

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

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Projected End Date: September 30, 2010

Objectives

- Develop materials and methods for low temperature (<85°C) release of pure hydrogen (99.99%) from chemical hydrides that can achieve DOE targets (>90g H₂/kg and >70g H₂/l):
 - Focus on quantitative measurements of impurities in H₂.
- Develop high efficiency methods for large scale synthesis of chemical hydrogen storage materials:
 - Fabricate reactor to prepare bench scale quantities of ammonia borane (AB).
- Develop high efficiency off-board methods for chemical hydride regeneration to achieve DOE targets (60%):
 - Coordinate with Argonne National Laboratory to do preliminary efficiency analysis of regen process.
- Support collaborators through expertise in chemistry and characterization to determine the kinetics and thermodynamics of hydrogen release and regeneration of H-storage materials:
 - Work with Center partners to characterize materials and novel approaches to store and release hydrogen.

Technical Barriers

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

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (R) Regeneration Processes
- (S) By-Product/Spent Material Removal

Technical Targets

Scheme 1 represents the focus of materials (ammonium borohydride, AB, diammoniate of diborane, lithium amidoborane and sodium amidoborane) currently under study and provides both the gravimetric and volumetric density of hydrogen. Table 1 presents a summary of the rates of hydrogen release, enthalpies of hydrogen release and impurities measured for various materials, temperatures and reaction conditions.

Solid phase chemical hydrogen storage materials studied

$\text{NH}_4\text{BH}_4 \rightleftharpoons \text{BNH}_x + \text{H}_2$	(240 g H ₂ /kg, 130 g H ₂ /l)
$\text{NH}_3\text{BH}_3 \rightleftharpoons \text{BNH}_x + \text{H}_2$	(195 g H ₂ /kg, 140 g H ₂ /l)
$[\text{NH}_3\text{BH}_2\text{NH}_3][\text{BH}_4] \rightleftharpoons \text{BNH}_x + \text{H}_2$	(195 g H ₂ /kg, 140 g H ₂ /l)
$\text{LiNH}_2\text{BH}_3 \rightleftharpoons \text{LiBNH}_x + \text{H}_2$	(109 g H ₂ /kg, 52 g H ₂ /l)
$\text{NaNH}_2\text{BH}_3 \rightleftharpoons \text{NaBNH}_x + \text{H}_2$	(76 g H ₂ /kg, 43 g H ₂ /l)

SCHEME 1. Materials currently under study and their gravimetric and volumetric density of hydrogen.



Accomplishments

- Scaled up AB synthesis (one-pot >95% yield, >99% purity).
- Determined stability of solution phase AB (to compare with solids).
- Quantified impurities in H₂ from AB and initiated approaches to mitigate and control.
- Optimized anti-foaming agents to retain solid state AB fuel morphology.
- Expanded studies of M-NH₂-BH₃: mechanisms of H₂ release, rates, stability studies, impurities

TABLE 1. Summary of the rates of hydrogen release, enthalpies of hydrogen release and impurities measured for various materials, temperatures and reaction conditions.

Compound	Gravimetric	Volumetric	Additive	Enthalpy	Peak Rate	Temperature	NH ₃	Bz	Notes
	g H ₂ /kg	g H ₂ /l		kJ/mol	g/s/kg	C	ppm	wt%	
NH ₃ BH ₃	194 (160)	146 (120)	none	-23	3.8	160	100-200	4-6	foams
NH ₃ BH ₃	"	"	none	-23	2.1	145	100-200	4-6	foams
NH ₃ BH ₃	"	"	none	-23	1.1	130	100-200	4-6	foams
NH ₃ BH ₃ + AF	155 (136)	117 (102)	anti foaming	-23	1.1	130	?	?	no foam
AB:MCM	"	"	scaffold (1:1)	-1 (-22)	2.8	130	100-200	<1	no foam
AB:MCM	"	"	scaffold (2:1)	-10	?	130	100-200	<1	no foam
AB:MCM	"	"	scaffold (3:1)	-12	1.9	130	100-200	<1	no foam
DADB	194 (160)	?	none	-16	1.8	145	?	?	little foam
DADB	"		none	-16	0.48	130	?	?	little foam
DADB	"		none	-16	0.2	100	?	?	little foam
NH ₄ BH ₄	240	130	none	-63	?	40	?	?	little foam
LiNH ₂ BH ₃	109	52	none	?	1.76	130	200	0	no foam
LiNH ₂ BH ₃	"	"	none	?	0.44	100	2,000	0	no foam
LiNH ₂ BH ₃	"	"	none	-2	0.08	90	2,000	0	no foam
LiNH ₂ BH ₃	"	"	none		0.01	80	2,000	0	no foam
NaNH ₂ BH ₃	76	43	none	?	0.044	80	?	0	no foam
NaMeNHBH ₃	30	?	none	?	0.043	100	?	0	no foam

Summary of rates, enthalpies and purity of hydrogen. theoretical density (measured density). Bz = borazine. ? = not yet measured, will be determined in future work. enthalpy in scaffold depends on isothermal or ramp heating

(International Partnership for the Hydrogen Economy [IPHE] collaboration).

