

### III.C.3 High Density Hydrogen Storage System Prototype Using NaAlH<sub>4</sub> Based Complex Compound Hydrides

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#### Objectives

- Improve the charging and discharging rates of the NaAlH<sub>4</sub> based hydrogen storage medium
- Determine the safety and risk factors associated with the enhanced compositions
- Design, develop and evaluate a hydrogen storage system having a 5-kg hydrogen capacity and installation capability in a fuel cell powered mid-size sedan

#### Technical Barriers

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

- B. Weight & Volume
- D. Durability
- E. Refueling Time
- M. Hydrogen Capacity and Reversibility

#### Approach

- Create combined atomistic/thermodynamic models of the NaAlH<sub>4</sub> system to determine catalyzed compositional ranges, sorption mechanisms, and the effects various catalyst additions have on these mechanisms.
- Cyclically evaluate selected complex compound hydride (CCH) compositions to determine degradation mechanisms and ameliorations as well as compatibility with construction materials.
- Conduct standardized safety testing related to the classification of hazardous materials.
- Develop preliminary designs through the evaluation of existing systems, generation of weight/volume/cost improvements, and high-level optimization to balance automotive demands.
- Perform heat and mass flow modeling for detailed optimization of the required system volume, mass and hydrogen sorption characteristics. Evaluate methods to enhance heat conduction into the CCH powder.
- Fabricate and evaluate 1-kg H<sub>2</sub> and 5-kg H<sub>2</sub> capacity hydrogen supply systems.

- Conduct preliminary system performance modeling analyses of the combined proton exchange membrane fuel cell (PEMFC)/H<sub>2</sub> storage system under steady state and transient conditions to establish system optimization and dynamic control requirements.

### Accomplishments

- Combined atomistic and thermodynamic modeling has been used to predict dopant lattice site locations and plateau pressure changes as a function of dopant and composition in both NaAlH<sub>4</sub> and Na<sub>3</sub>AlH<sub>6</sub>.
- Completed safety experiments resulting in no change in transportation packing class for these materials from their unmodified condition and identified these materials as being highly explosive in the finely divided and dispersed form.
- The hydrogen desorption and absorption kinetics for five alanate compositions has been experimentally determined under a wide range of temperature and pressure conditions. These results were used to determine a composition to be used in the 1-kg H<sub>2</sub> prototype.
- Final design and selection of construction materials based on volume, mass and cost estimates for a 1-kg H<sub>2</sub> storage system prototype have been completed.
- Completed synthesis of 25 kg of catalyzed media matching small batch kinetics.
- System components have been fabricated and assembly is in progress.
- A hydrogen storage system testing facility has been designed and installed to evaluate the 1-kg H<sub>2</sub> system being constructed.
- Initiated cell stack, balance of plant, and storage system modeling efforts with baseline system masses, volumes and operating conditions established.

### Future Directions

- Complete assembly of the first 1-kg H<sub>2</sub> storage system designated CCHSS#1.
- Evaluate CCHSS#1 under static and dynamic operating conditions.
- Continue characterization of alternately catalyzed NaAlH<sub>4</sub> media composition to identify optimum composition.
- Initiate design of second version of a 1-kg H<sub>2</sub> system capable of meeting DOE 2005 gravimetric and volumetric goals.

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### Introduction

One of the most significant barriers to the widespread application of hydrogen based propulsion is the development of on-board storage systems which can provide the needed quantity of hydrogen with acceptable volume, weight, cost, and safety risk. The major classes of established hydrogen storage methods – compressed gas, liquid, metal hydrides and chemical hydrides – all have advantages and disadvantages, but none is clearly superior for automotive transportation. Many chemical hydride materials, while having high capacities, are classified as irreversible, which requires that the entire material

be replaced during refueling rather than simply charging with hydrogen gas. The current project is focusing on the reversible chemical hydride, NaAlH<sub>4</sub>, with a theoretical hydrogen capacity of 5.5 wt%, and seeks to enhance the material for improved charging and discharging rates as well as increased capacity. Safety studies of the enhanced material will also be conducted to support the technology as it is driven toward commercialization. Additionally, the system developed here is designed to be altered to accommodate any other *in-situ* reversible hydride which may be developed having a higher gravimetric hydrogen storage density.

