Hydrogen Storage Systems Analysis Working Group Meeting

Held in Conjunction with the
DOE Hydrogen Program Annual Merit Review
Crystal Gateway Marriott, Arlington, VA

June 11, 2008

SUMMARY REPORT

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July 18, 2008

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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 and Discussion

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

Ned Stetson (DOE) opened the meeting and welcomed the meeting attendees. Romesh Kumar (ANL) presented the agenda, and indicated that the presentations and discussions would be necessarily short due to time constraints. The technical presentations began with Mike Heben (NREL) outlining the generic systems analysis needs from the perspective of the sorption-based hydrogen storage systems. Chris Aardahl (PNNL) then summarized the analysis plans and needs for chemical hydrogen storage systems. Don Anton (SRNL) did the same for the complex metal hydride hydrogen storage systems, with particular reference to the aspects to be covered by the materials and the engineering Centers of Excellence. Monterey Gardiner (DOE) gave a brief summary of the planned work on compression and liquefaction projects for hydrogen storage. Guido Pez (APCI) described an autothermal hydrogen storage and delivery concept using an organic liquid carrier for hydrogen. Joe Reiter (JPL) then discussed their modeling of hybrid hydride storage vessels (pressure vessels containing a metal hydride). Not presented at the meeting but included in this summary report is a discussion by Rajesh Ahluwalia (ANL) on the concept of using alane slurries in a light mineral oil for hydrogen storage.

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

The next meeting of the SSAWG is tentatively scheduled to be held in November or December 2008, in Washington, DC.

Analysis Needs for Sorption-Based Hydrogen Storage Systems
(Mike Heben, NREL)

The sorption materials developers need a spreadsheet-type model that includes system-level components, such as tanks and heat exchangers, so that the developers can gauge the impact of such balance-of-plant components on the gravimetric and volumetric capacities of the hydrogen storage systems based on their materials. Such models should also include other design and operating parameters, such as charging and discharging rates, sorption/desorption kinetics, thermal conductivity, heat capacity, material density, etc.

It is important to consider conformable tanks specifically designed for the relatively low pressures of 100 bar or less. Multiple conformable tanks, possibly in different locations, could permit de-rating of volumetric capacity targets (i.e., offer a credit), since the volumetric goals are based on the assumption of the hydrogen storage tanks being in one location in the vehicle.

It is also important to consider the storage system and the hydrogen production system in an integrated manner to obtain a complete picture of the round trip energy efficiency of hydrogen production and storage on-board the vehicle. Depending on the hydrogen production process used, there may be opportunities to gain performance efficiencies by closely integrating these subsystems. For example, the current H2A model includes considerations of fueling/energy costs for production and storage. Version 3 of H2A will also include novel hydrogen carriers. Other such models are known to exist, such as the one by Toyota, but those models are not readily available in the public domain.

Analysis Plans and Needs for Chemical Hydrogen Storage Systems
(Chris Aardahl, PNNL, and Kevin Ott, LANL)

The Chemical Hydrogen Storage Center is transitioning its engineering resources from analysis of on-board systems to addressing off-board issues. Thus, much of the capability developed for the engineering and analysis of sodium borohydride systems that was used in support of the go/no-go decision for that approach is directly portable to other candidate storage technologies. Such a transition is eased by being familiar with the DOE suite of tools and process simulation packages and by having experienced process engineers and industrial chemists on the team.

The focus of the current work is on ammonia borane (AB). The process steps that need to be analyzed include the regeneration of AB with integrated formic acid synthesis and hydrogen production. We need to assess the energy efficiency impact and CO_2 emissions from the process, as well as to determine the highest energy efficiencies achievable for the formate route for AB regeneration. We also need to analyze direct hydrogenolysis routes based on heterogeneous catalysis, which will require experimental validation and process development. A preliminary analysis is being conducted in collaboration with Argonne National Laboratory (ANL) on the hydrogen activation approach for AB regeneration. Various process chemistries can be considered, but it would perhaps be useful to just select one process chemistry and analyze it as a baseline case for comparison with alternative routes.

Other issues to be addressed include determining whether it is economical to recover hydrogen from partially spent fuel, perhaps as a function of the extent of hydrogen discharge on-board the vehicle. Also, AB is heat sensitive; the Center is exploring reactions that can protect the borane. Working with ANL, the Center will organize analysis workshops later in 2008.

