A GENERAL MODEL OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY
AND ITS APPLICATION TO HYDROGEN STORAGE MATERIALS

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by
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ABSTRACT

As the global need for energy increases, scientists and engineers have found a possible solution by using hydrogen to power our world. Although hydrogen can be combusted as a fuel, it is considered an energy carrier for use in fuel cells wherein it is consumed (oxidized) without the production of greenhouse gases.

The U.S. Department of Energy (DOE) formed a Center of Excellence for Chemical Hydrogen Storage, and this work stems from that project. The DOE has identified boron hydrides as being the main compounds of interest as hydrogen storage materials. The various boron hydrides are then oxidized to release their hydrogen, thereby forming a “spent fuel” in the form of a lower boron hydride or even a boron oxide. The ultimate goal of this project is to take the oxidized boron hydrides as the spent fuel and hydrogenate them back to their original form so they can be used again as a fuel. Thus this research is essentially a boron hydride recycling project.

One class of boron hydrides, called polyhedral boranes, became of interest to the DOE due to their ability to contain a sufficient amount of hydrogen and their physical and chemical safety attributes. Unfortunately, the research performed here has shown that polyhedral boranes do not react in such a way as to allow enough hydrogen to be released, nor do they appear to undergo hydrogenation from the spent fuel form back to the original hydride.

After the polyhedral boranes were investigated, the project goals remained the same but the hydrogen storage material was switched by the DOE to ammonia borane. Ammonia borane was found to undergo an irreversible hydrogen release process, so a
direct hydrogenation was not able to occur. To achieve the hydrogenation of the spent ammonia borane fuel, an indirect hydrogenation reaction is possible by using compounds called organotin hydrides. In this process, the organotin hydrides will hydrogenate the spent ammonia borane fuel at the cost of their own oxidation, which forms organotin halides. To enable a closed-loop cycle, my task was then to be able to hydrogenate the organotin halides back to their hydride form.

In addition to this experimental work, a parallel project was carried out to develop a new model of electrochemical impedance spectroscopy (EIS). The EIS technique is capable of probing complex chemical and electrochemical reactions, and this model was written into a computer code that allowed the input of experimental EIS data and the extraction of kinetic parameters based on a best-fit analysis of theoretical reaction schemes.
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Chapter 1

Introduction

It is all too clear that the demand for energy on a global scale is an ever-growing problem. One of the most promising solutions to this problem is to utilize hydrogen as an energy carrier. The benefits of harnessing hydrogen to carry energy are many; however, the main points are: a reduction in the use of fossil fuels, a corresponding reduction in the production of greenhouse gases, and an increased economic benefit by making other sources of energy available for consumers. However, the present limitation on this technology is a safe and effective method to store enough hydrogen for individual applications (these may vary in scale from powering a cellular phone or a laptop computer to powering an automobile or a standalone power unit as a primary or secondary source of electricity).

There are four primary areas of research that are required in order to make hydrogen a part of our daily lives: production, storage, transportation, and utilization. Typically, hydrogen is produced by the steam reforming of fossil fuels, although other methods are being developed in order to eliminate fossil fuels from the overall energy cycle; some of these methods include: algae bioreactors, fermentation of organic materials by anaerobic bacteria and enzymes, electrolysis of water (using non-carbon cycle power such as hydroelectric, solar, or nuclear power), and thermal decomposition of water (for example using solar power). The transportation of hydrogen is a separate task that will depend on the final form (solid, liquid, or gas) in which it will be
consumed; as such this will not be discussed further. The utilization of hydrogen is assumed here to be in a fuel cell where the only reaction product is water.

The most obvious method of storing hydrogen is in compressed gas or liquefied hydrogen tanks; nevertheless, the primary drawback of these methods is the limited quantity that is able to be stored. In recent years, the storage of hydrogen as a compressed gas entailed the use of large and heavy containers. For example, in a common steel tank only about 1% of the total weight was that of the hydrogen gas when it was fully compressed (14 MPa). Additionally, storing liquid hydrogen presents serious safety problems due to its extreme volatility if discharged and because of the temperatures required to maintain it as a liquid (20 K).

In order to address these problems, compressed hydrogen tanks are now being operated at extremely high pressures; most are in the range of 35 – 70 MPa. And although modern tanks are being designed for liquefied hydrogen storage, the major problem that still exists is boil-off. As a result, these hydrogen storage methods still present serious safety and engineering issues; this topic is discussed further in [1].

To overcome these downfalls, a vast quantity of research has been performed on various alternative mediums for hydrogen storage. These mediums include, but are not limited to: metal and chemical hydrides [2, 3], physisorption-based techniques [4, 5], and alloys such as Ti-Zr-Cr-V or lanthanum-rich intermetallic nickel alloys [6, 7]; some reviews of the recent research on hydrogen storage mediums can be found in [8, 9].

This dissertation stems from a five year research project through the Center of Excellence for Chemical Hydrogen Storage within the U.S. Department of Energy (DOE)
to study various hydrogen storage materials that are based upon boron hydrides. The idea of this research is to limit or eliminate fossil fuels to power our everyday needs.

Boron hydrides were chosen for this project in order to eliminate carbon from the overall lifecycle of the chemical hydrogen storage materials, and doing so would automatically reduce or do away with the production of greenhouse gases. One thing to note immediately about boron hydrides is the general trend that they are more reactive (less stable) in the more simple molecules, whereas the larger, more complex molecules of boron hydrides are more stable and less reactive.

To give the reader an idea of what is meant by stable and reactive, consider two such boron hydrides, namely borane (BH$_3$) and dodecahydrododecaborate (B$_{12}$H$_{12}$). Borane is a simple molecule (Figure 1-1) that is in the gaseous phase at ambient temperature and pressure and readily dimerizes to form diborane, B$_2$H$_6$ (Figure 1-2), which when released into an environment that contains oxygen and water vapor will spontaneously combust to form hydrogen (H$_2$) and boric acid, B(OH)$_3$.

![Figure 1-1: The borane molecule, BH$_3$.](image-url)
Figure 1-2: The diborane molecule, $\text{B}_2\text{H}_6$.

On the other hand, the $\text{B}_{12}\text{H}_{12}$ cluster molecule, often called a polyhedral borane or more simply a polyborane, is a complex icosahedral shape (Figure 1-3) and is found as an anion of various salts, for example potassium dodecahydrododecaborate ($\text{K}_2\text{B}_{12}\text{H}_{12}$).

Figure 1-3: The dodecahydrododecaborate cluster, $\text{B}_{12}\text{H}_{12}$.
The physical properties of dodecahydrododecaborate salts are such that they are found as powders at room temperature and pressure that are thermally stable up to a few hundred degrees Celsius. In addition, the chemical stability of these salts is such that they do not decompose unless they are in strongly acidic or caustic solutions. Figure 1-4 shows various polyhedral boranes ranging from four to twelve boron atoms in the polyborane; as mentioned before, the relative reactivity decreases as the number of boron atoms within the cluster increases.

Figure 1-4: The family of polyborane clusters from B₄H₄ up to B₁₂H₁₂. The terminal hydrogen atoms are omitted for clarity. Image from [10].
The immediate solution to the needs of chemical hydrogen storage would seem to be that borane, or more appropriately, diborane, is the most likely candidate due to its ease of reaction, i.e. we could simply have a container of diborane and expose it in a controlled manner to water, for example, in order to produce hydrogen spontaneously. Although this could be done, it is not in use due to safety issues of accidental release, which could cause catastrophic fires or explosions.

To address the requirements of the DOE, the original proposal made by Dr. Digby D. Macdonald was to use the salts of dodecahydrododecaborate as the first molecules to examine based on their safety qualities and ability to contain a sufficient amount of hydrogen (theoretically 8.2%, actual 6.2%). In addition, the proposal to use polyboranes as hydrogen storage materials is not only because they contain a sufficient quantity of hydrogen to meet the DOE goals, but also because virtually no work has been done to determine whether electrochemical transformations exist for these materials and if they do exist whether they are reversible as would be necessary to form a hydrogen storage system. Therefore, because this has not been investigated in the past I must emphasize that this work is primarily exploratory at the onset.

The results of this research are presented in Chapter 2 below, the goal of which is to identify whether the hydrogen release and uptake steps can be identified by electrochemical techniques.

Over time, the results of this research came to conclusions that spurred the DOE to stop investigating polyboranes as chemical hydrogen storage materials. The next
material of interest to the Department of Energy was ammonia borane, H$_3$BNH$_3$, (Figure 1-5) and it is the subject of Chapter 3 below.

![Ammonia Borane Molecule](image)

**Figure 1-5: The ammonia borane molecule, H$_3$BNH$_3$.**

The ammonia borane molecule follows a stepwise release of hydrogen from H$_3$BNH$_3$ to H$_2$BNH$_2$, then from H$_2$BNH$_2$ to HBNH, and finally from HBNH to BN. In traversing these reactions, the original ammonia borane fuel is capable of releasing 19.3% hydrogen by mass. My goal in this case was to determine whether the lower hydrides could be hydrogenated to the higher hydrides in a “refueling phase.” The process of hydrogenation was looked at in two different ways: a direct electrochemical hydrogenation, and an indirect hydrogenation. The indirect hydrogenation method results in the use of organotin halides (Figure 1-6) as intermediate hydrogenation materials (i.e., they hydrogenate the spent ammonia borane fuel at the cost of their own oxidation) that need to be recycled (hydrogenated) back to the hydride form; this is discussed in Chapter 3 below.
Finally, the ultimate goal of this research is to identify the reaction mechanisms that take place during hydrogen release and uptake reactions, therefore a novel model of electrochemical impedance spectroscopy (EIS) was developed. The EIS technique is able to probe reactions at time scales spanning approximately ten orders of magnitude, which makes it a very powerful tool for electrochemical analysis. The new model of EIS is presented below in Chapter 4.
References

Chapter 2

Polyhedral Boranes

Introduction

In order to overcome the hydrogen storage problems associated with many chemical hydrides and to achieve DOE goals for weight percent (9 wt. % by 2015) and volumetric density (80 g/L by 2015) of stored hydrogen, I began to explore the electrochemistry of complex polyhedral boranes (polyboranes) to assess their capabilities for the controlled release and uptake of hydrogen.

A literature review reveals that very little work has been reported on this topic [1-6] with virtually no work published since the mid-1970s. Due to a lack of knowledge about the electrochemical behavior of the polyboranes, I performed fundamental studies on these materials in an exploratory manner.

Neutral polyboranes and polyborane anion salts appear to be promising materials for hydrogen storage based on preliminary data. In order to determine if the polyborane anion salts would function as hydrogen-storage materials, I began to investigate whether electrochemically-mediated and reversible transitions between anions of different oxidation states could be achieved with an accompanied change in hydrogen content.

It was proposed that polyhedral borane (polyborane) anions and neutral species of the general formula $B_xH_y^+$ (where $x > 6$ and $y = 0 – 4$) are suitable in order to achieve sufficient gravimetric and volumetric hydrogen storage densities if electrochemically-
mediated and reversible transitions between polyboranes of different oxidation states could be achieved. Obtaining a suitable polyborane for this task was not a problem, although the selection process was more challenging because nearly 50,000 boron cluster compounds have been synthesized in the past half-century [7].

Because this was a new research project, I began by studying the electrochemistry of the dodecahydrododecaborate dianion, $\text{B}_{12}^2\text{H}_{12}^2$, as well as decahydrodecaborate dianion, $\text{B}_{10}^2\text{H}_{10}^2$, in nonaqueous solutions with acetonitrile as the solvent. I have noticed interesting differences in the cyclic voltammograms for various solutions that depend on: (1) the cation that is part of the polyborane salt, (2) the sweep rate of the electrode potential, and (3) the material of the working electrode. Also of interest is the effect of various concentrations of the polyboranes. For instance, a solution of triethylamine dodecahydrododecaborate, $[(\text{CH}_3\text{CH}_2)\text{NH}]_2\text{B}_{12}\text{H}_{12}$, at a concentration of 1 mM exhibits an oxidation wave whose potential value is dependent on the cycle number in a cyclic voltammogram. Additionally, by varying the polyborane concentration in a solution of tetra-$n$-butylammonium dodecahydrododecaborate, $[(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)\text{N}]_2\text{B}_{12}\text{H}_{12}$, from 1 to 10 mM, I noticed additional oxidation features occurring at the higher concentrations.

The initial data leads me to suspect that an ECE reaction mechanism is involved, i.e. a reaction where a chemical reaction is coupled in between preceding and following electrochemical reaction steps [8].
Experimental Approach

The first experiments were designed to study the complex electrochemical behavior of polyhedral borane anions as supplied by Dr. M. Frederick Hawthorne from his lab at The University of California at Los Angeles (currently at The University of Missouri). As such, the supplied polyboranes were in limited quantities because they were synthesized only when they were needed. This led me to design a small-volume electrochemical cell (V = 2.5 mL) in order to limit the need for large quantities of working materials.