- Developed approach to stabilize ammonium borohydride (NH₄BH₄) at room temperature.
- Demonstrated hydride transfer chemistry from 'activated' H₂ to digested fuels using non-precious metal reagents.

Approach

PNNL's approach is consistent with the philosophy Chemical Hydrogen Storage Center of Excellence. *A comprehensive understanding will enable the development of rational approaches to enhance rates of release, increase purity of hydrogen, and provide energy efficient regeneration schemes.* In addition to a focus on solid state chemical hydrogen storage, PNNL has responsibilities for theory and simulation and core science and engineering competencies within the Center. Therefore, PNNL's work within the Center is inherently multidisciplinary and highly collaborative with several of the Center partners.

PNNL has many activities including examination of mechanisms of hydrogen release from solid ABs, experimental work on the regeneration of spent ABs,

and addressing the materials handling issues associated with solid fuels. PNNL also leads the engineering activities within the Center, 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 Fiscal Year 2009 were focused on six major tasks: (i) scale up 'first-fill' synthesis of AB, (ii) stabilizing fuels, AB for regeneration and ammonium borohydride for first fill, (iii), quantifying the concentration of impurities, NH₃ and borazine in the hydrogen released from AB, (iv) optimization of anti-foaming additives for AB fuel formulations, (v) developed mechanistic understanding of hydrogen release from IPHE materials, metal amidoboranes and (vi) expanding the database of materials to enhance understanding of hydride affinity of borate esters and donors ability of metal hydrides for regeneration chemistry.

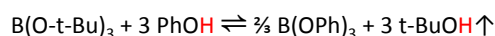
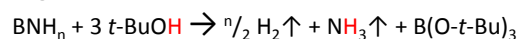
- First-Fill – PNNL designed and fabricated a bench scale reactor to prepare AB from sodium borohydride and an ammonium salt in a single pot to provide high yields (95-99%) and high purity (>99%) AB. The design concepts and materials

properties were shared with Center partner Rohm and Haas to provide an economic analysis to compare with procedures currently used to synthesis AB for first fill applications.

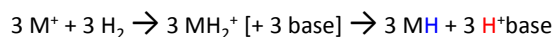
- **Stabilizing Fuels** – (a) ammonium borohydride was shown to be stable at room temperature in liquid ammonia. Little work has been previously performed on this unique borohydride in the last 50 years due to the lack of stability at room temperature. (b) AB decomposes by a second order reaction mechanism in solution. It is critical for regen to develop a stabilizer additive or protect the borane with a tertiary amine. AB can thus be recovered by a trans ammonization step (see results on regeneration).
- **Hydrogen Purity from AB** – Last year we demonstrated that ca. 16.5 wt% of the hydrogen is released from AB at temperature <150°C. Analysis of the hydrogen gas suggested that two impurities, ammonia and borazine are formed in the decomposition reaction. Subsequent work was performed to quantify the impurities in the H₂ gas stream. Ammonia is formed at levels of ca. 200 ppm when >15 wt% hydrogen is released. The yield of borazine is independent of heating rate and is formed in ca. 4±2% when >15 wt% hydrogen is released from AB. By keeping temperatures below 150°C the borazine yield can be significantly reduced.
- **Anti-Foaming Agents** – Methyl cellulose at 15 wt% prevents foaming of solid pellet fuel forms. This is a significant result; in that, pellets or monolithic fuels can now be formulated that can be handled in an engineered system.
- **IPHE Materials** – Metal amido boranes have been shown to decompose to release hydrogen by a different mechanism than AB hydrogen release. There is no induction period and steep temperature dependence.
- **Regeneration** – 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. Since then PNNL has 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-OR bonds). Methods using hydrides of sodium or aluminum are known. However, the cost of regenerating these hydrides makes their use prohibitive. Therefore, PNNL has been investigating approaches using transition metal hydrides. Studies began with one of the strongest transition metal hydride donors available: bis(dimethylphosphinoethane)rhodium hydride

