DOE Chemical Hydrogen Storage Center of Excellence

Low-Cost Precursors to Novel Hydrogen Storage Materials

Project ID# ST8

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Rohm and Haas Company
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Overview

**Timeline**

- Start: March 1, 2005
- End: February 28, 2010
- 60% complete

**Barriers**

- Cost
- Energy efficiency
- Regeneration processes
- System life cycle assessment

**Budget**

<table>
<thead>
<tr>
<th></th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Total Funding</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE</td>
<td>$1,136K</td>
<td>$632K</td>
<td>$1,768K</td>
</tr>
<tr>
<td>ROH</td>
<td>$537K</td>
<td>$285K</td>
<td>$822K</td>
</tr>
</tbody>
</table>

Overall 68:32 DOE:ROH Split

A Continuation Application with new scope and budget has been submitted to DOE.
Objectives

- Overall: Develop and advance novel hydrogen storage materials to meet DOE 2010 targets and with potential to meet 2015 targets
  - Leverage expertise and experience across Center: engineering requirements, economics, life cycle analysis
  - Support DOE Chemical H₂ Storage Systems Analysis Sub-Group
- Define and evaluate novel chemistries and processes for producing chemical hydrides (Phase 1)
  - Emphasis on low-cost routes to regenerate sodium borohydride from spent fuel leading to Go/No-Go Review
- Identify cost and energy efficient pathways to “first fill” and regeneration for ammonia borane (AB) and other borane materials (Phase 2)
  - Continue experimentation leading to selection of single pathway for low-cost NaBH₄ and further AB process technology development
  - Guide selection of a top AB regeneration scheme for experimental studies on most promising alternatives
Go/No-Go Process: Basis of Center Evaluations Moving Forward

- NaBH₄ process provided valuable experience in requirements for the life cycle of a chemical hydride system
  - Data requirements
  - Analysis assumptions
  - Applicable to AB and other systems of promise
- Independent Review Panel
  - University and National Laboratory experts
- Recommendations
  - No-Go for hydrolysis of NaBH₄ for on-board vehicular H₂ storage
  - Continue research activities on low cost NaBH₄ pathways
    - NaBH₄ is a key starting material for AB and other borane-based on-board H₂ storage systems under consideration
    - Improvements in NaBH₄ production will lead to cost-effective production (first fill) of these systems
Low Cost NaBH₄ is Essential to Center Success

- Low Cost Ammonia Borane (and other borane-based materials) requires low cost NaBH₄ for initial system fill
  - NaBH₄ is dominant component to AB costs
    \[ n\text{NaBH}_4 + (\text{NH}_4)_n\text{X} = n\text{NH}_3\text{BH}_3 + \text{Na}_n\text{X} + n\text{H}_2 \]
  - Lower cost NaBH₄ technologies needed

<table>
<thead>
<tr>
<th>DOE Storage System Cost Targets</th>
<th>$/kg H₂</th>
<th>$/kg AB *</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>200</td>
<td>8.7</td>
</tr>
<tr>
<td>2010</td>
<td>133</td>
<td>5.8</td>
</tr>
<tr>
<td>2015</td>
<td>67</td>
<td>2.9</td>
</tr>
</tbody>
</table>

* assume media is 33% of system cost
  (from TIAX SAH study)

Need < $5/kg NaBH₄ for 2010, < $3/kg for 2015

Impact of NaBH₄ on AB RM Costs
## Milestones

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No Go Decision</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 2007</td>
<td>Key chemistries demonstrated to validate leading NaBH₄ chemical pathways.</td>
</tr>
<tr>
<td>September 2007</td>
<td>Feasibility of leading NaBH₄ pathways established based on laboratory-scale experimental demonstration and cost analysis.</td>
</tr>
<tr>
<td>November 2007</td>
<td>No Go decision for NaBH₄ for on-board hydrogen release; <em>Go decision to progress R&amp;D on NaBH₄ synthesis for low cost first fill AB</em></td>
</tr>
<tr>
<td>July 2009</td>
<td>Top NaBH₄ synthesis route selected for development</td>
</tr>
</tbody>
</table>
Technical Approach

**Identify Leading Pathways**
- Develop screening and evaluation criteria specific to NaBH₄ regeneration cycles
- Review prior technical and patent literature
- Select leading NaBH₄ regeneration pathways based on theoretical energy efficiencies from reaction energetics and relevant metrics

