IV.B.1a 2009 Overview - DOE Chemical Hydrogen Storage Center of Excellence (CHSCoE)

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Objectives of the Center

- Implement a coordinated approach to identify, research, develop, and validate advanced on-board chemical hydrogen storage systems to overcome technical barriers and meet DOE Hydrogen Storage 2010 system goals.
- Design, synthesize, and test materials and compositions to control the thermochemistry and kinetics of hydrogen release.
- Develop energy and chemically efficient off-board spent fuel regeneration for the complete fuel cycle.
- Assess concepts and systems for hydrogen release and spent fuel regeneration using supporting engineering analysis and validation to rank viable candidates.
- Down select most promising chemical systems for more detailed materials and engineering development.
- Develop most promising chemical hydrogen storage materials with potential to meet 2010 targets.
- Perform lab-scale engineering studies to evaluate performance of hydrogen storage systems.
- Develop life cycle analysis.
- Transfer chemical hydrogen storage systems information to Hydrogen Storage Engineering Center of Excellence, and receive feedback from its analyses.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(J) Thermal Management
(K) System Life-Cycle Assessments
(R) Regeneration Processes
(S) By-Product/Spent Material Removal

Technical Targets

While all of the relevant targets detailed in the DOE MYRDDP will be addressed, the Center's main emphasis focuses on the material and efficiency requirements for storage of hydrogen in chemical bonds. The Center has developed interim technical guidelines to facilitate down-selection of promising materials for further development. The Center's key criteria for down-selection of storage materials include gravimetric and volumetric hydrogen capacities, as well as hydrogen release rate and temperature. Gravimetric capacity of materials must exceed 7 wt%, with the potential to exceed 9 wt%. The goal for temperature is for hydrogen release to occur with high rate below 100°C, with an interim goal of release occurring at high rates below 200°C. The Center's criterion for the rate of hydrogen release, 0.02 g H_2/s/kW, is the DOE 2010 target. A tabulation of all of the Center's interim targets is published in the Center's 2008 annual report, http://www.hydrogen.energy.gov/annual_progress08_storage.html#b.

The targets for regeneration of spent fuel include an interim target of 40% energy efficiency, with an ultimate goal of 60% energy efficiency, with chemical efficiencies approaching 100%, e.g. minimum losses to byproducts.

Accomplishments

Accomplishments from across the Center are organized into four main areas: 1). Hydrogen Release, 2). Spent Fuel Regeneration, 3). New Materials, and 4). Engineering Supporting R&D. The 2009 highlights from each of these areas are outlined below.

- Hydrogen Release from Ammonia Borane (AB):
  - Mitigation of foaming well demonstrated for solid AB with scaffold, nano BN, methylcellulose.

- Demonstrated ionic liquid/AB mixtures release hydrogen up to 10% wt% H_2 at temperatures less than 110°C.
- Demonstrated high rates at T as low as 70°C with non-precious group metal heterogeneous catalysts demonstrated.
- Identified liquid fuels of alkylamine borane/AB mixtures.
- Identification of impurities, mechanism of origin, and quantification studies underway for all pathways being actively pursued.

- Spent Fuel Regeneration, First Fill Processes, and Boron Resources Studies:
  - Demonstrated regeneration of AB from spent fuel.
  - Cost analysis of first fill AB synthesis completed for leading process candidates.
  - Identified additional promising first fill processes based upon direct digestion and reduction of spent fuel with hydrazine that may improve both cost and efficiency.
  - Added new partner, US Borax. Their work is to provide updated boron minerals reserves estimates that indicate U.S. supply of B is adequate to meet B-fuel requirements of DOE hydrogen vehicle market penetration scenarios.
- New Materials Development:
  - Li amidoborane demonstrated to have very high activation energy of release that is beneficial to onboard shelf life considerations.
  - Developed an ammonium borohydride synthesis that results in materials with vastly improved thermal stability, and has potential as a 'first fill' source of pure AB.
  - K, Mg, Ca-amidoboranes synthesized, hydrogen release characterized, and structures determined which assists our understanding of hydrogen release from these metal substituted AB derivatives.
  - Added new partner, University of Oregon. Synthesized a number of new cyclo-CBN compounds that are potentially onboard reversible.
- Engineering-Supporting R&D:
  - Developed a baseline cost analysis for regeneration of AB that is between $7-8/kg AB.
  - Developed cost analyses of most promising first fill pathways to prepare sodium borohydride and AB.
  - Developed improved resource reserves for borax minerals for both domestic and foreign sources indicating that there is no barrier to transition to boron fuels.
  - Collaborated with Argonne National Laboratory in estimation of regeneration pathways energy efficiency.

