Chemical Hydrogen Storage R&D at Los Alamos National Laboratory

Project ST6


2008 DOE Annual Merit Review
Arlington, VA

This presentation does not contain any proprietary or confidential information
Overview

Timeline
• Start: FY 05
• End: FY 09
• 60% Complete

Barriers
• Weight and Volume
• Flow Rate
• Energy Efficiency
• Cost
• Regeneration Process
• System Life-Cycle Assessments

Budget
• Estimated Project Funding
  - $9.61 M
• FY 07
  - $1,837 K
• FY 08
  - $2,455 K

Partners
• Chemical Hydrogen Storage Center of Excellence
• IPHE (Singapore, UK, New Zealand)
Objectives

• Develop and demonstrate heterogeneous catalysts and continuous flow reactor operation for hydrogen release

• Develop liquid ammonia-borane (AB) fuels and increase rate and extent of hydrogen release

• Identify and demonstrate new materials and strategies for near-thermoneutral hydrogen release ($\Delta G^\circ = \text{ideally no less negative than ca. } -0.8 \text{ kcal/mol}$)

• Demonstrate all chemical steps and conduct engineering assessment for energy efficient AB regeneration process (high yields, rates, and energy efficiency, integrate steps when possible)

• Develop materials and processes to minimize gas-phase impurities, and demonstrate adequate purity of hydrogen stream

✓ Provide materials chemistry support for PSU work on electrochemical conversion of B-O to B-H (completed as part of phase 1)
## Milestones

<table>
<thead>
<tr>
<th>Quarter</th>
<th>Milestone Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q4 FY07</td>
<td>Complete down-selection process for 2010 engineering &amp; 2015 science in collaboration with the entire Center</td>
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<tr>
<td>Q1</td>
<td>Define independent chemical steps for regeneration of spent fuel and document energy requirements per step. (DOE Joule Milestone)</td>
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<td>Q2</td>
<td>Complete laboratory scale demonstration of regeneration chemistries for at least two approaches and document reaction yields. (DOE Joule Milestone)</td>
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<td>Q3</td>
<td>Prepare and characterize variety of M-B-N-H compounds for high capacity, potentially reversible hydrogen storage</td>
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<tr>
<td>Q3</td>
<td>Determine thermodynamic efficiency of demonstrated spent fuel regeneration routes. (DOE Joule Milestone)</td>
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<td>Q4</td>
<td>Develop heterogeneous catalysis for hydrogen release from AB</td>
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<tr>
<td>Q4</td>
<td>Use mechanistic results and theory to guide catalyst design for optimal rates and extent of hydrogen release from liquid amine-borane fuels</td>
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<tr>
<td>Q4</td>
<td>Develop chemical hydrogen storage regeneration methods at laboratory-scale, obtain initial data for efficiency and cost analysis, and demonstrate lab-scale reactions capable of at least 40 percent energy efficiency</td>
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</tbody>
</table>
Approach: Los Alamos Technical Contributions

- Down-select materials and processes for Phase 2 to focus continuing research

- Engineering Guided Research
  - Use single cell PEM fuel cell for testing purity of hydrogen gas streams
  - Fabricate and operate continuous flow reactor for heterogeneous catalyst testing

- New hydrogen storage materials
  - Design and synthesis of near-thermoneutral release materials
  - Design and synthesis of liquid fuel compositions

- Hydrogen Release
  - Identify reaction pathways and mechanisms to maximal storage and release rates that lead to:
    - Design, synthesize, and demonstrate heterogeneous catalysts with high rates at $T < 100 \, ^\circ C$

- Regeneration
  - Use theory to guide toward most energy efficient matching of regeneration reactions
  - Demonstrate all individual steps to ammonia borane from spent fuel and begin process integration
  - Use ‘well-to-tank analysis’ and other engineering input to guide selection and improvement of reaction steps

- B-O to B-H (*completed: SBH go-nogo*)
  - Provide organic soluble borate salts for PSU electrochemistry
Down select results

Appendix 2. Decision Summary Spreadsheet

<table>
<thead>
<tr>
<th>Organic hydrides, alkoxides, and nanoparticles</th>
<th>Metal Alumidoboranes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
<td><strong>With 5%</strong></td>
</tr>
<tr>
<td><strong>DownSelect</strong></td>
<td><strong>Advantage</strong></td>
</tr>
<tr>
<td><strong>Ammonia Borane Materials</strong></td>
<td><strong>Figure 2. Decision Tree for the CH5CoE Materials Down-Selection Process</strong></td>
</tr>
<tr>
<td><strong>Table</strong></td>
<td><strong>With 5%</strong></td>
</tr>
<tr>
<td><strong>Material</strong></td>
<td><strong>With 5%</strong></td>
</tr>
</tbody>
</table>