Analysis Plans and Needs for Complex Metal Hydride Hydrogen Storage Systems
(Don Anton, SRNL)

Metal hydride data needed for engineering design and analysis include media characteristics (e.g., particle size, theoretical and bulk densities, energetics and volume change during hydriding/dehydriding, heat capacity), transport properties (e.g., thermal conductivity of the unsupported and supported storage medium, thermal contact resistance), and the kinetics of absorption and desorption (as functions of pressure, temperature, and state-of-charge), all as a function of composition.

These data needs must be met by the existing materials-focused Center of Excellence (CoE) and the new Engineering CoE working together. The materials CoE would address an element of the media that is representative of the bulk supported media characteristics, but which is free of any design constraints. The engineering CoE would address issues such as contact resistances and constrained expansion. There will also be items in the gray area, where the two Centers would overlap and on which they would need to collaborate closely, such as bed density.

Moving forward, then, we would need to identify the required materials parameters for candidate hydrogen storage media, and categorize them as to be addressed by the materials or the engineering CoE, or collaboratively by the two CoEs. We would need to identify appropriate testing methods and procedures (using ASTM standard procedures to the extent possible), and use existing capabilities and equipment at, for example, Sandia National Laboratory (SNL), United Technologies Research Center (UTRC), for cost effective determination of the needed properties. New measurement techniques and methodologies may need to be developed for reaction kinetics, expansion stress, cycling effects on parameters, vibration effects on materials separation, and the effects of contaminants in the hydrogen to be stored.

Thus, materials CoEs have capabilities that can be used by the engineering CoE and vice versa, so close collaboration among the Centers is essential. The new engineering CoE will be working with all the materials CoEs to identify data needs. When looking at leveraging efforts, international efforts should also be considered. A wide variety of data required by the engineering CoE may be available via such collaborations. Currently, systems models are being used to back calculate the data required.

Tube Trailer / Liquefaction Solicitation - A Brief Summary of Planned Work
(Monterey Gardiner, DOE)

This presentation summarized the new storage and delivery projects. Due to the projected funding limitations in FY 2009, these projects will start with approximately one-third of the funding, and they will be stretched to 15 months, in anticipation of new funding in FY 2010.

There will be two compression projects for a total funding of $2 million. Concepts ETI will develop a centrifugal hydrogen pipeline gas compressor. Mohawk Innovative Technologies will develop and demonstrate oil-free centrifugal hydrogen compression technology. We are examining electrochemical and centrifugal compression, and assessing how these technologies would scale for forecourt applications.

There will be two storage projects for a total funding of $1.5 million. Lawrence Livermore National Laboratory (LLNL) will develop and demonstrate inexpensive delivery of cooled hydrogen in high-performance glass fiber composite pressure vessels. For this project, TIAX will share information from their SBIR project on low-temperature, high-pressure hydrogen storage and delivery concept. Lincoln Composites will design and develop a tank for high-pressure storage and gaseous truck delivery. With low-pressure storage, footprint is an issue; therefore, high-pressure storage is being investigated.

There will be two hydrogen liquefaction projects for a total funding of $1.2 million. Praxair will address improvements in hydrogen liquefaction, while Prometheus Energy will work on an active magnetic regenerative liquefier approach.

Finally, the project at Air Products and Chemicals, Inc. (APCI), on the autothermal hydrogen carrier (see the next section of this report) will be wrapped up this year (FY 2008). Patent applications covering this technology have been filed.

It should be noted that issues related to the off-board/on-board storage systems interface at the dispenser are not considered in H2A, and they need to be looked at. Any input from the SSAWG would be useful.

Autothermal Hydrogen Storage and Delivery Using Organic Liquid Carriers
(Guido Pez, APCI)

There is currently is no liquid hydrogen carrier that can liberate hydrogen at a temperature below that at which waste heat is available from the fuel cell. To obtain the necessary heat of dehydriding for a current liquid hydrogen carrier, therefore, one needs to (a) burn a portion of the carrier, (b) burn some of the released hydrogen, or (c) burn something else. The new carrier developed by APCI not only provides hydrogen reversibly, but also eliminates the need for external heat to release the hydrogen. Instead, air is added to selectively oxidize a functional group on the liquid carrier in a catalytic reactor to release the hydrogen, without the need for an external heat source. The catalytic oxidative dehydration reaction is thermo-neutral.

