Hydrogen Storage Systems Analysis Working Group Meeting

Argonne DC Offices
L'Enfant Plaza, Washington, DC

December 4, 2007

SUMMARY REPORT

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Meeting Objectives

This meeting was one of a continuing series of biannual meetings of the Hydrogen Storage Systems Analysis Working Group (SSAWG). 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. The SSAWG typically meets twice a year, once in conjunction with the DOE Annual Hydrogen Program Review in May/June 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.

In the introductory remarks, Sunita Satyapal (DOE) welcomed the meeting attendees and stressed that the meeting is meant as a forum for discussion, not a technical review of the projects and work being presented. Romesh Kumar (ANL) presented the agenda, led the self-identification of those present in the room and the participants who were calling in, and offered an overview of the meeting. The technical presentations began with one on engineering and process models for hydrogen storage and dispensing systems by Bruce Hardy (SNL). Rajesh Ahluwalia (ANL) then discussed the analysis of off-board regeneration for different chemical hydrogen storage processes. Next, Daniel Dedrick (SNL) discussed the effects of metal hydride properties on the performance of hydrogen storage systems. Bob Bowman (JPL) presented a survey of metal hydride storage vessels built for or demonstrated on-board vehicles of various types. Kevin Ott (LANL) and Chris Aardahl (PNNL) gave presentations on preliminary chemistry and engineering studies of regenerating spent fuel from ammonia borane hydrogen storage systems. Leo Klawiter (R&H) discussed cost-estimating methodology for two different approaches to regenerating spent sodium borohydride storage media. Finally, Matt Ringer (NREL) provided an update on the H2A delivery models that now also include chemical hydrogen carriers. These discussions and the presentations at the meeting are summarized below.

The next meeting of the SSAWG is tentatively scheduled for June 12, 2008, during the Hydrogen Program's Annual Merit Review in Arlington, VA.

Engineering and Process Models for Hydrogen Storage Systems and Refueling Stations

(Bruce Hardy, SRNL)

This presentation reviewed SRNL's engineering models for hydrogen storage systems and process models for refueling stations. The engineering model was developed with specific reference to the sodium aluminate hydrogen storage material, in which the hydride bed has very low effective permeability and thermal conductivity. The model was used to evaluate storage system designs. The model includes reaction kinetics, which limit charging and discharging rates and bed capacity; system geometry, which is used to calculate vessel dimensions and to optimize location of heat transfer elements; and heat removal parameters, which determine the operation of the heat exchange system. These various processes are then coupled in two- and three-dimensional finite element models. These models were applied to the case of $TiCl_3$-catalyzed $NaAlH_4$ hydrogen storage medium in a modified shell-and-tube heat exchanger design, with radial fins for improved heat transfer. As the charging pressure is raised from 1 bar to 99% of the design 50 bar in 10 s, the model calculates profiles of hydrogen velocity, temperature, and hydride concentration. It was observed that the effect of the fins is much more pronounced with the higher reaction rates, and the hydride concentration is more uniform due to the fins, leading to better utilization of the sorbent bed. In future work, these models will be used to identify and develop an envelope of storage media properties (kinetic parameters, thermal conductivity, bulk density) that would be needed to meet DOE performance targets. The models will also be used to evaluate lighter and smaller heat removal systems, and to analyze the refueling of partially discharged beds.

The presentation also discussed an Aspen Plus process model for hydrogen storage and refueling station system requirements. In particular, the size and capacity of the off-board heat removal equipment was analyzed parametrically as a function of the number of simultaneous fueling points, the maximum capacity (in terms of the kilograms of H_2 dispensed per hour), and the enthalpy of sorption of the on-board hydrogen storage medium. Thus, for example, a fueling station with sixteen fueling points (eight fueling pumps, with a hydrogen dispenser on either side) servicing vehicles with a hydrogen storage medium that has an enthalpy of hydrogen sorption of -40 kJ/mole would require a cooling capacity of 600 tons. Such a large heat duty would entail a large capital cost. Conversely, this type of process modeling can be used to identify constraints on the properties of viable hydrogen storage media.

