

IV.B.1c Chemical Hydrogen Storage Research at PNNL

Chris Aardahl (Primary Contact), Tom Autrey, Don Camaioni, Dan Dubois, John Linehan, Abhi Karkamkar, Scot Rassat, Richard Zheng, Wendy Shaw, Jun Li, Dave Heldebrant, Robert Potter, Mike Mock, Avery Luedtke, Tricia Smurthwaite

Pacific Northwest National Laboratory (PNNL)
Box 999 Mail Stop P7-07
Richland, WA 99352
Phone: (509) 376-2529; Fax: (509) 376-5021;
E-mail: christopher.aardahl@pnl.gov

DOE Technology Development Manager:
Grace Ordaz

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

Start Date: March 1, 2005

Projected End Date: September 30, 2010

Objectives

- Quantify hydrogen release from solid ammonia borane (AB) and its derivatives and characterize mechanistic pathways.
- Employ release mechanism to understand how catalysts and additives can impact rates.
- 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 (3.3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight & Volume
- (B) System Cost
- (D) Durability
- (E) Charging/Discharging Rates
- (C) Efficiency

(J) Thermal Management

(R) Regeneration Processes

Technical Targets

The two tables below present current status as of July 2008. Table 1 provides release data for AB at various temperatures on the basis of 1 kg of material that is reacting to provide hydrogen. The release rate is a function of the number of equivalents of hydrogen released (1 equivalent ~6.5 wt%). Notice that the first equivalent of hydrogen from AB is evolved quickly, but as more hydrogen is extracted from AB, the rate slows dramatically. Higher temperature can be used to increase kinetics, but only to a limited degree. Table 2 shows release data for the AB derivatives developed in Fiscal Year 2008. These data generally indicate that capacity can be sacrificed in lieu of higher kinetics. The kinetics for Li-AB and ABH₂ are particularly fast.

TABLE 1. Release Characteristics for AB as a Function of Temperature

	1 eq H ₂	1.5 eq H ₂	2 eq H ₂	2.5 eq H ₂	Peak rate
160°C	50 sec (1.3 g/s)	80 sec (1.2 g/s)	240 sec (.54 g/s)	1,000 sec (.16 g/s)	3.8 g/s
145°C	70 sec (.93 g/s)	200 sec (.5 g/s)	1200 sec (.11 g/s)	----	2.1 g/s
130°C	150sec (.43 g/s)	1,000 sec (.1 g/s)	----	----	1.1 g/s

TABLE 2. Release Characteristics for AB Derivatives

	Wt%	Temp (°C)	2 Eq. Avg. Rate (130°C; g/s/kg)
Li-AB	11.2	<100	2.9
ABH ₂	12.2 - 21.4	40 - 130	VERY FAST
DADB	12	90 - 130	0.13

Accomplishments

- Developed Li-AB under International Partnership for the Hydrogen Economy (IPHE) collaboration; H₂ release kinetics increased by order of magnitude.
- Discovered additives that suppress foaming of AB, which enables pursuit of engineered systems based on solid materials.
- Demonstrated hydride transfer chemistry from 'activated' H₂ to spent fuel: confirms theory results from 2007.

- Theoretical calculations now point to energy efficient regeneration approach with non-platinum group metal reduction pathway resulting in reduced fuel cycle costs.
- Preliminary flow sheets for regeneration enabled identification of process knowledge gaps.



Approach

PNNL's approach is consistent with the philosophy of the Chemical Hydrogen Storage Center of Excellence (CHSCoE). In addition to unique scope, 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.

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 materials handling issues associated with solid fuels. PNNL also leads the engineering activities within the CHSCoE, which are now targeted toward 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 2008 were focused on three main areas: (i) increasing kinetics of hydrogen release, (ii) development of regeneration chemistry for spent AB fuels, and (iii) development of anti-foaming additives for AB fuel formulations.

Hydrogen release activities focused on increasing kinetics and controlling the morphology of materials. AB is a promising material due to its high gravimetric and volumetric capacity, but the release kinetics are slow and the material tends to foam during release. Foaming of materials limits the ability to engineer a solids handling system, which was a significant concern for solid AB. We started a study to investigate antifoaming additives at the outset of FY 2008. We found an additive that when added at 5-10% by mass can suppress foaming and enable morphological stability during release. Figure 1 shows three wafers. On the left is unreacted AB solid fuel. Addition of the additive allowed the wafer to retain its shape during hydrogen release, while the neat material foamed and eventually crumbled. This is a significant result; in that, pellets or monolithic fuels can now be formulated that can be handled in an engineered system.