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Introduction

Chemical hydrogen storage involves storing hydrogen in molecular chemical bonds where an on-board chemical reaction is used to release hydrogen. Currently, the resulting spent fuel may be regenerated off-board using chemical processing. In addition to the importance of on-board storage capacity and hydrogen release rates, the energy efficiency of the off-board regeneration of spent fuel is a key contributor to the overall energy efficiency of the fuel cycle. Chemical hydrogen storage provides a diversity of options to enable hydrogen for transportation as well as other niche and stationary applications, and could also be used for hydrogen delivery where it offers the opportunity for a liquid or solid fuel infrastructure with the potential for no direct hydrogen handling by the consumer.

During the four years of this project, CHSCoE researchers have made substantial strides toward developing nitrogen-boron based molecular hydrogen storage compounds that can meet DOE technical targets for on board hydrogen storage. The B-N materials, such as AB and related compounds, have unique chemical properties that enables facile hydrogen release at temperatures around 100°C using a number of approaches that give rise to high rates of release. The CHSCoE has also made dramatic strides in demonstrating that spent fuel from AB may be chemically regenerated off-board. Recent process modeling work from our partner Dow Chemical (formerly of Rohm and Haas) has shown that recycle may be done with an initial estimated cost of $7-8/kg of AB. Recent discoveries of more effective regeneration chemistries may lower this cost further.

Approach

The overall Center approach capitalizes on its broad spectrum of expertise ranging from chemical synthesis and characterization to catalysis to chemical engineering to molecular modeling and simulation to carry out research and development (R&D) in chemical hydrogen storage. The Center's activities fall into four general areas.

1. **Hydrogen Release from Ammonia Borane.** This activity is populated by a number of Center partners, and is directed at developing processes for the release of hydrogen from AB. The goal is to simultaneously improve the quantity of hydrogen released while improving the rate of hydrogen

release at the lowest temperatures achievable, and with mitigation of foaming or the release of volatile byproducts that could be deleterious to the eventual utilization of the hydrogen in for example, a fuel cell.

2. **Regeneration of Spent Fuel.** This activity is directed at the energy and chemically efficient regeneration of spent fuel that arises from dehydrogenation of AB. This represents a majority of the current work being performed within the Center. The Center's regeneration efforts are directed at digesting of the spent fuel to a readily chemically processable material, then adding hydrogen to this material, and recycling any auxiliary components required along the to provide for a chemically integrated spent fuel to fuel regeneration loop.
3. **Materials Discovery.** Much of the Center's focus is on developing AB as a hydrogen storage material. The Center maintains a smaller research effort to discover other potentially useful storage materials. These areas are currently focused on developing storage materials that release hydrogen less exothermically than AB, with the goal of discovering a material that releases hydrogen with little or no heat lost or gained. This could lead to a potentially reversible, on-board regenerable fuel.
4. **Engineering Supporting R&D.** This activity, along with theory and modeling, crosscuts all of the other activities within the Center, as engineering analyses are used to inform the R&D efforts as to what the practical implications of the systems targets entail for development of an efficient hydrogen storage system. This activity provides chemical engineering and process engineering expertise for analysis of potential hydrogen storage systems and spent fuel regeneration, and provides guidance for materials down selection processes.

The overall approach of the Center is to screen and assess concepts and ideas against a set of hierarchical criteria that are derived from the DOE technical targets for hydrogen storage.

Results

Because of space limitations, this report will describe only two of the major overarching accomplishments of the Center. More detailed and complete results from the Center's activities may be found in the individual reports of the CHSCoE partners.

Hydrogen Release. During previous years, the Center has demonstrated many compounds and processes that can release greater than 7 wt% hydrogen, with many compounds yielding in excess of 10-13 wt% hydrogen. AB, for example, in solid form, can readily release 13-15 wt% hydrogen. The key research issue that the Center has focused on is in increasing the rate and decreasing the temperature of release. A synopsis of results from the CHSCoE is shown in Figure 1.

Using ionic liquid/AB mixtures, very high rates of hydrogen release have been determined at temperatures between 100 and 120°C, where 8 wt% hydrogen is released within two minutes at 120°C.

