VI.A.2 High Density Hydrogen Storage System Demonstration Using $NaAlH_4$ Based Complex Compound Hydrides

Donald L. Anton (Primary Contact) and D.A. Mosher
United Technologies Research Center
411 Silver Lane
E. Hartford, CT 06108
Phone: (860) 610-7174; Fax: (860) 610-7253; E-mail: antondl@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

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QuesTek, LLC, Evanston, IL
Spencer Composites LLC, Sacramento, CA

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Objectives

- Optimize the charging and discharging rates of $NaAlH_4$.
- Determine the safety and risk factors associated with the enhanced compositions.
- Design, develop and demonstrate two solid state hydrogen storage systems having a 1 kg hydrogen. capacity

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:

- A. Cost
- B. Weight and Volume
- D. Durability
- E. Refueling Time
- M. Hydrogen Capacity and Reversibility
- O. Test Protocols and Evaluation Facilities
- Q. Thermal Management

Technical Targets

This project is optimizing catalyzed $NaAlH_4$ for performance and designing a system to initially utilize this material, but is easily reconfigurable to utilize any endothermically desorbing solid state hydrogen storage

media. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage systems that meet the 2010 hydrogen storage targets, especially specific energy, and energy density, charging time, minimum full flow rate, system fill time, transient response and storage system cost.

Approach

- Fabricate components and assemble the first prototype of a 1 kg H_2 capable solid state hydrogen storage system.
- Complete full-scale solid state hydrogen storage system evaluation facility.
- Develop high throughput media catalization method and synthesize 30 kg of 6m% TiF_3 catalyzed $NaAlH_4$.
- Develop a method for packing the media into aluminum foam disks in the highest density possible.
- Evaluate first 1 kg H_2 system prototype.

Accomplishments

- An effective large scale media synthesis was identified as critical in achieving target sorption goals and methods were developed to meet this requirement.
- High density media packing was identified as critical in achieving target volumetric goals and methods were developed to meet this requirement.
- The first prototype 1 kg H_2 storage system, Complex Compound Hydrogen Storage System (CCHSS) #1, has been safely assembled.
- A state-of-the-art full-scale hydrogen storage system testing facility has been completed to evaluate full-scale hydrogen storage systems.
- Performance characteristics of CCHSS#1 have been determined under static charging and discharging conditions after cycling.
- Initiated cell stack, balance of plant (BoP), storage system modeling efforts with base line system masses, volumes and operating conditions established.
- Projections were made and given in Table 1, based on CCHSS#1 performance, as to both fundamental and engineering design requirements to meet DOE 2007, 2010 and 2015 goals.
- A preliminary design has been completed for the 2nd prototype 1 kg H_2 system, CCHSS#2.

Future Directions

- Complete assembly of the first 1 kg H_2 hydrogen storage system designated CCHSS#1.
- Complete evaluation of CCHSS#1 following cyclic exposure under static operating conditions.
- Complete design of a second prototype storage system, CCHSS#2, having improved gravimetric and volumetric efficiencies.
- Characterize alternate media compositions to identify optimum sorption performance for introduction into CCHSS#2.
- Identify system filling techniques to obtain maximum media density within the heat exchange geometry.

Introduction

In a concerted effort to accelerate the development and demonstration of a solid state *in-situ* rechargeable hydrogen storage system, this project will design and develop two prototype systems and evaluate their performance. In designing, building and evaluating two near full-scale systems, all of the engineering hurdles which need to be overcome will be fully realized. The initial storage material to be used in these demonstrations is catalyzed $NaAlH_4$, but the system will be capable of rapid modification to accommodate any other endothermically discharging

hydride. Sodium alanate was selected as being currently the highest performing reversible chemical hydride, having a theoretical hydrogen capacity of 5.5wt% and a proven capacity of 3.5wt% within anticipated operating conditions. Kinetics have been routinely measured within an order of magnitude of those required to meet charging and discharging goals.

In order to design and build prototype systems, both materials and system level initiatives were instituted. The material efforts were initiated in order to facilitate introduction of active catalyzed media into the storage system and included: combined atomistic/thermodynamic models used to accurately predict the efficacy of numerous catalyst additions, a standardized media kinetics test methodology formulated to evaluate the kinetics of various catalyst compositions to gain a full understanding of the materials capabilities and limitations, cycling of the material utilizing commercial purity hydrogen elucidated contaminant degradation mechanisms, large scale media synthesis identified as a critical requirement in achieving system sorption goals, and high density media packing identified as a critical requirement in achieving volumetric goals.

