Process for the Regeneration of Sodium Borate to Sodium Borohydride

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## Overview

### Timeline
- **Project start date:** Fiscal Year 2004
- **Project end date:** Fiscal Year 2006
- **Percent complete:** 90%

### Barriers
- A. Cost
- C. Efficiency
- G. Life Cycle and Efficiency Analyses
- Q. Regeneration for Irreversible Systems
- R. By-Product Removal
- Other: Applicable to Off-Board Delivery and Storage

### Budget
- **Total funding:** $4.5 MM, 3 yrs
- **DOE share:** $3.6 MM
- **MCEL share:** $0.6 MM
- **APCI share:** $0.4 MM
- **Funding received in FY06:** $0.566 MM
- **Funding for FY07:** $0.120 MM

### Partners
- Millennium Cell - Na/B Separation, Engineering, Membrane development.
- Princeton University - Direct borate electrolysis.
**Objectives**

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Project Objectives</th>
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<tbody>
<tr>
<td><strong>A. Cost</strong></td>
<td>Develop regeneration process for NaBH₄ that significantly lowers its cost</td>
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<tr>
<td><strong>C. Efficiency</strong></td>
<td>Improve overall energy efficiency; Demonstrate feasibility of achieving ~50% “well-to-tank” efficiency.</td>
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<tr>
<td><strong>G. Life Cycle and Efficiency Analyses</strong></td>
<td>Conduct a high-level energy efficiency assessment based on the newly-developed re-generation process.</td>
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<tr>
<td><strong>Q. Regeneration Processes for Irreversible Systems</strong></td>
<td>Develop energy efficient and cost effective process for off-board regeneration of NaBH₄.</td>
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<tr>
<td><strong>R. By-Product Removal</strong></td>
<td>Develop a process that re-uses the by-product NaBO₂, thereby completing the recycling loop.</td>
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Status Against DOE Targets

**Objective:**
- Reduce SBH cost

**Status:**
- Current SBH: **$40-60** /kg purchased
- Reported in May 2005: estimated ~$7/kg production cost when NaOH electrolysis is implemented

**Further cost reduction:**
- Co-production of Na and Boric acid from recycled borate
- One-pot reaction from borate to SBH.

**DOE Target:**
- $2-3/kg H₂ is equivalent to $0.40-0.50/kg SBH.
Approach

- Use Electrochemical process to achieve high energy efficiency
  - Highly efficient pathway to key precursor for SBH.
  - Direct electrolysis of spent fuel
  - One-pot electrolysis for SBH synthesis

- Reduce number of steps in regeneration process
  - Eliminate costly and inefficient separation and purification steps

- Couple engineering development with bench scale testing
  - Safety and cost considerations

- Multi-discipline approach that includes chemistry, materials science, and engineering
  - Reaction kinetics studies
  - Materials compatibility and durability studies
  - Reactor and process designs
Approach
- utilizing recycled material

Spent fuel (NaBO₂/H₂O) → Electrolysis → 3 NaOH → Electrolysis → H₂

4 Na → H₂ → 3 NaOCH₃ → H₂O

B(OCH₃)₃ → MeOH

MeOH, H₂O → MeOH, H₂O → H₂O

NaBH₄ → H₂

Recycle

3 NaOH, NaBH₄, H₂O → 3 NaOH, NaBH₄, H₂O

MeOH, H₂O → B(OCH₃)₃/3MeOH azeotrope

Na₂B₄O₇ or H₃BO₃ → MeOH

H₂O → H₂
Accomplishments

**Reaction Chemistry**
- Measured current density in NaOH and NaBO$_2$ electrolysis
- Demonstrated that precursors to NaBH$_4$ synthesis can be made from the direct electrolysis of spent fuel
- Showed the feasibility of synthesizing BH$_4$ in ionic liquids at room temperature (current commercial NaBH$_4$ process: 275°C)

**Preliminary Engineering Assessment**
- Completed preliminary engineering:
  - PFDs, P&IDs, Equipment List, Equipment Specs
- Materials performance testing for reactor:
- Process modeling using HYSYS: 40% complete
- Safety and hazard assessment: 40% complete

