IV.B.4e Electrochemical Hydrogen Storage Systems

Dr. Digby D. Macdonald (Primary Contact),
Dr. Yancheng Zhang, Justin C. Tokash,
Jason B. McLafferty, JainEr Bao, Yingzi Chen

The Pennsylvania State University
Center for Electrochemical Science and Technology
201 Steidle Building
State College, PA 16802
Phone: (814) 863-7772; Fax: (814) 863-4718
E-mail: ddm2@psu.edu

DOE Technology Development Manager:
Grace Ordaz

Phone: (202) 586-8350; Fax: (202) 586-9811
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire

Phone: (303) 275-4795; Fax: (303) 275-4753
E-mail: James.Alkire@go.doe.gov

Contract Number: DE-FC36-05GO15054

Start Date: March 1, 2005
Projected End Date: September 30, 2009

Objectives

- Electrochemical reduction of B-O to B-H.
- Complex borane electrochemistry.
- Electrochemical borane hydrogenation.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) 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

Electrochemical Hydrogen Storage Systems:

This project has three objectives that are focused on conducting fundamental studies in order to reach the DOE 2010 hydrogen storage targets:

- To discover an electrochemical pathway to prepare sodium borohydride, $NaBH_4$, from sodium metaborate, $NaBO_2$.

- To explore and define the fundamental electrochemistry of polyboranes and polyborane anion salts.
- To explore the feasibility of developing a reversible hydrogen storage technology based on the polyborane system.

Accomplishments

- Developed a reliable and accurate *in situ* method for analysis of the borohydride ion in alkaline solutions, confirming and building upon previous work by Bard and Mirkin [1]; the concentration may be determined accurately down to 0.65 mM.
- We have been unable to detect the reduction of metaborate on Cu amalgam or Hg pool electrodes in 2 M NaOH at potentials down to -2,000 $mV_{Hg/HgO}$. Thus, we have been unable to confirm claims in the patent literature that 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 metaborate 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 Millennium Cell's borohydride regeneration process and by chemically modifying the electrode surface to concentrate metaborate ion at the interface. Experiments to explore these strategies are now underway.
- Developed a reliable reference electrode for performing electrochemical studies in non-aqueous media.
- Established 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.
- Cyclic voltammetry indicates that these polyborane transformations probably involve coupled chemical reactions, the nature of which is under investigation.

Introduction

The regeneration of borohydride ion (BH_4^-) from metaborate salts (e.g. $NaBO_2$) is considered to be a key step in one hydrogen storage concept currently being explored by DOE contractors. The patent literature

contains claims that this transformation can be affected electrochemically, but details of how the reaction can be made to occur are seldom given. One aspect of this project is exploring the feasibility of affecting an electrochemically-mediated transformation. Closely related to this task is the development of an *in situ* electrochemical method for borohydride analysis that would circumvent the need to remove aliquots of solution for external analysis by, for example, ^{11}B NMR. Linear sweep voltammetry was previously explored by Bard, et al. [1] as an analytical technique and our work, in part, was to confirm those previous results.

Finally, 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 has been reported in the open literature on this topic [2-4]. The possibilities of obtaining a suitable polyborane system are tremendous because over 50,000 boron cluster compounds are known to exist; among them are numerous polyborane species.

Approach

There were two routes to the regeneration of sodium borohydride ($NaBH_4$) that we investigated: electro-reduction of sodium metaborate ($NaBO_2$) and hydrogen plasma reduction of boric acid (H_3BO_3). While exploring the first route towards the electro-reduction of sodium metaborate, we needed to establish an *in situ* technique to quantify the concentration of sodium borohydride. We then identified some conditions under which reduction of metaborate might be favorable in aqueous solution (see Results for more details). Cyclic voltammetry experiments were performed on such systems to see if reduction of metaborate could be observed. In the second route taken, we utilized the highly energetic environment of a hydrogen plasma containing very reactive species such as atomic hydrogen; this environment is expected to be favorable for reduction reactions.

