IV.B.1a 2010 Overview and Wrapup: DOE Chemical Hydrogen Storage Center of Excellence (CHSCoE)

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Start Date: March 1, 2005
End Date: September 30, 2010

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 engineering analyses to evaluate cost and efficiency of hydrogen storage materials and spent fuel regeneration processes.
- Develop life cycle analysis.
- Transfer chemical hydrogen storage systems information to the Hydrogen Storage Engineering Center of Excellence, and receive feedback from its analyses.

Technical Barriers

This project addresses the following technical barriers from Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRDDP):

(A) System Weight & 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 have been addressed during the Center's activity, 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. The Center's criteria for materials down-selection, which are mapped to the DOE technical targets for storage systems, are tabulated in Table 1. 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 $gH_2/s/kW$, is the DOE 2010 target. A tabulation of all of the Center's interim targets are published in "2008 Overview - DOE Chemical Hydrogen Storage Center of Excellence", 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 for 2010 from across the Center are organized into four main areas: 1) Hydrogen Release, 2) Spent Fuel Regeneration, 3) New Materials, and 4) Engineering Supporting Research and Development

TABLE 1. Criteria for Materials Down-Selection

Criterion	Description	Metric
Material Wt. %	Maximum calculated hydrogen weight fraction, potential to exceed 9 wt %	> 7 wt. % H_2
Potential to Regenerate On-Board	Potential to rehydrogenate spent fuel directly	yes/no/potential
Regenerable	Ability to chemically reprocess fuel offboard	yes/no/potential
Acceptable Phase Change	Problematic liquid to solid phase change	yes/no/potential
Acceptable H_2 Release Rate	Maximum rate of hydrogen release	> .02g H_2/s/kW material
Stable Material < 50 °C	Stable in fuel tank< 50 °C to H_2 release, or decomposition	yes/no/potential
Temperature of Release	Demonstrated, or potential for release at T< 100 °C	< 200 °C

(R&D). The highlights from each of these areas are outlined below.

- Hydrogen Release from Ammonia Borane (AB):
  - Demonstrated increased rates at temperatures below 100°C for release from AB in ionic liquids using metal ion catalysts.
  - Kinetics data for ionic liquid/AB mixtures delivered to Argonne National Laboratory (ANL) for preliminary on board release system analysis.
  - Development of new ionic liquid fuel compositions with greater than 10 wt% hydrogen.
  - Demonstrated high rates at temperatures as low as 70°C with non-platinum group metal heterogeneous catalysts demonstrated.
  - Deselected amine borane/AB liquid fuels for further consideration because of unresolved catalyst deactivation issues.
  - Quantification of impurities and their rates of formation lead to demonstration that impurities may be mitigated by proper choice of process conditions.
- Spent Fuel Regeneration, First-Fill Processes, and Boron Resources Studies:
  - A complete **one pot** regeneration cycle has been proven with overall yield of spent fuel digestion through reduction steps exceeding 90%. This method works for multiple spent fuel forms including spent fuels from ionic liquids giving ammonia borane, and is chemically simple relative to previous regeneration schemes.
  - Cost analysis on this new regeneration process is underway in collaboration with Dow Chemical Company. Preliminary analysis indicates substantially reduced costs as compared to Dow's previous analysis of the thiocatechol route ($7-8/gasoline gallon equivalent, gge), but higher raw materials costs.
  - AB first-fill reactor capable of 100 gram batch.
  - 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:
  - All metal amidoborane materials currently known show exothermic hydrogen release. It is not possible to regenerate these materials efficiently and thus they are not considered further for onboard applications, but these materials are useful for stationary near-term applications.
  - University of Oregon demonstrated additional syntheses of endothermic/exothermic cyclo-carbon-boron-nitrogen (CBN) compounds, pathways for regeneration of spent fuel, first-fill syntheses, and measured thermodynamic paramaters that have corroborated computational studies on these molecules.
- Engineering-Supporting R&D
  - First order estimation of U.S. and global borate reserves completed, taking into account consumption by competing applications through initial fill timeframe.
  - Developed cost analyses of most promising first fill pathways to prepare sodium borohydride and AB.
  - Parametric studies to understand engineering scale up of first-fill reactor; semi-continuous flow reactor being designed.
  - Eliminated plasma-based process for $NaBH_4$ production to due to irreproducibility.
  - Identification of a scalable, solid-solid reactive milling technology has been met with challenges because of poor yields of $NaBH_4$.
  - Identified alternative, scalable solution route to $NaBH_4$ that has implications for successful scale up of any boron hydride-based fuel.

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 five 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 boron-nitrogen (BN) 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. A recent hydrazine-based one pot regeneration scheme has been demonstrated in the lab, and has substantially reduced separations and processing costs relative to prior regeneration schemes. The major cost in this scheme is the cost of the hydrazine, indicating that research to reduce this cost could lead to a very cost-effective regeneration of spent fuel.

