

## VI.B.4 DOE Chemical Hydrogen Storage Center of Excellence

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

*Los Alamos National Laboratory (LANL)*

*MS C346, Los Alamos, NM 87545*

*Phone: (505) 667-3803; Fax: (505) 667-4098; E-mail: [tumas@lanl.gov](mailto:tumas@lanl.gov)*

### *Partners:*

*Intematix Corporation, Xiao-Dong Xiang*

*Millennium Cell Inc., Ying Wu*

*Northern Arizona University (NAU), Clinton F. Lane*

*Pacific Northwest National Laboratory (PNNL), Christopher L. Aardahl*

*Pennsylvania State University (Penn State), Digby D. Macdonald*

*Rohm and Haas Company, Suzanne W. Linehan*

*US Borax, David Schubert*

*University of Alabama, David A. Dixon*

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

*University of California, Los Angeles (UCLA), M. Frederick Hawthorne*

*University of Pennsylvania (Penn), Larry G. Sneddon*

*University of Washington (UW), Karen I. Goldberg*

*DOE Technology Development Manager: Grace Ordaz*

*Phone: (202) 586-8350; Fax: (202) 586-9811; E-mail: [Grace.Ordaz@ee.doe.gov](mailto:Grace.Ordaz@ee.doe.gov)*

*DOE Project Officer: James Alkire*

*Phone: (303) 275-4795; Fax: (303) 275-4753; E-mail: [Jim.Alkire@go.doe.gov](mailto:Jim.Alkire@go.doe.gov)*

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### **Objectives of 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 2010 hydrogen storage 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 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 assess 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 Center**

The Chemical Hydrogen Storage Center of Excellence addresses the following technical barriers from the Hydrogen Storage section of the DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Cost
- B. Weight and Volume
- C. Efficiency
- D. Durability
- G. System Life-Cycle Assessment
- R. Regeneration Processes
- S. By-Product/Spent Material Removal
- T. Heat Removal

### Technical Targets Addressed by 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. These targets are described in detail in the DOE Multi-Year Research, Development and Demonstration Plan and include:

- 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.

### Overall Approach of Center

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. In ascending order, these criteria are:

- Hydrogen storage capacity of the material (weight and volume percent)
- Theoretical maximum possible efficiency for regeneration of storage material
- Experimental demonstration of hydrogen release from storage material
- Experimental demonstration of regeneration of storage material
- Engineering assessment of hydrogen release process from storage material
- Engineering assessment of regeneration process of storage material
- Systems engineering assessment

These concepts are applied in a rigorous and hierarchical manner in order to down-select to the systems with the most potential to meet DOE targets. The Center's efforts are divided into three Tiers with distinct goals:

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

Tier 2. "Novel Boron Chemistry:" 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.

Specifically, the Center is addressing the following tasks:

- Identify and assess past work, including proprietary work, on borate reduction (data mining).
- Develop and analyze new regeneration methods for reduction of borate and complexed borate to improve the energy efficiency of the regeneration of sodium borohydride.

- Design and synthesize new molecules or materials with potential hydrogen storage capacity.
- Use high-level quantum chemical computation to quantify thermodynamics for hydrogen release and regeneration as well as energetics of potential intermediates.
- Develop catalysts and processes for hydrogen release from chemical hydrogen storage candidates.
- Optimize catalysts and catalytic processes for hydrogen release.
- Develop concepts and processes for regeneration of spent material.
- Investigate the kinetics, thermochemistry, and mechanisms of hydrogen release and regeneration reactions.
- Assess concepts and systems for hydrogen release and regeneration using engineering analysis.
- Perform engineering-scale studies on hydrogen delivery systems.
- Develop life-cycle inventory of regeneration systems.
- Down-select best hydrogen storage candidates based on technical criteria and engineering and systems analysis.
- Develop and demonstrate a 1-kg storage prototype system.
- Pursue three tiers in parallel to maximize potential to achieve the DOE targets for hydrogen storage.
- Couple experimental and computational R&D with engineering assessment to facilitate the transition from discovery of new concepts through development to implementation.
- Assure coordination and integration of Center partners, capabilities and efforts.

### **FY 2005 Accomplishments of Center**

- Prepared a compendium of literature related to B-O to B-H conversion.
- Developed a methodology for engineering assessment of new chemical routes for hydrogen release or regeneration of spent material.
- Assembled block diagrams for generic solid and liquid fuel systems to be used for creating process flow sheets.
- Quantified, through quantum chemical calculations, the thermodynamics for hydrogen release and spent fuel regeneration from a number of key systems including ammonia-borane and heteroatom-containing organics.
- Demonstrated a more selective synthesis of polyhedral borane anions.
- Developed high-throughput screening and testing methodology, along with methodology for nanoparticle and thin film synthesis, for catalytic hydrogen release from borohydrides and dehydrogenated ammonia-borane (BNH) compounds.
- Discovered non-metal, non-precious metal, and general classes of transition metal catalysts for releasing hydrogen from ammonia-borane, which has a potential material hydrogen storage capacity of 19.6 weight %.
- Discovered several active heterogeneous catalysts for hydrogen release from ammonia-borane.
- Demonstrated that the process of hydrogen release from solid ammonia-borane occurs by nucleation and growth mechanism.
- Discovered that ammonia-borane in inorganic scaffolds leads to increased kinetics of hydrogen release with no borazines formation.
- Carried out systematic studies of boron nitride hydrohalogenation and halogenation reactions.
- Collected and compiled safety and reactivity data on borane-amines and borazines.
- Demonstrated hydrogen release from a heteroatom-containing "organic hydride."
- Demonstrated a coupled reaction with potential hydrogen storage capacity of > 6 weight %.
- Filed a number of provisional and non-provisional patents.

## **Future Directions of Center for FY 2006**

- Complete data mining activities for B-O to B-H.
- Publish compendium review on B-O to B-H. Theoretically predict the thermodynamics and rate constants for reactions of complexed borates with chemical reductants.
- Complete assessment of the most energy-efficient routes for direct regeneration of sodium borate to sodium borohydride (B-O to B-H).
- Continue work on electrochemical and chemical reduction of complexed borates.
- Identify catalysts for polyhedral borane hydrolysis.
- Utilize high-throughput catalyst screening methodology for hydrogen release from polyhedral boranes and borane-amines.
- Continue work on polyhedral borane synthesis.
- Complete preliminary work on homogeneous and nanoparticle catalysts to generate hydrogen from ammonia-borane.
- Continue work on scaffolds for ammonia-borane, including investigations of pore size effects.
- Characterize reaction products from ammonia-borane and borane-amine dehydrogenation.
- Finalize compilation of safety, reactivity and property data for borane-amines.
- Develop and test concepts for regeneration of spent material from borane-amines.
- Carry out mechanistic studies on dehydrogenation reactions including characterization of boron nitride (BN) intermediates on transition metals.
- Develop and test organic heteroatom compounds with higher hydrogen storage capacity.
- Continue work on coupled reactions on several candidate materials.
- Investigate hydrogen storage capacity of nanoparticle materials.
- Finalize Center spreadsheet for tracking chemical storage options under investigation along with properties (e.g., thermodynamics, theoretical storage capacity and regeneration efficiency, safety properties) for eventual down-selection.
- Continue integration and coordination of Center's efforts as called out in Center Implementation Plan.
- Continue engineering assessment work on hydrogen release and spent material regeneration.
- Patent, publish and present technical results.

## **Introduction**

Chemical hydrogen storage involves storing hydrogen in and releasing hydrogen from covalent chemical bonds in molecules and materials. 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. Key elements in the Center include 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; and engineering assessment of concepts and experimental results. Engineering studies in the Center will include assessment, modeling and testing ranging from process identification through optimization of hydrogen release and regeneration reaction conditions, including catalyst performance and lifetime, and mass transfer to the construction and testing of a prototype for hydrogen release and testing of a process for spent storage material regeneration. The assessment and performance criteria were developed using the DOE technical targets.

## **Approach of Center**

The Center's approach capitalizes on its broad spectrum of expertise to collaboratively carry out a number of focused projects listed below along with the collaborating institutions:

- 1.1 B-O to B-H Engineering Guided Research - *Rohm and Haas, Millennium Cell, Penn State, Alabama, PNNL, LANL*
- 1.2 Engineering Assessment for Hydrogen Release Systems - *PNNL, Rohm and Haas, Millennium Cell, LANL*
- 2.1 Polyhedral Borane Chemistry - *UCLA, Intematix, Penn State, PNNL, LANL*
- 2.2 Amine-Borane Chemistry - *Penn, Penn State, University of Washington, Northern Arizona University, Intematix, PNNL, LANL*
- 2.3 Amine-Borane Systems Engineering, Safety - *PNNL, Northern Arizona, LANL*
- 3.1 Organics and Coupled Reactions - *Alabama, PNNL, LANL*
- 3.2 Nanoparticles and Main Group Hydrides - *UC Davis, Alabama, LANL*

The tasks for accomplishing these projects are:

- Materials discovery and development: synthesis, testing, and optimization (including modeling, catalyst development and material optimization)
- Engineering assessment, modeling and testing
- Material scale-up
- Prototype design, construction and testing
- System, safety and economic analysis

Success in the Center's activities requires collaboration, coordination and integration where the right capabilities are targeted on the right problems at the right time. A key element of the Center is the ability to assess concepts and preliminary results against criteria to be established jointly with DOE. 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 base and critical evaluation to assist future R&D, technology demonstration, and policy decision-making. Our collaborative project structure will enable 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.

## **Results of Center Activities**

Work on Center activities started at LANL and PNNL in late January 2005 and at the other partners' laboratories around April 1, 2005. A number of significant preliminary accomplishments have been made within each Center project. Of particular note are a number of discoveries on catalysts and processes that enable hydrogen generation from ammonia-borane, including non-metal and transition metal homogeneous catalysts, nanoparticle heterogeneous catalysts, and inclusion in inorganic scaffolds. Ammonia-borane has a very high hydrogen storage capacity – up to 19.6 weight percent. The Center has also made significant strides in utilizing high-level quantum chemical calculations to calculate thermodynamics of reactions and key reaction intermediates, which has helped guide discovery and mechanistic experimental efforts. New classes of reactions involving heteroatom organic compounds and coupled reactions for hydrogen release have also been demonstrated.

## B-O to B-H Engineering Guided Research

Hydrolysis of sodium borohydride has been demonstrated by one of the Center partners, Millennium Cell, to 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 goal of this Center project is to develop more energy-efficient pathways for the synthesis of sodium borohydride from sodium borate using electrochemical methods and/or regenerable chemical reducing agents. In FY 2005, work focused on developing experimental capabilities as well as reviewing and assessing past efforts on converting B-O to B-H bonds. Much of this information is proprietary to Center partners, e.g., Rohm and Haas, and is not in the open literature. In addition, we have used computation to determine the energetics of potential reactions, intermediates and complexed borate species.

## Engineering Assessment for Hydrogen Release Systems

Understanding critical engineering aspects, designs and constraints is crucial for advancing chemical hydrogen storage discoveries into prototype on-board hydrogen generating systems. Engineering analysis is closely coupled to experimental work and results in the Center. For FY 2005, Millennium Cell has provided experimental results on a catalysis reactor to PNNL in order to initiate modeling activities. Block diagrams for generic solid and liquid fueling systems have been assembled. These diagrams include interface to the fuel cell system. These diagrams are being used to assemble process flow sheets for use in computer-aided design models.

Rohm and Haas expertise in chemical process engineering and life-cycle inventory is being used to develop down-selection criteria for borate reduction pathways in the assessment of potential regeneration pathways for Tier 1. These engineering capabilities will be critical for regeneration of systems from Tier 2 and 3 in the out years.