In order to determine whether meaningful electrochemical transitions occur among the polyboranes, we developed various techniques to handle and study these materials. Because of a lack of available safety data, all work has been performed in an inert argon atmosphere within a glovebox. Because we chose to study these materials in an aprotic organic solvent (acetonitrile), we had the task of developing a suitable reference electrode for this system. Commercially available reference electrodes are based on aqueous redox systems and are not suitable for electrochemical studies in non-aqueous systems. After this task was completed, our initial studies began on the polyborane $B_{12}H_{12}^{2-}$ anion. After a number of experiments, we discovered that the solubility of certain polyboranes of

interest were not sufficiently high to obtain meaningful results. As a result, we developed a technique to chemically exchange the cation (e.g., K^+) of the polyborane salt with a larger cation (e.g., R_4N^+, where R is an alkyl group) resulting in a new salt with a much higher solubility, because of the lower surface charge density of the cation.

Results

Cyclic voltammetry (CV) was found to be a suitable, quantitative analytical technique for the borohydride ion in alkaline solution. Figure 1 demonstrates that for a ten-cycle CV, the peak current is linearly related to concentration for all ten cycles. At this time, we have not determined why the peak current decreases with increased cycling; more work is needed.

The hypothetical reduction of metaborate (BO_2^-) has a standard potential of -1.36 V vs. Hg/HgO. In the 2 M hydroxide solutions we use, the equilibrium potential for hydrogen evolution is -0.97 V vs. Hg/HgO. Kinetic barriers to hydrogen evolution are known and some of these were studied to extend the cathodic limit (point at which hydrogen begins to evolve) for our media. Mercury and mercury-plated copper ("amalgamated copper") electrodes were used, along with thiourea and tetraethylammonium hydroxide. All of these are known to electrochemists to inhibit hydrogen evolution. Figure 2 illustrates that the cathodic limit observed is much more negative than the cathodic limit predicted from thermodynamics, i.e. -0.97 V vs. Hg/HgO. Nonetheless, we did not observe direct reduction of metaborate in any of these systems.

The microwave-induced hydrogen plasma experiment was performed using solid boric acid on two substrates: silica and graphite. The sample obtained from the silica substrate experiment was the
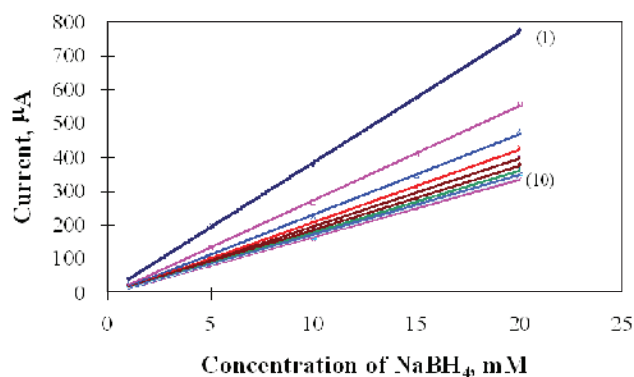

FIGURE 1. Peak current versus concentration for all ten cycles of cyclic voltammetry. Working electrode was a 1 mm diameter gold disk; counter electrode was a graphite disk. Sweep rate: 500 mV/s. All solutions are in 2 M NaOH + 0.2 M $NaBO_2$. The cycle numbers are indicated in the Figure from 1 to 10, consecutively.

easiest to analyze, and x-ray diffraction (XRD) and nuclear magnetic resonance (NMR) for boron (^{11}B) and hydrogen (^{1}H) were performed on this sample. The XRD analysis indicates that a boron hydride compound may be present. The NMR analysis did not clarify the identity of the sample. We must note that no attempt was made to collect a gas phase sample during or immediately after the operation of the plasma. This means that any volatile boron hydrides formed during the experiment would be lost. Clearly, more work is needed before the effectiveness of hydrogen plasmas can be ascertained.

With regard to the electrochemical studies performed on the polyboranes, the blank solution chosen was 0.100 M tetra-*n*-butylammonium hexafluorophosphate (TBA-PF$_6$) dissolved in HPLC grade acetonitrile; all samples were dissolved into portions of this solution for study.

The first sample studied was 1 mM triethylammonium dodecahydrododecaborate ([(CH$_3$CH$_2$)$_3$NH]$_2$B$_{12}$H$_{12}$, hereafter referred to as TEA$_2$B$_{12}$H$_{12}$). The 10-cycle CV for this sample is shown in Figure 3, where the arrow indicates the progression of the oxidation wave with successive cycles. The cause of this behavior is unknown at this point, however we believe that a coupled electrochemical-chemical (EC) reaction mechanism exists; this will be studied in more detail using electrochemical impedance spectroscopy (EIS).

