

IV.B.1k Electrochemical Hydrogen Storage Systems

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Objectives

- Demonstrate and characterize electrochemical transformations of ammonia borane (AB) and organotin hydrides.
- Investigate direct hydrogenation of AB in ionic liquids.
- Further develop electrochemical impedance spectroscopy (EIS) as a tool for mechanistic analysis of electrochemical systems.

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

Electrochemistry of AB and Organotin Hydrides

Our task is to determine the electrochemical behavior of AB and discover whether an electrochemical route to regenerating the spent AB fuel is possible. The regeneration of spent AB fuel is being investigated directly (without outside reducing agents) and indirectly (with organotin hydrides as an intermediate reducing agent). If the indirect route is chosen, we need to be able to regenerate the oxidized form of the organotin hydride in order to make the project a success.

Direct Hydrogenation of AB in Ionic Liquids

In addition to aqueous and organic solutions, we are attempting the direct hydrogenation of spent AB fuel (or organotin halide) in ionic liquids. Because we have no spent fuel at this time, a test hydrogenation process is being used to verify that the technique works. As such, we picked the hydrogenation of carbon dioxide (CO₂) to methanol in ionic liquid as our test system.

Mechanistic Analysis using EIS

In conjunction with other experiments, EIS can be used to identify the reaction mechanism of the system under study. By creating a general model and computer code for EIS, we can now extract kinetic parameters from reactions we are investigating. This will allow us in the future to optimize experimental conditions to achieve maximum reaction rates for systems of interest to this project.

Accomplishments

- Demonstrated complex electrochemical activity of AB.
- Attempted the hydrogenation of organotin halide using direct electrolysis techniques as well as beginning work to hydrogenate organotin halide in the Devanathan cell.
- Successfully hydrogenated several samples of styrene using the Devanathan cell in preparation for receiving samples of spent AB fuel.
- Finished the design and testing of a non-aqueous reference electrode to enable accurate potential measurements in organic solvents.
- Attempted direct hydrogenation of carbon dioxide in ionic liquids.
- Finished testing our general model of electrochemical impedance spectroscopy on a

simple reaction and successfully extracted kinetic information by a best-fit procedure.



Introduction

AB is a material capable of reaching DOE 2010 and 2015 goals for volumetric and gravimetric hydrogen storage densities. After the extraction of hydrogen from AB, the spent fuel needs to be regenerated in order for the overall process to continue. The spent AB fuel is polymeric in form and it can be digested using techniques from other researchers within the Chemical Hydrogen Storage Center of Excellence. The digested material can then be hydrogenated either directly using electrochemical regeneration or by reacting it with a reducing agent such as an organotin hydride [1]. If the latter method is used, the organotin hydrides become oxidized at the expense of hydrogenating the spent AB fuel, and as such the organotin compounds will need to be hydrogenated (electrochemically). Our work is being investigated in aqueous, organic (non-aqueous), and ionic liquid conditions.

Because many important reactions in this research are not fully understood, we want to be able to discover the exact reaction mechanism as well as the important kinetic parameters that control the overall system. Once the reaction mechanism and kinetic parameters are known for a system of interest, it would then be possible to setup the experimental conditions in such a way as to optimize the reaction rates, which would lead to increased efficiency.

Approach

Our focus for the hydrogenation of AB spent fuel will be to utilize a Devanathan cell for electrochemical reduction (hydrogenation) reactions. The Devanathan cell (shown in Figure 1) is a two- or three-compartment cell (depending on whether an additional solution separator is used) that uses a palladium or palladium alloy foil as the main solution separator as well as the working electrode for the hydrogenation reactions. The Devanathan cell works by generating hydrogen on one surface of the palladium foil and allowing it to diffuse through the foil (by chemical potential gradient) to the reaction side, where the hydrogen is supplied to hydrogenate the solution species either chemically or electrochemically. Because the Devanathan cell is not typically used to hydrogenate samples (its typical use is to study hydrogen diffusion through the membrane), we needed to test the process and chose the hydrogenation of styrene as an example until we receive spent AB fuel to study. We have also recently started using this technique to attempt the hydrogenation of organotin halides to support the indirect method of hydrogenation.

