Electrochemical Hydrogen Storage Systems

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Project ID
ST 26

Overview

Timeline

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

Barriers

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

Budget

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

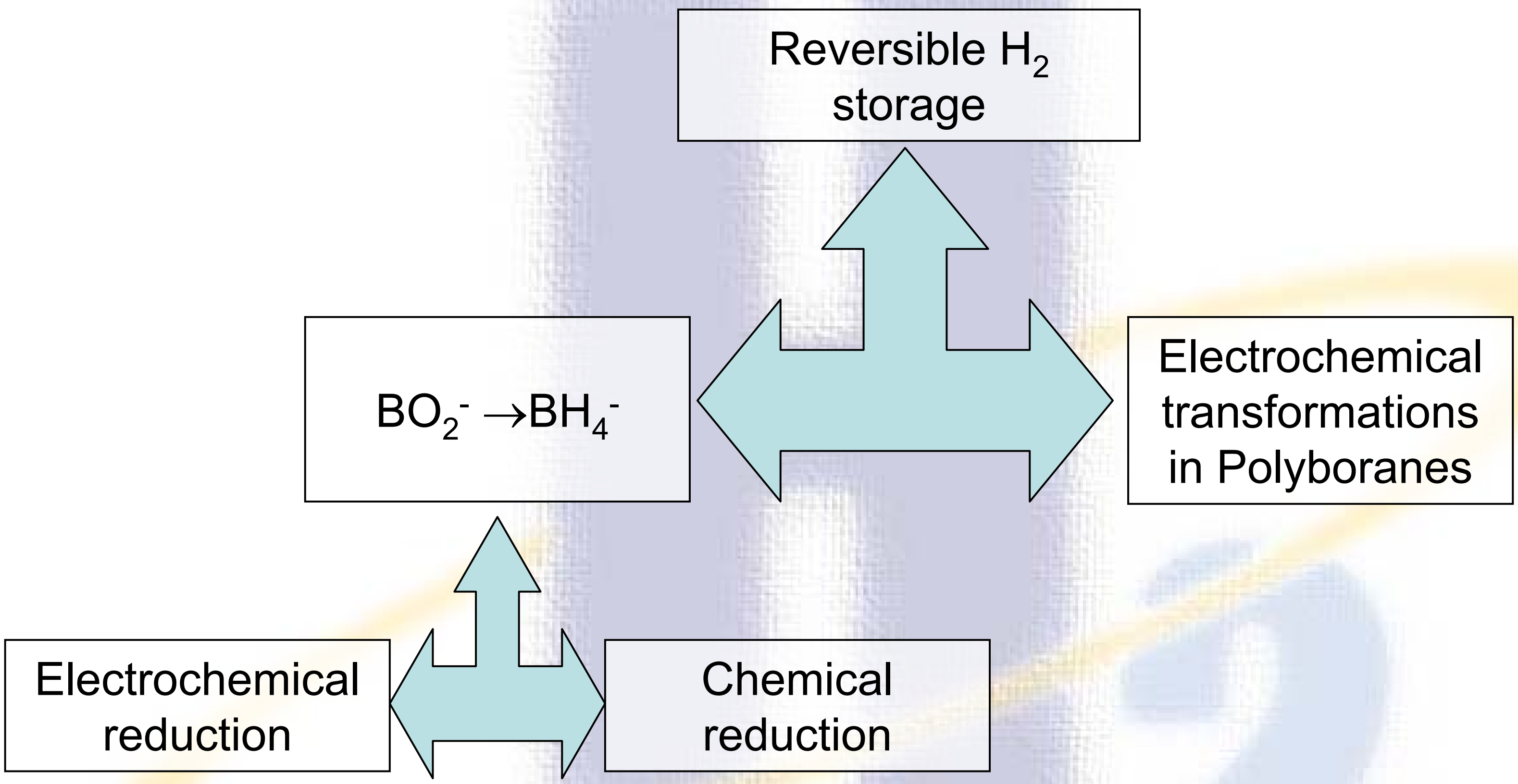
Partners

- 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



Technical Approach (cont.)

➢Electrochemical reduction of B-O to B-H

Analytical methods	Establish analytical methods for unequivocal determination of sodium borohydride: ➢Cyclic voltammetry ➢^{11}B NMR
Electroreduction experiments	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).
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

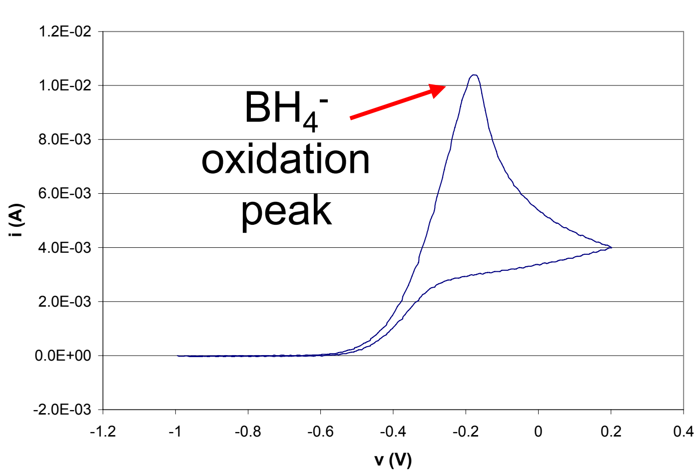
Electrochemistry of polyboranes	Exploring large boron/hydrogen compounds that contain both protic and hydridic hydrogen that should be electrochemically active and may release/absorb hydrogen reversibly upon changing the voltage
Electrochemical Impedance Spectroscopy	Used to discern mechanisms of complex, coupled charge transfer/chemical reactions.