The cell was built in our department’s glass shop by joining together four threaded glass joints (Chemglass, Inc.) with 7 mm internal diameter. The geometry of the electrochemical cell is a “cross shape” such that the working electrode and the counter electrode are facing one another and the reference electrode was able to be placed perpendicularly between the working and counter electrodes. The fourth glass joint is used as a septum port, while all other joints are sealed with o-rings to provide an airtight seal.

The chemical oxidation of polyboranes has been studied and reported in the literature [9-12], yet there is a limited quantity of open literature available on the electrochemistry of polyboranes [1,2,4,6]. Based upon the literature that was found, I decided to perform my initial experiments in an anhydrous, aprotic solvent. Acetonitrile was chosen because of its use in previous electrochemical studies, its wide, available potential range, and its ability to dissolve many inorganic salts.
All work has been conducted in a continuously purified argon glovebox with < 1 ppm H₂O and < 1 ppm O₂. The acetonitrile used throughout was HPLC grade (EMD Scientific, OmniSolv, 99.99%) and has been degassed by sparging with ultra-pure grade argon that was passed through a gas purifier (NuPure Corp., < 10 ppb impurities). The supporting electrolyte dissolved in all solutions was tetra-n-butylammonium hexafluorophosphate, (CH₃CH₂CH₂CH₂)₄N(PF₆), (Sigma Aldrich, electrochemical grade, 99.0%) at a concentration of 0.100 M; this forms the blank solution. Note that tetra-n-butylammonium hexafluorophosphate is referred to as TBA-PF₆ throughout the text.

I used the silver/silver ion couple in my reference electrode because it is nonaqueous and thus more compatible with my solutions than a customary aqueous reference electrode. The silver/silver ion couple has an equilibrium potential in this system that is +0.637 V vs. SHE (standard hydrogen electrode). The reference electrode was designed and built in-house. A 10 cm length of 6 mm outer diameter glass tube was fused at one end to a small length of 4 mm outer diameter glass tube and it was also fused at the other end to a threaded glass joint (Chemglass, Inc.) to form the electrode body.

A silver wire (Alfa Aesar, 99.9985%) runs coaxially inside the glass body where it was sealed at the threaded end allowing for electrical contact to be made. Inside the electrode body, the silver wire contacts a solution of 0.010 M AgNO₃ (Sigma Aldrich, 99.9995%), which was made by dissolving silver nitrate in a portion of the blank solution. The reference electrode has a small porous glass (Corning, Inc., Vycor #7930) frit as the liquid junction; it was cut to 3 mm in length and attached to the glass body onto the tip of the 4 mm glass tube by PTFE heat-shrink tubing.
The working electrode and the counter electrode were made from short lengths of platinum wire (Alfa Aesar, 99.99%) that are 1 mm and 2 mm in diameter, respectively. The platinum wires were soldered to longer lengths of copper wire and each was potted into chemically inert epoxy. The electrodes were removed from the epoxy molds and the platinum wire was polished flush to the end of the electrode making a disk-geometry for each electrode; the final polish used a 0.05 micron alumina suspension. External electrical contact was made via the copper wire extending from the opposite end of each electrode. The geometric surface area of the platinum working electrode is 0.00785 cm² and all electrochemical current measurements have been converted to apparent current density (A/cm²) for ease of comparison with other electrode dimensions. In addition, all potential values are automatically converted to the standard hydrogen scale by the data acquisition software (CorrWare, Scribner Associates Inc.).

Also of interest is the solubility of the polyborane salts in acetonitrile. I attempted to dissolve the potassium dodecahydrododecaborate methanolate salt, K₂B₁₂H₁₂•CH₃OH (BASF Corp., 95%), however I discovered that its solubility was quite low and also that particles were visible in solution. In order to increase the solubility, I exchanged the potassium cations for tetra-\(n\)-butylammonium, which has a different surface charge density and allows for more complete solvation. After performing the cation exchange, the solubility was determined to be well over 0.3 M in acetonitrile. This was determined by adding a sufficient amount of the salt to acetonitrile in order to form a saturated solution, then a known volume of the solution was collected and added to a different container whose mass had already been measured, finally after the solvent had
evaporated the mass of the salt was found, which allowed for a simple calculation to be made to yield the maximum soluble concentration in that solvent.

The cation exchange procedure was performed by mixing one equivalent of K$_2$B$_{12}$H$_{12}$$\cdot$CH$_3$OH in water (taking into account the methanol content) with slightly more than two equivalents of tetra-$n$-butylammonium bromide in water (in order to maintain this reactant in excess of the initial potassium polyborane salt). Upon mixing the two solutions, a white, paste-like slurry immediately precipitates. The precipitate was rinsed with Milli-Q deionized water (Millipore Corp.) and was then vacuum filtered with one-micron filter paper. The precipitate was collected from the filter paper in almost quantitative yield and it was allowed to air dry. After drying in air, the salt was further dried under vacuum to remove any remaining water. Once the sample was completely dry, it was transferred into the argon glovebox where it was recrystallized from pure acetonitrile several times. During this process, the methanol content is removed from the polyborane salt, and the identity of the final product was determined for this procedure by chemists at BASF [13].

**Results and Discussion**

In order to establish a starting point, a cyclic voltammogram (CV) was recorded for the blank solution (0.100 M TBA-PF$_6$ in acetonitrile). The 10-cycle CV for the blank solution is shown in Figure 2-1 where it can be seen that this combination of solvent and supporting electrolyte provides a wide available potential range with little background signal. Note that the arrows in Figure 2-1 indicate the directions of the potential sweeps;
all Figures follow this pattern by beginning at the cathodic limit and progressing toward the anodic limit on the forward sweep.

**Figure 2-1:** Cyclic voltammogram over 10 cycles for a blank solution containing only the supporting electrolyte (0.100 M tetra-n-butylammonium hexafluorophosphate) dissolved in acetonitrile. The arrows indicate the direction of the potential sweeps; each cycle begins at the cathodic limit. 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.

After verifying that the blank solution was suitable for electrochemical studies, I recorded a cyclic voltammogram for a sample of 1 mM triethylamine dodecahydrododecaborate, [(CH₃CH₂)₃NH]₂B₁₂H₁₂, which was dissolved in the blank solution. The 10-cycle CV for this sample is shown in Figure 2-2, where now the arrow indicates that the location of the oxidation wave is progressing to higher potential and current density values with successive cycles. The cause of this behavior is unknown at
this point, however the change in the oxidation wave appears to have no effect on the reduction wave located at –1.05 volts.

Figure 2-2: Cyclic voltammogram over 10 cycles for a sample of 1 mM triethylamine dodecahydrododecaborate ([CH₃CH₂)₃NH]₂B₁₂H₁₂) dissolved in the blank solution (0.100 M tetra-n-butylammonium hexafluorophosphate 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 progression of the oxidation wave with successive cycles toward higher potential and current values. The oxidation wave moves from 1.35 to 2.00 volts, and it becomes smaller with respect to the background on each additional cycle. The reduction wave is at –1.05 volts.

The next sample to be studied was 1 mM tetra-n-butylammonium dodecahydrododecaborate, [(CH₃CH₂CH₂CH₂)₄N]₂B₁₂H₁₂, also written as TBA₂B₁₂H₁₂. This polyborane is the product of the cation exchange reaction discussed earlier. Figure 2-3 shows the 10-cycle voltammogram of 1 mM TBA₂B₁₂H₁₂ under the same
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; the small nature of this wave should not be completely unexpected based upon the lack of oxidation features other than the small oxidation wave on the first cycle.

![Cyclic voltammogram over 10 cycles for a sample of 1 mM tetra-n-butylammonium dodecahydrododecaborate ([(CH₃CH₂CH₂CH₂)₄N]₂B₁₂H₁₂) dissolved in the blank solution (0.100 M tetra-n-butylammonium hexafluorophosphate 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. On the first cycle, an oxidation wave is seen at 1.25 V with a broad shoulder that appears to contain another small oxidation wave near 1.52 V. The small reduction wave is located at –0.55 V.](image)

The third solution studied was 10 mM tetra-ᵣ-butylammonium dodecahydrododecaborate ([(CH₃CH₂CH₂CH₂)₄N]₂B₁₂H₁₂). This solution was made with the same recrystallized polyborane salt as used for the 1 mM solution, so the results
are not due to any other factor than increased polyborane concentration. As shown in
Figure 2-4, the increase in polyborane concentration has a profound impact on the
oxidation features, however the reduction wave was virtually unchanged. A sharp
oxidation peak whose peak current is directly proportional to concentration is seen in
Figure 2-4 at 1.25 volts; this is at the same potential value as that of the 1 mM solution.

Figure 2-4: Cyclic voltammogram over 10 cycles for a sample of 10 mM tetra-n-
butylammonium dodecahydrododecaborate ([((CH₃CH₂CH₂CH₂)₄N]₂B₁₂H₁₂) dissolved in the blank solution (0.100 M tetra-n-butylammonium
hexafluorophosphate 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. A sharp oxidation peak is seen on the first
cycle at 1.25 V with another small oxidation wave at 1.53 V and a third oxidation
wave at 1.86 V. The small reduction wave is located at –0.57 V.

Additionally in Figure 2-4, 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
2-3. Finally, we now see in Figure 2-4 that a new oxidation peak is present at 1.86 volts.
I believe this is evidence of an ECE coupled reaction mechanism, and I investigated this further by adjusting the CV parameters as will be discussed below. Similar to Figure 2-3, the small reduction wave observed in Figure 2-4 is located at –0.57 volts.

An interesting observation for Figure 2-4 is the lack of oxidation peaks in the 1 – 2 V region at cycles beyond the first. Thus, the entities that are oxidized within this potential region are either removed irreversibly (and quantitatively) or their oxidation is inhibited on further cycling. Given the relatively high potential sweep rate, the time spent in the 1 – 2 V window is short (10 s) and noting that the current density is approximately 0.0025 A/cm² the total charge passed in the 1 – 2 V region on the first cycle is \( \sim 2 \cdot 10^{-4} \) C. Assuming a one-electron reaction, the number of moles removed is about \( 2 \cdot 10^{-9} \). This may be compared with \((2.5/1000) \cdot 0.01 = 2.5 \cdot 10^{-5}\) moles of the polyborane in the system; thus, only 0.008% of the polyborane is consumed on the first, forward potential sweep. If the reaction involves multiple electrons, the amount removed is even less. Thus, I conclude that the lack of oxidation peaks on the second and higher sweeps is not due to depletion of the reactant, leaving passivation of the surface by an adsorbed, inert oxidation product as being the most likely cause.

My examination of the electrochemical properties of the decahydrodecaborate dianion (\(B_{10}H_{10}^{2-}\)) in anhydrous acetonitrile began as I collected CV data on triethylamine decahydrodecaborate, \([(CH_3CH_2)_3NH]_2B_{10}H_{10}\), as shown in Figure 2-5.
The two oxidation peaks just below and above +1 volt form as hydrogen [1,4,6] is released, and we would expect to see a conjugate reduction peak for the hydrogenation reaction. The reduction peak near -1.3 volts was suspected to be the conjugate to one of the oxidation peaks, so further experiments were performed by changing the initial and switching potentials of the cyclic voltammograms.

Beginning with a fresh solution of triethylamine decahydrodecaborate, I collected CV data in the region of the reduction peak alone to determine if this peak is absent before the oxidation peaks are reached, see Figure 2-6.
Figure 2-6: Cyclic voltammogram of 1 mM triethylamine decahydrodecaborate, [(CH₃CH₂)₃NH]₂B₁₀H₁₀, in anhydrous acetonitrile with 0.05 M TBAPF₆ supporting electrolyte. WE = 0.5 mm Pt disk (area = 0.00196 cm²), CE = 2 mm Pt disk, RE = anhydrous Ag/Ag⁺ (+0.637 V vs. NHE). Scan rate = 100 mV/s.

I discovered that the reduction peak was in fact present after cycling the potential only in the region of the reduction peak; therefore, I conclude that the supplied polyborane salt contains some impurity that is able to be reduced electrochemically.

The study of the two oxidation peaks was more straightforward because there are no conjugate reduction peaks near to the potential region of the oxidation peaks – this indicates that the oxidation of the decahydrodecaborate dianion is irreversible. By starting the cyclic voltammogram at a potential value that is between the two oxidation peaks and then sweeping the potential higher to the anodic limit, I found that the more anodic peak (more positive potential) is not present, which indicates that the more anodic peak is due to a species that is formed by the lower potential value oxidation peak.
As indicated in References 1 and 2, the behavior of decahydrodecaborate dianion
\((B_{10}H_{10}^{2-})\) is paralleled by that of the dodecahydrododecaborate dianion \((B_{12}H_{12}^{2-})\), so it
was decided to examine the \(B_{12}H_{12}\) salts again in more detail.

By switching from the silver/silver ion reference electrode to a plain silver wire
pseudo reference electrode I was able to collect cyclic voltammogram data at higher
potential sweep rates. When using the silver/silver ion reference electrode, the internal
impedance of the reference electrode was sufficiently high to limit the potential sweep
rate to no more than 100 mV/s, however the sweep rate was able to reach 2500 mV/s
when using the silver wire pseudo reference electrode. The only drawback of using a
pseudo reference electrode is that potential values recorded are not able to be directly
corrected to any standard potential scale, such as the standard hydrogen electrode scale.
Therefore, each set of data then needs to be collected twice – the first set is collected as
usual, but the second set has a small amount of a known redox couple added to the test
solution. Such redox couples are then used as an internal standard to adjust the potential
scale after the data has been collected. In this work, ferrocene and ferrocenemethanol
were used with the choice of which one to use depending on the solubility of the
compound in the solvent being used for the sample under study.

