Hydrogen Storage Systems Analysis Working Group Meeting

Argonne National Laboratory DC Offices
955 L'Enfant Plaza, North, SW, Suite 6000
Washington, DC

December 12, 2006

SUMMARY REPORT

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Meeting Objectives

This meeting was one of a continuing series of biannual meetings of this Working Group. The objective of these meetings is to bring together the DOE research community involved in systems analysis of hydrogen storage materials and processes for information exchange and to update the researchers on related developments within the DOE program. A major thrust of these meetings is to leverage expertise, complement related work of different individuals and groups, and facilitate communication of storage related analysis activities. This Working Group typically meets twice a year (once in conjunction with the DOE Annual Hydrogen Program Review in May and for a second time in November/December at an appropriate venue).

Summary of Presentations

The meeting agenda is shown in Appendix A. The meeting participants are shown in Appendix B.

After introductory remarks by Sunita Satyapal (DOE) and Romesh Kumar (ANL), Don Anton and Bruce Hardy (SRNL) discussed engineering analyses of metal hydride storage at both the component and system level. Bob Bowman (JPL) described the planned work on evaluating the performance of candidate materials using their well-characterized experimental test beds that they have developed for reversible gas applications. Dan Mosher (UTRC) then discussed the second prototype sodium alanate system they are developing that offers significant reductions in system weight and volume compared to the first prototype. Philip Parilla (NREL) described the approach of the carbon Center of Excellence in designing materials with a compact scaffold, a high density of binding sites, and optimized hydrogen binding energies. Matt Ringer (NREL) and Steve Lasher (TIAX) discussed the use of H2A methodology for the analysis of advanced hydrogen storage systems, using the sodium borohydride system as a case study. Chris Aardahl (PNNL) summarized recent experimental studies and modeling analyses to determine the stability of solid ammonia borane for hydrogen storage. Rajesh Ahluwalia (ANL) discussed the results of analyzing four different options for sodium borohydride regeneration with FCHTool to evaluate the energy efficiencies of the sodium borohydride system over the well-to-engine life cycle for hydrogen storage.

These discussions and the presentations at the meeting are summarized below.

Overview of Hydrogen Storage Systems Research at Savannah River National Laboratory
(Don Anton and Bruce Hardy, SRNL)

Based on the operating conditions and targets established by DOE, the Engineering Analysis, Design, and Test (EADT) group at Savannah River National Laboratory has identified key parameters for the modeling of metal hydride-based hydrogen storage systems. The modeling is conducted at two levels of detail: a detailed model at the component level, including physical processes and kinetics, and an overall system model for the hydrogen fuel cell vehicle. Recent work on advanced cooling concepts, such as permeation cooling, and tank designs, such as conformal strut tanks, was discussed. The transport and chemical reaction kinetics equations used in the hydride bed model and the model parameters and geometry were presented. The model is flexible in that the parameters, as well as the form of the governing equations, can be readily modified to fit material properties or alternative tank designs. A preliminary evaluation of hydride formation in a sodium alanate bed indicated that even after 360 s, large areas of the bed would not be hydrided due to the relatively slow reaction kinetics of this material.

For the hydride vessel, SRNL has tested two materials: a graphite-reinforced epoxy composite (GREC), and stainless steel Type 316. Test results show that the gravimetric hydrogen storage density with GREC is higher than that with stainless steel and peaks at ~450 bar. These results are based on preliminary structural calculations, using a failure criteria derived for a GREC vessel. Only limited design formulas for such vessels are available, however, and those equations have major shortcomings. Because of the deficiencies in the existing design formulas, a set of three equations was derived for use as a design guide. This new design methodology will be published in an upcoming ASME paper.

A baseline automotive fuel cell system model has been completed. In future collaborative work with Argonne, accurate models will be developed for fuel cell operation integrated with the hydride system. An initial automobile/fueling station model will be developed to account for the rather large heat load management that will be required during vehicle fueling. Other future work will include the design and structural analysis of conformable tanks and continued development of heat and mass transfer models.

Prototype Hydride Storage Bed Analysis, Design, and Testing at Jet Propulsion Laboratory
(Bob Bowman, JPL)

The objectives of the work at JPL are to support the development of lighter weight and thermally efficient hydride storage vessels and to experimentally demonstrate their compatibility with the appropriate hydride materials. They will evaluate the performance of candidate materials using well-characterized experimental test beds over multiple cycles of hydrogen adsorption and desorption. Their analyses to date indicate that there are no viable candidate materials with a reversible hydrogen storage weight capacity greater than 2–3 wt% that can operate within the temperature range of polymer electrolyte fuel cell systems. Materials based on AB_2, AB_5, or other interstitial alloys can operate in the desired temperature range, but because of the heavy elements in them, their hydrogen storage capacities are generally less than 2 wt% just for the material itself.