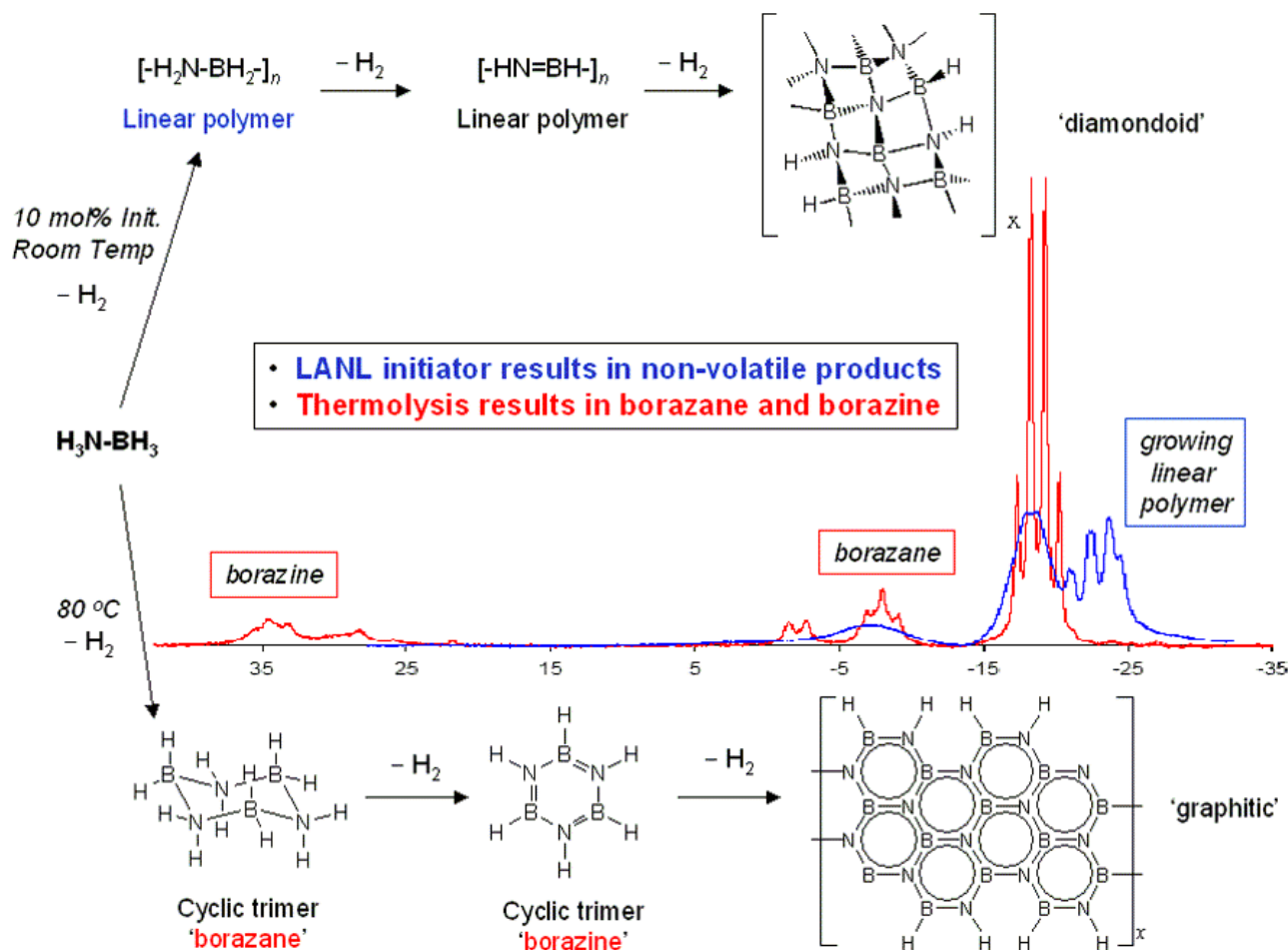
## Polyhedral Borane Chemistry

The Center is carrying out research to determine the potential of polyhedral boranes for hydrogen storage. Polyhedral boranes, e.g.,  $B_{12}H_{12}^{2-}$ , are cage molecules that contain both B-H and B-B bonds. Several concepts have been envisioned and are being explored, including hydrolysis, aminolysis and electrolysis. The focus of Center work in this area is to develop chemical pathways and catalysts to facilitate hydrogen release from polyhedral boranes. Researchers at UCLA have devised more selective routes to synthesizing polyhedral boranes. For example, heating tetraethylammonium borohydride at 185°C for 11 days gave *closo*- $B_{10}H_{10}^{2-}$  and *closo*- $B_{12}H_{12}^{2-}$  in 51% and 37% yield, respectively. Optimization of this process is currently in progress.

Intematix has developed high-throughput screening and testing methods for in-situ monitoring of hydrogen release from borohydrides or BNH compounds. This effort includes the development of high-quality nanoparticles and thin films using combinatorial synthesis methods and the synthesis and screening of hydrogen-release catalyst libraries (in nanoparticle or/and thin-film forms). Intematix has discovered several catalyst formulations that appear to be superior to the ruthenium-based catalysts for the hydrolysis of sodium borohydride and is now using this system for more complex boron-hydride systems.

## Amine-Borane Chemistry

The Center has made a number of significant discoveries relating to hydrogen release from ammonia-borane (AB), which has a potential hydrogen storage capacity to meet 2015 goals. Prior to the onset of Center work, there was some literature precedent that thermolysis and precious metal catalysts could affect hydrogen evolution from AB. Center researchers have found a number of proprietary homogeneous catalysts that consist of non-precious metals, or no metals at all, for release

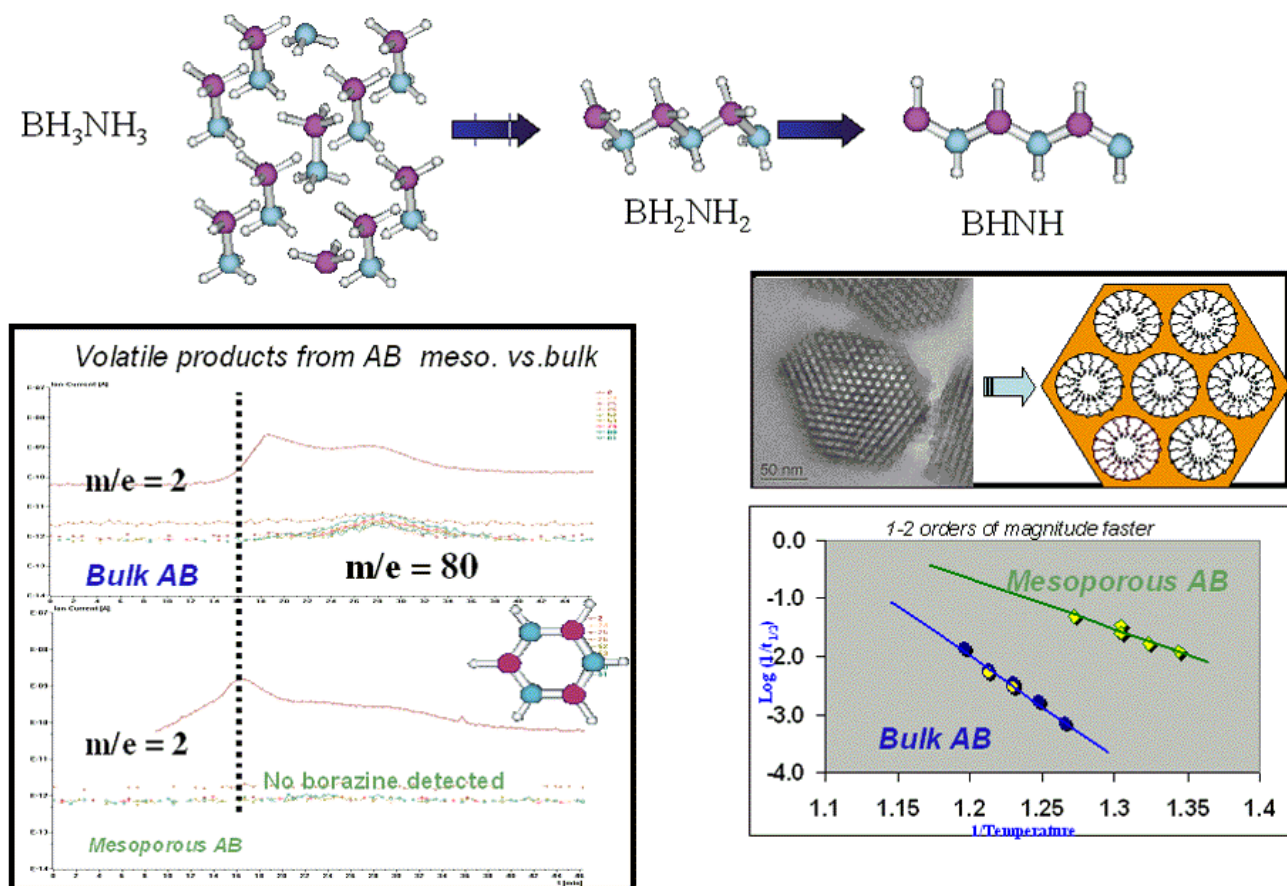


**Figure 1.** Comparison of Solution Reaction Chemistry for Hydrogen Release from Ammonia-Borane Using LANL Catalyst and Thermolysis

of hydrogen from AB (Figure 1). In addition, an ongoing systematic survey of nanoparticle catalysts for dehydrogenation has revealed several active catalysts for hydrogen release from AB. A number of provisional patents have been filed by Center partners in this area in FY 2005. The selectivity of the dehydrogenation is important as it appears that controlling the selectivity of amine-borane dehydrogenation away from borazine (and other volatile products) and towards non-volatile polymeric  $\text{BNH}_x$  species is important from the standpoint of overall energetics and regeneration. This is borne out by quantum chemical calculations of reaction and intermediate energetics. A number of these catalysts do not make borazine, and we are in the process of characterizing the polymeric products. Calculations have been used to predict nuclear magnetic resonance (NMR) chemical shifts for  $\text{BNH}_x(\text{CH}_3)_y$  polymers, which are aiding our characterization efforts.

When ammonia-borane is included in a scaffold consisting of mesoporous silica, the reaction rates increase substantially and no borazine is formed. The silica scaffolds appear to control the thermodynamics and kinetics of ammonia-borane decomposition as well as the reaction path to preferred linear polymer products. Figure 2 illustrates results in this area where more favorable energetics are found in the scaffold system than bulk AB.

Mechanistic work on hydrogen release from amine-boranes in solution and in the solid state was initiated in FY 2005. Some model complexes of amine-boranes with transition metals have been prepared and are being studied. Other work in progress has shown that the process of hydrogen release from solid ammonia-borane appears to occur by a nucleation and growth mechanism.



**Figure 2.** Illustration of Reaction Chemistry of Ammonia-Borane in a Mesoporous Scaffold Relative to Solid-State Thermolysis of Bulk Material

Means of regenerating amine-boranes from dehydrogenated BN or BNH<sub>x</sub> systems will need to be devised to capitalize on the hydrogen storage capacity of these systems. While these efforts will be a focal point in FY 2006 and out years, systematic studies of BN hydrohalogenation and halogenation reactions have already been initiated.

### Amine-Borane Systems Engineering, Safety

Given the potential promise of AB to reach even the 2015 goals, we initiated a project on engineering assessment which includes safety aspects of materials and handling.

A literature search for physical properties, chemical properties and safety aspects of borane-amines and borazines (including collection of Material Safety Data Sheets from manufacturers) was essentially completed this year. Collection of additional reactivity, stability and toxicity information from manufacturers of borane-amines and borazines is about 50% complete.

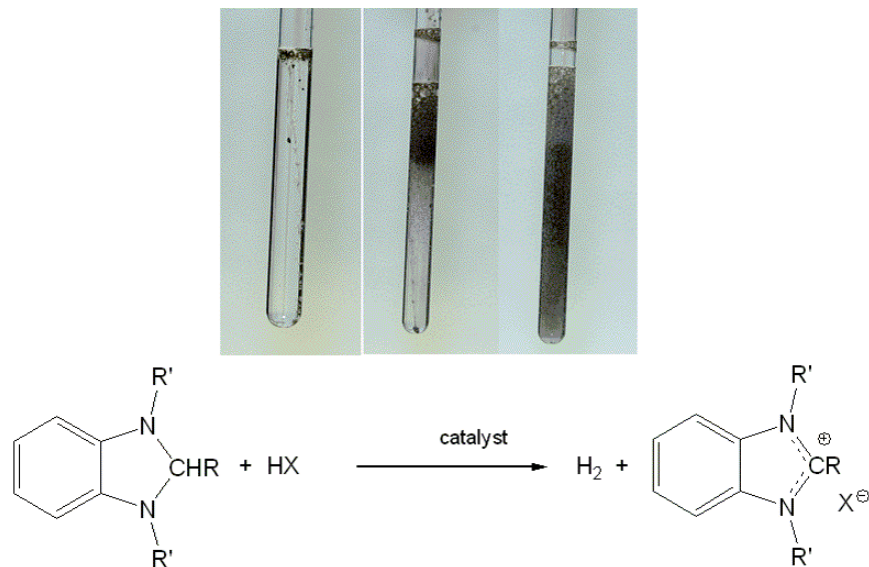
### Organics and Coupled Reactions

The Center is also investigating a number of organic systems for hydrogen storage using several approaches. Computation has revealed a number of molecules where the energetics of hydrogen release and regeneration are well within the DOE targets for energy efficiency. As illustrated in Figure 3, we have discovered a new reaction pathway for hydrogen evolution from organic systems whereby the organic



molecule behaves as a true chemical hydride in catalytic reactions with acids. While the initial molecule only has a hydrogen storage capacity of 1.2 weight %, it clearly demonstrates that heteroatom substitution within organic frameworks significantly alters the thermochemistry for hydrogen release (even from endothermic to exothermic). We are investigating other molecular systems based on this concept with potentially much higher storage capacity. The formation of 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 reactants are 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 liter 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.



