

## IV.B.4b PNNL Progress within the DOE Center of Excellence for Chemical Hydrogen Storage

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### Objectives

- Quantify hydrogen release from solid ammonia borane storage materials and determine associated chemical mechanism.
- Employ mechanism to understand rate limitations associated with release.
- Investigate the impact of exothermic hydrogen release on fuel stability and safety.
- Develop and validate multi-scale reactor models to better understand the impact of geometry, loading, pressure, and temperature on catalytic hydrogen release.
- Develop better understanding of thermodynamics for ammonia borane and other systems through comprehensive literature review, theoretical calculations, and thermochemistry experiments.

### Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (J) Thermal Management

### Technical Targets

Data reported are for solid ammonia borane either as a neat material or on a silica scaffold in a 1:1 ratio by weight. Here, values are 'material-based'; whereas, the DOE targets are on a system basis. For gravimetric and volumetric capacity, data are reported as 1<sup>st</sup> and 2<sup>nd</sup> equivalents, where 1<sup>st</sup> equivalent is obtained from  $\text{BNH}_6 \rightarrow \text{BNH}_4$ , and the 2<sup>nd</sup> equivalent is obtained from  $\text{BNH}_6 \rightarrow \text{BNH}_2$ . Rate of reaction is reported in terms of an estimate of the reaction volume required to obtain a rate of 0.02 g/kW/s (2010 target) using an 80 kW fuel cell as the basis. 2010 targets for gravimetric and volumetric capacity on a system basis are 6% and 0.045 kg/L, respectively.

AB specifics	1 <sup>st</sup> Eq. Wt % (T)	2 <sup>nd</sup> Eq. Wt % (T)*	Vol% (T)	Rxn Vol (L)
Neat material	5.5 (85°C) 6.5 (120°C)	~13 (> 120°C)	0.043	-
Seeded material	6.5 (120°C)	~13 (> 120°C)	0.043	6
1:1 Scaffold	3.2 (60°C)	~6.5 (> 120°C)	~0.02**	12

\*2<sup>nd</sup> Equivalent has not been quantified using pressure-composition-temperature (PCT). Quantities are inferred using nuclear magnetic resonance (NMR).

\*\*Assumes that the density of a settled powder is equal to that of neat ammonia borane.

### Accomplishments

- Quantitatively determined gravimetric and volumetric hydrogen density for 1<sup>st</sup> equivalent in table above.
- Determined that hydrogen release rate in solid ammonia borane is governed by a nucleation and growth mechanism. Nucleation seeds can be formed in the material using heat pretreatment. This allows a substantially higher hydrogen release rate from the material. Using this data it was determined that a reaction volume of 6 liters should be ample to meet the 2010 rate target.
- Using experimental kinetic data and simulated Avrami analysis, preliminary data show that exothermic chemistries can run away under extreme temperature and adiabatic conditions. The degree and speed of runaway is governed by the temperature of the fuel.

- Preliminary results on higher loading scaffolds show that as the ammonia borane content is increased beyond a 1:1 ratio, kinetics, thermodynamics, and byproducts begin to approach the neat material.
- A multi-scale reactor model was developed and handed off to Millennium Cell for the purposes of reactor optimization for sodium borohydride hydrolysis. The model will be used to support reactor development for other chemical systems within the Center.
- Complete thermodynamics have been determined for the cyclic products of ammonia borane dehydrocoupling.

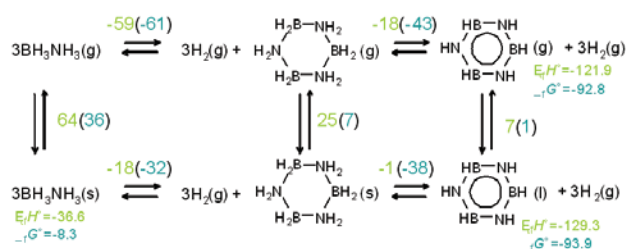
## Approach

PNNL is approaching the challenge in a means consistent with the Center philosophy. In addition to 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 2, PNNL has many activities including examination of mechanisms of hydrogen release from solid ammonia boranes, experimental work on the regeneration of spent ammonia boranes, and addressing the implications of exothermic hydrogen release on fuel safety. PNNL's efforts in Tier 3 are limited and composed primarily of computational and experimental investigations of high capacity hydrogen storage compounds built on oxygenates such as formaldehyde. PNNL also leads the engineering team working on sodium borohydride regeneration, life cycle and economic analysis, and on-board systems concepts. This group also interfaces on a regular basis with DOE's Storage System Analysis Working Group.