The next sample studied was 1 mM tetra-*n*-butylammonium dodecahydrododecaborate ([(CH$_3$CH$_2$CH$_2$CH$_2$)$_4$N]$_2$B$_{12}$H$_{12}$, hereafter referred to as TBA$_2$B$_{12}$H$_{12}$). This polyborane is the product of the cation exchange reaction discussed earlier (the original polyborane salt had potassium cations). Figure 4 shows the 10-cycle CV of 1 mM TBA$_2$B$_{12}$H$_{12}$ under identical experimental conditions as before. The oxidation peak at 1.25 V appears only on the first cycle with a broad shoulder

that appears to contain a very small oxidation wave near 1.52 V. A small reduction wave can be seen at −0.55 V.

Additionally, we studied a solution of 10 mM TBA$_2$B$_{12}$H$_{12}$. As shown in Figure 5, the increase in polyborane concentration has a profound impact on the oxidation features, however the reduction wave was virtually unchanged. This solution was made with the same recrystallized polyborane salt as used for the 1 mM solution, so these results can only be explained by an increase in the polyborane concentration. A sharp oxidation peak is seen in Figure 5 at 1.25 volts; this is at the same potential value as that of the 1 mM solution. Additionally in Figure 5, we notice that the small oxidation wave at 1.53 volts on the anodic shoulder of the first peak is more visible now as compared to that of Figure 4. Finally, we now see in Figure 5 that a new oxidation peak is present at 1.86 volts. We believe this is evidence of an electrochemical-chemical-electrochemical

FIGURE 3. A 10 cycle CV for 1 mM TEA$_2$B$_{12}$H$_{12}$ dissolved in the blank solution (0.100 M TBA-PF$_6$ in acetonitrile). The working electrode was a 1 mm Pt disk, the counter electrode was a 2 mm Pt disk, and the reference electrode was Ag/0.010 M Ag+. The scan rate was 100 mV/s. The arrow indicates the movement of the oxidation wave with successive cycles from 1.35 to 2.00 volts.
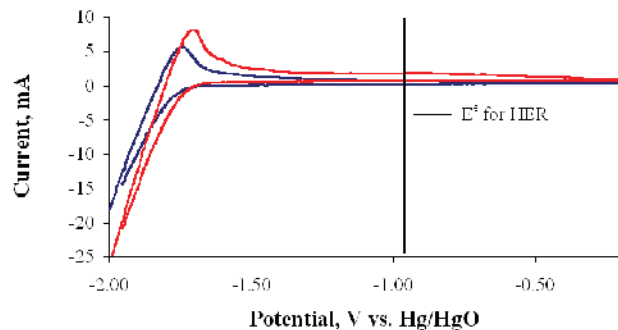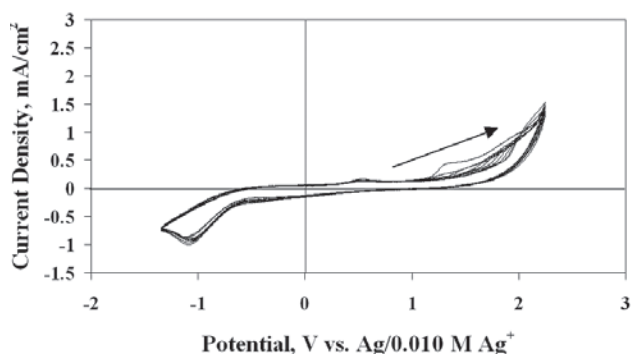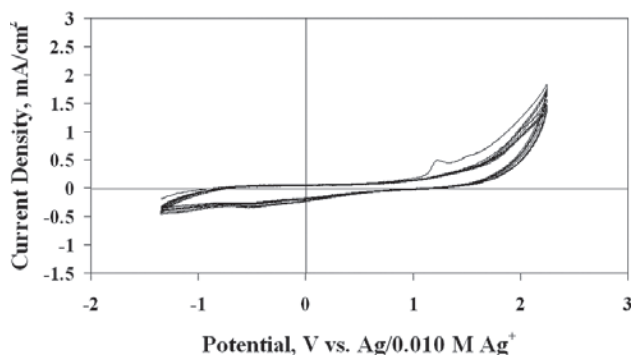
FIGURE 2. CV of blank solution (TEAH, blue) and NaBO$_2$ in TEAH (red). Working electrode was a 13 mm diameter mercury pool; counter electrode was a graphite disk. Sweep rate: 500 mV/s. The vertical line indicates the estimated equilibrium potential for hydrogen evolution in 2M TEAH solution.

