

## IV.B.5c Electrochemical Hydrogen Storage Systems

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### Objectives

- Demonstrate reduction of B-O compounds (e.g.  $\text{NaBO}_2$ ) to  $\text{NaBH}_4$  (i.e. B-H).
- Demonstrate electrochemical transformation among the complex polyboranes.
- Use electrochemical impedance spectroscopy (EIS) to determine the mechanism of electrochemical reactions of complex polyboranes.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (R) Regeneration Processes

### Technical Targets

#### Reduction of B-O to B-H

This project is concerned with the reduction of B-O compounds (e.g.  $\text{NaBO}_2$ ) to  $\text{NaBH}_4$ . There are many patents claiming that this reduction can be effected electrochemically. However, the claimed processes have not been replicated. Therefore, the first task is to demonstrate reduction of B-O to B-H. Once this is done, efficiency of the regeneration process can be determined.

#### Electrochemistry of Complex Polyboranes

This part of the project is concerned with demonstrating electrochemically-mediated transformations among the complex polyboranes and their reaction mechanisms. Some of these transformations have been demonstrated in our previous work, but they are not fully understood yet; polyboranes do not contain B-O bonds - they only involve varying numbers of B-H bonds. The capability and efficiency of hydrogen storage and release during the electrochemical transformations will be investigated.

### Accomplishments

- Continued reduction experiments for B-O to B-H using several different cathode materials. Titanium, gold, and lead have been investigated in addition to mercury and mercury-plated copper this year.
- Repeated and extended experimental work disclosed to us by Rohm and Haas for the electrochemical reduction of B-O compounds.
- Investigated the use of tetraalkylammonium cations, e.g. tetramethylammonium ( $\text{TMA}^+$ ), which can specifically adsorb at the cathode. These act to modify the profile of the electrical potential at the solution-electrode interface.
- Compared electrochemical activity of polyborane anions at gold and platinum working electrodes.
- Demonstrated electrochemical activity of polyborane anions using cyclic voltammetry (CV).
- Began studying polyboranes with EIS and began simulating reaction mechanisms with computer code provided from Dr. George R. Englehardt (consultant).



## Introduction

The regeneration of sodium borohydride from oxidized boron compounds (e.g. sodium metaborate,  $\text{NaBO}_2$ ) is considered to be a key step in one hydrogen storage concept currently being explored by DOE contractors. Henceforth, this process will be called B-O to B-H. The patent literature contains claims that the electrochemical reduction of B-O is feasible but, thus far, the claimed process has not been replicated. Thus, the first task is to demonstrate that B-O to B-H reduction occurs.

The polyborane anions appear to be promising materials for hydrogen storage, if reversible, electrochemically-mediated transitions between anions of different oxidation states (B/H ratios) can be achieved. Very little work in this area has been reported in the peer-reviewed literature.

## Approach

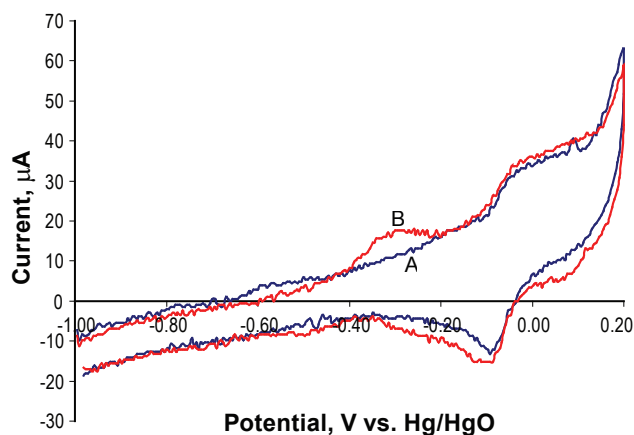
There are two essential themes for the B-O to B-H work. The first theme involves the hypothesis that Coulombic repulsion of borate anion from the cathode is inhibiting reduction. The standard potential for borate reduction is -1.24 V vs. the standard hydrogen electrode (SHE). At such a negative potential, the surface of many cathode materials will bear a significant negative charge. Therefore, our experimental approach is now aimed at minimizing repulsion of borate anion. The second theme is continuing the use of cathodes having a high overpotential for the hydrogen evolution reaction (HER). These materials present a large *kinetic* barrier to the evolution of hydrogen gas, which is an electrochemical reaction that competes with the B-O to B-H reduction. Because the kinetics of B-O reduction are not known and, like the HER, can depend upon the electrode material, we consider it important to continue investigating different cathode materials. Finally, to generate hydrogen plasma for the reaction with boric acid, two different types of plasma reactors (radio frequency and microwave) have been received, along with a residual gas analyzer. The reactors and analyzer are currently being installed; this equipment will be operational very shortly.

