

Design, fabrication and testing of NaAlH₄ based hydrogen storage systems

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Received 30 September 2006; received in revised form 4 January 2007; accepted 5 January 2007

Available online 14 January 2007

Abstract

To complement the vigorous search for novel hydrogen storage materials, efforts focused on system implementation of candidate compounds are important parallel activities to identify new or reprioritized system challenges and assess overall performance. The current paper will discuss the design, fabrication and testing of on-board rechargeable storage systems based on the complex hydride NaAlH₄. Emphasis is placed on the system elements affected by the different material characteristics compared with conventional metal hydrides such as LaNi₅. Design aspects include reaction kinetics modeling, finite element analysis and heat exchanger optimization. Materials related fabrication challenges are discussed associated with catalysis processing and powder densification. Testing facilities and techniques to evaluate a full-scale vessel containing nearly 20 kg of NaAlH₄ also are covered.

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Keywords: Energy storage materials; Hydrides; Mechanochemical processing; Solid state reactions; Kinetics; Thermal analysis

1. Introduction

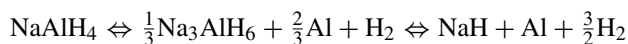
To accelerate the development of on-board rechargeable complex hydride based hydrogen storage systems, this research effort was initiated to design, fabrication and evaluate two prototype systems. The storage material used in these studies was NaAlH₄, selected as being the highest performing reversible complex hydride with a theoretical hydrogen capacity of 5.5 wt% and a proven reversible capacity of over 3.5 wt% under moderate charging pressures. During this development, specific material and system technical hurdles have been identified and addressed, which in many cases differ in character from those of conventional metal hydrides and systems. This paper addresses a range of topics associated with prototype system development including materials focused issues such as safety evaluations and effective compound/catalyst processing methods as well as system focused elements of component optimization, system assembly and evaluation. The design process and system hardware are sufficiently general for potential

accommodation of other, improved endothermically discharging hydrides as they are developed to meet higher performance system goals.

2. Prototype development

2.1. Material and system overview

From the material's perspective, the functions of the system components are to provide the necessary pressure and temperature conditions to drive the absorption and desorption reactions. The complex hydride NaAlH₄ has the advantage over conventional metal hydrides such as LaNi₅H₆ of a higher weight percentage of hydrogen stored, with the disadvantages of a two-step reaction,



slower reaction kinetics and the need for higher charging pressures of at least 100 bar. NaAlH₄ and other lightweight, complex hydrides are also low density, requiring greater volume for the pressure vessel. The higher pressure and greater volume both increase the mass of the pressure vessel and motivate the use of a carbon fiber reinforced epoxy composite material rather than

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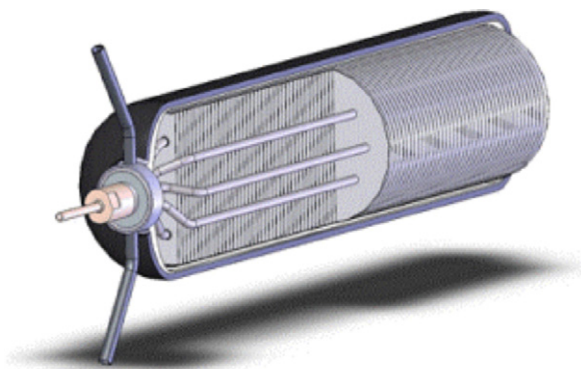


Fig. 1. Prototype 2 comprised of a carbon fiber composite vessel and finned tube heat exchanger.

a conventional stainless steel vessel. A sketch of the second-generation prototype is given in Fig. 1 showing a composite pressure vessel along with a finned tube heat exchanger to provide the needed temperature control. In addition to its low density of nominally 1.3 g/cc, NaAlH_4 also exerts low expansion forces upon hydriding [1] in contrast to LaNi_5H_6 , which reinforces the importance of improved powder densification as a focal point in the prototype development.

NaAlH_4 is also known to have greater reactivity with oxygen and water, which requires that all system fabrication be conducted within an inert gas glove box. It also necessitates the use of a non-reactive oil as the heat transfer liquid to mitigate the risk associated with a leak in the heat exchanger tubing. The design and fabrication activities identified these and other system technologies which were addressed, in part, with a first prototype and more completely with a second.