In Figure 2-7 we see the CV of triethylamine dodecahydrododecaborate,
\([(CH_3CH_2)_3NH]_2B_{12}H_{12}\), in which the more anodic oxidation peak is now slightly
suppressed.
The reason for the lowering of the second oxidation peak current is because as the potential is scanned very quickly past the lower potential value oxidation peak there is not sufficient time to form as much of the reaction product that is then oxidized a second time at the higher potential valued peak. This indicated that the chemical step that is coupled between the two electrochemical steps has a small reaction rate constant.

In addition to the triethylamine dodecahydridododecaborate, I also studied the potassium salt, K$_2$B$_{12}$H$_{12}$, in the same manner. This time, however, the results were drastically different as seen in Figure 2-8.
Figure 2-8: Cyclic voltammogram of 1 mM K$_2$B$_{12}$H$_{12}$ in anhydrous acetonitrile without supporting electrolyte. The background current density was subtracted. Scan rate = 50 mV/s, WE = 0.5 mm Pt disk, CE = 2 mm Pt disk, RE = anhydrous Ag/Ag+ (+0.637 V vs. NHE).

We can see in Figure 2-8 that the first sweep of potential in the cyclic voltammogram results in the usual oxidation peaks, but we notice that the current decreases for each subsequent cycle. This demonstrates the importance of the cation type that is used for the polyborane salts because in this case, for the potassium cation, the working electrode was being coated with a film as the experiments were taking place. I expect this is a similar problem as that shown above in Figure 2-4.
Effect of Working Electrode Material and Potential Sweep Rate

One problem that was present throughout the study of the polyboranes was the fact that the data looked different when collected on different working electrode materials. Although this is to be expected to a certain degree, the two materials used here were either platinum or gold – both of which are used extensively in the field of electrochemistry for being inert, i.e. they do not take part in electrochemical reactions as a general rule but rather they are simply the source/sink of electrons at the electrode surface.

In Figures 2-9 through 2-14 we see the cyclic voltammograms of 1 mM [Et₃NH]₂B₁₂H₁₂ in acetonitrile with 0.1 M TBA-PF₆ supporting electrolyte as the potential sweep rate is varied. For these Figures, the working electrode is a 0.5 mm platinum disk, the counter electrode is a 2 mm platinum disk, and the reference electrode is a silver wire pseudo reference electrode. Note that in Figures 2-9 through 2-14 the current density axis scale and the potential axis scale are the same for each Figure so that the effect of sweep rate is more obvious.
Figure 2-9: Cyclic voltammogram of 1 mM [Et$_3$NH]$_2$B$_{12}$H$_{12}$ in anhydrous acetonitrile with 0.1 M TBA-PF$_6$ supporting electrolyte. Scan rate = 250 mV/s, WE = 0.5 mm Pt disk, CE = 2 mm Pt disk, RE = silver wire pseudo reference electrode.
Figure 2-10: Cyclic voltammogram of 1 mM $[\text{Et}_3\text{NH}]_2\text{B}_{12}\text{H}_{12}$ in anhydrous acetonitrile with 0.1 M TBA-PF$_6$ supporting electrolyte. Scan rate = 500 mV/s, WE = 0.5 mm Pt disk, CE = 2 mm Pt disk, RE = silver wire pseudo reference electrode.
Figure 2-11: Cyclic voltammogram of 1 mM $[\text{Et}_3\text{NH}]_2\text{B}_{12}\text{H}_{12}$ in anhydrous acetonitrile with 0.1 M TBA-PF$_6$ supporting electrolyte. Scan rate = 1000 mV/s, WE = 0.5 mm Pt disk, CE = 2 mm Pt disk, RE = silver wire pseudo reference electrode.
Figure 2-12: Cyclic voltammogram of 1 mM \([\text{Et}_3\text{NH}]_2\text{B}_{12}\text{H}_{12}\) in anhydrous acetonitrile with 0.1 M TBA-PF₆ supporting electrolyte. Scan rate = 1500 mV/s, WE = 0.5 mm Pt disk, CE = 2 mm Pt disk, RE = silver wire pseudo reference electrode.
Figure 2-13: Cyclic voltammogram of 1 mM [Et₃NH]₂B₁₂H₁₂ in anhydrous acetonitrile with 0.1 M TBA-PF₆ supporting electrolyte. Scan rate = 2000 mV/s, WE = 0.5 mm Pt disk, CE = 2 mm Pt disk, RE = silver wire pseudo reference electrode.
In Figures 2-9 through 2-14, we notice that the potential sweep rate plays an important role in the electrochemical reactions that take place. For example, if the potential sweep rate was not varied while studying the polyboranes, then it would be possible to incorrectly assume that the samples were not electroactive – this is the case for extremely slow and extremely fast sweep rates (not shown) that are less than 50 mV/s or greater than 2500 mV/s. We can see through this series of experiments that the electroactivity increases as the sweep rate increases, but this trend only holds up to about 2000 mV/s after which it appears that the sweep rate is so fast that the electron transfer...
cannot proceed fast enough to oxidize the polyborane dianion. The reason for the large amount of electroactivity in Figure 2-13 is not known, but I hypothesize that the sweep rate of \(\sim 2000 \text{ mV/s}\) is at a sufficient rate to activate certain oxidation reactions that are not seen at slower sweep rates. The complex electrochemical behavior as shown in Figures 2-9 through 2-14 has not been reported in the literature before and as such I must point out that my exploratory work indicates that the polyborane electrochemistry is not fully understood.

On the other hand, in Figures 2-15 through 2-20 we see the cyclic voltammograms of 1 mM \([\text{Et}_3\text{NH}]_2\text{B}_{12}\text{H}_{12}\) in acetonitrile with 0.1 M TBA-PF\(_6\) supporting electrolyte as the potential sweep rate is varied; however, for these Figures the only difference is that the working electrode has been changed to a 0.5 mm gold disk rather than the platinum disk as before. The counter electrode is still a 2 mm Pt disk, and the reference electrode is once again a silver wire pseudo reference electrode. Note that in Figures 2-15 through 2-20 the current density axis scale and the potential axis scale are the same for each Figure (although they are different from Figures 2-9 through 2-14) so that the effect of sweep rate is more obvious.
Figure 2-15: Cyclic voltammogram of 1 mM [Et$_3$NH]$_2$B$_{12}$H$_{12}$ in anhydrous acetonitrile with 0.1 M TBA-PF$_6$ supporting electrolyte. Scan rate = 250 mV/s, WE = 0.5 mm Au disk, CE = 2 mm Pt disk, RE = silver wire pseudo reference electrode.
Figure 2-16: Cyclic voltammogram of 1 mM \([\text{Et}_3\text{NH}]_2\text{B}_{12}\text{H}_{12}\) in anhydrous acetonitrile with 0.1 M TBA-PF$_6$ supporting electrolyte. Scan rate = 500 mV/s, WE = 0.5 mm Au disk, CE = 2 mm Pt disk, RE = silver wire pseudo reference electrode.
Figure 2-17: Cyclic voltammogram of 1 mM [Et₃NH]₂B₁₂H₁₂ in anhydrous acetonitrile with 0.1 M TBA-PF₆ supporting electrolyte. Scan rate = 1000 mV/s, WE = 0.5 mm Au disk, CE = 2 mm Pt disk, RE = silver wire pseudo reference electrode.
Figure 2-18: Cyclic voltammogram of 1 mM [Et₃NH]₂B₁₂H₁₂ in anhydrous acetonitrile with 0.1 M TBA-PF₆ supporting electrolyte. Scan rate = 1500 mV/s, WE = 0.5 mm Au disk, CE = 2 mm Pt disk, RE = silver wire pseudo reference electrode.
Figure 2-19: Cyclic voltammogram of 1 mM [Et₃NH]₂B₁₂H₁₂ in anhydrous acetonitrile with 0.1 M TBA-PF₆ supporting electrolyte. Scan rate = 2000 mV/s, WE = 0.5 mm Au disk, CE = 2 mm Pt disk, RE = silver wire pseudo reference electrode.
As seen in Figures 2-15 through 2-20, the electroactivity of the polyborane sample on the gold working electrode is much less than what was shown on a platinum working electrode in Figures 2-9 through 2-14. As a result of these experiments, I have shown that the complex electrochemical behavior of the polyboranes can also be attributed to the nature of the working electrode material.
Conclusions

The complex electrochemistry of the polyhedral borane dianions $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$ has been investigated in depth for the first time in our laboratory. These anions were proposed for use as potential hydrogen storage systems from both gravimetric and volumetric standpoints.

After verifying that 0.100 M TBA-PF$_6$ in acetonitrile is a suitable blank solution with a wide potential range available, I 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 triethylamine dodecahydrododecaborate ($[(\text{CH}_3\text{CH}_2)_3\text{NH}]_2\text{B}_{12}\text{H}_{12}$) is unknown at present, but it is possible that the potential moves to higher values because on each cycle another hydrogen is removed from the polyborane cage, thus making it more difficult on successive cycles to remove further hydrogen atoms from the cage.

Once the potassium cations of $\text{K}_2\text{B}_{12}\text{H}_{12} \cdot \text{CH}_3\text{OH}$ were exchanged to tetra-$n$-butylammonium, the resulting dodecahydrododecaborate salt (not containing methanol) 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 (1 mM in this case) the oxidation features are more wave-like, however at higher concentrations (such as 10 mM shown in Figure 2-4) the oxidation features become much more prevalent 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.
In addition, I have shown for the first time that the sweep rate and the working electrode material are important factors to consider when studying polyhedral boranes. The complex electrochemical reactions that occur are not fully understood, although as proposed, it appears that the oxidation mechanism is a coupled ECE reaction path. In this ECE reaction, the first electrochemical step is the oxidation of the initial polyborane dianion, the product of this reaction is then able to dimerize in a chemical reaction step, and finally as the dimerized product is electrochemically oxidized we notice the second, more anodic oxidation peak.

The reduction peak that is observed throughout the cyclic voltammograms for the polyborane samples was shown to be present prior to any oxidation reactions, and therefore I conclude that it is due to an electroactive impurity in the samples. Because there are no conjugate reduction features present for the polyboranes in my exploratory experiments I therefore report that the oxidation reaction products follow an irreversible mechanism. Finally, I conclude that the polyboranes are not desirable materials for hydrogen storage after all because no hydrogenation (reduction) takes place that would allow for a closed-loop for the fuel life cycle.
References

Chapter 3

Ammonia Borane and Organotin Hydrides

Introduction

The U.S. Department of Energy (DOE) has set a target gravimetric capacity of materials such that they must exceed 7 wt% with the potential to exceed 9 wt% to meet future storage targets. Because the polyborane salts were not promising to the DOE, another material was sought after that would meet the target requirements. One such material is ammonia borane (H₃BNH₃), which has been shown by our partners at the University of Pennsylvania [1] to be able to release between 7.2 - 10.2% hydrogen by weight even though its theoretical limit for hydrogen release is 19.6 wt%. The reason that the current hydrogen release percent for ammonia borane (AB) is not pushed further toward its limit is because of the difficulty in regenerating the waste material back to a suitable fuel after dehydrogenation, which becomes more difficult as more hydrogen is released. The hydrogen release process below 100°C initially involves the formation of the diammoniate of diborane [(NH₃)₂BH₂⁺]BH₄⁻, then a mixture of linear, cyclic, and chain-branched polyamimoborane polymers [-H₂NBH₂-]ₙ is formed, and upon further dehydrogenation, the unsaturated product boron nitride (BN) is expected to be formed [2].
There are two ways in which attempts were made to electrochemically recycle (hydrogenate) the spent ammonia borane waste back to the fuel, these will be discussed below.

**Experimental Approach**

In order to hydrogenate the spent ammonia borane fuel, we can either directly or indirectly reduce the material by electrochemical means. The direct path to electrochemical reduction depends upon the particular waste material, but to date I have not been supplied with any spent fuel materials from our project partners so I began by investigating the general electrochemical properties of ammonia borane.

Because ammonia borane is soluble in aqueous and nonaqueous solvents, I was able to exploit the ability of nonaqueous solvents to achieve a more cathodic potential limit than in aqueous solutions. The ability to reach lower cathodic limits enables us to detect reduction (hydrogenation) features that would not be possible in aqueous solutions. The only drawback to working in nonaqueous solvents, as mentioned before, is that the use of a common (store bought) reference electrode such as the saturated calomel electrode (SCE) is not possible because they are aqueous in nature and form an unknown liquid junction potential when used in nonaqueous solvents. To overcome this problem, we have developed a new reference electrode that can be used directly in nonaqueous solvents as described below.
Development of a Nonaqueous Reference Electrode

I first attempted to use a nonaqueous reference electrode based on the metal/polypyrrole quasi-reference electrode [3]. This electrode is suitable for cyclic voltammetry; however, it is not suitable for steady state techniques such as controlled potential electrolysis or electrochemical impedance spectroscopy in the same way as other pseudo reference electrodes behave. In addition, the metal/polypyrrole reference electrode is not suitable for strongly oxidizing or reducing media [3], and although ammonia borane is known to have slightly hydridic and slightly acidic hydrogen atoms we must address this issue after the electrode has been constructed to determine if this will be a problem.