During the discussion, it was pointed out that in the model, the pressure and temperature are not uniform across the vessel but vary as the hydrogen is charged or discharged. Although the model does not optimize the size of the cooling tubes, the size and position of the tubes can be adjusted to evaluate the effect of such variations. For enhanced heat transfer in future analyses, pin fins, foams, spirals, pellets, etc., will be considered, using the performance targets as guidance. The engineering model can be adapted to sorption-based hydrogen storage media in about two weeks, if the relevant data or equations are available. Regarding the process model for the refueling stations, potential uses of the low-grade waste heat (available at ~100ºC), even if challenging, should be identified.

Fuel Cycle Efficiencies of Hydrogen Storage Options Requiring Off-Board Regeneration

(Rajesh Ahluwalia, ANL)

This presentation discussed the analysis of off-board regeneration of sodium borohydride (electrolysis pathways and metal reduction routes), organic liquid carriers (N-ethylcarbazole), and alane (liquid organometallic route, electrochemical method, and supercritical CO_2 extraction), as well as the regeneration of ammonia borane decomposition products. For the regeneration of sodium borohydride, the recovery of sodium is the most energy intensive step in the process. For the metal reduction routes, preliminary analysis shows that regeneration of the metal from the oxide accounts for 70–80% of the total primary energy required in the process. Analysis using the FCHtool showed that the overall well-to-tank efficiency for the sodium borohydride hydrogen storage approach is in the range of 12 to 17%.

The regeneration (hydrogenation) of N-ethylcarbazole is an exothermic reaction. For a three-stage hydrogenation process, with hydrogen quench and inter-stage regenerative cooling, the overall well-to-tank efficiency is just over 40% without any heat recovery. For alane (AlH_3) regeneration, all three approaches are still highly developmental. With the liquid organometallic route, AlH_3 has been synthesized as an adduct, but extraction from the adduct without decomposing the AlH_3 is difficult. Some initial success has been achieved by the electrochemical method using a high pressure, non-aqueous cell, but the yields are low. Work on using supercritical CO_2 extraction is just beginning. If one or more of these approaches is successful, however, the alane system may yield well-to-tank efficiencies of $\geq$55%.

During the discussions, it was clarified that hydrogen assisted electrolysis lowers the cell voltage, leading to reduced electrical energy consumption but increased hydrogen consumption. For the terminology used in the analyses, feedstocks referred to primary energy, while electricity is from the grid (assuming the 2015 EIA power generation mix). The analysis is preliminary and includes only for steam methane reforming for hydrogen production at this time. Since the different technologies are at different stages of development, these processes have different levels of uncertainty, which should be included when considering the results of the analyses. It was emphasized that heat recovery in processes that yield the heat at a central regeneration plant was not included in the analyses.

Effects of Metal Hydride Properties on the Performance of Hydrogen Storage Systems

(Daniel Dedrick, SNL)

This presentation summarized some of the results from the joint GM/SNL hydrogen storage project. This work used a range of physical (packing density), thermal (conductivity, specific heat), and thermodynamic (effective capacity, reaction enthalpy, pressure, temperature) properties of the storage medium in a MatLab-based analysis to obtain the relationship linking the properties of the material to the performance (e.g., gravimetric and volumetric energy densities) of the system. This relationship between the material's properties and the system performance involves five parameters: mass efficiency (ratio of hydride mass to system mass), volume efficiency (ration of hydride volume to system volume), enthalpy loss (for desorption of hydrogen), thermal loss, and the ratio of gaseous hydrogen to stored hydrogen. The medium's packing density and thermal load have the greatest effect on gravimetric efficiency, while the highest volumetric efficiency is achieved at low pressure, high thermal conductivity, and low heat duty. Results of sensitivity analyses showed that mass efficiency, packing density, and sorption enthalpy are the most critical hydride properties. In addition to the necessary high hydrogen capacity, the sorption enthalpy may be nearly as influential in determining the overall system performance. In the case where the waste heat from the power plant (fuel cell or internal combustion engine) can be used for hydrogen desorption, a heater would not be needed, which would reduce system complexity and increase the gravimetric and volumetric system capacities, perhaps by a factor of two.