A literature review of modeling approaches for hydride storage beds is being conducted with the metal hydride Center of Excellence and UTRC researchers to investigate input requirements and analysis methodologies for reversible gas applications, including hydrogen fuel storage, heat pumps, compressors, and sorption cryo-coolers. The emphasis is on modeling sorption and desorption behavior, including heat transfer, for predicting thermodynamic and kinetic parameters as well as comparing with laboratory tests. The models developed at JPL for sorption cryo-coolers using hydride beds have been validated, and the researchers have been able to predict the beds' thermal performance. It should be possible to adapt these models to different hydrides and to the integrated operation of sorbent beds and fuel cell systems.

High-Density Hydrogen Storage System Demonstration Using $NaAlH_4$ Complex Compound Hydrides at United Technologies Research Center

(Dan Mosher, UTRC)

Researchers at UTRC are working on a second, sub-scale sodium alanate prototype. The projected improvements over the first prototype are lighter weight composite vessels, lighter weight finned tube heat exchangers, and denser powder packing to improve both gravimetric and volumetric hydrogen storage densities.

Testing was conducted using a modified Sievert's apparatus. Low temperatures were observed due to slow kinetics during the adsorption phase. Results of the test indicate a gravimetric hydrogen storage capacity of 0.020 g of H_2/g system and a volumetric capacity of 0.021 g/cc of system volume (the 2007 DOE targets are 0.06 g of H_2/g and 0.036 g of H_2/cc). Just over half of the system weight was due to the hydrogen storage media, while the encasing vessel weight was ~10% of the total system weight. The discharge temperature of the system was 150°C. Only one cycling test had been conducted with this system.

Modeling the system for scale-up indicated that the gravimetric capacity of a full-scale vessel (an order of magnitude larger than the prototype) would be 3.4 wt% based on the active material and 2.3 wt% for the total system. Most of the improvement over the first prototype was due to the use of fins with the heat exchanger tubes.

It is recognized that sodium alanate is not a serious contender for the automotive on-board hydrogen storage application. It is a useful developmental material, however, in identifying and prioritizing issues in potential new hydrogen storage technologies, as well as in understanding specific reversibility mechanisms.

Carbon-Based Hydrogen Storage Research at National Renewable Energy Laboratory

(Philip Parilla, NREL)

At the carbon Center of Excellence, theoretical analyses are being used to help identify materials with better hydrogen storage properties, but the engineering characteristics of many materials are still unknown. The materials and approaches being investigated include:

- metal-organic frameworks with tailored nano-spaces, which have shown record hydrogen absorption capacities of ~7 wt% at 77 K and 60 bar;
- hybridization and boron-doping to improve binding energies;
- transition metals on carbon to exploit theoretically promising material storage properties;
- hydrogen storage via spillover, where the hydrogen dissociates at the metal doping sites and migrates to the substrate; and
- combined hydrogen binding and spillover.

In summary, the approach of the carbon Center of Excellence is based on designing materials with a compact scaffold, a high density of binding sites, and optimizing the hydrogen binding energy. A number of new materials have been designed that, theoretically, offer improved hydrogen storage properties. Experimental efforts are continuing to synthesize new carbon-based compounds for hydrogen storage. Temperature-programmed desorption tests of some of these materials have shown improved properties for hydrogen recovery from the tested materials.

Modeling of Advanced Hydrogen Storage Options in the H2A Framework
(Matt Ringer, NREL, and Steve Lasher, TIAX)

The objective of the H2A program is to develop a transparent, consistent methodology that can be used to compare different H_2-based systems. At present, H2A focuses only on off-board hydrogen storage (e.g., at the fueling station), but in the future it will incorporate hydrogen carriers. The H2A model is a spreadsheet-based tool that allows the user to determine a generic hydrogen cost for a particular delivery component. The component models are being modified to include chemical H_2 regeneration at a central plant, trucking, and forecourt inputs (i.e., H_2 is supplied "over the fence" at the fueling station). Thermal integration has not yet been considered, however.

TIAX has developed an H2A case study for hydrogen using the conventional sodium borohydride pathway. The results show that with the $NaBH_4$ distributed by liquid tanker truck, the cost of hydrogen would be approximately $10.6/kg. The analysis showed that the biggest contributor to this cost is the reprocessing facility cost of $9.85, of which utilities (mostly electricity at $0.05/kWh) account for $9.04. The analysis included the energy stored in the truck during the return trip and the requirements to store the spent material. The potential benefits from integrating the sodium borohydride regeneration plant with the hydrogen production plant have not yet been considered. This case study successfully implemented the H2A methodology into the analysis of an advanced hydrogen storage system and it opens the door to enhancing H2A models with other hydrogen storage systems as the various technologies evolve.

