

IV.B.4 DOE Chemical Hydrogen Storage Center of Excellence

William Tumas (Primary Contact),
R. Thomas Baker, Anthony Burrell,
David Thorn

Los Alamos National Laboratory
MS C331

Los Alamos, NM 87545

Phone: (505) 667-3803; Fax: (505) 667-4098

E-mail: tumas@lanl.gov

Partners:

Christopher L. Aardahl,

Pacific Northwest National Laboratory (PNNL)

Suzanne W. Linehan, Rohm and Haas Company (ROH)

Ying Wu, Millennium Cell Inc. (MCEL)

Digby D. Macdonald, Pennsylvania State University
(PSU)

M. Frederick Hawthorne, University of Missouri,
Columbia (UMC)

Larry G. Sneddon, University of Pennsylvania (Penn)

Karen I. Goldberg, University of Washington (UW)

Clinton F. Lane, Northern Arizona University (NAU)

Xiao-Dong Xiang, Intematix Corporation (IMX)

David A. Dixon, University of Alabama (Ala)

Philip P. Power, University of California, Davis
(UC Davis)

David Schubert, US Borax

DOE Technology Development Manager:
Grace Ordaz

Phone: (202) 586-8350; Fax: (202) 586-9811

E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire

Phone: (303) 275-4795; Fax: (303) 275-4753

E-mail: James.Alkire@go.doe.gov

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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 with the potential to meet the 2015 system goals.
- Develop materials, catalysts, catalytic processes, and new concepts for hydrogen release and spent fuel regeneration.
- Design, synthesize, and test structures/compositions to control the thermochemistry of hydrogen release and spent fuel regeneration.
- Assess concepts and systems for hydrogen release and regeneration using engineering analysis.

- Perform engineering scale studies to evaluate performance in hydrogen delivery systems.
- Develop life cycle inventory to assess regeneration energy requirements.
- Demonstrate a 1 kg prototype storage system.

Technical Barriers Addressed by the Center

The Chemical Hydrogen Storage Center of Excellence addresses the following technical barriers for On-Board Hydrogen Storage (section 3.3.4.2) in the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets Addressed by the Center

The Chemical Hydrogen Storage Center of Excellence is taking a multi-pronged approach to identifying and developing chemical hydrogen storage materials and systems capable of meeting the 2010 DOE goals for on-board hydrogen storage with the potential to meet the 2015 DOE targets. The Center has developed a set of quantitative metrics to track progress towards the DOE targets:

- Gravimetric capacity for the reaction system (i.e. the material and any solvent/catalyst), in wt% and kWh/kg.
- Volumetric capacity for the reaction system (i.e. the material and any solvent/catalyst), in kWh/L.
- Hydrogen release rate (reported as amount of material/catalyst needed to meet DOE target rate of 0.02 g H₂/sec/kW).
- Energy efficiency of the regeneration process (i.e. the ratio, in percent, of the amount of energy in hydrogen released to the sum of the energy in the hydrogen released and the amount of energy needed to regenerate spent storage material).

The capacity criteria above are not yet for a complete on-board storage system which would include the storage tank, reactor system, and ancillary components. Although much progress has been made

in FY 2006, the primary goal has been to understand the chemistry associated with the storage systems. Therefore, the systems under investigation are still being optimized for capacity, rate and regeneration efficiency. Progress towards these targets is being tracked at the Center level. For FY 2006, the progress towards these targets is provided in reports from each Center partner, which are appended to this report. The Center aims to meet the following DOE targets:

- By 2010, develop and verify on-board hydrogen storage materials achieving storage system targets of 2 kWh/kg (6 wt%), 1.5 kWh/L, and \$4/kWh.
- By 2015, develop and verify on-board hydrogen storage materials achieving storage system targets of 3 kWh/kg (9 wt%), 2.7 kWh/L, and \$2/kWh.