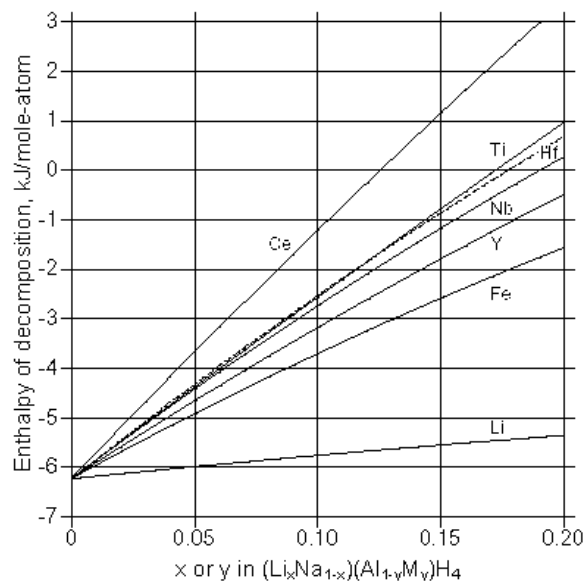
## Approach

This project seeks to apply  $\text{NaAlH}_4$  in the development of a system which will reversibly store a high wt% of hydrogen at low pressure for an indefinite amount of time. The storage system, which contains the CCH powder, must serve two primary functions: (1) exchange heat between the powder and a working liquid to drive the absorption/desorption of hydrogen; (2) support elevated hydrogen pressure during refueling. These functions must be performed with a minimum of weight, volume and cost. Secondly, the system should (i) allow for significant volumetric change of the powder, (ii) exchange hydrogen without the loss of the fine CCH powder particles, (iii) maintain chemical compatibility with the CCH powder and hydrogen, (iv) produce minimal impurities going to the PEMFC, and (v) fit into a conformable volume.

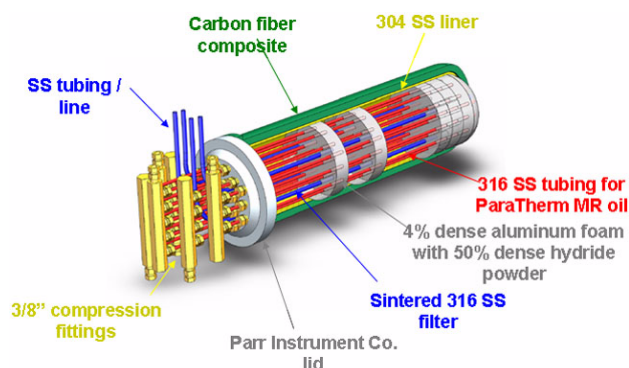
## Results

Atomistic models were created utilizing VASP (Vienna Ab-initio Simulation Package) for  $\text{NaAlH}_4$ ,  $\text{Na}_3\text{AlH}_6$  and  $\text{NaH}$  using known lattice parameters and atomic occupation sites. Full volume and site relaxations were allowed with resulting structures nearly identically replicating literature values. Catalyst substitutions of  $\text{Ti}^{+3}$ ,  $\text{V}^{+3}$ ,  $\text{Zr}^{+4}$ ,  $\text{Ce}^{+3}$ ,  $\text{Hf}^{+4}$ ,  $\text{Nb}^{+4}$ ,  $\text{Y}^{+3}$ ,  $\text{Fe}^{+3}$  and  $\text{Li}^{+1}$  were made in both the  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$  structures with transition metal substitution for  $\text{Al}^{+3}$  cations and alkaline metal substitutions for  $\text{Na}^{+1}$  cations showing the highest atomic activities for  $\text{Ce}^{+3}$ ,  $\text{Ti}^{+3}$  and  $\text{Hf}^{+4}$  respectively (see Figure 1).

A series of experiments were concluded to measure the reactivity of the catalyzed CCH media in the finely divided and dispersed form. Experimental details were taken from ASTM E1226, E 1515, E2019, and E1491 Dust Explosion Testing. Tests were conducted in two materials states: fully charged—primarily  $\text{NaAlH}_4$ , and fully discharged, composed of  $\text{NaH}$  and  $\text{Al}^0$  powders. All ignition tests were conducted in a sealed chamber in air and were instrumented to measure pressure and temperature rises. The results of these tests identified that these compounds are highly explosive in comparison to standards of coal dust and lycopodium spores.