Electrochemical reduction of B-O to B-H

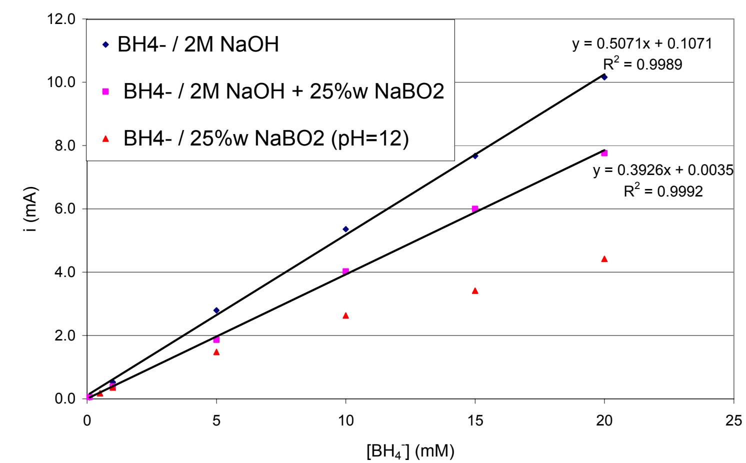
Cyclic Voltammetric Method for Sodium Borohydride Analysis

- **Fast and easy method for BH_4^- quantification** → ✓

- Using 6mm electrode the linearity range and sensitivity (slope) is higher than when using a1mm electrode.



Cyclic voltammetry of a 20mM BH_4^- solution in 2M NaOH

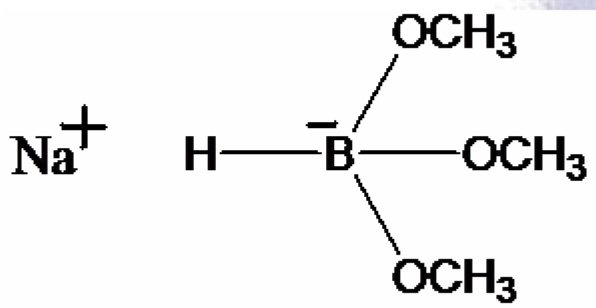


Calibration curves in different electrolytes

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

STMB Experiments

Experimental Parameters



Sodium trimethoxyborohydride - STMB

- 2 competing reactions:
  - Reduction

$NaBH(OCH_3)_3 + 6\cdot H^+ + 6e^- \rightarrow NaBH_4 + 3\cdot CH_3OH$

  - Disproportionation

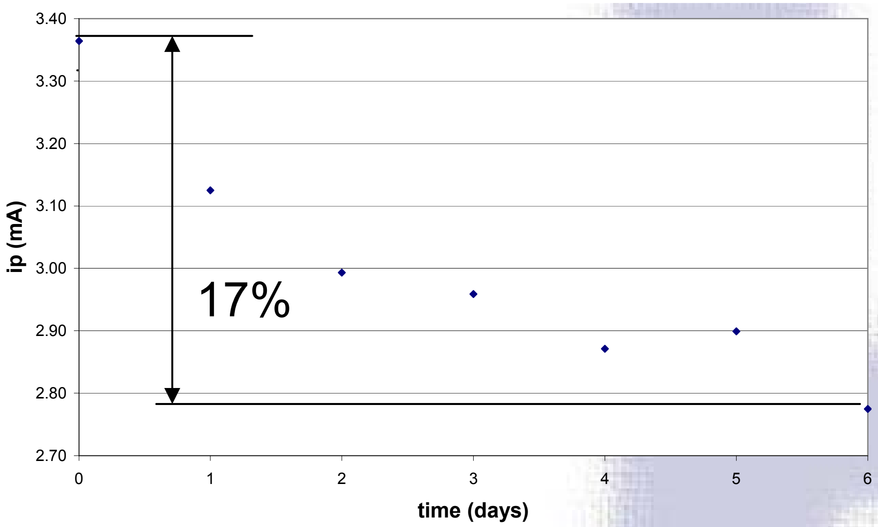
$4\cdot NaBH(OCH_3)_3 \rightarrow NaBH_4 + 3\cdot NaB(OCH_3)_4$

- 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)

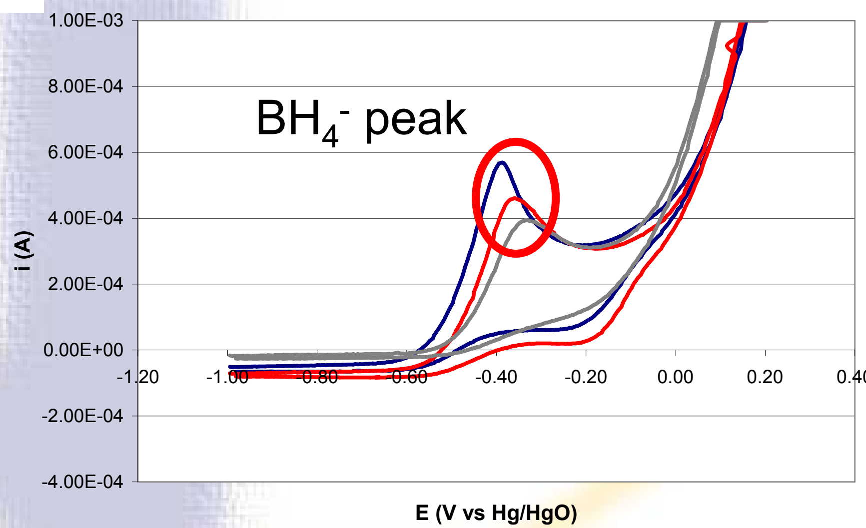
STMB Experiments

Stability test of STMB without electrolysis

10mM BH_4^- (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

Prior to electrolysis — After 4 hours of electrolysis — After 4 hours without electrolysis