2.2. Material safety tests

Since portions of this research would require kilogram quantities of NaAlH_4 and involve the associated increased risks, the safety characteristics of this material after catalysis, were evaluated. Standardized tests for burn rate, spontaneous ignition, dangerous self-heating, water immersion and dust explosion were performed on material catalyzed with 2 mol% TiCl_3 in the hydrided, partially dehydrided and fully dehydrided states. The tests were conducted using the United Nations “Recommendations on the Transport of Dangerous Goods – Manual of Tests and Criteria” and the ASTM test methods 1226, 1491, 1515

and 2019 for dust explosion. Images of the burn rate and water immersion tests are shown in Fig. 2.

A condensed compilation of results is listed in Table 1. While the catalyzed material is not pyrophoric at 20 °C according to the standard test method, the intermediate hydride, Na_3AlH_6 , is pyrophoric at the potential system operation temperature of 80 °C. As with the uncatalyzed material, both compound states are classified as dangerous when wet, which is the most restrictive behavior when determining the packing classification for material transportation. From the dust explosion tests, the material is considered highly explosive in air when finely divided with a minimum ignition energy of less than 7 mJ, making static electricity a concern as an ignition source. The hydride particles do coarsen and agglomerate significantly with absorption/desorption cycling, motivating additional testing for cycled material. The primary conclusions resulting from these tests are: (1) a high purity environment must be maintained when working with these materials both in glove boxes and within prototype systems; (2) a non-reactive oil, rather than the more commonly used and higher performance water, must be used as the heat transfer fluid due to the severe consequence of a leak; (3) the ultimate application of storage systems on-board vehicles using this or other highly reactive hydride materials will require the evaluation of air exposure, contact with water and dust explosion scenarios as well as mitigation approaches and risk acceptance criteria.

2.3. Material catalysis, processing and modeling

Catalysis of complex hydrides for hydrogen storage applications, performed primarily via ball milling, results in the interdependency of a number of factors that affect system design and performance. From a system perspective, the catalyst type and processing conditions ultimately determine the temperature dependence of the material’s effective capacity (capacity after certain temperature/pressure/time cyclic conditions), particularly for absorption during refueling where rapid rates are desired. When constructing prototypes with kilograms to tens of kilograms of storage material, it is desirable to apply catalysts and processing methods, which are both economical and effective. Finally, the mechanical processing techniques will also have a strong influence on the ability to densify the powder through vibratory settling, as discussed below, which has a direct influence on the volumetric performance of the hydrogen storage material and system.

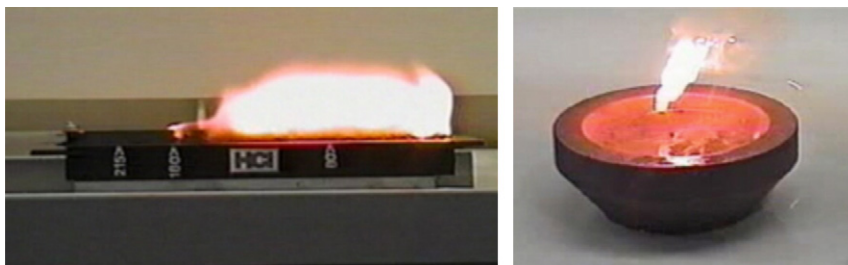


Fig. 2. Left: burn rate test; right: water immersion test.

Table 1
Subset of safety test results performed on NaAlH₄ catalyzed with 2 mol% TiCl₃ (pack Gp = packing group)

Test	Method	State A (NaAlH ₄)	State B (Na ₃ AlH ₆)	State C (NaH)
Burning rate, 20 °C	UN 33.2.1.4	51 mm/s	222 mm/s	27 mm/s
Burning rate, 80 °C	Note 1	127 mm/s	Spontaneous ignition	40 mm/s
Spontaneous ignition, 20 °C	UN 33.3.1.4	6 tries, not pyrophoric	6 tries, not pyrophoric	6 tries, not pyrophoric
Spontaneous ignition, 80 °C	Note 1	6 tries, no ignition	1 try, ignited	6 tries, no ignition
Dangerous when wet	UN 33.4.1	Yes, class 4.3, pack Gp 1	Yes, class 4.3, pack Gp 1	Yes, class 4.3, pack Gp 1
Min. Exp. Con., g/m ³	ASTM 1515	140		90
Minimum ignition energy, mJ	ASTM 2019	<7		<7

Note 1: variation from standard test to represent storage system operation.