**Figure 3.** Catalyzed Hydrogen Release from a Heteroatom-Containing Organic Hydride Reacting with an Acid (propionic acid used for illustration)

### Nanoparticles and Main Group Hydrides

The route to new, potentially high-yield hydrogen-capped silicon nanoparticles is under investigation. Detailed analysis will be carried out in the future to demonstrate whether or not this route will be successful.

## VI.B.4a Los Alamos National Laboratory

*William Tumas (Primary Contact), R. Thomas Baker, Anthony Burrell, Neil Henson, P. Jeffrey Hay, Kevin C. Ott, Bobbi Roop, David Thorn*

*Los Alamos National Laboratory*

*MS C346, Los Alamos, NM 87545*

*Phone: (505) 667-3803; Fax: (505) 667-4098; E-mail: tumas@lanl.gov*

*Start Date: January 21, 2005*

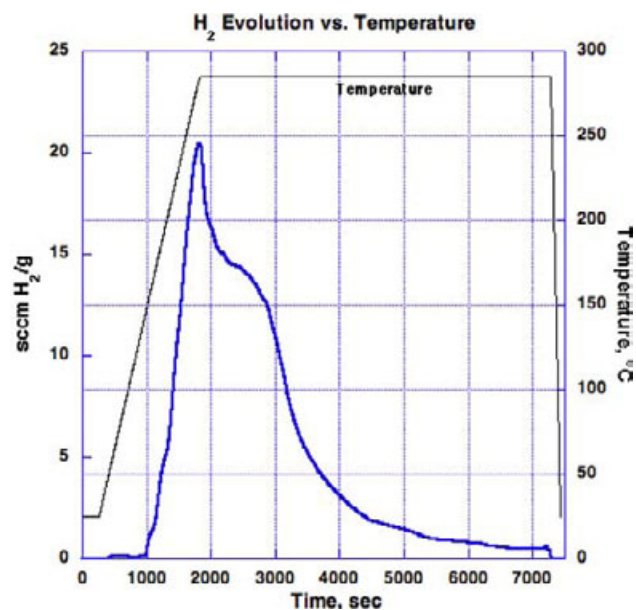
*Projected End Date: Project continuation and direction determined annually by DOE*

### Partner Approach

LANL is contributing to all experimental projects in the Center. In addition, LANL continues to be responsible for overall Center integration and coordination as well as providing core catalysis and complex instrumentation capabilities to Center partners. Within Tier 1, LANL is working with partners to identify and assess the most energy-efficient routes for regeneration of  $\text{NaBH}_4$ , including data mining and developing electrochemical approaches. Within Tier 2, LANL is working on polyhedral borane hydrolysis and regeneration and on mechanisms and development of catalyzed hydrogen release from and regeneration of amine-boranes. In Tier 3, LANL is working to identify new organic and main group element nanoparticle hydrogen storage media. We are also pursuing several coupled reaction strategies for chemical hydrogen storage. Other tasks include heterogeneous catalyst characterization, thermal analysis of  $\text{BNH}_x$  solids, and solid-state NMR characterization of  $\text{BNH}_x$  solids.

### Partner Results for FY 2005

- Discovered acid-initiated conversion of amine-boranes to hydrogen and acyclic aminoborane polymers by a novel mechanism (Figure 1) that avoids formation of volatile cyclic co-products and improves overall energetics and regeneration.
- Identified first examples of non-precious metal catalysts for amine-borane dehydrogenation.
- Demonstrated hydrogen release by acidification of organic nitrogen heterocycles.
- Demonstrated a coupled reaction sequence with potential material hydrogen storage capacity that meets 2010 targets.
- Coordinated and integrated Center efforts with PNNL through Center project development, site visits, regular conference calls, and other communication mechanisms.



**Figure 1.** Hydrogen Evolution from a Coupled Reaction as a Function of Time

### Partner FY 2006 Plans

- Complete data mining activities for B-O to B-H (with Millennium Cell, PNNL, and Rohm and Haas). Combine this information with calculated thermodynamics and rate constants (with PNNL and Alabama) to complete assessment of the most energy-efficient routes for direct regeneration of sodium borate to sodium borohydride.

- Complete preliminary survey of electrochemical and chemical reduction of complexed borates.
- Investigate coupled reaction concepts for Tier 1.
- Identify catalysts for polyhedral borane hydrolysis (with Intematix and UCLA) and assess suitability of Tier 1 B-O to B-H routes for direct polyhedral borane regeneration.
- Complete characterization (with PNNL) of  $\text{BNH}_x$  solids derived from amine-borane dehydrogenation and initiate experimental assessment of amine-borane regeneration routes.
- Develop and test heteroatom-containing organic compounds with higher hydrogen storage capacity (with Alabama).
- Continue work on coupled reactions on several candidate materials.
- Investigate hydrogen storage capacity of nanoparticle materials (with UC Davis).
- Finalize Center spreadsheet for tracking chemical storage options under investigation along with properties (thermodynamics, theoretical storage capacity and regeneration efficiency, safety properties) for eventual down-selection.
- Continue to integrate and coordinate Center's efforts as called out in Center Implementation Plan.
- Patent, publish and present technical results.

### **Conclusions of Partner Effort for FY 2005**

- Catalyzed dehydrogenation of amine-borane can afford acyclic aminoborane polymers without formation of volatile cyclic co-products while improving overall energetics and regeneration.
- Selected non-precious metal complexes are active catalysts for amine-borane dehydrogenation and are economical.
- Metal-catalyzed acidification of selected model nitrogen heterocycles provides a clean hydrogen stream at suitable rates.
- Hydrogen evolution from coupled reactions may offer robust alternatives for chemical hydrogen storage.

### **Los Alamos Special Recognitions & Awards/Patents Issued**

1. Acid-initiated Dehydrogenation of Amine-Boranes, provisional patent filed June, 2005.
2. Hydrogen-Evolving Organic Compounds, provisional patent filed June, 2005.
3. Non-precious Metal Catalysts for Amine-Borane Dehydrogenation, provisional patent to be filed August, 2005.
4. Two additional patents on coupled reactions for hydrogen evolution are in progress.
5. LANL Summer Student Chemistry Poster of the Year, 2005, Johanna Blacquiere.

### **Los Alamos FY 2005 Publications/Presentations**

1. W. Tumas, "Chemical Hydrogen Storage Center of Excellence" presentation at DOE EERE Hydrogen Review, Arlington, VA, May, 2005.
2. R. T. Baker, A. K. Burrell, F. H. Garzon, P. J. Hay, N. J. Henson, K. D. John, K. K. Jonietz, R. J. Keaton, K. C. Ott, B. J. Roop, D. E. Schwarz, F. H. Stephens, D. L. Thorn and W. Tumas, "Center of Excellence for Chemical Hydrogen Storage: LANL Tasks and Collaborations," poster at DOE EERE Hydrogen Review, Arlington, VA, May, 2005.
3. W. Tumas, "Chemical Hydrogen Storage Center of Excellence," poster at IPHE Conference on Hydrogen Storage, Lucca, Italy, June, 2005.
4. F. H. Stephens, R. T. Baker, D. Grant and D. A. Dixon, "Acid-initiated Hydrogen Evolution from Amine-boranes at Room Temperature," poster presentation at Inorganic Chemistry Gordon Research Conference, Newport, RI, July, 2005 (Joint with University of Alabama).

5. R. T. Baker, F. H. Stephens, R. J. Keaton and B. L. Scott, "Amine-boranes for Hydrogen Storage: Controlling Selectivity in Catalyzed Dehydrogenation," Invited lecture at 16<sup>th</sup> FEICHEM Conference on Organometallic Chemistry, Budapest, Hungary, September, 2005.
6. F. H. Stephens and R. T. Baker, "Acid-initiated Hydrogen Evolution from Amine-boranes," lecture presented at Fuel Chemistry symposium on *Research Challenges for the Hydrogen Economy: Hydrogen Storage* at the 230<sup>th</sup> American Chemical Society National Meeting, Washington, DC, August, 2005.
7. D. E. Schwarz, T. M. Cameron, B. L. Scott, P. J. Hay, W. Tumas, and D. L. Thorn, "Hydrogen Evolution from Organic Hydrides," lecture presented at Fuel Chemistry symposium on *Research Challenges for the Hydrogen Economy: Hydrogen Storage* at the 230<sup>th</sup> American Chemical Society National Meeting, Washington, DC, August, 2005.
8. D. E. Schwarz, T. M. Cameron, P. J. Hay, W. Tumas, and D. L. Thorn, "Catalyzed Evolution of Hydrogen from Organic 'Hydrides'," submitted to *Chemical Communications*.

## VI.B.4b Pacific Northwest National Laboratory

*Chris Aardahl (Primary Contact), S. Thomas Autrey, Maciej Gutowski, John Linehan, Scott Rassat, Michael Thompson*

*Pacific Northwest National Laboratory*

*Box 999 MS K6-28*

*Richland, WA 99352*

*Phone: (509) 376-7022; Fax: (509) 372-1861; E-mail: christopher.aardahl@pnl.gov*

*Start Date: March 1, 2005*

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### Partner Approach

PNNL is approaching the challenge in a manner consistent with Center philosophy. In addition to the specific scope within the Tier framework, PNNL has responsibilities for theory & simulation and core science & engineering competencies within the Center. Therefore, PNNL's work within the Center is inherently multidisciplinary and highly collaborative with several of the Center partners.

Within Tier 1, PNNL and LANL are exploring chemical routes to regeneration of NaBH<sub>4</sub>. Potential new chemical routes have been postulated, and experimental efforts are underway to assess the chemistry. Results from experiments are fed into analysis protocols to gauge improvements compared to existing production practices. Within Tier 2, PNNL has many activities, including examination of mechanisms of hydrogen release from ammonia boranes, experimental work on the regeneration of spent ammonia boranes, and investigation of the impact of novel supports on release/regeneration chemistry. PNNL's efforts in Tier 3 are limited and mainly composed of computational support to Center partners and minimal investigation of two new storage compounds at this point.

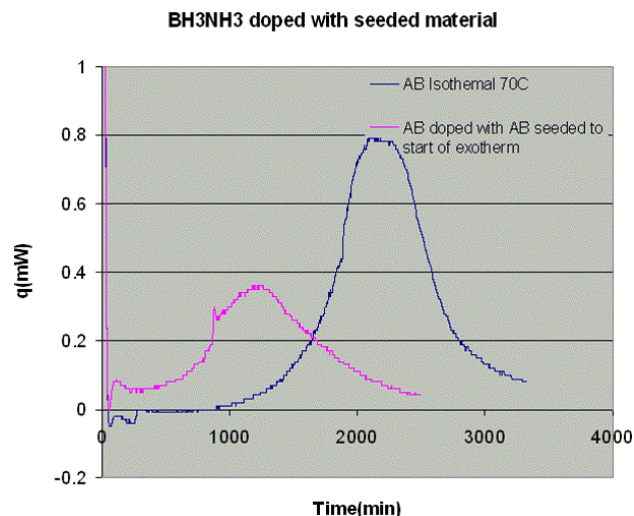
Theoretical computations are focused on materials belonging to all three Tiers. These are quantum chemical calculations on molecules, clusters, polymers and solids performed primarily at the density functional level of theory (DFT) with gradient-corrected and hybrid exchange-correlation functionals. The enthalpies and Gibbs free energies for gas phase reactions are for a temperature of 298 K and a pressure of 1 atmosphere.