FY 2006 Accomplishments of the Center

- Established performance-based metrics for quantitatively evaluating chemical storage system capacity, hydrogen release rate, and regeneration routes against DOE targets.
- Developed a Center-wide engineering assessment methodology for incorporating thermodynamics from known data or Center-derived quantum chemical calculations in the evaluation of new chemical routes for hydrogen release and regeneration of spent material.
- Completed a spreadsheet with energetics, potential capacity, and other critical information for chemical hydrogen storage options.
- Identified, assessed and prioritized new concepts for electrochemical reduction of B-OH(OR) bonds.
- Developed on-board storage engineering assessment tools using on-board release models of sodium borohydride hydrolysis as a prototypical system.
- Discovered heterogeneous catalysts for the controlled generation of hydrogen from the hydrolysis of salts of polyhedral borane anions, $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$ and $B_{11}H_{14}^{-}$, to release hydrogen with reaction system (material, catalyst, solvent) at material storage capacities up to 6.1 wt% (including consumed water) at rates up to $22 \times 10^{-3} \text{ min}^{-1}$ using 5 mole percent catalyst.
- Developed a convenient and safe method for the synthesis of ammonia triborane (AT) and demonstrated it was both soluble and stable in water.
- Demonstrated rhodium catalyzed hydrolysis of AT with a reaction system capacity of 6.1 wt% for a highly concentrated (22.7 wt%) aqueous AT solution – this example could meet the DOE 2007 system target of 4.5 wt%.
- Determined that hydrogen release rate from solid ammonia borane is governed by a nucleation and growth mechanism.
- Increased the rate and altered selectivity of ammonia borane (AB) dehydrogenation via extended studies of mesoporous scaffolds.
- Demonstrated that alternative reaction media such as ionic liquids can increase AB dehydrogenation rates and potentially open up new reaction pathways.
- Discovered that a system composed of a 90/10 mixture of ammonia-borane/lithium-amide was found to liberate 6.85 wt% H_2 after 6 h and 9.28 wt% H_2 after 15 h at 85°C.
- Discovered a number of catalysts for hydrogen release from AB in solution:
 - Studies using acid catalysts in concentrated AB solutions demonstrated multiple dehydrogenation at 60°C due to instability of acyclic $[BH_2NH_2]_n$ intermediates.
 - Iridium catalysts with ‘pincer’ ligands provide the fastest rate to date (complete in 14 minutes at 25°C with 1% catalyst) for release of one equivalent of hydrogen (rates up to 2.77×10^{-5} mole H_2 /sec) from AB to give exclusively cyclic $[BH_2NH_2]_5$.
 - Multiple dehydrogenation of AB to cyclic products such as borazine ($[BH=NH]_3$) is facile with several electron-rich precious metal complexes.
 - Non-precious metal complexes consisting of N-heterocyclic carbene ligands were found to be long-lived catalysts that afford linked borazines without build-up of $[BH_2NH_2]_n$ intermediates, as determined by *in situ* nuclear magnetic resonance (NMR) studies. The fastest rates observed to date are ca. 0.06 min^{-1} in diglyme solution which would require 153 g of AB (and ca. 14.6 g Ni catalyst) to provide a hydrogen release rate of 0.02 grams per sec.
 - New low-cost heterogeneous catalysts for AB dehydrogenation gave comparable rates to those for ruthenium-catalyzed AB hydrolysis.
- Developed concepts and demonstrated the key steps for regeneration of AB from spent dehydrogenated material:
 - Dissolution, hydride transfer, regenerable metal hydrides, ligand exchange.
- Demonstrated, in the laboratory, the individual key steps in the five step AB regeneration process: 1) digestion of dehydrogenated boron-nitrogen compounds by trifluoroacetic acid, 2) reduction of a B-X to B-H bond in chloro-catecholborane with a regenerable tin hydride as well as formation of the metal hydride from decarboxylation of a tin formate, 3) disproportionation of catecholborane to diethylaniline-borane, and 4) conversion of diethylaniline-borane to AB by reaction with ammonia.