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

$4HB(OMe)_3^- \rightarrow BH_4^- + 3B(OMe)_4^-$

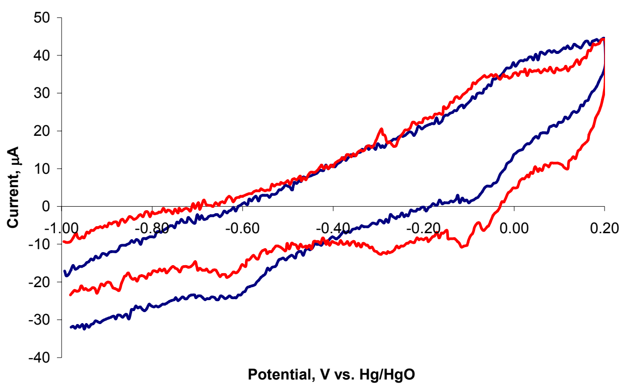
$BH(OCH_3)_3^- + CH_3OH \rightarrow H_2 + B(OCH_3)_4^-$

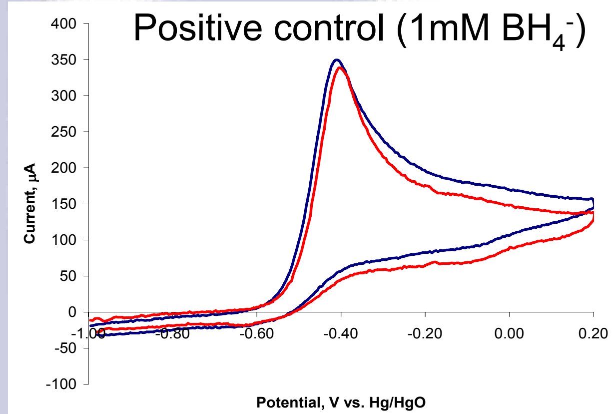
No evidence of BH_4^- generation using MeOH as a solvent

Graphite Felt Experiments

Results

— Prior to electrolysis
— After electrolysis



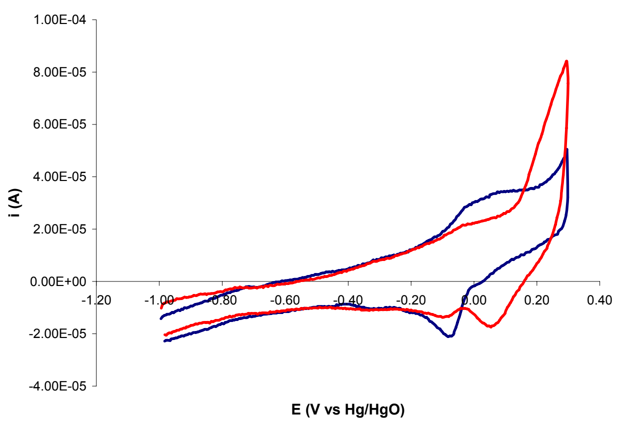


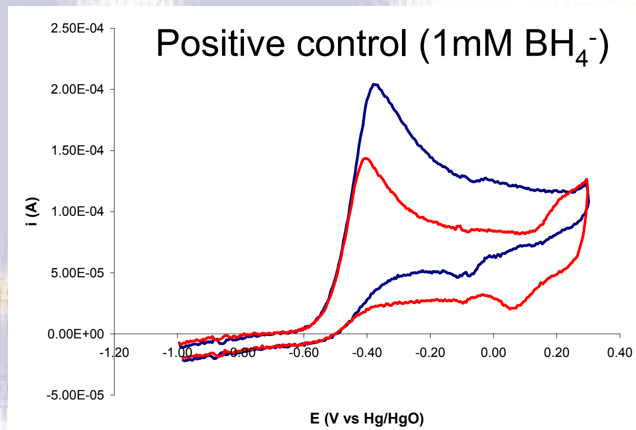
Symmetrical electrolyte:

25% $NaBO_2$ + 2M NaOH.

Current density: 5 mA/cm².

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





Symmetrical electrolyte:

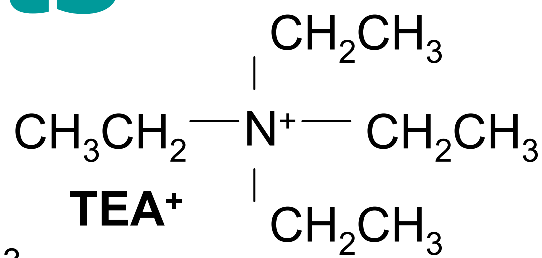
12.5% $NaBO_2$ + 1M TMAH.

Current density: 5 mA/cm².