### Partner Results for FY 2005

- Completed computational studies in Tier 1 to determine energetics of the following gas phase reactions:
  - $\text{B}(\text{NH}_2)_3 + 3 \text{H}_2 \rightarrow \text{BH}_3 + 3 \text{NH}_3$ ;  $\Delta\text{H}= 65.8 \text{ kcal/mol}$ ,  $\Delta\text{G}= 61.7 \text{ kcal/mol}$
  - $\text{B}_2(\text{NH}_2)_6 + 6 \text{H}_2 \rightarrow \text{B}_2\text{H}_6 + 6 \text{NH}_3$ ;  $\Delta\text{H}= 71.8 \text{ kcal/mol}$ ,  $\Delta\text{G}= 56.6 \text{ kcal/mol}$
  - $\text{B}(\text{OMe})_3 + 3 \text{H}_2 \rightarrow 1/2 \text{B}_2\text{H}_6 + 3 \text{MeOH}$ ;  $\Delta\text{H}= 68.9 \text{ kcal/mol}$ ,  $\Delta\text{G}= 66.0 \text{ kcal/mol}$
  - $\text{B}(\text{OMe})_3 + 3 \text{H}_2 \rightarrow \text{BH}_3 + 3 \text{MeOH}$ ;  $\Delta\text{H}= 86.5 \text{ kcal/mol}$ ,  $\Delta\text{G}= 78.4 \text{ kcal/mol}$
  - $\text{HB}(\text{NH}_2)_2 \rightarrow \text{H}^- + \text{B}(\text{NH}_2)_2^+$ ;  $\Delta\text{H}= 234.0 \text{ kcal/mol}$ ,  $\Delta\text{G}= 226.5 \text{ kcal/mol}$
  - $\text{HB}(\text{NH}_2)_2 \rightarrow \text{H}^+ + \text{B}(\text{NH}_2)_2^-$ ;  $\Delta\text{H}= 431.8 \text{ kcal/mol}$ ,  $\Delta\text{G}= 424.5 \text{ kcal/mol}$
  - $\text{HB}(\text{NH}_2)_2 \rightarrow \text{H} + \text{B}(\text{NH}_2)_2$ ;  $\Delta\text{H}= 105.8 \text{ kcal/mol}$ ,  $\Delta\text{G}= 97.6 \text{ kcal/mol}$
- Completed computational studies in Tier 2 to determine energetics of the following reactions:
  - $\text{NH}_4\text{BH}_4(\text{s}) \rightarrow \text{NH}_3\text{BH}_3(\text{s}) + \text{H}_2(\text{g})$ ;  $\Delta\text{E}= -2.3 \text{ kcal/mol}$
  - $\text{NH}_3\text{BH}_3(\text{s}) \rightarrow \text{NH}_2\text{BH}_2(\text{single strand polymer}) + \text{H}_2(\text{g})$ ;  $\Delta\text{E}= +8.8 \text{ kcal/mol}$
  - $\text{NH}_2\text{BH}_2(\text{single strand polymer}) \rightarrow \text{NHBH}(\text{single strand polymer}) + \text{H}_2(\text{g})$ ;  $\Delta\text{E}= -3.2 \text{ kcal/mol}$
  - $\text{NHBH}(\text{single strand polymer}) \rightarrow \text{BN}(\text{s}) + \text{H}_2$ ;  $\Delta\text{E}= -9.2 \text{ kcal/mol}$

- $\text{NH}_4\text{BH}_4(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \frac{1}{2}\text{B}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g}); \Delta E = +25 \text{ kcal/mol}$
- $\text{NH}_4\text{AlH}_4(\text{s}) \rightarrow \text{AlN}(\text{s}) + 4\text{H}_2(\text{g}); \Delta E = -60 \text{ kcal/mol}$

- Work in progress shows the process of hydrogen release from solid ammonia borane occurs by a nucleation and growth mechanism which may release hydrogen at lower temperature with the appropriate nucleation seed. Figure 1 illustrates the enhanced kinetics when fresh ammonia borane is seeded with BNH intermediates prepared in a previous ammonia borane thermolysis reaction.
- A methodology for engineering assessment of new chemical routes has been formulated and adopted by the Center. This methodology is being developed into a process for achieving go/no-go decision criteria in FY 2006.
- Block diagrams for generic solid and liquid storage systems and novel process concepts have been developed. These diagrams include interfacing of the storage system to the fuel cell system. These diagrams are being used to assemble process flow sheets for use in ChemCAD models to simulate hydrogen storage systems and optimize the mass and volume density of chemical-based hydrogen storage systems.
- Modeling activities have been initiated to build chemical fluid dynamics models for hydrogen release reactors in a hydrogen storage system. Again, these models will be useful for optimizing the mass and volume density of hydrogen in storage systems.



**Figure 1.** Influence of Nucleated Phase on Kinetics of Hydrogen Release from Ammonia Borane

### Partner FY 2006 Plans

Within Tier 1, major effort is going to be placed on data mining and brainstorming on proprietary resources available within the Center. This activity will be used to generate a list of options, and those options will be screened against go/no-go metrics assembled by the Engineering Team. This is part of the 'fail fast' approach adopted by the Center for screening new chemistries. For example, chemical routes to the synthesis of  $\text{NaBH}_4$  can be screened using computational chemistry to assess the thermodynamics of the proposed chemistry. If the chemistry is thermodynamically unfavorable, then minimal bench-scale work will be employed to examine the chemistry. This is particularly important for  $\text{NaBH}_4$  because it has received considerable attention in recent years. In parallel to computational and experimental work, PNNL will develop chemical reactor models that can be used to optimize catalytic reactor geometries for hydrogen release in a hydrogen storage system.

Within Tier 2, the FY 2006 focus is going to be on ammonia borane regeneration chemistry. Such chemistry needs to be defined such that cost models can be assembled for that system. This is presently the single most important question to answer for the ammonia borane system. It is unclear at this time whether direct hydrogenation of spent ammonia borane is possible. Results on silica supports suggest the chemistry is nearly thermoneutral, giving some chance of direct regeneration. If direct regeneration is not possible, then a suitable chemical process for taking spent ammonia boranes back to ammonia borane must be postulated and understood in the sense of number of unit operations and degree of difficulty on an energy basis. This will allow development of cost and efficiency models to make a go/no-go decision at the end of FY 2007.

Within Tier 3, PNNL will experimentally examine two undisclosed compounds that have potential to meet DOE's targets for on-board hydrogen storage. These compounds have already undergone screening using

computational chemistry approaches, and each appears to have the necessary energetics to be attractive. PNNL will also continue to support LANL in coordination activities within the Center, particularly in support of computational chemistry, advanced analytical instrumentation, and engineering & analysis.

### Conclusions of Partner Effort for FY 2005

- It has been demonstrated that an 'active' phase is nucleated in ammonia borane during hydrogen evolution. This phase will be useful to limit transient effects at the start of hydrogen release. Once this phase is formed, rate of release is a direct function of temperature, and there is no 'induction' period. Identification of this phase is underway. It is important to understand the mechanism of this phase transition to be able to control the rate of hydrogen release from BNH<sub>x</sub> materials.
- Two Tier 3 compounds have been postulated and examined computationally. The bench-scale chemistry of these compounds will be evaluated using NMR and thermochemistry techniques. Both compounds have hydrogen mass density capable of meeting DOE targets, but little is known of their bench-scale operation.
- Engineering block diagrams have been constructed for baseline solid and liquid systems. These diagrams will be used to build flow sheets suitable for process simulations.
- Computational fluid dynamics modeling has been initiated to model hydrogen release for an arbitrary geometry reactor. A Lattice-Boltzmann algorithm is being used to simulate the microstructural effects of catalysts on transport in the system. This modeling is critical to obtain tools for system optimization.
- Computations on the B-N family of chemicals indicate there is no thermodynamic "sink" for hydrogen release from the BNH<sub>x</sub> (x=2-8) compounds. In addition, the release of ammonia from BNH<sub>8</sub> is thermodynamically not favorable. These calculations indicate that energetics for regeneration could be favorable and that unwanted byproducts will be avoided.
- Computations show that the release of hydrogen from AlNH<sub>x</sub> is more exothermic than from BNH<sub>x</sub>, indicating that BNH<sub>x</sub> compounds are likely more promising for further study.

### PNNL FY 2005 Publications/Presentations

1. A. Gutowska, L. Li, Y. Shin, Ch. Wang, S. Li, J. Linehan, R. Scott Smith, B. Kay, B. Schmid, W. Shaw, M. Gutowski, and T. Autrey, Nano-Scaffold Mediates Hydrogen Release and Reactivity of Ammonia Borane, *Angew. Chem. Int. Ed.*, 44, 2, (2005).
2. D. A. Dixon and M. Gutowski, Thermodynamic Properties of Molecular Borane Amines, BH<sub>4</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> for Chemical Hydrogen Storage Systems from Ab Initio Electronic Structure Theory, *J. Phys. Chem. A.*, 109, 5129, (2005).
3. "Computational Studies of Materials for Hydrogen Storage. The NBH<sub>6</sub> Compounds", presentation by M. Gutowski at the Johns Hopkins University, Baltimore, MD, January 20<sup>th</sup>, 2005.
4. "The Challenge of On-Board Hydrogen Storage. Thermolysis of the NBH<sub>x</sub> (x=1-4) Materials", presentation by M. Gutowski at the University of Calgary, Calgary, Alberta, Canada, February 9<sup>th</sup>, 2005.
5. "High Level Computational Approaches to the Prediction of the Thermodynamics of Chemical Hydrogen Storage Systems and Hydrocarbon Fuels", D. A. Dixon, M. Gutowski, L. Pollack, T. L. Windus, W. A. deJong, 229<sup>th</sup> ACS National Meeting, San Diego, California, March 13-17, 2005; also *Prep. Pap. - Am. Chem. Soc., Div. Fuel Chem.*
6. "Mechanistic Studies of Hydrogen Formation from Amineborane Complexes", R. Scott Smith, B. D. Kay, L. Li, B. A. Schmid, N. J. Hess, M. Gutowski, and T. Autrey, 229<sup>th</sup> ACS National Meeting, San Diego, California, March 13-17, 2005; also *Prep. Pap. - Am. Chem. Soc., Div. Fuel Chem.*
7. "Theoretical Characterization of the NH<sub>x</sub>BH<sub>x</sub> Compounds", M. Gutowski, 2005 National APS Meeting, Los Angeles, California, March 21-25, 2005.
8. "The Grand Challenge of Hydrogen Storage", presentation by M. Gutowski at the Simons' Reunion Mini-symposium, Park City, Utah, June 19<sup>th</sup>, 2005.
9. "Relative Stability of (NH<sub>3</sub>BH<sub>3</sub>)<sub>2</sub>, [NH<sub>3</sub>-BH<sub>2</sub>-NH<sub>3</sub>]<sup>+</sup> BH<sub>4</sub><sup>-</sup>, and [BH<sub>3</sub>-NH<sub>2</sub>-BH<sub>3</sub>]<sup>-</sup> NH<sub>4</sub><sup>+</sup>", M. Gutowski, R. Bachorz, T. Autrey, J. Linehan, 230<sup>th</sup> ACS National Meeting, Washington, DC, August 28-September 1, 2005, also *Prep. Pap. - Am. Chem. Soc., Div. Fuel Chem.* submitted.

## VI.B.4c Pennsylvania State University

*Dr. Digby D. Macdonald (Primary Contact), Justin C. Tokash, Jason B. McLafferty, Yancheng Zhang, Dr. Wendy Coulson*

*The Pennsylvania State University*

*Center for Electrochemical Science and Technology*

*201 Steidle Building*

*State College, PA 16802*

*Phone: (814) 863-7772; Fax: (814) 863-4718; E-mail: ddm2@psu.edu*

*Contract Number: DE-PS36-03GO93013*

*Start Date: March 1, 2005*

*Projected End Date: February 26, 2010*

### Partner Approach

This project is addressing the DOE 2010 hydrogen storage targets by conducting fundamental research in three areas of electrochemical study. The first objective is focused on discovering an electrochemical pathway to prepare sodium borohydride,  $\text{NaBH}_4$ , from sodium metaborate,  $\text{NaBO}_2$ . The second and third objectives entail research on complex, polyhedral boranes (polyboranes). As such, the second direction of our research is focused on exploring and defining the fundamental electrochemistry of polyboranes and polyborane anion salts. As a final course of action, we will explore the feasibility of developing a reversible hydrogen storage technology based on the polyborane system.

Our work is being accomplished in close cooperation with scientists from Rohm and Haas, Inc.; Millennium Cell, Inc.; Pacific Northwest National Laboratory; Los Alamos National Lab; The University of California at Los Angeles; and The University of Alabama. In studying the B-O to B-H electrochemical pathway, we will concentrate on characterizing the mechanisms of the reaction(s) that display exceptionally high over-potentials for hydrogen evolution for the production of sodium borohydride from sodium metaborate. We emphasize that our research is on fundamental mechanistic studies for the conversion from B-O to B-H. Once the mechanism is known, we will transfer our findings to our partners in industry, who will evaluate the information for large-scale production of sodium borohydride.

The initial activities investigating complex boranes are concentrated on the identification of electrolysis reaction products and definition of reaction mechanisms. Various techniques will be employed in this work, including electrochemical impedance spectroscopy, cyclic voltammetry (CV), and rotating disk and rotating ring/disk voltammetry.

