Electrochemical Hydrogen Storage Systems

Dr. Digby Macdonald, Justin Tokash, Samin Sharifi, Sang-Kwon Lee, Krys Williams, Matthew Taylor, Dr. Amr Saleh, Dr. Rezwana Sharna

Center for Electrochemical Science and Technology
Department of Materials Science and Engineering
Pennsylvania State University
University Park, PA 16802

Dr. George Engelhardt (Consultant)
OLI Systems, Morris Plains, NJ 07950

June 9 2010

Project ID # ST058

Overview

Timeline

- Project start date: 3/1/05
- Project end date: 6/30/10
- Percent complete: 99%

Barriers

- Barriers addressed:
  - A: System Weight and Volume
  - C: Efficiency
  - R: Regeneration Processes.

Budget

- Total project funding (Phase 2)
  - DOE share: $615,403
  - Contractor share: $153,861
- Funding FY08: $241,445
- Funding for FY09: $280,000
- Funding for 2010: $135,802

Partners

- LANL
- PNNL
- University of Alabama
- Rohm & Haas
- University of Missouri

Objectives

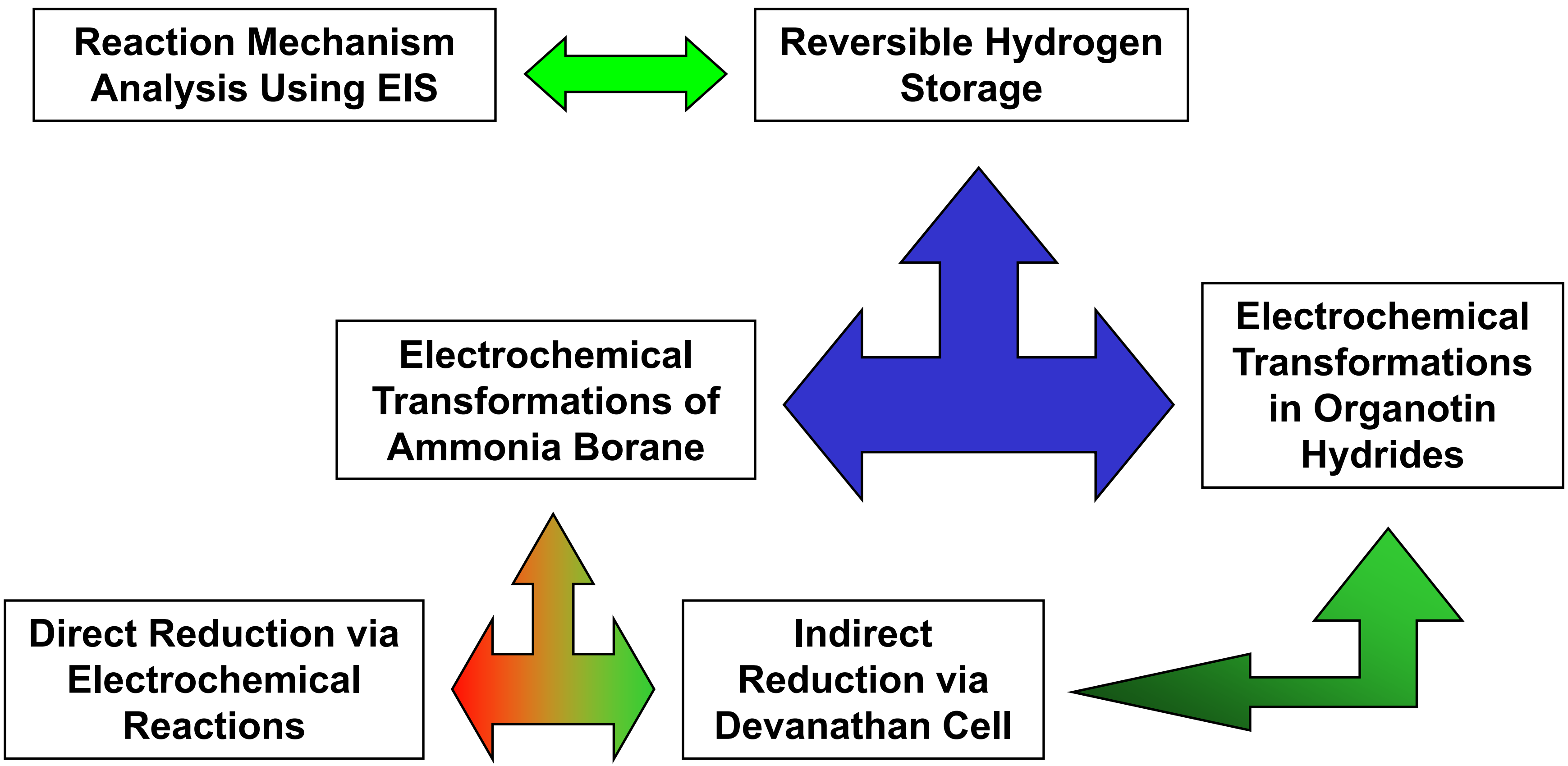
- Demonstrate an electrochemical route to the conversion of spent ammonia borane (lower hydride) back to ammonia borane fuel (higher hydride) to meet DOE 2010 regeneration process goals.

- Explore the feasibility of electrochemical regeneration of organotin hydrides for use as a reagent in the regeneration of ammonia borane.

