

Electrochemical Hydrogen Storage Systems

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**Project ID #
STP 25**

Overview

Timeline

Start Date: FY 2005

End Date: FY 2009

Percent Complete: 25

Barriers

Low-cost, energy efficient regeneration processes have not been established.

Budget

DOE: \$1,215,637

PSU: \$303,910 (Cost Sharing)

FY2005: \$172,000

FY2006: \$ 200,000

Partners

DOE Center of Excellence in Chemical Hydrogen Storage

Center Collaborations

- **LANL**

- New electrode fabrication
- Complexation of borate to adjust electrochemical properties
- Electrocatalyst development
- Stoichiometric chemical reduction

- **PNNL/Alabama**

- Computation of reaction intermediates and energetics

- **Rohm & Haas**

- Access to proprietary information on borate electrochemistry
- Engineering assessment
 - Data mining results
 - PSU electrochemical results

- **Millennium Cell**

- Data mining and background information

- **UCLA**

- Synthesis and characterization of polyboranes
- Expertise on chemical reactivity and properties of polyboranes

Table 1. DOE Technical Targets for On-Board Hydrogen Storage Systems (Abridged)

Storage Parameter	Units	2005	2010	2015
Usable specific energy	kg H₂/kg total	0.045	0.06	0.09
Usable energy density	kg H₂/L	0.036	0.045	0.081
Storage system cost	\$/kg H₂	200	133	67
Fuel cost	\$/gallon equiv. gasoline	3	1.5	1.5
Start time to full flow at 20 °C.	Seconds	4	0.5	0.5
Cycle life	Cycles	500	1000	1500
Refueling rate	kg H₂/min	0.5	1.5	2
Loss of useable hydrogen	(g/hr)/kg H₂ stored	1	0.1	0.05

The complexity of boron/hydrogen chemistry –complexity means opportunity

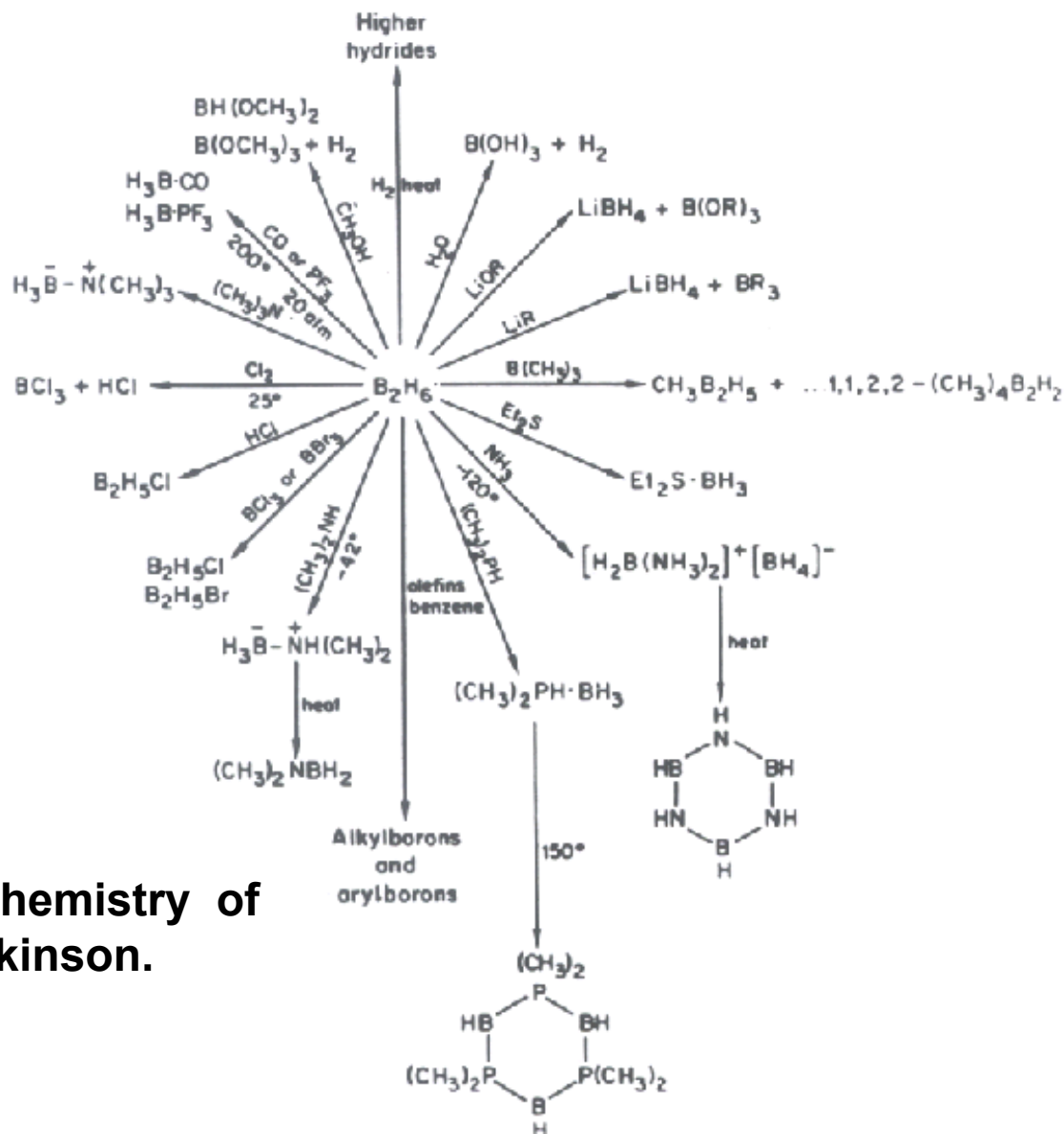
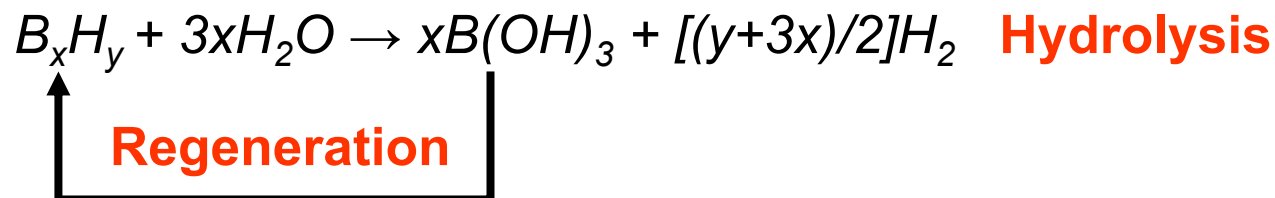


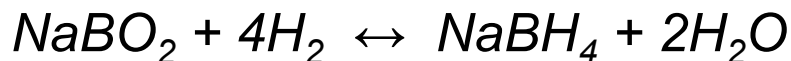
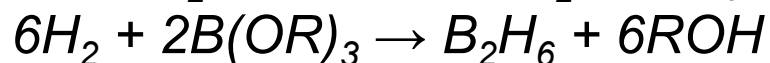
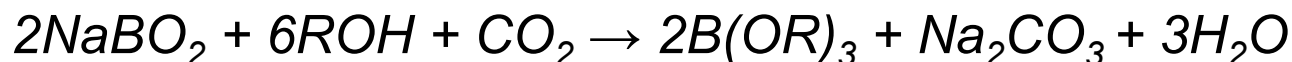
Figure 1. Summary of the chemistry of diborane. After Cotton and Wilkinson.