No evidence of BH_4^- generation

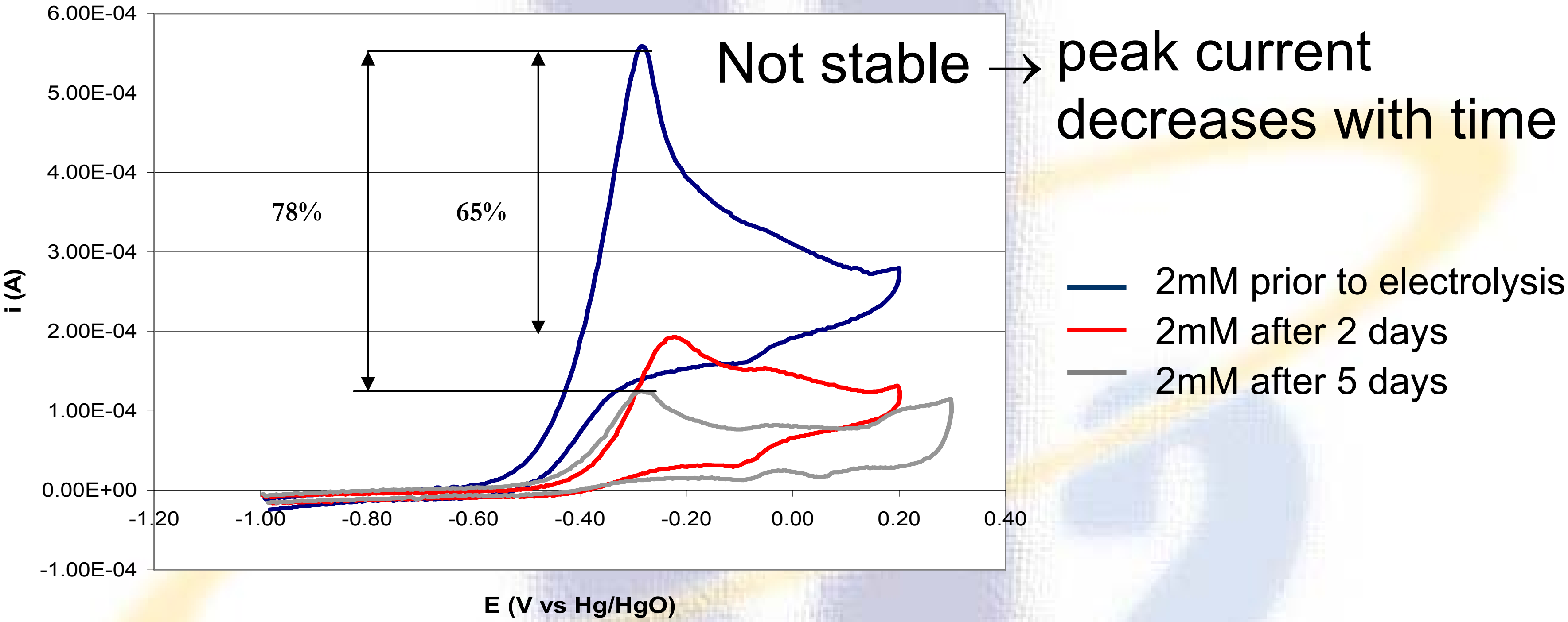
Hg Experiments

- **Results**



Cathode: Hg pool (13mm diameter)

Positive control (2mM BH_4^-) in 2M TEAH + 0.2M H_3BO_3



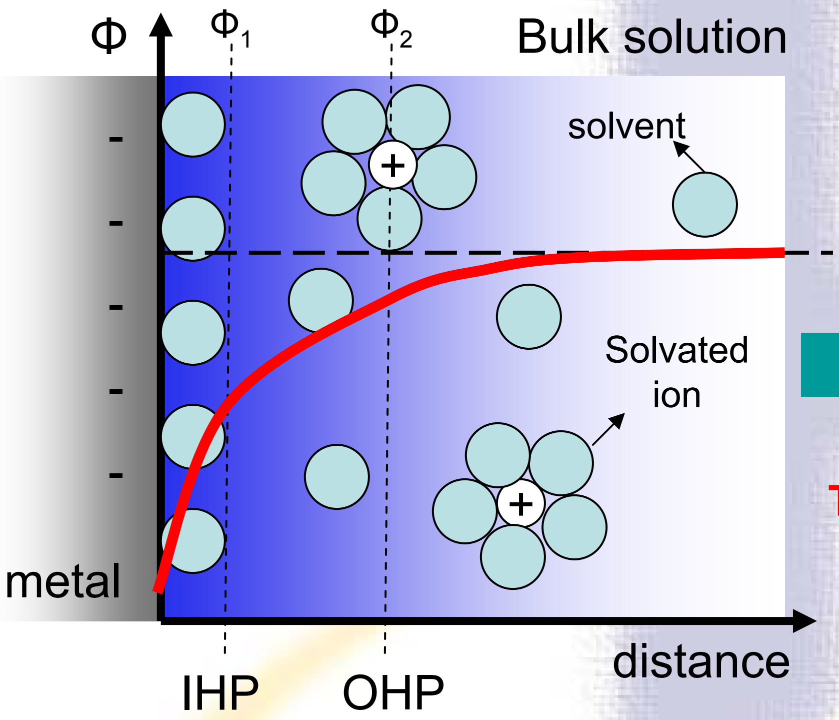
Not stable → peak current decreases with time

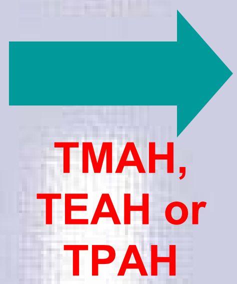
- Increase in the reduction rate using R_4NOH may be possible
- Important observation: electrolysis at 10 mA, tiny Hg droplets were observed in solution.

Double layer modification

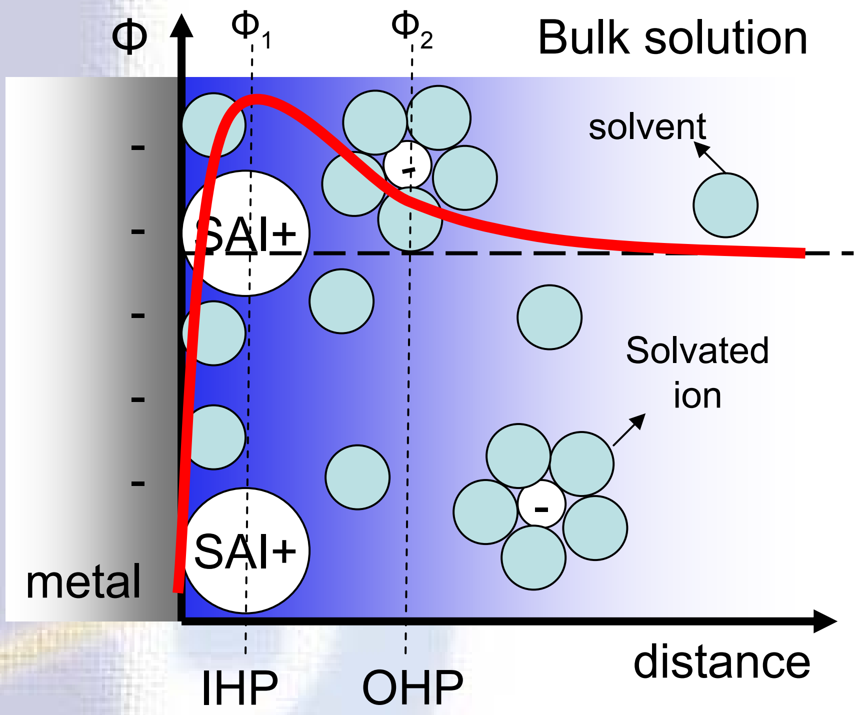
Objective: Modify potential profile in the interphase region to encourage close approach of $B(OH)_4^-$ ion for reduction.