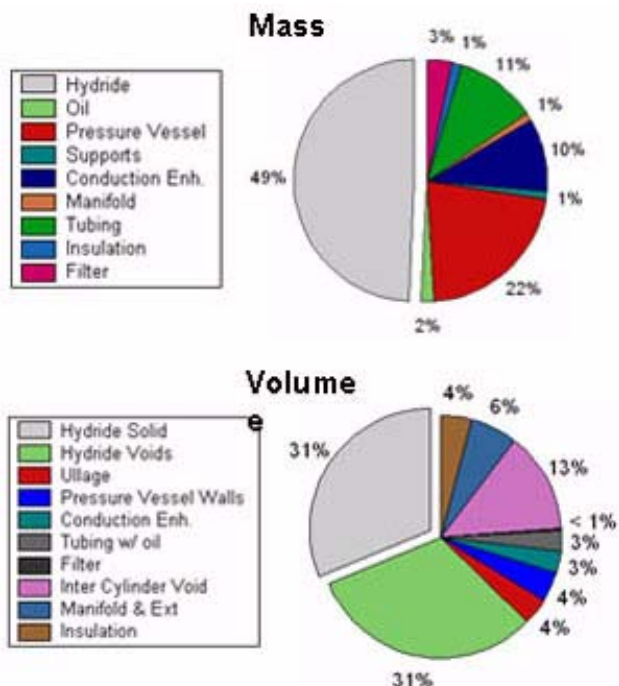


**Figure 1.** Results of Combined Atomistic and Thermodynamic Modeling Showing Relative Changes in Enthalpy of Decomposition for  $\text{NaAlH}_4$  Doped with Various Concentrations of Cations



**Figure 2.** Cut-away View of 1-kg  $\text{H}_2$  Storage System, CCHSS#1

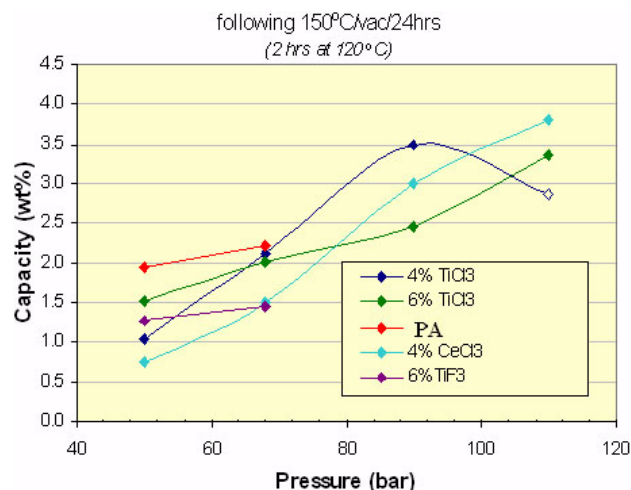
The primary elements of the  $\text{NaAlH}_4$  based hydrogen storage system are shown in Figure 2. Due to the high pressures in the range of 70 to 100 atm required for acceptable charging kinetics, a carbon fiber composite vessel has been designed and fabricated. Powder densification is a particular challenge for  $\text{NaAlH}_4$  compared with conventional metal hydrides such as  $\text{LaNi}_5$ . It is also of great importance since  $\text{NaAlH}_4$  has a reversible hydrogen density that is approximately half that of  $\text{LaNi}_5$ .



**Figure 3.** Masses and Volumes of Prototype 5-kg H<sub>2</sub> System Based on Current CCHSS#1 Design

To facilitate the densification as well as glove box assembly, a fully open end will be used in this first prototype, also allowing post-test inspection. During assembly, metal foam disks are first filled with powder and then installed onto stainless steel tubing. Hydrogen lines and particulate filters are also present.

The updated gravimetric and volumetric component system percentages are shown in Figure 3. The underlying calculations are based on a charging pressure of 70 atm, media with 4 weight percent capacity and 50% powder relative density. A system of five cylinders holding nominally 1 kg of hydrogen each was used, which affects elements such as the inter-cylinder void volume. The mass of the pressure vessel does not contain the heavy stainless steel lid, but rather is a projection for the next generation prototype having two partially open end bosses. The tubing and conduction enhancement (metal foam) have been optimized for a 15 minute refueling time and 1% parasitic loss associated with pumping power, resulting in 24 tube passes of 3/8" diameter tubing and 4% dense aluminum foam.



**Figure 4.** Isothermal Charging Results after 2 Hours at 120°C

An extensive characterization was completed for a number of catalyst compositions in NaAlH<sub>4</sub>. This characterization consisted of three phases: (i) Isobaric Absorption at 80, 100, 120 & 140°C/68 bar following 150°C/vacuum/24 hr desorption; (ii) Isobaric Desorption at 70, 80, 90, 100, 110, & 120°C/1 bar following 120°C/68 bar/16 hr absorption; and (iii) Isothermal Absorption at 120°C/50, 68, 90 & 110 bar H<sub>2</sub> pressure after 150°C/vacuum/24 hr desorption. The catalyst compositions evaluated under these tests were 6% TiCl<sub>3</sub>, 4% TiCl<sub>3</sub>, 4% CeCl<sub>3</sub>, 6% TiF<sub>3</sub> and finally a proprietary catalyst composition denoted PA.

