Hydrogen Storage Systems Analysis Working Group Meeting

2007 Hydrogen Program Annual Review
Crystal Gateway Marriott, Arlington, VA

May 17, 2007

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), Dan Mosher (UTRC) discussed finite-element analysis of charging the sodium alanate Prototype 2 with hydrogen. Bob Bowman (JPL) reviewed a survey they have initiated on solid state hydride tanks for hydrogen storage and other energy conversion applications. The IPHE (International Partnership for the Hydrogen Economy) safety program to assess storage media's safety characteristics was then outlined by Don Anton (SRNL). He also provided a brief summary of the planned hydrogen storage research activities at SRNL. Rajesh Ahluwalia (ANL) then summarized his analysis of hydrogen storage in liquid carriers. Finally, Chris Aardahl provided an update on the Chemical Center of Excellence's analysis of sodium borohydride regeneration options. The next meeting of the SSAWG was tentatively set for early December 2007.

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

FEA Analysis of $NaAlH_4$ Prototype 2 Charging
(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.

A finite element simulation using three-dimensional solid elements has been carried out for the hydrogen charging behavior of sub-scale Prototype 2. A sorption kinetics model derived from the Sievert's test data has been implemented and verified over the pressure range of 75 to 105 bar and a temperature range of 60ºC to 180ºC. For this simulation, the fin/hydride composite was represented as a homogeneous material. With minor adjustments to the effective thermal conductivity, very good agreement was obtained for the transient thermochemical simulation and measured data during the hydrogen absorption test warm-up period. The better powder packing resulted in higher thermal conductivity. However, it also resulted in increased mass transfer resistances, which were not incorporated in the FEA model. Presumably because of the transport resistances, the observed temperature rise during charging was lower and slower than that projected by the simulation. Introducing a reaction rate reduction factor of approximately 0.5 yielded good agreement in temperature profiles and the amount of hydrogen charged, indicating that enthalpy, heat capacity, and heat transfer were being modeled consistently. The feeding of cold hydrogen doses into the system produced secondary decreases in the temperature near the entrance filter; this phenomenon is not included in the present model.

In summary, the Prototype 2 was designed, fabricated, and tested to meet the September 30, 2006, DOE Joule milestone, achieving significant improvements over the earlier system. The finned tube heat exchanger used in this prototype is expected to reduce system weight by 30% compared to that of the foam heat exchanger used earlier. The media packing density was increased from 0.44 to 0.72 g/cc, yielding a gravimetric hydrogen storage capacity of 2% and a volumetric capacity of 700 Wh/L.

Survey of Solid State Hydride Tanks for Hydrogen Storage and Energy Conversion Applications
(Bob Bowman, JPL)

Researchers at the JPL, along with colleagues at UTRC, SRNL, and SNL are assessing the status of metal hydride storage bed design configurations and performance models reported in the published literature to produce a benchmark review by the end of FY 2007. This review will summarize the state-of-the-art modeling and performance analyses of metal hydride sorbent beds for hydrogen storage (as well as for heat pumps, compressors, and sorption cryo-coolers). The emphasis is on modeling absorption and desorption behavior, including heat transfer, for predicting thermodynamic and kinetic parameters and comparing them with results from laboratory tests.

It was pointed out in the discussions that in typical analyses, only one or two specific candidate materials that show good results are considered, but when a system-level analysis is carried out (i.e., including kinetic and thermal effects), other candidate materials may also become viable.