**Preliminary Cost Assessment**
- Established plant scale
- Gathered initial information on electrolyzer cost
“One-Pot” Borohydride Electrochemical Generation

\[
\begin{align*}
\text{LiBr} & \rightarrow \text{Li} + \text{Br}_2 \quad \text{eq 1} \\
\text{Li} + \text{H}_2 & \rightarrow \text{LiH} \quad \text{eq 2} \\
\text{LiH} + \text{B}_2\text{O}_3 & \rightarrow \text{LiBO}_2 + \text{LiBH}_4 \quad \text{eq 3}
\end{align*}
\]

- Reaction sequence takes place in one pot, with no need for separations
- Yield is currently low (<10%), most likely due to the low solubility of \( \text{H}_2 \) in the melt at reaction temperature (275 °C).
- Work at subcontractor (Princeton) **focused on utilizing melts with higher \( \text{H}_2 \) solubility**

**Status:**
- **1st Step:** Demonstrated the hydride transfer chemistry with commercially available hydrides and borate
- **2nd Step:** Will Attempt electrochemical synthesis of hydride when the chemistry and analysis methods are in hand
One-pot SBH synthesis in ionic liquids

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>M.P. (°C)</th>
</tr>
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<tbody>
<tr>
<td>1-butyl-1-methyl-pyrrolidinium tris(pentafluoroethyl)trifluorophosphate</td>
<td>-50</td>
</tr>
<tr>
<td>Trihexyl-tetradecyl-phosphonium tris(pentafluoroethyl)trifluorophosphate</td>
<td>-50</td>
</tr>
<tr>
<td>1-butyl-2,3-dimethylimidazolium chloride</td>
<td>89</td>
</tr>
</tbody>
</table>

- **Step 1**: successfully demonstrated the synthesis of NaBH$_4$ in the first two ionic liquids at room temperature, with hydride starting material.
- **Remain to be shown**: same reactions can take place with electrochemically generated hydride.
Experimental Focus:
- Electrochemical generation of hydride with subsequent formation of BH$_4^-$ in the same cell.
- Trimethyl borate species has been shown to be electrochemically activated at Pt and Li electrodes.

Results so far:
- In the absence of Li or Na as counter cations to the hydride, B-O species was converted into B-F species.
- Conversion of B-O to B-F occurs only with applied voltage indicating electroactivity.

Future experiments:
- Will include addition of H$_2$ at cathode as well as Li or Na to make borohydride.
**Method:**
Direct recovery of Na metal and borate from NaBO₂ spent fuel, for use in SBH synthesis

**Experimental Set-up**

**NaSICON membrane**
- Aqueous NaBO₂
- Molten Sodium Pool
- NaSICON Membrane
- Nickel Plate
- Cathode
- Anode

**Na-β”-alumina membrane**
- Aqueous Metaborate
- Molten Sodium Pool
- Alumina Tube
- Nickel Plate
- Cathode
- Anode
Sodium and Boron Separation
- Effect of Applied Potential

Cathode Rxn: \[ 4 \text{Na}^+ + 4 \text{e}^- \rightarrow 4 \text{Na} \]
Anode Rxn: \[ 4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \]
Anode Solution Rxn: \[ 4 \text{B(OH)}_4^- \rightarrow 4 \text{B(OH)}_3 + 4 \text{OH}^- \]
Overall Rxn: \[ \text{NaB(OH)}_4 \rightarrow \text{Na} + \text{B(OH)}_3 + \frac{1}{4} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} \]

- Onset potential = 3.2 V
- Higher potential required to achieve sufficient reaction rate

Example Experimental Results

<table>
<thead>
<tr>
<th></th>
<th>Potential (V)</th>
<th>Current (mA)</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run A</td>
<td>3.5</td>
<td>4.8</td>
<td>85%</td>
</tr>
<tr>
<td>Run B</td>
<td>5.0</td>
<td>125</td>
<td>96%</td>
</tr>
</tbody>
</table>
Sodium and Borate Separation