- Completed a survey document report that details safety aspects, synthesis, properties and applications of N-B-H compounds and materials.
- Demonstrated hydrogen storage in organic systems:
 - Used high-level theory to obtain accurate thermodynamic data for hydrogen release from heteroatom-containing organics.
 - Hydrogen release demonstrated in laboratory for heteroatom-containing organics (1,1-elimination) with the potential for over 7 wt% storage in the material.
 - Demonstrated first examples of coupled endo/exothermic reactions with the potential for over 7 wt% storage in the material.
- Developed solution synthetic routes to boron nanoparticles and characterized H-loaded silicon nanoparticles.
- Coordinated overall Center R&D efforts through implementation of monthly conference calls, project level meetings, semi-annual meetings, site visits, and Coordinating Council meetings.

Introduction

Chemical hydrogen storage involves storing hydrogen in chemical bonds in molecules and materials where an on-board reaction is used to release hydrogen and generate spent storage material. In addition to the importance of on-board storage capacity and hydrogen release rates, the energy efficiency of the regeneration of spent storage material, which will likely be off-board the vehicle, is vital. Chemical hydrogen storage provide a diversity of options 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.

Researchers in the Center are advancing a number of integrated projects involving the development of materials, catalysts, catalytic processes, and new concepts for hydrogen release and regeneration of spent material, as well as the development of engineering feasibility of the processes. The objectives of the Center are to develop and assess new methods for on-demand release of hydrogen from chemical systems that can achieve DOE targets and to develop high yield, energy efficient off-board methods for regeneration of spent storage material. The key elements in the Center's collaborative activities are computation and modeling; the design, synthesis, and testing of structures and compositions to control the thermochemistry and kinetics of hydrogen release and spent fuel regeneration; development of chemical processes and catalysts for hydrogen release and regeneration; and iterative engineering assessment including evaluation, modeling

and testing ranging from process identification through optimization of hydrogen release and regeneration reaction conditions.

Center Approach

The overall Center approach capitalizes on its broad spectrum of expertise to carry out collectively a number of focused projects listed below that are divided into three Tiers with distinct goals:

Tier 1. "Borohydride": Develop new borate-to-borohydride (B-OH to B-H) regeneration alternatives and assess economics and life cycle analysis of borohydride/water to hydrogen.

Tier 2. "Novel Boron Chemistry": Alternative boron chemistry that avoids thermodynamic sinks using catalytic hydrogen release from polyhedral boranes (B_xH_y) or amine-boranes. Develop alternative boron chemistry approaches including polyhedral boranes and amine-boranes.

Tier 3. "Innovation Beyond Boron": Develop new compounds and concepts beyond boron for chemical hydrogen storage using coupled endo/exothermic reactions, nano-scale materials, and heteroatom-substituted organic systems for thermodynamic control.

Pursuing three-tiers of material discovery in parallel will maximize our ability to achieve the DOE targets for hydrogen storage. The goal is to provide DOE with several working options for chemical hydrogen storage, as well as an evolving knowledge and critical evaluation to assist future R&D, technology demonstration, and policy decision-making. The overall approach of the Center is to screen and assess concepts and ideas against a set of hierarchical criteria which are derived from the DOE technical targets for hydrogen storage (Figure 1).

The specific Center projects are listed in Table 1. Our collaborative project structure enables the close coupling of experimental and computational R&D with engineering assessment to facilitate the transition from discovery of new concepts through development to implementation. The Center is addressing storage capacity by developing, synthesizing, and testing molecular compounds with high hydrogen density, appropriate energetics, and potential pathways for hydrogen release. Theory and modeling as well as engineering assessment are being used to provide insight and down-select the diversity of options. We are developing and optimizing catalysts and chemical processes for hydrogen release and studying their rates and mechanisms. Work on regeneration is focused on developing pathways closer to the thermodynamic limits by avoiding intermediates with high energy content, i.e. reducing agents that can be regenerated by low energy routes.