Because I initially wanted to use cyclic voltammetry to study the electrochemistry of ammonia borane, I proceeded to build the metal/polypyrrole reference electrode as outlined in Reference 3 and summarized below.

The body of the metal/polypyrrole reference electrode can be made of any metal although it is recommended to use platinum or stainless steel [3]. For this electrode, I used a 5 cm length of type 316 stainless steel with a diameter of 1/16” and attached it to a length of copper rod to extend the overall length to 15 cm (the copper rod is the external electrical connection). The junction between the stainless steel and copper rods was insulated by PTFE shrink tube and the whole assembly was potted into chemically inert epoxy. The PTFE shrink tube was adjusted so that only 1 cm of the stainless steel rod was left exposed. After the epoxy for the electrode body was cured, the exposed portion of the stainless steel rod was immersed into a solution of 0.01 M pyrrole and 0.1 M
TBA-PF₆ in acetonitrile. The polymerization of the pyrrole onto the stainless steel rod was performed in a three-electrode electrochemical cell with the stainless steel rod acting as the working electrode; a graphite rod was used as the counter electrode and a silver/silver ion reference electrode completed the cell. The electropolymerization occurs as the stainless steel working electrode is cycled 50 times through the redox region of pyrrole at a scan rate of 0.1 V/s. The polypyrrole (PPy) film grows thicker upon each cycle and the stainless steel rod is then removed on the final cycle so that the film is only partially oxidized so that the film is PPy/PPy⁺PF₆⁻ [3].

The newly fabricated metal/polypyrrole reference electrode was then characterized as outlined in [3] by examining a solution of ferrocenemethanol as a known redox couple and treating its oxidation peak potential on a gold working electrode as a standard for calibrating the metal/polypyrrole reference electrode. I found that the potential of the stainless steel/polypyrrole reference electrode was -0.208 V versus SHE.

As mentioned above, the metal/polypyrrole reference electrode is not suitable for controlled potential electrolysis or electrochemical impedance spectroscopy, so a different type of nonaqueous reference electrode based on the silver/silver chloride redox couple was designed for later use. This design was discussed in depth by McLafferty [4], but it will be summarized below. As a note to the reader, Jason McLafferty [4] was a fellow graduate student working on the same project so this reference electrode was fabricated and characterized by McLafferty and the author simultaneously.

The construction of a nonaqueous silver/silver chloride reference electrode has been attempted with little success in the past [5]. The reason for this is because the silver chloride layer that is deposited onto a silver wire within the reference electrode body is
known to dissolve in chloride-containing aprotic solvents, and the filling solution for the silver/silver chloride reference electrode by definition contains chloride so dissolution of silver chloride is inevitable. To get around the problem of silver chloride dissolution in the reference electrode filling solution [4], a sufficient amount of trimethylethylammonium chloride and silver chloride were added to obtain a saturated solution, which also contained 0.1 M TBA-PF$_6$ in acetonitrile. The addition of trimethylethylammonium chloride enables the formation of an equilibrium between the silver chloride layer on the silver wire and the free chloride ions in the filling solution.

In addition to the filling solution, we also needed to design the body of the nonaqueous silver/silver chloride reference electrode in such a way as to eliminate any leaking of the filling solution through the porous liquid junction. The primary reason why this is so important is to eliminate contamination of the test solution by the reference electrode filling solution, but it is also important because standard frit materials such as zirconia ceramic or porous Vycor glass have high leak rates and require frequent refilling of the reference electrode filling solution.

To address the problem of the porous liquid junction frit, we designed [4] our reference electrode body in such a way as to incorporate a layer of anion exchange polymer within the porous frit material, thereby allowing electronic conduction across the liquid junction and yet eliminating bulk flow of filling solution through the frit and into the test solution. For this task, we chose to use a cross-linked poly (4-vinylpyridine) polymer layer as described below [4]:
A 25% w/w solution of poly (4-vinylpyridine) (Sigma Aldrich, average molecular weight 60,000) in methanol was prepared. Two grams of this solution, containing 0.5 grams of poly (4-vinylpyridine) were stirred with 0.026g of 1,4-dichlorobutane [the cross-linking agent] for one hour in a closed glass vial. A 4 mm diameter zirconia frit was attached to a 5mm outer diameter glass tube with PTFE heat shrink tubing. The mixture of poly (4-vinylpyridine), methanol, and 1,4-dichlorobutane was applied over the frit using a Pasteur pipette; the thickness of the layer was about 5-6 mm. The tube was left open overnight on the bench top, to evaporate the methanol. The next day, the above assembly was heated at 110°C in an oven for 5 hours, 20 minutes. After cooling, acetonitrile was placed in the tube and the open end of the tube was closed with parafilm to check for leaks. After leaving overnight, no leaks were found, and the tube was emptied of the acetonitrile. The assembly was then filled with a solution of 0.1M TBAPF₆ in acetonitrile saturated with silver chloride and tetramethylammonium chloride.

The next step after fabrication of the new nonaqueous silver/silver chloride reference electrode was to determine its stability and calibrate it so that potentials measured on it are able to be adjusted to an accepted potential scale, such as the standard hydrogen scale (SHE). By examining cyclic voltammetry data for the oxidation of ferrocene on a platinum working electrode in acetonitrile with 0.1 M TBA-PF₆ as supporting electrolyte, we conclude that the nonaqueous silver/silver chloride reference electrode has a potential that is +345 mV above the standard hydrogen electrode (SHE) potential.

**Results and Discussion**

I studied ammonia borane by cyclic voltammetry in both aqueous and nonaqueous solvents as shown in Figures 3-1 and 3-2 below.
Figure 3-1: Electrochemical activity of 10 mM ammonia borane in aqueous 2 M sodium hydroxide. WE = 5 mm Au disk, CE = Pt mesh, RE = SCE. Scan rate = 50 mV/s. In this cyclic voltammogram the two peaks correspond oxidation reactions that take place on forward and reverse sweeps; no reduction peaks are observed that would indicate rehydrogenation of the newly created (oxidized) species. The oxidation peak near 0 volts is because the gold working electrode becomes oxidized and it is then becoming active once again as the potential is swept toward more negative values.
Figure 3-2: Electrochemical activity of 5 mM ammonia borane in 1:1 acetonitrile:dioxane with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte. WE = 0.5 mm Pt disk, CE = 2 mm Pt disk, RE = Ag (pseudo). Scan rate = 100 mV/s. This cyclic voltammogram shows only one oxidation (dehydrogenation) peak without any subsequent reduction peaks. The feature near -2 volts is related to the discharge limit of the solvent and has nothing to do with the electrochemical behavior of the ammonia borane.

We can see from Figures 3-1 and 3-2 that ammonia borane exhibits oxidation peaks (removal of hydrogen), however we see no reduction peaks that would correspond to a direct path of hydrogenation. In Figure 3-1, the solvent is aqueous 2 M sodium hydroxide so if any reduction reactions were able to occur in the available potential window of the solvent, the solvent itself could act as the hydrogen source and donate the protons to the reduction reaction; however, the ammonia borane sample does not exhibit any reduction (hydrogenation) features.
Because of the limited cathodic potential limit that is available in aqueous solutions, I switched over to an organic solvent that allows for the cathodic potential limit to be extended at least one volt beyond that of aqueous solutions. The organic solvent that I chose to use was a 1:1 mixture of acetonitrile and dioxane; although the individual solvents are aprotic, this fact was taken into consideration by adding phenol (work done in conjunction with that of McLafferty in Reference 4) in some cases or by sparging hydrogen gas through the solution in other cases as a source of protons for any possible reduction reactions. Even though the cathodic limit was extended in the acetonitrile:dioxane mixture to nearly -2 volts, I still did not observe any reduction features indicative of a hydrogenation reaction.

Due to these results, the indirect reduction of spent ammonia borane back to a fuel has been looked upon by the DOE as the most likely reaction to succeed. The idea is to use a separate reducing agent to hydrogenate spent AB fuel at the cost of having to regenerate the auxiliary reducing agent. The reducing agent chosen by the DOE was an organotin hydride such as tributyltin hydride. Once the tributyltin hydride is used as a reducing agent to hydrogenate the ammonia borane spent fuel, it will be left as a tributyltin halide (most likely tributyltin chloride) so my task will then be to attempt to electrochemically reduce Bu₃SnCl back to Bu₃SnH. One possible reduction mechanism is as follows: $Bu₃SnCl + H + e^- \rightarrow Bu₃SnH + Cl^-$.

In order to accomplish this task, I used a Devanathan cell because this provides a convenient source of hydrogen atoms on the surface of the working electrode. The Devanathan cell is shown below in Figure 3-3 where we can see the bi-polar membrane (Pd in the schematic) that is used as the working electrode for both sides of the cell;
additionally we see two counter electrodes and the possibility to add a separator membrane on the reaction side, but the reference electrodes were omitted on each side for clarity.

![Diagram of the Devanathan cell]

Figure 3-3: A schematic drawing of the Devanathan cell. The center membrane is a bi-polar electrode made from palladium or palladium:silver alloy. Counter electrodes complete the electrical circuits; however, the two reference electrodes have been omitted for clarity. A separator membrane can be added to the reaction side of the cell if the products are likely to be re-oxidized during the hydrogenation. The charging side is controlled galvanostatically (indicated by “I” in the circle) and the reaction side is controlled either potentiostatically or galvanostatically (indicated by “I/V” in the circle).

During the operation of the Devanathan cell, hydrogen atoms are produced in the charging side by the electrolysis of aqueous solutions (typically sulfuric acid or potassium hydroxide), the hydrogen then diffuses through the working electrode membrane, and it finally emerges on the other surface in the reaction side where it is used to reduce (hydrogenate) the species in solution on that side of the cell. Because the
membrane for the working electrode is made from palladium or palladium:silver alloy, the electrode surface is also catalytic so that chemical hydrogenation is possible along with electrochemical hydrogenation. The addition of palladium black to the palladium surface on the reaction side has been shown to increase the reactivity by up to 40 times [6] so this was also used in these studies.

In order to test whether the Devanathan cell was operating properly, I attempted to hydrogenate styrene [7] as follows: \( \text{C}_6\text{H}_5\text{CH}═\text{CH}_2 + 2\text{H}_{\text{ads}} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \), in which styrene \((\text{C}_6\text{H}_5\text{CH}═\text{CH}_2)\) reacts chemically with two adsorbed hydrogen atoms on the palladium/silver membrane to produce ethylbenzene \((\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3)\).

Each experiment began with a sample solution of styrene that was 50 mL in volume on the reaction (left) side of the Devanathan cell, and the charging side contained a solution of 6 M KOH that was approximately 100 mL in volume. Each solution was degassed with ultrahigh purity argon for 30 minutes prior to the start of the experiment, and the argon gas was allowed to remain flowing above the solutions so that evaporation was minimized and yet oxygen could be excluded continuously. Hydrogenation occurred after galvanostatic electrolysis of the KOH solution was started by applying a current density of \(-20 \text{ mA/cm}^2\) to the Pd:Ag membrane and using a platinum counter electrode to complete the circuit. The cell potential was monitored in time with a mercury/mercury oxide reference electrode.

The experiments were allowed to run for various times from one to six days. The results obtained by gas chromatography-mass spectrometry (GC-MS) indicate that the amount of ethylbenzene produced increases linearly with time and that the Coulombic efficiency is nearly constant for all experiments. The rate of ethylbenzene production is
2.90% per day and the Coulombic efficiency is ~79%. The results can be seen in Figure 3-4 below. These experiments clearly demonstrate the effectiveness of the Devanathan cell for hydrogenating unsaturated organic materials; the next task was to apply this technique to attempt the reduction of tributyltin chloride. Because tributyltin hydride might not be the only reaction product [8-9], I will identify the resulting species in the solution by cyclic voltammetry.

![Amount Hydrogenated and Coulombic Efficiency versus Time](image)

**Figure 3-4**: Experimental results for the hydrogenation of styrene using a Devanathan cell. The amount of ethylbenzene produced is shown in blue diamonds with a best-fit line shown in light blue indicating a rate of production of 2.90% per day. The Coulombic efficiency is shown in red dots with the average value (79%) shown as the black line.

Although the reaction seems fairly straightforward for the reduction (hydrogenation) of tributyltin chloride, the results (not shown) indicate that the organotin
halide cannot be directly hydrogenated in a common, undivided three-electrode electrochemical cell. I first determined whether cyclic voltammetry could distinguish the hydride apart from the halide form of the organotin compounds, and this is definitely the case as shown in Figure 3-5 where we see two oxidation peaks on the forward scan and one (larger peak current) oxidation feature on the reverse scan.