Two B/H Hydrogen Storage Strategies of Interest in this Work

Strategy 1: Hydride Hydrolysis/Regeneration



Millenium Cell Regeneration



Theoretical Specific Energy = 0.108 kg H₂/kg Reactants

Practical Specific Energy < 0.060 kg H₂/kg Total

Two B/H Hydrogen Storage Strategies of Interest in this Work (Cont.)

Strategy 2: Polyborane Transformations

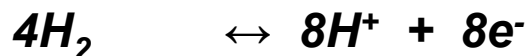
- A large number of polyboranes (B_xH_y) and polyborane anions ($B_xH_y^{z-}$) are known with formal boron oxidation states ranging from 3 (BH_3 , B_2H_6 , BH_4^-) to about 0.8 ($B_{20}H_{16}$, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$).
- This change in formal oxidation state may be used to devise theoretical hydrogen storage schemes that show considerable promise, if the reactions can be made to occur.
- The transformations might be affected chemically, e.g.



which will almost certainly require novel catalysts, or electrochemically, e.g.



and



- Literally, thousands of such schemes may be written, but so little is known about B/H electrochemistry that it is not possible to judge *a priori* which of the schemes might be practical.

Theoretical Specific Energies (kgH₂/kg Reactants) for Various Inter-polyborane Transformations

Reaction (Note that the reaction is the same whether it is carried out chemically or electrochemically).	Theoretical Specific Energy
$B_6H_{10} + 4H_2 \leftrightarrow 3B_2H_6$	0.108
$Li_2B_{12}H_{12} + 18H_2 \leftrightarrow 2LiBH_4 + 10BH_3$	0.186
$Li_2B_{10}H_{10} + 19H_2 \leftrightarrow 2LiBH_4 + 8BH_3$	0.220
$B_{20}H_{16} + 22H_2 \leftrightarrow 10B_2H_6$	0.157

Comparison of Theoretical Specific Energies (kgH₂/kg Reactants) for Various Hydrogen Storage Technologies

Technology	Specific Energy
$Li_2B_{10}H_{10} + 19H_2 \leftrightarrow 2LiBH_4 + 8BH_3$	0.220
$B_{20}H_{16} + 22H_2 \leftrightarrow 10B_2H_6$	0.157
$LiH \leftrightarrow Li + 1/2H_2$	0.065
$MgH_2 \leftrightarrow Mg + H_2$	0.076
$AlH_3 \leftrightarrow Al + 3/2H_2$	0.100
$H_2S \leftrightarrow S + H_2$	0.059
$NH_3 \leftrightarrow N + 3/2H_2$	0.176
$H_2O \leftrightarrow 1/2O_2 + H_2$	0.111
$BeH_2 \leftrightarrow Be + H_2$	0.182
OVONICS (Proprietary alloy)	0.065
AMMINEX (Proprietary material)	0.090

Pressing Needs

- An accurate, *in situ* analytical method for detecting and measuring the concentration of borohydride, BH_4^- .
- A simple, direct, lower cost method for converting borate (BO_3^{3-} , BO_2^-) into borohydride (BH_4^-). Electrochemical reduction appears to be the most promising.
- Definition of the electrochemistry of the polyboranes, in order to assess the feasibility of advanced hydrogen storage systems based upon inter-polyborane transformation. Potentially, these systems could meet DOE's 2015 goal of a specific energy of $0.09 \text{ kgH}_2/\text{kg}$ total weight.

Objectives

Tier 1: B-O to B-H work

- Develop an *in-situ* electro-analytical method for BH_4^- .
- Find an electrode system having a very negative cathodic limit for reducing B-O to B-H.
- Demonstrate reduction of B-O to B-H.
- Explore alternate routes from B-O to B-H via the electro-reduction of B-X intermediates, where $\text{X} \equiv \text{OCH}_3$, SCH_3 , etc.

Tier 2: Polyhedral borane work

- Explore the electrochemistry of various polyhedral boranes to ascertain if electrochemical transformations can be affected between various polyboranes that reversibly absorb and release hydrogen and hence could form the basis of a new hydrogen storage technology.

Approach

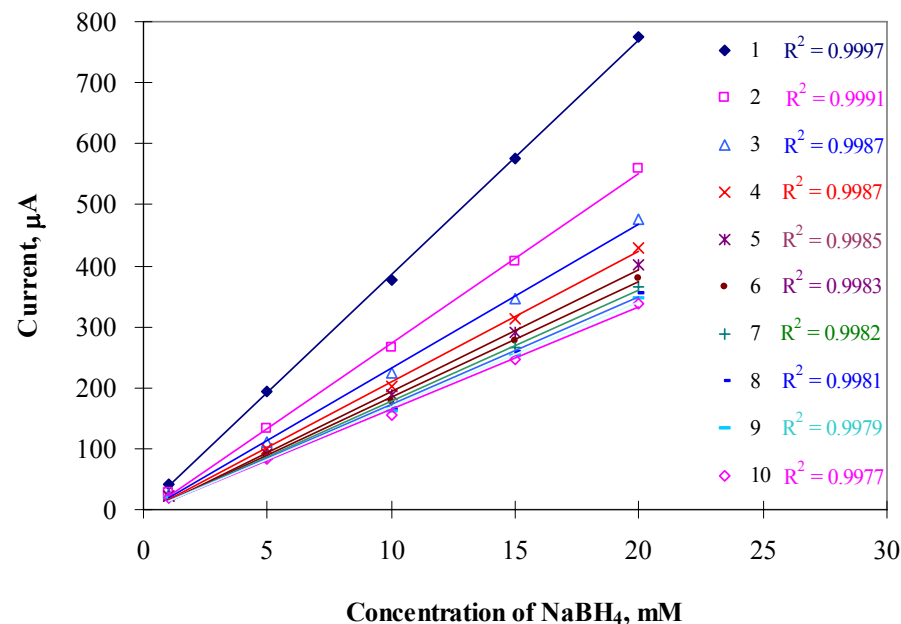
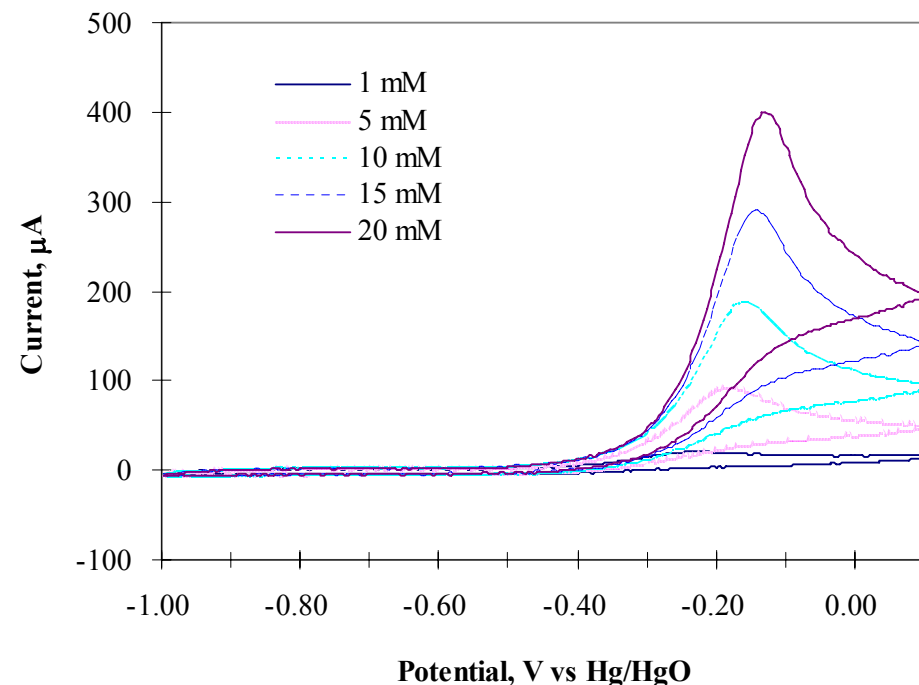
Tier 1: B-O to B-H work