<table>
<thead>
<tr>
<th>Aqueous Solution</th>
<th>Na-β”-alumina</th>
<th>NaSICON</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBO₂ (concentrated)</td>
<td>100% Current Efficiency</td>
<td>No reaction</td>
</tr>
<tr>
<td>NaBO₂ (dilute)</td>
<td>Failed – 0% yield</td>
<td>60-70% yield</td>
</tr>
<tr>
<td>NaOH (concentrated)</td>
<td>100% Current Efficiency</td>
<td>No reaction</td>
</tr>
<tr>
<td>NaOH (dilute)</td>
<td>To be tested</td>
<td>Partial rxn, membrane damaged</td>
</tr>
<tr>
<td>Borax (concentrated)</td>
<td>100% Current Efficiency</td>
<td>To be tested</td>
</tr>
<tr>
<td>Borax (dilute)</td>
<td>To be tested</td>
<td>30-35% yield</td>
</tr>
<tr>
<td>“Spent Fuel” from HOD®</td>
<td>100% Current Efficiency</td>
<td>Failed, membrane damaged</td>
</tr>
</tbody>
</table>

Initial Experiments Appear to Indicate:
• Na-β”-Alumina is more effective with concentrated solutions while NaSICON is more effective with dilute solutions
• Further experimentation needed to obtain additional insight
• Higher current densities were achieved in hydroxide solutions than in the corresponding borate solutions.

• Membranes exhibited better stability in borate solutions.

• Use of β”-alumina allowed 99+% current efficiencies in both the borate and the hydroxide melts tested.

Note: β”-Alumina membranes with Ni counter electrode
Theoretical Minimum Potential = 2.94 V at 115 °C

- Increasing applied potential increases current density but also decreases the voltage efficiency.

Optimized Current Density

Measured Current Density vs. Voltage Efficiency
Effects of Membrane Composition

Of the two types of $\beta''$-membranes tested, Membrane A exhibits higher current densities and is more resistant to failure than Membrane B.
Preliminary Engineering

**Tasks**

- Based on results generated from bench scale experiments, design a process for scale up operation and cost estimates
- Determine materials of construction for components of electrochemical reactor.
- Verify physical properties of membrane.
- Design of electrochemical reactor for continuous flow operation.
- Perform safety and hazard analysis (e.g. FMEA)

**Accomplishments**

- Established basic Process Flow Diagram (PFD)
- Started to generated equipment list and equipment specifications
- Developed Piping and Instrumentation Diagram (P&ID)
- Completed preliminary mass balance
- Process simulation (modeling) using Aspen HYSYS software
Preliminary Engineering

Molten salt electrolysis requires converting spent fuel to anhydrous starting materials – high cost

Aqueous electrolysis allows the direct use of spent fuel – low cost

Trade-off: lower current density, therefore more membrane required
Process Flow Diagram

Initial Process Flow Design

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**System Components:***

- Sodium Storage Vessel T-101
- Sodium Heater HX-101
- E-Reactor R-101
- Caustic Soda Heater HX-102
- Caustic Soda Pump P-102
- Caustic Soda Storage Vessel T-102

**Flow Pathways:**

4. Sodium is heated in Sodium Heater HX-101.
5. Sodium flows to E-Reactor R-101.
7. Process water from Process Water Tank T-105 is used in the process.

**Additional Components:**

- Caustic Condenser HX-103
- Small Flash Drum T-104
- Water-05-T-031

**To Atmosphere:**

- Vapor-05-T-007

**System Notes:**

- The system uses a variety of heat exchangers and pumps to control the flow and temperature of sodium and other chemicals.
- The process is designed to efficiently manage the flow of materials between the various vessels and components.
Cost Reduction Summary

- Of the 3 options investigated, only the route via Na cost reduction is mature enough to allow for a reasonable preliminary cost analysis.
- For the Na/B co-production route and the direct BH route, more data is needed on reaction yields and electrolytic efficiency before conducting cost analysis.