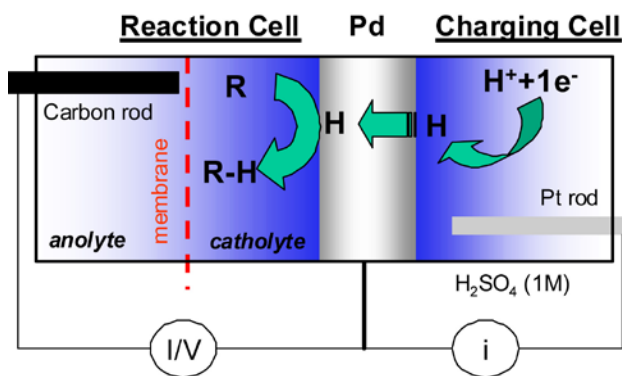


FIGURE 1. Schematic diagram of the Devanathan-Stachurski cell. In the styrene hydrogenation reactions, we do not need a separator membrane or a counter electrode on the reaction side since the hydrogenation occurs chemically. Also, for this work, we are using 6 M KOH as opposed to 1 M H_2SO_4 on the charging side.

In addition to the Devanathan cell work, we have also attempted the direct hydrogenation method in ionic liquid solutions. Again, because we do not have spent AB fuel to study, we have worked with the hydrogenation of carbon dioxide as a test reaction. To support both the direct and indirect hydrogenation methods, we have developed (in conjunction with Dr. George Engelhardt of OLI Systems) a general mathematical model of electrochemical impedance spectroscopy and a computer program to simulate and best-fit results based on the reaction mechanism. The mathematical modeling of reaction mechanisms will be applied to the AB and organotin hydride samples.

Results

In light of the findings from literature [2-7], our work has employed both acetonitrile (ACN) and dimethoxyethane (glyme) as solvents. We consider the electrochemical activity of hexaalkyldistannane to be important. This is because most radicals are highly reactive species and thus their reactions have very low activation energies. Furthermore, in contrast to ionic reactions, solvent effects are rather minimal in the vast majority of radical reactions. For these reasons, we speculate that little can be done to avoid dimerization of trialkyltin radicals and therefore conditions must be chosen to allow the reduction of hexaalkyldistannanes. Most of the work in the literature has used either mercury or amalgamated working electrodes; we used these in some experiments. Additionally, a silver working electrode was used in some experiments. Silver was chosen because it is known to be a good electrocatalyst for the reduction of alkyl halides, and therefore it would be interesting to see if it exhibits similar behavior in the reduction of trialkyltin halides [8].

Figure 2 shows cyclic voltammograms (CVs) obtained at a 1 mm silver disk working electrode

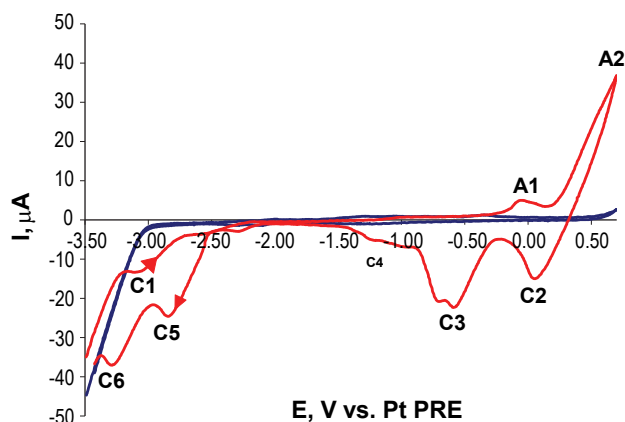


FIGURE 2. CV at 1 mm diameter silver disk working electrode. Sweep rate: 250 mV/s. CE: platinum wire. RE: Pt pseudo-reference. Blue: blank (0.1 M TBAPF₆ in glyme). Red: 10 mM Bu₃SnCl in 0.1 M TBAPF₆/glyme. Arrows indicate direction of sweep. The labels are described in the text.