- Literature/patent search (**complete**).
- Develop electroanalytical technique for BH_4^- ion (**complete**).
- Calculated standard potentials for some reduction reactions of B-O species (**complete**).
- Used amalgamated Cu disk and Hg pool electrodes to increase cathodic range for electrolysis and perform electrolysis studies at elevated temperatures – up to 150°C (**on-going**).
- Used reagents known to be catalytic poisons to the HER in trying to push cathodic range to more negative potentials (**on-going**).
- Explore electro-reduction of B-X to B-H, where $\text{X} \equiv \text{OCH}_3$, SCH_3 , etc., to devise an alternative route from B-O to B-H (**not yet started**)

Tier 2: Polyhedral borane work

- Literature/patent search (**complete**).
- Establish a suitable organic solvent and supporting electrolyte to be used for electrochemical studies (**complete**).
- Developed an appropriate reference electrode for non-aqueous studies (**complete**).
- Study various polyborane salts (both B_{10} and B_{12} species) and neutral carborane samples to identify electrochemical transformations (**on-going**).
- Identify transformations that involve the reversible absorption and release of hydrogen and hence that might form the basis of a new hydrogen storage technology (**not yet started**).

Electroanalysis of BH_4^- Ion



This method, which builds on the work of Bard and Mirkin, demonstrates the utility of cyclic voltammetry as a quantitative electroanalytical method for BH_4^- ion.

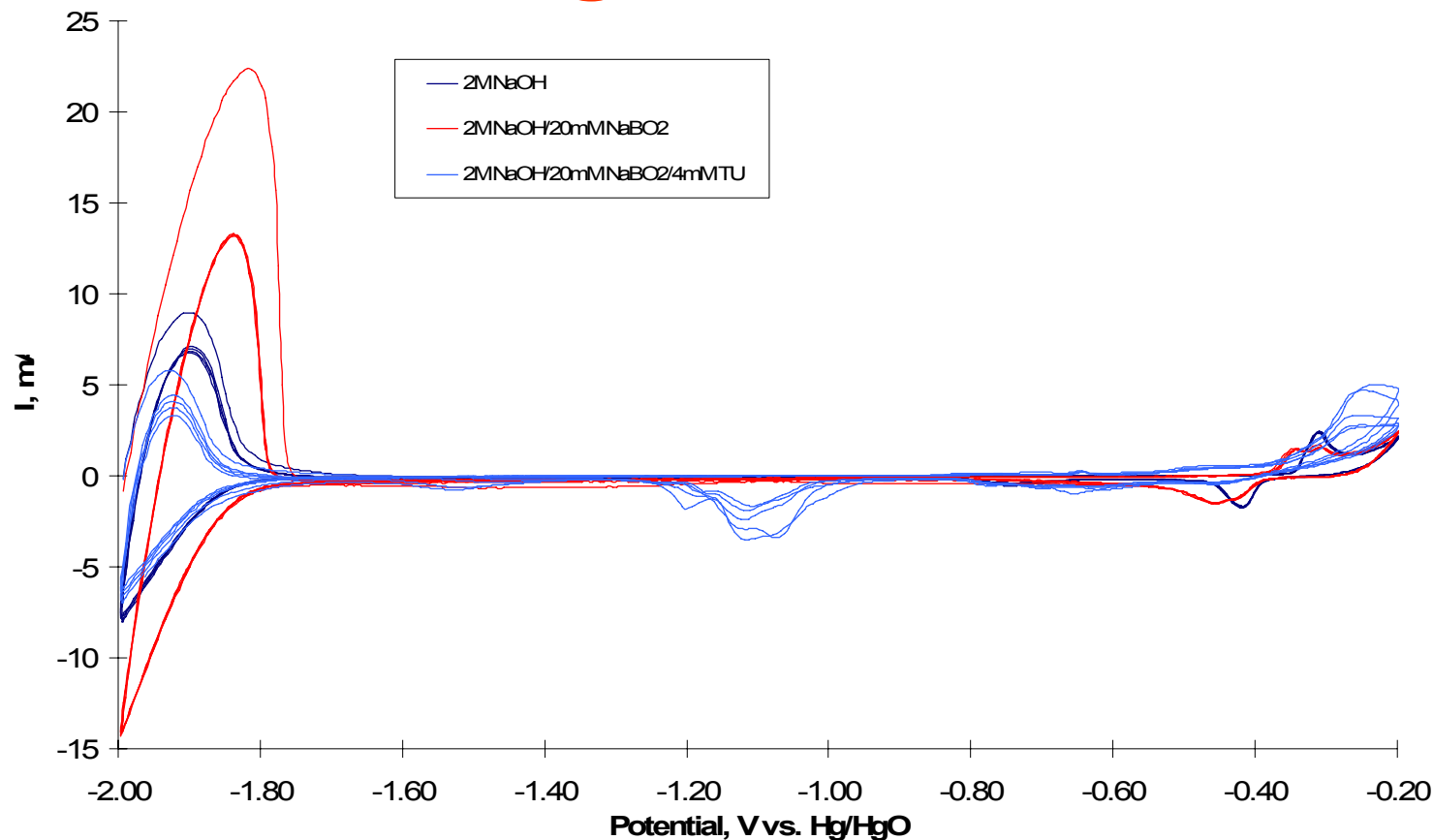
- An excess of NaBO_2 was present, yet the CV's show excellent selectivity towards BH_4^- ion ($\text{BO}_2^-/\text{BH}_4^- \geq 10$).
- Compared to other methods, such as spectroscopy (e.g. NMR), this method is simple and inexpensive.
- This method also has the advantage of allowing for real-time, *in situ* monitoring of BH_4^- concentration.

Thermodynamic Calculations

Reaction	E vs. SHE (V)	K
$B(OH)_4^- + 4H_2O + 8e^- \rightarrow BH_4^- + 8OH^-$	-1.24 (25°C) -1.65 (250°C)	1.46×10^{-168} (25°C) 1.33×10^{-127} (250°C)
$B(OH)_3 + 4H_2O + 8e^- \rightarrow BH_4^- + 7OH^-$	-1.21 (25°C) -1.64 (250°C)	6.96×10^{-164} (25°C) 2.88×10^{-127} (250°C)
$B(OH)_3 + 3H_2O + 6e^- \rightarrow BH_3 + 6OH^-$	-1.47 (25°C) -1.87 (250°C)	2.79×10^{-149} (25°C) 1.23×10^{-108} (250°C)

- The equilibrium potential for the HER in 2M hydroxide solution is -0.85V vs. SHE.
- Because the equilibrium potential for the HER is higher than the equilibrium potential for B-O reduction, reduction of B-O may not be expected to occur.
- However, electrode kinetics are very important. By judicious choice of electrode material, the over potential for the HER can be made very large, thereby making it possible to study reduction reactions at potentials that are much more negative than the equilibrium potential of the HER.. Reagents that act as catalytic poisons to the HER are also known and described in literature.