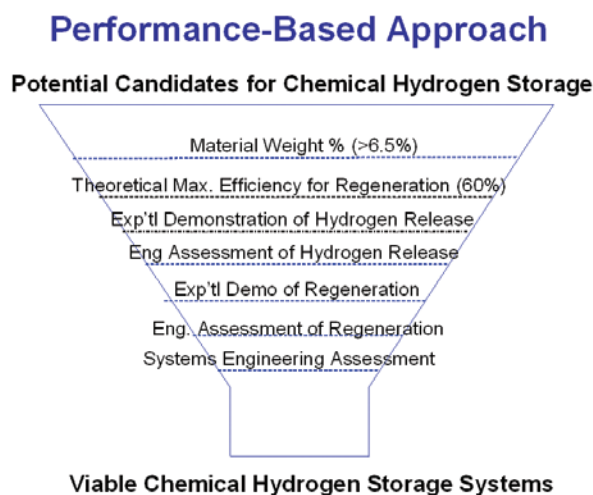


FIGURE 1. Performance-Based Criteria for Assessment of Center Concepts

TABLE 1. Center Projects

#	Project	Partners
1.1	B-O to B-H Engineering Guided Research	ROH, MCEL, PSU, Ala, USB, PNNL, LANL
1.2	Engineering Assessment of Hydrogen Generation Systems	MCEL, ROH, LANL, PNNL
2.1	Polyhedral Borane Chemistry	UCLA, IMX, PSU, PNNL, LANL
2.2	Amine-Borane Chemistry	Penn, UW, NAU, Ala, IMX, PNNL, LANL
2.3	Amine-Borane Systems Engineering, Safety	PNNL, NAU, LANL
3.1	Organics and Coupled Reactions	Ala, PNNL, LANL
3.2	Nanoparticles and Main Group Hydrides	UC Davis, Ala, LANL

Maintaining the synergy of the Center technical approaches and avoiding duplication are key goals that are achieved through frequent interaction and communication. Each project has a monthly conference call that allows principal investigators and their co-workers at each institution to share results and collectively plan their paths forward for the next month. In addition, our Center coordination approach maximizes the number of face-to-face discussions through semi-annual meetings, project level meetings, personnel exchange, and site visits as well as discussions at technical conferences attended by Center partners.

Results of Center Activities

The Center has made considerable progress in FY 2006 on all of the Center projects. Results from individual partners are provided in their reports

appended to this summary which also provide more detailed information on specific discoveries and findings. Work on Center activities started circa March 2005.

B-O to B-H Engineering Guided Research

Hydrolysis of sodium borohydride has been demonstrated by one of the Center partners, Millennium Cell (MCEL), to potentially meet the 2010 goals for hydrogen storage capacity; however, the current regeneration of spent storage material, aqueous sodium borate, is energy intensive owing to the use of sodium metal as a reductant. The energy efficiency regeneration of sodium borohydride from spent sodium borate solution is of primary importance for the utility of sodium borohydride hydrolysis for on-board hydrogen storage. DOE has targeted the end of FY 2007 for a go/no-go decision on sodium borohydride. The Center has created a set of milestones to develop energy efficient and cost-effective options for the conversion of B-OH (borate) to B-H (along with recommended performance criteria) to be able to provide a timely recommendation for this decision. Engineering-guided research is being used for down-selection to chemical pathways and processes for converting boron-oxygen bonds to boron-hydrogen bonds. In FY 2006, we evaluated several potentially energy-efficient and cost-effective regeneration routes: metal (e.g. Al, Zn, Si) reduction of borates; electrochemical reduction (one-step and two-step routes); and borane-based routes that do not rely on NaBH₄ as a starting material. Penn State University (PSU) developed a reliable and accurate in situ method for analysis of the borohydride ion to enable electrochemical investigations which will be employed to study some potential routes for electroreduction identified by Rohm and Haas (ROH), PSU, MCEL and Los Alamos National Laboratory (LANL) based on proprietary ROH data. In other experimental work, we prepared a number of complexed borates with nitrogen and sulfur donor ligands, but to date these have not proved advantageous for the B-O reduction chemistry.

