Electrochemical Hydrogen Storage Systems

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Project ID
ST 26

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Overview

Timeline
- Project start date: 3/1/05
- Project end date: 9/20/09
- Percent complete: 40%

Budget
- Total project funding
  - DOE share: $1,215,637
  - Contractor share: $303,910
- Funding FY06: $250,000
- Funding for FY07: $280,000

Barriers
- Barriers addressed:
  - R: Regeneration processes for sodium borohydride.
  - Determine whether, electrochemically, the polyboranes can reversibly store hydrogen.

Partners
- Technical guidance for B-O to B-H:
  - LANL
  - Millennium Cell
  - Rohm and Haas (R&H)
- Technical guidance for polyboranes:
  - Fred Hawthorne
## Objectives

| Overall | ➢ Demonstrate an electrochemical route to the conversion of metaborate to sodium borohydride to meet DOE 2010 regeneration process goals.  
➢ Explore the feasibility of reversible electrochemical hydrogen storage in the polyboranes. |
Technical Approach

Reversible H\textsubscript{2} storage

Electrochemical reduction

BO\textsubscript{2}\textsuperscript{-} → BH\textsubscript{4}\textsuperscript{-}

Chemical reduction

Electrochemical transformations in Polyboranes
These experiments include attempts to reproduce Rohm and Haas’ past positive results:
- One-step reductions in aqueous media using high hydrogen overpotential cathode materials (Hg pool, graphite felt, Ni/PTFE, other novel materials).
- Reductions in non-aqueous media of sodium trimethoxyborohydride (STMB).

Electroreduction experiments

Analytical methods

Establish analytical methods for unequivocal determination of sodium borohydride:
- Cyclic voltammetry
- $^{11}$B NMR

High temperature experiments

Enhance the rate to overcome kinetic limitations.
Technical Approach (cont.)

- **Chemical reduction of B-O to B-H**
  - *Plasma*
  - Hydrogenate boric acid with plasma-generated hydrogen atoms in the absence of electrochemical limitations (e.g., coulombic repulsion of anionic borate ion from a negatively-charged electrode surface)

- **Electrochemistry of polyboranes**
  - *Electrochemistry of polyboranes*
  - Exploring large boron/hydrogen compounds that contain both protic and hydridic hydrogen that should be electrochemically active and may release/absorb hydrogen reversibly upon changing the voltage

- **Electrochemical Impedance Spectroscopy**
  - Used to discern mechanisms of complex, coupled charge transfer/chemical reactions.
Electrochemical reduction of B-O to B-H
Cyclic Voltammetric Method for Sodium Borohydride Analysis

- Fast and easy method for BH$_4^-$ quantification

- Using 6mm electrode the linearity range and sensitivity (slope) is higher than when using a 1mm electrode.

Cyclic voltammetry of a 20mM BH$_4^-$ solution in 2M NaOH

Calibration curves in different electrolytes

- The detection limit and quantification limit depends on the electrolyte composition.
Experimental Parameters

Current

- 100mA, 300mA
- Cell potential was measured to be about 18V at 100mA.
- Maybe the cell resistance is too high

Catholyte:

- 2M KOH/MeOH + STMB
- 0.5M KOH/MeOH + STMB
- Isopropylamine → suggested by ROH (in progress)

STMB Experiments

Stoichiometry:

\[
\text{NaBH(OCH}_3\text{)}_3 + 6\cdot \text{H}^+ + 6\text{e}^- \rightarrow \text{NaBH}_4 + 3\cdot \text{CH}_3\text{OH}
\]

- Reduction
- Disproportionation

\[
4\cdot \text{NaBH(OCH}_3\text{)}_3 \rightarrow \text{NaBH}_4 + 3\cdot \text{NaB(OCH}_3\text{)}_4
\]
STMB Experiments

Stability test of STMB without electrolysis
10mM BH₄⁻ (2M KOH/MeOH)

Electrolysis of STMB in 2M KOH/MeOH

Not stable → peak current decreases with time even in 2M KOH

Peak current after electrolysis decreased and temperature increased to 35ºC

Even in 2M KOH/MeOH there is a tendency for the peak current to decrease
STMB decomposing or converting to SBH?