By using cyclic voltammetry on the polyborane samples, we have been able to determine voltage regions of interest where oxidation and reduction reactions occur. Much of our work until now has been toward gaining experience in dealing with anhydrous electrochemical systems with solution impedances. We have found that gold is not suitable for electrode materials because it appears to act as a catalyst for chemical reactions which interfere with the electrochemical reactions. By using platinum electrodes with cyclic voltammetry, we have preliminary information that suggests that the polyboranes undergo a

coupled reaction. After using CV to discover the proper conditions to further study the polyborane reaction mechanisms, we are now ready to investigate the polyboranes with EIS.

## Results

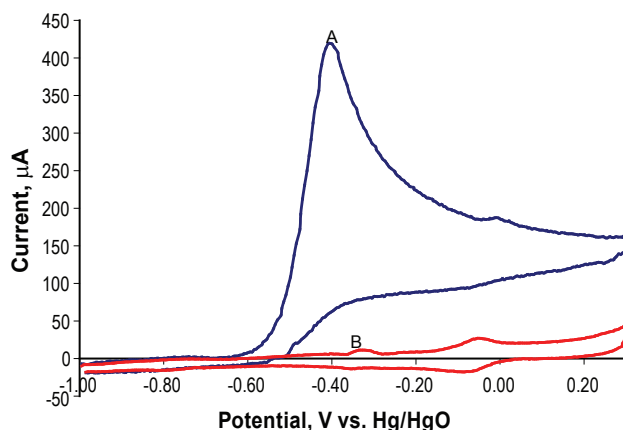
Tetraalkylammonium hydroxides in aqueous solutions have been investigated as solvents for  $\text{NaBO}_2$  in our electro-reduction experiments this year. There were three reasons for choosing these compounds: (1) to avoid the presence of alkali metal cations, while maintaining a high pH, (2) to allow specific adsorption of the tetraalkylammonium cation, which can change the profile of the electrical potential at the electrode/solution interface, and (3) to increase the overpotential for the HER. Item (1) is important in avoiding the formation of alkali metal amalgams when a mercury pool cathode is used. Item (2) relates to the theme of minimizing Coulombic repulsion of borate anion from the cathode. Figure 1 shows the results of a reduction experiment where tetraethylammonium hydroxide (TEAH) was used as the electrolyte; the solution was 2M TEAH + 0.2M boric acid ( $\text{B}(\text{OH})_3$ ). The total time of electrolysis was five days, and the analysis shown in Figure 1 was cyclic voltammetry (CV) using a 6mm diameter gold-disk working electrode. *This is the first result indicating that the reduction of borate ion may be occurring.* This experiment was performed using a constant current of 10 mA. In addition to TEAH, tetramethylammonium hydroxide (TMAH) and tetra-n-propylammonium hydroxide (TPAH) were used. It should be noted that in most of the constant potential electrolyses, finely dispersed (colloidal) Hg could be seen shortly after electrolysis started. It seems that a tetraalkylammonium ‘amalgam’ can be formed that reacts strongly with water [1]. Furthermore, it appears that the colloidal mercury (resulting after the dispersed amalgam reacts with water), being at open circuit, can



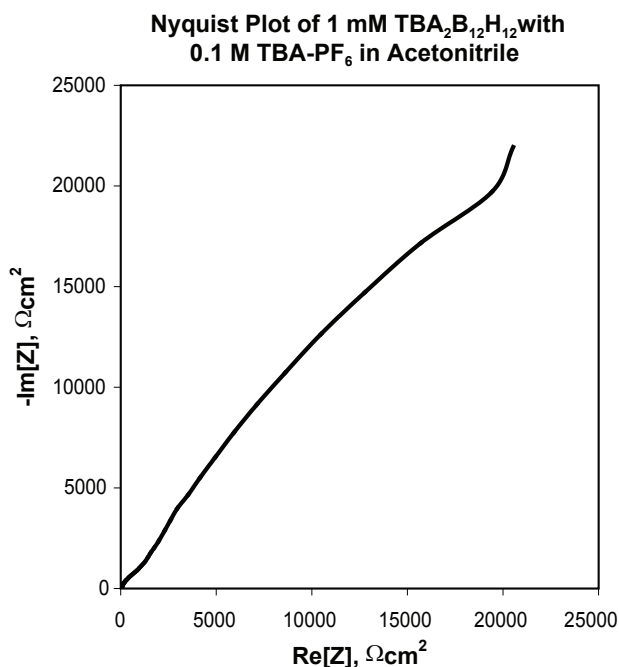
**FIGURE 1.** Hg Pool Electrolysis of 2M TEAH + 0.2M  $\text{B}(\text{OH})_3$  Before (A) and After (B) Electrolysis at 10 mA for Five Days