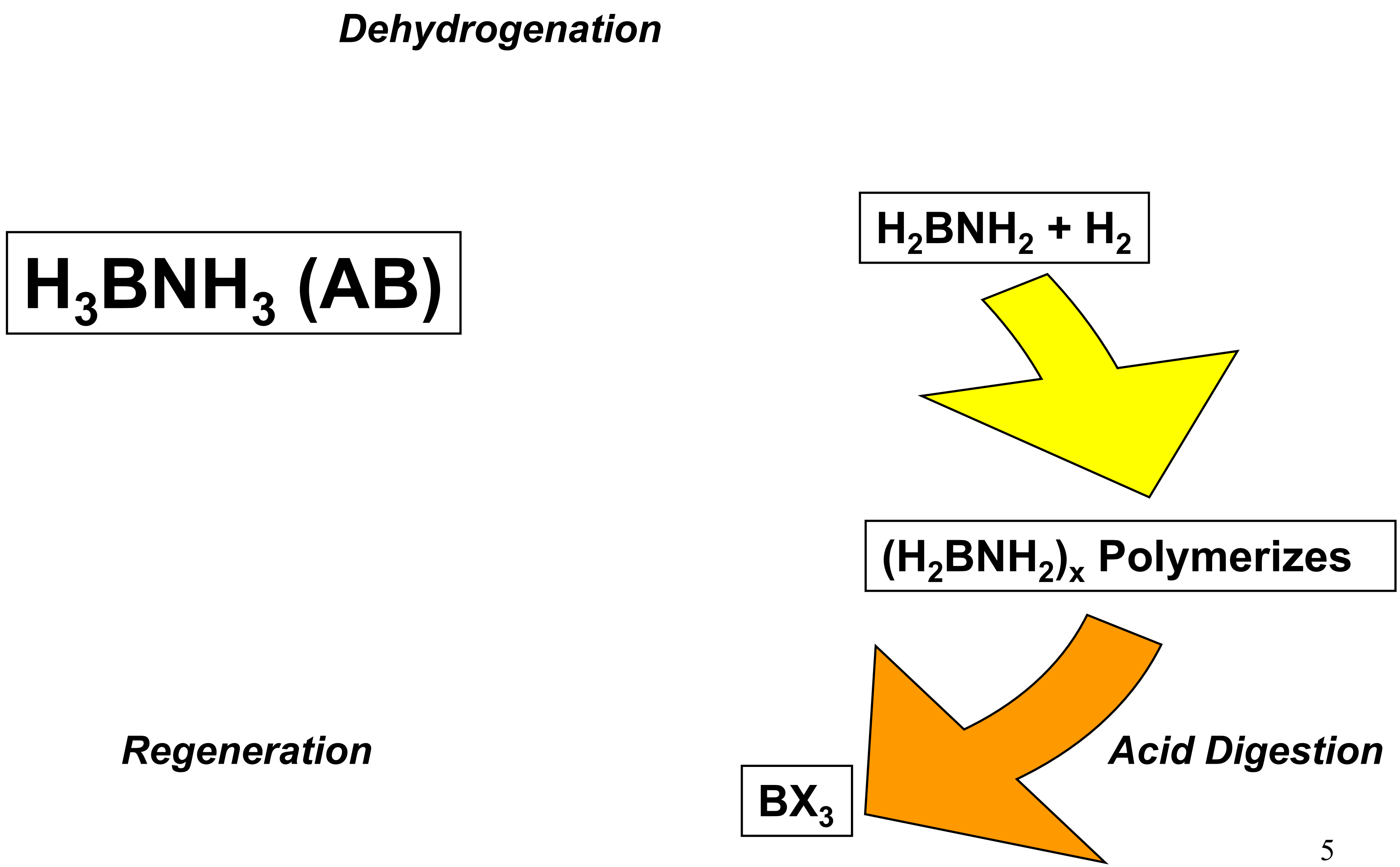
- Develop a general model of Electrochemical Impedance Spectroscopy to study coupled reaction mechanisms and utilize the model to extract kinetic parameters from experimental data.

- Explore the feasibilities of indirect and direct electrochemical methods for hydrogenating materials.

Technical Approach



Ammonia Borane (AB) Lifecycle



Ammonia Borane Regeneration

- **Digestion: $BNH_x + 3 \cdot HX \rightarrow BX_3 + NH_3 + H_2$**
- Regeneration via two different approaches:

1) $BX_3 + 3 \cdot MH + NH_3 \rightarrow H_3BNH_3 + 3 \cdot MX$

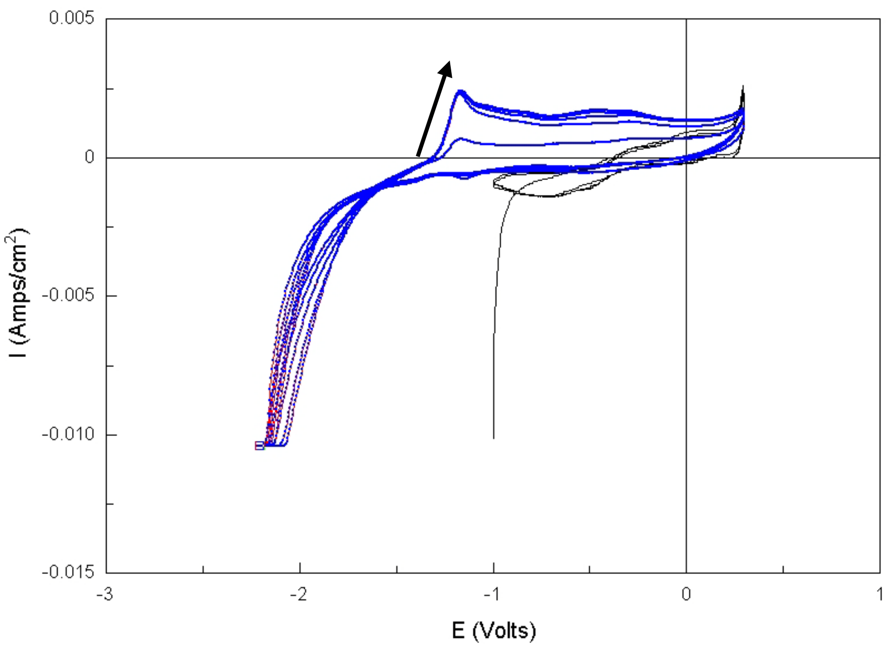
MX regeneration

2) $R_nSnH_{4-n} + BX_3 \rightarrow R_nSnX_{4-n} + BH_3$

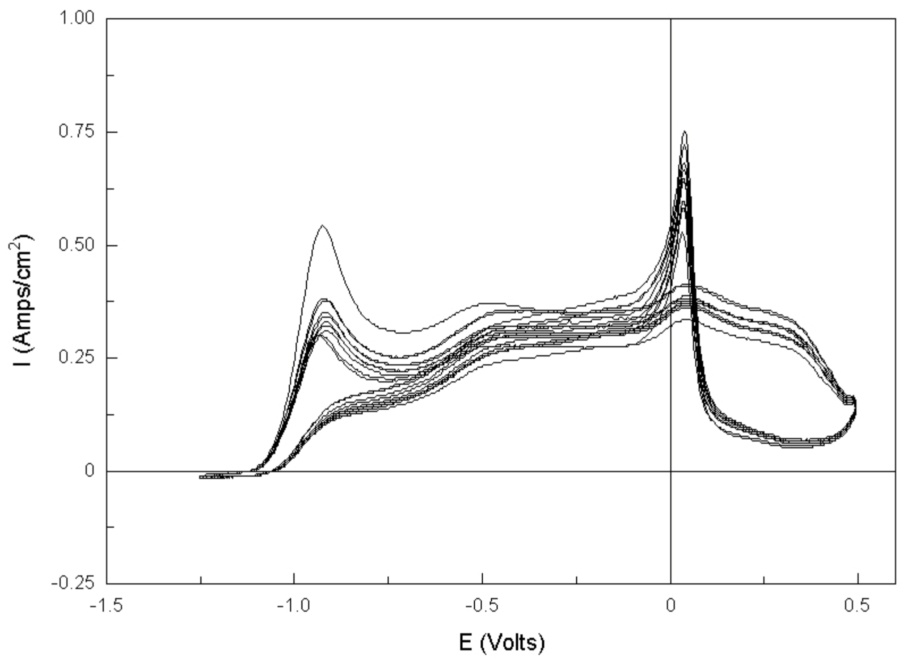
H_3BNH_3

R_nSnH_{4-n} regeneration

Ammonia Borane Electrochemistry



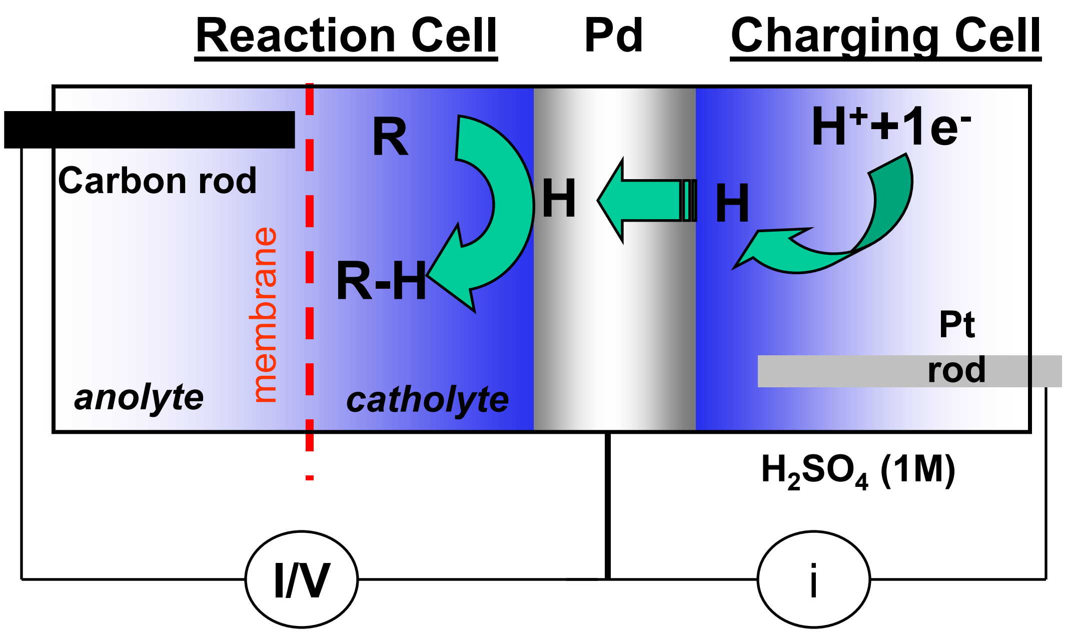
CV of 5 mM ammonia borane in anhydrous acetonitrile/dioxane (1:1) with 0.1 M $TBAPF_6$ as supporting electrolyte. WE = 0.5 mm Pt disk, CE = 2 mm Pt disk, RE = Ag (pseudo). Scan rate = 100 mV/s. Blue line is the AB sample, black line is the blank solution. The arrow indicates that the oxidation peak grows with each successive cycle.



CV of 10 mM ammonia borane (AB) in 2 M NaOH. WE = 5 mm Au disk, CE = Pt mesh, RE = SCE. Scan rate = 50 mV/s.