No evidence of BH₄⁻ generation using MeOH as a solvent

4HB(OMe)₃⁻ → BH₄⁻ + 3B(OMe)₄⁻

BH(OCH₃)₃⁻+CH₃OH → H₂+B(OCH₃)₄⁻
Graphite Felt Experiments

Results

> Use of TMAH to increase $H_2$ overpotential on the carbon felt → suggested by R&H

Symmetrical electrolyte:
25% $NaBO_2 + 2M NaOH.$
Current density: 5 mA/cm$^2.$

Symmetrical electrolyte:
12.5% $NaBO_2 + 1M TMAH.$
Current density: 5 mA/cm$^2.$

No evidence of $BH_4^-$ generation
Hg Experiments

Results

Cathode: Hg pool (13mm diameter)
Positive control (2mM BH$_4^-$) in 2M TEAH + 0.2M H$_3$BO$_3$

- Increase in the reduction rate using R$_4$NOH may be possible
- Important observation: electrolysis at 10 mA, tiny Hg droplets were observed in solution.

Not stable → peak current decreases with time

Positive control (2mM BH$_4^-$) in 2M TEAH + 0.2M H$_3$BO$_3$
Double layer modification

Objective: Modify potential profile in the interphase region to encourage close approach of B(OH)$_4^-$ ion for reduction.

EDL in absence of specific adsorption

EDL in presence of specific adsorption

Legend
- SAI: Specifically Adsorbed Ion
- IHP: Inner Helmholtz Plane
- OHP: Outer Helmholtz Plane
- Red: Potential Profile

Specifically adsorbable cations include $R_4N^+$, Cs$^+$, Tl$^+$.  
[Habib and Bockris. Specific Adsorption of Ions, in: Comprehensive Treatise of Electrochemistry, v.1.]
Hg Experiments

**Results**

Cathode: Hg pool (13mm diameter); 10 mA during 5 days

- **Current:**
  - 10mA
- **Symmetrical electrolyte**
  - 2M TEAH + 0.2M H$_3$BO$_3$.

Possible presence of BH$_4^-$

Potential, V vs. Hg/HgO

First Positive Result
Results

Cathode: Au foil (7.5 cm²)

Positive control (2mM BH₄⁻) at open circuit in 2M TEAH + 0.2M H₃BO₃

Metal surfaces catalyzes BH₄⁻ hydrolysis at open circuit

BH₄⁻ not stable

peak current decreases with time

It may explain lack of reproducibility with Hg experiments
High Temperature Aqueous Experiments

- Voltammogram of 2M NaOH + 0.2M NaBO₂ at Hg-plated copper electrode.
- Electrode was rotated at 100rpm; sweep rate was 50mV/s.
- H₂ was bubbled through electrolyte at a pressure of 20psi.
- Red circle shows a small cathodic hump ca. -1.60V vs. Ag/AgCl that is visible when a temperature of 175°C was used.

Presence of a small hump! Almost certainly not of borohydride.
# Summary of the Electrochemical Experiments Performed

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Catholyte</th>
<th>Current</th>
<th>BH$_4^-$ generation?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon felt experiments</td>
<td>Carbon felt, 25% w NaBO$_2$ (pH=12), 25% w NaBO$_2$ + 2M NaOH</td>
<td>7.5 mA, 37.5 mA</td>
<td>None Detected</td>
</tr>
<tr>
<td>Ni-PTFE</td>
<td>Ni-PTFE, 1M TMAH + 0.5M H$_3$BO$_3$ (pH&gt;13.5)</td>
<td>100 mA, 300 mA</td>
<td>Tentative Positive Result In progress</td>
</tr>
<tr>
<td>Hg Experiments</td>
<td>Hg, Hg/Cu, 2M TEAH + 0.2M H$_3$BO$_3$</td>
<td>1 mA Hg pool (13 mm diameter), 10 mA Hg pool (13 mm diameter), 25 mA Cu/Hg</td>
<td>First Positive Result In progress</td>
</tr>
<tr>
<td>STMB</td>
<td>Pd, 2M KOH/MeOH</td>
<td>100 mA, 300 mA</td>
<td>In progress (other solvents)</td>
</tr>
<tr>
<td>High temperature</td>
<td>Hg/Cu, 2M NaOH + 0.2M NaBO$_2$</td>
<td>Exploratory CV</td>
<td>None Detected</td>
</tr>
</tbody>
</table>
Chemical reduction of B-O to B-H
Hydrogen Plasma

Determine B-H compounds produced via Hydrogen plasma reactions below

\[ B(OH)_3 + H \rightarrow B(OH)_2 + H_2O \]
\[ B(OH)_2 + H \rightarrow BH(OH)_2 \]
\[ BH(OH)_2 + H \rightarrow BH(OH) + H_2O \]
\[ BH(OH) + H \rightarrow BH_2(OH) \]

etc

Determine reaction conditions that produced the desired B-H species
Hydrogen Plasma