Engineering Assessment for Hydrogen Release Systems

Engineering analysis in the Center is being closely coupled to experimental work as results are obtained for hydrogen release and regeneration. Understanding critical engineering aspects, designs and constraints is crucial for advancing chemical hydrogen storage discoveries into prototype on-board hydrogen generating systems. A multi-scale reactor model was developed and is being used by PNNL and MCEL for reactor optimization for sodium borohydride hydrolysis as a baseline. The steady-state profiles of temperature, NaBH₄ concentration, pressure drop, and H₂ flow rate were simulated and used to validate the modeling by comparison with corresponding experimental data.

The effects of fuel flow rate, fuel concentration, and system pressure were modeled. The model has been constructed with flexibility to be used to support reactor development for other chemical systems within the Center.

Center expertise in chemical process engineering and life cycle inventory has been used to examine work in Tier 1 and Tier 2. A baseline life cycle inventory has been completed for the current commercial Schlesinger NaBH_4 process. Preliminary cost estimates for AB synthesis based on current routes have also been completed.

Polyhedral Borane Chemistry

Hydrolysis of polyborane anions, e.g. $\text{B}_n\text{H}_n^{2-}$ ($n = 10$ and 12), $\text{B}_{11}\text{H}_{14}^-$ and their derivatives offer hydrogen storage capacity comparable to sodium borohydride without requiring high pH media for stability. Center partners at the University of California at Los Angeles (UCLA) have discovered several heterogeneous transition metal (cobalt, nickel, rhodium) boride catalysts for the hydrolysis of $\text{B}_{11}\text{H}_{14}^-$, $\text{B}_{12}\text{H}_{12}^{2-}$ and $\text{B}_{10}\text{H}_{10}^{2-}$ anion salts. Hydrolysis of $\text{NaB}_{11}\text{H}_{14}$ was faster than any $\text{B}_{12}\text{H}_{12}^{2-}$ or $\text{B}_{10}\text{H}_{10}^{2-}$ salts investigated and proceeded in the presence of all three boride catalysts. The hydrolysis rate was faster with rhodium boride compared to nickel and cobalt borides. Material storage capacities and hydrogen release rates were determined and found to be up to 6.15 wt% (including consumed water) and $22 \times 10^{-3} \text{ min}^{-1}$, respectively, using 5 mole percent catalyst. The University of Pennsylvania developed a method for the synthesis of ammonia trborane (AT) and studied its hydrolysis reactions. AT was demonstrated to be both soluble and stable in water, but that upon addition of acid or an appropriate transition metal catalyst it rapidly released hydrogen. Hydrolysis of highly concentrated (22.7 wt%) aqueous solutions of AT produced hydrogen corresponding to a reaction system capacity of 6.1 wt% using a rhodium/alumina catalyst over three hours at 21°C . Intematix has screened a hundred combinatorial compositions for catalytic hydrogen release from hydrolysis of polyhedral boranes and AB. They found a couple of potentially low-cost compositions with catalytic activity on par with the rates for ruthenium-catalyzed hydrolysis of sodium borohydride.

Amine-Borane Chemistry

Due to the high hydrogen content (up to 19.6 wt%) and the polarity of the bonding, amine-boranes, such as AB, are unique when compared to other chemical hydrogen storage options in their potential ability to store and deliver large amounts of molecular hydrogen through dehydrogenation and hydrolysis reactions. In FY 2006, understanding the chemistry and potential

of AB as a storage medium was one of the focal points for the Center. A number of important advances and discoveries were made. We continue to increase our understanding of the solid-state and solution reactivity of AB. We have also developed concepts for regeneration of AB from spent dehydrogenated material, $(\text{BNH}_x)_y$. Computational work in the Center is helping us fully characterize the thermodynamics of AB hydrogen release and regeneration chemistry.

