PNNL Progress as Part of the Chemical Hydrogen Storage Center of Excellence

Chris Aardahl, PNNL
June 2008
Overview

Timeline
- Start 3/2005
- End 3/2010
- 60% Complete

Barriers Addressed
- Volumetric Density
- Gravimetric Density
- Hydrogen Release Rate
- Fuel Cost
- Fuel Cycle Energy Efficiency

Budget
- FY07: $1700K
- FY08: $2050K

Center Collaborations

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy
Project Objectives

Center
- Develop methods for on-demand, low temperature hydrogen release from chemical hydrides that can achieve DOE targets
- Develop high efficiency off-board methods for chemical hydride regeneration

PNNL
- Meet Center objectives through studies and development of high capacity chemical hydrides (NH$_3$BH$_3$ (& isomers), NH$_4$BH$_4$, B-N/M-H hybrids)
  - Increase kinetics while maintaining high capacity
  - Hybrid materials to control thermodynamics
  - Controlling morphology: materials engineering
  - Regeneration of NH$_3$BH$_3$: matching digestion and reduction
Specific Approach for this Review Period

- Increase rate for the second equivalent of hydrogen release from NH$_3$BH$_3$ or related systems to achieve rate target
- Develop methods to control morphology of NH$_3$BH$_3$ during H$_2$ release to enable solids handling
- Develop experimental program to explore use of ‘activated’ H$_2$ as a means to regenerate spent B-N fuels to reduce fuel cycle costs
- Use theory to guide matching of digestion and reduction chemistry in regeneration schemes
- Develop preliminary flow sheets for PNNL regeneration scheme to identify knowledge gaps
- Examine hybrid materials based on BH$_3$NH$_3$ and LiH/NaH to explore a new class of materials
- Quantify H$_2$ impurities from the B-N and B-N-X systems to understand potential impacts on fuel cell operation
Major Achievements for the Review Period

• Developed Li-NH₂-BH₃ under IPHE collaboration: worth additional pursuit; H₂ release kinetics increased by order of magnitude
• Discovered additives that suppress foaming of NH₃BH₃: enables pursuit of engineered system
• Demonstrated hydride transfer chemistry from ‘activated’ H₂ to spent fuel: confirms theory results from 2007 AMR
• Theoretical calculations now point to energy efficient regeneration approach with non-PGM reduction pathway: reduced fuel cycle costs
• Preliminary flow sheets for regeneration enables identification of process knowledge gaps
## Milestones – FY 2008

<table>
<thead>
<tr>
<th>Quarter</th>
<th>Milestone Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Q4</strong></td>
<td>Complete characterization of mechanism for second equivalent of hydrogen from ammonia borane. Deliver research direction for development of additives to accelerate release of second equivalent without destabilization of the fuel.</td>
</tr>
<tr>
<td><strong>Q3</strong></td>
<td>Quantify the purity of hydrogen released thermally from ammonia borane as a function of temperature. Understand gap between observed data and 2010 target.</td>
</tr>
<tr>
<td><strong>Q2</strong></td>
<td>Finish characterization of alternative ammonia borane-scaffold materials and quantify thermochemistry. Quantify kinetics and thermodynamics. Deliver assessment versus 2010 targets and neat ammonia borane.</td>
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<tr>
<td><strong>Q4</strong></td>
<td>Demonstrate bench scale regeneration at 40% energy efficiency (Center milestone with LANL, Penn, UC Davis).</td>
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<tr>
<td><strong>Q3</strong></td>
<td>Complete characterization of mechanism for foaming during hydrogen release from ammonia borane solids. Deliver research direction and list of options for mitigation of foaming.</td>
</tr>
<tr>
<td><strong>Q4</strong></td>
<td>Complete the characterization (NMR, TGA/DSC) of the LiH/AB system and assess capacity and reversibility</td>
</tr>
<tr>
<td><strong>Q4</strong></td>
<td>Submit a minimum of 1 joint publication from the IPHE activities with the UK, Singapore, New Zealand, and the US</td>
</tr>
<tr>
<td><strong>Q2</strong></td>
<td>Complete down-selection process for 2010 engineering &amp; 2015 science in collaboration with the entire Center</td>
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</table>
Progress on Hydrogen Release (2008 vs. 2007)