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

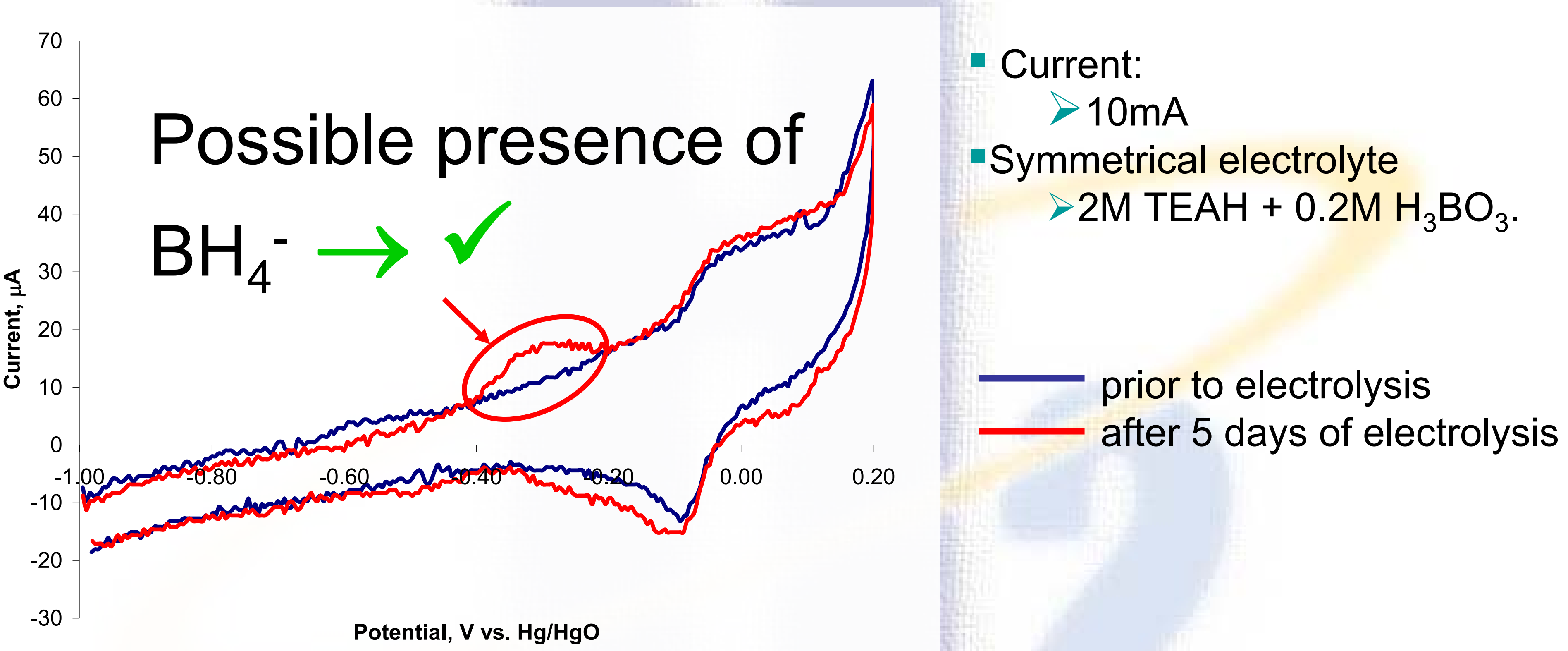
Specifically adsorbable cations include R_4N^+, Cs^+, Tl^+.

[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_3BO_3.