This year, we confirmed that dehydrocoupling of solid AB proceeds through a nucleation and growth pathway that can be fit to the Avrami equation. *In situ* solid state NMR analysis revealed that the diammoniate of diborane, $[(\text{NH}_3)_2\text{BH}_2][\text{BH}_4]$, is formed and could be the nucleation seed for the reaction prior to formation of the product $[\text{NH}_2\text{BH}_2]_n$. Building on previous results showing that the rate and selectivity of dehydrocoupling are modified for AB contained in mesoporous scaffolds, we showed that loading beyond the 1:1 AB:scaffold ratio gave kinetics, thermodynamics and byproducts that begin to approach unsupported AB. In other work to lower the temperature and increase the extent of hydrogen release from solid AB, the University of Pennsylvania found that a system composed of a 90/10 mol% mixture of AB/ LiNH_2 was found to liberate 6.85 wt% H_2 over 6 h and 9.28 wt% H_2 over 15 h at 85°C .

In order to develop sufficiently fast hydrogen release reactions of AB that can be controlled, we have been investigating dehydrogenation catalysis in solution. A wide range of catalysts (based on metals, acids, and bases) were evaluated for their ability to effect hydrogen release. We are examining kinetics and mechanisms as well as characterizing intermediates and products in order to develop the optimal systems for capacity and hydrogen release rates. Strong Lewis and Bronsted acids promote hydrogen release even at room temperature to afford $[\text{BH}_2\text{NH}_2]_n$ oligomers. The mechanism for this process was elucidated by a combination of experiment and theory through Center partner collaboration. Concentrated (20 wt%) solutions of ammonia-borane in glyme react at least twice as fast as solid AB at 80°C and yield significantly more hydrogen.

A number of advances in transition metal catalysis have been made. For example, we discovered that an iridium 'pincer' complex is a very active catalyst for rapid dehydrogenation of AB (complete in 14 minutes at 1% catalyst loading) in organic solvents to produce one equivalent of hydrogen and what appears to be the cyclic pentamer $(\text{NH}_2\text{BH}_2)_5$. We also found that non-precious transition metal complexes consisting of N-heterocyclic carbene ligands can be long-lived catalysts that afford linked borazines without build-up of $[\text{BH}_2\text{NH}_2]_n$ intermediates, as determined by *in situ* nuclear magnetic resonance (NMR) studies. The fastest rates observed to date are ca. 0.06 min^{-1} in diglyme solution at 80°C which would require 153 g of AB (and ca. 14.6 g Ni catalyst) to provide a hydrogen release rate

of 0.02 grams per sec. Rapid screening has identified active catalyst compositions with potentially very reasonable costs. Center partners have also shown that reactions in ionic liquids increase the rate and extent of thermolytic hydrogen release from ammonia borane and several systems have been identified that have potential to meet DOE targets. For example, the reactions of AB dissolved in the 1-butyl-3-methyl-imidazolium chloride (bmimCl) ionic liquid at 85°C showed no induction period for hydrogen release producing 0.5, 0.91 and 1.10 equivalents of hydrogen after only 1, 3 and 6 h, respectively. The degree and rate of dehydrogenation could also be significantly increased by raising the temperature.

In the important area of regeneration of spent storage material, we have conceptualized an overall regeneration process that is currently based on five chemical transformations: digestion, activation, reduction, disproportionation and ligand exchange (Figure 2). We have demonstrated each step individually in the process. We have shown that trifluoroacetic acid can be used to digest the dehydrogenated boron-nitrogen product. We have also demonstrated the net reduction of the B-Cl bond in chloro catecholborane (ClBCat) with hydrogen mediated by a tin hydride. This tin hydride can be regenerated by decarboxylation of the tin formate. The latter can be formed by reaction of formate (itself generable from the hydrogenation of carbon dioxide) and the corresponding tin hydride. Diethylaniline was found to drive the redistribution of HBCat to (diethylaniline)-BH₃ which reacts quantitatively with ammonia to make AB.