The Center is the team comprised of researchers at LANL, the University of Pennsylvania, Dow Chemical Company, Pacific Northwest National Laboratory (PNNL), Pennsylvania State University, the University of California, Davis, the University of Alabama, the University of Washington, the University of Oregon, U.S. Borax, and the University of Missouri. The Center has been supported in our work through analyses performed by ANL and TIAX, and our interactions with the Hydrogen Storage Engineering Center of Excellence.

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 R&D in chemical hydrogen storage. The Center's activities fall into four general areas of hydrogen release from AB or its mixtures, regeneration of spent fuel from AB, materials discovery, and engineering supporting R&D. The goals of these four parallel approaches is to increase the rates of hydrogen release from BN compounds at moderate temperatures, regenerating the spent fuel that results from dehydrogenation of boron-nitrogen-hydrogen (BNH) compounds, and discovering new release materials with more favorable thermodynamics that may enable direct rehydrogenation of the spent fuel. All of these activities are supported and guided by modeling and simulation of the related molecular processes and engineering-based analysis that provides direction to the experimental efforts that are focused on developing a practical hydrogen storage material that meets DOE's 2010 technical targets.

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. For example, AB in solid form, can readily release 13-15 wt% hydrogen. Because of the engineering issues surrounding the handling of solids onboard, the Center has focused significant effort at developing stable liquid fuels comprising AB in ionic liquids, or AB in liquid alkylamineboranes. The latter approach, while potentially realizing greater hydrogen capacity because of the contribution of the dehydrogenation of the liquid alkylamineborane, has run into difficulty because of catalyst deactivation for which the Center at present has no straightforward solution.

The Center this year has provided ANL with kinetics data for the dehydrogenation of AB/ionic liquid mixtures. With this data, ANL has provided a preliminary onboard hydrogen release system analysis. Their preliminary findings are that the exothermicity of hydrogen release drives adequately rapid release of hydrogen, but the heat released provides a challenge for onboard heat management. Several configurations of onboard release reactor are suggested to accommodate these features, but more work is necessary.

New Materials

By synthesizing metal-substituted derivatives of AB, a wide array of new metal amidoborane (M-AB) storage materials have been previously discovered and characterized by researchers at PNNL, LANL, and Missouri. As one example, PNNL has shown that Li-AB releases 5 wt% hydrogen in 2 minutes at 100°C. This year, additional thermodynamics data have been obtained on a subset of these compounds. The thermodynamics of release indicate that all of the mono metalamidoborane compounds studied to date are still too exothermic to enable direct rehydrogenation of spent fuel (Figure 1). Because of this, and the fact that there are no energy-efficient pathways to regenerate spent fuel from metal amidoboranes, that this line of research should be curtailed. There remains the possibility that multimetallic metalamidoboranes may have more favorable thermodynamics. Also, some of these metal amidoboranes may find use in small niche non-vehicular applications such as portable power.

Another line of research into new materials by our University of Oregon partner has shown that exothermic release of hydrogen from the BN segment of a cyclo-CBN compound coupled with the endothermic release of carbon-carbon (C-C) segments achieves more thermodynamically favorable release of hydrogen as compared to highly exothermic ammonia borane (Figure 2). The thermodynamics of release in these systems that was previously explored using theoretical techniques in collaboration with our University of Alabama partner have been corroborated experimentally. Because of the more favorable thermodynamics, regeneration of spent fuel using H_2 directly in concert with H^+ and H^- reagents under mild conditions has been demonstrated.

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. Last year, 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 that indicated that AB regeneration could cost as little as $7-8/gge. Based on our lessons learned from this process, the Center has discovered a very simple, one-pot regeneration of AB spent fuels using hydrazine in liquid ammonia that results in fast, high conversions back to AB (see Figure 3). Dow has performed a preliminary cost analysis of this hydrazine route, and has found that because of the simpler process that requires far fewer separations steps, that process energy and capital equipment costs are substantially reduced vs. the multistep thiocatechol route. They also find that the most significant cost is in the cost of hydrazine. An