Figure 3-5: Cyclic voltammograms of tributyltin chloride (black line) and tributyltin hydride (red line) with 0.1 M TBA-PF₆ in acetonitrile. Working electrode = 5 mm gold disk, counter electrode = platinum wire (5 cm length), reference electrode = nonaqueous silver/silver chloride. Potential sweep rate = 50 mV/s.

The first oxidation peak near +0.18 V is attributed [8] to the oxidation of neutral tributyltin hydride to form the neutral radical species $Bu_3Sn^*$. The radical species then
has two options: (1) the radical can chemically dimerize to the hexabutylditin molecule, $Bu_3SnSnBu_3$, or (2) the radical can undergo an electrochemical oxidation at approximately +0.38 V to form the non-radical cation species, $Bu_3Sn^+$. The final oxidation around +0.78 V is due to the electrochemical oxidation of hexabutylditin, which forms the non-radical cation species, $Bu_3Sn^+$, once again. On the reverse sweep of the cyclic voltammogram in Figure 3-5 we see a single, larger oxidation peak. This peak is attributed to the reactivation of the gold working electrode, because as it is swept to the anodic limit the gold surface becomes oxidized and this peak simply indicates the removal of the surfaceoxide.

Now that we know that it is possible to differentiate between the tributyltin hydride and the tributyltin chloride, the next step was to attempt the electrochemical reduction (hydrogenation) process of the organotin halide in the Devanathan cell. The problem in this case is that the experiments take many hours to perform, and as such the applied potential to the Devanathan cell was found to drift in time due to a slightly unstable nonaqueous reference electrode in the reaction solution (its own potential drifts slowly with time so any applied potential will likewise drift in time). As a result, I was unable to conclusively determine whether the Devanathan cell is a viable option for the electrochemical hydrogenation of organotin halides.

An analysis of the solutions that were reacted in the Devanathan cell, even though the reference electrode was not fully stable in time, revealed that no organotin hydride was formed even for positive control solutions where an initial quantity of organotin hydride was spiked into the reaction solution (so at the very least we expect to see the
initial quantity of organotin hydride after the Devanathan cell electrolysis). The results of a 24 hour electrochemical reduction at -2.3 V of a solution of 0.05 M tributyltin chloride, 1 mM tributyltin hydride (the initial spike), and 0.1 M TBA-PF₆ as the supporting electrolyte in acetonitrile are shown in Figure 3-6.

![Figure 3-6: Cyclic voltammograms of 0.05 M tributyltin chloride, 1 mM tributyltin hydride (the initial spike), and 0.1 M TBA-PF₆ as the supporting electrolyte in acetonitrile before Devanathan cell electrolysis at -2.3 V (black line) and after 24 hours of electrolysis (red line). Working electrode = 5 mm gold disk, counter electrode = platinum wire (5 cm length), reference electrode = nonaqueous silver/silver chloride. Potential sweep rate = 50 mV/s.](image)

As we see in Figure 3-6, the results after 24 hours of electrolysis at -2.3 V in the Devanathan cell indicate that even the initial quantity of tributyltin hydride is absent.
These results point toward two explanations: either (1) the applied potential of the working electrode has drifted far enough to oxidize any organotin hydride that is present, or (2) any organotin hydride that is formed is then consumed at the counter electrode of the Devanathan cell. The former issue could only be solved by the development of a more stable nonaqueous reference electrode. The latter issue could be addressed by utilizing a three-part Devanathan cell where the reaction side is separated into two parts rather than just one part as in these studies. The only downfall to this would be the additional potential loss across the extra separating membrane, which in the case of organic solutions that have poor conductivity could lead to potentials that might exceed the discharge potential of the solvent or the applied potential/current output of the potentiostat/galvanostat.

**Conclusions**

Although ammonia borane is a very promising material for hydrogen storage, it has been shown in this work that it is not able to be directly electrochemically reduced (hydrogenated) in aqueous or nonaqueous solutions. The reduction of spent ammonia borane fuel is critical to the success of the overall fuel cycle; therefore, as an alternative approach, I investigated the feasibility of electrochemically reducing organotin halide back to organotin hydride for use as indirect hydrogenation materials.

The initial experiments revealed that the reduction of tributyltin chloride did not take place in an ordinary three-electrode undivided electrochemical cell, so I then explored the use of the bipolar Devanathan cell in order to electrochemically reduce the
organotin halide species. I first began by testing the Devanathan cell using the chemical hydrogenation of styrene as a reaction that is known to occur. The results were very promising, so I then moved on by attempting to electrochemically reduce tributyltin chloride to tributyltin hydride. Even though I built and characterized a nonaqueous reference electrode, the results of the Devanathan cell electrolysis indicated that no tributyltin hydride was formed after 24 hours even for positive control test solutions that contained an initial quantity of tributyltin hydride. I therefore conclude that the Devanathan cell needs to be redesigned with a separating membrane and/or the choice of nonaqueous reference electrode is not the best suited one for this task.
References


Chapter 4

General Model of Electrochemical Impedance Spectroscopy

Introduction

The power of electrochemical impedance spectroscopy (EIS) cannot be overstated and it is clear that this technique has a profound impact in the electrochemical field as proof by the tens of thousands of publications in the open literature about this technique. Due to the vast amount of information obtained from an EIS data set, the application of this technique to study reaction mechanisms is very desirable. One of the main reasons for this applicability of using EIS for a mechanistic analysis of a reaction (or coupled reactions) is because the data span many orders in the time (or frequency) domain, thus allowing us to probe reactions steps of varying rates.

A brief summary of the electrochemical impedance spectroscopy technique is as follows: the system under study is first brought to a steady state by applying a fixed steady-state potential to the working electrode, next a small perturbing sinusoidal voltage amplitude (typically less than 20 mV) is superimposed over the steady-state potential as the frequency of the perturbing sinusoidal voltage wave is stepped from one value to the next, finally we measure how the current responds to the sum of the applied potentials. To keep this summary of the EIS technique brief, it will simply be mentioned that the measured current contains a phase shift relative to the applied potential and therefore we treat this by using complex numbers to describe the impedance; i.e. the impedance is
\[ Z = E / I \], where \( E \) is the applied potential and \( I \) is the measured current, and this impedance is then treated as having real and imaginary components. For more information on the electrochemical impedance spectroscopy technique, see for instance Reference 1.

In order to use the EIS technique as a tool to study reaction mechanisms, it is very common in the literature to find discussions wherein the reaction mechanism is described by an analogous equivalent electronic circuit. Although it is possible to describe an electrochemical system as being analogous to an electronic circuit, it must be emphasized that when doing this the choice of equivalent circuit is quite ambiguous. The reason for the lack of a specific equivalent circuit that describes a true electrochemical system is because there is the possibility that any number of circuit elements can be added to the equivalent circuit analogue that allows for the impedance data to match the experimentally collected data, therefore the extraction of various parameters (resistances, capacitances, etc.) becomes impractical. In addition to this, even if an analogous equivalent circuit is found to describe the experimental data very well, the individual electronic components of the analogous circuit can sometimes be non-physical, which then leads us to question the validity of using equivalent circuit analysis for the study of reaction mechanisms.

The aim here is then to strictly avoid using equivalent circuit analogs and to describe the electrochemical impedance in a more classical mathematical manner. The idea of this approach is not new, however various attempts in the past have been found to have limitations that I wish to overcome in this model of electrochemical impedance spectroscopy. A short review of the previous work of others will be discussed below; the
main contributions are from: D. A. Harrington [2-6], B. Tribollet [7], S. K. Rangarajan [8-10], and H. Anderson [11-15]. It is not my goal to degrade the work of those mentioned above, because their contributions are significant to the science; however, I simply want to provide the proper motivation and justification as to why the model presented below is more applicable than the work of others that has been done in the past. In fact, the model described below contains some ideas from past work, in a classical mathematical approach, so not only does this model compliment previous work but it also extends it further.

The first contribution to be discussed, namely that of D. A. Harrington [2-6], shows a thorough analysis of electrochemical impedance for multistep reaction mechanisms including treatments for diffusing, static, and adsorbed species, as well as presenting a reduction of his model to equivalent circuit analogies [6]. However, the treatment of Harrington is limited to being able to handle only electrochemical reactions because he explicitly excludes from consideration any mechanisms that include homogeneous chemical reactions. Due to this restriction, the applicability of this model to actual reaction mechanisms (which can and do include coupled homogeneous chemical steps) is quite limited.

The work of Tribollet [7] is similar in restriction to that of Harrington in that Tribollet’s model does not handle homogeneous chemical reaction steps either. In Tribollet’s discussion, he says that his model “has [the] provision for an arbitrary number of simultaneous homogeneous and heterogeneous reactions,” and yet his mathematical treatment does not have even the slightest treatment of coupled homogenous chemical
reaction steps. Again, due to this restriction (similar to Harrington’s model) I do not consider the model of Tribollet very practical.

One of the more elaborate treatments of coupled reaction mechanisms that include both electrochemical and chemical steps has been proposed by S. K. Rangarajan [8-10], wherein he describes his model as the “Scheme of Squares.” Although his analysis of the problem is very sophisticated it still has its flaws. For example, even though the Scheme of Squares model can handle coupled reaction mechanisms with an arbitrary number of steps, I must emphasize that Rangarajan’s treatment is restricted to handle a maximum of second order reactions, which cannot describe all of the possible reaction steps able to be written down.

It should be clear to the reader that even though the Scheme of Squares model by Rangarajan is quite powerful and capable of handling an arbitrary number of coupled reaction steps, it has a drawback in that the individual (elementary) chemical and electrochemical steps that it considers are not the most universal or applicable to all mechanisms that are able to be conceived. It is because of this drawback in Rangarajan’s Scheme of Squares that I find it not applicable to all situations and find room to extend the theory in the model presented below to handle mechanisms that have been written with reaction steps that are higher than second order.

Finally, the work of Anderson in his thesis [11] and subsequent journal articles [12-15] are to be considered because the treatment within his model is of a similar nature as my model; however, it will be shown that his model is not without its drawbacks. The general idea of Anderson’s work is that various mechanisms are chosen in advance,
theoretical data are calculated, and the experimental data are then compared manually (by eye) to choose which is the best model that describes the experimental data [11].

Regarding the applicability of Anderson’s model, he considers coupled chemical steps in two cases: those with fast or slow rates; whereas in the new model described below I allow the chemical reactions rates to be of any value, not just fast or slow ones.

One last point to be made about Anderson’s model is based upon his analysis of impedance spectra. Anderson has this to say about the two ways in which it is possible to analyze the impedance spectra [12]:

The spectrum can be fitted by a least-squares method to some equations [equation numbers are omitted by this author to avoid confusion], which will give the corresponding parameters A, B, D, T [note that these parameters are not used in my model] … This is a non-linear problem which requires sophisticated mathematical tools and will not be treated here. The second and more common approach is to use electrical equivalent circuits [emphasis added by this author]… In order to obtain information about the kinetics for the electrochemical reaction the electric quantities associated with the [equivalent] circuit must be related to the parameters in the corresponding admittance equation.

The point being that Anderson eventually resorts to an equivalent circuit analog to analyze impedance data for some situations and this is also the case in Anderson’s other work [14]. It is this point that once again shows how my model is an improvement over Anderson’s model because I cannot emphasize enough that an equivalent circuit analog cannot fully describe true physical and chemical properties of an actual reaction mechanism.

Now with the proper motivation I present here the new model for electrochemical impedance spectroscopy, which has already been described in our publication by Tokash, Engelhardt, and Macdonald [16].
I begin by reminding the reader that since the amplitude of the perturbation to the system is quite small, we can assume that the corresponding mass transfer equation’s relative perturbation concentrations are generally also in linear form even for the case of arbitrarily complicated (and nonlinear) systems. However, the solution of these equations also depends upon the steady-state concentrations of species, which in turn depend on the steady-state value of the applied potential. Thus, in order to calculate the impedance of a system and compare to experimental data I must solve steady-state mass transfer equations. In general, these transport equations are often nonlinear due to the presence of nonlinear electrochemical and chemical reactions, migration effects, concentration dependences of transport coefficients, and any other factors that cause the deviation of the system from dilute-solution behavior. As a result, a complete analysis of impedance data for nonlinear systems, as mentioned by Anderson [12], can only be accomplished by applying numerical methods because impedance is defined only for linear systems and numerical methods allow us to linearize a nonlinear system.

The model described below, and its associated computer code, generates theoretical electrochemical impedance spectroscopy (EIS) data for a one-dimensional system of heterogeneous and/or homogeneous reaction steps of arbitrary complexity (in terms of reactions and number of species) based on a small periodic (sine wave) perturbation of the potential, \( E \), applied to this system. My task is then to determine whether a certain mechanism is the appropriate choice for an unknown system under study by optimizing the theoretical model onto experimental EIS data with the determination being made by using “goodness of fit” criteria. Once a mechanism is deemed acceptable based upon the goodness of fit of the optimization process, we are
presented with values for various model parameters that we desire to know (such as reaction rates or transfer coefficients).