In FY 2007, PNNL examined increased temperature as a means to increase release rate of hydrogen from solid AB, but results fell short of what is needed to

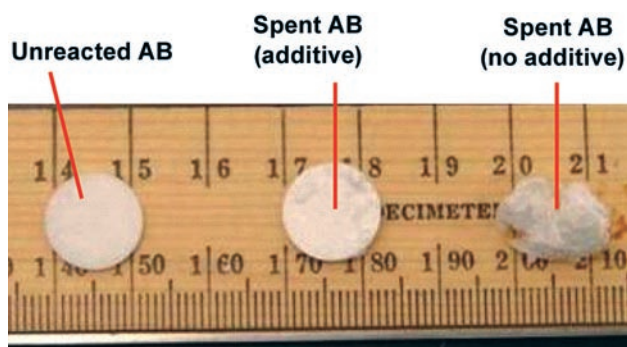


FIGURE 1. Impact of Additive on the Foaming Behavior of AB

meet the 2010 DOE targets. Catalysis is difficult in solid phase reactions because it is virtually impossible to have all the material access a catalytic site. We have previously shown that additives mixed into AB powders can accelerate release. We probed the mechanism further, which indicated that subtle changes in the degree of protonic and hydridic hydrogens in the material can impact rates.

To manipulate the protonic and hydridic nature of the material, we started looking at metal substitution for hydrogen on the N-atom in AB. Through an international partnership (IPHE), Li-AB and other variants were synthesized and tested. The results are shown in Figure 2 where release of hydrogen from AB is compared to Li-AB. Hydrogen mass spectrometry (MS-H₂) was used to measure hydrogen release from the material. The middle trace in Figure 2 shows that hydrogen comes off at a lower temperature (92 vs. 108°C). Moreover, 2 equivalents of hydrogen come off the material at low temperature with fast kinetics (sharp peak shape). This is a marked improvement over

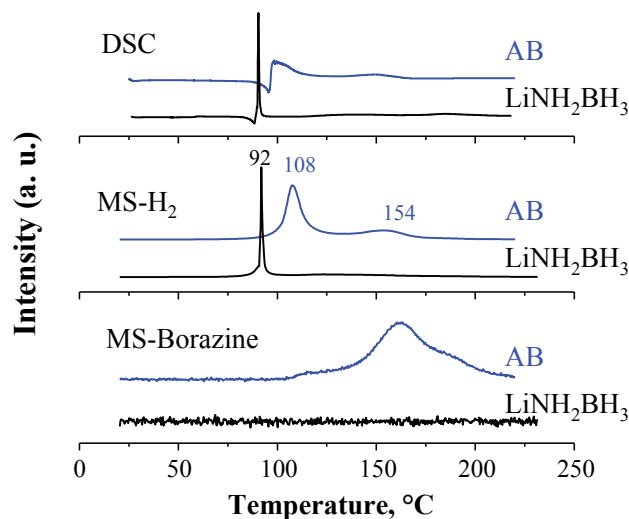


FIGURE 2. Release Data Collected for Li-AB Demonstrating Increased Release Rate and Hydrogen Purity

the release characteristics for AB. The bottom trace in Figure 2 shows the borazine impurity in the hydrogen gas. The chemical structure of Li-AB, does not allow volatile byproducts, which is another benefit of this system.

Another key aspect of the PNNL 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 the fuel must be digested into a liquid solvent. In FY 2007 and early FY 2008 we showed that alcohols are suitable for this purpose. Throughout FY 2008 we have been looking at reduction chemistry to put hydrogen back into the spent material. This effectively involves making B-H bonds from the digestion product (B-O-X bonds). Theoretical arguments pointed to organometallic Rh hydrides as suitable hydrogen donors to these chemical systems. Experimental work in FY 2008 has now shown that hydride transfer does take place as expected, but that the full regeneration cycle cannot be completed. To better understand this, we have been using theory to better understand the matching required between the digestion agent and the reducing agent within the cycle. Figure 3 shows a cartoon of the desired features for each of the steps. It is critical that the hydride transfer hydrogen (requirement 1), but it is also critical that H^+ leaves as ROH during the hydrogen activation step (requirement 2). With the Rh system, requirement 1 was satisfied, but requirement 2 was not. Theory has been instrumental in setting a more promising direction that is under experimental investigation at the time of this report. Figure 4 shows how the hydricity of the donor and the acidity of the digestion agent need to be matched to enable the complete cycle. In the top figure, the reducing agent must be to the left of the digestion product in order to

