

IV.B.5f PNNL Progress within the DOE Center of Excellence for Chemical Hydrogen Storage

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Objectives

- Quantify hydrogen release from solid ammonia borane and determine associated chemical mechanism.
- Employ release mechanism to understand how catalysts and additives can impact rates of release.
- Investigate the impact of exothermic hydrogen release on fuel stability and safety.
- Develop engineering tools to help compare bench scale data to system level metrics.
- Develop better understanding of thermodynamics for ammonia borane and other systems through comprehensive literature review, theoretical calculations, and thermochemistry experiments.
- Develop efficient pathways for the chemical regeneration of spent fuel.

Technical Barriers

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

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

Technical Targets

Data reported in the following table are for solid ammonia borane (AB). Here, values are 'material' based, whereas, the DOE targets are on a system basis. 2010 targets for gravimetric and volumetric capacity on a system basis are 6% and 0.045 kg/L, respectively.

Temp (°C)	Weight % H ₂		Vol. Cap. (kg/L) (loose powder)	Max. Rate (gH ₂ /s/kgAB)	kgAB Required for 2010 Rate**
	2006	2007			
60 (scaffold)*	3.2	3.2	---	---	---
86.5	5.5	5.5	---	---	---
120	6.5	7	0.021	1	2
140	---	>13	0.039	1.8	1
155	---	>16	0.048	>3	0.8

*Data applicable to a 1:1 AB to silica material.

**Indicative of the amount of material required to be in a reactor to meet the H₂ release rate.

Accomplishments

- Determined mechanism for the release of the 1st equivalent of hydrogen from ammonia borane. Reaction proceeds quickly after the formation of an ionic intermediate, diammoniate of diborane (DADB).
- Demonstrated that additives with chemical functionality like DADB reduce the induction period typically observed for hydrogen release at temperatures below 140°C.
- Demonstrated that fuel can be formulated that is stable to 60°C indicating that AB will not spontaneously release hydrogen in hot climates. This temperature corresponds to the 2015 DOE target. This work showed that purity of the fuel is critical to meeting this stability metric.
- Demonstrated that spent AB fuel analogues, such as polyborazylene, can be digested using *t*-butyl alcohol. Moreover, digestion coupled with ammonia (NH₃) overpressure allows recovery of residual B-H bonds in the spent fuel as AB. Recovery of B-H allows more efficient regeneration of spent fuels.
- Performed engineering analysis to evaluate the potential of solid AB to meet 2010 and 2015 targets for volumetric capacity. Results show that pelletized or particulate fuels might meet 2010 targets, but not 2015 targets. Ultra-low void volume concepts

will be required to enable an approach to the 2015 volumetric capacity targets.



Approach

PNNL is approaching the challenge in a means consistent with the Chemical Hydrogen Storage Center of Excellence (CHSCoE) philosophy. In addition to specific scope within the tier framework, PNNL has responsibilities for theory and simulation and core science and engineering competencies within the CHSCoE. Therefore, PNNL's work within the CHSCoE is inherently multidisciplinary and highly collaborative with several of the CHSCoE partners.

Within Tier 2 (focus on B-N chemical systems), 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 also leads the engineering within the CHSCoE and its efforts in support of on-board release systems as well as off-board regeneration of fuels. This group interfaces on a regular basis with DOE's Storage System Analysis Working Group.

Results

Efforts at PNNL in FY 2007 were focused on four main areas: (i) quantification of hydrogen release, (ii) development of methods for digestion of spent fuels, (iii) fuel thermal stability, and (iv) understanding how engineered forms affect the volumetric capacity of ammonia borane.

Experimental studies involved determining the mechanism for the onset of hydrogen release. Nuclear magnetic resonance (NMR) techniques coupled with thermochemical analysis were used to confirm that DADB is the critical intermediate formed during the initial stages of release. NMR spectroscopy was used to study the mechanism of hydrogen release. The insight gained from this approach allowed the discovery of additives that could accelerate the release of hydrogen at lower temperatures. Seeding solid AB with DADB or ammonium chloride completely eliminates the induction time required to release hydrogen.