As a final note on the mathematics that are presented below: the procedure that I follow is to solve equations that are nonlinear (the source of nonlinearity is mentioned above) by linearizing them and then I allow the numerical analysis method to determine whether the solutions are converging. The reason that we can trust the results of the optimization process is because I constrain the optimized parameters to a range of realistic values. Finally, the stability of this solution procedure is termed “asymptotically stable” because I limit the perturbations of the system to small amplitudes around the critical points. This can be explained in another way by an analogy to a simple pendulum under the force of gravity that has a damping force (be it mechanical friction or air resistance or both). We know from experience that one stable equilibrium point is gravitationally downward where the system will come to rest if we perturb it slightly. On the other hand, there exists a second equilibrium point for a pendulum, namely gravitationally upward. However, this second equilibrium point is unstable because slight perturbations from the equilibrium position do not bring it back to the same equilibrium point. So mathematically speaking, we need to assure we are near stable equilibrium points and as mentioned above I accomplish this by constraining the optimized values to those within a range of values that we know to exist in real life situations. Further, I assure that we do not go too far from the stable equilibrium point by restricting the system perturbation to a small-amplitude (as is the case for EIS experiments). By following this procedure, the solutions are "asymptotically stable," meaning that the system will eventually find a stable equilibrium solution.
The model that follows is exactly that which was presented in our publication [16] and it is written here in the same format as our publication with only minor changes being made.

**Mathematical Model**

I will describe both homogeneous and heterogeneous reactions by the single equation:

\[ \sum_i V_{m,i} A_i^{z_i} \rightarrow \sum_i \mu_{m,i} A_i^{z_i} + n_m e^-, \quad m = 1, 2, \ldots \]  

(1)

Here \( A_i^{z_i} \) is the chemical symbol of species \( i \) with charge \( z_i \). For each reaction, \( m \), the stoichiometric coefficients of species \( i \) in the left and right sides are \( \nu_{m,i} \) and \( \mu_{m,i} \), respectively. It is assumed that the change in valence, \( n_i \), is positive if the electrochemical reaction is anodic (oxidation) and negative if this reaction is cathodic (reduction). For non-electrochemical heterogeneous and homogeneous reactions we set \( n_m = 0 \).

The rate of production (or depletion) of species \( i \) due to chemical reactions is expressed as:

\[ R_i = \sum_m \mu_{m,i} V_m - \sum_m \nu_{m,i} V_m = \sum_m \lambda_{m,i} V_m \]  

(2)

where \( \lambda_{m,i} = \mu_{m,i} - \nu_{m,i} \) and \( V_m \) is the rate of reaction \( m \). The summation in Equation 2 takes place for all chemical homogeneous or heterogeneous reactions depending on the type of reaction considered.
In general, the rates $V_m$ and $R_i$ are functions of concentrations, $C_i$, Kelvin temperature, $T$, and in the case of electrochemical reactions on the potential of the electrode, $E$. In this model, I assume that $V_m$ can be presented in the form:

$$V_m = k_m \prod_i C_i^{\nu_i}.$$  

(3)

It is important to note that if some species is present in excess in the system its concentration is considered to be constant and it is included in the parameter $k_m$, which depends also on temperature and in the case of electrochemical reactions on the potential of the electrode. In this case, the rate expressions for second order reactions are conveniently reduced to linear form. Here I assume that the rate constant of an electrochemical reaction has the Tafel form:

$$k_m = k_m^0 \exp \left( \frac{\alpha_m F E}{RT} \right).$$  

(4)

where, $k_m^0$ is the standard rate constant, $R$ is the universal gas constant, $F$ is the Faraday constant, and $\alpha_m$ is the transfer coefficient with $\alpha_m$ being positive for an anodic reaction and negative for cathodic one.

Here I will consider two hydrodynamic cases: Nernst diffusion layer and forced convection for the case of a rotating disk electrode (RDE). From a mathematical point of view the task reduces to the solution of the following set of mass transfer equations:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} - V(x) \frac{\partial C_i}{\partial x} + R_i, \quad i = 1, 2, \ldots, N$$  

(5)

where $N$ is the total number species in the solution, whose concentrations have to be found, $x$ is the distance from the electrode surface, $t$ is the time, $D_i$ is the diffusion coefficient, $V$ is the hydrodynamic velocity, and $R_i$ is the source (sink) of species $i$. For
the case of the Nernst diffusion layer the hydrodynamic velocity is zero, and for the case
of the RDE we have [17]:

\[
V(x) = -0.51023x^2 \Omega^{1.5} / \sqrt{\nu}
\]  

(6)

where \( \Omega \) is the rotation speed of the disk (in rad/s) and \( \nu \) is the kinematic viscosity.

Two boundary conditions exist – one far from the electrode surface and the other
at the electrode surface, and each one is of a different type. This case, in mathematics, is
referred to as a mixed boundary condition, i.e. we have both a Dirichlet boundary
condition (Equation 7) as well as a Neumann boundary condition (Equation 8).

Far from the metal we have all concentrations equal to their bulk solution values:

\[
C_i = C_{i,\infty} \quad \text{at} \quad x = \Delta x, \quad i = 1,2,\ldots,N
\]  

(7)

Here, \( C_{i,\infty} \) is the bulk concentrations of species “\( i \)”, which is assumed to be established by
equilibrium with other components at a “sufficiently far” distance from the surface. In
equation 7, \( \Delta x \) is the width of the Nernst layer for quiescent solutions, but for the case of
a RDE I choose \( \Delta x = 2d \), where \( d = 1.61D_{\max}^{1/3} \nu^{1/6} / \sqrt{\Omega} \) is the width of the Levich layer
[17] and \( D_{\max} \) is the maximum diffusion coefficient among all \( D_i \).

On the metal surface we have:

\[-D_i \frac{\partial C_i}{\partial x} = J_i, \quad i = 1,2,\ldots,N, \quad \text{at} \quad x = 0\]

(8)

where the flux densities of species, \( J_i \), are considered to be a known function of surface
concentrations and potential in accordance with Equations 6.

It should be mentioned here that the diffusion equations (Equations 5) are
parabolic partial differential equations, but in Equations 9 below I have removed the time
dependence in order to find the stationary solution, which results in elliptic equations. The nonlinear system of equations can be solved by usual linearization method using a Taylor series expansion. Let us denote \( C_{old,i}^0 \) as some guess for the solution \( C_i^0 \). On the first step it can be simply assumed that \( C_{old,i}^0 = C_{i,\infty}^0 \). After expanding the expression for \( R_i \) in a Taylor series about the point \( C_{old,i}^0 \) and keeping only the linear terms

\[
( R_i = a_i + \sum_{k=1}^{N} b_{i,k} C_k ) , \quad \text{Equation 5 can be presented in linear form:}
\]

\[
D_i \frac{d^2 C_i^0}{dx^2} - V(x) \frac{dC_i^0}{dx} + a_i + \sum_{k=1}^{N} b_{i,k} C_k = 0, \quad i = 1, 2, ..., N
\]

where

\[
b_{i,k} = \left. \frac{\partial R_i}{\partial C_k} \right|_{old} \quad \text{and} \quad a_i = \left. R_i \right|_{old} = \sum_{k=1}^{N} b_{i,k} C_{old,k}^0 \]

By analogy, the boundary conditions to Equations 9 at \( x = 0 \) have the form:

\[
- D_i \frac{dC_i^0}{dx} = \xi_i + \sum_{k=1}^{N} \xi_{i,k} C_k^0, \quad i = 1, 2, ..., N, \quad \text{at} \quad x = 0
\]

where

\[
\xi_{i,k} = \left. \frac{\partial J_i}{\partial C_k} \right|_{old} \quad \text{and} \quad \xi_i = J_i \bigg|_{old} = \sum_{k=1}^{N} \xi_{i,k} C_{old,k}^0
\]

and the boundary conditions to Equations 9 at \( x = \Delta x \) are described by Equations 7.

The linear boundary value problem that is described by Equations 11, 12, and 7 can be solved by the finite difference method. It should be noted that (approximate) solutions obtained by the linearization of nonlinear differential equations are valid only under certain restricted conditions. One such valid scenario is when the perturbation to
the system is of small amplitude, as is the case for this model. This treatment, by using small amplitude perturbations, is quite common in physics and mathematics for the analysis of the harmonic oscillator, for example.

Diffusion terms in the governing equations are approximated by the central scheme and the convective term is approximated by an up-wind scheme [18]. The obtained system of linear equations is solved by using Thomas algorithm for block tridiagonal matrixes [19,20]. After finding the solution \( C_i^0 \) it is declared to be \( C_{\text{old},i}^0 \) and solution is continued until the convergence is achieved. In some cases, in order to insure convergence, it is necessary to use the method of lower relaxation, which means that after each solution of Equation 15 is found a new value of \( C_i^0 \) is recalculated via the relation:

\[
C_i^0 = \alpha C_i^0 + (1 - \alpha) C_{\text{old},i}^0
\]

where \( \alpha < 1 \) is the relaxation parameter (not to be confused with the transfer coefficient).

After obtaining the stationary solution, the transient perturbation solution can be obtained in the following way: I assume that \( E = E_{dc} \) at \( t < 0 \) and that for \( t > 0 \) a sufficiently low amplitude sinusoidal perturbation, \( \Delta E \), is applied to the system, i.e.

\[
E = E_{dc} + \Delta E \cos(\omega t) = E_{dc} + Re\{\Delta E e^{j\omega t}\} \quad \text{at} \quad t > 0
\]

Here, \( \omega \) is the modulation frequency, and \( \Delta E \) is the real amplitude for the potential of the electrode. If the amplitude, \( \Delta E \), is sufficiently small, the dependence of electrochemical rate constants as a function of time can be presented as:

\[
k_m = k_m^0 + \frac{\partial k_m}{\partial E} \bigg|_0 Re\{\Delta E e^{j\omega t}\}
\]

and accordingly, the response of the system may be presented as:
\begin{equation}
C_i = C_i^0 + \text{Re}\{\Delta C_i e^{j\omega t}\} \tag{16}
\end{equation}

and

\begin{equation}
i = i^0 + \text{Re}\{\Delta i e^{j\omega t}\} \tag{17}
\end{equation}

where $C_i^0$ and $i^0$ are the steady-state values and $\Delta C_i$ and $\Delta i$ are the complex amplitudes for the concentrations and current density, respectively.

After substituting Equation 16 into Equations 5 we have:

\begin{equation}
j\omega \Delta C_i = D_i \frac{d^2 \Delta C_i}{dx^2} - V(x) \frac{d\Delta C_i}{dx} + \sum_{k=1}^{N} b_{i,k} \Delta C_k, \quad i = 1, 2, ..., N \tag{18}
\end{equation}

where parameters $b_{i,k}$ are calculated by Equations 10 at point $C_k = C_k^0$.

The set of $N$ complex equations (Equations 18) can be separated into a set of $2N$ equations corresponding to the real and complex parts of the concentration amplitude

\[\Delta C_i = \Delta C_{i,\text{Re}} + j\Delta C_{i,\text{Im}} \tag{19}\]

\begin{equation}
D_i \frac{d^2 \Delta C_{i,\text{Re}}}{dx^2} - V(x) \frac{d\Delta C_{i,\text{Re}}}{dx} + \sum_{k=1}^{N} b_{i,k} \Delta C_{k,\text{Re}} + \omega \Delta C_{i,\text{Im}} = 0, \quad i = 1, 2, ..., N
\end{equation}

\begin{equation}
D_i \frac{d^2 \Delta C_{i,\text{Im}}}{dx^2} - V(x) \frac{d\Delta C_{i,\text{Im}}}{dx} + \sum_{k=1}^{N} b_{i,k} \Delta C_{k,\text{Im}} - \omega \Delta C_{i,\text{Re}} = 0, \quad i = 1, 2, ..., N
\end{equation}

The boundary conditions are:

\[\Delta C_{i,\text{Re}} = \Delta C_{i,\text{Im}} = 0 \text{ at } x = \Delta x, \quad i = 1, 2, ..., N \tag{21}\]
in which parameters $\zeta_{i,k}$ are calculated by Equations 12 at the point $C_k = C^0_k$.

The solution of the formulated system of linear equations is performed by the same method that was described above for the steady-state case. After that, the real and imaginary components of the complex current amplitude $\Delta i = \Delta i_{_{\text{Re}}} + j\Delta i_{_{\text{Im}}}$ are determined via the relations:

\[
\Delta i_{_{\text{Re}}} = -F \sum_{j=1}^{N} z_j D_j \left( \frac{d\Delta C_{i,\text{Re}}}{dx} \right)_{x=0} \quad \text{and} \quad \Delta i_{_{\text{Im}}} = -F \sum_{j=1}^{N} z_j D_j \left( \frac{d\Delta C_{i,\text{Im}}}{dx} \right)_{x=0}
\]

Finally, the faradic admittance of the system is calculated as:

\[
Y = \frac{\Delta i}{\Delta E} = \frac{\Delta i_{_{\text{Re}}}}{\Delta E} + j \frac{\Delta i_{_{\text{Im}}}}{\Delta E}
\]

Accordingly, the faradic impedance of the system is:

\[
Z_j = \frac{1}{Y} = \frac{\Delta i_{_{\text{Re}}}/\Delta E}{\sqrt{(\Delta i_{_{\text{Re}}}/\Delta E)^2 + (\Delta i_{_{\text{Im}}}/\Delta E)^2}} - j \frac{\Delta i_{_{\text{Im}}}/\Delta E}{\sqrt{(\Delta i_{_{\text{Re}}}/\Delta E)^2 + (\Delta i_{_{\text{Im}}}/\Delta E)^2}}
\]
Example of Application

As an example I consider the application of the developed code to the case of electrochemical-chemical-electrochemical (ECE) mechanism [21]. I assume that the following reactions (in both directions) take place:

\[
O + e^- \leftrightarrow R \quad (28)
\]

\[
R \leftrightarrow 2X \quad (29)
\]

\[
X + e^- \leftrightarrow 2Y \quad (30)
\]

This mechanism has been chosen, because it cannot be reduced in principle to linear mass transfer equations when species X and Y are not present in the bulk electrolyte, unless the pseudo first order approximation is adopted by utilizing large concentrations of X and Y in the solution such that these concentrations remain constant as the reactions proceed.