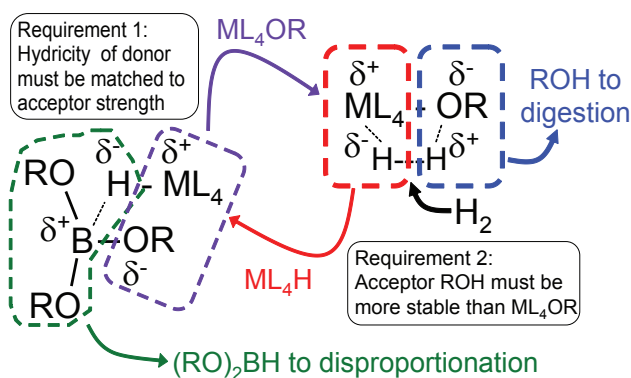


FIGURE 3. Pictorial of Regeneration Pathway being Developed at PNNL

transfer hydrogen to the boron center. In the bottom figure, the alcohol used for digestion must be to the left of the hydrided donor moiety. In other words the alcohol must be more stable than the complex formed when H_2 reacts with the metal center. This will allow hydrogen to be split into H^+ (to the alcohol) and H^- (to the hydride donor). It is readily seen from Figure 4 that Rh cannot satisfy all the criteria. It is also seen that Co complexes appear to satisfy these criteria simultaneously, and that is now the direction of the experimental project.

Conclusions and Future Directions

In sum, FY 2008 has resulted in the continued growth in knowledge of B-N materials. We now understand that hydrogen release rate can be increased substantially in solid systems. We also have a formulation that will allow development of solids handling architectures. We have hands-on experience using hydrogen activation as a regeneration step,

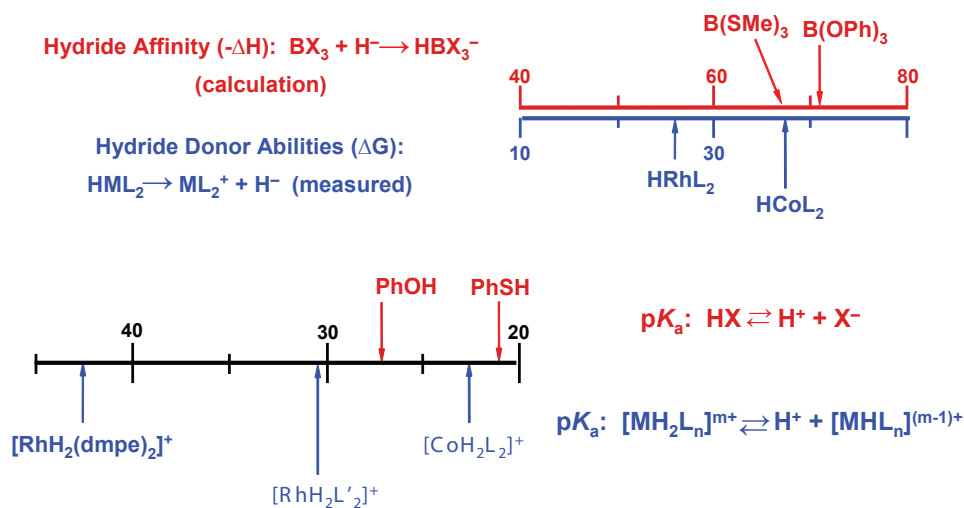


FIGURE 4. Energy Diagrams Pertaining to the Suitable Matching of Digestion and Reduction in Regeneration Strategies

and theory is guiding us to improved organo-metallic hydride systems. New materials based on AB and its derivatives will continue to be our focus on the release portion of the project. Regeneration is the key for all these chemistries, where we are driving to bench demonstration of 40% efficiency with potential to meet the 60% target from DOE. The following bulleted list is indicative of the areas we will pursue in FY 2008:

- New materials based on AB-metal hydrides such as MgH_2 .
- Materials synthesis based on ABH_2 to explore higher capacity materials.
- Explore the limitations (mass, heat transfer, kinetics) of monolithic fuels.
- Thoroughly explore cobalt hydrides as a means to match digestion and reduction in regeneration schemes.
- Continue to develop process concepts and flow sheets for AB regeneration and fill technology gaps in the area of separations.

