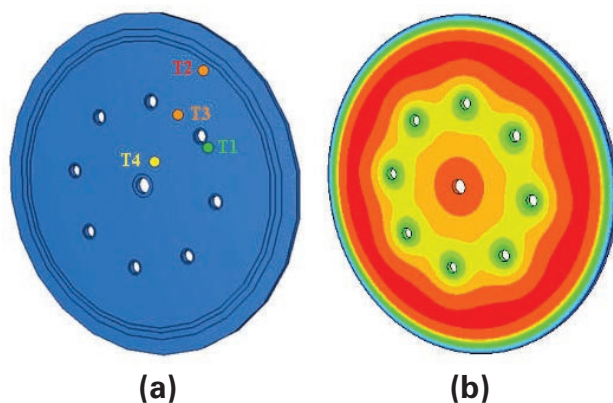


FIGURE 3. Prototype 2 FEA Cross-Section Model: (a) Solid Model and Thermocouple Locations; (b) Representative Temperature Contour during Refueling

given in Figure 3a for the plane positioned one-quarter of the way along the straight, cylindrical section of the vessel. Temperature data for an absorption test, including the circulated heat transfer oil inlet and exit are shown in Figure 4 along with simulation results.

Thermochemical finite element analysis (FEA) simulations using the ABAQUS code were conducted first by recalibrating the reaction kinetics model for the specific material used in the prototype. The associated data were obtained from Sievert's apparatus experiments on 1 g powder samples for pressures of 75 and 105 bars

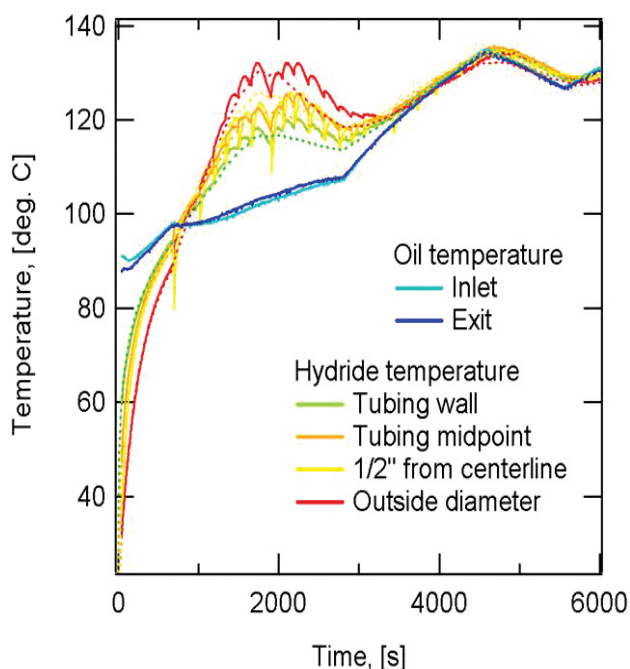


FIGURE 4. Temperature Data for an Absorption Test (Solid Lines) and Simulation Results for Reaction Kinetics Reduced by a Factor of Two (Dashed Lines)

and temperatures ranging from 60 to 180°C. Transient simulations were conducted using the inputs for the experimental hydrogen pressure and oil temperature histories. A representative temperature distribution is shown in Figure 3b. The results indicated that the simulated absorption occurred much more rapidly than experiment, with a higher hydride temperature rise of 60°C above the oil temperature compared with a measured value of 30°C. The simulated hydrogen mass flow rate for the initial linear section of the mass versus time curve also was twice that of experiment, but the ultimate capacity levels were nearly identical. The cause of this difference was hypothesized to be restricted mass flow due to the high level of powder packing. Mass transport had not been included in the NaAlH₄ modeling framework due to the material's slow kinetics, high system charging pressures and initially low powder packing densities. However, the results from the Prototype 2 testing, due to the success in powder loading, indicate mass transport should now be included. To mimic the effect, the reaction kinetics were reduced

by a factor of 1/2, producing the simulated temperature results shown in Figure 4. The hydrogen mass curve also was well matched, confirming consistency for the reaction enthalpies and thermal properties.

Methods to neutralize NaAlH₄ (in its discharged state) were developed using real time X-ray diffraction studies and experiments on increasingly larger quantities of material, starting with 10 g, then 25 g, 50 g, 1,000 g and finally with the ultimate application to Prototype 1 containing 19,000 g of hydride. In contrast to methods developed to neutralize hydride powder in an easily accessible container, the current approach can be used on storage systems in which the hydride is packed and unable to be easily manipulated.

Conclusions and Future Directions

- The project concluded technical research as of 3/31/07.
- Safety studies and neutralization efforts will be expanded in another contract, broadening the study of risk assessment and mitigation for a number of materials-based storage systems.

FY 2007 Publications/Presentations

1. D. Anton, D. Moshier, M. Fichtner, N. Kuriyama, R. Chahine and D. Dedrick, "Fundamental Safety Testing and Analysis of Hydrogen Storage Materials and Systems," submitted for publication in the Proceedings of the 2nd International Conference on Hydrogen Safety, San Sebastian, Spain, September 2007.
2. D. Moshier, S. Opalka, X. Tang, S. Arsenault and B. Laube, "Development and Application of New High Capacity Hydrogen Storage Materials," IEA Task 22 Meeting, Monterey, California, January 29, 2007.
3. M. Cao, S. Arsenault, and D. Moshier, "Preliminary Study on Nanometer-scale Gamma-aluminum Powder Densification Through Vibration," Proceedings of IMECE2006, 2006 ASME International Mechanical Engineering Congress and Exposition, November 5–10, 2006, Chicago, Illinois, USA.
4. D. Moshier, S. Arsenault, X. Tang and D. Anton, "Design, Fabrication and Testing of NaAlH₄ Based Hydrogen Storage Systems," MH2006 International Symposium on Metal-Hydrogen Systems, Lahaina, Maui, Hawaii, USA, October 1–6 2006.