FIGURE 4. A 10 cycle CV for 1 mM TBA$_2$B$_{12}$H$_{12}$ dissolved in the blank solution (0.100 M TBA-PF$_6$ in acetonitrile). The working electrode was a 1 mm Pt disk, the counter electrode was a 2 mm Pt disk, and the reference electrode was Ag/0.010 M Ag$^+$. The scan rate was 100 mV/s.

FIGURE 5. A 10 cycle CV for 10 mM $TBA_2B_{12}H_{12}$ dissolved in the blank solution (0.100 M $TBA-PF_6$ in acetonitrile). The working electrode was a 1 mm Pt disk, the counter electrode was a 2 mm Pt disk, and the reference electrode was $Ag/0.010$ M Ag^+. The scan rate was 100 mV/s.
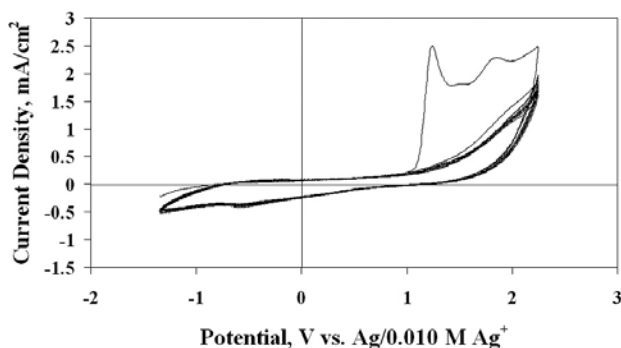
coupled reaction mechanism, which will be investigated further in a mechanistic study involving EIS.

A fascinating observation for Figure 5 is the lack of oxidation peaks in the 1–2 V region for cycles other than the first one. Consequently, the constituents that are oxidized within this potential region are either removed irreversibly (and quantitatively) or their oxidation is inhibited on further cycling. To explain this behavior, we have performed calculations which show that only 0.008% of the polyborane is consumed on the first, forward potential sweep. In our calculations we assume that the reaction progresses via a one-electron reaction; however, if the reaction involves multiple electrons, the amount of polyborane removed is even less. Thus, we conclude that the lack of oxidation peaks on the second and higher sweeps is not due to depletion of the polyborane reactant; rather, we feel that passivation of the surface by an adsorbed, inert oxidation product is the most likely cause.

Conclusions and Future Directions

Based on our observations in trying to reduce metaborate in alkaline, aqueous solution, we plan the following future work: (1) 'indirect' reduction of metaborate, 'indirect' meaning chemical reduction may occur through reaction with adsorbed hydrogen or alkali metals formed at the cathode during electrolysis; (2) investigate methods that should enhance adsorption of metaborate at the cathode, e.g. neutral or positively charged oxidized boron species as starting material, chemically-modified electrodes; (3) continue studies of borohydride oxidation to determine why the peak current decreases with increased cycling; and (4) further investigate hydrogen plasma for reduction of metaborate.

Since the electrochemical reduction of B-O to B-H apparently does not occur at room temperature, some high temperature work (up to 200ºC) will be carried out

to investigate if this process will become feasible when the kinetics are facilitated. A controlled hydrodynamic electrochemical cell with an annular flow channel will be used at elevated temperatures (up to 200ºC), of which, the hydraulic properties have been characterized previously in our laboratory. To maintain the system in a single aqueous phase, a high pressure liquid chromatography (HPLC) pump and a pressure control valve will be employed, with the pressure being set at a value at least 200 psi (1.38 MPa) higher than the water vapor pressure at that temperature. The same type of solution will be used here as for the room temperature studies ($NaOH + NaBO_2$), with the impeller rotating at a high speed, and both with and without the hydrogen gas dissolved in the solution. A schematic of this system is shown in Figure 6.

After verifying that 0.100 M $TBA-PF_6$ in acetonitrile is a suitable blank solution with a wide potential range available, we studied solutions with low concentrations of polyboranes. The cause of the oxidation wave moving toward higher potential and current density values for the solution of 1 mM $TBA_2B_{12}H_{12}$ is unknown at present, but it is currently under investigation.

