

IV.B.1d Electrochemical Hydrogen Storage Systems

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Objectives

- Demonstrate electrochemical reduction of boron oxides to borohydride in aqueous solution.
- Demonstrate and characterize electrochemical transformations of polyboranes and ammonia borane.
- Further develop electrochemical impedance spectroscopy (EIS) as a tool for electrochemical mechanistic analysis.

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 Borate (B-O) to Sodium Borohydride (B-H, NaBH₄)

This project is concerned with the reduction of B-O compounds (e.g. NaBO₂) to NaBH₄. 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.

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.

Electrochemistry of Ammonia Boranes

The electrochemical study of ammonia boranes is a new aspect of our project that is meant to replace the polyborane research in the future. The ammonia boranes are already part of other (external) research that has shown that they are a good medium for hydrogen storage; however, the regeneration of the spent fuel is still a necessary aspect of the overall project. Our task is to determine the electrochemical behavior of ammonia boranes and discover whether an electrochemical route to regenerating the spent ammonia borane fuel is possible.

Accomplishments

- Continued reduction experiments for B-O to B-H using materials having a high overpotential for the hydrogen evolution reaction. Gold, titanium and lead were used in addition to mercury and mercury-plated copper.
- Repeated and modified work disclosed to us by Rohm and Haas on electrochemical regeneration of NaBH₄.
- Investigated the use of tetraalkylammonium cations, pulsed current or potential, and modified electrodes to try to overcome electrostatic repulsion of borate anion from cathode.

- Demonstrated that electrochemical reduction of boron oxides to borohydride is not feasible in aqueous solution.
- Determined that the oxidation of polyboranes (the hydrogen releasing reaction) is complicated by a polymerization of the polyboranes onto the electrode surface, thus inhibiting the reaction to continue.
- Began studying the ammonia boranes in non-aqueous and aqueous solvents. The results in aqueous solutions are being studied in greater detail to understand the oxidation mechanism before proceeding to investigate the reduction of the spent ammonia borane fuel.



Introduction

NaBH_4 is currently prepared by the Brown-Schlesinger process, an energy intensive process with low yields. In order for NaBH_4 to be accepted as a hydrogen storage material, alternative, low-cost, high-yield synthetic routes are required. Electrochemical regeneration was the primary alternative route explored by PSU. Several patents were granted to others in which electrochemical methods were claimed to yield NaBH_4 [1]. Our findings suggest that electrochemical regeneration of NaBH_4 , at least in aqueous solution, is not possible.

In both the hot and cold hydrogen plasma systems, boric acid was subjected to hydrogen plasma over time. The plasma systems were designed to determine if more or less energetic plasma is required for a reaction to occur, and which system can produce the desired B-H compounds more efficiently. Due to severe operational problems with the equipment, leading to lengthy downtime, the experiments were discontinued.

Complex polyhedral boranes were considered as a suitable hydrogen storage material owing to their theoretical gravimetric and volumetric storage capacities and the lack of boron-oxygen bonds, which are inherently hard to reduce electrochemically. Although these molecules were discovered in the 1950s, very little is known about their electrochemical behavior. We are also investigating ammonia borane molecules as they are already being used as hydrogen storage materials; however, our research is on the electrochemical regeneration of the spent ammonia borane fuel.

Approach

PSU focused on electrochemical regeneration of NaBH_4 in aqueous solutions for the following two reasons: the spent fuel (primarily NaBO_2) was expected to be in an aqueous medium, and electrochemical

experiments in aqueous solutions are generally simpler to perform and have less ecological considerations than do experiments in non-aqueous solutions. The patent literature in this area is generally focused on cathodes having a high overpotential for water electrolysis, in order to try to minimize the rate of this competing process; some of our work also used cathodes materials from this class. Additionally (and not considered in these patents), attempts to overcome electrostatic repulsion of the negatively charged borate anion (BO_2^-) from the negatively charged cathode surface were explored. Three methods were tried: application of a current or potential pulse, modification of the cathode-solution interface by specific adsorption of cations, and use of polymer-modified cathodes.

In order to understand the electrochemical behavior of the polyboranes, we began by studying their oxidation and reduction reactions in non-aqueous solutions due to their limited solubility in aqueous solutions. We focused on determining the reaction mechanism taking place during the oxidation (hydrogen release) of the polyboranes. To aid in this step, we developed (in conjunction with Dr. George Engelhardt of OLI Systems) a general mathematical model of electrochemical impedance spectroscopy and a computer program to simulate results based on the model. The new task of studying ammonia boranes will parallel the work done on the polyboranes.