Using catalysts, release of hydrogen from AB may be accelerated. The University of Washington has demonstrated release of 5.8 wt% hydrogen in three minutes at 25°C. Using heterogeneous catalysts LANL researchers have demonstrated hydrogen release of 8 wt% in 120 minutes at 70°C, or in 8 minutes at 110°C.

By synthesizing metal-substituted derivatives of ammonia borane, a wide array of new metal amidoborane (M-AB) storage materials have been discovered and characterized by researchers at the Pacific Northwest National Laboratory (PNNL), LANL, and the University of Missouri. As one example, PNNL has shown that Li-AB releases 5 wt% hydrogen in 2 minutes at 100°C. Li-AB also has a very high activation energy, a feature with positive implications for adequate storage lifetimes at 50-60°C. LANL has also worked closely with Center partners at the University of Missouri to characterize the hydrogen release and thermochemical properties of aluminum-based amidoborohydride compounds being prepared at Missouri.

These are but a few examples from the Center that indicate that hydrogen release from B-N systems results in good capacity delivered at high rates. To summarize, during the last four years, Center researchers have made

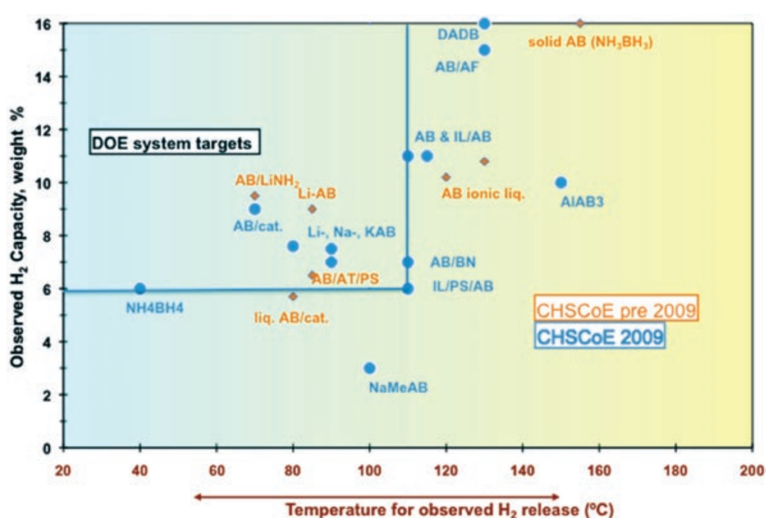

FIGURE 1. Synopsis of results for the release of hydrogen from a variety of materials as a function of temperature.

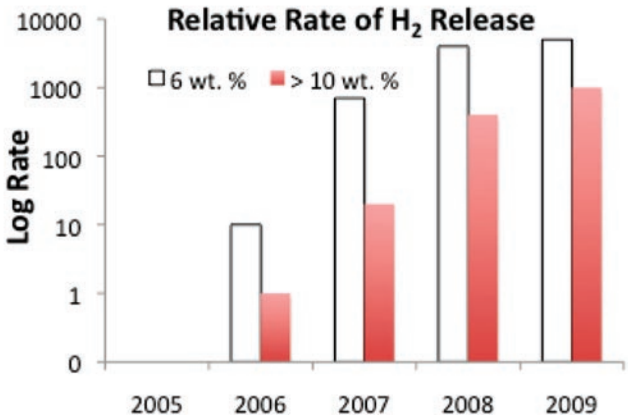

FIGURE 2. Improvements in rate of hydrogen release from AB. Rates to release the first equivalent (6.5 wt%) (unshaded) and the rate to release 10 wt% (shaded) have improved 100-1,000 fold.

continuous improvements in the rates of hydrogen release from B-N materials that now are 2-3 orders of magnitude greater rate than rates reported in 2006 (see Figure 2).

Regeneration. Center researchers have previously described and/or demonstrated several chemical reprocessing schemes to convert spent fuel back to ammonia borane. The best developed scheme involves the use of thiocatechol to 'digest' the spent fuel to a more reactive form, followed by subsequent amine exchange for ammonia, and a reduction using a tin hydride. Replacing the amine with ammonia regenerates AB. Recycling the tin reagent back to tin hydride completes the cycle. LANL demonstrated lab-scale regeneration of ammonia borane, and demonstrated the proof-of-principle recycle of tin hydride. With this information in hand, process engineers at Rohm and Haas (now Dow) performed process modeling of this regeneration scheme to obtain a baseline estimate of the cost of this process. This first analysis indicated that AB regeneration could cost as little as $7-8/kg of AB. The analysis indicated substantial opportunities to improve both the cost and the energy efficiency of the thiocatechol regeneration scheme, particularly in the area of improved separations and reduced mass of reagents.