There are \( N = 4 \) species in this system, \( M = 4 \) electrochemical reactions and \( L = 2 \) chemical reactions. First of all, I assign indexes to these species and describe their properties (see Table 4-1).

**Table 4-1: Properties of species.**

<table>
<thead>
<tr>
<th>Index</th>
<th>Species</th>
<th>( D, \text{ cm}^2/\text{s} )</th>
<th>( z )</th>
<th>( C_\infty, \text{ M} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( O )</td>
<td>( 10^{-5} )</td>
<td>-1</td>
<td>( 0.01 )</td>
</tr>
<tr>
<td>2</td>
<td>( R )</td>
<td>( 10^{-5} )</td>
<td>-2</td>
<td>( 0 )</td>
</tr>
<tr>
<td>3</td>
<td>( X )</td>
<td>( 10^{-5} )</td>
<td>-1</td>
<td>( 0 )</td>
</tr>
<tr>
<td>4</td>
<td>( Y )</td>
<td>( 10^{-5} )</td>
<td>-1</td>
<td>( 0 )</td>
</tr>
</tbody>
</table>
After that, I have to describe the properties of chemical and electrochemical reactions (see Table 4-2 and 4-3).

**Table 4-2: Properties of electrochemical reactions.**

<table>
<thead>
<tr>
<th>Index</th>
<th>Reaction</th>
<th>Non zero $v_{m,i}$</th>
<th>$\mu_{m,i}$</th>
<th>$\alpha$</th>
<th>$k^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$O + e^- \rightarrow R$</td>
<td>$v_{1,1} = 1$</td>
<td>$\mu_{1,2} = 1$</td>
<td>-0.5</td>
<td>1, cm/s</td>
</tr>
<tr>
<td>2</td>
<td>$R \rightarrow O + e^-$</td>
<td>$v_{2,2} = 1$</td>
<td>$\mu_{2,1} = 1$</td>
<td>0.5</td>
<td>0.1, cm/s</td>
</tr>
<tr>
<td>3</td>
<td>$X + e^- \rightarrow 2Y$</td>
<td>$v_{3,3} = 1$</td>
<td>$\mu_{3,4} = 2$</td>
<td>-0.5</td>
<td>$2 \times 10^{-2}$, cm/s</td>
</tr>
<tr>
<td>4</td>
<td>$2Y \rightarrow X + e^-$</td>
<td>$v_{4,4} = 2$</td>
<td>$\mu_{4,3} = 1$</td>
<td>0.5</td>
<td>$3 \times 10^{-3}$, cm$^3$/mol*s</td>
</tr>
</tbody>
</table>

**Table 4-3: Properties of chemical reactions.**

<table>
<thead>
<tr>
<th>Index</th>
<th>Reaction</th>
<th>Non zero $v_{m,i}$</th>
<th>$\mu_{m,i}$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$R \rightarrow 2X$</td>
<td>$v_{1,2} = 1$</td>
<td>$\mu_{1,3} = 2$</td>
<td>2000, 1/s</td>
</tr>
<tr>
<td>2</td>
<td>$2X \rightarrow R$</td>
<td>$v_{2,3} = 2$</td>
<td>$\mu_{2,3} = 1$</td>
<td>1000, cm$^3$/mol*s</td>
</tr>
</tbody>
</table>

Some general properties of the system must be also defined: electrode potential, temperature and hydrodynamic conditions (see Table 4-4). Here the case of RDE is considered.

**Table 4-4: General Properties of the system.**

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>$E_{dc}$, V (SHE)</th>
<th>$\Omega$, rpm</th>
<th>$v$, cm$^3$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.1</td>
<td>500</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The calculated impedance data are presented in Figures 4-1 and 4-2.
Figure 4-1: Nyquist plot for ECE mechanism (described by Equations 28-30). $E_{dc} = 0.1$V. Numbers denote some characteristic frequencies in Hz. Other parameters are defined in the Tables 4-1 through 4-4 above.

As we can see from Figure 4-1 there are two well defined time constants for the chosen ECE mechanism and for the chosen set of parameters. For comparison purposes Figure 4-2 yields the corresponding Nyquist plot for the EC mechanism (described by Equations 28 and 29) and for the E mechanism (described by Equations 28) and for the same set of parameters.
Figure 4-2: Nyquist plot for EC mechanism (described by Equations 28 and 29) is shown in Curve 1 and the E mechanism (described by Equation 28) is shown in Curve 2. $E_{dc} = 0.1V$. Other parameters are defined in the Tables 4-1 through 4-4 above.

For the case of the EC mechanism, there are also two time constants visible, but for the case of a single electrochemical reaction we can see only one time constant, as expected.

Also for comparison purposes Figure 4-3 yields Bode plots for different values of initial constant potential, $E_{dc}$.
Figure 4-3: Bode plots for ECE mechanism and for different values of the initial constant potential, $E_{dc}$. Other parameters are defined in the Tables 4-1 through 4-4 above.
We see in Figure 4-3, for example, that at low frequencies the impedance of the system reduces to the resistance component that does not depend on frequency. However, the value of this resistance component increases as $E_{dc}$ is decreased. This fact is the result of the observed current approaching the limiting current value, which is determined by the transport of species X to the electrode surface.

**Evaluation of Unknown Parameters from Experimental Data**

Each of the parameters that characterize a given species (e.g., the diffusion coefficient) or the kinetics of the chemical or electrochemical reactions (standard rate constant, transfer coefficient) can be considered as unknown values, which can be determined by optimizing the model onto the experimental data. Practically, optimization reduces to the minimization of some value, $S$, which describes the discrepancy between calculated and experimentally measured values. In this study I choose:

$$S = \sum_{i} \frac{|Z_{\text{Re},i} - Z_{\text{exp},i}|}{Z_{\text{exp},i}}$$

where $Z_{\text{exp},i}^{\text{exp}}$ is the experimentally-measured real component of the impedance and index $i$ numerates different frequencies. That is, I considered the minimization of the relative deviation of the real component of the impedance. If optimization is performed in the proper manner, a satisfactory agreement between calculated and measured imaginary
components must be also observed (or equivalently, amplitude of the impedance and phase angle).

It is important to note that the impedance of the experimental system, $Z$, is related to the faradic impedance, $Z_f$, that is described by Equation 27 by the relation:

$$Z = R_{el} + \frac{Z_c Z_f}{Z_c + Z_f}$$  \hspace{1cm} (32)

where

$$Z_c = \frac{1}{j\omega C_d}$$  \hspace{1cm} (33)

is the impedance of the double layer with the capacitance $C_d$ and $R_{el}$ is the resistance of the electrolyte between the metal surface and the tip of the Luggin probe.

Experimental impedance measurements were performed for 1 mM potassium ferricyanide + 1 mM potassium ferrocyanide + 2 M NaOH at a 5 mm diameter platinum RDE (1000 RPM) at 23°C. The frequency range was 100,000 Hz to 0.1 Hz and the perturbation potential amplitude was 20 mV peak-to-peak. A platinum wire counter electrode and Hg/HgO reference electrode were used.

The polarization behavior of this system is described by the Butler-Volmer equation:

$$i = Fk_R^0 C_{R,s} \exp\left[\frac{(1-\beta)FE}{RT}\right] - Fk_O^0 C_{O,s} \exp\left[-\frac{\beta FE}{RT}\right]$$  \hspace{1cm} (34)

where index $O$ denotes ferricyanide and index $R$ denotes ferrocyanide, $C_{O,s}$ and $C_{R,s}$ are the surface concentrations of O and R, respectively, and $\beta$ is the symmetry factor for the reaction. The parameters to be determined by optimization are: $k_R^0$, $k_O^0$, $\beta$, $D_O$, $D_R$, $R_s$.
and $C_{dl}$. The surface concentrations are readily calculated from the bulk concentrations and the limiting currents as [21]:

$$C_{O,s} = C_{O,b} \frac{i_{l,r} - i}{i_{l,r}}$$  \hspace{1cm} (35)

and

$$C_{R,s} = C_{R,b} \frac{i_{l,f} - i}{i_{l,f}}$$  \hspace{1cm} (36)

where $i_{l,f}$ and $i_{l,r}$ are the limiting current densities in the forward ($R \rightarrow O + ne^-$) and reverse directions ($O + ne^- \rightarrow R$), respectively and $i$ is the current density.

The results of optimization that was performed by using the Monte Carlo method for the real part of impedance at $E_{dc} = 304$ mV vs. SHE (the equilibrium potential of the reaction is $E^e = 0.379$ V vs. SHE), yields: $k^0_R/k^0_O = 3.55 \cdot 10^{-7}$, $\beta = 0.5$, $D_O = 4.06 \cdot 10^{-5}$ cm$^2$/s, $D_R = 4.66 \cdot 10^{-5}$ cm$^2$/s, $R_e = 0.8$ $\Omega$cm$^2$ and $C_{dl} = 43$ $\mu$F/cm$^2$. Experimental measurements of the resistance of the electrolyte and the double layer capacitance in the absence of the redox couple yield results that are close to the fitted values, namely: $R_e = 0.76$ $\Omega$cm$^2$ and $C_{dl} = 46$ $\mu$F/cm$^2$.

Figure 4-4 shows that the theoretical curve, which was calculated numerically (line) by using the values of the optimized parameters compares very well with the experimental data (dots) for real part of the impedance. The same values of the optimized parameters also yield excellent agreement between the calculated and experimental data for the imaginary part of the impedance (Figure 4-5).
Figure 4-4: Comparison between experimental (dots) and calculated (line) values of real part of impedance at $E_{dc} = 304 \text{ mV (SHE)}$.

Figure 4-5: Comparison between experimental (dots) and calculated (line) values of imaginary part of impedance at $E_{dc} = 304 \text{ mV (SHE)}$. 
Experimental measurements also were performed for $E_{dc} = 329, 354, 379, 404, 429$ and $454$ mV vs. SHE. At all of these values of the steady-state potential of the electrode, except for 454 mV, excellent agreement has been observed between the calculated and measured real and imaginary parts of the impedance. Thus, for example, Figures 4-6 and 4-7 show comparison between calculated and measured values for $E_{dc} = 429$ mV vs. SHE.

![Graph showing comparison between experimental and calculated values of real part of impedance at $E_{dc} = 429$ mV (SHE).](image)

**Figure 4-6:** Comparison between experimental (dots) and calculated (line) values of real part of impedance at $E_{dc} = 429$ mV (SHE).
Figure 4-7: Comparison between experimental (dots) and calculated (line) values of imaginary part of impedance at $E_{dc} = 429$ mV (SHE).

However, for $E_{dc} = 454$ mV (SHE), some discrepancy is observed (see Figures 4-8 and 4-9). The reason for the discrepancy is not clear at this time. However, I would like to remind the reader that only the experimental data for the real part of impedance at $E_{dc} = 304$ mV (SHE) was used for optimization. The fact that the impedance data that were calculated by using the optimized parameters at only one potential satisfactory coincides with the majority of the experimental data at different potentials confirms the adequacy of the fitted values.
Figure 4-8: Comparison between experimental (dots) and calculated (line) values of real part of impedance at $E_{dc} = 454$ mV (SHE).

Figure 4-9: Comparison between experimental (dots) and calculated (line) values of imaginary part of impedance at $E_{dc} = 454$ mV (SHE).
It is important to note that the described procedure of optimization failed to
determine the standard rate constants of the reactions, $k^0_R$ and $k^0_O$, separately (only their
ratio could be obtained for the given system), because their values appear to be
excessively high. Thus, the following approximate, but very accurate, analytical
expression for the faradic impedance can be derived:

$$Z_f = \frac{\Delta i}{\Delta E} = \frac{1}{k^0_O} + \frac{\exp\left[\frac{(1 - \beta)FE}{RT}\right]}{\sqrt{j\omega D_o}} \arctan\left[\frac{j\omega L_O}{D_o}\right] + \frac{(k^0_R/k^0_O)\exp\left[-\frac{\beta FE}{RT}\right]}{\sqrt{j\omega D_R}} \arctan\left[\frac{j\omega L_R}{D_R}\right]$$

(35)

Here $C^0_{R,s}$ and $C^0_{O,s}$ are steady surface concentration of ferricyanide and
ferrocyanide, correspondingly and $L_R$ and $L_O$ are the corresponding thicknesses of the
Nernst diffusion layers. We see that as $k^0_O \to \infty$, (practically for $k^0_O > 100$ cm/s) $Z_f$
becomes independent of both $k^0_O$ and $k^0_R$, which is the case here. This example shows
that, in some cases, not all unknown parameter values can be found by optimization, by
using the impedance method.