[HRh(dmpe)₂]. Theoretical analysis showed that B(OPh)₃ has sufficient hydride affinity to react and indeed PNNL found that HRh(dmpe)₂ does transfer H⁻ to B(OPh)₃. A process then was envisioned as shown in Scheme 2; where R is an alcohol such as *tert.*-butanol; PhOH is phenol; M is a transition metal complex. Through FY 2009 PNNL developed process flow sheets, performed proof-concept experiments, and worked to advanced understanding of factors that affect reactivity and efficiency in the process steps. PNNL has found precedent for and demonstrated all the steps individually. The remaining challenge is to develop a transition metal complex with suitable properties such that the steps can be integrated into a process. Ideally, the acidity of the MH₂ complex should be similar to the acidity of phenol and the H⁻ donor abilities of MH should be matched to the H⁻ accepting abilities of B(OPh)₃. The properties of the HRh(dmpe)₂ are not optimal in this regard. For example, the deprotonation of H₂Rh(dmpe)₂⁺ requires base that is much stronger than PhO⁻ and HRh(dmpe)₂ is a stronger H⁻ donor than is needed to reduce B(OPh)₃. Structure-reactivity trends for known transition metal complexes pointed to cobalt complexes. PNNL synthesized complexes with dmpe and other bis phosphine ligands and explored their properties and reactivities. The results show that HCo(dmpe)₂ is not strong enough of a hydride donor to transfer a hydride to B(OPh)₃. However, it readily transfers H⁻ to B(OC₆F₅)₃, which has greater H⁻ affinity compared to B(OPh)₃. Also, it transfers H⁻ to B(SPh)₃ which has an intermediate hydride affinity. On the basis of these observations and recent theoretical analyses, PNNL is examining the use of chlorophenols in place of phenol in the above process with complexes of Co.

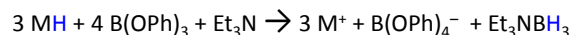
1) Digestion



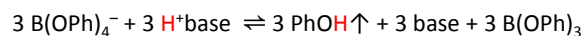
2) Transition Metal Hydride Formation



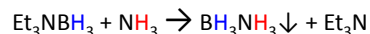
3) Hydride Transfer/Ligand Redistribution



4) Recycle

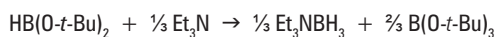
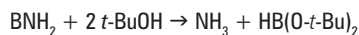


5) Ammoniation



SCHEME 2. Process Using Transition Metals Catalysts to Regenerate Spent AB Fuel

Argonne National Laboratory performed an energy and efficiency analysis of the above process. Their preliminary analysis estimated a well-to-tank efficiency of 25-47%. Scenarios leading to higher efficiencies assumed hydridic H in spent fuel may be recovered as a BH₃ adduct by the following reaction sequence:



Work is in progress to evaluate the efficiency of for recovering hydridic H in spent ammonia borane fuels which have released greater than 2 equivalents of H₂.

Conclusions and Future Directions

In sum, FY 2009 has resulted in the continued growth in knowledge of B-N materials. We can prepare large-scale quantities of AB of sufficient purity to meet DOE stability targets. We demonstrated for the first time that ammonium borohydride can be stabilized at room temperature in ammonia solvents. This enhance stability is key to first fill engineering requirements and provides initial insight into stabilizing ammonium borohydride for storage applications. We demonstrated that concentrated solutions of AB are not stable due to the second order decomposition pathways. These insights lead to alternative approaches to stabilize boranes in the regeneration process. Additives such as methyl cellulose can prevent foaming of AB during the hydrogen release and preserve fuel form factors – critical for transferring solid fuel forms in a reactor. PNNL, in collaboration with University of California, Davis, has quantified impurities, i.e. ammonia and borazine, in the hydrogen released from solid phase AB. The work shows that borazine concentrations are not dependent on heating rate but are dependent on final temperature used to release hydrogen from solid AB. IPHE collaborations continue to provide insight into the hydrogen release properties of metal amido boranes, e.g., LiNH₂BH₃. Mechanistic studies show that decomposition has steep temperature dependence – a valuable property for stability at 60°C and high release rates at 85°C. Also, they yield of ammonia varies dependent on reaction conditions. In AB regeneration work we have demonstrated that we can activate hydrogen at ambient temperature and pressure with transition metal hydrides. Judicious matching of the metal, the base and the borate ester will lead to optimized energy efficiency.