System level efforts were instituted to aid in the design, fabrication and evaluation of the prototype systems and included: systematic safety studies performed to quantify the risks to be encountered in both design and large scale synthesis efforts, system level models made to predict the interaction of the fuel system with a full-scale automotive polymer electrolyte membrane fuel cell system to establish the system level trade offs in weight, volume and performance, kinetic and thermal models developed to predict system performance under static and transient conditions, heat exchanger design optimization utilizing a systematic convex-hull approach, system assembly methods developed to safely load and transport a 1 kg H_2 storage system, and a testing facility constructed in order to safely evaluate full-scale solid state hydrogen storage systems performance under static and transient operating conditions.

Results

System

Construction of the first full-scale prototype, CCHSS#1, has been completed safely. A cut-away solid model of this system is shown in Figure 1. This design incorporated 24 stainless steel tubes embedded in 4wt% aluminum foam for enhanced thermal conductivity. All assembly was completed under an inert gas cover in a glove box as depicted in Figure 2. The final prototype was filled with 19 kg of catalyzed $NaAlH_4$. After fabrication, CCHSS#1 was moved into the recently completed system evaluation test facility which incorporated controlled and measured hydrogen flow to pressures of 150 bar, controlled heating and cooling via a closed-loop oil flow with controlled temperatures from ambient to 200C. Figure 3 illustrates this facility with CCHSS#1 installed, oil manifold outward, in its secondary containment prior to sealing for evaluation.

Initial testing was conducted under static charging and discharging conditions. Continual increased performance was observed during charging experiments, indicating continuing incorporation of the catalyst into the media. To achieve optimum performance, 20 charge/discharge cycles were given to the system. The system will be tested in the coming year for final performance characteristics.

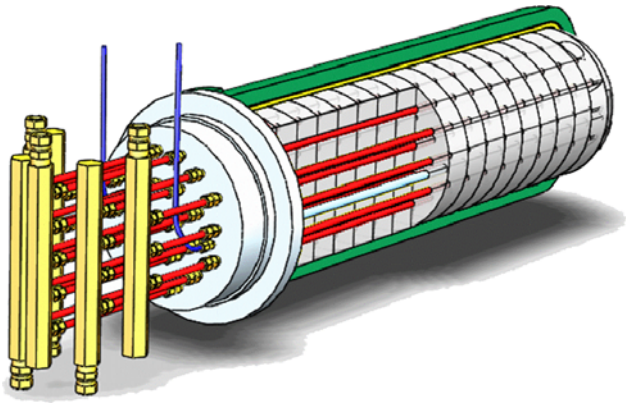

Figure 1. Cut-away solid model of CCHSS#1 utilizing a tube-foam heat exchange design incorporated in an open end configuration which allows the easiest loading of both heat exchanger and media.

Figure 2. Dual glove box assembly used to fabricate CCHSS#1. The left hand glove box was used to fill the foam disks while the right hand box served as the loading station for the vessel which is mounted vertically and required an electrically driven press to drive the foam disks over the stainless steel tubes.

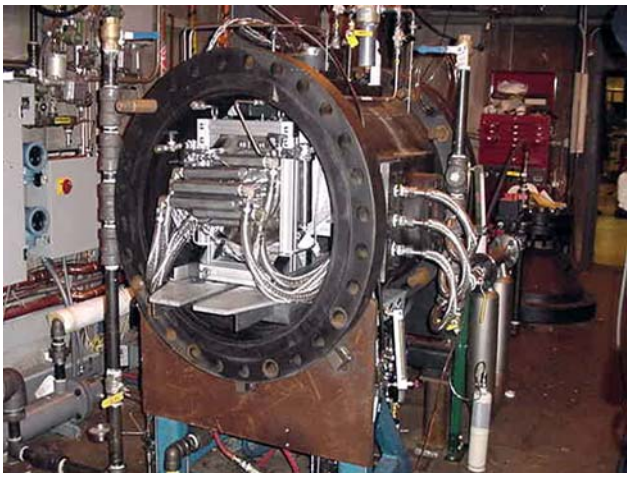

Figure 3. Full-scale hydrogen storage system evaluation facility with CCHSS#1 inserted into secondary inert gas containment. The facility is capable of controlled temperature and pressure testing of full-scale hydrogen storage systems.