- Order of magnitude increase in release rates
- ABH₂ kinetics too fast to measure with existing methods

PNNL: Karkamkar, Choi, Daschbach, Autrey

Modified from Thomas & Sandrock, DOE
## Summary Table

### 2007 – Neat AB (per kg on rates)

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>1 eq H₂</th>
<th>1.5 eq H₂</th>
<th>2 eq H₂</th>
<th>2.5 eq H₂</th>
<th>Peak rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>160°C</td>
<td>50 sec</td>
<td>80 sec</td>
<td>240 sec</td>
<td>1000 sec</td>
<td>3.8 g/s</td>
</tr>
<tr>
<td></td>
<td>(1.3 g/s)</td>
<td>(1.2 g/s)</td>
<td>(.54 g/s)</td>
<td>(.16 g/s)</td>
<td></td>
</tr>
<tr>
<td>145°C</td>
<td>70 sec</td>
<td>200 sec</td>
<td>1200 sec</td>
<td></td>
<td>2.1 g/s</td>
</tr>
<tr>
<td></td>
<td>(.93 g/s)</td>
<td>(.5 g/s)</td>
<td>(.11 g/s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>130°C</td>
<td>150 sec</td>
<td>1000 sec</td>
<td></td>
<td></td>
<td>1.1 g/s</td>
</tr>
<tr>
<td></td>
<td>(.43 g/s)</td>
<td>(.1 g/s)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 2008 – AB Derivatives

<table>
<thead>
<tr>
<th></th>
<th>Wt %</th>
<th>Temp (°C)</th>
<th>2 Eq. Avg. Rate (130°C; g/s/kg)</th>
<th>Foam?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-AB</td>
<td>11.2</td>
<td>&lt; 100</td>
<td>2.9</td>
<td>NO</td>
</tr>
<tr>
<td>ABH₂</td>
<td>12.2 - 21.4</td>
<td>40 - 130</td>
<td>VERY FAST</td>
<td>NO</td>
</tr>
<tr>
<td>DADB</td>
<td>12</td>
<td>90 - 130</td>
<td>0.13</td>
<td>NO</td>
</tr>
</tbody>
</table>
Additive Discovered Allows High Volumetric Density & Prospect of an Engineered System for Solid AB

- System targets are difficult for granulated materials
- Addition of a spent fuel tank cuts the volumetric density in half
  - AB foams when it releases hydrogen – not conducive to engineering
  - Potential show stopper
- Campaign on anti-foaming initiated in Q1, FY08
  - More than 50 additive formulations tested with 2-3 successful (Patent Filed)
  - Scaffold materials also demonstrate foam suppression at lower AB:scaffold loadings
  - Paves the way to systems with monolithic fuels & high volumetric density

_PNNL: Choi, Karkamkar, Aardahl, Autrey_
$^{11}$B NMR: No Evidence of Reaction Between AB & Additive

155°C: 2 – 2.2 Eq. H$_2$

120°C: 1.3 Eq. H$_2$

PNNL: Choi, Karkamkar, Autrey
Measurements of Volatile Impurities Show Small Amounts of Borazine and NH$_3$

- Pass H$_2$ though THF to trap borazine → measure via NMR
  - 1 °C/min (detected)
  - 0.1 °C/min (not detected)
- Daigger tube (Kitagawa)
  - Measure [NH$_3$] in H$_2$ from gas burette
  - Isothermal (120 °C; 1.3 eq H$_2$): NH$_3$ ca. 170 ±10 ppm
  - Unclear whether a decomposition product or residual from synthesis
- Impurities at low levels can be handled through filtration or reactor design approaches
**Li-AB: Fast Kinetics & Little Barrier on Second Equivalent of H₂ (all release < 100°C)**