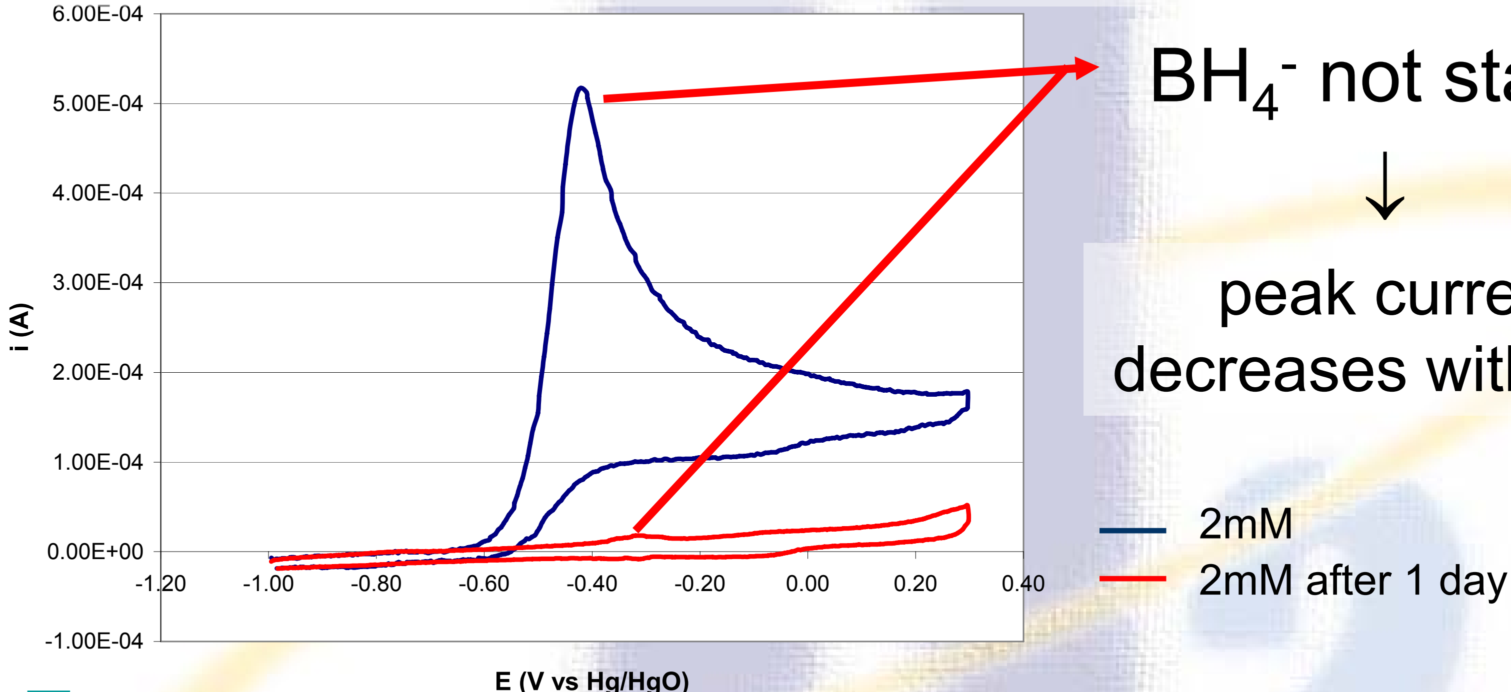
First Positive Result

Au Experiments

- **Results**

Cathode: Au foil (7.5 cm^2)

Positive control (2mM BH_4^-) at open circuit in 2M TEAH + 0.2M H_3BO_3



BH_4^- not stable

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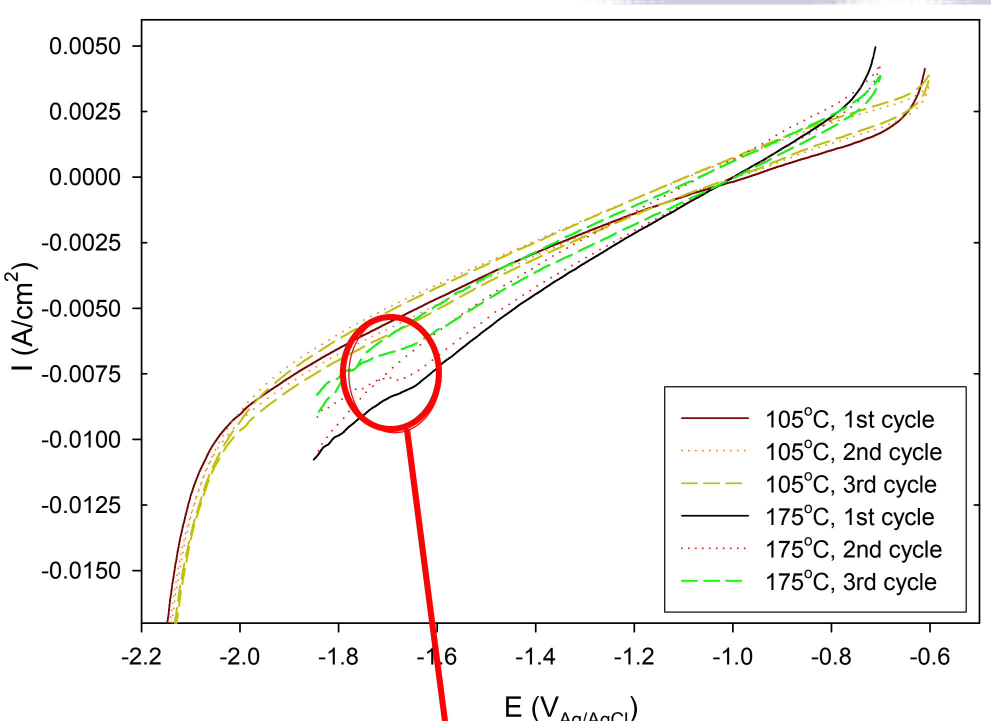
peak current decreases with time

Metal surfaces catalyzes BH_4^- hydrolysis at open circuit

It may explain lack of reproducibility with Hg experiments

High Temperature Aqueous Experiments



- Voltammogram of 2M NaOH + 0.2M $NaBO_2$ at Hg-plated copper electrode.
- Electrode was rotated at 100rpm; sweep rate was 50mV/s.
- H_2 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

	Electrode material	Catholyte	Current	BH_4^- generation?
Carbon felt experiments	Carbon felt	•25%w $NaBO_2$ (pH=12) •25%w $NaBO_2$ + 2M NaOH	•7.5 mA •37.5mA	None Detected
Ni-PTFE	Ni-PTFE	1M TMAH + 0.5M H_3BO_3 (pH>13.5)	•100 mA •300 mA	Tentative Positive Result In progress
Hg Experiments	•Hg •Hg/Cu	2M TEAH + 0.2M H_3BO_3	•1 mA Hg pool (13 mm diameter) •10 mA Hg pool (13 mm diameter) •25 mA Cu/Hg	First Positive Result In progress
STMB	Pd	2M KOH/MeOH	•100 mA •300 mA	In progress (other solvents)
High temperature	Hg/Cu	2M NaOH + 0.2M $NaBO_2$	Exploratory CV	None Detected