Rather unusual electrochemical behavior – complex mechanism. The lower peak occurs on the forward sweep (negative to positive potential) while the higher peak occurs on the reverse sweep; both grow on successive cycles.

Devanathan-Stachurski Cell



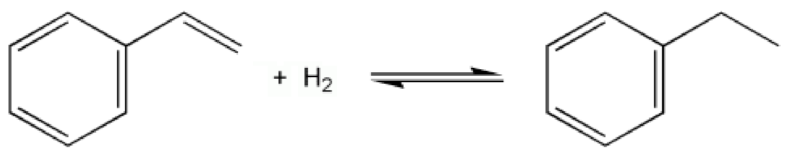
- Pump atomic H from the charging cell to the reaction cell through palladium foil.
- Apply a potential / current in the reaction cell with the H source to hydrogenate R to R-H.

- The use of the Devanathan cell will be employed to:

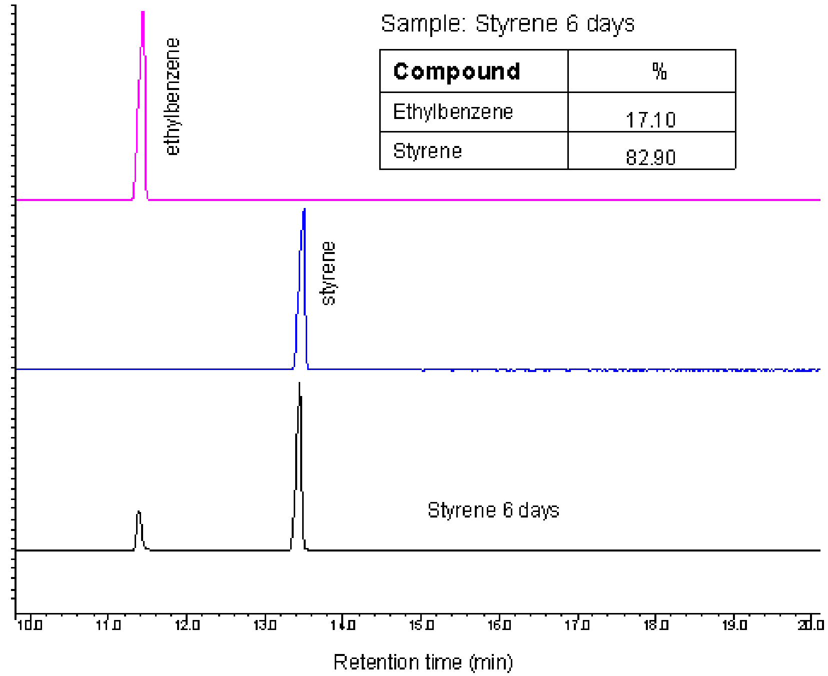
1. Explore reductions important to the regeneration of AB.
2. Regeneration of metal ammonia boranes [$M(AB)_n$; e.g., $Ca(AB)_2$].
3. Regeneration of tin hydride (SnH_y).

Devanathan-Stachurski Cell

As a test of the ability for this cell to hydrogenate a sample, we have attempted to hydrogenate styrene to ethylbenzene – essentially this is a conversion of a ethylene group into an ethyl group that is attached to a benzene ring, as shown below.



Styrene Ethylbenzene



Sample: Styrene 6 days

Compound	%
Ethylbenzene	17.10
Styrene	82.90

Will this work for organotin halide or ammonia borane reductions? We will soon find out!!

After six days of hydrogenation using the Devanathan cell, the styrene was hydrogenated by 17.10% to ethylbenzene at a coulombic efficiency of 81.5%.

Metal Hydride Electrodes

The hydride-forming materials may be classified as

- classic hydride formers (e.g. Zr, Ti, Ta…)
- 'reactive' hydride formers (e.g. Li, Be, Mg…)

Both hydride-forming materials may be employed as intermediates in hydrogenating other species in regeneration schemes.

- The use of metal hydride electrodes will be explored to:

1. The direct formation of hydride metal surfaces under conditions compatible with the regeneration schemes .
2. We also propose to explore the use as hydrogenation media of:
   - Molten salts
   - Ionic liquids

Electrochemical Generation of Solution Based Inorganic Hydrides

In an extension of Task 2 we examined hydride transfer reagents:

$$BX_3 + 3 \cdot MH + NH_3 \rightarrow H_3BNH_3 + 3\,MX$$

The current thinking is the use of tin hydrides (reactions not balanced):

$$R_nSnH_{4-n} + BX_3 \rightarrow BH_3 + R_nSnX_{4-n}$$

X is probably sulfide R-S

Then recycle the SnX using formate as the H source:

$$R_nSnX_{4-n} + HCO_2H \rightarrow R_nSn(CO_2H)_{4-n} + HX$$

(this may involve NaOH as a reagent!)

$$R_nSn(CO_2H)_{4-n} \rightarrow R_nSnH_{4-n} + CO_2$$

These hydride transfer reagents can facilitate the conversion of electrode-based hydrides to active solution-based hydride transfer reagents.