Additionally, I wanted to test the new EIS model on a more complex, coupled
reaction scheme to determine whether the model can fit the various reaction parameters
for a more complicated case than the ferricyanide reduction discussed above. The two
coupled reactions I studied were the reduction of nitromethane [22] and the reduction of
ortho-bromonitrobenzene [23]. After verifying that the model works properly on one of
these complex reaction mechanisms, I intend to use it to discover the mechanisms and kinetic parameters for various boron hydride reactions as mentioned above.

The reduction of nitromethane has been explored by other groups and the original consensus among various researchers was that this reaction followed a coupled ECCE mechanism [24] as shown in Figure 4-10.

![Figure 4-10: The proposed ECCE reaction mechanism for the electrochemical reduction of nitromethane, from [24].](image)

During the electrochemical reduction of nitromethane, the blank solution is 1M NaCl + 0.15M NaH₂PO₄ + 0.05M citric acid. The sample of nitromethane is then made so that it contains 5mM nitromethane and the remainder is the same as the blank. At 23 degrees Celsius, the viscosity of the blank solution was 0.0010478 cm²/s and the viscosity of the nitromethane sample solution was 0.0010631 cm²/s.
Figure 4-11 displays cyclic voltammograms (collected at 0 RPM with a scan rate of 50 mV/s) and linear sweep voltammograms (collected at 1000 RPM and a scan rate of 5 mV/s) for the redox reactions of nitromethane, in 1 M NaCl + 0.15 M NaH₂PO₄ + 0.05 M citric acid at 23 °C.

Figure 4-11: Black line is blank CV (0 RPM with a scan rate of 50 mV/s), blue line is nitromethane sample CV (0 RPM with a scan rate of 50 mV/s), red line is blank LSV (1000 RPM and a scan rate of 5 mV/s), and green line is nitromethane sample LSV (1000 RPM and a scan rate of 5 mV/s).

EIS data were collected at the following steady-state potentials versus SHE: 0.150V, 0.050V, -0.025V, and -0.100V. The peak-to-peak amplitude of the perturbing
voltage signal was 20 mV. Table 4-5 presents the steady state current density, solution resistance, and double layer capacitance:

**Table 4-5: Electrochemical properties during the reduction of nitromethane.**

<table>
<thead>
<tr>
<th>SS Potential (vs. SHE)</th>
<th>SS Current Density (A/cm^2)</th>
<th>R_s (Ohm*cm^2)</th>
<th>C_{dl} (F/cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.150V</td>
<td>-6.131x10^{-6}</td>
<td>2.312</td>
<td>3.2594x10^{-5}</td>
</tr>
<tr>
<td>0.050V</td>
<td>-8.6602x10^{-6}</td>
<td>2.321</td>
<td>3.2871x10^{-5}</td>
</tr>
<tr>
<td>-0.025V</td>
<td>-9.1696x10^{-6}</td>
<td>2.334</td>
<td>3.4530x10^{-5}</td>
</tr>
<tr>
<td>-0.100V</td>
<td>-12.226x10^{-6}</td>
<td>2.348</td>
<td>3.8539x10^{-5}</td>
</tr>
</tbody>
</table>

Figure 4-12 shows the Nyquist and Bode plots of the nitromethane solution:

**Figure 4-12: Nyquist and Bode plots for 5mM nitromethane in 1 M NaCl + 0.150 M NaH_2PO_4 + 0.05 M citric acid. Frequency range was 100,000 Hz to 0.1 Hz. The green line corresponds to the steady-state potential of -0.100 V (vs. SHE), all other potential values yield data that overlap one another.**
When the collected EIS data were introduced into the computer code and a best-fit analysis was performed, I discovered that the real-value component results (Figure 4-13) were not suitable for extracting the necessary reaction parameters, with any degree of accuracy, even though the imaginary-value component results were fitted quite well (Figure 4-14).

![Figure 4-13: EIS fitting of reduction of nitromethane at 25 mV vs. SHE, real values shown.](image-url)
Upon reviewing more literature on the subject or the electrochemical reduction of nitromethane, a paper was found [25] in which the reaction mechanism is not just a simple ECCE, but rather is as shown in Figure 4-15.
Figure 4-15: The proposed reaction mechanism for the electrochemical reduction of nitromethane, from [25].

Due to the complexity of this reaction mechanism it was not explored any further and work was started on investigating the electrochemical reduction of ortho-bromonitrobenzene [23,26].
The proposed reaction mechanism from the literature is shown below in Figure 4-16.

![Diagram of the proposed reaction mechanism for the reduction of ortho-bromonitrobenzene (o-BNB)](image)

**Figure 4-16: The proposed reaction mechanism for the reduction of ortho-bromonitrobenzene, from [26].**

EIS experimental data for the reduction of 2 mM ortho-bromonitrobenzene (o-BNB) with 100 mM tetrabutylammonium perchlorate (TBAP) as supporting electrolyte in acetonitrile were collected using a 5 mm gold RDE disk working electrode at 1000 RPM, a 1 mm platinum wire as the counter electrode with 5 cm length in solution, and a silver wire pseudo-reference electrode.
Within the filenames shown in Figures 4-17 through 4-20, the numbers at the end correspond to different steady-state potential values (all perturbation voltage amplitudes are 20 mV): 01 = -0.900 V; 02 = -0.945 V; 03 = -0.990 V; 04 = -1.035 V; 05 = -1.080 V; 06 = -1.125 V, all potentials are measured versus silver wire pseudo-reference electrode. The frequency range for each data set is from 65535 Hz down to 0.1 Hz.

Figure 4-17: Nyquist plot for the reduction of 2 mM o-BNB in 100 mM TBAP in acetonitrile measured by EIS. Experimental parameters defined in the text above.
Figure 4-18: Same as Figure 4-17, just a different scale.
Figure 4-19: Same as Figures 4-17 and 4-18, just a different scale.
Figure 4-20: Same as Figures 4-17 through 4-19, just a different scale.

Figure 4-21 shows the cyclic voltammogram of 2 mM o-BNB when the working electrode is stationary (0 RPM) and when it is rotated at 1000 RPM.
Results from other experiments (not shown) revealed that, even though the purity of the ortho-bromonitrobenzene I purchased was stated to be greater than 99%, there was a sufficient amount of its isomer, para-bromonitrobenzene, to interfere with the EIS analysis because the para- isomer undergoes a competing electron transfer process at virtually the exact same potential value. As a result of the chemical contamination (from the source) and lack of a higher purity sample of ortho-bromonitrobenzene, these results could not be used to validate this model on a more complex, yet known, reaction mechanism.
Summary and Conclusions

A general model and computer code have been developed for writing down by inspection the impedance of one-dimensional systems involving arbitrary numbers of coupled electrochemical and chemical processes under activation or mass transport control. This code is based on the direct solution of the mass transport equations by using the finite difference up-wind scheme. In the first step, the steady-state distributions of concentration, $C_i$, and potential, $E$, are found and in the second step the periodic reaction of the concentrations, electric potential in the solution, and current density to the small periodic perturbation of $E$ are determined. In this last step, the number of unknown values is doubled (we have to find the real and imaginary components of the perturbation and responses) and, accordingly, the number of governing equations is also doubled. The current version of the code is able to handle any arbitrary number (and complexity) of homogeneous and heterogeneous reactions in the frame of dilute solution theory. However, it can be easily generalized to the case of concentrated electrolytes. This code simulates, and can be used for optimization, coupled chemical/electrochemical reaction mechanisms at rotating disk electrode (RDE) or by using the Nernst diffusion layer approximation. The code executes rapidly and the output is formatted for easy comparison with experimental impedance measurements. On the other hand, the models are presented in a form that allows them to be readily optimized on experimental EIS data, in order to determine values for various model parameters (rate constants, transfer coefficients, diffusivities, etc). The application of the code was illustrated with “synthetic” EIS data and with the experimental data obtained on the RDE.
Overall Summary and Recommendations for Future Work

This project began based on requirements from the US Department of Energy for researching chemical hydrides that were likely candidates to meet their ultimate goals (high storage capacity, good safety qualities, ability to be regenerated). The first chemical hydrides that were proposed to be studied by our group were the polyborane salts. Although they were shown to be electroactive, I discovered that the oxidation was irreversible and no hydrogenation could take place. This generality of the polyboranes’ lack of electrochemical reversibility is found in the decahydrodecaborate and dodecahydrododecaborate salts with various cations in the salts.

As a result of the less than favorable outcome of the polyboranes, the DOE then requested that I study ammonia borane in the same manner. Once again, I found that the electrochemical oxidation for ammonia borane was irreversible. In order to take a second attempt at the hydrogenation of ammonia borane, I looked into using the Devanathan cell as a tool for indirect hydrogenation using organotin hydrides. Unfortunately, the organotin halides were not able to be hydrogenated, thus a closed-loop cycle could not take place.

In parallel with the work on chemical hydrogen storage, I developed a new model of electrochemical impedance spectroscopy. The new model was originally supposed to be used to determine the reaction mechanism(s) within the chemical hydrogen storage materials (though it applies to any reaction mechanism and not just chemical hydrogen materials), however I ran out of time to validate the model and collect EIS data from the chemical hydrogen storage materials. The new model of EIS was shown to extract...
accurate kinetic information from various sets of experimental data based on the redox
couple ferricyanide anion and ferrocyanide anion. I attempted to find a more complex
(and yet known) reaction mechanism that I could use as a standard for validating the
model, but the two compounds that I chose were found later to be not well suited for the
task at hand.

In the future, the greatest benefit would be found in researching the nonaqueous
silver/silver chloride reference electrode in more depth. Having this electrode available
to the investigator would provide the means to perform long-term electrolyses and
electrochemical impedance spectroscopy measurements. In order to make this reference
electrode a reality, a new junction mater is needed that allows for good electronic
conductivity but at the same time it should limit the bulk flow of filling solution into the
test cell, which thereby contaminates the working solution.
References


Appendix

Non-Technical Abstract

Hydrogen has been chosen as an energy carrier to address the global need for energy. Because of the physical and chemical properties of hydrogen, we are in some instances able to store more hydrogen per unit mass and/or volume in the form of a chemical hydride as opposed to compressed hydrogen gas, liquefied hydrogen, or various other forms of hydrogen storage.

The chemical hydrides in this work are forms of boron hydrides. The first boron hydride that was investigated here is from a class of materials called “cluster molecules” and hydrides in this class are called polyhedral boranes. These molecules can be produced as inorganic salts that have excellent physical and chemical properties in terms of hydrogen storage capacity as well as safety (they are relatively inert to heat as well as acids and bases).

I found that due to the stability of the polyhedral borane molecules, they were unable to release a sufficient amount of hydrogen for this project. As a result of these findings, I then investigated ammonia borane as another candidate for chemical hydrogen storage. Ammonia borane suffers from an irreversible hydrogen release step and therefore we cannot directly hydrogenate it from a spent fuel form back to the original hydride. To get around this problem, organotin hydrides were found to be able to indirectly hydrogenate the spent ammonia borane fuel, but then the organotin hydrides are converted to a halide that then needs hydrogenated.

To complement the experimental work on boron hydrides, I developed a new model of electrochemical impedance spectroscopy, which is a technique that is capable of probing complex chemical and electrochemical reactions. The model was written into a computer code that allows us to extract kinetic parameters of interest from experimental data by performing a best-fit analysis of the experimental data onto the theoretical reaction scheme.
Justin Charles Tokash

Justin was born on April 8, 1980 in DuBois, PA, and was raised in Foxburg, PA. He graduated from Punxsutawney Area High School in the academic curriculum in 1998. After high school, Justin attended the DuBois, PA campus of Penn State University for two years to obtain the majority of his general education course requirements. After these first two years, Justin moved to the Erie, PA campus of Penn State for two more years to complete the core requirements for his Bachelor of Science degree in physics and his minor in mathematics. After completing his Bachelor’s degree, Justin moved on to study physics at The University of Akron in Akron, Ohio for his Master’s of Science degree. During his time at The University of Akron, Justin began his studies while also being a teaching assistant for the physics department. After one year of being a TA, Justin was able to start research with Professor Rex Ramsier in the field of surface physics. This research led to nine refereed scientific journal articles and a broad knowledge of surface science. Finally, in the fall of 2004 Justin came to Penn State University to begin working toward his Ph.D. degree under the guidance of Professor Digby Macdonald. Justin initially began his Ph.D. studies in the Materials Science and Engineering department, but transferred to the Engineering Science and Mechanics department after two years while continuing to work on the same chemical hydrogen storage project and then was co-advised by Professor Mirna Urquidi-Macdonald. This research has lead to the publication of three refereed scientific journal articles and the development of a new model of electrochemical impedance spectroscopy.