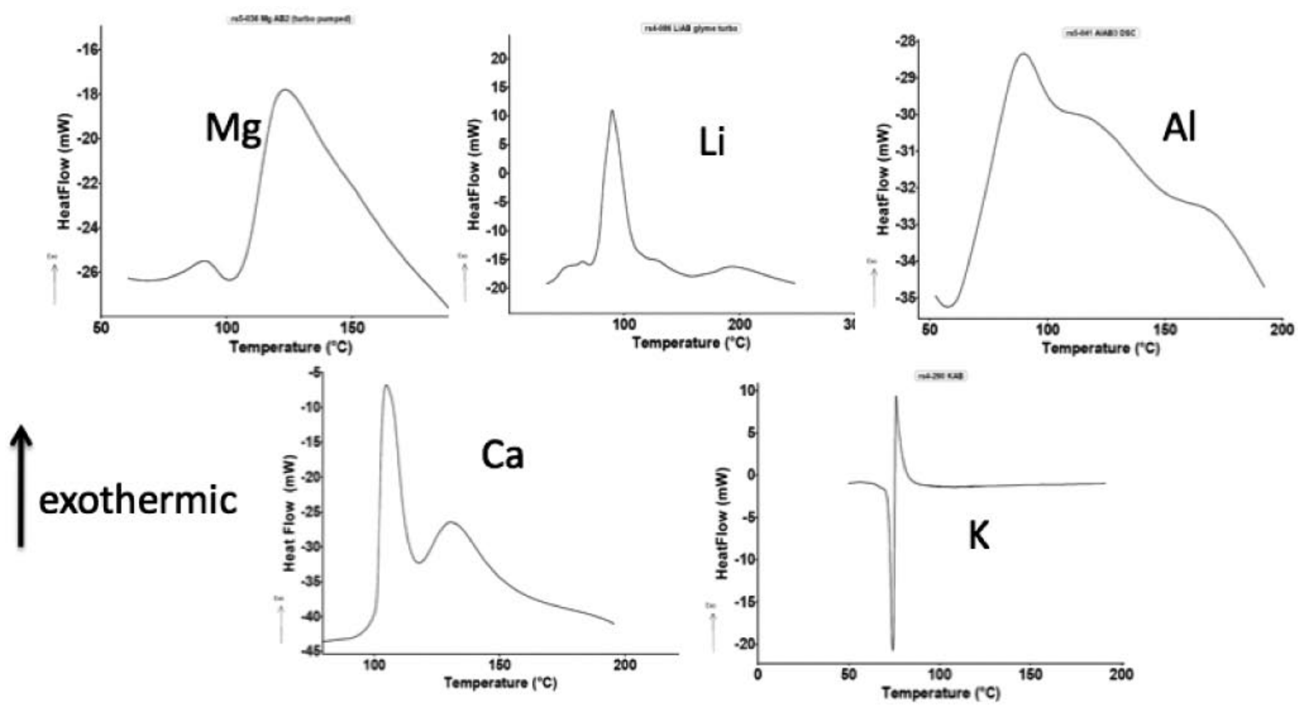

FIGURE 1. Measured heat flow during hydrogen release for a series of metal amidoboranes $M(NH_2BH_3)_n$ compounds. Hydrogen release temperature, rate of release, and heat released vary with the identity of the metal ion. All of the heat flow measurements indicate that these compounds release hydrogen exothermically.

