Fluid Phase H$_2$ Storage Material Development

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2013 Annual Merit Review, May 15th

Los Alamos National Laboratory
LA-UR-13-22354

Project ID # ST040

This presentation does not contain any proprietary or confidential information.
Overview

Timeline
- Project Start Date: Oct 1st 2010
- Project End Date: 2014
- Percent Complete: 73%

Barriers
- Barriers Addressed
  - A. Weight/Volume
  - C. Efficiency
  - D. Durability/Operability
  - E. Discharging Rates

Budget
- Total project funding
  - DOE share: $225k
- Funding received in FY12: $330k
- Funding for FY13: $225k

Partners
- LANL (lead)
- University of Ottawa
Relevance and Overall Objectives

Relevance

Materials with good H₂ storage capacity and efficient regeneration are required for transportation, stationary, and portable power applications.

2017 system target = 5.5 wt. %; ultimate 7.5 wt. %

Objectives

Develop liquid ammonia-borane (~15 wt. % usable H₂)/ionic mixtures that have sufficient H₂ capacity, release kinetics, stability, and fluid phase properties upon H₂ release.

Integrate design specifications from Hydrogen Storage Engineering Center of Excellence (HSECoE) and ensure compatibility with system designs.
Chemical Hydrogen Storage Center

AB/IL: Good Capacity, Kinetics

\[
\begin{align*}
\text{H} & \text{N} \quad \text{H} \\
\text{H} & \text{H} \\
\text{HN} & \text{B} \\
\text{B} & \text{N} \\
\text{H} & \text{N} \\
\text{HB} & = \text{NH} \\
\end{align*}
\]

60-120 °C

BmimCl (m.p. 70 °C)

Colorless solid @ RT

\[
\begin{align*}
\text{HB} & = \text{NH} \\
\text{HN} & \quad \text{B} \quad \text{N} \\
\text{B} & \quad \text{N} \\
\text{B} & \quad \text{NH} \\
\text{HN} & \quad \text{B} \quad \text{N} \\
\text{B} & \quad \text{NH} \\
\text{B} & \quad \text{NH} \\
\text{HB} & = \text{NH} \\
\end{align*}
\]

7-11 wt. % H₂

Larry Sneddon, UPENN

A - 110 °C
B - 105 °C
C - 95 °C
D - 85 °C
E - 75 °C
Approach

Technical Limitation: Ammonia borane mixtures can form insoluble products after extensive $\text{H}_2$ release

Our Method: Use additives which react with ammonia borane, yielding smaller molecular weight products that are less prone to precipitation. By adjusting the functionality of the additive, we can control solubility of the products in various media

2013 Goals:
1) Design and synthesize amine-boranes tethered to ionic liquids
2) Characterize neutral functionalized amine-boranes and AB blends

Two different classes of additives will be used to address phase change
**Approach – Ionic Additives**

**Advantage:** excellent solubility in ionic liquids; less impurities

![Ionic liquid structure]

**Disadvantage:** unknown compounds, must be synthesized

*Ionic additives give better solubility in ionic liquids*
**Approach – Neutral Additives**

**Advantage:** easy to synthesize; liquid products; good H₂ capacity

![AB/hexylAB](image1.png) ![Copolymer product (@ 20°C)](image2.png)

140°C  6 wt. % H₂

**Disadvantage:** may generate volatile intermediates

Neutral Additives Yield Promising Results in FY12

US Nonprovisional Application (# 13850959)
Ionic Additive Development
Approach

**Initial Sneddon Mixture:**

**Final Sneddon Products:**

**Proposed Target:**

**Proposed Products:**

Insoluble
2013 Accomplishments

Attempted three independent syntheses

Gabriel Synthesis

Silyl Protecting Groups

Nitrile Precursors
2013 Accomplishments

Successful Synthesis of Amine-Borane tethered to an Ionic Liquid

\[ \text{Cl} \cdot \text{(CH}_2\text{)}_n \cdot \text{NH}_3^+ + \text{TMS-Cl} \rightarrow \text{TEA} \rightarrow \text{Cl} \cdot \text{(CH}_2\text{)}_n \cdot \text{N} \cdot \text{SiMe}_3 \]

\[ \text{R} \cdot \text{N} \rightarrow \text{R} \cdot \text{N} \cdot \text{Cl}^- \cdot \text{SiMe}_3 \rightarrow \text{HCl} \rightarrow \text{R} \cdot \text{N} \cdot \text{2Cl}^- \cdot \text{(CH}_2\text{)}_n \cdot \text{NH}_3^+ \]

\[ \text{NaBH}_4 \rightarrow \text{R} \cdot \text{N} \cdot \text{Cl}^- \cdot \text{SiMe}_3 \rightarrow \text{TMS-X} \rightarrow \text{R} \cdot \text{N} \cdot \text{X}^- \cdot \text{(CH}_2\text{)}_n \cdot \text{NH}_2\text{BH}_3 \]
2013 Accomplishments

Tethered Ionic liquid/Amineboranes Remain Liquid!