R_3SnH Regeneration

- Polarographic studies in protic solvents ($MeOH/LiClO_4$) (1,2)

$$2R_3SnX + 2\,e^- \rightarrow 2X^- + 2R_3Sn^{\cdot} \rightarrow R_3SnSnR_3$$

$$\downarrow\ 2e^-$$

$$2R_3Sn^- \rightarrow R_3SnSnR_3$$

- Polarographic studies in acetonitrile (3)

$$2R_3SnX + 2\,e^- \rightarrow 2X^- + 2R_3Sn^{\cdot} \rightarrow R_3SnSnR_3$$

$$\downarrow\ 2e^-$$

$$2R_3Sn^-$$

- Reactions to consider

$$Ph_3Sn^{\cdot} + H^+ + e^- \rightarrow Ph_3SnH \text{ (4)}$$

$$Ph_3Sn^- + PhOH \rightarrow Ph_3SnH + PhO^- \text{ (3)}$$

1. A. Savall and G. Lacoste. *Chemical Engineering Science*, Vol 35 (1980) 389-395.
2. A. Savall, G. Lacoste and P. Mazerolles. *Journal of Applied Electrochemistry*, 11 (1981) 61-68.
3. G. Mazzochin, R. Seeber and G. Bontempelli. *Journal of Organometallic Chemistry*. 121 (1976) 55-62.
4. D. White. *Organoelemental and Coordination Compounds*. In Organic Electrochemistry: and introduction and guide, 2nd ed. 1983, Marcel Dekker, NY.

R_3SnH Regeneration

- Possible side/competing reactions

1. Formation of distannates

$$2R_3Sn^{\cdot} \rightarrow R_3SnSnR_3$$

$$2R_3Sn^{-} \rightarrow R_3SnSnR_3$$

$$2R_3SnH \xrightarrow{\text{Catal (Pd)}} R_3SnSnR_3 + H_2 \ (1)$$

$$R_3SnH + R'_3SnX \rightarrow R_3SnSnR'_3 + HX \ (2)$$

2. Oligostannanes formation

$$R_3Sn^{\cdot} + e^{-} \rightarrow R^{-} + R_2Sn \rightarrow (R_2Sn)_x \ (3)$$

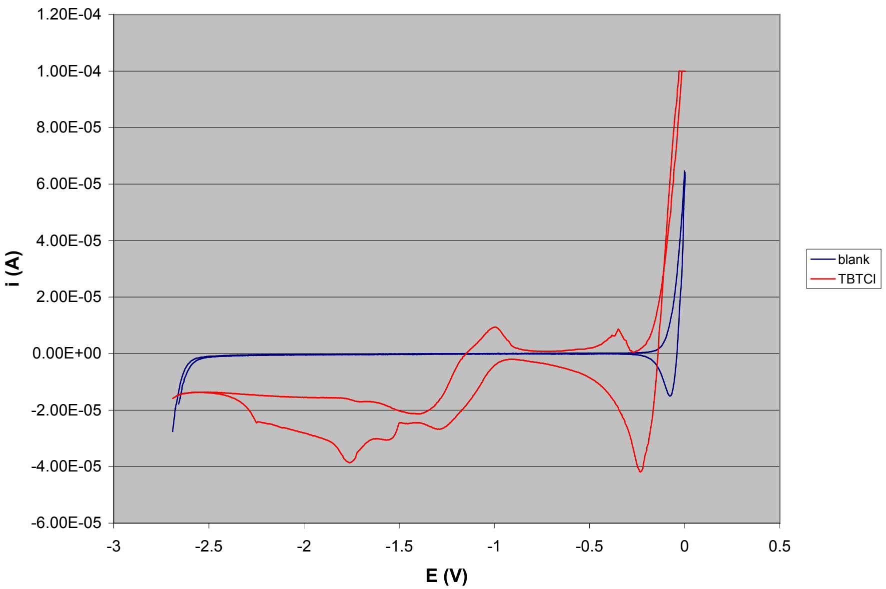
3. Moisture sensitive

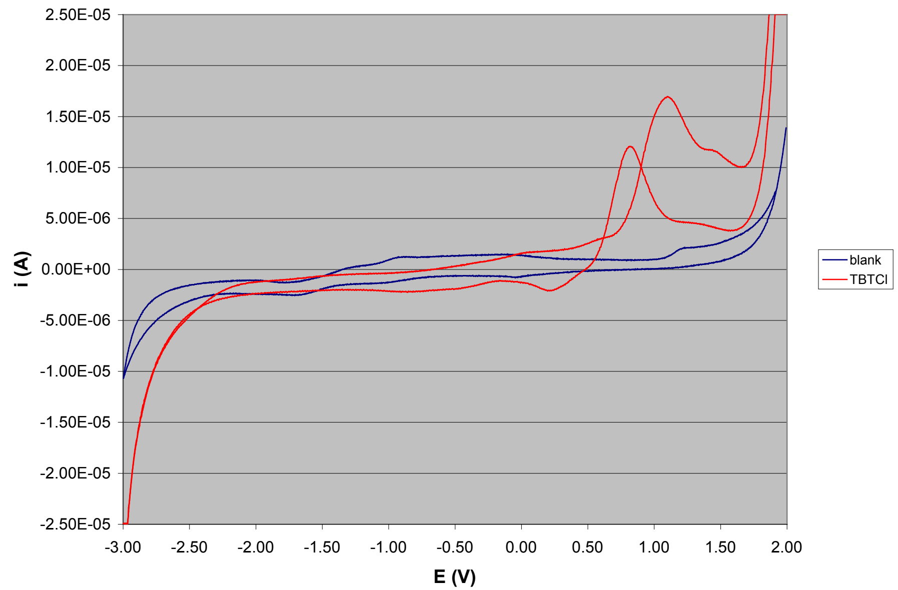
$$R_3SnX + H_2O \rightarrow R_3SnOH \rightarrow R_3SnOSnR_3$$

1. B. Jousseaume. *Mikrochimica Acta*, 109 (1992) 5-12.
2. A. Davies. *Organotin Chemistry*, 2nd ed, 2004, Wiley-VCH
3. A. Savall, G. Lacoste and P. Mazerolles. *Journal of Applied Electrochemistry*, 11 (1981) 61-68.