### Partner Results for FY 2005

The experimental results of our preliminary investigations are shown in Figures 1 and 2, in which we followed the work of Gyenge, who performed cyclic voltammetry on sodium borohydride solutions using platinum and gold working electrodes [Electrochimica Acta 49 (2004) 965-978]. These experiments were executed to verify our experimental set-up and the reproducibility of our methods. The cyclic voltammograms, shown in Figures 1 and 2, display the same general features as those published by Gyenge. This data is from the first cycle and may include influence of the surface preparation of the working electrode due to incomplete electrode conditioning. The effects of electrode polishing and conditioning will be investigated to establish methods with reproducible results on multiple scans. This is essential to our success since electrochemical

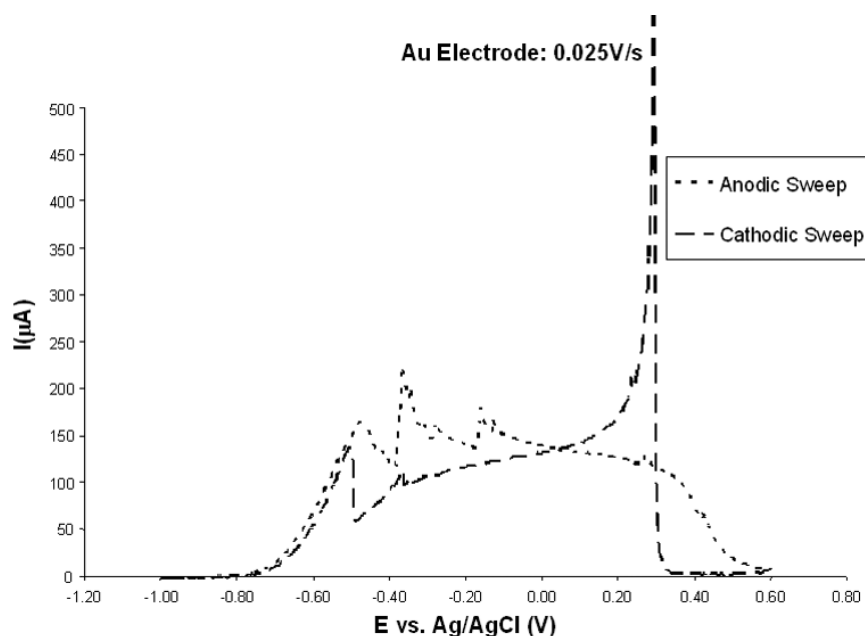


analyses are surface sensitive. The multiple peaks in the forward (anodic) scan on the gold working electrode appear to be due to adsorption of a species in the liquid phase onto the electrode. The objective of future experiments will be to determine whether adsorption effects are occurring on the gold electrode.

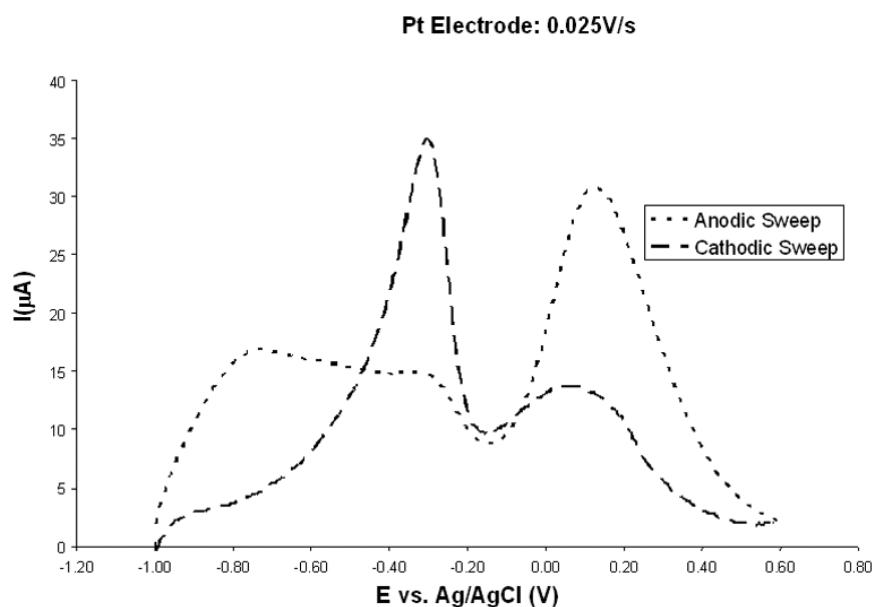
It is significant that there are no reduction peaks in the preliminary data. We hypothesize that the multiple oxidation peaks indicate that a species that forms on the forward (anodic) scan is oxidized later at a different potential, giving rise to the anodic peaks seen on the reverse (cathodic) scan. Our subsequent experiments will test this hypothesis.

During the course of this initial work on the electrochemical pathway from sodium metaborate to sodium borohydride, other efforts have been focused on preparing the laboratory for the studies on the polyboranes. These materials require special handling, and we have recently completed the installation of an inert atmosphere glovebox in our laboratory. The glovebox purifies the argon atmosphere to remove oxygen and water vapor to less than one part per million. The sealed electrochemical cell will be located within the glovebox, and ultra-pure argon gas (contamination of less than one part per billion) will be bubbled through the polyborane samples prior to and during any electrochemical analyses.

In addition, a comprehensive review of the electrochemistry of the B:H system has been compiled. To date, the most recent review of the literature on the electrochemistry of boron compounds was published in 1985.



**Figure 1.** CV Plot of 0.03M NaBH<sub>4</sub> in 2M NaOH with a Gold Working Electrode



**Figure 2.** CV Plot of 0.03M NaBH<sub>4</sub> in 2M NaOH with a Platinum Working Electrode

### **Partner FY 2006 Plans**

Fundamental mechanistic studies for the conversion from B-O to B-H will be continued. Investigations of complex boranes will concentrate on the identification of electrolysis reaction products, definition of reaction mechanisms, and the determination of relevant transport parameters (e.g., diffusion coefficients).

### **Conclusions of Partner Effort for FY 2005**

- Two graduate students (Jason McLafferty and Justin Tokash), one Post Doctoral Scholar (Dr. Yancheng Zhang), and one Senior Research Associate (Dr. Wendy Coulson) have been retained on the project.
- An approved safety plan has been put in place, and the intellectual property memorandum of understanding has been negotiated.
- A comprehensive review of the electrochemistry of the B:H system, covering articles in the open, peer-reviewed literature, the patent literature, and any proprietary sources that have been made available to us, has been prepared, and sections of that review have been posted to the Center's web site as they have been completed.
- Experimental systems have been designed and various components have been purchased for studying the electrochemical reduction of B-H to B-O and for exploring electrochemically-mediated transformations between the boranes and other boron compounds. These systems are located in a dedicated laboratory with restricted access.
- Thermodynamic calculations of the standard potentials for the reduction of B-H to B-O and other hydrides (hydrides of Al, C, S, N, As, P, and Se) show that the reduction of B-H is thermodynamically the most difficult (most negative standard potential) of all of the hydrides explored.
- Experimental work on the electrochemical oxidation of borohydride to metaborate has been initiated to reproduce and confirm the work reported in the literature (e.g., that by Bard).
- Theoretical work on defining reaction mechanisms for the reduction of metaborate to borohydride has also been initiated.

## VI.B.4d Intematix Corporation

*Xiao-Dong Xiang*

*46410 Fremont Boulevard*

*Intematix Corporation*

*Fremont, CA 94538*

*Phone: (510) 668-0227; Fax: (510) 668-0793; E-mail: XDxiang@intematix.com*

*Contract Number: DE-FC36-05GO15052*

*Start Date: March 1, 2005*

*Projected End Date: February 26, 2010*

### Partner Approach

Intematix puts the emphasis on developing cost-effective catalysts for hydrogen release based on chemical hydrides using proprietary combinatorial synthesis and high-throughput screening technologies. The primary tasks of this project are listed below:

- Development of high-throughput screening and testing methods for in-situ monitoring of hydrogen release from borohydrides or BNH compounds
- Development of high-quality nanoparticles and thin films using combinatorial synthesis methods
- Synthesis and screening of hydrogen-release catalyst libraries (in nanoparticle or/and thin-film forms)
- Synthesis and screening of hydrogen-regeneration catalyst libraries
- Characterization of materials properties of candidate catalysts

In designing catalysts for borohydrides (“polyhedral boranes”), Intematix collaborates closely with Los Alamos National Laboratory, Pacific Northwest National Laboratory, and UCLA.

In exploring the effectiveness of the designed catalysts for hydrogen release from the hydrides, Intematix uses its proprietary combinatorial synthesis technology that is capable of generating hundreds of different catalyst combinations (thin-film or nanoparticle) in one experiment.

In evaluating the catalysts’ performance and optimizing the efficiency of the catalysts, Intematix fully utilizes its proprietary high-throughput screening technology to narrow in and down-select promising catalysts under realistic reaction conditions in a cost-effective and time-efficient way.

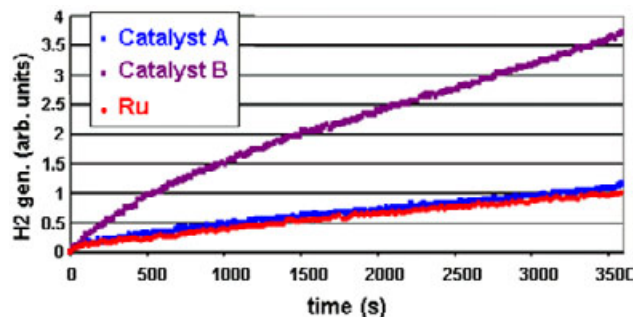
### Partner Results for FY 2005

- Validated combinatorial molecular beam epitaxy (MBE) and ion beam sputtering (IBS) systems for synthesizing thin-film complex hydrides containing air-sensitive elements, such as Li, Na, Mg. Installed an additional high-temperature effusion cell (up to 1900°C) in the MBE system for catalyst element (such as Ti) incorporation. Added a getter pump on the combinatorial IBS system to reduce the residual O<sub>2</sub>.
- Completed setting up an oxygen-free glovebox for *in situ* sample transfer and characterization. The glovebox is integrated with the MBE system to allow samples be transferred in oxygen-free environment.
- Developed a combinatorial nanoparticle (CNP) synthesis system as the third proprietary combinatorial materials synthesis technique, with the advantages of small particle size of ~10-50 nm, narrow particle-size distribution, and accessibility to most elements, as well as rapid size and composition optimization capabilities.
- Designed and constructed micro-reactor arrays for combinatorially screening catalyst libraries.

- Made preliminary discovery of alternative low-cost metal catalysts for hydrogen release in  $\text{NaBH}_4$  (see Figure 1).

### Partner FY 2006 Plans

- Perform high-throughput in-situ catalyst screening.
  - Identify key parameters for high-throughput in-situ screening.
  - Demonstrate effectiveness of catalyst screening methodology for model reaction:  
 $\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{H}_2 + \text{NaBO}_2$  (using effective catalysts).
- Validate the capability of CNP for synthesizing catalyst nanoparticles.
  - Synthesize and screen catalyst libraries for hydrogen release in polyhedral boranes, e.g.,  
 $\text{Na}_2\text{B}_{10}\text{H}_{10} \cdot 16\text{H}_2\text{O} \rightarrow 2\text{NaBO}_2 + 4\text{B}_2\text{O}_3 + 21\text{H}_2$  (using effective catalysts).
- Validate the characterization of material properties of lead catalysts.
  - Examine crystal structure, grain size, and alloy composition of catalyst materials.



**Figure 1.** Pressure Build-Up of Hydrogen Gas Released from  $\text{NaBH}_4$  as a Function of Time Using Different Metal Catalysts

### Conclusions of Partner Effort for FY 2005

- Completed instrumentation validation for combinatorial synthesis of complex metal hydrides and catalysts.
- Initiated high-throughput screening and characterization of metal hydrides.

## VI.B.4e Millennium Cell Inc.

*Ying Wu (Primary Contact), Jeffrey V. Ortega, Richard M. Mohring*  
*One Industrial Way West*  
*Millennium Cell Inc.*  
*Eatontown, NJ 07724 USA*  
*Phone: (732) 544-5718; Fax: (732) 542-2846; E-mail: wu@millenniumcell.com*

*Contract Number: DE-FC36-05GO15056*

*Start Date: March 1, 2005*

*Projected End Date: February 28, 2010*

### Partner Approach

The primary goal of the project is to develop a chemical hydrogen storage and release system, which will meet the DOE 2010 gravimetric and volumetric storage density targets of 2.0 kWh/kg and 1.5 kWh/L, respectively. The system will incorporate Millennium Cell's state-of-the-art technology to provide a practical on-board hydrogen generator. Knowledge and experience gained in this area will not only improve NaBH<sub>4</sub>-based technology, but also provide valuable insight to the controlled hydrogen release from new and novel materials identified by the collective efforts of the Center in the interim. The successful execution of this system engineering research will significantly advance hydrogen storage technology for transportation.