The catalyst TiCl₃ has been demonstrated to provide reversibility of the NaAlH₄ reaction [2], and is widely considered the baseline catalyst with 4 mol% loadings being the most common for a balance of kinetics and ultimate capacity. However, the cost of this material has become significant for kilogram scale quantities of catalyzed NaAlH₄. One alternate catalyst form with significantly lower cost is TiF₃ which has been shown to possess nearly the same catalytic performance [3]. However, this similarity is dependent upon processing with small scale, high energy milling producing comparable catalysis while larger scale, lower energy processing using TiF₃ can result in decreased performance due to inferior incorporation of the Ti³⁺ cation. A second alternative catalyst form is the mixture TiCl₃·1/3AlCl₃ which has demonstrated superior absorption kinetics and moderately reduced desorption kinetics using both small scale (5 g batch) SPEX milling and larger scale (100 g batch) attrition milling [4]. The absorption performance of commercial purity NaAlH₄ with 3 mol% TiCl₃·1/3AlCl₃ processed using attrition milling (50 g batch size), is shown in Fig. 3.

In order to represent the thermochemical behavior of the material in finite element analyses for system design and evaluation, a reaction kinetics model has been developed that is described in [5]. The model is specified in rate form to be valid for arbitrary temperature and pressure histories that may occur when simulating a specific system test or transient operation sce-

nario. Comparison of the model with experimental data is also shown in Fig. 3.

2.4. Component optimization

2.4.1. Pressure vessel

The optimal charging pressure was determined based on the trade-off between material capacity and system mass. The material absorption capacity was measured experimentally using a Sievert's apparatus over a wide range of temperatures and pressures. For a temperature in the optimal range of 120 °C, additional absorption experiments were conducted over a wider range of pressures up to 200 bar. From these results, the pressure dependent material capacity was determined at a fixed time of 2 h after saturation had occurred for most pressures. Formulas for the pressure dependent system mass of the heat exchanger tubing and composite pressure vessel were determined and used along with other system component mass representations to calculate the overall system capacity of (kg H₂/kg system) as a function of pressure. The optimum system capacity occurred in the neighborhood of 100–140 bar, with the value of 100 bar being selected for prototyping due to the desire to keep pressures low.

2.4.2. Heat exchanger

The heat exchanger for this class of hydrogen storage system is comprised of tubing passes that are connected by conduction enhancement to facilitate heat transfer, since the thermal conductivity of NaAlH₄ and other hydrogen storage powders is low. Thermal conductivity can vary with conditions such as particle geometry, packing density and hydrogen pressure. We have measured typical values of 0.5 W/(m °C), which is in general agreement with [6]. The heat transfer process can be divided into three stages: (1) short range heat transport through the hydride layer or cell to the conduction enhancement; (2) long range transport along the conduction enhancement to the tubing; (3) and convection from the tubing to the heat transfer liquid.

The conduction enhancement used in our first prototype was an open celled aluminum foam. This approach has the advantage of small cell sizes to facilitate stage 1 short range conduction, good strength even for low relative densities on the order of 4% and fabrication convenience for specific system designs. However, foam also has the disadvantage that its effective or