During the discussion, it was pointed out that the type of high-filament steel used in this analysis does not have the problem of hydrogen embrittlement. For these analyses, the van der Waals equation of state was used for H_2. A parametric analysis of cost was not conducted, as that would involve placing a value on manufacturability, which is difficult for the researchers to do; perhaps input from original equipment manufacturers would be needed for this. In the storage vessels analyzed, although no internal heater was included, a source of heat may be required, depending on the design. It was also pointed out that a hydrogen discharge temperature of less than 80ºC is required for optimal heat utilization from the fuel cell power plant.

Survey of Metal Hydride Storage Vessels for Fuel Cell Systems

(Bob Bowman, JPL)

This presentation summarized the configuration and system requirements for hydride beds, including the bed design features, thermal management, and other issues. The survey covered metal hydride storage systems that have been demonstrated in a variety of vehicles. Although there are literally hundreds of metal hydrides and hydride phases known, only a few of them are viable for vehicular applications. The required attributes of hydride storage systems are driven by the DOE targets for use with fuel cell vehicles. In addition to the pressure-temperature relationships for the various hydride storage media, the storage system design needs to include thermal components for effective heat transfer.

Examples of metal hydride (MH) beds developed for vehicular applications include: Ti-Zr-Mn-V-Fe-Ni and misch metal-Ni-Al (misch metal: La-Ce-Pr-Nd) beds for a golf cart that were designed, built, and tested by Sandia National Laboratory in 1998 (but not integrated into the golf cart); a low pressure tank for 3.5 kg of H_2 and a high pressure tank for 7.3 kg of H_2 Ti-Cr-Mn alloy beds described by Toyota in 2005 (neither has been integrated into a demonstration vehicle); and sodium alanate storage vessels built and tested by Sandia (2005) and United Technologies Research Center (2002 to 2007). Vehicle demonstrations using MH hydrogen storage beds include the Hydrogen Hybrid Electric Bus, Augusta, GA (1997–1998), with 15 kg H_2 in two beds of misch metal-Ni-Al; the SRTC Gator vehicle, York and Columbia, SC (1998–2001); the HICE scooter with Ovonic metal hydride storage integrated with an internal combustion engine, Rochester Hills, MI (2002); Ovonic Hydrogen Systems LLC metal hydride bed for a modified Toyota Prius (2002–2006); the Sandia RATLER (Robotic All Terrain Lunar Exploration Rover) with two beds of Ti-Fe-Mn alloy; a four-ton mine locomotive (1999–2002) and an underground mine loader (2001–2007); and the German Navy, Class 212, submarine (2003).

All of the reviewed designs were compromises between conflicting properties and performance requirements. The thermal management issues usually dominate the design and performance of the system. Very few long-term cycling assessments of full size operating systems have been conducted. In addition, the complex hydrides being investigated currently have low thermal conductivities, low reaction kinetics, low powder densities, and issues of safety due to their high chemical reactivities.

The researchers are planning to publish the results of this survey in early 2008.

Regeneration Chemistries of Spent Fuel from Ammonia Borane

(Kevin Ott, LANL)

Ammonia borane (AB, NH_3BH_3) is being investigated as a hydrogen storage medium. The release of H_2 from AB is exothermic, but the process is not directly reversible with accessible pressures of H_2. Thus, the spent fuel must be chemically processed to regenerate the AB; the structure and properties of the spent fuel itself vary with the different dehydrogenation processes used, and those differences may affect the choice of regeneration chemistry that can be used. The typical regeneration process involves digestion (dissolution and pretreatment) of the spent fuel, reduction/hydriding, and ammoniolysis to replace the ammonia. For highest regeneration process efficiencies, the exothermic digestion step needs to be balanced against the endothermic reduction/hydriding step. Three different digestion routes are being explored that use a halide, thiol, or alcohol (thiacatechol) reagent. The overall calculated thermodynamic efficiency of the thiacatechol regeneration scheme, for example, is 75%, which could increase to 79% if 20% heat recovery can be achieved within the process.

