

IV.A.1 High Density Hydrogen Storage System Demonstration Using NaAlH₄ Based Complex Compound Hydrides

Daniel A. Mosher (Primary Contact),
Xia Tang and Sarah Arsenault
United Technologies Research Center
411 Silver Lane
E. Hartford, CT 06108
Phone: (860) 610-7011; Fax: (860) 660-1284
E-mail: mosherda@utrc.utc.com

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

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

Contract Number: DE-FC36-02AL67610

Subcontractors:

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

Start Date: May 1, 2002
Projected 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 On-Board Hydrogen Storage section (3.3.4.2) 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

The development efforts are optimizing catalyzed NaAlH₄ performance to achieve high capacity and rapid kinetics with processing methods which can produce kilograms of material for prototype fabrication. System components are being designed and fabrication processes developed to minimize weight and volume. Charging rates are also addressed both with the material catalysis and heat exchanger optimization elements. The primary targets are listed in Table 1. Additional details and future projections are provided in Table 2.

TABLE 1. UTRC Progress Towards Meeting DOE On-Board Hydrogen Storage Targets

Storage Parameter	Units	2007 Target	Prototype 2 estimates
System Gravimetric Capacity	kg H ₂ / kg system	0.045	0.023
System Volumetric Capacity	kg H ₂ / L system	0.036	0.021
System Fill Time	min	10	30
Minimum Full Flow Rate	(g/s)/kW	0.02	0.005

Accomplishments

- Completed evaluation testing of the first prototype up to 25 cycles under a range of charge/discharge pressure and temperature conditions. Performed comparison of test data against model predictions.
- Developed alternative low-cost catalysts and demonstrated processing methods to produce kilogram level quantities of NaAlH₄ for the second prototype with a nominal absorption capacity of 3.5 wt% in 30 minutes.
- Conceived and constructed a powder densification apparatus to examine both fundamental consolidation of hydride powders as well as procedural development for loading system heat exchanger structures to densities between 0.65 and 0.75 g/cc for catalyzed NaAlH₄ with a nominal solid density of 1.3 g/cc.

TABLE 2. System Gravimetric and Volumetric Projections Estimated to Balance Demands on Storage Material and System Performance

Material & catalysis:		NaAlH ₄	NaAlH ₄	TBD	TBD	DOE Targets	
		TiCl ₃ /AlCl ₃	ultimate	hydride	hydride	2007	2010
Characteristics & Metrics	Units						
Material gravimetric capacity	% kg H ₂ / kg hydride	3.7%	5.4%	6.5%	8.0%		
H ₂ charging pressure	bar	100	100	70	50		
Packed powder density	kg hydride / m ³ powder	750	900	800	850		
Material volumetric capacity	kg H ₂ / m ³ powder	28	49	52	68		
System gravimetric efficiency	kg hydride / kg system	0.55	0.60	0.67	0.75		
System volumetric efficiency	m ³ powder / m ³ system	0.67	0.67	0.67	0.67		
Normalized compressed gas	% kg H ₂ gas / kg hydride	0.4%	0.3%	0.3%	0.2%		
System gravimetric capacity	% kg H ₂ / kg system	2.3%	3.4%	4.5%	6.1%	4.5%	6.0%
System volumetric capacity	kg H ₂ /m ³	20.7	34.3	36.2	46.5	36	45
	kWh / kg	0.8	1.1	1.5	2.0	1.5	2.0
	kWh / L	0.69	1.14	1.21	1.55	1.2	1.5

Notes

- a: Improved catalysts & processing
- b: Further powder packing improvements
- c: Pressure vessel liner improvement

- d: Materials discovery
- e: Reduction of charging pressure & vessel mass

- Designed the second storage system prototype at sub-scale including heat exchanger optimization, internal structures for powder loading, compact manifolding and assembly hardware to realize a >2.0 wt% NaAlH₄ system.

Introduction

As an early effort to accelerate the development of on-board rechargeable complex hydride-based hydrogen storage systems, this project will design, fabricate and evaluate two prototype systems. During this development, new or reprioritized engineering hurdles differing from those of conventional metal hydride systems will be identified, addressed and implemented. These include safety evaluation, materials catalysis, component optimization and system assembly. The initial storage material to be used in these demonstrations is NaAlH₄, 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 will be sufficiently general for modification to accommodate other endothermically discharging hydrides as they are 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 involve the design, fabrication and evaluation of two prototype systems and include: 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 H₂ storage system and construction of a testing facility in order to evaluate full-scale solid state hydrogen storage system performance.