In order to accomplish the long-term goal of developing a working prototype, reactor modeling to optimize the system engineering conditions will be performed first in the short-term in collaboration with Pacific Northwest National Laboratory (PNNL), who is also a participant in the Center. The modeling expertise residing at PNNL will be leveraged and is expected to greatly accelerate the modeling effort at Millennium Cell. More specifically, the effort on the hydrogen-release system during the first year will include the following:

- Increase the system storage capacity and performance of the catalytic reactor.
  - Conduct computational fluid dynamics (CFD) modeling of the reactor.
    - Improve catalyst activity.
    - Better understand reactor dynamics.
    - Reduce liquid hold-up in the reactor.
    - Improve overall heat integration and water management.

In addition to the hydrogen-release-system-focused activity, Millennium Cell will continue to assist the Center partners in their efforts to develop low-cost, energy-efficiency processes for the off-board regeneration of sodium borohydride. Understanding the chemical reaction fundamentals that transform a boron-oxygen (B-O) compound to a boron-hydrogen (B-H) compound is critical to solving the off-board regeneration problem. An improved NaBH<sub>4</sub> regeneration process will bring this chemical hydrogen storage technology closer to DOE cost and energy efficiency targets. Millennium Cell's role in the development of re-generation chemistry will include the following:

- Assist in the engineering development and assessment of electrochemical regeneration processes of borohydride.
  - Increase understanding of reaction kinetics and rate-limiting step(s).
  - Improve reaction yield by rational selection of solvent systems.
  - Lower the cost relative to current technology limitations.

- Mine data on B-H chemistry literature.
- Partners involved: PNNL, LANL, Rohm and Haas, Penn State.

### **Partner Results for FY 2005**

In the short period of time since the project start in March of 2005, Millennium Cell has completed the following activities:

- Distributed a report titled “Summary of Synthetic Processes for the Production of Sodium Borohydride” to the Center partners.
- Provided experimental results on the catalyzed reactor to PNNL in order to initiate modeling activities.
- Disclosed results of recent efforts to synthesize sodium borohydride electrocatalytically to Digby McDonald’s group at Penn State.
- Provided a summary of analytical techniques, both from the literature and those developed in-house at Millennium Cell, for detecting sodium borohydride and related compounds to the Center partners.

### **Partner FY 2006 Plans**

In the remainder of FY 2005 and the first half of FY 2006, our efforts will mainly be focused on the system modeling for hydrogen release:

- Model catalytic reactor using CFD to provide insight into improving efficiency/reducing reactor size.
  - Investigate means of improving gas/liquid separation in the HOD™ system.
  - Determine optimum conditions for heat and water management.
  - Leverage engineering expertise at PNNL.
- Initiate the design of the interim, laboratory-scale prototype system based on the modeling results.

### **Conclusions of Partner Effort for FY 2005**

The reactor modeling activity has commenced. Millennium Cell has supplied PNNL with confidential experimental results on the performance of a generic HOD™ catalyzed reactor design. This data will help PNNL to decide which modeling package/technique to use and will serve as an initial point for the optimization of the next generation of catalyzed hydrolyzing reactor. Starting with the reactor, we will be able to optimize the rest of the system from an inside to outside approach during the following years.

Millennium Cell has also provided Center partners with summaries of both synthetic and analytical methods with regards to borohydride chemistry. In sharing these documents, the Center partners will have more knowledge to draw upon when evaluating new methods for making borohydride. Previous electrocatalytic research performed at Millennium Cell has also been disclosed to the Center partners. This information will help prevent overlap (or the duplicating) of prior work and will provide a course for Center partners to pursue.

### **Millennium Cell FY 2005 Presentations**

1. 2005 DOE Hydrogen Program Review, May 23-26, Washington, DC.

## VI.B.4f Northern Arizona University

*Clinton F. Lane*

*Northern Arizona University*

*Department of Chemistry, PO Box 5698*

*Flagstaff, AZ 86011-5698*

*Phone: (928) 523-6296; Fax: (928) 523-8111; E-mail: Clint.Lane@nau.edu*

*Contract Number: DE-FC36-05GO15060*

*Start Date: March 1, 2005*

*Projected End Date: February 28, 2010*

### **Partner Approach**

NAU is performing two tasks in support of the DOE Chemical Hydrogen Storage Center of Excellence. First, we are providing guidance for safe handling of amine-borane and related boron hydrides based on years of previous industrial experience. We will conduct a thorough technical survey of all knowledge relating to amine-borane and borazines. Insights gained from this survey will be applied across the Center to ensure that the design and synthesis of amine-borane-based hydrogen storage materials meet or exceed all applicable safety and toxicity standards as defined by DOE.

In addition, we will evaluate hydrogen on-board release and off-board regeneration capability and capacity of N-substituted amine-boranes to determine if a laboratory-scale system can be developed that safely meets the DOE 2015 target of 9 wt% hydrogen. This project will conduct basic and applied research studies of N-substituted amine-boranes and borazines. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that will meet the DOE 2015 hydrogen storage targets, especially for gravimetric and volumetric capacity and quality of delivered hydrogen.

### **Partner Results for FY 2005**

- Completed literature searches for physical properties, chemical properties and safety aspects of amine-boranes and borazines.
- Completed collection of Material Safety Data Sheets from manufacturers of amine-boranes and borazines.
- Collection of additional reactivity, stability and toxicity information from manufacturers of amine-boranes and borazines is about 50% complete.
- Collection of anecdotal observations from organizations and research groups (outside of the Center) currently or formerly active in amine-borane chemistry is about 10% complete.

### **Partner FY 2006 Plans**

- A report on hazards associated with preparation and handling of amine-boranes, borazines and related boron hydrides and means to mitigate these hazards will be disseminated to all partners in the Center.
- We will prepare various N-substituted amine-borane compounds and determine their solubility and stability in a few inert high-boiling solvents. The best candidates will be studied to see if a safe decomposition can be achieved at a reasonable temperature and if an expected borazine product is produced. This will be done by studying the effect of time and temperature on the evolution of hydrogen from these solutions and by isolation and identification of any intermediates. In collaboration with other

Center partners, catalytic processes will be studied for the evolution of hydrogen from these solutions to see if a system can be developed that cleanly forms a borazine product plus pure hydrogen at a temperature low enough to use the waste heat from fuel cells.

- We will prepare a sample of the borazine mixture from above and then study the effect of time, temperature and pressure on its hydrogenation. In collaboration with other Center partners, catalytic processes will be studied for the hydrogenation of the borazine mixture to see if a process can be developed that cleanly regenerates the amine-borane-based chemical hydrogen storage fuel.

### **Conclusions of Partner Effort for FY 2005**

- Amine-boranes meet the safety and capacity criteria to warrant further intensive work at NAU in collaboration with Center partners LANL, PNNL, Penn, UW, Alabama, and Intematix.



## VI.B.4g Rohm and Haas

*Suzanne W. Linehan*

*Rohm and Haas Company*

*60 Willow Street*

*North Andover, MA 01845*

*Phone: (978) 689-1589; Fax: (978) 689-1555; E-mail: slinehan@rohmmaas.com*

*Contract Number: DE-FC36-05GO15053*

*Subcontractors:*

*Innochem, Inc., Boxford, MA*

*Electrolytica, Inc., Amherst, NY*

*Start Date: March 1, 2005*

*Projected End Date: December 31, 2009*

### Partner Approach

This project is organized around four main technical tasks:

- **Task 1 — Data Mining.** Compile existing technical information to identify viable pathways from B-O to B-H. Develop technical targets, criteria and metrics to ensure consistent evaluation of options.  
Partners: Rohm and Haas, US Borax, LANL, PNNL, University of Alabama, Millennium Cell, Penn State
- **Task 2 — Electrochemical Reduction of Borates.** Optimize the efficiency of the overall reaction:  

$$\text{B(OH)}_4^- + 4\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{BH}_4^- + 8\text{OH}^-$$
 Optimize previous Rohm and Haas success with aqueous systems; investigate non-aqueous electrochemical reduction.  
Partners: Rohm and Haas, Penn State, Millennium Cell, LANL
- **Task 3 — Complexation and Reduction of Borates.** Screen and evaluate various complexing agents for their efficacy in facilitating borate reduction.  
Partners: Rohm and Haas, LANL, University of Alabama
- **Task 4 — Engineering-Guided Research on Chemical Borate Reduction Routes.** Conduct detailed engineering assessment of as many chemical borate reduction routes as possible, against established metrics. Reduce options: identify routes that do not meet the established criteria and identify leading routes to be pursued experimentally by Center participants.  
Partners: Rohm and Haas, LANL, PNNL, Millennium Cell

### Partner Results for FY 2005

- **Electrochemical Reduction.** Kick-off meeting for electrochemical reduction working group held in March 2005. Identified work practices and Year 1 milestones. Began review of prior intellectual property (IP) and literature. Currently compiling relevant Rohm and Haas background data and experimental information. Collaborating with Penn State to establish appropriate laboratory equipment set-up and to develop experimental program.
- **Engineering.** Kick-off meeting held in March 2005. Clarified Statement of Work, established work practices for the group, and defined regeneration chemistries that were outlined in our respective proposals. A strawman for an options reduction matrix has been drafted. Preliminary discussions were held on conducting life cycle inventory studies. Currently compiling relevant Rohm and Haas background information on all possible borate chemical reduction routes to prepare for brainstorming session.

- **Safety.** Safety Plan submitted to DOE in February 2005.

### **Partner FY 2006 Plans**

- **Data Mining**
  - Complete data mining.
  - Define goals and strategies, boundaries and assumptions; develop performance criteria and metrics.
- **Engineering**
  - Document all possible chemical pathways and process options for B-O to B-H, including contributions from Center participants.
  - Utilize options reduction matrix and develop basic reaction envelopes and process flowsheets. Conduct preliminary technical and economic analysis for regeneration chemistries.
  - Identify leading pathways for experimental studies.
  - Develop criteria and conduct preliminary life cycle inventory studies.
- **Complexation and Reduction of Borates**
  - Establish experimental program.
  - Provide information on solubility, stability, and physical/chemical properties.
  - Provide process support and engineering/economic analysis for promising concepts.
- **Electrochemistry**
  - Identify and establish appropriate analytical methodology and laboratory equipment for electrochemical reduction studies.
  - Establish metrics for evaluating and comparing different electrochemical approaches.
  - Identify pathways and constraints for B-O to B-H; identify leading options meeting the selected criteria and progress to studies on leading systems.
  - Collaborate with Penn State to build upon Rohm and Haas' past success with aqueous borate electrolytic reduction.

### **Conclusions of Partner Effort for FY 2005**

Although this project started on March 1, 2005, activities that may lead to co-invention between Center participants have been avoided (brainstorming sessions, sharing of new ideas or extensions of existing detailed technical confidential information). The reason for this is that it has not yet been possible to execute an IP agreement between Center participants that addresses jointly invented IP. While we believe this has slowed progress somewhat, we anticipate that we will have an IP agreement in place in the July – August 2005 time frame, at which time we expect the work to accelerate quickly.

### **Rohm and Haas FY 2005 Publications/Presentations**

1. Poster presentation at 2005 DOE Hydrogen Program Review, Washington, DC, May 23 – 26, "DOE Chemical Hydrogen Storage Center of Excellence - Novel Approaches to Hydrogen Storage: Conversion of Borates to Boron Hydrides, Project ID# STP11," S. W. Linehan.

## VI.B.4h University of Alabama

David A. Dixon (Primary Contact), Anthony J. Arduengo, III

Chemistry Department, Shelby Hall, Box 870336

Tuscaloosa, AL 35487-0336

Phone: (205) 348-8441; Fax: (205) 348-4704; E-mail: dadixon@bama.ua.edu

Contract Number: DE-FC36-05GO15059

Start Date: January 1, 2005

Projected End Date: December 31, 2009

### Partner Approach

The focus of the work is the development of new chemistries for chemical hydrogen storage systems to enable DOE to meet the technical objective: “By 2010, develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%), 1.5 kWh/L, and \$4/kWh.; by 2015, 3 kWh/kg (9 wt%), 2.7 kWh/L, and \$2/kWh”. We are developing and implementing imidazolium-based H<sub>2</sub> activation chemistry; developing and implementing chemical systems based on polyhydrides of main group elements, *e.g.*, phosphorous; developing and implementing cyanocarbon systems for H<sub>2</sub> storage; and providing computational chemistry support (thermodynamics, kinetics, properties prediction) to the experimental efforts of the DOE Center of Excellence for Chemical Hydrogen Storage to reduce the time to design new materials and develop materials that meet the 2010 and 2015 DOE objectives.