## Results

A significant amount of effort was centered on obtaining thermodynamics of the ammonia borane system with particular focus on the differences between gas and liquid phase. This was accomplished using literature sources [1,2,3] and computational methods as needed. Figure 1 shows the energetics for the system where the products are cyclic. Good agreement between measured values and calculated values has been obtained and the relationship between gas phase and liquid phase calculations is understood. Based on these thermodynamics it is virtually impossible to regenerate ammonia borane using hydrogen pressure alone, which

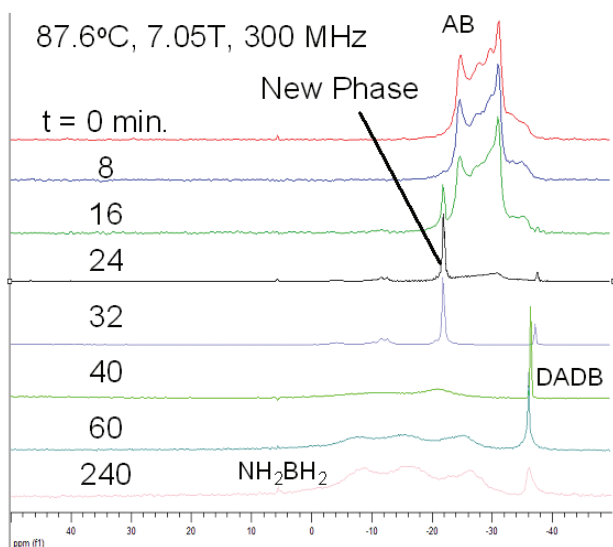


**FIGURE 1.** Thermodynamics for Hydrogen Release from Ammonia Borane: Dehydrocoupling to form Perhydroborazine and Borazine (All values are in kcal/mol.)

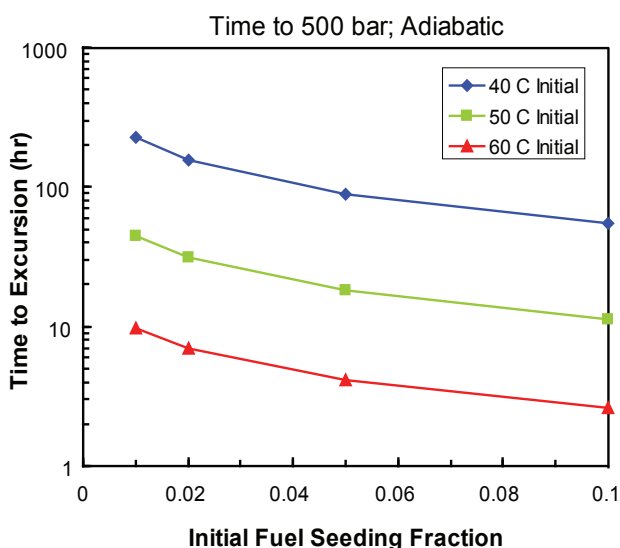
indicates that a chemical pathway will be required to allow fuel recycling.

In addition to investigation of thermodynamics, mechanistic studies were used to understand how solid ammonia borane releases hydrogen. Last year, we reported that solid ammonia borane appeared to dehydrocouple through a nucleation and growth pathway. During FY 2006 this was confirmed and the mechanism illuminated. The in situ, solid state NMR spectra shown in Figure 2 clearly show that the diammoniate of diborane (DADB),  $[(\text{NH}_3)_2\text{BH}_2][\text{BH}_4]$ , is formed prior to formation of the product  $[\text{NH}_2\text{BH}_2]_n$ . We believe that this is the nucleation seed material that is the intermediate required for ammonia borane to release hydrogen. Also interesting is that ammonia borane undergoes a phase change prior to isomerizing to DADB. This new phase has not been previously reported, but the sharpening of the peak would indicate a highly mobile or liquid-like phase.