R_3SnH Regeneration

- Exploratory CVs performed in acetonitrile





CV of 10mM tributyltin chloride in acetonitrile with 0.1M $TBAPF_6$ supporting electrolyte.
Sweep rate: 100mV/s.
WE: Hg/Cu (1mm disk).

CV of 10mM tributyltin chloride in acetonitrile with 0.1M TBAP supporting electrolyte.
Sweep rate: 100mV/s.
WE: Pt (1mm disk).

R_3SnH Regeneration

- Direct electrolysis performed in acetonitrile (undivided cell)

0.1M Tributyltin chloride (TBTCl)

Electrolyte: 0.1M Tetrabutylammonium perclorate (TBAP)

Anode: Pt gauze

40mA during 3.5h

a) Cathode: Pd flag

1. **Solution yellowish and partialy cloudy**
2. **Using PhOH as a hydrogen source** → **Tar formation on the anode**
3. **Sparging the anode with 10%H_2** → **White solid** → **$(R_2Sn)_x$ (?)** → **to identify**

b) Cathode: Cu/Hg flag

Sparging the anode with 10%H_2 → **Yellow oil (?)** → **to identify**

Reaction Mechanism Analysis
(Electrochemical Impedance Spectroscopy)

Technique for discerning mechanisms of complex, coupled electrochemical (charge transfer) and chemical reaction processes.

Coupled reaction mechanisms are indicated by cyclic voltammetry on the tin hydride / halide system and on the ammonia borane system.

High level of mathematical sophistication is utilized:

- **to differentiate between various coupled mechanisms.**
- **extract kinetic information by constrained optimization of the models on the experimental impedance data.**

Present treatment handles:

- **reaction mechanisms involving up to ten species in ten reactions.**
- **non-linear problems involving semi-infinite and forced convection mass transport modes.**

It is probably the most sophisticated and powerful electrochemical mechanism solver ever devised.

General Mathematical Model for EIS

- **Existing work to model EIS data almost always assumes linear system behavior and dilute-solution behavior. But not all of the important electrochemical reactions follow these behaviors.**

- **Our goal is to develop a general model and computer code to describe the response of any reaction (chemical or electrochemical) of arbitrary complexity to small periodic potential perturbations.**

- **Model is capable of accounting for behavior at a stationary or rotating disk electrode with varying diffusion layer thicknesses.**

Results for EIS Model: ECE Mechanism

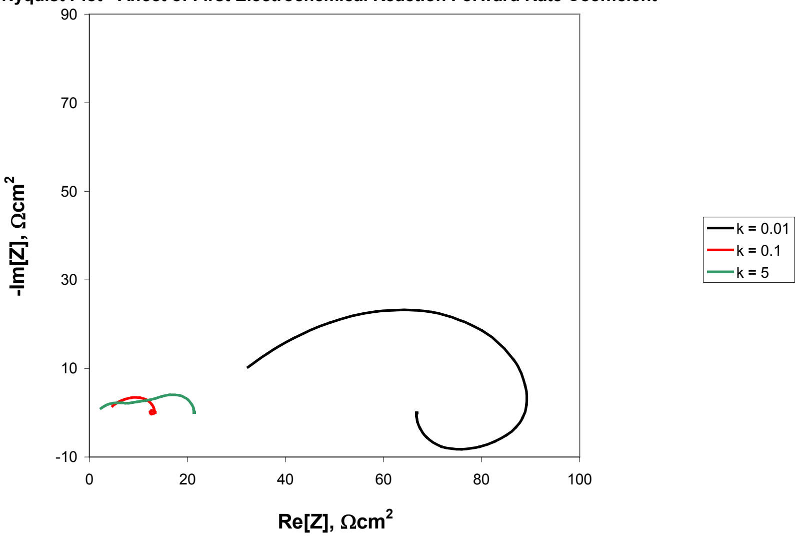
$$O + e^{-} \Leftrightarrow R$$

$$R \Leftrightarrow 2X$$

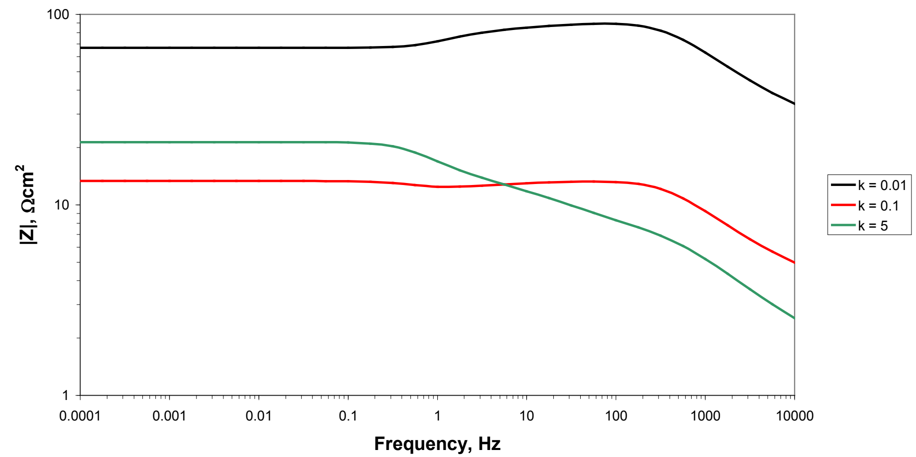
$$X + e^{-} \Leftrightarrow 2Y$$

Forward and reverse reaction rates varied for each step to see how each one affected the data.