Amine-borane systems engineering, safety

Given the potential promise of AB to reach even the 2015 goals, we are examining the engineering aspects, including safety aspects of materials and handling.

Regeneration Concept for Ammonia Borane

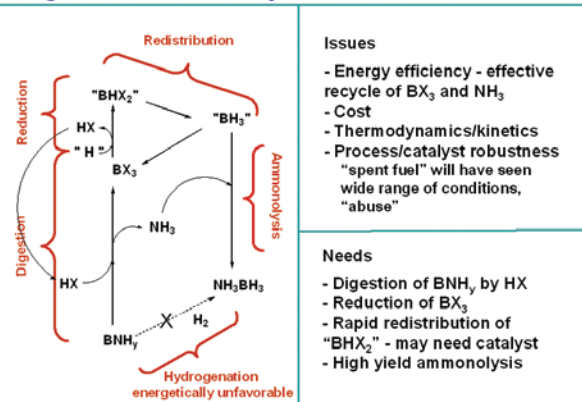


FIGURE 2. Scheme for Regeneration of Ammonia Borane from Dehydrogenated Material (BNH_y)

A thorough literature search for the preparation, physical properties, chemical properties and safety aspects of amine-borane compounds and borazines was completed which culminated into a survey document report that detailed safety aspects, synthesis, properties and applications of N-B-H compounds and materials. We have also investigated the thermal stability of solid AB which will be needed for fuel formulation concepts as we move forward. In FY 2007, we expect work in this area to increase and to incorporate findings from our other engineering assessment tasks.

Organics and Coupled Reactions

Organic molecules are capable of storing significant amounts of hydrogen in C-H bonds and offer potential advantages as storage materials (e.g. liquid storage materials); however, the dehydrogenation reactions are typically endothermic. Two general approaches to reducing the energy requirements for dehydrogenation are: 1) employing heteroatom substitution, particularly for 1,1-elimination reactions, and 2) investigating methods for mechanistically coupling endothermic hydrogen release reactions with other exothermic reactions. **Substantial progress has been made this year in heteroatom-containing organics with our experimental and computational efforts in carbene and cyanocarbon chemistry. Computation has revealed a number of molecules where the energetics of hydrogen release and regeneration are within the DOE targets for energy efficiency. Details include synthesis of a polycarbene architecture and addition of water to release additional hydrogen through both 1,1 and 1,2 pathways. A new pyridazine hydrogen storage candidate has been identified that appears to have favorable thermodynamics (weakly endothermic) of hydrogen release. The formation of novel imidazolium carbene adducts with hydrogen has also been demonstrated.**

Exploration of compounds that evolve hydrogen by way of coupled reactions has yielded interesting results where the evolution of hydrogen is driven by a co-reaction having a more favorable thermodynamic driving force generated by reaction of a co-product with the storage component precursor. We have examined a reaction to generate hydrogen at reasonable rates and quantities when heated in the presence of a suitable catalyst. Hydrogen evolution starts to occur at 150°C with a total quantity of hydrogen released during a temperature ramp to 245°C of 0.4-0.5 standard liters per gram of material which corresponds to 30-40% of the theoretical maximum. We are currently attempting to increase the total amount of hydrogen evolved from this compound to its full potential, and to decrease the temperature of hydrogen evolution. As the preliminary results are promising, we will also initiate studies of the regeneration reaction analogous to the reverse of the equation above.