The results of the Isobaric Absorption tests showed the highest recharging rates were observed for 6% TiCl<sub>3</sub> and PA compositions occurring at ~100°C. These rates reflect an ~1 hr full 5 kg charging time, one order of magnitude lower than that required for a 5 min. recharging time. The compositions PA, 4 & 6% TiCl<sub>3</sub> held the highest discharge rates under isobaric discharge testing, increasing linearly with 1/T. The CeCl<sub>3</sub> and TiF<sub>3</sub> compositions displayed desorption rates approximately 1/5 that of the former group. Isothermal Absorption test results given as capacity vs. charging pressure are displayed in Figure 4. The capacity was determined as the wt% of H<sub>2</sub> absorbed after two hours of charging. All compositions charged more hydrogen with increasing pressure up to a maximum of 3.7 wt% at 110 bar.

## **Conclusions**

Numerous experiments were carried out on catalyzed  $\text{NaAlH}_4$  in various phases of decomposition. The results indicate these materials to be flammable when in contact with water or water vapor in the air. The partially discharged material containing a mixture of  $\text{Na}_3\text{AlH}_6$  and aluminum powder was found to be somewhat more reactive than the fully charged material, but in all cases, the packing classification did not change.

Significant advances have been made in modeling of the media utilizing a combination of atomistic and thermodynamic methods which has proven to be state-of-the-art in its methodology and enlightening in its results. If the catalytic additions can be made to stay within the host structure upon repeated sorption cycles, the full 5.5 wt% of hydrogen should be accessible at pressures above 1 bar.

Kinetic modeling of a new catalyst type with associated processing methods, denoted as PA here, holds promise of lowering the charging pressure while increasing charging and discharging rates.

System designs have been completed and projections made as to the gravimetric and volumetric density of CCHSS#1. It is projected that improvements to the current catalyst compositions and system designs will be required to meet future DOE goals.

## **FY 2004 Publications/Presentations**

1. D.A. Moser, *High Density Hydrogen Storage System Development*, IEA Task XVII, Fall 2003, Hawaii.
2. Z. Dardas, *High Density Hydrogen Storage System Development*, IEA Task XV, Fall 2003, Miami Beach, FL.
3. D.L. Anton and C. Reade, "A Review of On-Board Hydrogen Storage Alternatives for Fuel Cell Powered Automotive Applications," (a comparison of solid hydride storage methods), National Hydrogen Association Annual Meeting, Los Angeles, CA, April 26-30, 2004.
4. D.L. Anton, *Hydrogen Desorption Kinetics in Transition Metal Modified  $\text{NaAlH}_4$* , *J. Alloys & Compounds*, 356-357, pp. 400-4 (2003).
5. S.M. Opalka and D.L. Anton, *First Principles Study of Sodium-Aluminum-Hydrogen Phases*, *J. Alloys & Compounds*, 356-357, pp. 486-9 (2003).
6. C. Qiu, G.B. Olsen, S.M. Opalka & D.L. Anton, A Thermodynamic Assessment of the Al-H System, in press.
7. S.M. Opalka & O.M. Lovvik, "Bulk Hydrogen Diffusion within Undoped and Titanium-Doped Sodium Alane," Hydrogen-Metal Systems Gordon Research Conference, Waterville, ME, July 13-18, 2003.
8. O.M. Lovvik and S.M. Opalka, "Calculation of Hydrogen Mobility near the Surface of Doped and Undoped  $\text{NaAlH}_4$ ," Hydrogen-Metal Systems Gordon Research Conference, Waterville, ME, July 13-18, 2003.
9. O.M. Lovvik, S.M. Opalka, H.W. Brinks and B.C. Hauback, *Crystal Structure and Thermodynamic Stability of the Lithium Alanes  $\text{LiAlH}_4$  and  $\text{Li}_3\text{AlH}_6$* , *Phys. Rev. B* **69**, 134117 (2004).
10. C. Qiu, G.B. Olson, S. Opalka and D.L. Anton, *A Thermodynamic Evaluation of the Al-H System*, submitted to *J. of Phase Equilibria and Diffusion*.
11. O.M. Lovvik and S.M. Opalka, *Density Functional Calculations of  $\text{NaAlH}_4$  with Added Ti*, submitted to *Phys. Rev. B*.