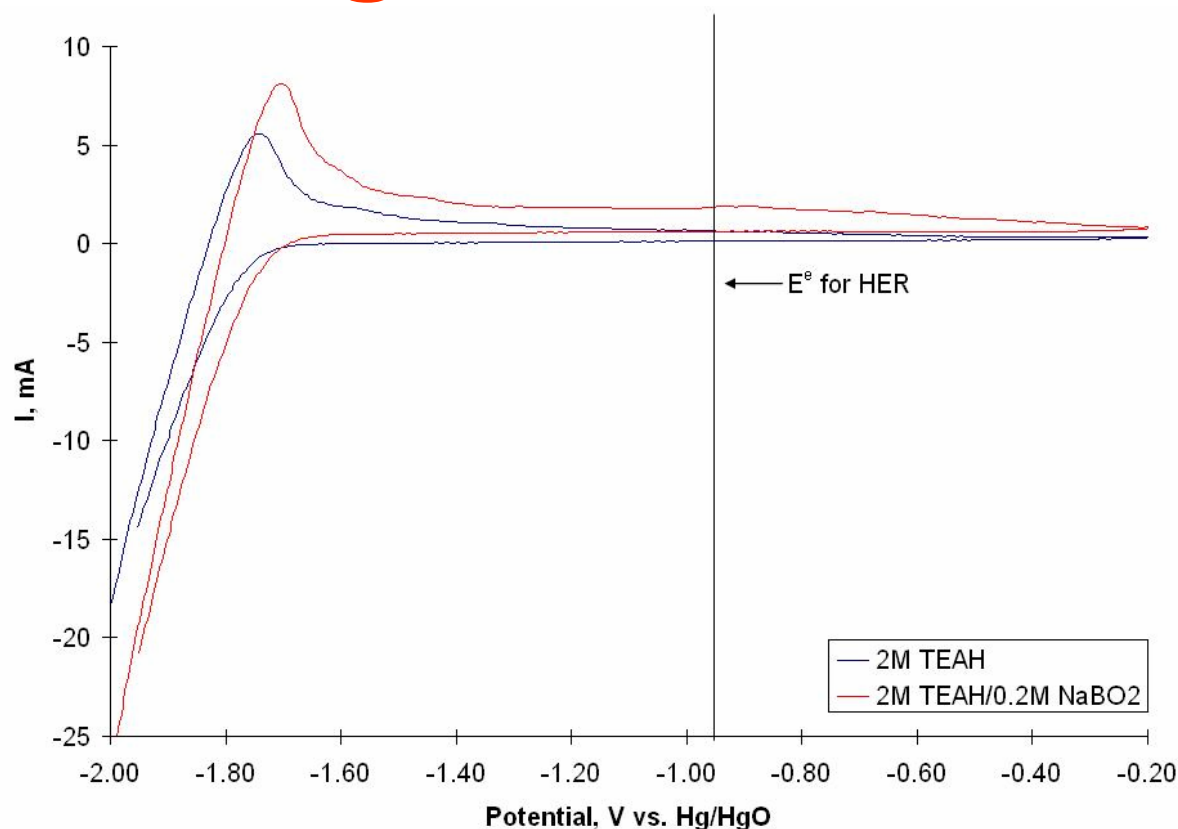
CV at amalgamated Cu disk



Shown is CV at a 6mm amalgamated Cu disk. Hg surfaces are known to have a large overpotential for the HER.

- Thiourea (TU) $[(\text{NH}_2)_2\text{CS}]$ is described in literature to increase overpotential of HER.
- Despite addition of TU, the onset of a large cathodic current occurs at very nearly the same potential.
- New cathodic peaks were noted but these are due to some reaction of the TU and not any reaction of BO_2^- ion.

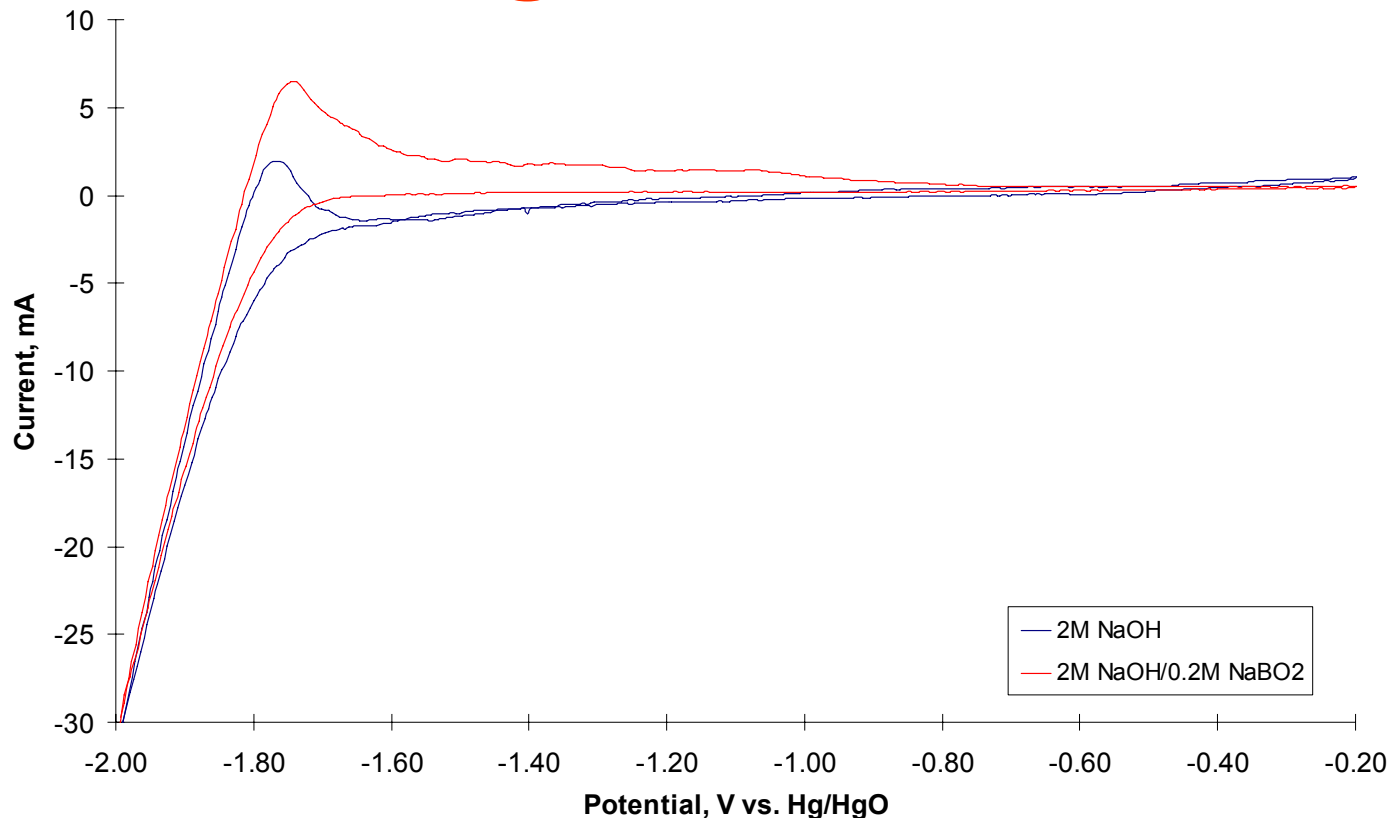
CV at Hg Pool Electrode



Shown is CV of 2M TEAH (blue) and 2M TEAH/0.2M NaBO₂ at a 13mm diameter Hg pool working electrode .