This process is based on fluorenone-perhydrofluorene-fluorene hydriding/dehydriding cycle. Liquid fluorenone ($C_{13}H_8O$) is hydrided off-board by the addition of 8 moles of hydrogen and the removal of 1 mole of water (over Pd/SiO_2 catalyst at 70ºC and 8 bar, or over Ru/Al_2O_3 catalyst at 160ºC and 60 bar) to form perhydrofluorene ($C_{13}H_{22}$), which is the liquid hydrogen carrier. On-board, 6 mole of hydrogen are released by the endothermic conversion of perhydrofluorene to fluorene ($C_{13}H_{10}$) over 5% Pt/Al_2O_3 catalyst at 235ºC and 1 bar. The heat for this reaction is provided by the exothermic oxidation of fluorene to fluorenone over Fe/V_2O_5

catalyst at 350ºC and 1 bar (gas phase). It is important that the regeneration reaction should yield >99% *cis-cis* conformer; "natural" mixtures of *cis-trans* conformers would need higher dehydrogenation temperatures and may not achieve 99% conversion.

During the discussion, it was emphasized that in the regeneration of the oxidized carrier, all *cis* conformers must be utilized. There is also the issue of pressure – the delivered hydrogen needs to be at an elevated pressure >1 atm; therefore, the feed air into the oxidation reaction needs to be at higher pressure, unless a high-temperature backpressure valve is used between the dehydrogenation reactor and the oxidation reactor. Although the process concept has been developed, engineering design and analysis is needed to verify the applicability of this process to a real-world automotive system, similar to what was done by Argonne for the N-ethylcarbazole as an organic liquid carrier for hydrogen.

Although the hydrogen storage project on this technology has been completed, a hydrogen delivery project will continue through 2010 to develop a dehydrogenation reactor prototype. This has been enabled by the direct participation of an automotive company. In this continuing project, alternative materials and catalysts are being developed and evaluated by APCI.

"Hybrid" Hydride Storage Vessels: Parametric and FEA Modeling
(Joe Reiter, JPL)

A "hybrid" tank design is one that combines compressed hydrogen with solid-state hydride storage. Such an approach, when combined with an effective heat-exchanger design, may be able to realize good system response, fast filling, and simplified thermal management, possibly eliminating the need for off-board cooling. In such systems, the high-pressure plenum provides a buffer for startup-up and transient operation, and absorption time constants do not have to be small to provide the needed transient performance.

One such design is the Toyota hybrid tank, which is a 35 MPa high-pressure tank that can be used as a low-temperature metal hydride storage vessel. In this design that has been tested in the laboratory but not in a vehicle, sieved metal hydride powder supported on an aluminum foam matrix offers good bulk thermal conductivity. Published information indicates that for this hybrid tank, there is no need for an external cooling facility, even when achieving 80% fill in 5 min.

A second example of a hybrid design is a prototype tank developed by Ovonic Hydrogen Systems, a subsidiary of Energy Conversion Devices. This tank also uses metal hydride powder packaged in a tank with a support and heat exchange system. The hybrid tank has the same volume as a 350 bar tank, but it is heavier. With an operating pressure of 2 MPa instead of 35 MPa, this tank was installed in a modified Toyota Prius, in which application, it provided a range of ~200 miles, similar to the range with the 35 MPa non-hybrid compressed hydrogen tank. This hybrid tank does require external cooling for charging, however.

Researchers at JPL are developing a model to predict the performance of such hybrid tanks. This effort initially consisted of a one-node, simple Excel-based model. However, the simplicity of that model limited its usefulness. The modeling effort then expanded into a thermal-mass finite element model, comparing AB_2- and AB_5-type alloys. Known systems were used to validate the model. Preliminary model results indicate that relatively fast fill (5 min) can be accomplished by increasing the filling pressure, but this would also require a reduction in the thermal resistances in the cooling loop and an increase in the thermal conductivity of the alloys.

With appropriate modifications, the current model can be used as a basis for developing a fundamental numerical model to understand hydrogen charging and discharging for sorbents, metal hydrides, and chemical hydrogen storage materials.

On-Board Storage of Hydrogen in Alane Slurries: Preliminary Results
(Rajesh Ahluwalia, ANL)

This material was not presented at the SSAWG meeting. It was presented during the Hydrogen Program Annual Merit Review, however, and it is summarized here for completeness.

A preliminary system model has been developed and analyzed for the alane slurry (70-wt% AlH_3 loading in a light mineral oil) hydrogen storage concept. The key assumptions in the concept include (1) a single, volume-exchange tank with a bladder suitable for handling slurries, (2) Xceltherm heat transfer fluid (HTF) since ethylene glycol is unsuitable for the operating temperature range, (3) Avrami-Erofeyev rate expression for AlH_3 dehydrogenation kinetics, (4) compact, microchannel heat exchangers, and (5) a hydrogen buffer tank to provide hydrogen during startup and transient operation.