Temperature processing of AB solids at 120°C yields only 7 wt% H₂. Therefore, we have begun looking at higher temperatures to increase the degree and rate of release. Figure 1 shows the impact of increasing the temperature on hydrogen release from neat AB. As the temperature increases to 140°C and beyond, the induction period is eliminated. Moreover, raising the release temperature to 155°C results in more than

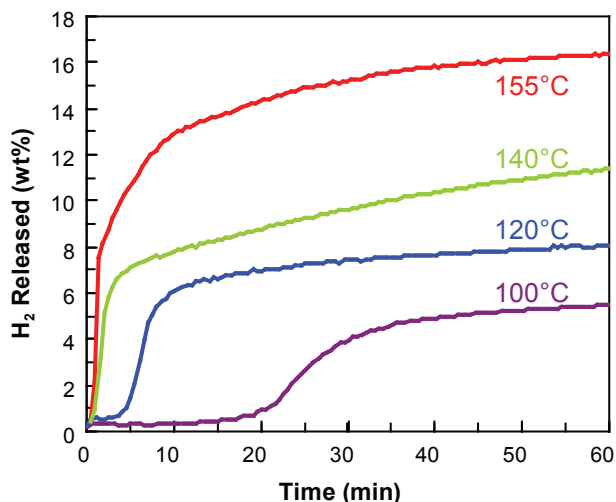


FIGURE 1. Impact of higher temperature on release of ammonia borane. Greater than 16% wt% H₂ can be achieved at 155°C.

two equivalents of hydrogen (greater than 16% H₂ by weight). The maximum release rate takes place in the first minute and is roughly 3 gm H₂/s/kgAB. Although the release continues beyond a minute, it slows considerably. The high rate observed in the first minute of reaction is sufficient to enable a small processor for on-board hydrogen release, but some of the capacity is sure to be lost when such bursts are needed. This indicates that the focus must turn to accelerating release beyond the first equivalent of hydrogen.

Another key aspect of the project is chemical regeneration. The first regeneration hurdle with solids is getting the spent fuel into a chemical form where reduction chemistry can be employed. In general, this implies that the fuel must be digested into a liquid solvent. PNNL has had some success using alcohols for digestion; in particular, *t*-butyl alcohol has been a good performer. Most spent AB fuels have residual hydrogen. It is desirable to preserve this hydrogen as B-H bonds, because doing so reduces need for energy later in the regeneration process. Figure 2 shows that *t*-butyl alcohol recovers these bonds as AB through a disproportionation reaction. Recovery is particularly good when an overpressure of ammonia is used during the digestion. By comparison, a similar approach with methanol results in digestion but no recovery of B-H. It is likely that methanol is acidic enough to allow reaction with the B-H to form H₂. The H₂ gas is then lost from the digested fuel and is not recoverable as AB.

Engineering studies are becoming more of a focus in PNNL's work as the CHSCoE matures. One aspect of these studies has been to understand the impact of working with chemicals that release hydrogen exothermically. Using an accelerated rate calorimeter at Rohm and Haas, we have shown that high purity AB fuel can remain stable for many days at 60°C. This is