DOE Chemical Hydrogen Storage Center
Key accomplishments since last review

• New materials have been prepared that have lower exothermicity, higher rates to higher extents of release at lower temperatures compared to ammonia borane which exceed 2010 targets
• Liquid fuel compositions have been expanded, and liquid range to -30 °C has been demonstrated
• Heterogeneous base metal catalysts for hydrogen release have been prepared and demonstrated to have high rates of release to > 9 wt % H₂ at 70 °C
• All individual steps in a “first pass” AB regen cycle have been proven with overall yield of spent fuel digestion through reduction steps exceeding 70%
• Flow reactor for catalyst screening and process development has been assembled and screening heterogeneous catalysts underway
• Hydrogen stream purity analysis system has been assembled and is operating to identify and quantify impurities in H₂ stream
• PEM fuel cell apparatus for hydrogen stream purity testing has been assembled and is operating
New solution routes to new AB derivatives
Extensive portfolio of storage materials with lower exothermicity, higher rates and extent of release, with reduced impurities in H₂ stream

Metal Amidoborane Derivatives

MgCl₂ + 2NaNH₂BH₃ → Mg(NH₂BH₃)₂ + 2NaCl
MgCl₂ + NaNH₂BH₃ → Mg(NH₂BH₃)Cl + NaCl
ZnCl₂ + 2NaNH₂BH₃ → Zn(NH₂BH₃)₂ + 2NaCl
TiCl₄ + 4NaNH₂BH₃ → Ti(NH₂BH₃)₄ + 4NaCl
LiNH₂ + NH₃BH₃ → LiNH₂BH₃ + NH₃

NaH + NH₃BH₃ → NaNH₂BH₃ + H₂
CaH₂ + 2NH₃BH₃ → Ca(NH₂BH₃)₂ + 2H₂
AlH₃ + 3NH₃BH₃ → Al(NH₂BH₃)₃ + 3H₂
LiAlH₄ + 4NH₃BH₃ → LiAl(NH₂BH₃)₄ + 4H₂
Li₃(ZnH₄) + 4NH₃BH₃ → Li₃Zn(NH₂BH₃)₄ + 4H₂
Li(ZnH₃) + 3NH₃BH₃ → LiZn(NH₂BH₃)₃ + 3H₂

e.g. Ca(NH₂BH₃)₂ has greater thermal stability than AB but undergoes faster catalytic release of H₂ at room temperature

Example
W(NH₂BH₃)₆ = 8.3 wt%

Fluoride systems

NH₃BH₃ + MFₙ → NH₃BH₂F + M + ½H₂

• Future Examination of potential for direct rehydrogenation to explore potential of onboard regeneration
**We Now Understand the Catalytic Mechanism of $H_2$ Release from Ammonia-Borane to Guide Catalyst Design**

\[
H_3NBH_3 \rightarrow n\ H_2 + (H_2NBH_2)_n \rightarrow n\ H_2 + (HNBH)_n \rightarrow n\ H_2 + BN
\]

- **2007**: proposed that ejection of reactive aminoborane ($H_2NBH_2$) from metal center allows for release of $> 2$ equiv. of $H_2$

- **2008**: confirmed mechanistic details*

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*V. Pons (DEFG02-05ER15719-AO)
Understanding Mechanism Leads to New Class of Modular Iron Hydrogen Release Catalysts

2008 work

\[
[M]-\text{NRR}' + \text{H}_3\text{NBH}_3 \rightarrow \left[ \begin{array}{c}
\text{H}_2\text{B} \longrightarrow \text{NH}_2 \\
\text{H} \quad \text{H} \\
[M]-\text{NRR}' 
\end{array} \right] \rightarrow [M]-\text{NHRR}' + \text{H}_2\text{NBH}_2
\]

\[
\text{Fe}[\text{N(SiMe}_3)_2]_2 \xrightarrow{\text{R}_2\text{P} / \text{PR}'_2 / \text{HR}''\text{N} / \text{NHR}''' } \text{- HN(SiMe}_3)_2
\]

Route to Supported Iron Dehydrogenation Catalysts

\[
(\text{dcpe})(\text{dpen})\text{Fe}[\text{N(SiMe}_3)_2]_2
\]

Fast but only 1 Equiv. H\text{H}  
0.026 g s^{-1} kW^{-1}

\[
(\text{PCy}_3)_2\text{Fe}[\text{N(SiMe}_3)_2]_2 > 1 \text{ H}_2 \text{ but slower}
0.004 g s^{-1} kW^{-1}
\]

• Future Improved rates of hydrogen release from new catalysts that can be prepared on supported catalysts employing the new synthesis robot
2008: Identified Effective Heterogeneous Catalysis for the Release of H₂ with cleaner hydrogen stream

2006 homogeneous catalyst:
  high rate, limited capacity

2008 heterogeneous catalyst:
  higher capacity, higher initial rate

2007 homogeneous catalyst:
  higher capacity, limited rate

2006 homogeneous catalyst:
  high rate, limited capacity

Non-precious metal catalyst identified!