Results

Testing of the first prototype, described in previous reports, was completed involving a total of 25 cycles conducted for the system containing 19 kg

of NaAlH_4 . Improvement in performance with cycling was noted to saturate at an ultimate hydrogen capacity of 0.45 kg at 100 bar. The first prototype served to identify the key technical challenges for such complex hydride-based systems including 1) scaled-up material catalysis and processing, 2) higher performance finned tube heat exchanger, 3) powder loading and densification compatible with prototype fabrication, and 4) lightweight domed composite vessel design with compact heat transfer fluid manifolding.

To address scaled-up material processing, the alternate catalyst form $\text{TiCl}_3 * 1/3 \text{AlCl}_3$ was evaluated for its substantially lower cost than TiCl_3 and potential performance improvement. Doping level evaluations were conducted first with gram-scale quantities using SPEX milling. Results indicated that a 3% level gave the best compromise of initial kinetics and capacity. Comparison with the standard 4% TiCl_3 revealed slightly superior absorption performance for $\text{TiCl}_3 * 1/3 \text{AlCl}_3$ but slower desorption kinetics. Processing was scaled up to 50 g batches of $\text{NaAlH}_4 + 3\% \text{TiCl}_3 * 1/3 \text{AlCl}_3$ using attrition milling. The performance was found to be comparable with that of the SPEX mill processing. Temperature dependence of the absorption for this material is given in Figure 1 along with the kinetics model of Ref [1] which was recalibrated to this data and shows good agreement. This model was used for heat exchanger optimization simulations and performance predictions.

The thermal conduction enhancement in the heat exchanger was changed from aluminum foam in the first prototype to fins for the second prototype. This latter approach has higher thermal performance, is more adaptable to advanced loading methods and would have substantially lower cost in high rate production. To optimize the finned heat exchanger design variables of

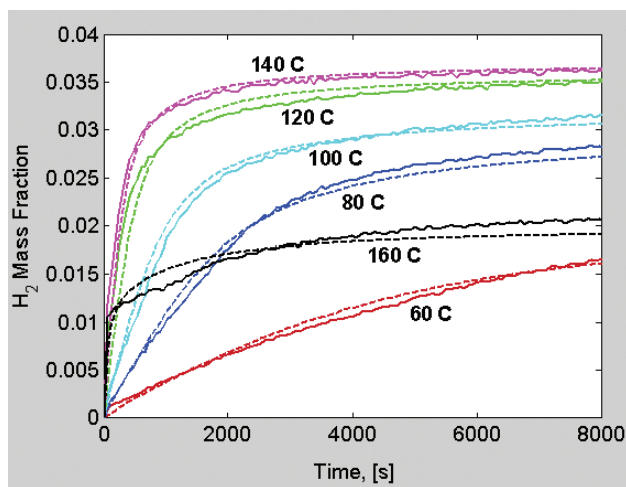


FIGURE 1. Absorption kinetics data (solid lines) and model (dashed lines) for $\text{NaAlH}_4 + 3\% \text{TiCl}_3 * 1/3 \text{AlCl}_3$ at 110 bar.

fin thickness, fin spacing, tubing diameter and tubing spacing, a novel methodology was developed using scripted finite element analysis of a low length scale fin unit cell which included variability of important parameters such as thermal contact resistance between the hydride powder and fin. Example results from this optimization procedure are given in Figure 2 in which each point represents a different set of design variables. Not only is there an optimal heat exchanger density, but also certain designs which make more effective use of the heat exchanger mass.

The system volumetric capacity depends directly on the ability to load and densify the hydride powder within the system's heat exchanger and pressure vessel. An apparatus has been developed for studying hydride powder fundamental settling behavior as well as the system loading procedure. In these experiments, vibratory displacements parallel and perpendicular to the densification axis are controlled independently. Methods of enhancing the powder densification have been developed that are compatible with fabrication of a lightweight composite vessel. Powder densities depend significantly on milling methods and densification conditions, varying from less than 0.6 g/cc to over 0.8 g/cc. Figure 3 shows a disassembled fin structure used to develop NaAlH_4 powder loading and densification procedures. Average densities of 0.66 g/cc have been achieved to date using non-optimal powders, and a value of over 0.70 g/cc is targeted for the second prototype.