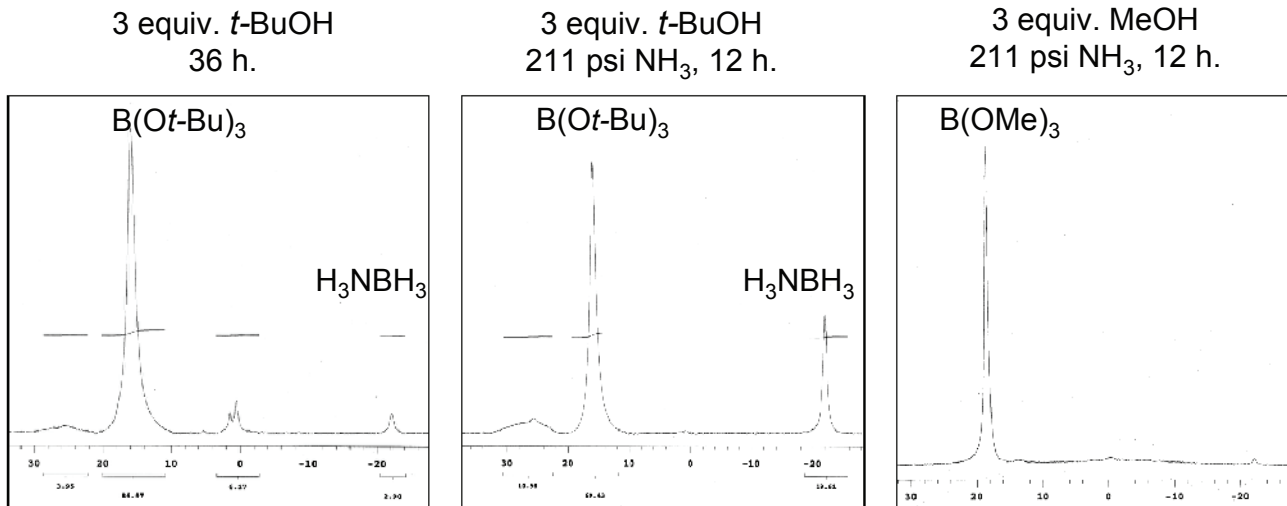


FIGURE 2. NMR spectra taken during the digestion of polyborazylene with alcohols. *t*-butyl alcohol shown to be preferable to methanol due to reduction in protonolysis. Ammonia overpressure results in dramatic improvement in B-H recovery.

key because DOE has set 2015 targets for in-tank fuel stability in terms of hydrogen losses at this temperature. As temperature is reduced to 50°C, more impurities can be tolerated.

PNNL has also been looking at the impact of morphology on the volumetric capacity of solid AB. Figure 3 shows how the void volume within the material impacts the volumetric capacity assuming two equivalents of hydrogen (13.1 wt%) release from AB. For comparison, the system targets for 2010 and 2015 are also shown. Note that closely packed spheres have a void fraction of 30%, so that is really the best case possible with pellets. With loose powders we have measured void fractions close to 60%. When volumetric capacity is considered, void fraction is effectively unused volume. The single crystal hydrogen density is just under 0.1 kgH₂/L, but for a loose powder this drops to 0.04, a significant loss. In fact, there is no chance of attaining the 2010 volumetric capacity target with loose powder. The 2010 target could be met by spheres with high packing density, but not the 2015 target. As a result of this analysis, PNNL has chosen to take two paths to increase volumetric capacity: (1) work to release more hydrogen from the fuel; and (2) work on monolithic, low voidage fuel morphologies to limit the degree of dead volume.

Conclusions and Future Directions

In sum, FY 2007 has seen the continued growth in knowledge of B-N materials. The release mechanism and the potential hydrogen content for solid forms of AB is now understood in quantitative terms. Understanding of the thermodynamics and kinetics has been improved, which is critical to pursuing system level work, where

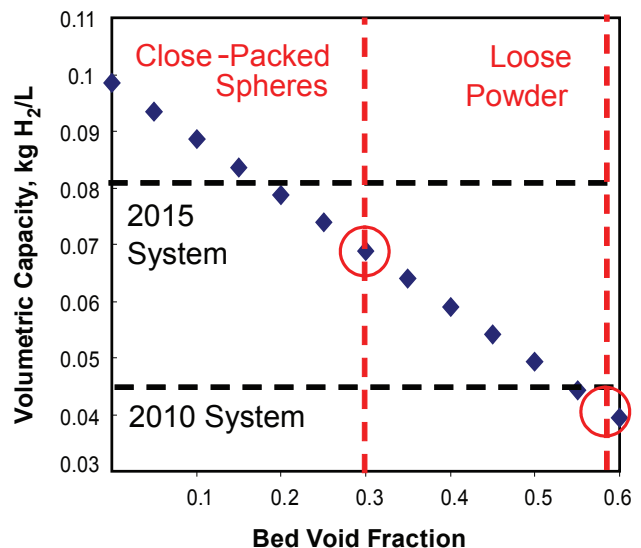


FIGURE 3. Impact of void fraction on the volumetric capacity of solid AB. Data corresponds to two equivalents of H₂ or 13.1 wt%.

heat integration and management are going to be of utmost importance. It is now believed that the key to increased rates is better understanding and acceleration of the 2nd hydrogen equivalent from AB. This will be a key focus. Regeneration will also be a key focus, where we are driving to bench demonstration of 40% efficiency with potential to meet the 60% target from DOE.

The following are indicative of the areas to be pursued in FY 2008:

- Investigate mechanism for 2nd+ equivalent of hydrogen release from AB. Use mechanistic

information to propose additives for higher release rates.