Nanoparticles and Main Group Hydrides

This project is focused on the design and synthesis of light element compounds and nanomaterials that will reversibly produce molecular hydrogen for hydrogen storage materials. The large surface area of nanoparticles should facilitate a favorable weight to volume ratio, and low molecular weight elements such as boron, nitrogen and silicon exist in a variety of inexpensive and readily available precursors. Two primary routes were explored for the production of nanoparticles smaller than 10 nm in diameter. The first was the reduction of the elemental halides to achieve nanomaterials with chloride surface termination that could subsequently be replaced with amine or hydrogen. The second was the reaction of metal main group intermetallics with ammonium halides to produce hydrogen-capped nanomaterials. These materials were characterized via x-ray powder diffraction, transmission electron microscopy (TEM), fourier transform infrared (FTIR), thermogravimetric/differential scanning calorimetry (TG/DSC), and NMR spectroscopy. A simple low temperature route to hydrogen-capped silicon nanoparticles has also been demonstrated. X-ray powder diffraction along with TEM images show discrete nanoparticles consistent with diamond structure silicon. Hydrogen termination was demonstrated using solid state NMR. Reversible hydrogen release and uptake has not yet been demonstrated for these new nanomaterials.

Conclusions and Future Directions of Center for FY 2007

On-board hydrogen storage is a formidable problem for which scientific advances and engineering assessment are needed and a multi-disciplinary collaborative approach is required.

The Center has made significant progress towards its project objectives and towards DOE storage targets. In the area of borohydride regeneration from borate spent fuel, potential pathways have been identified, assessed and prioritized. The most promising candidates will be investigated aggressively as we approach the FY 2007 go/no-go decision on sodium borohydride. Detailed analysis of product mixtures will also be conducted to see if some regeneration schemes afford significant amounts of polyborane anions such as $(B_{12}H_{12})^{2-}$ without having to go through borohydride.

The Center's combination of experiment and theory has afforded a great deal of new information on ammonia borane dehydrogenation with discoveries of a number of catalysts, alternative reaction media and pathways, and the beneficial effects of additives and supports. In FY 2007, we will capitalize on partners' developments and have an even more coordinated

Center effort in catalyst development for this important area to identify the most promising systems with the potential to meet DOE storage targets in preparation for our down-select. Intimately intertwined with this selection is the development of energy-efficient processes for the regeneration of AB from the spent fuel (BNH_x). We expect work scope and Center partner participation on AB regeneration will more than double over the next six months. Engineering assessment of AB solution stability and of both hydrogen release and AB regeneration processes will also get underway in earnest in FY 2007 as we prepare for larger scale evaluations with Southwest Research Institute. Chemical process development for the efficient preparation of ammonia borane on pilot plant scale will be conducted at Northern Arizona University (NAU) with engineering input from Center partners.

While organic systems do not offer the high storage capacities of AB, the potential for thermodynamic control and reversible release and regeneration continue to make them attractive targets for the Center. We will continue to use theory and experiment to identify promising candidates that can be synthesized economically, release hydrogen at suitable rates below 90°C, and be rapidly regenerated using low to moderate hydrogen pressures. Similar qualities will be looked for in the light element nanomaterials. For the coupled reactions, materials that exhibit good hydrogen release rates and selectivity need to undergo engineering analysis to determine the mode of operation that offers the most efficient hydrogen release. For FY 2007 the Center will:

- Determine if B-O to B-H is possible with better energy efficiency and provide a go/no-go recommendation for on-board $NaBH_4$ hydrolysis storage system based on modeling and laboratory-scale experimental demonstration of energy-efficient off-board regeneration.
- Increase the capacity and rates of hydrogen release from polyboranes and amine boranes through catalyst development, mechanistic studies, and reaction media.
- Enhance spent AB regeneration process(es) by improving reactions for digestion and activation, developing lower energy metal hydrides and other reductants and combining/integrating steps.
- Develop energy-efficient metal hydrides for AB regeneration.
- Investigate new chemistry concepts for organics with >6-7 material wt% hydrogen storage potential.
- Determine effects of nano-scale on hydrogen storage capacity and energetics.
- Develop mechanisms to more closely couple endothermic and exothermic reactions.