The nucleation seeding of ammonia borane is of interest for several reasons. It allows evolution of hydrogen at lower temperature, and the kinetics of release is faster, which drives toward meeting the 2010 target for hydrogen release rate. This benefit, however, comes at a cost because the fuel is effectively destabilized. In an exothermic hydrogen release system this can cause some safety concerns. We therefore went through a preliminary analysis on the impact of seeding on fuel stability. This was accomplished by fitting kinetics data to the Avrami equation,  $X = 1 - \exp[-(kt)^n]$ , where X is the partial conversion, k is a rate constant, and t is time. It was assumed that the fuel bed was adiabatic, resulting in a slow temperature rise over time due to the exothermic reaction. Focus was on obtaining the pressure evolved due to fuel destabilization. Figure 3 shows the results of the analysis for a 1,000 mol bed of AB with no temperature gradients. The time required to reach 500 bar is plotted as a function of the seeding fraction. This analysis is somewhat conservative in that there is no allowance for cooling of any kind. In a real system heat is lost due to conduction and convection, so this is a 'worst case' scenario. Nevertheless, the analysis



**FIGURE 2.** In Situ, Solid State NMR Spectra Obtained During the Dehydrocoupling of Ammonia Borane



**FIGURE 3.** Results of a Stability Analysis on Solid Ammonia Borane Fuels

does point out that fuel stability could be a concern for solid ammonia borane systems.

## Conclusions and Future Directions

In all, FY 2006 has resulted in a great expansion in knowledge with B-N materials. We now understand the release mechanism and the hydrogen content of ammonia borane in quantitative terms. We have a good grasp on the thermodynamics and kinetics. This information is critical to pursue system level work where heat integration and management are going to

be of utmost importance. In the next year we intend to continue examination of ammonia borane and begin to study some compounds built around oxygenated hydrocarbons. The following bulleted list is indicative of the areas we will pursue in FY 2007:

- Quantitative measurement of rates for seeded and unseeded materials. Extrapolation to obtain status vs. 2010 target. This is critical to determine impact of kinetics on system volume.
- Quantitative measurements of release for the 2<sup>nd</sup> H<sub>2</sub> equivalent from AB. This is critical to determine the limits of system gravimetric capacity.
- Scaffold work to determine whether lightweight supports like carbon allow thermodynamic and kinetic control similar to silica. Also of interest is the impact of pore size, shape and surface chemistry on the decomposition of ammonia borane.
- Engineering studies: infrastructure for semi-continuous and continuous work to start to look at real rate information from the processing perspective. All measurements to date have been on batch samples.
- Complete multi-scale model for catalytic reactor used for hydrogen release. Build infrastructure for ChemCAD process models. Such component models are critical for system level work and understanding how material-based metrics translate to system-based metrics.
- Finish the stability study on ammonia borane and propose paths forward for heat management. Model serves as a general method for any exothermic system.
- Regeneration of AB via chemical pathways (in situ NMR, then yield quantification).
- Computational and synthetic work on new systems such as oxygenated hydrocarbons.

## FY 2006 Publications/Presentations

1. *The Grand Challenge of Hydrogen Storage*. Maciej Gutowski, Simons Reunion Mini-symposium, Park City, UT 84060, June 19, 2005.
2. *Computational Studies of BNH<sub>x</sub> Materials*. M. Gutowski, R.A. Bachorz, T. Autrey, J. Linehan, Gordon Research Conference, Hydrogen-Metal Systems, Colby College, Waterville, ME, July 10-15, 2005.
3. *The Challenge of On-Board Hydrogen Storage. Thermolysis of III-V Hydrogen-Rich Materials*, Maciej Gutowski, Anna Gutowska, Tom Autrey, John Linehan, Stanford University, Global Climate & Technology Project, August 4, 2005.
4. *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>*. Maciej Gutowski, Rafal Bachorz, Tom Autrey, and John C. Linehan, the 230th ACS National Meeting, in Washington, D.C., Aug 28-Sept 1,

2005; also Prep. Pap. - Am. Chem. Soc., Div. Fuel Chem. 50 (2), 496 (2005).