- TEAH [(C₂H₅)₄NOH] has also been described in literature as increasing overpotential for the HER.
- In aqueous 2M hydroxide solution, the equilibrium potential for HER is -0.97V vs. Hg/HgO.
- The above CV demonstrates potentials quite negative of the equilibrium HER potential are achieved on Hg for this system
- Despite this, no new cathodic peaks are seen in the presence of NaBO₂.

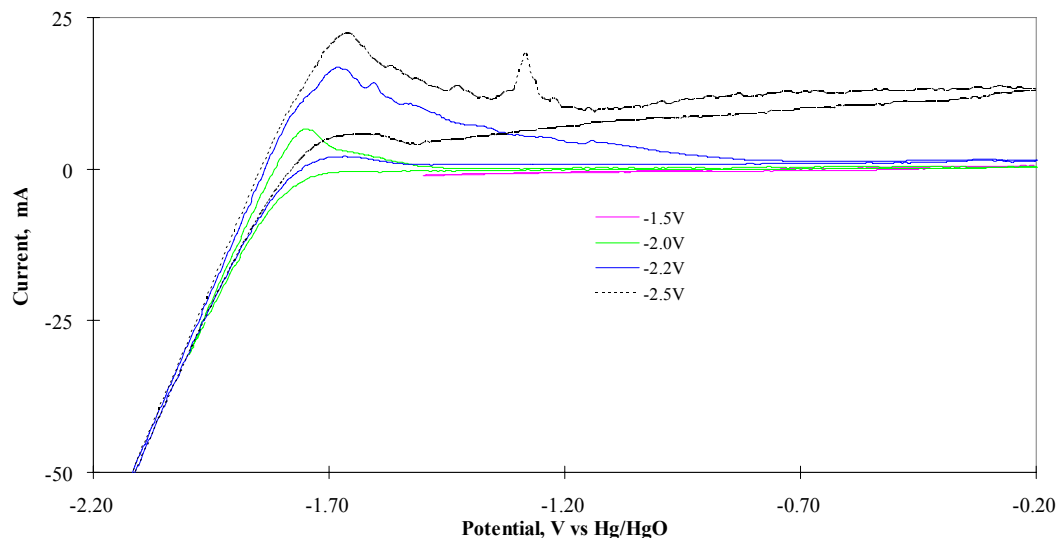
CV at Hg Pool Electrode



Shown is CV of 2M NaOH (blue) and 2M NaOH/0.2M NaBO₂ (blue).

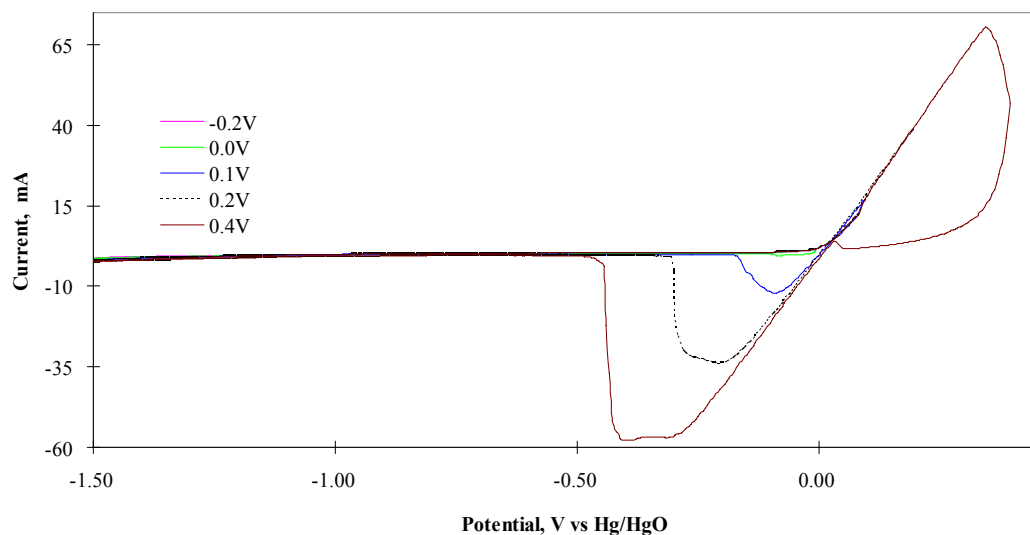
- Once again, no peaks that can be attributed to the reduction of BO₂⁻ are seen.
- The standard reduction potential of sodium metal is -2.83V vs. Hg/HgO.
- The formation of a sodium amalgam occurs at potentials positive to the standard reduction potential of sodium metal. [Kita, et al. *Electrochimica Acta*, 1975, 20, 441]
- The exact value of the amalgam formation potential depends upon the activity of sodium in the amalgam and the activity of Na⁺ in solution, and in this case we believe that the cathodic current below -1.80V is due to the formation of sodium amalgam.
- Behavior in KOH is similar to what is seen for NaOH and TEAH solutions.

Effect of Scan Range



Shown are CVs for 2M NaOH solution at a mercury pool electrode.

- Top: Effect of different starting potentials. For starting potentials lower than -2V, the amalgam is unstable and H_2 evolution causes instability in the current.



- Bottom: Effect of different switching potentials. For potentials greater than 0V, oxidation of the mercury occurs, which gives rise to the peaks shown in the plot.

Major Accomplishments in the B-O to B-H Studies

- Developed a reliable and accurate *in situ* method for analyzing for borohydride in alkaline solutions, confirming and building upon previous work by Bard and Mirkin. Concentration may be determined accurately down to 1-2 mM.
- Determined that the accuracy of the technique is greatly enhanced by employing the oxidation current density after a set number of voltage sweep cycles.
- Determined that borate does not interfere with the analysis of borohydride.
- Unable to detect the reduction of borate on Cu amalgam or Hg pool electrodes in 2 M NaOH at potentials down to -2000 mV_{Hg/HgO}. We have been unable to confirm claims in the patent literature that borate (metaborate) can be reduced electrochemically to borohydride, even though the reaction is possible thermodynamically.
- Developed an explanation for the lack of electrochemical activity in terms of an electrostatic barrier to adsorption of borate onto the electrode surface.
- Devised strategies to overcoming the electrostatic barrier by employing neutral boron derivatives [e.g., B(OR)₃] that are intermediates in Millemium Cell's borohydride regeneration process and by chemically modifying the electrode surface to concentrate borate ion at the interface. Experiments to explore these strategies are now underway.