To achieve this goal, we are using novel chemistry approaches to synthesize compounds for easily reversible addition/elimination of H<sub>2</sub> based on our novel, stable carbene chemistry; using first principles computational chemistry approaches on advanced computer architectures to predict the electronic structure of molecules to obtain thermodynamic and kinetic information in support of the design of hydrogen storage materials and of catalysts to effect easy release and addition of H<sub>2</sub>; developing a thermodynamic approach for chemical H<sub>2</sub> storage based on exploiting H and G coupled with Le Chatelier’s principle to manage H<sub>2</sub> addition and release in chemical compounds, which is a potential approach for dealing with cold-start issues. For the experimental effort, there are close interactions with the partners, LANL and UC Davis. The computational effort supports the entire Center, with special interactions with LANL, PNNL, UW, Penn, UC Davis, and UCLA.

### Partner Results for FY 2005

- Formation of carbene·H<sub>2</sub> adducts demonstrated.
- Reliable computational chemical prediction of H<sub>2</sub> release energetics from borane amines and carbenes has been achieved, demonstrating the methodology and further developing G/H concepts. Developed approaches for dealing with gas-phase molecules and salts.
- Model compound available for cyanocarbon·H<sub>2</sub> adducts.
- Performed structural characterization of an imidazolium borohydride.
- Predicted NMR chemical shifts for analysis of BNH<sub>x</sub>(CH<sub>3</sub>)<sub>y</sub> polymers for analysis of LANL data.
- Predicted energetics for H<sub>2</sub> release from isoelectronic compounds based on the boron amines with other main group elements in support of work at PNNL and UC Davis.
- Website completed for Center partners.

### Partner FY 2006 Plans

- Conduct experimental and computational characterization of cyanocarbons for H<sub>2</sub> storage.
- Continue experimental and computational studies on carbene-H<sub>2</sub> adducts.
- Conduct experimental and computational studies on imidazol(in)ium borohydrides and carbene-borane adducts.
- Continue computational chemistry studies in overall support of DOE Center of Excellence for Chemical Hydrogen Storage.
- Predict the thermodynamics and rate constants for reactions of alkoxyboron compounds with metal hydrides (disproportionation/conproportionation, hydride exchange).
- Predict reaction mechanisms for borane amine reactions, including dehydro-oligomerization reactions, Lewis acid base addition reactions, hydride extraction, and proton loss, and predict NMR chemical shifts, infrared spectra, and UV-visible spectra for use in analyzing experimental data.
- Electronic infrastructure support: Support and continue to develop website for Center partners to share data, publications, and presentations, and develop and construct database for thermodynamic, kinetic, and spectroscopic data for the Center.

### Conclusions of Partner Effort for FY 2005

- Developed a reliable computational chemistry approach based on molecular orbital theory and density functional theory to predict the thermodynamics for chemical H<sub>2</sub> storage.
- Developed synthetic approaches for carbenes for chemical H<sub>2</sub> storage.
- Developed synthetic approaches for cyanocarbons for chemical H<sub>2</sub> storage.

### University of Alabama Special Recognitions & Awards/Patents Issued

1. 2nd Undergraduate Research Symposium, Arts and Sciences, University of Alabama, April 8, 2005, "High level computational approaches to the prediction of the thermodynamics of chemical hydrogen storage systems," Jacob Batson and David A. Dixon, 2nd place in science category.

### University of Alabama FY 2005 Publications/Presentations

1. Invited Presentation at the 229th National American Chemical Society Meeting, San Diego, CA, March, 2005, Division of Fuel Chemistry, Computational Methods and Modeling in Fuel Chemistry Symposium (+ 2-page extended abstract): "High Level Computational Approaches to the Prediction of the Thermodynamics of Chemical Hydrogen Storage Systems and Hydrocarbon Fuels," D. A. Dixon, M. Gutowski, L. Pollack, T. L. Windus, and W. de Jong (partner with PNNL)
2. "Thermodynamic Properties of Molecular Borane Amines and the [BH<sub>4</sub><sup>-</sup>][NH<sub>4</sub><sup>+</sup>] Salt for Chemical Hydrogen Storage Systems from Ab Initio Electronic Structure Theory," D. A. Dixon and M. Gutowski, *J. Phys. Chem. A*, **2005**, *109*, 5129. (partner with PNNL)
3. "Thermodynamic Properties of the C<sub>5</sub>, C<sub>6</sub>, and C<sub>8</sub> n-Alkanes from Ab Initio Electronic Structure Theory," L. Pollack, T. L. Windus, W. A. de Jong, and D.A. Dixon, *J. Phys. Chem. A*, published WEB ASAP, July, 2005. (partner with PNNL).
4. "Thermodynamic Properties of Molecular Borane Phosphines, Alane Amines, and Phosphine Alanes as well as the [BH<sub>4</sub><sup>-</sup>][PH<sub>4</sub><sup>+</sup>], [AlH<sub>4</sub><sup>-</sup>][NH<sub>4</sub><sup>+</sup>], and [AlH<sub>4</sub><sup>-</sup>][PH<sub>4</sub><sup>+</sup>] Salts for Chemical Hydrogen Storage Systems from Ab Initio Electronic Structure Theory," D. J. Grant and D. A. Dixon, *J. Phys. Chem. A*, to be submitted, July, 2005.
5. "Heats of Formation of the Arduengo Carbene and Various Adducts Including H<sub>2</sub> from Ab Initio Molecular Orbital Theory," D. A. Dixon and A. J. Arduengo, III, *J. Am. Chem. Soc.*, to be submitted, July, 2005.

## VI.B.4i University of California, Davis

*Philip P. Power (Primary Contact), Susan Kauzlarich*  
*Chemistry Department, UC Davis*  
*One Shields Avenue*  
*Davis, CA 95616*  
*Phone: (530) 752-6913; Fax: (530) 752-8995; E-mail: pppower@ucdavis.edu*

*Contract Number: DE-FC36-05GO15055*

*Start Date: January 1, 2005*

*Projected End Date: December 31, 2005*

### Partner Approach

The proposed project is focused on the synthesis of compounds that will reversibly adsorb molecular hydrogen in the design of 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. Furthermore, the small particles are non-toxic and non-corrosive. Particular attention will be focused on silicon or Group III-V containing compounds, concentrating primarily on capped and uncapped nanoparticles and investigating the interconversion of the nanoparticles through their hydrogenation/dehydrogenation reactions. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the DOE 2010 hydrogen storage targets, especially cost, hydrogen capacity and reversibility.

### Partner Results for FY 2005

The route to new, potentially high-yield hydrogen-capped silicon nanoparticles is under investigation. Detailed analysis is necessary to be able to demonstrate whether or not this route will be successful. Results to date are summarized as follows:

- Preparation of gram-scale hydrogen-capped silicon nanoparticles has been attempted by both solid-state and solution reaction routes. The precursors are NaSi and Mg<sub>2</sub>Si, and for hydrogen sources, NH<sub>4</sub>X (X= Cl and Br) have been used.
  - The X-ray powder patterns of the resulting materials correspond to nc-Si. Initial scanning electron microscopy (SEM) images indicate that these materials are on the nanometer scale.
- Preparation of octaoxy terminated silicon nanoparticles from reduction of SiCl<sub>4</sub> with sodium naphthalide has been demonstrated.
  - Transmission electron microscopy, fluorescence, NMR, UV-vis, and Fourier transform infrared analysis fully characterized the sample and confirmed that we had 4 nm diameter particles.
- Preparation of amine-capped silicon nanoparticles from reduction of SiCl<sub>4</sub> with sodium naphthalide has been demonstrated.
  - The product has been characterized by NMR and thermogravimetric analysis.
- Silica nanoparticles have been prepared by the Stober method.
  - The nanoparticles have been characterized by SEM.

**Partner FY 2006 Plans**

- Identify hydrogen storage material enabling DOE targets and increase the understanding of synthetic approaches and physical properties of main group element clusters, such as Si/SiO<sub>2</sub>, Al-alloys, BP and BN. Designing simple routes to such compounds using mild conditions will provide commercially viable materials, and the high percentage of surface atoms offers promising reactivity towards hydrogen and alkyl or amide groups.
- Investigate the viability of the synthesized materials for commercial application by studying their weight and volume as well as the reversibility of hydrogen uptake. Measurements will be analyzed to identify compounds that offer relatively lightweight, easily handled solid materials capable of hydrogen storage and that are synthesized, activated and regenerated in a simple manner.
- Engineer and synthesize the most efficient hydrogen adsorbent.

**Conclusions of Partner Effort for FY 2005**

The project is as yet in its infancy, but inroads have been made towards the synthesis of similar-sized, capped silica nanoparticles, which relates to the materials development aspect of the DOE technical targets. The hydrogen storage potential of these materials will be investigated in order to address the DOE's objective to develop and verify on-board hydrogen storage systems achieving 2 kWh/kg (6 wt%) by 2010.

## VI.B.4j University of California, Los Angeles (UCLA)

*M. Frederick Hawthorne*

*Department of Chemistry and Biochemistry, UCLA*

*Los Angeles, CA*

*Phone: (310) 825-7378; Fax: (310) 825-5490; E-mail: mfh@chem.ucla.edu*

*Contract Number: DE-FC36-05GO15058*

*Start Date: January 1, 2005*

*Projected End Date: December 31, 2009*

### Partner Approach

Borohydride compounds offer the potential for significant hydrogen storage capacity, but most work to date has focused on one particular anion,  $\text{BH}_4^-$ , which requires high pH for stability and large energy costs for regeneration. Other borohydride compounds, in particular polyborane anions, may offer comparable hydrogen storage capacity without requiring high-pH media and with significantly reduced energy costs for regeneration.

The UCLA project will provide the overall program focal point for the investigation of polyhedral borane anions  $\text{B}_n\text{H}_n^{2-}$  ( $n = 10$  and  $12$ ),  $\text{B}_{11}\text{H}_{14}^-$  and their derivatives as reservoirs for stored electrons available for hydrogen release upon catalyzed hydrolysis, as a substitute for electrochemical studies leading to reversible electron storage, and as reactants in reversible hydrogen storage.

Objectives of the Project:

- Develop heterogeneous catalysts for the controlled release of hydrogen from the hydrolysis of salts of  $\text{B}_{12}\text{H}_{12}^{2-}$ ,  $\text{B}_{10}\text{H}_{10}^{2-}$  and  $\text{B}_{11}\text{H}_{14}^-$  ions.
- Determine the kinetics and mechanism of these catalyzed borane anion hydrolysis reactions to provide design data for large-scale hydrogen release devices.
- Investigate blends of two or more anionic polyhedral borane salts of variable purity as commercially viable sources of hydrogen (analogous to hydrocarbon blends for optimized gasoline), with cost and performance as working parameters.
- Optimize existing processes for the conversion of diverse  $>\text{BH}$  sources to  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  and  $\text{Na}_2\text{B}_{10}\text{H}_{10}$  for direct use in hydrogen release without extensive purification.

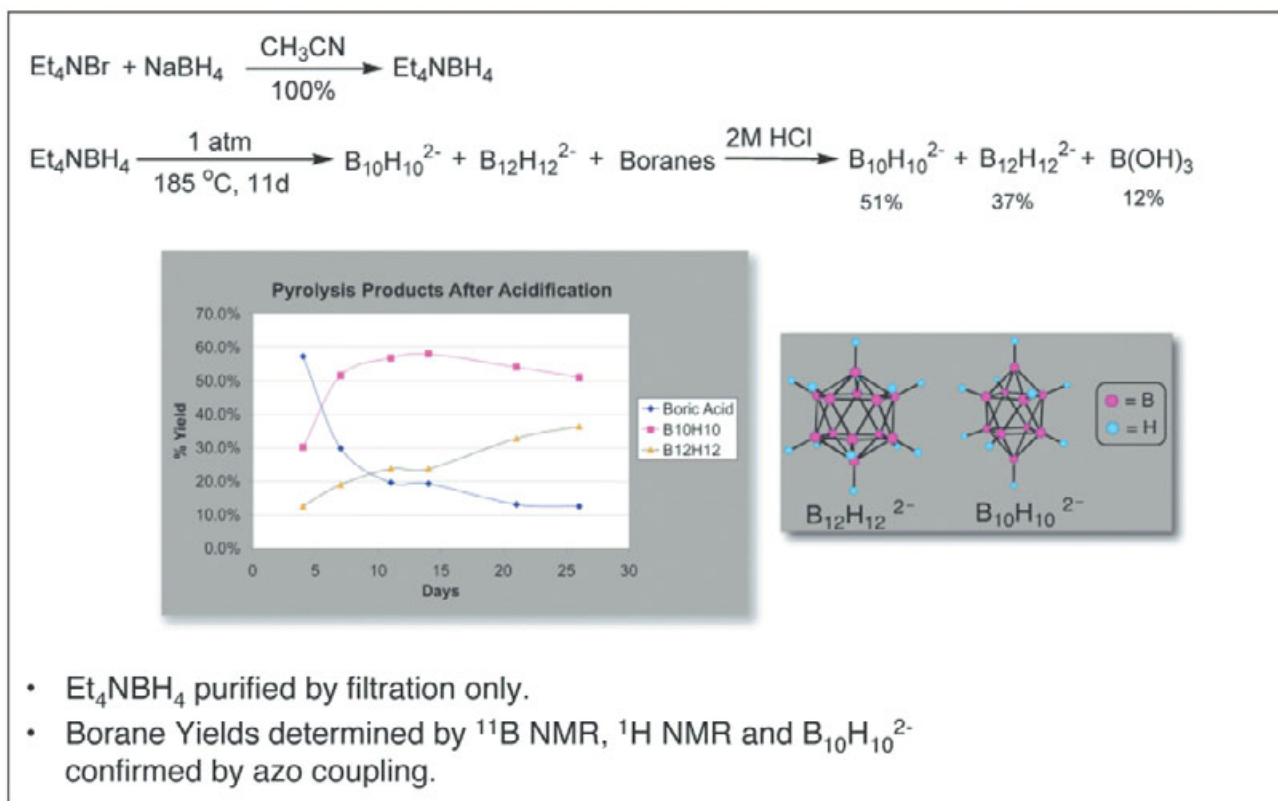
Collaborations and Partners:

- Penn State University (Digby McDonald) for electrochemical studies of polyhedral borane species identified through consultation with UCLA and supplied by UCLA.
- Los Alamos National Laboratory (Tom Baker) for collaborative studies of selected amine borane derivatives supplied by UCLA and used in reversible hydrogen uptake reactions.
- Pacific Northwestern National Laboratory (Tom Autrey) for collaborative kinetic studies of catalyzed polyhedral borane hydrolysis using microcalorimetry to obtain reaction kinetics and thermodynamic data.