catalyze decomposition of sodium borohydride. For this reason, we are having problems with reproducibility with the mercury pool electrolysis experiments. Consequently, we are currently investigating constant-potential electrolyses that prevent the formation of the highly-reactive amalgam. Additionally, as described above, various cathode materials have been investigated that have moderate to high overpotential for the HER. Metals studied this year included gold, titanium, lead and mercury. Interestingly, the literature recommends gold as an electrode in direct borohydride fuel cells, since it is not supposed to catalyze hydrolysis of sodium borohydride [2]. However, in our experiments with gold as a cathode material, it appears that it is catalyzing decomposition of borohydride. Figure 2 shows CV at a gold-working electrode of sodium borohydride solution before and after stirring in contact with a gold foil. The decrease in peak current after electrolysis indicates decomposition of borohydride.

During the past year, we have overcome many barriers to adequately studying the polyborane samples. We have replaced a faulty potentiostat that was introducing a great deal of noise into the collected data. By perfecting a technique to exchange the cation on the polyborane salts, we are now able to achieve a tremendous improvement in the solubility and purity of the polyboranes in anhydrous acetonitrile. And, as shown in our previous quarterly reports, we have used cyclic voltammetry to obtain voltage regions of interest for use in EIS to determine the reaction mechanism. To this end, we have just begun using a computer code to simulate EIS data based on a set reaction mechanism. The user adjusts the code to the desired mechanism and inputs the necessary electrochemical parameters to obtain the EIS data as output. By systematically varying the available reaction choices and system parameters, we should be able to determine the reaction mechanism followed by the polyboranes by comparing



**FIGURE 2.** CV of 1mM  $\text{NaBH}_4$  in 2M  $\text{NaOH}$  + 25%  $\text{NaBO}_2$  Solution Before (A) and After Stirring (B) in Contact with a Gold Foil



**FIGURE 3.** Nyquist Plot of 1 mM  $\text{TBA}_2\text{B}_{12}\text{H}_{12}$  with 0.1 M  $\text{TBA-PF}_6$  Supporting Electrolyte in HPLC Grade Acetonitrile at 1 mm Diameter Pt-Disk Working Electrode

the theoretical and experimental data. Our most recent EIS data is shown in Figure 3 for a sample of 1 mM  $\text{TBA}_2\text{B}_{12}\text{H}_{12}$  with 0.1 M  $\text{TBA-PF}_6$  supporting electrolyte in high performance liquid chromatography (HPLC) grade acetonitrile.

## Conclusions and Future Directions

- A method has been perfected to exchange polyborane cations to increase solubility as well as improve sample purity.
- The initial stages of EIS studies have begun and we plan to continue characterizing reaction products with CV and elemental analysis techniques to gain a more fundamental understanding of these samples.
- Means of overcoming electrostatic repulsion of borate anion from the cathode will continue to be investigated. These include applying a square wave pulse to the cathode, continuing experiments with tetraalkylammonium hydroxides, and the use of a Devanathan-Stachurski (bi-polar palladium membrane) cell.
- Decomposition of borohydride solutions in contact with metals, e.g. as observed with Au will continue to be investigated. Preventing or minimizing this reaction is critical for electro-reduction experiments employing metallic cathodes.
- We will continue development and use of the EIS mechanism software to aide in determining the

polyborane reaction mechanism in conjunction with collecting the necessary EIS data from the polyborane samples to compare to the various simulated reactions.

### FY 2007 Publications/Presentations

1. J. McLafferty, D.D. Macdonald, Y-Z. Zhang, J. Tokash, and J-E. Bao, "B-O to B-H Conversion Activities at Penn State University," Meeting at Penn State University, August 29, 2006.
2. D.D. Macdonald, S. Colominas, J. Tokash, J. McLafferty, V. Bao, and J. Nollinger, "Chemical Hydrogen Storage Activities at Penn State University," Denver, CO, November 14, 2006.
3. D.D. Macdonald, S. Colominas, J. McLafferty, V. Bao, J. Nollinger, Y. Chen, and J. Tokash, "Boron Compounds for Hydrogen Storage," Penn State Hydrogen Day poster presentation, November 14, 2006.
4. D.D. Macdonald, S. Colominas, J. Tokash, J. McLafferty, V. Bao, and J. Nollinger, "Hydrogen Storage Tech Team Meeting," Meeting at PNNL, March 22, 2007.
5. D.D. Macdonald, S. Colominas, J. Tokash, J. McLafferty, V. Bao, J. Nollinger, G. Engelhardt, "Electrochemical Hydrogen Storage Systems," Annual Merit Review Meeting, Washington, D.C., May 18, 2007.

### References

1. B.C. Southworth, et al. *Anal. Chem.* 33 (1961) 208 – 212.
2. See, for example: S.C. Amendola et al. *J. Power Sources.* 84 (1999) 130 – 133.