B-O to B-H Unanswered Questions

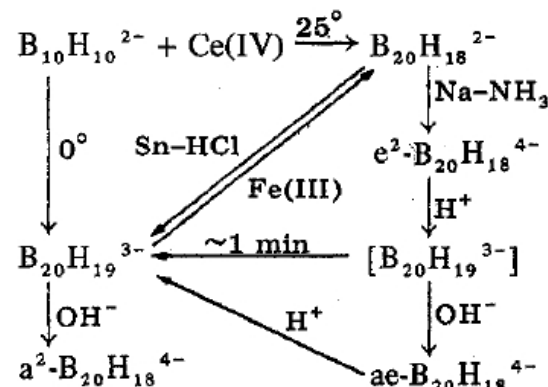
Question	Response
<p>Why does peak current decrease with increasing cycle for CV of BH_4^- at Au electrode?</p>	<ul style="list-style-type: none">• Intermediate species formed in electro-oxidation of BH_4^- are adsorbing to surface of electrode, decreasing the true working area of the electrode.
<p>Potentials greatly negative of HER have been achieved on Hg. Why don't we see reduction of BO_2^-?</p>	<ul style="list-style-type: none">• BO_2^- reduction may occur with alkali metal amalgams via chemical steps.• Adsorption of BO_2^- and/or negatively charged intermediates may be important in reduction. At highly negatively potentials, adsorption is less favored.
<p>What is the anodic peak seen in CVs near -2V?</p>	<ul style="list-style-type: none">• The source of this peak is still undetermined.• Peak is seen for amalgamated disk and Hg pool electrodes.• Peak is seen for all solutions studied.• Must be due to some species present initially and is oxidized at quite negative potentials, because the initial scan in all cases starts at -2V and sweep towards positive potentials.

Polyhedral Borane Results

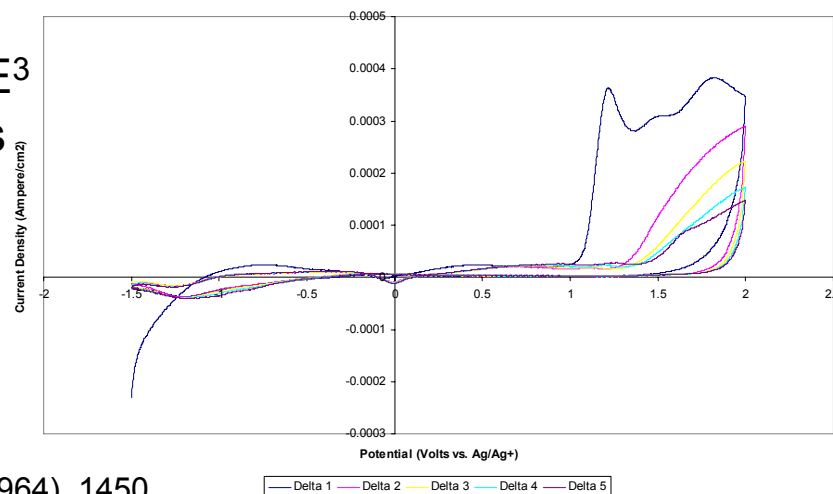
- The most favorable solvent examined was acetonitrile (CH_3CN), and the supporting electrolyte chosen was tetrabutylammonium hexafluorophosphate (TBA) $[(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{NPF}_6]$.
- For a reference electrode, we chose to build a non-aqueous $\text{Ag}/0.01\text{M Ag}^+$ (CH_3CN) electrode to avoid junction potentials and possible water contamination possible from standard reference electrodes, i.e. the aqueous saturated calomel electrode. The reference potential for this electrode is +0.637 V vs. NHE.
- Because of poor solubility of the samples provided by UCLA and BASF, we have developed a procedure to exchange the cation of the polyborane salt with one that has a lower surface charge density. The TBA cation has been found to work very well for this procedure.

Some Previous Borane Electrochemistry

- The chemical oxidation of $B_{10}H_{10}^{2-}$ and its derivatives have been extensively examined¹
- $B_{10}H_{10}^{2-}$ was studied with a platinum RDE²
 - a one-electron transfer is followed by a second-order chemical reaction to form $B_{20}H_{19}^{2-}$ which is oxidized to $B_{20}H_{18}^{2-}$
 - the second-order chemical rate constant is $k = 2.8 \times 10^3 \text{ l/mol/sec}$
- $B_{12}H_{12}^{2-}$ was also studied with a platinum RDE³
 - The reaction parallels $B_{10}H_{10}^{2-}$ and follows a one-electron transfer followed by a dimerization reaction to yield $B_{24}H_{23}^{2-}$



CV of K₂B₁₂H₁₂ in Acetonitrile



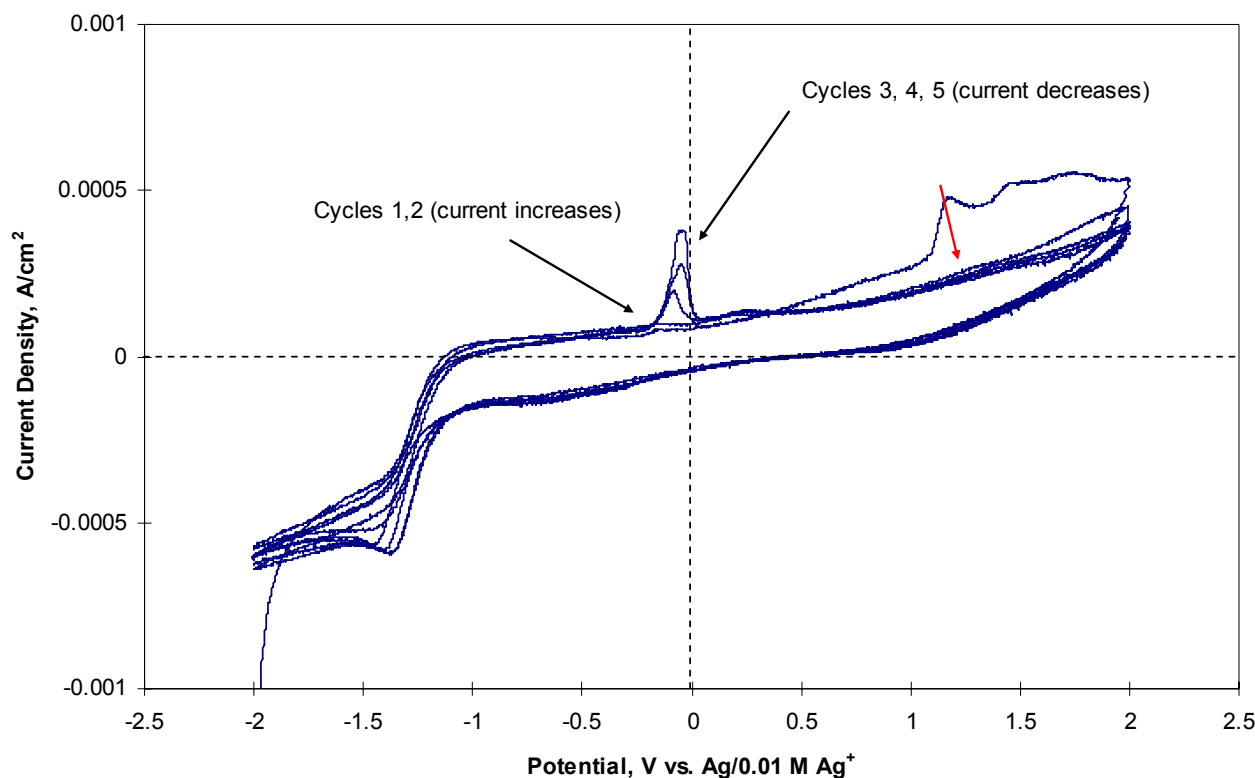
CV of 1mM K₂B₁₂H₁₂ in anhydrous acetonitrile.