Results

Previously, the stability of NaBH_4 in aqueous, alkaline solutions was evaluated at PSU. Because electrolysis experiments continued to yield no positive results for BH_4^- formation, the role of cathode material was investigated. Stability tests were performed at open circuit, and with electrolysis (positive control – the catholyte had a small amount of NaBH_4 added at the beginning) with the cathode material present. The cyclic voltammetry (CV) method described in previous reports was used to quantify changes in peak current for NaBH_4 oxidation over time. These experiments demonstrated a stability problem both at open circuit and during constant current electrolysis, even with materials not expected to be a problem (e.g. Au). Figure 1 shows results at open circuit for Au and Ag with 3 mM NaBH_4 in 2 M NaOH + 25% NaBO_2 . Note that there was a definite tendency for the peak current to decrease in time, signaling loss of BH_4^- . Because the literature indicates that Au is not catalytic for BH_4^- hydrolysis, this result was not expected [see, for example, 2]. However, it was realized that oxygen was not removed from the solutions. Thus, the cathode material (at least Au) could be catalyzing *oxidation* of NaBH_4 in the presence of O_2 . Figure 2 shows results for a copper electrode, again with 3 mM NaBH_4 in 2M NaOH + 25% NaBO_2 . In Figure 2, the series for electrolysis at 10 mA showed a

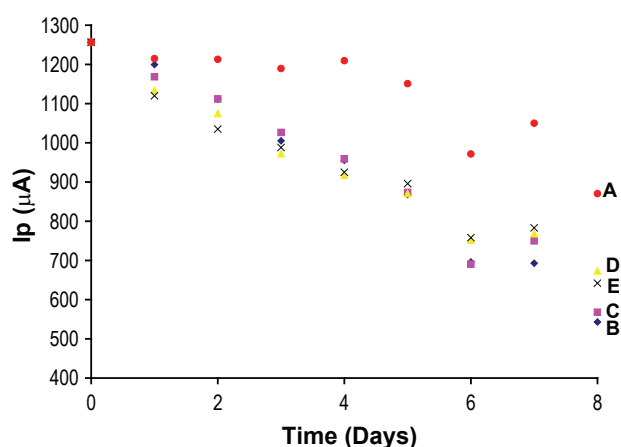


FIGURE 1. Peak Current (from CV measurement) vs. Time for 3 mM NaBH_4 in 2 M NaOH + 25% NaBO_2 in Contact with Au and Ag Electrodes – Series: A: 3 mM standard, no metal; B: Au, sample a; C: Au, sample b; D: Ag, sample a; E: Ag, sample b.

more rapid decrease. In these experiments, an H-cell with a Nafion[®] membrane divider was used, and 1 M H_2SO_4 was used as the anolyte. The more rapid decrease could be due to proton cross-over, which would neutralize (in part) the alkalinity of the catholyte. This could increase rate of hydrolysis of NaBH_4 . Sulfuric acid was not typically used as the anolyte previously; its use was suggested in a publication [3]. Interestingly, the electro-osmosis effect reported previously by PSU was not observed when 1 M H_2SO_4 was used as the anolyte. In addition to these stability experiments, aqueous reduction experiments were continued, with focus on overcoming electrostatic repulsion of borate anion (as described in the Approach section). The cathode modifications included 1-thioglycerol on Au, which forms a self-assembled monolayer with the diol functionality needed to chelate borate, and polymer modifications using quaternized poly (4-vinylpyridine). None of the electrolysis experiments yielded any convincing evidence of BH_4^- production. Thus, electrolytic production of NaBH_4 is not feasible in aqueous solution, at least as explored in this work.

Two plasma reactors were purchased, received, and installed. The first system operates at 13.56 MHz (cold plasma) and the second system operates at 2.54 GHz (hot plasma). Also a residual gas analyzer was purchased, received, and installed. The residual gas analyzer should greatly aid in the initial determination of reaction conditions because of the available real-time process monitoring. However, an air leak was detected in the radio frequency plasma reactor system. This has not allowed the collection of data from this system to date.