Regeneration of Spent AB Solids

(Chris Aardahl, PNNL)

This presentation continued the discussion of the regeneration of the spent AB solids. The digestion step converts the spent solids to more readily processed BX_3 compounds (where X may be a halogen, sulfur, or a nitrogen and oxygen-containing ligand). A reduction step then converts the B-X bonds to B-H bonds. The next step is elemental redistribution, i.e., $LBHX_2$ to LBH_2X and (BX_3 + LBH_2X) to (LBH_3 + BX_3). Finally, the LBH_3 is reacted with NH_3 to regenerate the NH_3BH_3. Different preliminary digestion and reduction process flowsheets are being analyzed. Some of the trade-offs being considered are whether the hydrogen in the spent fuel should be captured as a hydride or as hydrogen gas for use during the reduction step, which involves a trade-off between energy penalty and process complexity. Separation of BX_3–BHX_2 is a critical step, for which data on thermal stability, relative volatility, solubility, etc., are needed, as are data on the physical properties of organic boron compounds for process design and analysis.

Cost Estimating Methodology for Regenerating $NaBH_4$

(Leo Klawiter, Rohm & Haas)

The objective of this work is to develop a methodology for determining the costs of regenerating sodium borohydride in a manner that is consistent with the assumptions and parameters used in the H2A model to determine the cost of delivered hydrogen. The costing process starts with a conceptual process flowsheet, from which an equipment list and the material and energy balances are obtained. The equipment list, energy balance, physical properties, and the appropriate heuristics are used to size the equipment. This, in turn, is used along with labor requirements and wage rates to determine labor-related costs that are fed to the H2A model. The equipment size data are also used to determine the capital investment, and the maintenance and property overhead that are also fed to the H2A model. Finally, the material and energy balances are used to determine the raw material and energy/utility costs, which complete the input to the H2A model. The regeneration process efficiency is determined from the energy balance and equipment data using FCHtool.

Two conceptual processes were analyzed, one based on metal reduction, and the other based on carbothermal reduction. Based on certain assumptions and a range of costs associated with changes in yield, production volume, capital investment, utility costs, byproduct credits, and labor costs, the metal reduction process resulted in delivered hydrogen costs of \$6–12/kg, while the carbothermal reduction process resulted in delivered hydrogen costs of \$2–7/kg.

During the discussion, it was pointed out the costing approach is based on earlier models developed by TIAX, which have been adapted to sodium borohydride regeneration for the present study. Although these analyses indicate that the carbothermal process yields a much lower cost of delivered hydrogen than the metal reduction process, a down select to pursue only the former process has not yet been made. The \$2/kg H_2 estimated for the low end of the delivered hydrogen cost for the carbothermal process is very optimistic and would only be realized with high yields and suitable credits for byproduct CO and H_2.

H2A Delivery Models Update: Improvements and Advanced Carrier Inclusion

(Matt Ringer, NREL)

This presentation provided an update on the improvements and developments in the H2A hydrogen delivery models. Specific major improvements include: components sized to meet demand profiles (to eliminate capacity factors); pathway storage optimization (including plant outage, summer/Friday/hourly peaks, and "hose occupied fraction" peak); variable sizes of refueling stations (50–6000 kg/day); added pathways (mixed-mode deliveries, plant outage and summer peak handling); refueling station optimization (both gaseous and liquefied hydrogen, based on total station cost); practical limitations on component sizes (liquefiers, compressors); and land area calculations (stations and terminals). Nine delivery pathways are now included in H2A, three that involve liquid hydrogen distribution, four involving compressed hydrogen distribution, and two with pipeline delivery.

Preliminary hydrogen carrier analysis has also been added to H2A. Initial results indicate that: carriers that can be used in all phases of delivery can have many off-board advantages, but hydrogen release can be more difficult on-board the vehicle; carriers that can be easily loaded and off-loaded from a truck allow for simple materials handling, but result in additional station requirements; certain novel carriers have restrictions necessitating that they remain contained in a single container; the process of unloading hydrogen during delivery reduces the need to drop-off vehicles, but increases storage/compression requirements; certain carriers have the ability to be shipped via pipeline and stored at the forecourt for steady-state or on-demand H_2 release; and certain carrier materials may be permanently stored as “bricks,” which can be loaded and off-loaded to the vehicle without requiring any storage.