With this information and guidance from Dow's process analysis in hand, LANL researchers developed and demonstrated a streamlined process of potentially simpler separations, and markedly fewer steps using light weight hydrazine as digesting agent and reducing agent as shown in the right panel of Figure 3. Analysis of this process is currently being performed. With the lower mass of reagents that are required, and the simpler separations schemes, this streamlined process is may have potentially reduced cost and increased energy efficiency.

Conclusions and Future Directions

Research within the CHSCoE has demonstrated that chemical hydrogen storage may be a viable approach to on board storage. Materials with high hydrogen capacities having high rates of release, good stability, and proven recycle have been synthesized, characterized, and demonstrated in the laboratory. Preliminary baseline costs for off-board regeneration have been modeled, and may be reduced further, and energy efficiencies may still be improved.

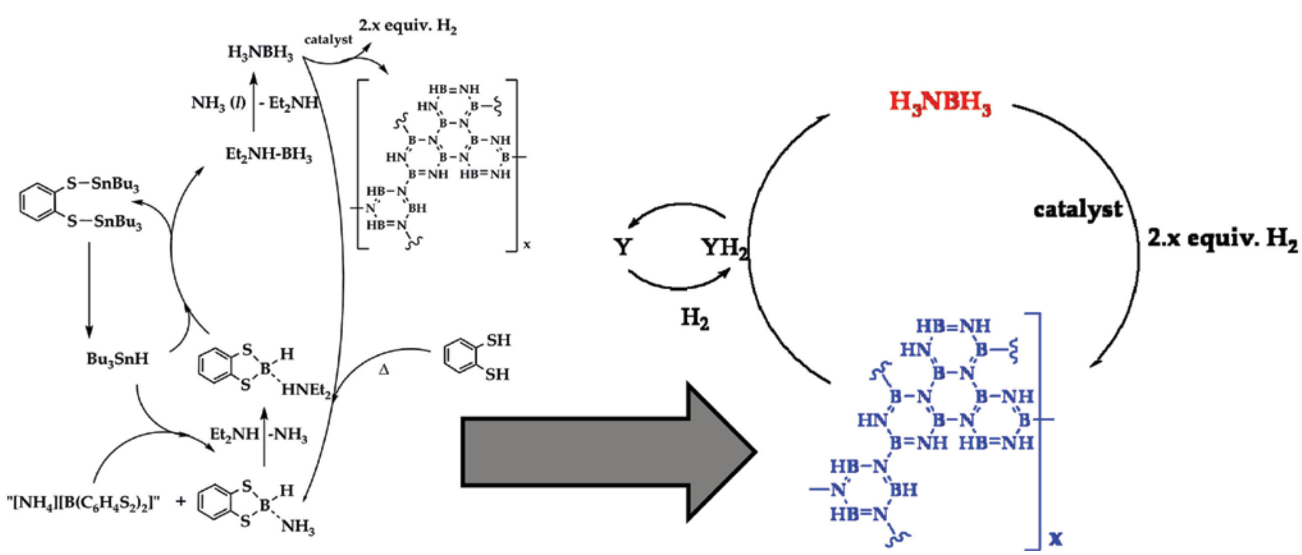

FIGURE 3. Evolution of spent fuel regeneration schemes. Left side depicts the 'thiocatechol route'. The right panel depicts an improved, simplified regeneration process using hydrazine as digesting agent and reducing agent (Y=hydrazine).

Future work within the last year of the Center will be focused on:

- Engineering support – analyze progress with respect to key barriers, provide quantitative input to prioritization, down select processes, complete additional cost estimates.
- Regeneration – use baseline cost analysis to prioritize improvements in efficiency, cost, down-select most promising regeneration pathway.
- New materials – Continue search for reversibility in covalent materials with goal of discovering on board regenerable materials.
- Hydrogen release – Finalize optimization of catalyst, ionic liquid, additive-mediated release processes, develop and describe mitigation of impurities, complete release studies for catalytic, ionic liquid-activated, and thermolytic approaches.
- Preparation of a final report of Center activities – analyze pros/cons of materials, regeneration processes, and give final recommendations to DOE.

Special Recognitions & Awards/Patents Issued

All Awards, Patents, Publications and Presentations resulting from work within the Chemical Hydrogen Storage Center are given in the accompanying partner reports.