References

- (1) B.L. Chamberland and E.L. Muetterties, *Inorganic Chemistry*, 3, 10, (1964), 1450.
- (2) R.L. Midaugh and F. Farha, Jr., *J. Am. Chem. Soc.*, 88, 18, (1966), 4147.
- (3) R.J. Wiersema and R.L. Midaugh, *J. Am. Chem. Soc.*, 89, 19, (1967), 5078.
- (4) A.P. Schmitt and R.L. Midaugh, *Inorganic Chemistry*, 13, 1, (1974), 163.

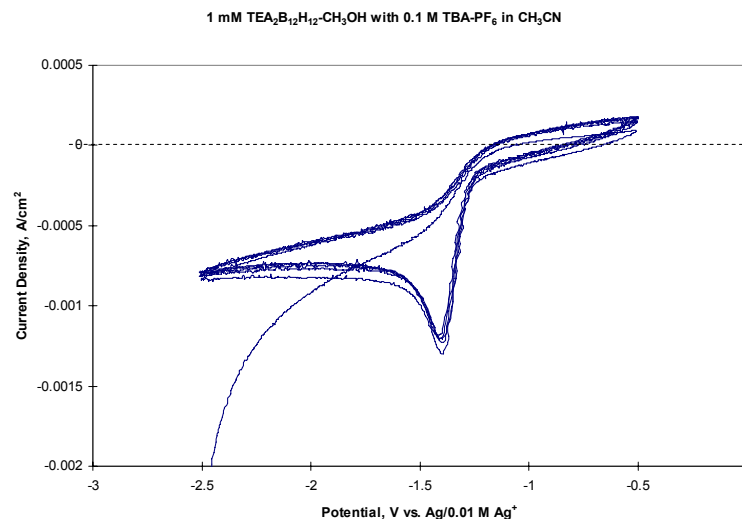
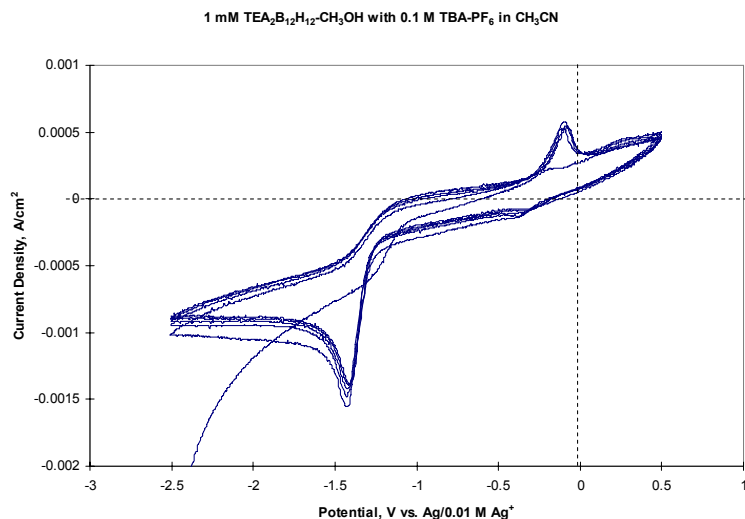
Polyhedral Borane Results

1 mM $\text{TEA}_2\text{B}_{12}\text{H}_{12}\text{-CH}_3\text{OH}$ with 0.1 M TBA- PF_6 in CH_3CN



Cyclic voltammetry (CV) of tetraethylammonium $\text{B}_{12}\text{H}_{12}$ methanolate (as received from BASF). WE = 0.5 mm Pt disk, CE = 2 mm Pt disk, scan rate = 10 mV/sec. The oxidation peak near 0 volts is unlikely due to the RE, since that reaction would produce Ag^{2+} from Ag^+ . The origin of the reduction peak at -1.4 V is unknown.

Polyhedral Borane Results

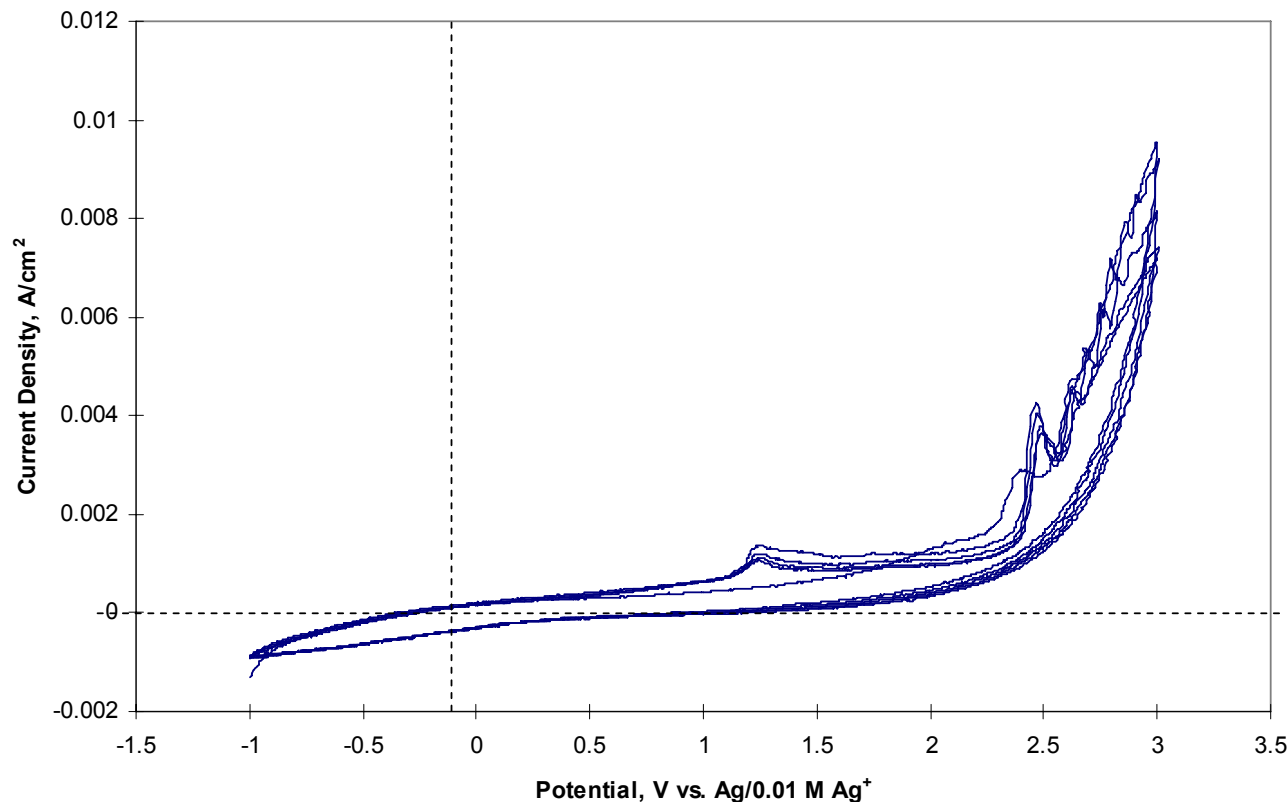


Shown above are two experiments (also on the $\text{TEA}_2\text{B}_{12}\text{H}_{12}$ salt) to determine the origin of the peak near -1.4 Volts. It was suspected that the oxidation peaks (near 0 Volts and +1.2 Volts) were producing an oxidized species that was being reduced upon the cathodic cycle.