H₂ Charged State (@ 20°C)

H₂ Released State (@ 20°C)

US Nonprovisional Application (#13850959)
### First Round of Derivatives

<table>
<thead>
<tr>
<th>Additive</th>
<th>Identifier</th>
<th>Initial State (20°C)</th>
<th>Spent State (20°C)</th>
<th>Wt. % H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure A" /></td>
<td>A</td>
<td>Solid</td>
<td>Solid</td>
<td>2.5</td>
</tr>
<tr>
<td><img src="image" alt="Structure B" /></td>
<td>B</td>
<td>Solid</td>
<td>Solid</td>
<td>1.5</td>
</tr>
<tr>
<td><img src="image" alt="Structure C" /></td>
<td>C</td>
<td>Solid</td>
<td>Solid</td>
<td>2.3</td>
</tr>
<tr>
<td><img src="image" alt="Structure D" /></td>
<td>D</td>
<td>Oily Wax</td>
<td>Solid</td>
<td>1.4</td>
</tr>
<tr>
<td><img src="image" alt="Structure E" /></td>
<td>E</td>
<td>Solid</td>
<td>Solid</td>
<td>2.1</td>
</tr>
</tbody>
</table>

F: Liquid | Viscous liquid | 1.4

G: Liquid | Liquid | 1.0

US Nonprovisional Application (#13850959)
2013 Accomplishments

Anion Choice Has Pronounced Effect on Properties

Control H₂ release with anion choice; better match with AB = less impurities

\[ \text{H}_2 \text{Release: } 133°C \]

\( \text{(E)} \)

\[ \text{H}_2 \text{Release: } 82°C \]

\( \text{(F)} \)

\[ \text{H}_2 \text{Release: } 75°C \]

\( \text{(G)} \)
## 2013 Accomplishments

### Amineborane-IL/AB mixtures

<table>
<thead>
<tr>
<th>Material</th>
<th>AB/Additive</th>
<th>Initial State (20°C)</th>
<th>Spent State (20°C)</th>
<th>Wt. % H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.5</td>
<td>Solid</td>
<td>Solid</td>
<td>2.0</td>
</tr>
<tr>
<td>F</td>
<td>0.5</td>
<td>Milky Suspension</td>
<td>Solid</td>
<td>1.8</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>Milky Suspension</td>
<td>Flaky Solid</td>
<td>2.3</td>
</tr>
<tr>
<td>G</td>
<td>0.5</td>
<td>Milky Suspension</td>
<td>Viscous Liquid</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Ionic Additives blended with AB yields fluid phase products**

US Nonprovisional Application (#13850959)
Neutral Additive Development
### 2013 Accomplishments

**Surveyed Alternative Amine Boranes**

<table>
<thead>
<tr>
<th></th>
<th>n-C4</th>
<th>iso-C4</th>
<th>sec-C4</th>
<th>tert-C4</th>
<th>n-C5</th>
<th>iso-C5</th>
<th>sec-C5</th>
<th>1,2-DMP</th>
<th>neo-C5</th>
<th>n-C6</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRH₂ b.p. (°C)</td>
<td>78</td>
<td>68</td>
<td>63</td>
<td>45</td>
<td>104</td>
<td>95</td>
<td>93</td>
<td>85</td>
<td>83</td>
<td>130</td>
</tr>
<tr>
<td>RH₂N•BH₃ m.p.</td>
<td>10</td>
<td>65</td>
<td>0</td>
<td>96</td>
<td>5</td>
<td>85</td>
<td>-5</td>
<td>-</td>
<td>-</td>
<td>~20</td>
</tr>
</tbody>
</table>

Synthesized by Ottawa

<table>
<thead>
<tr>
<th>Amine</th>
<th>n-C5</th>
<th>iso-C5</th>
<th>sec-C5</th>
<th>1,2-DMP</th>
<th>neo-C5</th>
<th>n-C6</th>
</tr>
</thead>
<tbody>
<tr>
<td>50g ($)</td>
<td>97</td>
<td>70</td>
<td>1390</td>
<td>128</td>
<td>264</td>
<td>17</td>
</tr>
</tbody>
</table>
2013 Accomplishments

Benzylamine-borane Pursued

R = H, m.p. 10°C
R = o-CH₃, m.p. = < 20°C
b.p. ~200°C

R = H, m.p. 57°C
R = o-CH₃, m.p. = 110°C

Interact with ionic liquids = greater solubility

All stored H₂ released!
2013 Accomplishments

Benzylamine-borane/AB Mixtures

Spent fuel of BzAB + AB in [EMIm]EtSO₄ (1.8 wt. % H₂) still flows while above 100°C!