- Material mixtures allow engineering thermodynamics and kinetics
- Demonstrated release of 2 equivalents (~11 wt%) of hydrogen below 100°C; release of 2nd equivalent is very fast compared to AB
- No borazine impurity in the hydrogen released
- Faster kinetics for a given wt% than neat ammonia borane

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**Chemical Structures**

- Red – H
- Blue – N
- Pink – B
- Purple – Li

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**Graphs and Data**

- DSC curves showing reaction temperatures for LiNH₂BH₃ and AB
- Mass spectrometry (MS) data for H₂ and LiNH₂BH₃

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**References**


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**Contributors**

- PNNL: Autrey, Shaw, Karkamkar
- NUS: P. Chen; RAL: W. David; Oxford: P. Edwards
Ammonium Borohydride Has Potential

• Fast kinetics for 12 wt%
• Literature indicates compound not stable: PNNL has demonstrated that stability enhancement possible with careful synthetic approaches
  – More stable than previously reported: stable at -30°C
  – Opens up opportunities to look at materials based on ABH₂
• Step 1: ABH₂ → AB + H₂
• Step 2: ABH₂ + AB → DADB → PAB + H₂
• Complete reaction (150°C): 20 wt% H₂

XRD of ABH₂: $t_{1/2} = 16$ hrs under ambient

PNNL: Karkamkar, Heldebrant, Autrey
Proposed at 2007 AMR: Regeneration of AB with ‘Activated’ H₂

Focus on Alcohols t-BuOh, PhOH to make Borate Esters

Transition Metal Hydrides from H₂
- RhL₄H
- CoL₄H

Spent fuel + H₂ in

AB out

Disproportionation Followed by Reaction with Ammonia Forms AB

Hydride Transfer Enabled by Acid-Base Chemistry

PNNL: Camaioni, Dubois, Mock, Potter, Heldebrant, Rassat, Zheng
NMR Characterization Key to Confirming Efficient Regeneration Chemistry

- ≥ 2 eq H₂ gives polyborazylene-like products
- Polyborazylene undergoes digestion relatively easily
- Spent fuel characterization complete
- Digestion pathways in good shape
- Principle focus in FY08 on reduction chemistry

Solid $^{11}$B: 800 MHz

Solution $^{11}$B: 300 MHz

$t$-BuOH

NH$_3$

B(OBu')$_3$

BH$_3$NH$_3$

PNNL: Camaioni, Shaw, Potter, Karkamkar, Heldebrant
NMR confirms (dmpe)$_2$RhH can reduce B(OPh)$_3$: Points to Efficient Pathway for Regeneration

$^{11}$B NMR spectra at 55 °C ($^1$H decoupled and coupled):

Area Ratio: > 60% B-H

Doublet indicates B-H formation

Shift in $^{31}$P NMR Confirms

Proposed for FY08

$^{31}$P NMR Spectrum

PNNL: Mock, Potter, Dubois, Camaioni
Use of Theory and Experiment to Understand Energetics is Key to Efficient Regeneration

Step 1: $\text{H}_2$ Activation
$\text{H}_2 + \text{pressure} + \text{heat}$
Metal: $\text{H}_2 \rightarrow \text{H}^+ & \text{H}^-$ (not $\text{H}^*$)
Step 2: Reduction
Hydricity of donor must be matched to acceptor strength

Acidity of proton donor critical: acceptor ROH must be more stable than ML₄OR
Understanding the Mechanism & Energetics
Key to Solving Regeneration Problem

ML₄OR

ML₄H

(RO)₂BH to disproportionation

ROH (digestion)
Matching Hydricity and $pK_a$ for MH$_2$ and HX

M, L, & R are the tuning parameters!!