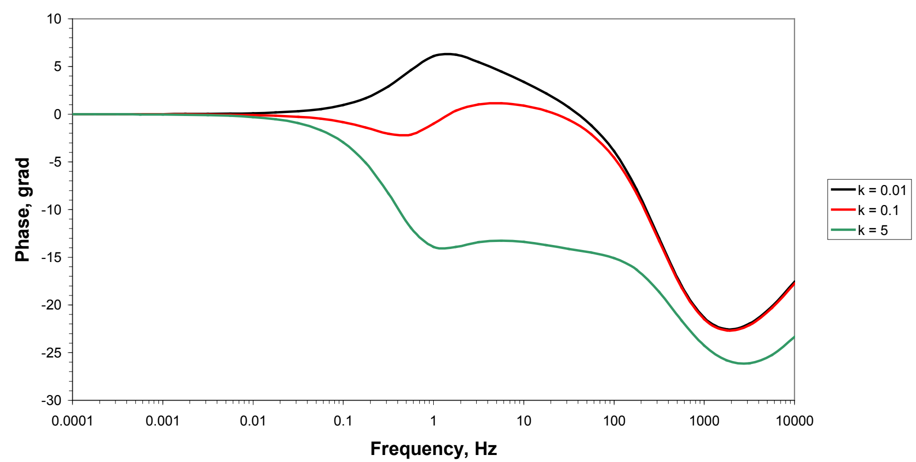
Nyquist Plot - Affect of First Electrochemical Reaction Forward Rate Coefficient



Bode Plot - Affect of First Electrochemical Reaction Forward Rate Coefficient

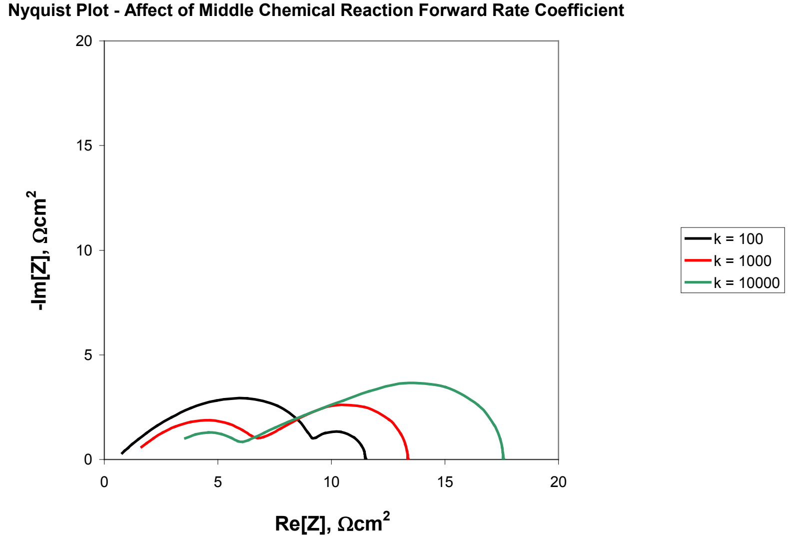


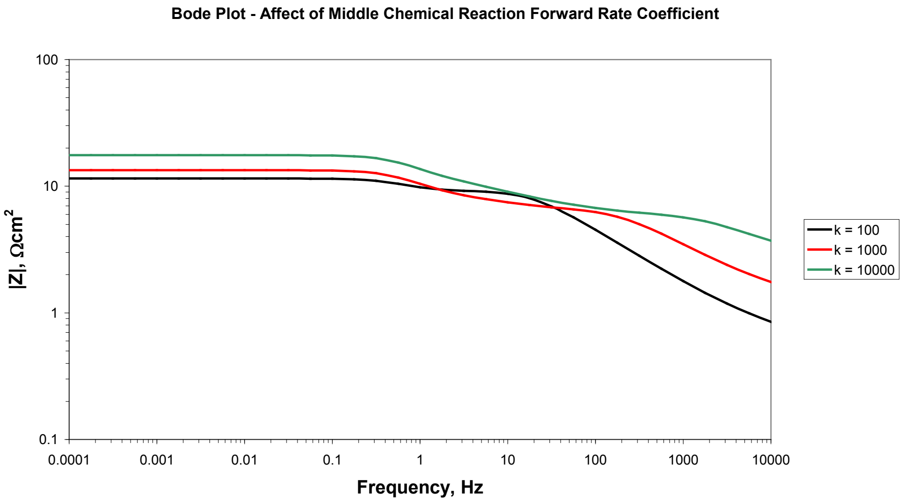
Bode Plot - Affect of First Electrochemical Reaction Forward Rate Coefficient

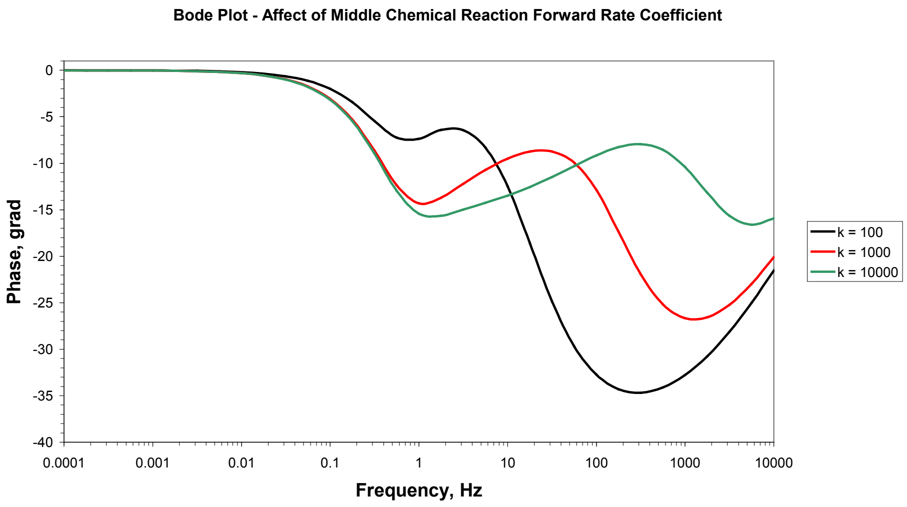


Nyquist and Bode plots for simulated ECE mechanism showing the affect of the first electrochemical reaction's forward rate coefficient.