for 10 mM tributyltin chloride (Bu₃SnCl) in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆)/glyme. A large amount of electrochemical activity is evident in the CV of 10 mM Bu₃SnCl. Peak C1, a cathodic peak, occurs on the forward sweep near -3 V. Peak C2 is most likely related to peak A2. The identity of peak A2 is not clear. The shape and location suggests that it is related to the oxidation of solvent (glyme) or supporting electrolyte (TBAPF₆). On the other hand, this peak is not seen in the blank. However, since a platinum wire is being used as a pseudo-reference, the potential scale may have shifted upon addition of the Bu₃SnCl. Peak C3 is seen here as what appears to be two closely-spaced peaks. In some experiments, however, it appears as one broad peak. The reason for this behavior is not clear at this time. By analogy to the results of Mazzocchin's group, it would seem that this peak is due to reduction of Bu₃SnCl to Bu₃Sn radical. Peak C5 or C6 look similar to the peak observed by Mazzocchin et al. for Ph₃SnCl in ACN. These workers attributed the peak to reduction of Ph₃SnSnPh₃, which formed by dimerization of Ph₃Sn radicals (described above).

Some experiments were performed where phenol (PhOH) was added to the electrolyte solution. Some of these experiments employed holds for various times at potentials corresponding to various peaks (particularly C5 and C6), but no evidence of Bu₃SnH formation was found in the voltammograms. Exploratory CV was performed on a ~13 mM Bu₃SnSnBu₃ solution; the CVs are shown in Figure 3. In these CVs, no peak corresponding to Bu₃SnSnBu₃ reduction is seen. However, when comparing the red curve (Bu₃SnSnBu₃) with the green curve (Bu₃SnSnBu₃ with PhOH), a significant change is evident. The CV for Bu₃SnSnBu₃

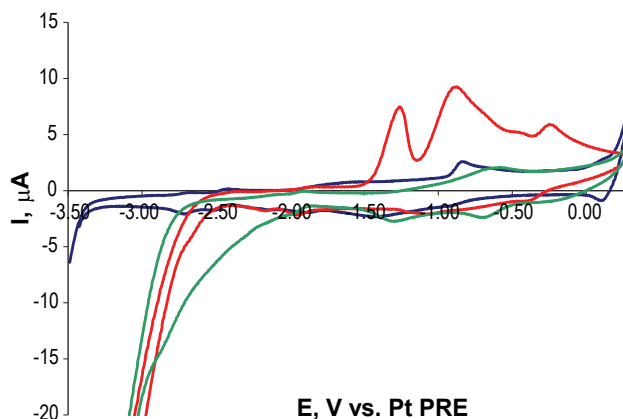


FIGURE 3. CV at 1 mm diameter silver disk working electrode. Sweep rate: 300 mV/s. CE: platinum wire. RE: Pt pseudo-reference. Blue: blank (0.1 M TBAPF₆ in glyme). Red: ~13 mM Bu₃SnSnBu₃ in 0.1 M TBAPF₆/glyme. Green: ~13 mM Bu₃SnSnBu₃ with 10 mM PhOH in 0.1 M TBAPF₆/glyme.

shows three anodic peaks on the forward sweep. After addition of PhOH, these peaks are extinguished.

The meaning of the results of these CV experiments is not clear at this time. As mentioned above, peak C5 or C6 in Figure 2 resemble the peak attributed to Ph₃SnSnPh₃ reduction observed by Mazzocchin et al. However, when a known sample of Ph₃SnSnPh₃ was used, this peak was not evident. Perhaps C5 or C6 are not due to reduction of Bu₃SnSnBu₃. Evidently, more experiments to identify the source of these peaks are required.

To test the Devanathan cell, we attempted the hydrogenation of styrene, which is known to form ethylbenzene. The reaction was carried out by applying a fixed current to the palladium alloy membrane for various periods of time. An analysis using gas chromatography-mass spectrometry revealed that the rate of production (hydrogenation) is 2.90% per day at an average efficiency of 79%, see Figure 4.