DOE target 0.02 g s⁻¹ kW⁻¹
Measured for Heterogeneous catalyst 0.04 g s⁻¹ kW⁻¹
With no borazine detected!

• Future Find additional non-precious metal catalysts with high rates and stability under continuous flow reaction conditions.
New Fuels that are Liquid Down to -30 °C Have Been Developed

• 2007 Initial work using methylamine-borane was terminated in 2008 due to volatility and instability of MeAB containing liquid mixtures

• 2008 New liquid systems have been prepared

<table>
<thead>
<tr>
<th>wt%</th>
<th>Formula</th>
<th>Temperature</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>H₂N</td>
<td>120 °C</td>
<td>Liquid</td>
</tr>
<tr>
<td>5.6</td>
<td>NH₂</td>
<td>-2 H₂</td>
<td>Liquid</td>
</tr>
<tr>
<td>7.8</td>
<td>H₃B</td>
<td>120 °C</td>
<td>Liquid</td>
</tr>
<tr>
<td>5.6</td>
<td>H₂N</td>
<td>-2 H₂</td>
<td>Liquid</td>
</tr>
<tr>
<td>2.3</td>
<td>Et₂N</td>
<td>120 °C</td>
<td>Liquid</td>
</tr>
</tbody>
</table>

• Future Optimize fuel mixture for highest wt% H₂ and target liquid range using synthesis robot
Regeneration: Demonstrated spent fuel recycle

2007

- Amines digested spent fuel, but products **did not** undergo other required reactions
- Proposed thiols as digestion agents
- Screened a variety of reducing agents with a variety of B-X bonds; showed that the boron-sulfur bond in B(SPh)$_3$ could be reduced by Bu$_3$SnH
- Route for tin hydride recycling via formate route was proposed

2008 Progress

- **New digestion agent:** Demonstrated that benzenedithiol digests spent fuel in high yield (**100% isolated yield**)
- Demonstrated that thiol-based digestion products undergo reduction to yield AB (**70% isolated yield of LBH$_3$**)
- **Tin hydrides reduce digestion products and can be recycled:**
  - Extensive calculations *and* experiment confirm tin mono- and dihydrides as reducing agents for digestates
  - Decreased reaction temperature for reduction enabled using auxiliary ligands -- results in higher yields, rates of reduction
  - Reduction co product (C$_6$H$_4$S$_2$)(SnBu$_3$)$_2$ reacts with formic acid en route to recycling the MH (ongoing work)
  - Direct hydrogenation replaces formic acid steps
LANL Has Demonstrated Fuel Regeneration Process

- Benzenedithiol fully digests BNH$_x$ into two products at 55 °C
- After treatment with diethylamine, tributyltin hydride reduces mixture to H$_3$B·Et$_2$NH

Spent fuel + H$_2$ in

AB out

- Addition of formic acid and heat to tin byproduct recycles MH
- Et$_2$NH will be displaced by NH$_3$ to form AB

Digestion — Reduction

MH Recycle — Ammoniation
Stepwise Regen of AB: Solving the Problems

Cycle as envisioned

1st problem = co product chemistry ✓ solved
How we utilize the Theory – Experiment Interface: Choosing the Best Ligand for Reduction and Ammoniation by Matching Energetics

2nd problem = matching digestion with reduction chemistry ✓ solved

• Tech Team 08: LANL showed exchange of \( \text{NH}_3 \) for \( \text{NEt}_3 \) permitted reduction of \( \text{HB}(\text{C}_6\text{H}_4\text{S}_2)\cdot\text{L} \) at lower temperature

• Now energy balance required for Rxns A-C: \( \text{HNET}_2 \) (ongoing work)
ANL Engineering Assessment Identifies CO₂ Compression as a Major Energy Concern in Regen Cycle

Have to replace CO₂ as a hydrogen transfer reagent

+2H₂ =

(HOOC)SnBu₃ → CO₂ + HSnBu₃  12.9 kcal/mol
H₂ + CO₂ → HCOOH  -22.5 kcal/mol

3rd problem = engineering issues in formic acid synthesis

Theory

C₆H₄(SSnBu₃)₂ (l) + 2 H₂ (g) → C₆H₄(SH)₂ (l) + 2 Bu₃SnH (l)  4.2

Relevant work at PNNL using rhodium homogenous catalysis

RhH + B(OPh)₃ → Rh⁺ + HB(OPh)₃⁻

Leads to LANL experiments

Examining alternatives to tin for easy hydrogenation (Philip Power, Davis)

2008 Top Priority
Investigate
Direct Rehydrogenation
LANL’s Current Engineering-Guided Ammonia-Borane Regeneration Process