Future Work

- Economic analysis of first-fill AB to compare to conventional methods. Optimize a continuous process from lessons learned in batch reactor.

- Mechanistic studies of ammonia and borazine formation from AB decomposition to develop rational approach to mitigate impurities in hydrogen.
- Develop additives that reduce foaming as well as increase kinetics and decrease volatile impurities.
- Mechanistic studies of ammonia formation from IPHE materials to develop procedures to maximize hydrogen purity.
- Examine Ni and Fe metals as Hydride transfer agents in regeneration.
- Provide the Hydrogen Storage Engineering Center of Excellence with property information on solid chemical hydride species that show promise to meet optimal DOE targets.

2009 Publications

- Christopher L Aardahl, Scot D Rassat. Overview of Systems Considerations for On-Board Chemical Hydrogen Storage. *Int. J. Hydrogen Energy*. 2009, accepted.
- Doinita Neiner, Abhijeet Karkamkar, John C. Linehan, Bruce Arey, Tom Autrey, and Susan M. Kauzlarich Promotion of Hydrogen Release from Ammonia Borane with Mechanically Activated Hexagonal Boron Nitride *J. Phys Chem. C*. 2009, 113, 1098.
- Brandon Dietrich, Karen Goldberg, D. Michael Heinekey, Tom Autrey, John Linehan. Iridium-Catalyzed Dehydrogenation of Substituted Amine Boranes: Kinetics, Thermodynamics, and Implications for H₂ Storage. *Inorg. Chem*, 2008.
- Zhitao Xiong, Yong Shen Chua, Guotao Wu, Weiliang Xu, Ping Chen, Wendy Shaw, Abhi Karkamkar, John Linehan, Tricia Smurthwaite, and Thomas Autrey. Interaction of Lithium Hydride and Ammonia Borane in THF. *Chem. Comm.* 2008, DOI: 10.1039/b812576g.
- Wendy Shaw, John Linehan, Nathaniel Szymczak, David Heldebrant, Clem Yonker, Donald M. Camaioni, R. Tom Baker, Tom Autrey. In Situ Multinuclear NMR Studies of the Thermal Decomposition of Ammonia Borane in Solution. *Angew. Chem. Int. Ed.* 2008, 47, 7493.
- Feng Zheng, Scot D. Rassat, David J. Heldebrant, Dustin D. Caldwell, Christopher L. Aardahl, Tom Autrey, John C. Linehan, and Kenneth G. Rappé, Automated gas burette system for evolved hydrogen measurements. *Review Scientific Instruments* 2008, 79, 084103.
- David Heldebrant, Abhi Karkamkar, Nancy Hess, Mark Bowden, Scot Rassat, Feng Zheng, Kenneth Rappe, Tom Autrey. The Effects of Chemical Additives on the Induction Phase in Solid-State Thermal Decomposition of Ammonia Borane. *Chem. Materials*. 2008, 20, 5332.
- Zhitao Xiong, Chaw Keong Yong, Guotao Wu, Ping Chen, Wendy Shaw, Abhi Karkamkar, Tom Autrey, Martin Jones, Simon Johnson, Peter Edwards, William David. High Capacity Hydrogen Storage in Lithium and Sodium Amidoboranes. *Nature Materials*, 2008, 7, 138.

9. Mark Bowden, Tom Autrey, Ian Brown, Martin Ryan. The thermal decomposition of ammonia borane: A potential hydrogen storage material. *Current Applied Phys.* 2008, 8, 498.

2009 Presentations

1. ST Autrey Workshop on Clean Energy Technology, Tiayuan, China (Sept 2008).
2. ST Autrey LANL-NEDO-AIST Meeting on H2 Research, San Diego, CA (Sept 2008).
3. CL Aardahl LANL-NEDO-AIST Meeting on H2 Research, San Diego, CA (Sept 2008).
4. DJ Heldebrant Chem Department Colloquium, Queens College, Canada (Oct 2008).

5. ST Autrey Materials Science Dept Colloquium, Seattle, WA (Oct 2008).
6. WJ Shaw Materials Science Institute Workshop, Gleneden Beach, OR (Dec 2008).
7. CL Aardahl TMS2009 Meeting, San Francisco, CA (February 2009).
8. AJ Karkamkar APS 2009 Annual Meeting, Pittsburgh, PA (March 2009).
9. D Neiner ACS National Meeting, Salt Lake City, UT (March 2009).