Table 1 gives actual and projected system gravimetric and volumetric densities based on practical experience in building CCHSS#1. The actual gravimetric density achieved for CCHSS#1 is 0.4 wt%. This included all of the extended safety factors as well as the massive flat stainless steel head used to facilitate media loading. The ultimate embodiment of a 100 bar pressure vessel would include a dual hemispherical head arrangement to minimize system mass. After appropriate modifications are taken to account for a dual hemispherical enclosure, elimination of excess safety factors beyond ASME Pressure Vessel Code Section X requirements, incorporation of the best powder packing method and optimized coolant manifolding,

Table 1. CCHSS#1 & 2 Design Parameters Along With Projected Requirements to Meet DOE 2007 and 2010 Goals

Solid State Hydrogen Storage System Performance Metrics

United Technologies

D.L. Anton

	Symbol	units	CCHSS #1.0	CCHSS #1.1a	CCHSS #1.1b	CCHSS #2	CCHSS #3	CCHSS #4	CCHSS #5	CCHSS #6	DoE 2007 Goal	DoE 2010 Goal	DoE 2015 Goal
	Media		$NaAlH_4$ 6%TiF_3	$NaAlH_4$ 4%$TiCl_3$	NaAlH4 enhanced	NaAlH4 enhanced	NaAlH4 advanced	NaAlH4 ultimate					
Media Gravimetric Density	$\Box^m_g$	wt%	0.025	0.035	0.04	0.04	0.05	0.054	0.065	0.075			
System Gravimetric Density	$\Box^s_g$	wt%	0.4%	1.7%	1.9%	2.2%	3.0%	3.5%	4.5%	6.0%	4.5%	6.0%	9.0%
	$\Box^s_g$	kWh/kg	0.1	0.6	0.6	0.7	1.0	1.2	1.5	2.0	1.5	2.0	3.0
System Volumetric Density	$\Box^s_v$	kgH_2/m^3	9.4	17.2	19.6	24.3	32.9	37.1	46	53	36	45	81
	$\Box^s_v$	kWh/l	0.31	0.57	0.65	0.81	1.09	1.24	1.53	1.77	1.2	1.5	2.7
Gravimetric Engineering Efficeincy	E^g_f		0.14	0.48	0.48	0.55	0.60	0.65	0.69	0.80			
Volumetric Engineering Efficiency	E^v_f		0.62	0.65	0.65	0.67	0.67	0.67	0.67	0.67			
Powder Packing Density	$\Box^m_p$		0.40	0.50	0.50	0.60	0.65	0.68	0.7	0.7			
	system parameters												
	media parameters												

Increase Gravimetric Efficency 34 pts.
Two hemespherical ends
Eliminate excess factors of safety
Best large scale powder packing achieved
Increase media gravimetrics 0.01wt%
Increase Volumetric Efficiency 3 pts
Optimize Manifold

Increased media gravimetrics 0.005wt%

Increase gravimetric efficiency 7 pts.
Tube/Fin HX
Increase powder packing 10 pts.
Increase volumetric efficency 2 pts.
Compact external manifold

Increase gravimetric efficiency 5 pts.
Increased media gravimetrics 0.01wt%
Increase powder packing 5 pts.

Increase gravimetric efficiency 4 pts.
Increased media gravimetrics 0.04wt%
Increase powder packing 3 pts.

Increase Gravimetric Efficiency 4 pts.
Increase media gravimetrics 0.011wt%
Decrease charging pressure to 70 bar
Increase media packing 2 pts.

Increase Gravimetric Efficiency 11 pts.
Increase media gravimetrics 0.01wt%
Decrease charging pressure to 50 bar

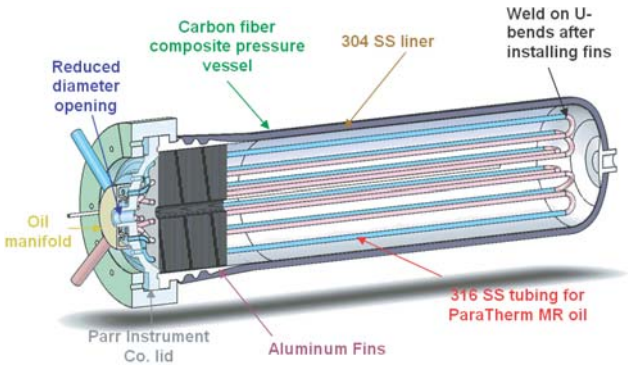

Figure 4. Cut-away solid model of 2nd generation solid state hydride storage system utilizing a tube/fin heat exchange design incorporated in a dual hemispherical end configuration which will allow for the highest hydrogen capacity in a 100 bar system. (Only the first section of fins is shown for clarity.)

a gravimetric density of 1.7 wt% is projected. Via incorporation of a 4% media, this density can be increased to 1.9%. The goal of the 2nd prototype is to increase gravimetric capacity by 7 points through enhanced heat exchanger design and increased powder packing density in addition to increasing volumetric efficiency 2 points through optimized manifolding, yields a system gravimetric density of 2.2%. To reach a 3% gravimetric density, gravimetric efficiency needs to be increased by 5 points through increased media gravimetric capacity and increased powder packing. Subsequent iterations to system densities of 3.5, 4.5 and 6 wt% are also given with required technical advances. The two overriding technical hurdles are media gravimetric density and media packing density.