Once the potassium cations were exchanged to tetra-*n*-butylammonium, the resulting dodecahydrododecaborate salt exhibits approximately a 100-fold increase in solubility in acetonitrile, allowing for a wider range of concentrations to be studied. We notice that at low concentrations the oxidation features are more wave-like (Figure 4), however at higher concentrations the oxidation features become much more prevalent (Figure 5) with a new peak present that was not noticed at lower concentrations. The entities that are oxidized within the 1–2 V region during the first cycle apparently inhibit further oxidation during subsequent cycles.
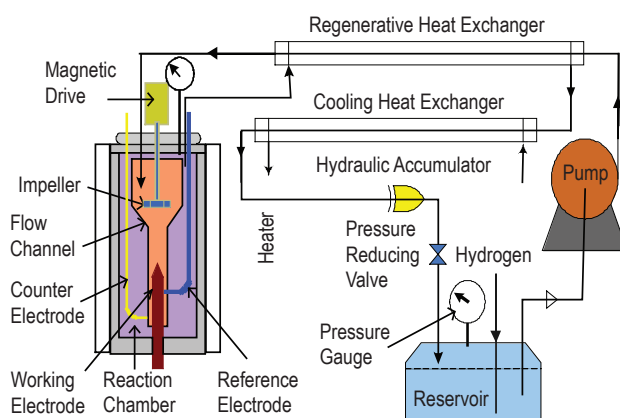

FIGURE 6. A schematic of the experimental apparatus that will be used for the high temperature studies of the electrochemical reduction of B-O to B-H.

Our future experiments will be to study the effects of concentration in more depth for various polyboranes. Additionally, we plan to investigate the reaction mechanism for selected polyborane anions utilizing electrochemical impedance spectroscopy. In order to assist in discovering the reaction mechanism, we plan to perform controlled potential electrolysis and to collect the reaction products from a divided electrochemical cell by utilizing high performance liquid chromatography as a detection and separation technique. The separated materials will be further identified by mass spectroscopy and nuclear magnetic resonance techniques.

Special Recognitions & Awards/Patents Issued

1. D. D. Macdonald and J. McLafferty, "Conversion of Oxides into Hydrides Using a Hydrogen Plasma", Invention Disclosure, Pennsylvania State University, February 28, 2006.

2. J. McLafferty and D. D. Macdonald, "Novel Modified Electrodes for the Electrochemical Reduction of Boron-Oxygen Entities to Boron-Hydrogen Species", Invention Disclosure, Pennsylvania State University, April 20, 2006.

FY 2006 Publications/Presentations

1. D. D. Macdonald, W. Coulson, Y. Zhang, J. McLafferty, and J. Tokash, "Electrochemical Hydrogen Storage", CHS CoE Center Meeting, Salt Lake City, UT, October 27, 2005.

2. D. D. Macdonald, W. Coulson, Y. Zhang, J. McLafferty, and J. Tokash, "Electrochemical Hydrogen Storage", Penn State University, September 20, 2005.

3. J. McLafferty, J. Tokash, Y. Zhang, and D. D. Macdonald, "Electrochemical Hydrogen Storage", CHS CoE Center Meeting, Los Alamos, NM, March 22, 2006.

4. J. McLafferty, J. Tokash, Y. Zhang, W. J. Coulson, and D. D. Macdonald, "Electroanalysis of Borohydride Ion", Electrochemical Society Spring Meeting, Denver, CO, May 7-12, 2006.

5. J. Tokash, J. McLafferty, Y. 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.

6. J. McLafferty, J. Tokash, Y. Zhang, W. J. Coulson, and D. D. Macdonald, "Electroanalysis of Borohydride Ion", ECS Transactions, submitted.

7. J. Tokash, J. McLafferty, Y. Zhang, W. J. Coulson, and D. D. Macdonald, "Polyhedral Boranes as Electrochemical Hydrogen Storage Materials", ECS Transactions, submitted.

References

1. M. Mirkin and A. Bard, *Anal. Chem*., **63**, 532 (1991).

2. R. L. Middaugh and F. Farha, Jr., *J. Am. Chem. Soc.*, **88**, 4147 (1966).

3. R. J. Wiersema and R. L. Middaugh, *J. Am. Chem. Soc.*, **89**, 5078 (1967).

4. R. J. Wiersema and R. L. Middaugh, *J. Am. Chem. Soc.*, **92**, 223 (1970).