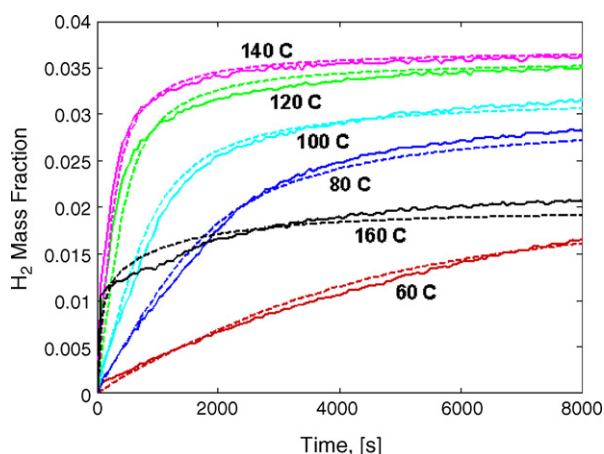


Fig. 3. Absorption data (solid lines) and model of [5] (dashed lines) for NaAlH₄ + 3% TiCl₃·1/3AlCl₃ under 100 bar of hydrogen pressure.

homogenized thermal conductivity associated with stage 2 long range transport for an isotropic foam is nominally

$$k_{\text{foam}} \approx \frac{\rho_{\text{rel}} k_{\text{solid}}}{3}$$

Intuitively, the factor of 1/3 arises because on average only 1/3 of the cell struts are aligned parallel to the heat flux vector, which is oriented radially when near the tubing. The remaining 2/3 of the conduction enhancement material participates in short range transport only. Additional disadvantages are high cost and lack of flexibility in tailoring to minimize contact resistance with the tubing or to facilitate powder densification as discussed below.

The second prototype utilized a finned tube design to improve upon the disadvantages listed for aluminum foam, with the challenge now shifted to fabricate the heat exchanger with fine length scales to minimize thermal resistances for short range conduction. In order to optimize the heat exchanger design involving tubing diameter, tube spacing, fin thickness and fin spacing, a modeling framework was developed which made use of low length scale finite element simulations of a single fin unit cell. With a focus on the challenging rapid vehicle refueling step and assuming the system begins recharging at an operational temperature of nominally 80 °C, the behavior can be approximated reasonably as steady state, greatly simplifying the analyses. The tube/fin/hydride structure was modeled as a two dimensional, axisymmetric domain including thermal contact resistances between the tube & fin and between the fin & hydride. Variabilities in thermal properties were also included to estimate the temperature distribution for the entire system's hydride as an ensemble average for a collection of unit cells. By conducting over 3000 automated simulations, an optimal set of design variables for tubing diameter, tubing spacing, fin thickness and fin spacing was determined. Results and a unit cell thermal contour plot are shown in Fig. 4. These detailed analyses were also used to develop a simplified thermal model for inclusion in an analysis framework given in [7] to estimate optimized system performance from material data of different hydrides without the need for system design decisions.

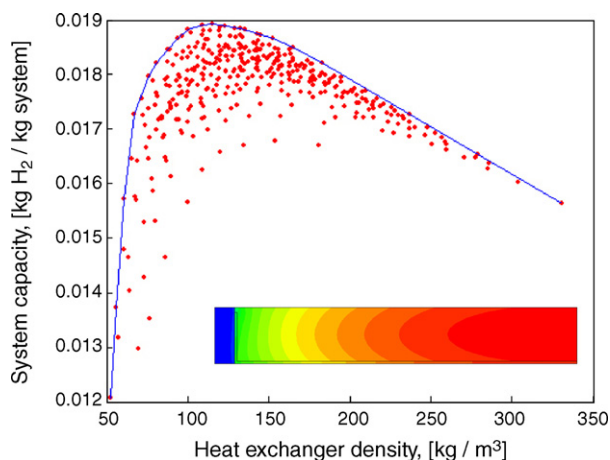


Fig. 4. Heat exchanger optimization of the second prototype. Inset is a temperature contour for a single fin unit cell model.

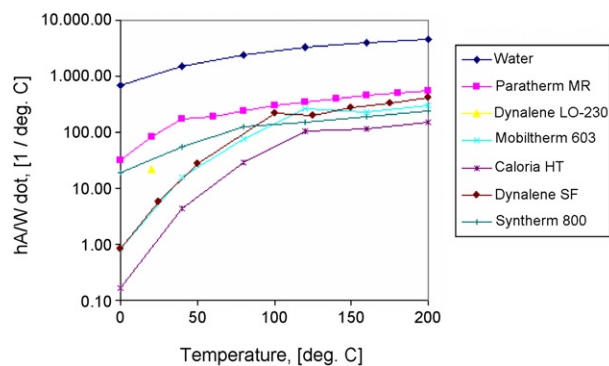


Fig. 5. Figure of merit, η_h , for selection of heat transfer oil.