Experiments:

- Two reactors have been purchased and are currently being installed
  - 13.56 MHz (RF or “cold” plasma)
  - 2.54 GHz (microwave or “hot” plasma)

- Volatile B-H compounds will be analyzed via in-line residual gas analyzer
  - Provides real-time process monitoring
Electrochemistry of polyboranes

- Demonstrate electrochemical activity in the polyboranes (accomplished)
- Demonstrate reversible hydrogen storage (underway)
- Explore complex reaction mechanisms (underway)
Electrochemical Activity

Compounds with large boron/hydrogen that contain both protic and hydridic hydrogen

these should be electrochemically active and may release/absorb hydrogen reversibly upon changing the voltage

Polyboranes show multiple electrochemical transformations

Cyclic voltammetry has been used to study these transformations
Demonstration of Electrochemical Activity

CV of 9.49 mM [(C$_2$H$_5$)$_3$NH]$_2$B$_{12}$H$_{12}$-CH$_3$OH in 1.000 M TBA-PF$_6$ at 1000 mV/s

Multiple peaks!

We suspect a coupled reaction mechanism in this case.

We are investigating this by using electrochemical impedance spectroscopy.

B$_{12}$H$_{12}^2^-$ cyclic voltammetry in acetonitrile with 1M tetrabutylammonium hexafluorophosphate as a supporting electrolyte.

WE = 1 mm Pt disk, CE = 2 mm Pt disk, RE = Ag (pseudo). Sweep rate = 1000 mV/sec.

Demonstrated electrochemical activity in the polyboranes
Reversible Hydrogen Storage

- Electrochemical Impedance Spectroscopy (EIS) is being used to model and analyze the reaction mechanism.

- Because very little work has been done in this area:
  - we will examine $H_2$ absorption/desorption with a volumetric gas burette apparatus attached to the electrochemical cell.
  - all proposed reaction mechanisms are entirely hypothetical until more data is gathered.

- Hypothetical reaction mechanisms:

$$B_xH_y^{z-} + ne^- \leftrightarrow B_xH_{y'}^{(z+n)-} + \frac{y-y'}{z}H_2$$
Reaction Mechanism Analysis
(Electrochemical Impedance Spectroscopy)

Technique for discerning mechanisms of complex, coupled charge transfer/chemical reaction processes.

Coupled reaction mechanisms are indicated by cyclic voltammetry on the borate/borohydride system and on the polyborane system.

High level of mathematical sophistication required to differentiate between various coupled mechanisms to extract kinetic information by optimization of the models on the experimental impedance data.

Present treatment handles reaction mechanisms involving up to ten species in ten reactions capable of handling non-linear problems involving semi-infinite and forced convection mass transport modes.

It is probably the most sophisticated and powerful electrochemical mechanism solver ever devised.
Electrochemical Impedance Spectroscopy

Efficacy on a non-linear mechanism involving four species among six reactions in an ECE configuration has been demonstrated.

Example of Reaction Mechanism (ECE)

\[
\begin{align*}
O + e^- & \Leftrightarrow R \\
R & \Leftrightarrow 2X \\
X + e^- & \Leftrightarrow 2Y
\end{align*}
\]

Impedance

\[
Z = \frac{1}{Y} = \frac{\frac{\Delta i_{\text{Re}}}{\Delta E}}{\sqrt{\left(\frac{\Delta i_{\text{Re}}}{\Delta E}\right)^2 + \left(\frac{\Delta i_{\text{Im}}}{\Delta E}\right)^2}} - j \frac{\frac{\Delta i_{\text{Im}}}{\Delta E}}{\sqrt{\left(\frac{\Delta i_{\text{Re}}}{\Delta E}\right)^2 + \left(\frac{\Delta i_{\text{Im}}}{\Delta E}\right)^2}}
\]

Graph showing impedance vs. frequency.
## Approach/Accomplishments

### FY 2006

#### I. B-O to B-H
- Literature search completed
- Reduction experiments using Hg pool and Hg-plated copper in NaOH solution
- Explored use of thiourea as poison for HER reaction
- Focus was on avoiding the H$_2$ evolution reaction, which is thermodynamically favored.