In order to keep fabrication hardware to a reasonable size and capital investment, the second prototype has been scaled to contain approximately 3 kg of hydride. Detailed design of the second prototype components has been conducted including additional heat exchanger finite element simulations to optimize tube positioning. Figure 4 shows a model of the second prototype with its finned tube heat exchanger and two

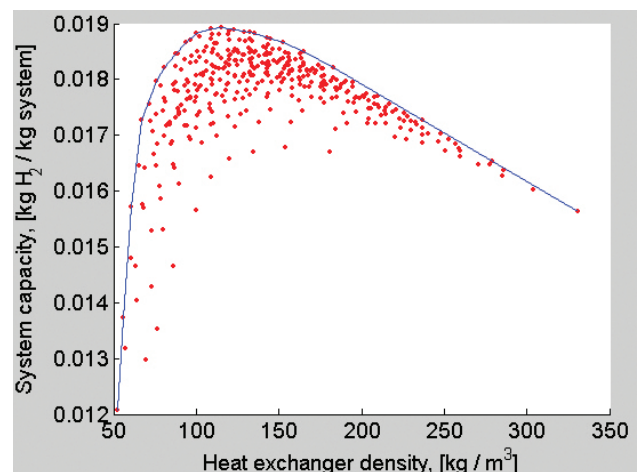


FIGURE 2. Heat exchanger optimization plot of system gravimetric capacity (without compressed gas component) for each design point.

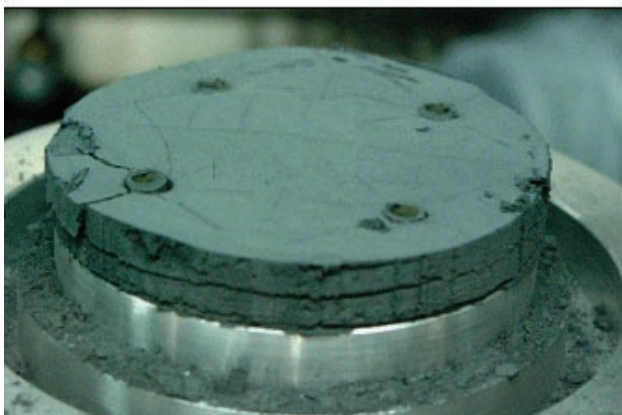


FIGURE 3. Filled fin structure which can be disassembled for developing powder loading techniques.

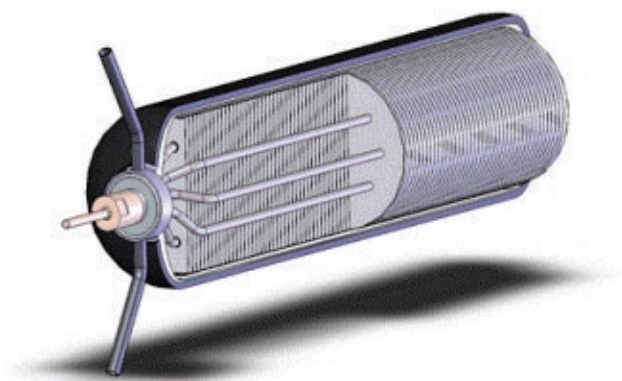


FIGURE 4. Sectioned model of the second prototype revealing the finned tube heat exchanger.

conventional domed ends for the carbon fiber composite vessel capable of 100 bar hydrogen charging pressure. To perform the powder loading process, a 4 ft by 5 ft by 5 ft glove box, high capacity vibratory shakers and other hardware have been developed for prototype assembly in the final quarter of FY 2006.

Conclusions and Future Directions

- Scaled-up material processing, heat exchanger advancements and powder loading procedures have been developed to improve predicted performance of the second NaAlH₄ prototype to nominally 2.0 wt% system gravimetric capacity.
- Future efforts will complete the fabrication and testing of the second prototype to demonstrate the developed technologies and provide guidance for projecting system performance of future enhancements to this class of on-board reversible, moderate pressure, complex hydride storage system.
- Safety studies initiated early in the project will be continued to evaluate the reactivity of catalyzed NaAlH₄ when exposed to ambient conditions and to develop neutralization procedures for storage systems.

FY 2006 Publications/Presentations

1. D. Mosher, DOE Annual Peer Review Meeting poster, May 18, 2006.
2. D. Mosher, "Complex Hydride Materials, Systems and Safety," IEA Task 17 / IPHE Joint Meeting, Windermere, UK, May 1-4, 2006.
3. D. Mosher, X. Tang and S. Arsenault, "Material Processing and Densification for Complex Hydride Based Storage Systems," MRS Spring Meeting, San Francisco, CA, April 17-21, 2006.
4. D. Anton, D. Mosher, F. Lynch and J. Senecal, "Risk Assessment of High Capacity Solid State Hydrides," TMS Annual Meeting, San Antonio, TX, March 13-16, 2006.
5. D. Mosher and S. Opalka, "Hydrogen Storage System Demonstration for a Fuel Cell Vehicle Base on NaAlH₄," IEA HIA Task 17 Workshop, Tateshina, Japan, October 23-27, 2005.

References

1. X. Tang, D. Mosher and D. Anton, "Practical Sorption Kinetics of TiCl₃ Catalyzed NaAlH₄," in *Materials and Technology for Hydrogen Storage and Generation*, Mater. Res. Soc. Symp. Proc. 884E, Warrendale, PA, 2005, GG4.4.