Hydride Affinity (-$\Delta H$): $BX_3 + H^- \rightarrow HBX_3^-$
(calculation)

Hydride Donor Abilities ($\Delta G$):
$HML_2 \rightarrow ML_2^+ + H^-$ (measured)

$B(SMe)_3$  $B(OPh)_3$

$[RhH_2(dmpe)_2]^+$  $[CoH_2L_2]^+$  $[RhH_2L'_2]^+$

$PhOH$  $PhSH$

40  30  20

$pK_a$: $HX \rightleftharpoons H^+ + X^-$

$pK_a$: $[MH_2L_n]^{m+} \rightleftharpoons H^+ + [MHL_n]^{(m-1)+}$
Preliminary flow sheets can indicate gaps:
Digestion

- **CRUSHING**
  - Spent Fuel
  - Recovered Ammonia

- **DIGESTION**
  - Solvent
  - Co-Solvent

- **LIQ – SOL SEPARATION**
  - Undigested Dregs

- **EXTRACTION**
  - BX$_3$ to Reduction

- **SEP**
  - Co-Solvent Recycle
  - Solvent Recycle

- **CRYSTALLIZATION**
  - Recovered AB

-PNNL: Zheng, Rassat, Aardahl, Camaioni-
Reduction

H₂ ACTIVATION
(MX + H₂ to HM + HX)

HYDRIDE TRANSFER
(HM + BX₃ to HBX₂ + MX)
Lessons Learned from Flow Sheeting: Technical Gaps to Address in Phase 2

• Although processes have been conceived: very limited optimization of operating envelopes
  – Demonstration of the chemistry in small scale, batch mode
  – Continuous processing still quite an extrapolation from here
• Spent Fuel: Residual BH Recovery
  – Do we capture H\(^+\) in spent fuel as hydride during digestion or as H\(_2\) to be converted to hydride during reduction?
  – Assessment of energy penalty vs. process complexity still in progress
• Hydride Separation
  – Critical separation step: BX\(_3\)-BHX\(_2\)
  – Need data on thermal stability, relative volatility, solubility, etc.
• Mixed Solvents
  – Digestion and reduction processes may require different solvents
  – Separations: Is solubility the only consideration?
• Ammonia Borane Heat Sensitivity
  – Difficult to separate AB from other hydrides based on volatility
• Physical Properties of Organo-boranes
  – Needed for process design
• Additional focus on the separations will be required moving ahead
Summary

• Release
  – Kinetics can be increased dramatically through hybrid materials (LiAB)
  – Method for foam suppression in AB discovered
    • Can now pursue solids handling in earnest
    • Enables system volumetric density much higher than previously possible
  – Initial results indicate ABH$_2$ worth further study

• Regeneration
  – Experiments confirm theory for reduction of B(OPh)$_3$ w/MH
  – Digestion well in hand; reduction pathway becoming clearer
  – Preliminary regeneration flow sheets have helped identify needed separations work

• Milestones on track & Phase 2 now underway
Future Work

• Release – focus now on materials down-selected by the Center
  – Additional focus on materials within the metal-AB family: LiAB is interesting; others?
  – ABH$_2$; exactly how stable can it be?
  – B-N-C materials
  – Characteristics of monolithic solid AB

• Regeneration
  – Push toward matching energetics of reduction with digestion agent choice
    • Synthetic challenges in the Co system
    • Quantification of yields and process envelopes
  – Work toward filling gaps in process knowledge (with ROH, LANL, Penn, UC Davis) and understand efficiency/cost
  – Help LANL, Penn by matching PNNL reduction strategy with their digestion chemistries
Team & Collaborators

PNNL supports collaboration through expertise in materials science, instrumentation, theory & simulation, inorganic chemistry, high field NMR, general characterization of hydrogen bearing materials, and engineering support for on-board and off-board

Center of Excellence for Chemical Hydrogen Storage

International Partnership for the Hydrogen Economy
PNNL Team

**FUEL REGENERATION**
- Don Camaioni
- Dan Dubois
- Jun Li
- Mike Mock
- Jerry Potter
- Wendy Shaw
- Dave Heldebrant

**H₂ RELEASE**
- Tom Autrey
- Abhi Karkamkar
- John Linehan
- Daiwon Choi

**ENGINEERING**
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- Richard Zheng
- Ken Rappe
- Chris Aardahl

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