Fundamental Safety Testing and Analysis of Hydrogen Storage Materials & Systems
(Don Anton, SRNL)

As part of the IPHE, SRNL is participating in a project that covers risk assessment, chemical kinetics, risk mitigation, and prototype system testing of solid-state hydride materials. This effort to test hydrogen storage materials for various safety-related criteria is not specifically for a go/no-go decision on the different materials; rather, the objective is to gain an understanding of the materials' safety characteristics. The proposed standard tests include flammability (flammability, spontaneous ignition, burn rate, pyrophoricity), water contact (immersion, surface exposure, water drop, water injection), impact sensitivity, and the magnitude and rate of pressure increase due to the ignition of combustible dusts (including the concentration of the powder and its ignition temperature and energy). Details of the respective test methods and test protocol development were presented, as was a participation matrix that includes U. S. and non-U. S. organizations and laboratories. It was brought out in the ensuing discussion that while it is necessary to conduct basic materials testing, system level tests are also needed to identify or develop engineering solutions for the mitigation of any identified safety issues.

Summary of Planned Hydrogen Storage Activities at Savannah River National Laboratory
(Don Anton, SRNL)

The focus of these activities is on heat removal in metal hydride-based hydrogen storage systems. Bases have been developed for general numerical models using COMSOL, MSC/Patran-Thermal, and other software to simulate coupled hydrodynamics, heat transfer, and chemical kinetics in these systems. A major issue being analyzed is the refueling rate, which is limited by the heat removal rate for the system (on a volumetric basis), and by the transport of hydrogen and/or coolant within the hydride bed. Potential resolution of this issue is by use of one or more of structured beds, micro-channel heat exchangers, modified media particles and supports, and phase-change cooling. For the hydride pressure vessels, structural analyses will include the effects of fittings on the vessels, durability under the occurrence of off-normal events, conformal tanks, and composite tanks using different epoxies, fiber materials, and winding angles. During the discussions, it was pointed out that research similar to certain aspects of this work is also being carried out at LLNL. It was recommended that the researchers ensure that there is more interaction between the two laboratories and that there is no duplication in the tasks carried out at the two organizations. DOE requested that SRNL not conduct work on conformable tanks because significant activities had already been undertaken at LLNL.

Hydrogen Storage in Liquid Carriers
(R. Ahluwalia, ANL)

R. Ahluwalia presented recent hydrogen storage systems analysis conducted at Argonne on a fuel cell system with the on-board hydrogen stored in an organic liquid carrier (such as N-ethylcarbazole being investigated by APCI). The reference pressurized fuel cell system analyzed uses a once-through anode gas flow with controlled hydrogen utilization, where the anode exit gas is burned in a tail gas burner using a portion of the cathode exhaust stream. The burner exhaust is expanded in a gas turbine to recover additional power. For a particular set of design and operating conditions and parameters, the results of the analysis show that the storage system efficiency (defined as the fraction of hydrogen liberated in the dehydrogenation reactor that is available for use in the fuel cell stack) can be close to 100% if the enthalpy of hydriding is less than 40 kJ/mol and the dehydrogenation reaction temperature is less than the operating temperature of the fuel cell; if the dehydrogenation temperature is higher than the fuel cell temperature, then the storage system efficiency would be reduced to about 78%. For the specific case of N-ethylcarbazole as the liquid hydrogen carrier (ΔH = 51 kJ/mol, 5.8 wt% intrinsic capacity), the system capacity based on stored H_2 is 4.4 wt% or 35 g-H_2/L, Assuming 95% conversion in the dehydrogenation reactor and 68% storage system efficiency for N-ethylcarbazole, this translates to 2.8 wt% and 23 g/L system capacity based on usable H_2. To meet the automotive driving cycle's transient requirements, however, such a fuel cell-hydrogen storage system would need a 20-g hydrogen buffer tank, as well.

Preliminary results from this analysis indicate that the dehydrogenation reactor will need to use a supported catalyst, operate at a liquid hourly space velocity greater than 20 h^{-1}, and achieve 95% conversion of the liquid chemical hydride. To meet the 2007, 2010, and 2015 DOE targets of 4.5, 6.0, and 9.0 wt% storage system capacity, the liquid carrier medium would need to have a hydrogen storage capacity of 6.0, 8.6, and 14.5 wt%, respectively (for the last case, however, the 20-g hydrogen buffer would have to be reduced if the 81 g/L volumetric target is to be achieved).