During the discussion, it was reiterated that the new version of H2A will have several significant changes from the pervious version, particularly regarding the forecourt fueling station. Along with the release of the new version, user documentation will be issued that describes the changes. It is likely that some of the earlier analyses by users of the previous version will need to be re-worked, such as, for example, what to do with the capacity factor that is no longer a user parameter in the new version. It was emphasized that changes to H2A and comparison of assumptions and results using the old and the new versions should be made transparent and publicized.

Next Steps

The Hydrogen Storage Systems Analysis Working Group meets biannually. The Group will next meet on June 12, 2008, in Arlington, VA, during the 2008 Hydrogen Program Annual Review.

Abbreviations and Acronyms

ANL	Argonne National Laboratory
DOE	U. S. Department of Energy
EIA	Energy Information Administration (DOE)
JPL	Jet Propulsion Laboratory
LANL	Los Alamos National Laboratory
NREL	National Renewable Energy Laboratory
PNNL	Pacific Northwest National Laboratory
R&H	Rohm and Haas
SNL	Sandia National Laboratory
SRNL	Savannah River National Laboratory
SRTC	Savannah River Technology Center (predecessor of SRNL)
SSAWG	Hydrogen Storage Systems Analysis Working Group

APPENDIX A

AGENDA

Hydrogen Storage Systems Analysis Working Group Meeting

December 4, 2007
Argonne National Laboratory DC Offices
955 L'Enfant Plaza, North, SW, Suite 6000, Washington, DC 20024-2168
(North Tower, 6th Floor)

Energy Inputs and Process Efficiencies

09:30	Welcome	Sunita Satyapal / DOE
09:40	Meeting overview	Romesh Kumar / ANL
09:45	Engineering Model for Hydrogen Storage Systems	Bruce Hardy / SRNL
10:15	Process Efficiencies	Rajesh Ahluwalia / ANL
10:45	Hydrogen Storage Systems Engineering at Sandia National Laboratory, CA	Daniel Dedrick / SNL
11:15	Survey of Metal Hydride Storage Vessels for Fuel Cell Systems	Bob Bowman / JPL
11:45	Lunch Break	
12:40	Preliminary Engineering Studies of Chemical Hydride Regeneration	Chris Aardahl / PNNL Kevin Ott / LANL Leo Klawiter / R&H
13:20	H2A: Delivery Modeling & Carrier Options	Matt Ringer / NREL
14:00	Discussion	All
14:20	Wrap-up	R. Kumar / S. Satyapal

Next SSAWG Meeting: at the 2008 Hydrogen Program Annual Merit Review, June 10-13, Arlington, VA

APPENDIX B

Meeting Attendees

Last	First	Organization	
Aardahl	Chris	Pacific Northwest National Laboratory	
Ahluwalia	Rajesh	Argonne National Laboratory	
Berry	Gene	Lawrence Livermore National Laboratory	Call-in
Bowman	Robert	Jet Propulsion Laboratory	
Deason	Kristin	Sentech	
Dedrick	Daniel	Sandia National Laboratory - Livermore	
Gardiner	Monterey	U. S. Department of Energy	
Hardy	Bruce	Savannah River National Laboratory	
Hua	Thanh	Argonne National Laboratory	Call-in
Klawiter	Leo	Rohm & Haas	
Kumar	Romesh	Argonne National Laboratory	
McClaine	Andrew	SafeH2	
McKenney	Kurtis	TIAX	Call-in
Moreno	Oscar	Millennium Cell	
Ordaz	Grace	U. S. Department of Energy	
Ott	Kevin	Los Alamos National Laboratory	
Parilla	Philip	National Renewable Energy Laboratory	Call-in
Read	Carole	U. S. Department of Energy	
Reiter	Joe	Jet Propulsion Laboratory	Call-in
Ringer	Matt	National Renewable Energy Laboratory	
Satyapal	Sunita	U. S. Department of Energy	
Semelsberger	Troy A.	Los Alamos National Laboratory	
Stetson	Ned	U. S. Department of Energy	