**Na Metal Production Cost**

*via electrolysis of NaOH or NaCl*

- NaCl (anhydr.)
  - Na Price: $3.50/kg Na
  - Est'd Prod. Cost ($/kg Na): $1.50
  - Est'd elec input (kWh/kg Na): 10 kWh/kg Na

- NaOH ( melt) w/ H2 assist
  - Na Price: $1.13/kg Na
  - Est'd Prod. Cost ($/kg Na): $1.13
  - Est'd elec input (kWh/kg Na): 1.7 kWh/kg Na

- NaOH (aq.)
  - Na Price: $0.90/kg Na
  - Est'd Prod. Cost ($/kg Na): $0.90
  - Est'd elec input (kWh/kg Na): 3.6 kWh/kg Na

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**NaBH₄ Cost Reduction Roadmap**

- Current
  - Production Cost ($/kg NaBH₄) = $1.2/kg Na
- 1st Improv't
  - Achieved
- 2nd Improv't
- Final Target
Improvements in Efficiency

Producing Na from NaOH instead of NaCl is more energy efficient

**Cell Temp**
- NaCl (anhydr.)
- NaOH (melt) w/ H2 assist
- NaOH (aq.)

**Cell Voltage**
- NaCl (anhydr.)
- NaOH (melt) w/ H2 assist
- NaOH (aq.)

**Elec Efficiency**
- NaCl (anhydr.)
- NaOH (melt) w/ H2 assist
- NaOH (aq.)

NaOH Electrolysis is
Lower in Temperature
Lower in Voltage
Higher in Efficiency
## Comparison of Electrical Energy Input

<table>
<thead>
<tr>
<th></th>
<th>NaCl (anhydrous)</th>
<th>NaOH (Anhydrous)</th>
<th>Aqueous NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Current efficiency</strong></td>
<td>80 %</td>
<td>100 %</td>
<td>100 %</td>
</tr>
<tr>
<td><strong>Voltage efficiency</strong></td>
<td>56 %</td>
<td>90% (with H₂-assist)</td>
<td>70 %</td>
</tr>
<tr>
<td><strong>Overall electrical efficiency</strong></td>
<td>45%</td>
<td>90%</td>
<td>70%</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>600 °C</td>
<td>350 °C</td>
<td>110 °C</td>
</tr>
<tr>
<td><strong>Cell Operating Voltage</strong></td>
<td>6 - 7 V</td>
<td>2.8</td>
<td>4.2</td>
</tr>
<tr>
<td><strong>Electrical energy input per kg Na produced</strong></td>
<td>10 kWh/kg</td>
<td>1.6 – 3.6 kWh/kg</td>
<td>2.4 – 4.2 kWh/kg</td>
</tr>
<tr>
<td><strong>Estimated Na production cost</strong></td>
<td>$ 1.57 /kg</td>
<td>$1.22 /kg</td>
<td>$0.90 /kg</td>
</tr>
</tbody>
</table>
Well-to-Tank Efficiency

Energy Input for the Production of NaBH₄ via 3 different methods of Na production

- The majority of the energy input is in the Na production
- Producing Na by H₂-assisted electrolysis dramatically reduced the upfront energy input in the NaBH₄ manufacturing process.
- US production of Na metal uses hydro-electric energy almost exclusively, resulting in very little CO₂ emission.

W-t-T Efficiency: 25% 54% 60%
Future Work

**Preliminary Engineering Assessment**
- Continue materials chemical compatibility tests
- Complete HYSYS process modeling for the process
- Complete safety and hazard assessment

**Membrane Testing**
- Explore methods to increase current densities in borate electrolysis
- Additional experiments using other inexpensive sodium salts, e.g. borax or borate-caustic mixtures
- Long-term stability tests
- Equivalent quantitative experiments with NaSICON membranes
- Explore new electrochemical cell configuration

**Preliminary Cost Assessment**
- Complete cost assessment associated with electrolysis of borate
- Coordinate with TIAX

**Project Go/no-go Decision with DOE**
After demonstration SBH regeneration cost reduction via NaOH electrolysis last year, further demonstrated feasibility of direct electrolysis of spent fuel (NaBO₂) to obtain precursors to SBH synthesis, namely Na metal and non caustic borates.

- Expanded the one-pot reaction of borohydride synthesis in medium temperature halide melt to room temperature ionic liquids.
- Initiated process engineering assessment in order to establish cost estimates of SBH regeneration
- Gained significant insight into the concentration sensitivity of the electrolytic processes, particularly its effect on various membranes
- Continue down the path of cost reduction and efficiency improvement