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

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Objectives

- Develop materials and methods for low temperature (<85°C) release of pure hydrogen (99.99%) from chemical hydrides that can achieve DOE targets (>90 g H₂/kg and >70 g 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.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction</th>
<th>Gravimetric Density</th>
<th>Volumetric Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄BH₄</td>
<td>NH₄⁺ + H₂</td>
<td>240 g H₂/kg</td>
<td>130 g H₂/l</td>
</tr>
<tr>
<td>NH₂BH₃</td>
<td>NH₂⁺ + H₂</td>
<td>195 g H₂/kg</td>
<td>140 g H₂/l</td>
</tr>
<tr>
<td>[NH₂BH₄][BH₄]</td>
<td>[NH₂⁺][BH₄⁻]</td>
<td>195 g H₂/kg</td>
<td>140 g H₂/l</td>
</tr>
<tr>
<td>LiNH₂BH₃</td>
<td>Li⁺ + H₂</td>
<td>109 g H₂/kg</td>
<td>52 g H₂/l</td>
</tr>
<tr>
<td>NaNH₂BH₃</td>
<td>NaN⁺ + H₂</td>
<td>76 g H₂/kg</td>
<td>43 g H₂/l</td>
</tr>
</tbody>
</table>

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
Developed approach to stabilize ammonium borohydride (NH$_4$BH$_4$) at room temperature.

Demonstrated hydride transfer chemistry from ‘activated’ H$_2$ 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, NH$_3$ 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Gravimetric</th>
<th>Volumetric</th>
<th>Additive</th>
<th>Enthalpy</th>
<th>Peak Rate</th>
<th>Temperature</th>
<th>NH$_3$</th>
<th>Bz</th>
<th>Notes</th>
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<tbody>
<tr>
<td>NH$_4$BH$_4$</td>
<td>194 (160)</td>
<td>146 (120)</td>
<td>none</td>
<td>-23</td>
<td>3.8</td>
<td>160</td>
<td>100-200</td>
<td>4-6</td>
<td>foams</td>
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<tr>
<td>NH$_4$BH$_4$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>none</td>
<td>-23</td>
<td>2.1</td>
<td>145</td>
<td>100-200</td>
<td>4-6</td>
<td>foams</td>
</tr>
<tr>
<td>NH$_4$BH$_4$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>none</td>
<td>-23</td>
<td>1.1</td>
<td>130</td>
<td>100-200</td>
<td>4-6</td>
<td>foams</td>
</tr>
<tr>
<td>NH$_4$BH$_4$ + AF</td>
<td>155 (136)</td>
<td>117 (102)</td>
<td>anti foaming</td>
<td>-23</td>
<td>1.1</td>
<td>130</td>
<td>?</td>
<td>? no foam</td>
<td></td>
</tr>
<tr>
<td>AB:MCM</td>
<td>&quot;</td>
<td>scaffold (1:1)</td>
<td>-1 (-22)</td>
<td>2.8</td>
<td>130</td>
<td>100-200</td>
<td>&lt;1</td>
<td>no foam</td>
<td></td>
</tr>
<tr>
<td>AB:MCM</td>
<td>&quot;</td>
<td>scaffold (2:1)</td>
<td>-10</td>
<td>?</td>
<td>130</td>
<td>100-200</td>
<td>&lt;1</td>
<td>no foam</td>
<td></td>
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<tr>
<td>AB:MCM</td>
<td>&quot;</td>
<td>scaffold (3:1)</td>
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<td>1.9</td>
<td>130</td>
<td>100-200</td>
<td>&lt;1</td>
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<tr>
<td>DADB</td>
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<td>?</td>
<td>none</td>
<td>-16</td>
<td>1.8</td>
<td>145</td>
<td>?</td>
<td>? little foam</td>
<td></td>
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<td>&quot;</td>
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<td>?</td>
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<td>-16</td>
<td>0.2</td>
<td>100</td>
<td>?</td>
<td>? little foam</td>
<td></td>
</tr>
<tr>
<td>NH$_4$BH$_4$</td>
<td>240</td>
<td>130</td>
<td>none</td>
<td>-63</td>
<td>?</td>
<td>40</td>
<td>?</td>
<td>? little foam</td>
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<tr>
<td>LiNH$_2$BH$_3$</td>
<td>109</td>
<td>52</td>
<td>none</td>
<td>-44</td>
<td>1.76</td>
<td>130</td>
<td>200</td>
<td>0 no foam</td>
<td></td>
</tr>
<tr>
<td>LiNH$_2$BH$_3$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>none</td>
<td>-44</td>
<td>1.76</td>
<td>130</td>
<td>200</td>
<td>0 no foam</td>
<td></td>
</tr>
<tr>
<td>LiNH$_2$BH$_3$</td>
<td>&quot;</td>
<td>&quot;</td>
<td>none</td>
<td>-44</td>
<td>1.76</td>
<td>130</td>
<td>200</td>
<td>0 no foam</td>
<td></td>
</tr>
<tr>
<td>NaNH$_2$BH$_3$</td>
<td>76</td>
<td>43</td>
<td>none</td>
<td>-0.044</td>
<td>80</td>
<td>?</td>
<td>0</td>
<td>no foam</td>
<td></td>
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<tr>
<td>NaNH$_2$BH$_3$</td>
<td>30</td>
<td>?</td>
<td>none</td>
<td>-0.043</td>
<td>100</td>
<td>?</td>
<td>0</td>
<td>no foam</td>
<td></td>
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</tbody>
</table>