**Determine Feasibility of Leading Pathways**
- Demonstrate key chemical and process steps in laboratory studies
- Develop flow sheets and preliminary energy requirements and cost estimates for leading systems

**Detail Performance to Select Single Pathway**
- Establish complete material balance to determine intermediates and purification requirements
- Demonstrate all chemical and process steps
- Investigate scalability

**Single Pathway Selected**
- Develop single NaBH₄ process
- Update economics
Technical Accomplishments

Overview

• Feasibility of 2 new low-cost NaBH₄ routes identified
  – Metal reduction of borate
  – Carbothermal reduction of borate

• Key chemistry step of NaBH₄ formation demonstrated

• Conceptual processes developed show significantly improved energy efficiency and lower cost compared to current Schlesinger technology

• Research on electrochemical reduction pathways to NaBH₄ discontinued (Penn State)

• Spent AB regeneration analysis support initiated
Leading NaBH₄ Pathways Identified

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schlesinger (current)</td>
<td>4NaH + B(OCH₃)₃ → NaBH₄ + 3NaOCH₃ - 25% utilization of Na metal</td>
</tr>
<tr>
<td>Metal Reduction</td>
<td>1-step: NaBO₂ + 2x/y M + 2H₂ → NaBH₄ + 2/y MₓOᵧ</td>
</tr>
<tr>
<td></td>
<td>2-step: 2x/y M + 2H₂ → 2x/y MH₂yₓₓ ⟷ NaBO₂ + 2x/y MH₂yₓₓ → NaBH₄ + 2/y MₓOᵧ</td>
</tr>
<tr>
<td></td>
<td>- lower-cost metal and lower usage vs. Na</td>
</tr>
<tr>
<td></td>
<td>- reactive milling</td>
</tr>
<tr>
<td>Carbothermal Reduction</td>
<td>NaBO₂ + 2CH₄ → NaBH₄ + 2CO + 2H₂</td>
</tr>
<tr>
<td></td>
<td>- methane instead of metal reductant</td>
</tr>
<tr>
<td></td>
<td>- syn gas (CO/H₂) byproduct</td>
</tr>
<tr>
<td></td>
<td>- high temperature to convert B-O to B-H</td>
</tr>
</tbody>
</table>
Metal-Based Reduction Feasibility Established

11B NMR confirms and quantifies NaBH₄ formation

Lab reactive milling capabilities established

High NaBH₄ yields demonstrated with metal hydrides
Carbothermal Reduction Feasibility Established

Reactions favored at high temperatures

INL claims NaBH₄ formation under plasma conditions

**Pre-combustion:**
\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
3\text{CH}_4 + \text{CO}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{CO} + 8\text{H}_2 \\
\text{Net: } 4\text{CH}_4 + 2\text{O}_2 & \rightarrow 4\text{CO} + 8\text{H}_2
\end{align*}
\]

**Borate Reduction:**
\[
\text{NaBO}_2 + 2\text{CH}_4 \rightarrow \text{NaBH}_4 + 2\text{CO} + 2\text{H}_2
\]

**Chemical flame torch**
**Electric Arc**
**Electrode**
**Insulator**
**Feeds**
**Collection chamber**

From US Patent 7,354,561
NaBH₄ Regeneration Conceptual Process Using Metal Reduction

\[ \text{NaBO}_2 + \frac{2x}{y} \text{M} + 2\text{H}_2 \rightarrow \text{NaBH}_4 + \frac{2}{y} \text{M}_x\text{O}_y \]
NaBH₄ Regeneration Conceptual Process Using Carbothermal Reduction

NaBO₂ + 2CH₄ → NaBH₄ + 2CO + 2H₂

Lower cost and higher efficiency process expected with elimination of metal recovery.
Cost Estimating Methodology Established

- Conceptual Process Flowsheets
  - Equipment List
    - Physical properties
    - Heuristics
  - Labor Requirements
    - Wage Rates
- Material Balance
- Energy Balance
- Process Efficiency
- Aspen IPE™
- Capital Investment
- H2A
- Raw Material Costs
- Energy/Utility Costs
- Delivered H₂ Cost
- Maintenance Property Overhead
- Capital Cost
Regenerated NaBH$_4$ Costs Approach DOE Fuel Targets

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Cost, $/kg H$_2$</th>
<th>Fuel Energy Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE 2010 Target</td>
<td>2-3</td>
<td>60%</td>
</tr>
<tr>
<td>Metal Reduction</td>
<td>6-12</td>
<td>43(19)%</td>
</tr>
<tr>
<td>Carbothermal Reduction</td>
<td>2-7</td>
<td>50(19)%</td>
</tr>
</tbody>
</table>

Cost ranges reflect sensitivities in yield, production volume, capital investment, utility costs, byproduct values, and labor costs.