The technique used to monitor the hydrogenation of CO₂ in ionic liquids was CV; and this was carried out with a computerized electrochemical workstation (Gamry Instrument). To analyze the reaction product, Fourier transform infrared-attenuated total reflectance spectroscopy has been employed.

All experiments were carried out in 0.01 M 1-butyl 3-methyl imidazolium hexafluorophosphate aqueous solution. A platinum metal plate was employed as a working electrode. The surface of the electrode was etched by hot concentrated sulfuric acid. The electrode potential of the cathode was measured with respect to Ag/AgCl (sat. KCl) reference electrode. A platinum wire was used as counter electrode. Pure N₂ gas

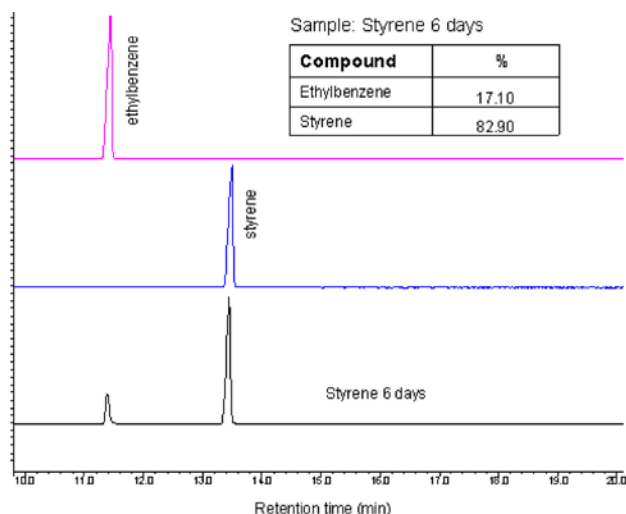


FIGURE 4. Gas chromatography–mass spectroscopy results for a sample of styrene that was hydrogenated using the Devanathan cell.

was bubbled into the solution for an hour to remove dissolved oxygen. The electrolysis was carried out in a closed U-cell and the solvent was saturated with CO_2 for 120 minutes. The cell was usually operated at room temperature under H_2 atmosphere. The cyclic voltammetry responses for platinum plate in CO_2 saturated ionic liquid solution are featureless over the potential region between 0.5 to -0.3 V.

We have tested our general model of EIS using real data collected from the reduction of ferricyanide anion to ferrocyanide anion as a known reaction. Our results are in excellent agreement with those found in literature and we are continuing to improve our model to include better fitting algorithms.

Conclusions and Future Directions

- The electrochemical behavior of organotin halide/hydride systems is not fully understood, however it appears to be possible to successfully hydrogenate organotin halides to their respective hydride using electrolysis or Devanathan cell techniques.
- The direct hydrogenation of carbon dioxide (as a test system) was attempted in ionic liquids, however the results did not indicate any hydrogenated species.

- Our general mathematical model of EIA has been tested on real data and yields very good results.
- Future work includes Devanathan cell reduction reactions of organotin halides, improved techniques for ionic liquid direct hydrogenation, and more complex testing of the EIS model using another known reaction from the literature.

FY 2009 Publications/Presentations

1. J.B. McLafferty, J.C. Tokash, S. Colominas, and D.D. Macdonald, “PSU Group Activity Summary,” Meeting at Rohm & Haas, Philadelphia, PA, August 2008.
2. S. Colominas, J.B. McLafferty, and D.D. Macdonald, “Electrochemical Studies of Sodium Borohydride in Alkaline Aqueous Solutions Using a Gold Electrode,” *Electrochim. Acta*, in press (2009).
3. J.B. McLafferty, S. Colominas, and D.D. Macdonald, “Attempts to Cathodically Reduce Boron Oxides to Borohydride in Aqueous Solution,” *Electrochim. Acta*, in preparation (2009).
4. J.C. Tokash, G.R. Engelhardt, and D.D. Macdonald, “On the Development of a General Electrochemical Impedance Model,” *Transactions of the Electrochemical Society*, in preparation (2009).

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