2.4.3. Heat transfer fluid

Because of the safety risks due to potential leaks in the heat exchanger tubing, the use of water as a heat transfer fluid was excluded. A number of non-reactive oils were considered as replacements. Since oils, in general, have significantly lower heat transfer capability, a figure of merit termed the *convection efficiency* was developed to rank prospective oil candidates and was defined as the ratio of convective heat transfer rate divided by the fluid pumping power. Based on accepted formulas for flow and heat transfer within tubes [8], the convection efficiency, denoted as η_h , was derived and expressed as factors involving oil properties (ρ = density, k = thermal conductivity, c_p = specific heat and μ = viscosity) and other variables (D_h = hydraulic diameter and V = velocity),

$$\begin{aligned} \eta_h &= \frac{hA}{\dot{W}} = \frac{\text{heat transfer per degree}}{\text{pumping power}} \\ &= 0.582 \times \left(\frac{\rho^{0.05} k^{0.65} c_p^{0.35}}{\mu^{0.70}} \right) \left(\frac{D_h^{0.05}}{V^{1.95}} \right) \end{aligned}$$

A plot of the convection efficiency for water and the oil candidates is given in Fig. 5 for a liquid velocity of 1 m/s and hydraulic diameter of 1 cm. From this analysis, the oil Paratherm MR was selected for prototype testing.

2.5. Powder densification

NaAlH_4 has a low solid density (1.3 g/cc theoretical) and low powder relative density (nominally 30% before packing or settling) for an overall material density of 0.39 g/cc, increasing the importance of powder densification. The densification methods must not damage the lightweight and moderately fragile heat exchange structure. In addition, the composite pressure vessel resin is cured at 200 °C, which essentially requires that the powder be loaded after vessel construction. A filling procedure has been developed for the second prototype that obtained moderately high hydride powder densities of over 0.7 g/cc within a finned heat exchanger structure contained inside the composite vessel. This process uses biaxial vibration and other methods to enhance loading of the system. To support procedure development, an apparatus was constructed to study the densification of a column of powder and examine the more

Table 2
Densification results in [g/cc] for NaAlH₄ powder with different ball milling processing

	Milling method A	Milling method B	Milling method C
Original density	0.46	0.32	0.50
Vibratory settling	0.74	0.47	0.63
Enhanced densification	0.75	0.63	0.84

fundamental aspects of the material consolidation. Through this, mechanical processing of the material was determined not only to affect the reaction kinetics as described above, but also the ability to densify the powder. Representative results are listed in Table 2 giving variability due to milling method in the range of 15–40% for the powder density and related hydrogen storage volumetric performance.

2.6. System assembly and testing

Because the systems must be loaded with hydride and undergo final assembly in an oxygen and water vapor free environment, this poses restrictions and additional challenges on the approaches used. For the first prototype, constructed at full-scale, two glove boxes were connected together, the first being used to load the hydride powder into 5 cm thick aluminum foam disks. The system vessel penetrated through the floor of a second glove box in which the foam disks were pressed onto the heat exchanger tubing and down into the vessel. A total of 19 kg of catalyzed NaAlH₄ was loaded in this manner into the first prototype. The second prototype was designed to contain approximately 3 kg of NaAlH₄ and has been fabricated within a larger 1.3 m × 1.6 m × 1.6 m glove box in which the entire prototype can be vibrated for loading of the hydride powder.