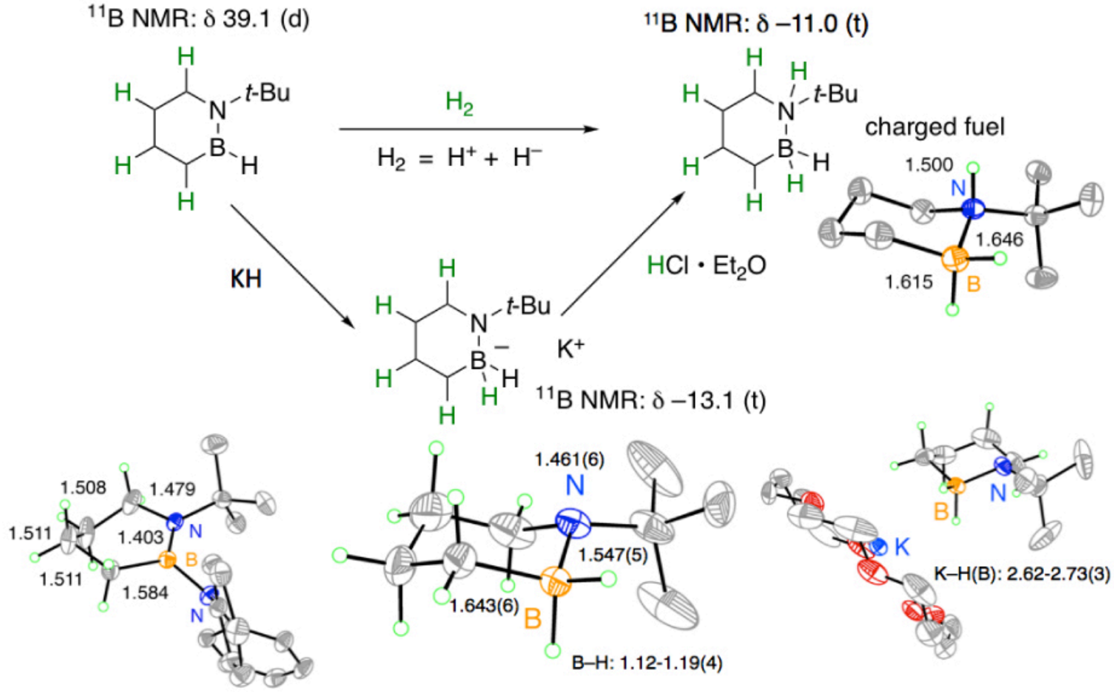

FIGURE 2. Cyclo-CBN compounds such as shown in this figure may be interconverted using chemical approaches. The intermediates along the hydrogenation-dehydrogenation pathway have been structurally characterized using single crystal X-ray diffraction techniques, and are depicted at the bottom of the figure.

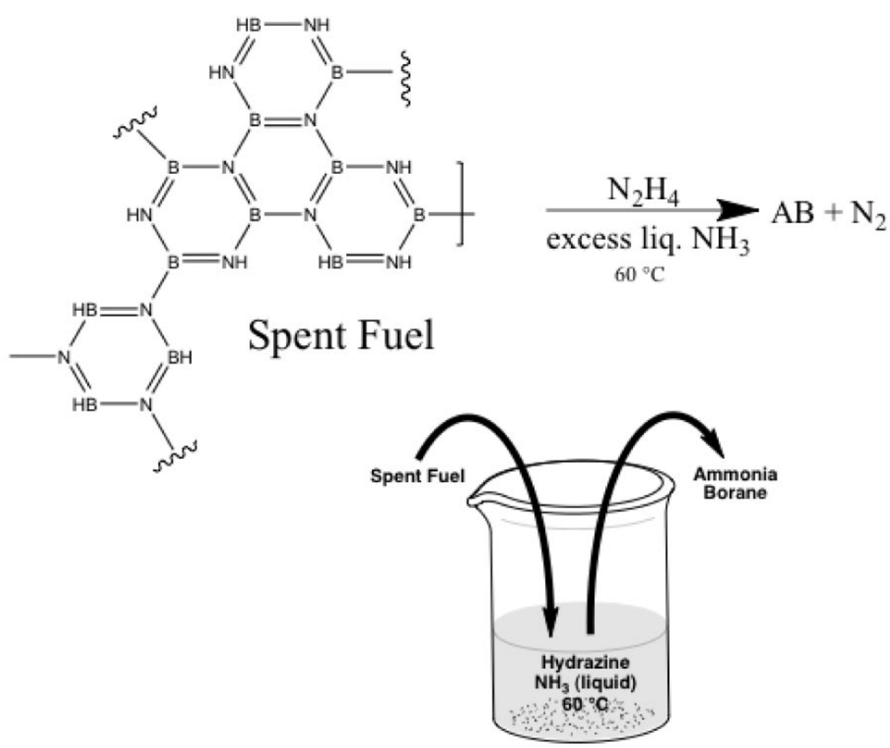

FIGURE 3. One-pot regeneration scheme using hydrazine as the digestion and reduction agent. Digestion of spent fuel in a mixture of hydrazine and ammonia results in near quantitative conversion to ammonia borane. This approach also works for regeneration of other forms of BNH_x spent fuels that arise from ionic liquid/AB mixtures, and from the 'pentamer' that results from the release of one equivalent of hydrogen from AB using specific homogeneous transition element catalysts.

additional feature of the hydrazine route is that multiple spent fuel forms may be readily regenerated, such as the spent fuel from ionic liquid/AB liquid mixtures, or the 'pentamer' spent fuel that results from rapid room temperature release of one equivalent of hydrogen using certain homogeneous Co and Ir pincer ligand catalysts. This latter observation may be interesting for certain stationary applications, where rapid release at room temperature is required and where only the heat related to the release of one equivalent of hydrogen is generated.

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. Liquid fuels that have the potential to remain liquid during the dehydrogenation cycle may enable simplified reactor designs. Heat management of these exothermic processes will remain a challenge. Preliminary baseline costs for off board regeneration have been modeled, and may be reduced further, and energy efficiencies may still be improved.

Remaining issues include:

- Regeneration – develop inexpensive hydrazine synthesis routes, or develop alternative regeneration schemes.
- New materials – continue search for reversibility in covalent materials such as the cyclo-CBNs or multimetallic amidoboranes with goal of discovering on board regenerable materials, or materials that are less exothermic. Search for liquid hydrogen storage materials.
- Hydrogen release – measure and understand any catalyst deactivation or lifetime issues, develop and describe mitigation of any and all impurities and their impact on fuel cell operation if any, develop stable optimal liquid fuels, develop reactor schemes to handle the exothermicity of hydrogen release from this class of materials.

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.