Impact of Solid Ammonia Borane Fuel Formulation on an On-Board Storage and Hydrogen Release System, Center of Excellence for Chemical Hydrogen Storage
(Chris Aardahl, PNNL)

The objective of this part of the work at the Center of Excellence for chemical hydrogen storage is to study the stability of on-board solid ammonia borane (AB) fuel using experimental and modeling methods. The Center has studied heat transfer conditions of AB through a number of activities, namely: Avrami kinetic analysis (kinetics of phase transformation), thermal stability calculations, heat management, calorimetric analysis, and thermal stability tests. An accelerated rate calorimeter was used to conduct thermal stability tests at 60ºC on AB from different suppliers. Purity of the material was found to be a very important factor in determining its stability (presumably, impurities act as initiators for decomposition). Stability increases at lower temperatures. Multi-day stability was demonstrated experimentally at 50°C and 60°C.

The model developed at PNNL can be used to assess the mass and volume of solid AB needed for hydrogen generation at peak vehicle load. To meet the needed hydrogen flow rate requirements, 1 kg of AB would be needed, which corresponds to 3.3 L of bulk particulate or 1.9 L of closely packed pellets (30% void). A 5-kg H_2 storage system would require 38 kg of AB, corresponding to 74 L of packed AB pellets. Feeding and removing solids at high pressures (~8 bar) are still issues, however, that need to be investigated further. The energy required for startup has not yet been included in the calculations.

Sodium Borohydride Regeneration Analysis – Energy Requirements and Efficiencies, Argonne National Laboratory
(R. Ahluwalia, ANL)

Argonne has used data from Millennium Cell (MCell) to calculate energy requirements and efficiencies of a sodium borohydride system with sodium recovery. According to MCell, the possibility of recycling sodium in a closed loop system has been demonstrated experimentally by electrolysis of $NaBO_2$ in a small electrochemical cell. The Argonne model assumes 100% sodium recovery using the electrochemical process. The theoretical current efficiency for this process is ~50% without MCell's membrane (commercial cells achieve ~40% current efficiency). With MCell's membrane, the current efficiency of NaOH and $NaBO_2$ electrolysis is reported to be close to 100%, with or without H_2 assist. The H_2-assisted process requires less electricity, but the energy savings are offset by the need to provide H_2 to the process.

Sodium recovery is the most energy intensive step in the regeneration of sodium borohydride. Four sodium regeneration options were analyzed with FCHTool. The analyses assumed 50% thermal integration within the process, and a 2015 projected U. S. electrical grid for the electricity needed for electrolysis, which is the major energy-consuming step. The results show that sodium recovery accounts for 45–80% of the total energy consumed in the regeneration of sodium borohydride. The calculated well-to-engine efficiency is 17–23% for the H_2-assisted electrolysis options, and 14–19% without H_2 assist. Loss of materials from the closed-loop processes, especially the loss of sodium, can significantly reduce this calculated efficiency.

Next Steps

The Hydrogen Storage Systems Analysis Working Group meets biannually. The Group will next meet in conjunction with the 2007 Annual Merit Review of the DOE Hydrogen Program, May 15–18, 2007, in Arlington, VA.

APPENDIX A

MEETING AGENDA

Hydrogen Storage Systems Analysis Working Group Meeting

December 12, 2006
955 L'Enfant Plaza, North, SW, Suite 6000, Washington, DC 20024-2168

10:00	Welcome	Sunita Satyapal / DOE
10:10	Meeting overview	Romesh Kumar / ANL
10:15	Overview of Hydrogen Storage Systems Research at Savannah River National Laboratory	Bruce Hardy / SRNL
10:45	Second $NaAlH_4$ Prototype	Dan Mosher / UTRC
11:10	Carbon-Based Materials Center of Excellence: Update on Activities	Philip Parilla / NREL
11:35	Modeling of Advanced Storage Options in the H2A Framework	Matt Ringer / NREL Steve Lasher / TIAX
12:30	Lunch Break	
13:15	Impact of Solid Ammonia Borane (AB) Fuel Formulation on an On-Board Storage and Hydrogen Release System	Chris Aardahl / PNNL
14:00	SBH Regeneration Analysis – Energy Requirements and Efficiencies	R. Ahluwalia / ANL
14:45	Discussion	All
15:15	Wrap-up	R. Kumar / S. Satyapal

Next SSAWG Meeting: at the 2007 Hydrogen Program Annual Merit Review, May 15–18, Arlington, VA

APPENDIX B

MEETING PARTICIPANTS

Hydrogen Storage Systems Analysis Working Group Meeting

December 12, 2006, Washington, DC

Last	**First**	**Org**
Aardahl	Christopher	PNNL
Ahluwalia	Rajesh	ANL
Blair	Larry	DOE
Bowman	Robert	JPL
Brown	Ken	Safe H2
Hardy	Bruce	SRNL
Inbody	Michael	LANL
Kumar	Romesh	ANL
Lasher	Stephen	TIAX
McClaine	Andrew	Safe H2
Moreno	Oscar A.	MCell
Mosher	Dan	UTRC
Ordaz	Grace	DOE/EE
Parilla	Philip A.	NREL
Read	Carole	DOE/EE
Reiter	Joe	JPL
Ringer	Matthew	NREL
Satyapal	Sunita	DOE/EE
Tullman	Sig	Safe H2
Verduzco	Laura	DOE/EE