#### II. Polyboranes
- Literature search completed
- Began experiments in non-aqueous media
- Performed experiments to identify a suitable non-aqueous RE

### FY 2007

#### I. B-O to B-H
- Revisited CV method; used 6mm Au WE; completed statistical validation of method.
- Reduction experiments using Hg pool and Hg-plated copper avoiding presence of alkali metal cations.
- Focus is on overcoming electrostatic repulsion of B(OH)$_4^-$ from cathode.

#### II. Polyboranes
- Compared electrochemical activity at Pt and Au WE.
- Increased the solubility of polyborane salts in organic media through cation exchange.
- Demonstrated electrochemical activity of polyboranes through CV experiments.
Important Accomplishments

- Developed a quantitative method for BH$_4^-$ analysis in aqueous solution.
- Demonstrated electrochemical reduction of B-O to B-H.
- Discovered BH$_4^-$ hydrolysis on several metal surfaces.
- Demonstrated multiple redox transitions in polyboranes.
- Developed a computer algorithm for mechanistic analysis of electrochemical processes using EIS data.
Future Work: B-O to B-H

Theme: Overcome Coulombic repulsion of $\text{B(OH)}_4^-$ from cathode.

- **Approach I: Specific adsorption of cations**
  - Modify potential profile in interphase region
- **Approach II: Square wave reduction**
  - During ‘off’ portion of wave, $\text{B(OH)}_4^-$ approaches electrode; during ‘on’ portion it might be reduced.
- **Approach III: Modify gold electrode**
  - Use compounds that can chelate $\text{B(OH)}_4^-$ to get anion close enough for electron transfer.
Future Work: B-O to B-H

- Key milestones that have been addressed:
  - Development of Analytical Method: CV method is complete
  - Demonstration of B-O to B-H transformation: Hg pool cathode and Ni-PTFE show some activity.

- Remaining milestones:
  - Determination of reaction kinetics: Will largely use EIS with models and software developed by George Englehardt
  - Specification of Optimal System: Can be specified once kinetics data is available.
Future Work: Polyboranes

Key milestones addressed:
- Demonstration of electrochemical transformations

Key milestones remaining:
- Demonstration of practically useful oxidation state change
- Demonstration of reversible H$_2$ storage
Acknowledgements

- DOE for funding through Award DE-FC36-05GO15054
- Rohm and Haas for providing technical support as well as sodium borohydride
- Prof. Fred Hawthorne for the synthesis of polyboranes
- Millennium Cell for technical assistance
- Valuable advice of Tony Burrell and Bill Tumas at LANL
- BASF inorganics division for providing polyborane samples
The End
STMB Experiments

Experimental Parameters

- Cell: ESC C-600, small compartment used for cathode, large compartment for anode
- Cathode: Pd. Electrode area: 7.5 cm² (2.5 cm wide and 3 cm long)
- Anode: Pt flag electrode, 5 cm²
- Separator: DuPont Nafion N-112
- Agitation with magnetic stirring apparatus

- Current
  - 100 mA, 300 mA
  - Cell potential was measured to be about 18 V at 100 mA.
  - Maybe the cell resistance is too high

- Catholyte:
  - 2M KOH/MeOH + STMB
  - 0.5M KOH/MeOH + STMB
  - Isopropylamine → suggested by ROH (in progress)
Graphite Felt Experiments

**Experimental Parameters**

- **Cell:** ESC C-600 small compartment used for cathode, large compartment for anode
- **Cathode:** Graphite felt, ESC GF-S6, provided by Rohm and Haas.
  Electrode area: 7.5 cm² (2.5 cm wide and 3 cm long)
- **Anode:** Pt flag electrode, 5 cm²
- **Separator:** DuPont Nafion N-112 and Reinforced Nafion
- **Stirring with magnetic stirring apparatus**

- **Current density:**
  - 1 mA/cm², 5 mA/cm²
- **Catholyte**
  - 25% NaBO₂ (pH=12)
  - 25% NaBO₂ + 2M NaOH
- **Anolyte**
  - 1M NaOH
  - Symmetrical with catholyte

**Experimental Parameters**

- **ΔV**
  - Catholyte
  - Anolyte

Hg Experiments

- **Experimental Parameters**
  - H-Cell.
  - Cathode: 13mm Hg pool or Cu/Hg electrode.
  - Anode: Pt flag electrode (5cm²) or 6mm diameter graphite rod.
  - Separator: DuPont Nafion N-112.
  - Agitation with magnetic stirring apparatus.
  - Current
    - 10mA Hg pool
    - 25 mA Hg/Cu
  - Symmetrical electrolyte
    - 2M TEAH + 0.2M H₃BO₃