To conduct safe system testing, the first prototype was placed within a containment vessel as shown in Fig. 6 and experiments were performed inside of a test cell with reinforced

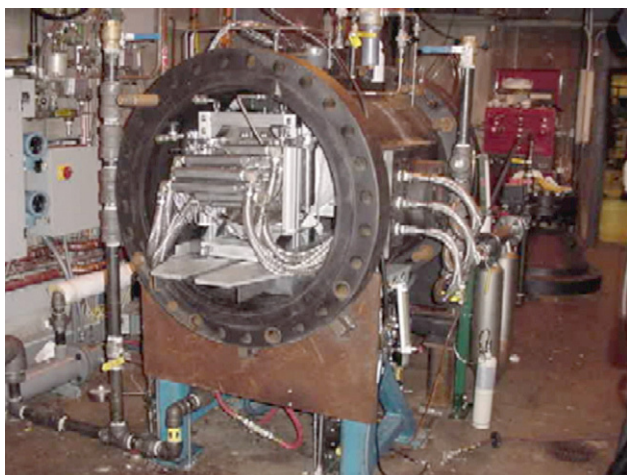


Fig. 6. First NaAlH₄ prototype installed within a containment vessel that is located in a remote controlled testing cell.

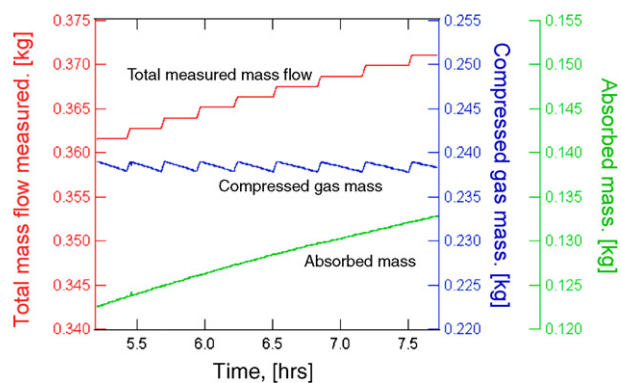


Fig. 7. “Burst flow” testing technique to improve flow meter accuracy which produces a smooth absorbed mass curve.

concrete walls and remote control of all functions. Hydrogen measurements of total mass flow into or out of the system were made using a Coriolis force flow meter. The amount of hydrogen exchanged in the absorption or desorption reactions was calculated by subtracting the amount of hydrogen present as compressed gas, determined from pressure and temperature data, as well as measurements of the free volume. In contrast to most Sievert’s devices, the majority of the compressed gas volume was within the void space of the hydride powder. From data analysis, the difference in free volume for the hydrided versus dehydride states could be determined (33 l versus 34.5 l). In order to improve the accuracy of the Coriolis force flow meter at low flow rates, a method was devised in which valves to the system were closed and opened based on pressure measurements to produce bursts of flow while maintaining a nominally constant pressure during the test. Example data using this technique are shown in Fig. 7 in which the saw-tooth shaped compressed gas trace is subtracted from the stepped total mass data, resulting in a smooth absorbed mass curve. The system was evaluated under static charging and discharging conditions, with initial tests indicating increasing kinetics and capacity over cycling. A total of 25 cycles were completed with an ultimate system capacity of 0.45 kg H₂ for the first prototype.

Assembly of the second prototype has recently been performed with successful powder loading, leading to an increase in average hydride density from 0.44 g/cc for the first prototype to 0.72 g/cc for the second system. Based on initial tests with desorption occurring at 150 °C, the NaAlH₄ system gravimetric capacity and volumetric density were measured to be 2.0 wt% and 21 kg/m³, respectively.

3. Conclusions

With the current level of activity searching for high performance hydrogen storage compounds, companion efforts examining their incorporation into complete systems are beneficial not only to demonstrate overall performance, but also to identify critical systems technologies that have greater importance for new classes of storage materials. The current paper has presented a range of technical elements associated with the development of prototypes based on the complex hydride

NaAlH₄. In addition to safety and component optimization, powder densification compatible with heat exchanger and composite vessel fabrication is of particular importance. The gravimetric capacity of 2.0 wt% falls short of 4.5 wt% and greater viability targets motivating the need for higher capacity materials as well as system designs and fabrication techniques that are optimized to the material's particular characteristics and properties.

Acknowledgements

Support for this effort was provided by the U.S. Department of Energy under contract DE-FC36-02AL67610 with the guidance of C. Read, J. Adams and S. Satyapal. Partners in the project include Frank Lynch of Hydrogen Components, Inc., Brian Spencer of Spencer Composites Corporation and Will Lyons of Lyons Tool and Die. The contributions of R. Brown, S. Saitta, R. Dold and M. Cao are gratefully acknowledged.

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