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

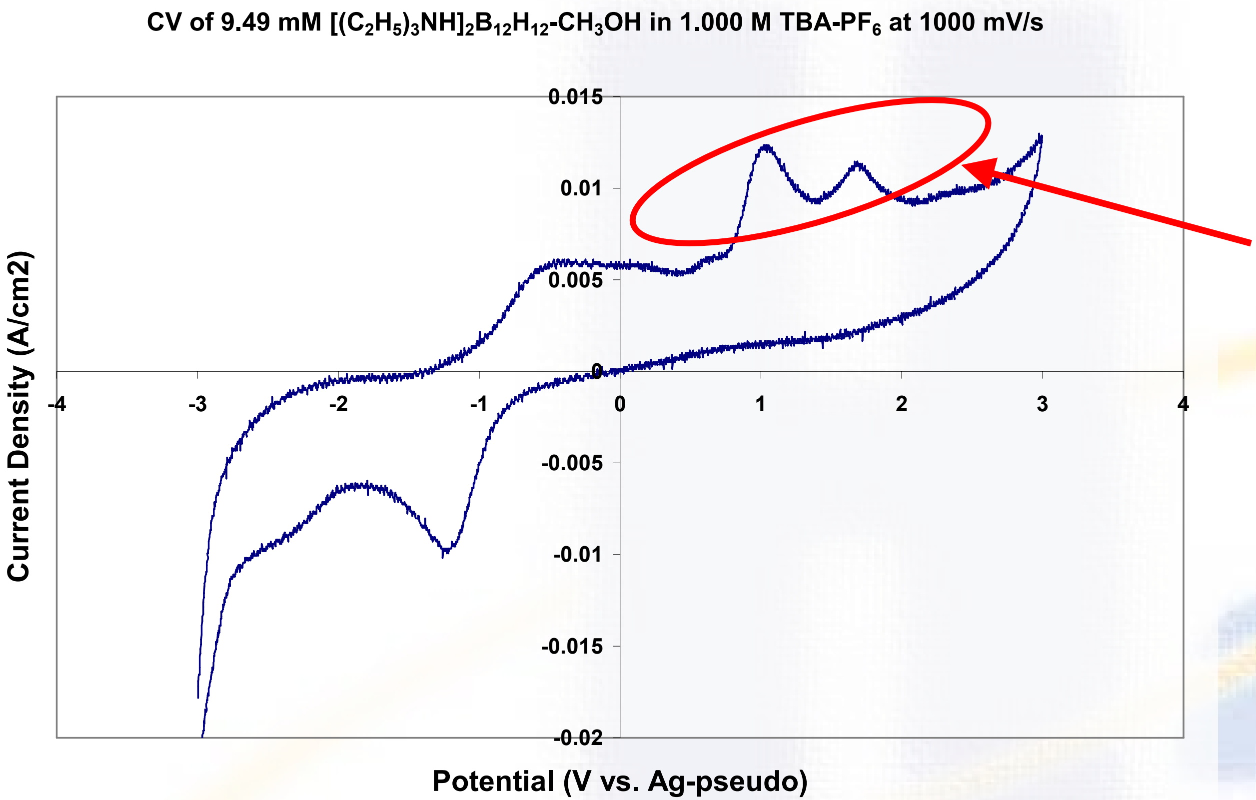
↓

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



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:

$$B_x H_y^{z-} + ne^- \leftrightarrow B_x H_{y'}^{(z+n)-} + \frac{y-y'}{z} H_2$$

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

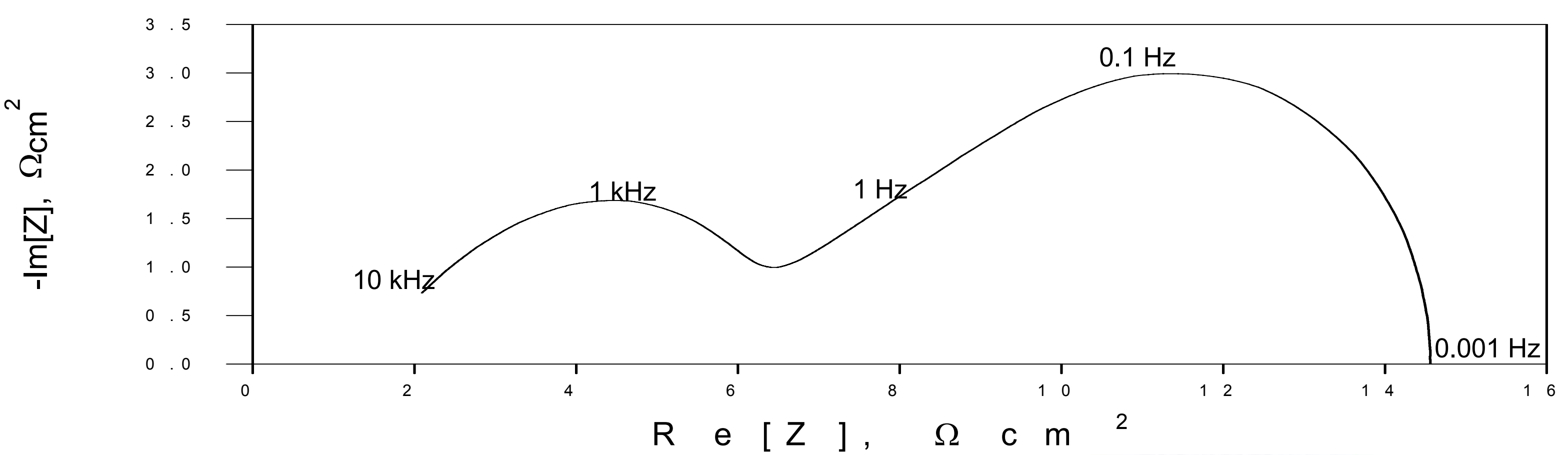
Efficacy on a non-linear mechanism involving four species among six reactions in an ECE configuration has been demonstrated.