Evidence of copolymerization; 2 wt. % IL mixture flows above 100°C
### 2013 Accomplishments

**Benzylamine-Boranes Outselected**

<table>
<thead>
<tr>
<th>Fuel Blend</th>
<th>time (h)</th>
<th>temp (°C)</th>
<th>solvent</th>
<th>Spent Phase?</th>
<th>Wt. % H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>BzAB/AB</td>
<td>24</td>
<td>80</td>
<td>neat</td>
<td>RT: solid, 80°C; liquid</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BzAB/AB</td>
<td>18</td>
<td>130</td>
<td>neat</td>
<td>RT: solid, 130°C; solid</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BzAB/AB</td>
<td>22</td>
<td>130</td>
<td>[EMIm]EtSO₄</td>
<td>RT: liquid, 130°C; liquid</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BzAB/AB</td>
<td>18</td>
<td>130</td>
<td>[EMIm]EtSO₄</td>
<td>RT: solid, 130°C; liquid</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-MeBzAB/AB</td>
<td>7</td>
<td>130</td>
<td>neat</td>
<td>RT: liquid, 130°C; liquid</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-MeBzAB/AB</td>
<td>18</td>
<td>130</td>
<td>[EMIm]EtSO₄</td>
<td>RT: solid, 130°C; liquid</td>
<td>1.7</td>
</tr>
</tbody>
</table>

**Benzylamineboranes outselected for future work**
2013 Accomplishments (joint with ECoE)

Volatile Limits Conversion

Non-volatile additives may facilitate greater conversion and prevent phase change.
Neutral AmineBorane/AB Blends: Batch Evaluation

Excellent H₂ release; Some impurities detected; Better AB mixing for future runs

Heating to 130°C releases 98% of stored H₂ (assume 2.5 eq. for AB)

AB (JSC Aviobor, as received)

AB (finely dispersed)
Stability Additive Development
2013 Accomplishments

Stability Additives

PVP – inert, nonvolatile
prevents isomerization and resulting H₂ release from glyme solutions at room temperature

PVP improves AB stability; related additives may work in ionic liquids
## Collaborations

<table>
<thead>
<tr>
<th>External Collaborators</th>
<th>Effort</th>
<th>Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ Codes and Standards</td>
<td>General Guidance</td>
<td>C. Padro (LANL)</td>
</tr>
<tr>
<td>Centre for Catalysis Research and Innovation</td>
<td>Neutral Additive Design, Characterization</td>
<td>T. Baker (Ottawa)</td>
</tr>
<tr>
<td>Chemical Hydrogen System Architect (HSECoE)</td>
<td>System Designs</td>
<td>Troy Semelsberger (LANL)</td>
</tr>
</tbody>
</table>
Proposed Future Work

Continue amine-borane/ionic liquid additive development
  FY13 Upscale synthesis; determine maximum AB loading
  FY13-FY14 Assess H₂ release, phase of AB blends
  FY13-FY14 Incorporate ECoE feedback for better additive design

Assess efficacy of diaminoborane additives
  FY13 Synthesize known materials
  FY13 Evaluate product phase with borazine, polyborazylene
  FY14 Generate AB blends and perform batch experiments

Interface with HSECoE
  FY13-FY14 Upscale candidate materials for HSECoE reactor/component testing
**Project Summary**

**Relevance:** Developing materials that store H₂, supporting the HSECoE effort to meet the 2017 system target of 5.5 wt. %; 7.5 wt. % ultimate

**Approach:** Create amineborane additives which, when blended with ammonia borane, yield a good storage capacity material that remains fluid after H₂ release. Ionic and neutral additives were targeted.

**Accomplishments and Progress:** synthesized first amineborane/ionic liquid additive; demonstrated blends with AB remain liquid post H₂ release; searched for new neutral additives; evaluation of neutral additives in HSECoE reactor suggests volatility may limit conversion

**Collaborations:** Hydrogen Storage Engineering Center of Excellence

**Proposed Future Research:** Continue amineborane/ionic liquid additive development; investigate diaminoborane additives

**Benjamin Davis**

bldavis@lanl.gov
Technical Back Up Slides
Previous Additive Development

- Explored alkylamine boranes to solubilize AB

- UPENN evaluated amine additives and substituted borazines to maintain fluid phase (2011)

\[ \text{AB/IL + 5\% dipentylamine} \rightarrow 85^\circ C \rightarrow \text{solid (2.2 eq. } H_2 \text{ released)} \]

\[ \text{AB/IL + 5\% trimethylborazine} \rightarrow 85^\circ C \rightarrow \text{solid (2.3 eq. } H_2 \text{ released)} \]