The conversion of alane is a function of the liquid hourly space velocity (LHSV) in the dehydrogenation reactor, with higher LHSVs leading to smaller reactor volumes. At LHSVs of 10–60 h^{-1}, the dehydrogenation reaction requires temperatures of 200–260ºC to achieve 95% conversion of undoped alane. While doping significantly destabilizes alane at low temperatures, the effect of doping is small at the high conversions needed in this system.

Preliminary results of the analysis show that starting with the intrinsic material storage capacity of 10 g-H_2/g-AlH_3, the capacity in the slurry decreases to 7 g-H_2/g-slurry, which decreases to a usable capacity of 5.6 g-H_2/g-slurry for reasonable states of charge and discharge. This value translates to a gravimetric hydrogen storage capacity of 4.2 g-H_2/g-system and a volumetric capacity of 49.8 g-H_2/L-system. For such a system with 5.6 kg usable H_2 and sized to provide 1.6 g/s of maximum hydrogen flow rate, the “fuel” accounts for 75% of the total system weight of 132.8 kg, and 73% of the total system volume of 112.4 L.

Next Steps

The Hydrogen Storage Systems Analysis Working Group meets twice a year, once during the DOE Hydrogen Program Annual Merit Review in May/June and once in November/December. The spring meeting is necessarily short, due to the other activities at the Merit Review. The fall meeting is generally a longer meeting that provides an opportunity for more detailed discussions.

The Group will next meet in November or December 2008, tentatively in Washington, DC.

Abbreviations and Acronyms

ANL	Argonne National Laboratory
APCI	Air Products and Chemicals, Inc.
DOE	U. S. Department of Energy
JPL	Jet Propulsion Laboratory
LANL	Los Alamos National Laboratory
NREL	National Renewable Energy Laboratory
PNNL	Pacific Northwest National Laboratory
SRNL	Savannah River National Laboratory
SSAWG	Hydrogen Storage Systems Analysis Working Group

APPENDIX A

AGENDA

Hydrogen Storage Systems Analysis Working Group Meeting

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Mike Heben, NREL	Analysis Needs for Sorption-Based Hydrogen Storage Systems
Chris Aardahl, PNNL Kevin Ott, LANL	Analysis Plans and Needs for Chemical Hydrogen Storage Systems
Don Anton, SRNL	Analysis Plans and Needs for Complex Metal Hydride Hydrogen Storage Systems
Monterey Gardiner, DOE	Tube Trailer / Liquefaction Solicitation - A Brief Summary of Planned Work
Guido Pez, APCI	Autothermal Hydrogen Storage and Delivery Using Organic Liquid Carriers
Joe Reiter, JPL	“Hybrid” Hydride Storage Vessels: Parametric and FEA Modeling
Rajesh Ahluwalia, ANL	On-Board Storage of Hydrogen in Alane Slurries: Preliminary Results (*Not presented due to time constraints*)

APPENDIX B

Meeting Attendees

Last	First	Organization
Aardahl	Chris	Pacific Northwest National Laboratory
Ahluwalia	Rajesh	Argonne National Laboratory
Berry	Gene	Lawrence Livermore National Laboratory
Bonner	Brian	Air Products and Chemicals, Inc.
Bowman	Robert	Jet Propulsion Laboratory
Brown	Ken	Safe Hydrogen, LLC
Chin	Artie	Rohm & Haas
Dedrick	Daniel	Sandia National Laboratory - Livermore
Gardiner	Monterey	U. S. Department of Energy
Gray	Joshua	Savannah River National Laboratory
Hardy	Bruce	Savannah River National Laboratory
Heben	Mike	National Renewable Energy Laboratory
Herling	Darrell	Pacific Northwest National Laboratory
Hua	Thanh	Argonne National Laboratory
Klawiter	Leo	Rohm & Haas
Kumar	Romesh	Argonne National Laboratory
Lasher	Steve	TIAX, LLC
McClaine	Andrew	Safe Hydrogen, LLC
Mosher	Dan	United Technologies Research Center
Ott	Kevin	Los Alamos National Laboratory
Pez	Guido	Air Products and Chemicals, Inc.
Reiter	Joe	Jet Propulsion Laboratory
Sandrock	Gary	U. S. Department of Energy
Satyapal	Sunita	U. S. Department of Energy
Stetson	Ned	U. S. Department of Energy
Thomas	George	DOE/Sandia National Laboratory
Toseland	Bernie	Air Products and Chemicals, Inc.
Weg	James	Brookhaven National Laboratory
Yuzugullu	Elvin	Sentech, Inc.
Zan	Jason	Jet Propulsion Laboratory