**5. Hydrogen Release from Ammonia Borane Mediated by a Nanoscaffold of Silica.** Maciej Gutowski, Rafal A. Bachorz, Tom Autrey, John C. Linehan, the 361st WE-Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials, Bad Honnef, Germany, October 23-28, 2005.

**6. The Challenge of On-Board Hydrogen Storage. Theoretical and Experimental Studies of BNH<sub>x</sub> (x=8-2) Materials.** Maciej Gutowski, Heriot-Watt University, Department of Chemistry, Edinburgh, UK, December 2, 2005.

**7. Understanding of hydrogen storage in the NBH<sub>x</sub> materials through computational studies.** Maciej Gutowski, Rafal A. Bachorz, Jun Li, Greg Schenter, Shawn Kathmann, Tom Autrey, John Linehan, Anna Gutowska, Wendy Shaw, 231 ACS National Meeting, Atlanta, Georgia, March 26-30, 2006.

**8. Hydrogen Storage in HNBH Systems.** Liyu Li, Benjamin Schmid, R. Scott Smith, Bruce D. Kay, John Linehan, Wendy Shaw, Nancy Hess, Ashley Stowe, Craig Brown, Luke Daemen, Maciej Gutowski & Tom Autrey. Materials Research Society Meeting, San Francisco, April 2006.

**9. Amine Boranes for Chemical Hydrogen Storage.** Tom Autrey & Maciej Gutowski. Hydrogen Initiative Symposium sponsored by The Energy Center, Purdue University, West Lafayette, IN, April 2006.

**10. Mechanistic studies of molecular hydrogen formation from borane ammonia complexes.** R. Scott Smith, Bruce D. Kay, Liyu Li, Nancy Hess, Maciej Gutowski, Wendy Shaw, John Linehan, Ashley Stowe, Benjamin Schmid & Tom Autrey. Carnegie Institute, Washington, D.C., February 2006.

**11. On-board Hydrogen Storage -- Breakthroughs and Barriers.** Tutorial: Materials Research Society Fall 2005. Tom Autrey, Weifang Luo, Phil Parilla. [http://www.mrs.org/meetings/fall2005/tutorial\\_a.html](http://www.mrs.org/meetings/fall2005/tutorial_a.html)

**12. Novel Approaches for On-board Chemical Hydrogen Storage.** Tom Autrey, Anna Gutowska, John Linehan, Liyu Li, R. Scott Smith, Bruce D. Kay, Yongsoon Shin, Wendy Shaw, Nancy Hess, Benjamin Schmid. Presented at the International Partnership for the Hydrogen Economy – Hydrogen Storage Technology Conference, Lucca, Italy, June 22, 2005.

**13. Controlled Hydrogen Release From Ammonia Borane Using Mesoporous Scaffolds.** Anna Gutowska, Benjamin Schmid, Liyu Li, R. Scott Smith, Bruce D. Kay, John Linehan, Wendy Shaw, Nancy Hess, Yongsoon Shin, Maciej Gutowski & Tom Autrey Presented at the American Physical Society Meeting, Los Angeles, March 2005.

**14. Research Challenges for the Hydrogen Economy; Hydrogen Storage.** Presented at New York City College, April 4, 2005, Tom Autrey.

**15. Hydrogen gets onboard,** RSC Chemistry World, March 2006, Maciej Gutowski & Tom Autrey <http://www.rsc.org/chemistryworld/Issues/2006/March/HydrogenOnBoard.asp>

## References

1. NIST Chemistry WebBook, NIST Standard Reference Database, Lange's Handbook of Chemistry.
2. Wolf, G. in *W. E.-Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials*, October 23-27, 2005, Bad Honnef, Germany.
3. Leavers, D. R.; Long, J. R.; Shore, S. G.; Taylor, W. J. *J. Chem. Soc. (A)*, **1969**, 1580.