1 - Delivered H$_2$ cost to auto
2 - Energy content of H$_2$ delivered to auto relative to total energy to process including fuel input energy of H$_2$ and any other fuel streams used for generating process heat and electrical energy. Electricity from hydroelectric. () indicates efficiency based on US Electrical Grid.
Sensitivity Analysis Shows Scenarios to Achieve DOE Fuel Cost Targets

Carbothermal Reduction Route (Base = $6.0/kg)

- Fuel Gases as Feedstock
- Electricity Cost
- Investment Cost
- Regen Conversion
- Plant Capacity
- Labor Cost
- Natural Gas Cost
- NaBH4 Content and HOD Yield

Fuel Cost, $/kg H₂

Target

1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5

Grid 5.5¢/GJ

Fuel value

Hydro 3¢/GJ

Fuel value

Grid 5.5¢/GJ

Carbothermal Reduction Route (Base = $6.0/kg)

- Fuel Gases as Feedstock
- Electricity Cost
- Investment Cost
- Regen Conversion
- Plant Capacity
- Labor Cost
- Natural Gas Cost
- NaBH4 Content and HOD Yield

Fuel Cost, $/kg H₂

Target

1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5

Grid 5.5¢/GJ

Fuel value

Hydro 3¢/GJ

Fuel value

Grid 5.5¢/GJ

Carbothermal Reduction Route (Base = $6.0/kg)
Low Cost NaBH₄ Routes Will Help AB Meet DOE Storage System Cost Targets

- With No-Go decision for on-board NaBH₄ hydrolysis, focus turns to low cost means for first charge of fuel (AB)
- Project scope unchanged - NaBH₄ paths applicable to borate as raw material or as spent fuel
- With lower NaBH₄ demand, efficient energy sources (i.e., hydroelectric) may be practical

<table>
<thead>
<tr>
<th>Pathway</th>
<th>H₂ Cost, $/kg</th>
<th>AB Cost, $/kg * (NaBH₄ RM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Reduction</td>
<td>6-12</td>
<td>1.6-3.1</td>
</tr>
<tr>
<td>Carbothermal Reduction</td>
<td>2-7</td>
<td>0.5-1.8</td>
</tr>
</tbody>
</table>

* Excludes borate feed cost; 100% yield to AB
Assuming AB media is 33% of storage system costs, AB media cost targets are $5.8/kg AB in 2010 and $2.9/kg AB in 2015.
Future Work

- Progress process R&D to create high-yield, low-cost scalable NaBH₄ process for first fill AB
  - Continue studies on both metal-based and carbothermal reduction
    - Identify byproduct formation
    - Define chemistry and process window
    - Identify scale-up options and evaluate viability
    - Develop separation and purification needs
    - Detail conceptual process and costs
  - Select single top pathway
    - Continue R&D to define and develop process
    - Update flowsheets and economics
    - Develop life cycle impacts
Future Work (cont.)

• Support AB synthesis and regeneration research
  – Apply NaBH₄ metrics-based process to select top AB pathways
  – Provide conceptual process development and cost estimates
  – Conduct “first fill” AB synthesis process analysis

Define high yield, low cost, scalable processes

• Leverage Rohm and Haas competencies across Center
  – Process development
  – Engineering assessment
Summary

• Experimental studies confirmed feasibility of two leading pathways for regenerating NaBH₄ from spent borate fuel
  – Metal reduction
  – Carbothermal reduction
  – *Both show potential for significant cost improvement over current Schlesinger process*

• Independent Panel Review found
  – Sound chemistry, but early stage
  – NaBH₄ analysis methodology valuable: tool applicable to AB and other promising storage materials

• Research on low-cost pathways to NaBH₄ will continue
  – NaBH₄ is a key starting material for AB and other borane-based materials under consideration
  – Improvements in NaBH₄ production will lead to cost-effective “first fill” for these systems

• Phase 2 focus
  – Detailing conceptual process and cost for top NaBH₄ pathway
  – Applying metrics-based NaBH₄ pathway analysis to AB assessments
Collaboration and Technology Transfer
Phase 2

• AB regeneration processes
  – Rohm and Haas, PNNL, LANL, U. Penn

• “First fill” AB process analysis
  – Rohm and Haas, PNNL, LANL
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