Analysis of Chemical Storage Systems: Sodium Borohydride
(Chris Aardahl, PNNL)

The most critical hurdle for the use of sodium borohydride for automotive hydrogen storage is the off-board regeneration of the hydride while meeting the DOE targets for hydrogen storage system efficiency. Several alternative regeneration pathways may be possible, with the well established Brown-Schlesinger process as a benchmark for comparison. These pathways include metal reduction, electrochemical, carbothermal, elemental synthesis, borane-based, and metathesis. For each of these pathways, a theoretical regeneration energy efficiency can be calculated. The results indicate that several of them can potentially meet the DOE target. To assist in down-selecting to a short list of candidate pathways to pursue further, a scorecard approach was adopted to apply different weighting factors to the different process metrics, such as demonstrated chemistry, manufacturing cost, capital cost, EHS (environment, health, and safety), and logistics. This analysis led to a prioritized list of candidate pathways: metal reduction > carbothermal, elemental > electrolytic (requires high-efficiency electricity source) > borane-based, metathesis. Note that the DOE's H2A model for hydrogen production and

delivery is being expanded to include component tabs for chemical hydrogen carriers, such as sodium borohydride. It was also noted that sometimes the researchers involved in bench-scale chemistry do not fully understand the implications of results from the related H2A-based big-picture analyses.

For the on-board part of the sodium borohydride hydrogen storage system, the dehydrogenation reactor is the heart of the system. Its design and operating conditions affect the size of the reactor and greatly impact the balance-of-plant (heat exchangers, separators, etc.). Increased capacity may be achieved by using a higher concentration of the sodium borohydride in the solution, higher space velocity and pressure, and a single, volume-exchange tank design. The dehydrogenation reactor is being modeled using the Lattice-Boltzmann approach coupled to computational fluid dynamics (transitioning to STAR-CD) for enhanced visualization and the ability to model complex geometries. The reactor simulations are being used for process optimization using UniSim.

Next Steps

The Hydrogen Storage Systems Analysis Working Group meets biannually. The Group will next meet in early December 2007, in Washington, DC. Among the items to be included in that meeting will be progress in the IPHE systems project and a discussion of life-cycle costs to ensure consistency with similar analyses being conducted by TIAX.

Abbreviations and Acronyms

ANL	Argonne National Laboratory
APCI	Air Products and Chemicals, Inc.
DOE	U. S. Department of Energy
IPHE	International Partnership for the Hydrogen Economy
JPL	Jet Propulsion Laboratory
LLNL	Lawrence Livermore National Laboratory
PNNL	Pacific Northwest National Laboratory
SNL	Sandia National Laboratory
SRNL	Savannah River National Laboratory
SSAWG	Hydrogen Storage Systems Analysis Working Group
UTRC	United Technologies Research Center

APPENDIX A

MEETING AGENDA
Hydrogen Storage Systems Analysis Working Group Meeting

May 17, 2007

Crystal Gateway Marriott, Arlington, VA
Conference Room: Lee (Lobby Level)

4:30 PM	Welcome	Sunita Satyapal / DOE
4:35 PM	Meeting notes	Romesh Kumar / Argonne
4:40 PM	FEA Analysis of $NaAlH_4$ Prototype 2 Charging	Dan Mosher / UTRC
4:55 PM	Survey of Solid State Hydride Tanks for Hydrogen Storage and Energy Conversion Applications	Bob Bowman / JPL
5:10 PM	IPHE Safety program	Don Anton / SRNL
5:25 PM	H_2 Storage Cost & Life-Cycle Analyses at TIAX	Steve Lasher / TIAX (*Not presented*)
5:40 PM	H_2 Storage Systems Analysis at Argonne	R. Ahluwalia / ANL
5:55 PM	Sodium Borohydride Chemical Storage: A Progress Report	Chris Aardahl / PNNL
6:10 PM	Next Steps / Wrap-up / Adjourn	

Next SSAWG Meeting: early December 2007 in Washington, DC