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.
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 degradation 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)3]. Theoretical analysis showed that B(OPh)3 has sufficient hydride affinity to react and indeed PNNL found that HRh(dmpe)3 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)3 are not optimal in this regard. For example, the deprotonation of H2Rh(dmpe)3− requires base that is much stronger than PhO− and HRh(dmpe)3 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(OC3F7)3, which has greater H− accepting abilities compared to B(OPh)3. Also, it transfers H− to B(ScH)3 which has an intermediate hydride affinity. On the basis of these observations and recent theoretical analyses, PNNL is examining the use of chlorophenol in place of phenol in the above process with complexes of Co.

1) Digestion

\[
\text{BNH}_n + 3 \text{ t-BuOH} \rightarrow \frac{n}{2} \text{H}_2 \uparrow + \text{NH}_3 \uparrow + \text{B(O-t-Bu)}_3 \\
\text{B(O-t-Bu)}_3 + 3 \text{PhOH} \rightleftharpoons \% \text{B(OPh)}_3 + 3 \text{t-BuOH} \uparrow
\]

2) Transition Metal Hydride Formation

\[
3 \text{M}^+ + 3 \text{H}_2 \rightarrow 3 \text{MH}_3^+ [+ \text{base}] \rightarrow 3 \text{MH} + 3 \text{H}^+ \text{base}
\]

3) Hydride Transfer/Ligand Redistribution

\[
3 \text{MH} + 4 \text{B(OPh)}_3 + \text{Et}_3\text{N} \rightarrow 3 \text{M}^+ + 3 \text{B(OPh)}_3^- + 3 \text{Et}_3\text{NBH}_3
\]

4) Recycle

\[
3 \text{B(OPh)}_3^- + 3 \text{H}^+ \text{base} \rightleftharpoons 3 \text{PhOH} \uparrow + 3 \text{base} + 3 \text{B(OPh)}_3
\]

5) Ammoniation

\[
\text{Et}_3\text{NBH}_3 + \text{NH}_3 \rightarrow \text{BH}_2\text{NH}_3 \downarrow + \text{Et}_3\text{N}
\]

**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 BH$_3$ adduct by the following reaction sequence:

$$\text{BNH}_3 + 2 \text{t-BuOH} \rightarrow \text{NH}_3 + \text{HB(O-t-Bu)}_2$$
$$\text{HB(O-t-Bu)}_2 + \frac{1}{3} \text{Et}_3\text{N} \rightarrow \frac{1}{3} \text{Et}_3\text{NBH}_3 + \frac{1}{3} \text{B(O-t-Bu)}_3$$

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 H$_2$.

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., LiNH$_2$BH$_3$. 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


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).