In order to better understand the electrochemical behavior of the polyboranes, we have used both CV and EIS techniques. By examining the CV data for

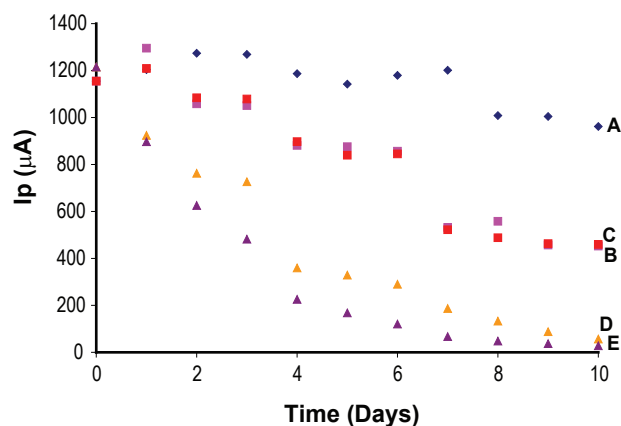


FIGURE 2. Peak Current (from CV measurement) vs. Time for 3 mM NaBH_4 in 2 M NaOH + 25% NaBO_2 in Contact with Cu Electrodes – Series: A: 3 mM standard, no metal, no electrolyte; B: Cu, sample a; C: Cu, sample b; D: Cu, electrolysis at 10 mA a; Cu, electrolysis at 10 mA b.

the polyboranes, we feel that the reaction mechanism associated with the oxidation (hydrogen release) is a coupled electrochemical-chemical-electrochemical reaction (a chemical step appears to be present between two separate electrochemical steps). In order to verify this, we utilized EIS to gather additional data and we analyzed it in terms of the mathematical reaction mechanism model that we developed. We have experienced two main problems: (1) the polyboranes produce a polymerized film on the electrode surface during prolonged constant-potential electrolysis (which is part of an EIS experiment), and (2) we have yet to successfully verify our mathematical model due to the lack of a different sample with a well known reaction mechanism that would act as a standard for calibration and comparison. We are examining the reduction of nitromethane as a standard mechanism for the EIS modeling research, due to its in-depth investigation by other groups.

We have also started to study the oxidation of ammonia boranes in both non-aqueous as well as in aqueous solutions. By understanding the oxidation, we feel that we will be better prepared to investigate the reduction of the spent ammonia borane spent fuel. So far we have found that the samples have greater electrochemical activity in aqueous solutions and that their oxidation reaction is unusual in that there are two visible oxidation steps occurring and that the more anodic oxidation step proceeds more readily while sweeping the potential from positive to negative potential, which is the opposite way that it is expected to occur.

Conclusions and Future Directions

- The results of work at PSU on NaBH_4 regeneration suggest that electrolytic production of NaBH_4 is

not feasible in aqueous solutions. This finding was part of the reason that the DOE reached a no-go decision for NaBH_4 as a chemical hydrogen storage material. Thus, all future work will be in support of aminoborane regeneration work.

- Current aminoborane regeneration schemes call for organotin hydrides as reducing agents. The literature indicates that electrochemical reduction of organotin compounds, such as the halides, may yield the hydrides; work has begun in this area.
- Experiments on direct electrochemical reduction of boron complexes from spent aminoborane digestion are planned.
- Devanathan cell hydrogenations are being explored in support of aminoborane regeneration work.
- Polyboranes appear to be suitable for hydrogen storage based on theoretical gravimetric and volumetric hydrogen content; however, the problem of electrode filming due to a polymerization of the polyboranes needs to be overcome for this to be a useful hydrogen storage medium.
- EIS is being used in conjunction with our mathematical reaction mechanism model to identify unknown electrochemical mechanism. We are studying the electrochemical reduction of nitromethane as a known reaction so that in the future we can verify our mathematical model.
- Ammonia boranes are just beginning to be studied in our lab, and so far they appear to have an unusual oxidation mechanism. We are waiting to receive a sample of the spent ammonia borane fuel from another laboratory. Once it arrives we can begin to study its reduction (hydrogenation reaction) based on our findings of its oxidation mechanism.

FY 2008 Publications/Presentations

1. D.D. Macdonald, S. Colominas, J. Tokash, J. McLafferty and J. Nollinger, "DOE Go/No-Go Meeting," Meeting at ANL, September 10, 2007.
2. D.D. Macdonald, S. Colominas, and, J. McLafferty,, "212th ECS meeting," Meeting at Washington DC, October 7, 2007.
3. 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 5, 2007.

References

1. E. Gyenge and C.W. Oloman. *Journal of Applied Electrochemistry* 28 (1998) 1147.
2. C.P. de Leon et al. *Journal of Power Sources* 155 (2006) 172.
3. W. Jianquang, S. Yanping, and L. Zhehan. *Journal of Taiyuan University of Technology* 37 (2006) 539. Translated version courtesy of Rohm and Haas.