If polyhedral boranes show promise for hydrogen storage, we will reexamine the best synthesis routes to develop the most efficient and economical variant.

### Partner Results for FY 2005

- Achieved conversion of  $\text{Et}_4\text{NBH}_4$  to *Closo*- $\text{B}_{10}\text{H}_{10}^{2-}$  and *Closo*- $\text{B}_{12}\text{H}_{12}^{2-}$  ions by thermolysis (see Figure 1).
- $\text{Et}_4\text{NBH}_4$ , when heated at  $185^\circ\text{C}$  for 11 days, gave *Closo*- $\text{B}_{10}\text{H}_{10}^{2-}$  and *Closo*- $\text{B}_{12}\text{H}_{12}^{2-}$  in 51% and 37% yield, respectively. Optimization of this process is currently in progress.



**Figure 1.** Conversion of  $\text{Et}_4\text{NBH}_4$  to  $\text{Closo-B}_{10}\text{H}_{10}^{2-}$  and  $\text{Closo-B}_{12}\text{H}_{12}^{2-}$  Ions by Thermolysis

- Synthesis of  $\text{NaB}_{11}\text{H}_{14}$  was achieved.
- Reaction of  $\text{B}_{10}\text{H}_{14}$  with  $\text{NaBH}_4$  in 1,4-dioxane at  $110^\circ\text{C}$  gave  $\text{NaB}_{11}\text{H}_{14}$  in 70% yield. Further optimization of the reaction is under investigation.
- Catalytic hydrolysis of  $\text{NaB}_{11}\text{H}_{14}$ ,  $\text{Closo-B}_{10}\text{H}_{10}^{2-}$  and  $\text{Closo-B}_{12}\text{H}_{12}^{2-}$  was achieved.
- Various cobalt, nickel, ruthenium and rhenium catalysts are under investigation. For example, the  $\text{Co}_2\text{B}$ -catalyzed reaction of  $\text{NaBH}_4$  with water liberates  $\text{H}_2$  at a faster rate than the uncatalyzed reaction. Studies are underway to quantitatively determine rate and amount of  $\text{H}_2$  released in the reaction.

### Partner FY 2006 Plans

- Prepare appropriate quantities of  $\text{Na}_2\text{B}_{10}\text{H}_{10}$ ,  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  and  $\text{NaB}_{11}\text{H}_{14}$  to support catalyst studies.
- Identify active catalyst for  $\text{B}_{11}\text{H}_{14}^-$  hydrolysis, determine mechanism of polyhedral borane anion hydrolysis reactions and secure an efficient catalyst for the same.
- Identify appropriate polyhedral borane anions for electrochemical regeneration (with Penn State).
- Identify appropriate polyhedral borane-amine complexes and ammonium salts for catalytic dehydrogenation studies (with Center).

### Conclusions of Partner Effort for FY 2005

Achieved conversion of  $\text{Et}_4\text{NBH}_4$  to  $\text{Closo-B}_{10}\text{H}_{10}^{2-}$  and  $\text{Closo-B}_{12}\text{H}_{12}^{2-}$  ions by thermolysis.



**UCLA FY 2005 Publications/Presentations**

1. Quarterly report was presented at DOE Chemical Hydrogen Storage meeting held in Washington, DC, May, 2005.

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## VI.B.4k University of Pennsylvania

Larry G. Sneddon

University of Pennsylvania, Department of Chemistry

231 South 34<sup>th</sup> Street

Philadelphia, PA 19104-6323

Phone: (215) 898-8632; Fax: (215) 573-6743; E-mail: lsneddon@sas.upenn.edu

Contract Number: DE-FC36-05GO15051

Start Date: January 1, 2005

Projected End Date: December 31, 2009

### Partner Approach

Because of their protonic amine-hydrogens and hydridic borane-hydrogens, amine-boranes are unique in their potential ability to store and deliver large amounts of molecular hydrogen through either intramolecular or intermolecular dehydrogenation reactions. The goals of this project are to (1) develop new ways of inducing amineborane dehydrogenations at lower temperatures and elucidate the important controlling factors in these reactions; (2) develop efficient methods for the regeneration of ammonia borane or other hydrogenated amineborane species from amorphous boron nitride or  $\text{BNH}_x$  materials; and (3) investigate the hydrogen storage potentials of higher aminopolyborane and/or boron-nitrogen polymeric materials. Successful execution of this project will provide the chemistry necessary to construct a rough life cycle analysis of amineboranes as efficient hydrogen storage media.

To accomplish these objectives, we are collaborating with Center partners LANL, PNNL, University of Washington, Northern Arizona University and University of Alabama to develop (1) new transition metal catalyzed pathways for key amineborane dehydrogenation reactions that lower the dehydrogenation temperature and increase the extent of dehydrogenation, and (2) new amineborane regeneration reactions based on either transition metal catalyzed hydrogenation or stoichiometric hydrohalogenation reactions.

### Partner Results for FY 2005

- Appropriate quantities of key amine-boranes, including ammonia borane, ammonia triborohydride and borazine, have been prepared.
- An ongoing systematic survey of catalysts for dehydrogenation activity has identified several active catalysts, and studies of  $\text{H}_2$  release as a function of catalyst, temperature and solvent are underway
- Systematic studies of BN hydrohalogenation and halogenation reactions have been initiated.

### Partner FY 2006 Plans

The potential high hydrogen storage capacities of ammonia borane,  $\text{NH}_3\text{BH}_3$  (19.6 wt%, 0.16 kg/L  $\text{H}_2$ ), and ammonia triborohydride,  $\text{NH}_3\text{B}_3\text{H}_7$  (17.8 wt%, 0.14 kg/L  $\text{H}_2$ ), will make them focal point materials for FY 2006. Planned dehydrogenation/regeneration studies are briefly described below.

In FY 2006, our ongoing studies of the metal-catalyzed dehydrogenation of ammonia borane and ammonia triborohydride will be focused on the use of nanoparticle catalysts. Such catalysts have been shown to have high activity for organic hydrogenation/dehydrogenation processes, suggesting they should have comparable activities for isoelectronic boron-nitrogen species. Our initial studies in this area have already led to the identification of several active catalysts. In addition to optimizing the reaction conditions for these catalysts,

we plan to complete our initial screenings of the other known nanoparticle-based dehydrogenation catalysts in FY 2006.

A key to the successful utilization of amine-boranes for hydrogen storage is to develop efficient methods for their regeneration. Therefore, the second main focus of our work in FY 2006 will be directed toward achieving the formation of ammonia borane and/or other hydrogenated amineborane species (i.e., polyborazylene, borazine or cyclotriborazane) from amorphous boron nitride and/or  $\text{BNH}_x$  materials. We plan to use spectroscopic and analytical methods to characterize the structures and compositions of the amorphous boron-nitride and/or  $\text{BNH}_x$  products obtained from the dehydrogenation of ammonia borane and ammonia triborohydride and to complete our screening of the reactivities of these materials for both hydrogenation and hydrohalogenation reactions.

## VI.B.4I University of Washington

*Karen I. Goldberg (Primary Contact), D. Michael Heinekey*

*Department of Chemistry*

*University of Washington*

*Box 351700*

*Seattle, WA 98195-1700*

*Phone: (206) 616-2973; Fax: (206) 685-8665; E-mail: Goldberg@chem.washington.edu*

*Contract Number: DE-FC36-05GO15057*

*Start Date: March 1, 2005*

*Projected End Date: February 28, 2010*

### Partner Approach

The dehydrogenation and hydrogenation of BN compounds using transition metal catalysts are under investigation. We are engaged in determining and carrying out detailed studies of the key steps in the catalytic mechanism. Current efforts are concentrated on the coordination of the BN species to the metal center. These studies are guided by our prior experience with the binding and activation of sigma bond ligands such as dihydrogen and silanes. Unsaturated metal centers which bind hydrogen well may also bind and activate amine boranes.

Interactions with our partners at the University of Pennsylvania, PNNL and LANL are integral to our research, and in-person meetings and phone conversations are advancing the project goals.

### Partner Results for FY 2005

- Coordination of the product of the dehydrogenation of amine borane to transition metal species has been observed. Examples of the coordination of amine boranes to transition metal complexes have recently been reported by Shimoi and coworkers [1]. In their studies, they showed that  $(\text{CO})_5\text{M}(\eta^1\text{-BH}_3\text{.L})$  can be prepared by photolysis of  $(\text{CO})_6\text{M}$  in the presence of  $\text{BH}_3\text{.L}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ;  $\text{L} = \text{NMe}_3, \text{PMe}_3, \text{PPh}_3$ ). They also report that the corresponding  $\text{Me}_2\text{NHBH}_3$  compound could be neither isolated nor observed due to dehydrogenation and formation of the cyclic dimer  $(\text{Me}_2\text{N-BH}_2)_2$  [2]. We have found a different outcome for this reaction with observation of the coordination of the product of dehydrogenation to give  $[\text{Cr}(\text{CO})_5(\eta^1\text{-BH}_2=\text{NMe}_2)]$  (**1**).  $[\text{Cr}(\text{CO})_5(\text{H}_2)]$  and the bridging hydride dimer  $[(\text{CO})_5\text{Cr}(\text{m-H})\text{Cr}(\text{CO})_5]^-$  are also observed. Attempts to isolate complex **1** for complete characterization are continuing. Interesting preliminary results have also been obtained for the ruthenium system  $[\text{Cp}^*\text{Ru}(\text{P}^{\wedge}\text{P})]^+$ .
- A general class of transition metal catalysts for efficient dehydrogenation of amine boranes has been discovered. A provisional patent is being filed by UW.

### Partner FY 2006 Plans

Research will continue on the modeling efforts as described above. A variety of unsaturated metal complexes will be prepared, and their formation of adducts and/or reactions with amine boranes will be examined. Full characterization will be obtained for all adducts, and kinetic and mechanistic studies of reactions will be pursued. In addition, reactions of the BN products of dehydrogenation of amine boranes with hydrogen in the presence of transition metal species will be examined.

We will also study and develop the effective catalyst systems for amine borane dehydrogenation described in a provisional patent filed by UW in July 2005.

### **Conclusions of Partner Effort for FY 2005**

Novel BN adducts with transition metal species have been observed. Leads as to the nature of the transition metal species needed to stabilize different BN species are being identified.

Highly effective catalysts for amine borane dehydrogenation have been developed.

### **University of Washington Special Recognitions & Awards/Patents Issued**

1. A provisional patent on efficient dehydrogenation of amine boranes by transition metal catalysts has been filed by the University of Washington.

### **University of Washington FY 2005 Publications/Presentations**

1. Coordination of B-N Species to Transition Metal Complexes. Pons, V.; Denney, M. C.; Goldberg, K. I.; Heinekey, D. M. ACS National Meeting, Washington, DC, 2005. Prepr. Pap-Am. Chem. Soc., Div. Fuel Chem, 2005, 50, (1), paper # 51.

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