In order to achieve projected performance, one critical obstacle is the incorporation of a dual hemispherical domed containment. This geometry requires prefabrication and installation of the heat exchange system into the pressure vessel prior to curing. The high temperature cure of 250°C makes the preloading of the media impractical for safety reasons. The media must thus be packed after system assembly. To utilize the 2nd one end open tank previously purchased, a preliminary design for CCHSS#2 has been developed and is pictorially given in Figure 4. This design incorporates a tub/fin heat exchanger and will be filled through a small, 1-1.5" opening in one end to approximate the requirement for a two-end closed design.

Media

Due primarily to cost considerations, a media composition of 6%TiF_3 catalyzed $NaAlH_4$ was used as the hydrogen storage media for CCHSS#1. Investigations were conducted as to the best method of producing 30kg of this composition in a timely manner. Tumble milling and power milling in 0.5 kilogram batches were employed and kinetic studies performed on resulting materials. Power milling was identified as the best approach, however, resulting kinetics were inferior to those achieved in 3 gram batch SPEX milling which incorporates a higher energy attrition methodology. Extensive studies into the thermodynamics and kinetics of TiF_3 incorporation into $NaAlH_4$ showed sluggish incorporation due to reduced thermodynamic driving forces which are overcome in SPEX milling, but which power milling only partially completes.

The utilization of $TiCl_3$*1/3$AlCl_3$ as a catalyst for $NaAlH_4$ has subsequently been identified as having better kinetics and capacity performance than TiF_3. $TiCl_3$*1/3$AlCl_3$ is readily available at a much lower price than both $TiCl_3$ and TiF_3. Therefore $TiCl_3$*1/3 $AlCl_3$ will be considered as the catalyst precursor for this second prototype if $NaAlH_4$ is utilized. Experiments are under way to optimize catalyst doping level.

Due to the irregular geometry of the finned heat exchanger, a solvent assisted media loading method is currently under development. The current achievable packing density is 46-50% for milled $NaAlH_4$. The milled $NaAlH_4$ has much better hydrogen storage performance than the dehydrided materials after extensive agitation with nonreactive fluids. This is due to component separation of dehydrided materials. Fluid assisted infiltration will be used in loading the fully hydrided media, even though the dehydrided materials have a high density and possibly higher volumetric density.

Conclusions

$NaAlH_4$ has a wide charging operational temperature range facilitating heat transfer design. Full-scale solid state hydrogen storage systems based on catalyzed $NaAlH_4$ can be safely built and evaluated. Powder packing density of nano particulates is an important requirement for

achieving high gravimetric and volumetric hydrogen storage density. High energy/high throughput mechanico-chemical processing needs to be developed in order to achieve the performance requirements needed for successful commercial application.

FY 2005 Publications/Presentations

1. C. Qiu, S. M. Opalka, G. B. Olson, and D. L. Anton, "The Na-H System: from First Principles Calculations to Thermodynamic Modeling," submitted to Phys. Rev. B.
2. O. M. Lovvik and S. M. Opalka, "First-Principles Calculations of Ti-Enhanced $NaAlH_4$," Phys. Rev. B 71 054103-1-10 (2005).
3. C. Qiu, G. B. Olson, S. M. Opalka and D. L. Anton, "A Thermodynamic Evaluation of the Al-H System," J. of Phase Equilibria and Diffusion 25(6) 520-527 (2004).
4. Xia Tang, D. A. Mosher and D. L. Anton, "Practical Sorption Kinetics of $TiCl_3$ doped $NaAlH_4$" Materials Research Society Spring Meeting, San Francisco, California, March 28 to April 1, 2005.
5. D. A. Mosher and D. L. Anton, "Beyond Weight Percent – The Influence of Material Characteristics on Hydrogen Storage System Performance," Materials Research Society Spring Meeting, San Francisco, California, March 28 to April 1, 2005.
6. C. Qiu, S. M. Opalka, D. L. Anton, G. B. Olson, "Thermodynamic Modeling of Sodium Alanates," Materials Science & Technology 2005 to be held in Pittsburgh, PA, September 25-28, 2005.
7. O. M. Løvvik and S. M. Opalka, "First-Principles Calculations of Ti-Enhanced $NaAlH_4$." Presentation at the International Symposium of Metal Hydrogen Systems (MH2004), Krakow, Poland, September 10, 2004.