FY 2008 Publications/Presentations

1. Karkamkar AJ, CL Aardahl, and T Autrey. 2007. "Recent Developments on Hydrogen Release from Ammonia Borane." *Material Matters* 2(2):6-9.
2. Matus MH, K Anderson, DM Camaioni, T Autrey, and DA Dixon. 2007. "Reliable Predictions of the Thermochemistry of Boron-Nitrogen Hydrogen Storage Compounds: $B_xN_xH_y$, $x=2,3$." *Journal of Physical Chemistry A* 111(20):4411-4421.
3. Xiong Z, CK Yong, G Wu, P Chen, WJ Shaw, AJ Karkamkar, T Autrey, MO Jones, S Johnson, P Edwards, and B David. 2008. "High-capacity Hydrogen Storage in Lithium and Sodium Amidoboranes." *Nature Materials* 7(2):138-141.
4. Sepehri S, AM Feaver, WJ Shaw, CJ Howard, Q Zhang, T Autrey, and G Cao. 2007. "Spectroscopic Studies of Dehydrogenation of Ammonia Borane in Carbon Cryogel." *Journal of Physical Chemistry B* 111(51):14285-14289.
5. Karkamkar AJ and T Autrey. 2008. "On-Board Hydrogen Storage Breakthroughs and Barriers: A Tutorial."
6. Bowden M, T Autrey, I Brown, and M Ryan. 2008. "The Thermal Decomposition of Ammonia Borane: A Potential Hydrogen Storage Material." *Current Applied Phys.* 8:498.
7. Feaver A, S Saghar, P Shamberger, A Stowe, T Autrey, and G Cao. 2007. "Coherent Carbon Cryogel-Ammonia Borane Nanocomposites for H_2 Storage." *J. Phys. Chem. B* 111:7469.
8. Stowe, AC, WJ Shaw, JC Linehan, B Schmid, and T Autrey. 2007. "Reliable Predictions of the Thermochemistry of Boron-Nitrogen Hydrogen Storage Compounds: $B_xN_xH_y$, $x = 2$." *J. Phys. Chem. A* 111:4411.
9. Karkamkar AJ, AC Stowe, NJ Hess, and T Autrey. 2007. "Kinetic and Thermodynamic Investigations of Ammonia borane on Various Mesoporous scaffolds." Presented by Abhijeet J Karkamkar at Gordon Research Conference, Waterville, ME on July 10, 2007.
10. Rassat SD, T Autrey, DM Camaioni, and CL Aardahl. 2007. "Amine Boranes for Chemical Hydrogen Storage." Presented by Scot D. Rassat at MS&T - Fall 2007, Detroit, MI on September 20, 2007.
11. Karkamkar AJ. 2007. "Experimental Studies of Ammonia Borane for Hydrogen Storage." Presented by Abhijeet Karkamkar at Washington State University - Pullman, Pullman, WA on December 13, 2007.
12. Aardahl CL, S Linehan, FJ Lipiecki, A Chin, L Klawiter, SD Rassat, F Zheng, T Semmlsberger, and O Moreno. 2008. "Engineering Developments within the Chemical Storage COE: On-board & Off-board Issues." Presented by Chris Aardahl at Freedom CAR Hydrogen Storage Tech Team Review, Detroit, MI on January 17, 2008.
13. Camaioni DM, DL DuBois, DJ Heldebrant, JC Linehan, AJ Karkamkar, MT Mock, RG Potter, T Autrey, CL Aardahl, and FH Stephens. 2008. "Pacific Northwest National Laboratory Ammonia Borane Regeneration Overview." Presented by Frances Stephens at Chemical Hydrogen Storage Technical Team Review, Detroit, MI on January 17, 2008.
14. Heldebrant DJ, JC Linehan, DM Camaioni, SD Rassat, F Zheng, and T Autrey. 2007. "Effect of Additives on the Thermolysis of Ammonia Borane." In *234th American Chemical Society Conference Proceedings*.
15. Camaioni DM, DJ Heldebrant, JC Linehan, WJ Shaw, J Li, DL DuBois, and T Autrey. 2007. "Towards Regeneration of Ammonia Borane from Spent Fuel." In *234th American Chemical Society Conference Proceedings*.
16. Ott K, CL Aardahl, and F Lipiecki. 2008. *Milestone Report: 2Q FY08 Downselect of Chemical Hydrogen Storage Materials, Catalysts, and Spent Fuel Regeneration Processes*.
17. Rassat SD, F Zheng, DD Caldwell, JL Daschbach, DJ Heldebrant, S Berds, WJ Shaw, JC Linehan, DM Camaioni, and T Autrey. 2007. "Volumetric Approaches to Study Release of Hydrogen from Chemical Hydrogen Stores." Abstract submitted to 2007 MRS Fall Meeting, Boston, MA.
18. Autrey T. & D. Camaioni. 2007. "Solid State Chemical Hydrogen Storage." Presentation at Material Innovations in an Emerging Hydrogen Economy, Cocoa Beach, FL.
19. Autrey T. 2007. "Solid State Chemical Hydrogen Storage in NH_xBH_x Materials." Presentation at Materials Research Society Meeting, San Francisco, CA.
20. Bowden ME, NJ Hess, WJ Shaw, DJ Heldebrant, SD Rassat, T Autrey, T Kemmitt, and I Brown. 2007. "Initiation of Hydrogen Release from Ammonia Borane." Presented by Mark Bowden at International Symposium on Materials Issues in a Hydrogen Economy, Richmond, VA on November 14, 2007.
21. Camaioni DM, F Zheng, and CL Aardahl. 2007. "Pacific Northwest National Laboratory Ammonia Borane

Regeneration Overview” Presented by Chris Aardahl
at Storage System Analysis Working Group Meeting,
Washington, D.C. on December 4, 2007.