However, by comparing these two figures to the figure on the previous slide, it can be seen that the reduction peak is still present regardless of the switching potential. The reduction potential is near -0.8 V vs. NHE.

Polyhedral Borane Results

10 mM $\text{TBA}_2\text{B}_{12}\text{H}_{12}$ with 0.1 M TBA- PF_6 in CH_3CN



The experimental conditions are the same as all other cases, however this sample is one that the cation was exchanged from potassium to tetrabutylammonium. Some literature describe the oxidation of the $\text{B}_{12}\text{H}_{12}^{2-}$ anion as similar to the $\text{B}_{10}\text{H}_{10}^{2-}$ anion, and the oxidation peaks here near +1.25 V are similar to the $\text{B}_{10}\text{H}_{10}^{2-}$ case.

Major Accomplishments in the Polyborane Studies

- Determined that acetonitrile is a suitable solvent for exploring electrochemical transformations in polyboranes.
- Developed a reliable reference electrode for performing electrochemical studies in non-aqueous media.
- Developed a cation exchange procedure to enhance the solubility of polyborane salts in acetonitrile, to a level that meaningful electrochemical experiments can be performed.
- Determined that electrochemical transformations occur in the $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ systems.
- The CVs indicate that these transformations probably involve coupled chemical reaction, the exact nature of which is currently unknown.

Polyborane Unanswered Questions

Question	Response
<p>The presence of peaks in the cyclic voltammograms (CVs) is unequivocal evidence that electrochemically-mediated transformations are taking place. What are these reactions?</p>	<p>The reactions must involve the electron rich/electron deficient cage structures, because of the absence of redox sensitive derivative groups.</p>
<p>Some evidence exists from the CVs that chemical reactions are coupled to the charge transfer reactions. If so, what is the nature of these reactions. If they involve cage opening, can the overall process be reversible?</p>	<p>This question can only be answered by controlled potential electrolysis and product analysis (NMR, chromatography), electrochemical impedance spectroscopy, and rotating ring-disk voltammetry. A cell is currently being fabricated to explore this issue.</p>
<p>Is hydrogen released or absorbed in these transformations? Can the transformations form the basis of a novel hydrogen storage technology?</p>	<p>This question can only be answered using coulometry and hydrogen volumetry, coupled with product analysis. A cell for performing these specific experiments is currently being designed.</p>

Future Work

Tier 1: B-O to B-H work

- More experiments are required to test hypotheses:
 - Choose metals with more negative PZC for cathodes.
 - Use B-X species that are neutral or have positive charge.
 - Use capacitance-based measurements to determine if reactant or intermediate adsorption occurs for B-O to B-H and also in electro-oxidation of BH_4^- .
 - Explore chemically-modified electrodes as a means of overcoming electrostatic repulsion of borate from the electrode surface.
- Explore the reduction of B-O to B-H at elevated temperatures (up to 150°C).
- For any reduction reactions that occur for B-O, the mechanisms will be studied using techniques such as CV, EIS, and RRDE voltammetry.
- Explore the reduction of B-X to B-H, where $\text{X} \equiv \text{OCH}_3$, SCH_3 , etc., to identify alternate routes from B-O to B-H.

Tier 2: Polyhedral borane work

- Continue using cyclic voltammetry to detect electrochemical transformations in the polyboranes.
- Perform controlled potential electrolysis within a divided cell and determine the identities of the reaction products.
- Investigate the polyborane electrochemistry within other media, e.g., ionic liquids or water.
- Identify electrochemical transformations that result in the reversible absorption/release of hydrogen that could be the basis of a new hydrogen storage technology. These studies will make use of coulometry coupled to hydrogen volumetry, in order to establish the relationship between charge passed and the amount of hydrogen released or absorbed.
- Continue and expand mechanistic analyses of the transformations detected in the $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$ systems. These studies will employ electrochemical impedance spectroscopy (EIS) as the principal analytical tool.

Summary

Tier 1: B-O to B-H work

- Demonstrated CV with Au electrode as quantitative analytical technique for BH_4^- .
- Explored Hg and amalgamated copper electrodes for cathodes in B-O reduction.
- Explored some catalytic poisons for HER to extend cathodic range in aqueous systems.
- Demonstrated that systems with a very negative cathodic limit still do not allow for reduction of BO_2^- .
- This indicates that reactant and/or intermediate adsorption may be very important in B-O to B-H reduction.
- Devised a strategy, using chemically-modified electrodes, to enhance the adsorption of B-O oxyanion at highly negatively-charged electrode surfaces.

Tier 2: Polyhedral borane work

- Determined that acetonitrile is a suitable organic solvent with a wide potential range available for electrochemical studies.
- Developed a non-aqueous reference electrode that performs well.
- Developed a cation exchange technique for enhancing the solubility of polyborane salts in low dielectric media.
- Discovered several new oxidation and reduction peaks that are not identified in the literature. These peaks arise from electrochemical transformations that appear to be coupled to chemical steps.

Publications, Presentations, and Intellectual Property

- **D. D. Macdonald, W. Coulson, Y-C. Zhang, J. McLafferty, and J. Tokash, “Electrochemical Hydrogen Storage”, CHSCoE Center Meeting, Salt Lake City, UT, Oct. 27, 2005.**
- **D. D. Macdonald, W. Coulson, Y-C. Zhang, J. McLafferty, and J. Tokash, “Electrochemical Hydrogen Storage”, Penn State University, September 20, 2005.**
- **J. McLafferty, J. Tokash, Y-C. Zhang, and D.D. Macdonald, “Electrochemical Hydrogen Storage”, CHSCoE Center Meeting, Los Alamos, NM, March 22, 2006.**
- **J. McLafferty, J. Tokash, Y-C. Zhang, W. J. Coulson, and D. D. Macdonald, “Electroanalysis of Borohydride Ion”, Electrochemical Society Spring Meeting, Denver, CO, May 7-12, 2006.**
- **J. Tokash, J. McLafferty, Y-C. Zhang, W. J. Coulson, and D. D. Macdonald, “Polyhedral Boranes as Electrochemical Hydrogen Storage Materials”, Electrochemical Society Spring Meeting, Denver, CO, May 7-12, 2006.**
- **D. D. Macdonald and J. McLafferty , “Conversion of Oxides into Hydrides Using a Hydrogen Plasma”, Invention Disclosure, Pennsylvania State University, Feb. 28, 2006.**
- **J. McLafferty and D. D. Macdonald, “Novel Modified Electrodes for the Electrochemical Reduction of Born-Oxygen Entities to Boron-Hydrogen Species”, Invention Disclosure, Pennsylvania State University, April 20, 2006.**

Acknowledgements

- Rohm and Haas for providing sodium borohydride.
- UCLA for synthesizing polyboranes.
- BASF for supplying additional polyborane samples.
- DOE and PSU for funding.
- Penn State University for facilities.
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