Example of Reaction Mechanism (ECE)

$$\begin{cases} O + e^- \Leftrightarrow R \\ R \Leftrightarrow 2X \\ X + e^- \Leftrightarrow 2Y \end{cases}$$

Impedance

$$Z = \frac{1}{Y} = \frac{\Delta i_{\mathrm{Re}} / \Delta E}{\sqrt{(\Delta i_{\mathrm{Re}} / \Delta E)^2 + (\Delta i_{\mathrm{Im}} / \Delta E)^2}} - j \frac{\Delta i_{\mathrm{Im}} / \Delta E}{\sqrt{(\Delta i_{\mathrm{Re}} / \Delta E)^2 + (\Delta i_{\mathrm{Im}} / \Delta E)^2}}$$



Summary Table

Approach/Accomplishments

Project	FY 2006	FY 2007
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.	▪ 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	▪ Literature search completed ▪ Began experiments in non-aqueous media ▪ Performed experiments to identify a suitable non-aqueous RE	▪ 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 $B(OH)_4^-$ from cathode.

- Approach I: Specific adsorption of cations
  - Modify potential profile in interphase region
- Approach II: Square wave reduction
  - During 'off' portion of wave, $B(OH)_4^-$ approaches electrode; during 'on' portion it might be reduced.
- Approach III: Modify gold electrode
  - Use compounds that can chelate $B(OH)_4^-$ 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

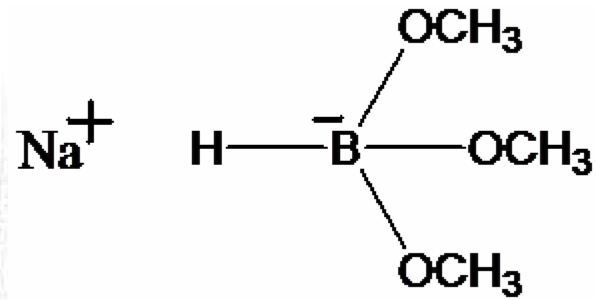
- DOE for funding through Award DE-FC36-05GO15054
- Rohm and Haas for providing technical support as well as sodium borohydride
- Prof. Fred Hawthorne for the synthesis of polyboranes
- Millennium Cell for technical assistance
- Valuable advice of Tony Burrell and Bill Tumas at LANL
- BASF inorganics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

The End

R&H patent 2005/0224364A1 "Electrolytic method for producing borohydride"

STMB Experiments

➢ <u>Experimental Parameters</u>



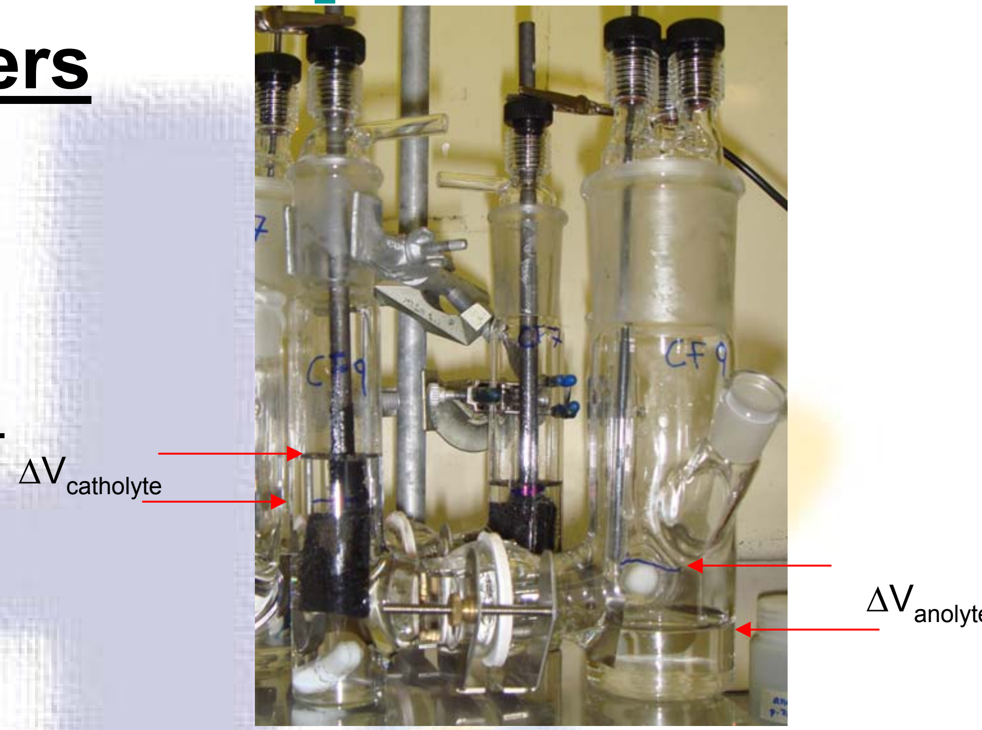
- Cell: ESC C-600, small compartment used for cathode, large compartment for anode
- Cathode: Pd. Electrode area:7.5 cm^2 (2.5 cm wide and 3cm long)
- Anode: Pt flag electrode, $5cm^2$
- Separator: DuPont Nafion N-112
- Agitation with magnetic stirring apparatus
- Current
  - ➢100mA, 300mA
  - ➢Cell 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)

R&H patent 2005/0224365A1 “One [step] electro-synthesis of borohydride”

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 cm^2 (2.5 cm wide and 3cm long)
- Anode: Pt flag electrode, 5cm^2
- Separator: DuPont Nafion N-112 and Reinforced Nafion
- Stirring with magnetic stirring apparatus



- Current density:
  - 1 mA/cm^2, 5 mA/cm^2
- Catholyte
  - 25% $NaBO_2$ (pH=12)
  - 25% $NaBO_2$ + 2M NaOH
- Anolyte
  - 1M NaOH
  - Symmetrical with catholyte

Hg Experiments

- **Experimental Parameters**
  - H-Cell.
  - Cathode:13mm Hg pool or Cu/Hg electrode.
  - Anode: Pt flag electrode ($5cm^2$) 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 H_3BO_3