**Future:** Complete most steps in one pot, with separations facilitated by solid-supported reagents and identify an energy efficient, non-gas phase hydrogen transfer reagent (in progress)
LANL’s **NEW** Engineering-Guided Ammonia-Borane Regeneration Process

**Future:** Complete most steps in one pot, with separations facilitated by solid-supported reagents and identify an energy efficient, non-gas phase hydrogen transfer reagent (in progress)
Engineering Assessment of Catalysts/Processes using Continuous Flow Reactor is Underway to Determine Catalysis Lifetime Issues

**2007** bread-board designs

**2008** reactor assembled and testing underway

- Future All heterogeneous metal catalysts will be characterized in the flow reactor
Hydrogen Stream Purity Capability is Enhanced

We can use spectroscopy and spectrometry for determining H₂ purity.
But what about effects of very small, perhaps undetectable contaminants over long operating times?
PEM Fuel Cell Provides the Final Word On H₂ Purity

2008 reactor assembled and testing underway

Small surface area fuel cell (1 cm²) is used as a sensitive detector of hydrogen purity -- and acts as a dosimeter
Impacts from the H₂ Stream on Fuel Cell Operation can be determined

Raw H₂ from thermal treatment of AB contains borazine, which is known to poison Pt fuel cell catalyst.

Fuel cell recovered under clean hydrogen and analysis indicates catalysis was poisoned, not the membrane.

- Future Test hydrogen release systems H₂ purity using long term fuel cell operation

Collaboration with Rod Borup of the LANL Fuel Cell Durability Team
Future Work

• Storage materials
  – Prepare fuels that meet DOE targets for operability (temperature, stability)
  – Identify, test new materials with potential for on-board regeneration

• Release
  – Identify, demonstrate additional non-precious metal heterogeneous catalyst with yet higher rates and with high durability for AB release

• Regeneration of AB
  – Improve process efficiency (replace CO₂ in the hydrogen transfer step)
  – Optimize and quantify yield of recycle using “real” spent fuel
  – Lab scale integrated regen process demonstration

• Engineering Guided Research
  – Hydrogen purity testing of release materials (including regenerated fuel using fuel cell as dosimeter)
  – Identify and mitigate any impacts of impurities using in situ FC performance and post-mortem analysis of FC components
  – Flow reactor catalysis testing of catalyst (kinetics, durability, extent)
  – Process modeling of liquid systems, regen complete cycle and energy efficiency analysis
Summary of LANL Technical Accomplishments

• Engineering integration is now the major driver for the chemical storage systems under development
• Heterogeneous catalysis have been identified and proven to be effective with hydrogen release from AB
• Liquid storage options for AB fuels are major priority and have multiple paths forward
• Large numbers of new materials are now under investigation for direct rehydrogenation potential for onboard regeneration
• Regen scheme is being optimized with input from ANL, with replacement of major energy intensive steps the priority
• Hydrogen gas stream purity is being examined with working fuel cell and multiple paths forward for preventing impurities
• As we move along in Phase 2 greater communication with the new Engineering Center of Excellence will be vital
## Materials Comparisons and Progress; Selected Results

### Thermolysis

<table>
<thead>
<tr>
<th>Material</th>
<th>Grav. density (Mat. wt%)</th>
<th>H₂ Flow Rate (g/s) per kg*</th>
<th>Vol. density (kg-H₂/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-aminodicoborane</td>
<td>7.2</td>
<td>.02</td>
<td>.05 (est.)</td>
</tr>
<tr>
<td>LiZnAB₃</td>
<td>9.3</td>
<td>.02</td>
<td>.07 (est.)</td>
</tr>
<tr>
<td>ScAB₃</td>
<td>11.1</td>
<td>New work</td>
<td>.05 (est.)</td>
</tr>
<tr>
<td>Homog. Fe catalyst-1</td>
<td>1 eq. H₂/AB</td>
<td>.058</td>
<td>Not measured</td>
</tr>
<tr>
<td>Homog. Fe catalyst-2 2007</td>
<td>1.8 eq. H₂/AB</td>
<td>.008</td>
<td>Not measured</td>
</tr>
<tr>
<td>Not measured</td>
<td></td>
<td></td>
<td></td>
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### Catalysis

<table>
<thead>
<tr>
<th>Material</th>
<th>DOE System Targets for Hydrogen Storage Systems</th>
</tr>
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<tbody>
<tr>
<td>Volumetric Density (kg-H₂/L)</td>
<td>0.036 (2007), 0.045 (2010), 0.081 (2015)</td>
</tr>
</tbody>
</table>

* DOE target = .02 g/s/kW; rate/kg is roughly equal to rate/kW
Team & Collaborators

Chemical Hydrogen Storage COE Partners

IPHE Partners