- Continue to examine fuel stability for AB formulations that have been enhanced by additives.
- Make a critical assessment of the hydrogen purity. Specifically examine released hydrogen for partial decomposition products like ammonia and diborane. Quantify whether high temperature results in excessive sublimation of AB.
- Examine digestion routes that result in destabilized B centers that will allow facile reduction. In particular, we will examine polyols, phenol, and thiols as a means to allow efficient reduction.
- Examine acid-base chemistry as a means to promote the splitting of H₂ into H⁺ and H⁻ for energy efficient hydride transfer reactions.
- Undertake engineering studies that examine the quasi-fluid state of AB and associated volumetric expansion that takes place during hydrogen release reactions. Develop methods to allow monolithic fuels and control foaming.
- Develop process concepts and flow sheets for AB regeneration.

FY 2007 Publications/Presentations

1. Camaioni and Autrey (2006), "Thermochemistry of Boron-nitrogen Hydrogen Storage Compounds," presented at the Fall 2006 ACS Meeting, San Francisco, CA.
2. Gutowski, Schenter, Li, Camaioni, Kathman, and Bachorz (2006), "Computational Studies of Materials for Chemical Hydrogen Storage," presented at the International Symposium on Metal-Hydrogen Systems, Maui, HI.
3. Gutowski, Bachorz, Kathman, Schenter, Autrey, and Linehan (2006), "Hydrogen Release from Ammonia Borane Mediated by a Nanoscaffold of Silica, presented at symposium on *Predicting Catalysis: From Ammonia Production to the Hydrogen Economy*, June 21-23, Leiden, Netherlands.
4. Heldebrant, Autrey, Linehan, Karkamkar, Stowe (2006), "Spectroscopic Investigations of Ammonium Borohydride and Diammoniate of Diborane: Evaluating the Potential of a Hydrogen Storage Material, presented at the Fall 2006 ACS Meeting, San Francisco, CA.
5. Karkamkar, Stowe, Hess, Autrey (2006), "Kinetic and Thermodynamic Investigations of Ammonia Borane on Various Mesoporous Scaffolds," presented at the Fall 2006 ACS Meeting, San Francisco, CA.
6. Rassat, Aardahl, Smith, Autrey, Karkamkar, Chin, Magee, Van Sciver, Lipiecki (2006), "Impact of Solid Ammonia Borane Fuel Formulation on an On-board Storage and Hydrogen Release System, presented at the Fall 2006 ACS Meeting, San Francisco, CA.
7. Wu, Ortega, Sun, and Rector (2006) "Optimization of a Catalyzed Reactor Utilizing Sodium Borohydride for Hydrogen Generation," presented at the Fall 2006 ACS Meeting, San Francisco, CA.
8. Shoemaker, McGowan, Thomas, Klymyshyn, Hernandez, Linehan, Gateley, Quadrel, Moon, Li, Kathman, Schenter, Gutowski (2006), "Experimental and Computational Investigations of NBH Chemical Hydrogen Storage Compounds," presented at the Fall 2006 MRS Meeting, Boston, MA.
9. Hernandez, Matus, Anderson, Dixon, Autrey, Camaioni (2007), Reliable Predictions of the Thermochemistry of Boron-nitrogen Hydrogen Storage Compounds," presented at the Energy Center Hydrogen Initiative Symposium, West Lafayette, IN.
10. Bowden, Autrey, Hess (2006), "*In situ* Raman Investigations of Hydrogen Release from Ammonia Borane," Presented at the Spring 2007 MRS meeting, San Francisco, CA.
11. Autrey, Stowe, Schmid, Shaw, Linehan (2006), "Hydrogen Release from Ammonia Borane," presented at the Spring 2007 MRS Meeting, San Francisco, CA.
12. Aardahl, Rassat, Smith, Autrey, Karkamkar, Chin, Magee, Van Sciver, Lipiecki (2006), Impact of Solid Ammonia Borane Fuel Formulation on an On-board Storage and Hydrogen Release System," presented at the Fall 2006 MRS Meeting, Boston, MA.
13. Autrey, Heldebrant, Karkamkar, Shaw, Linehan (2006), Hydrogen Release from Ammonia Borane," presented at the Fall 2006 MRS Meeting, Boston, CA.
14. Aardahl (2006), "Engineering Considerations for Solid Ammonia Borane Fuels," presented to the Hydrogen Storage System Analysis Working Group. Washington, DC.
15. Aardahl (2007), "The DOE Center of Excellence for Chemical Hydrogen Storage," presented at the IEA Task 22 Meeting, Monterey, CA.
16. Autrey (2007), "Release of Hydrogen from Ammonia Boranes," presented at the IEA Task 22 Meeting, Monterey, CA.