Results for EIS Model: ECE Mechanism

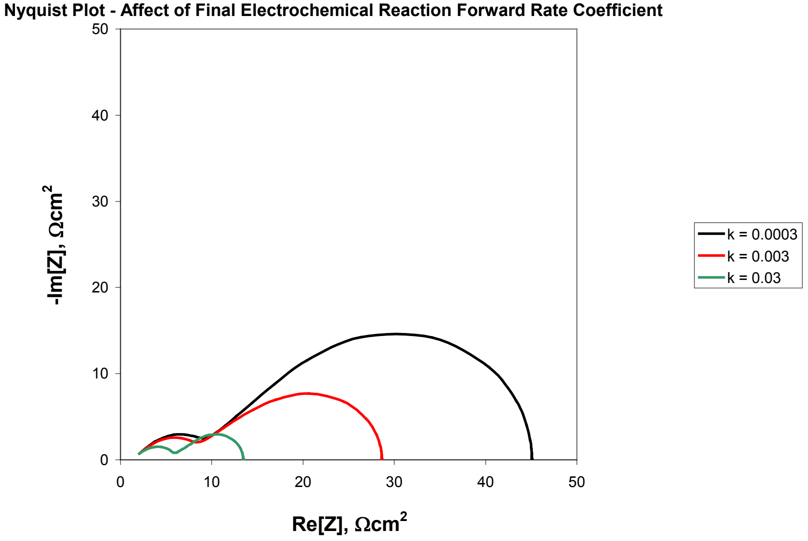


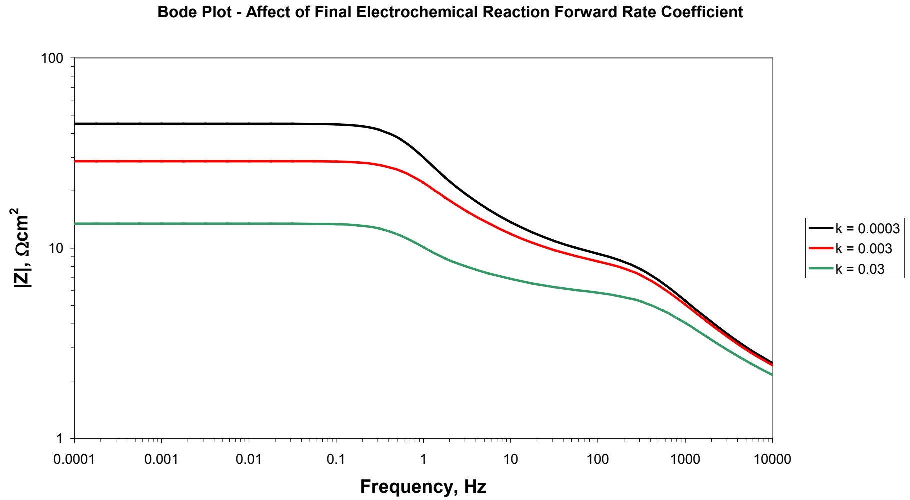


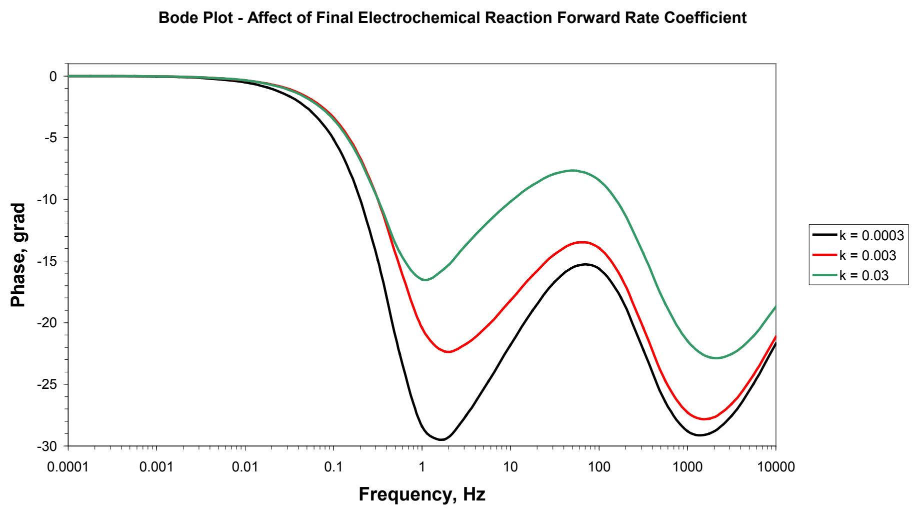


Nyquist and Bode plots for simulated ECE mechanism showing the affect of the middle chemical reaction's forward rate constant.

Results for EIS Model: ECE Mechanism







Nyquist and Bode plots for simulated ECE mechanism showing the affect of the last electrochemical reaction's forward rate constant.

Results for EIS Model: ECE Mechanism

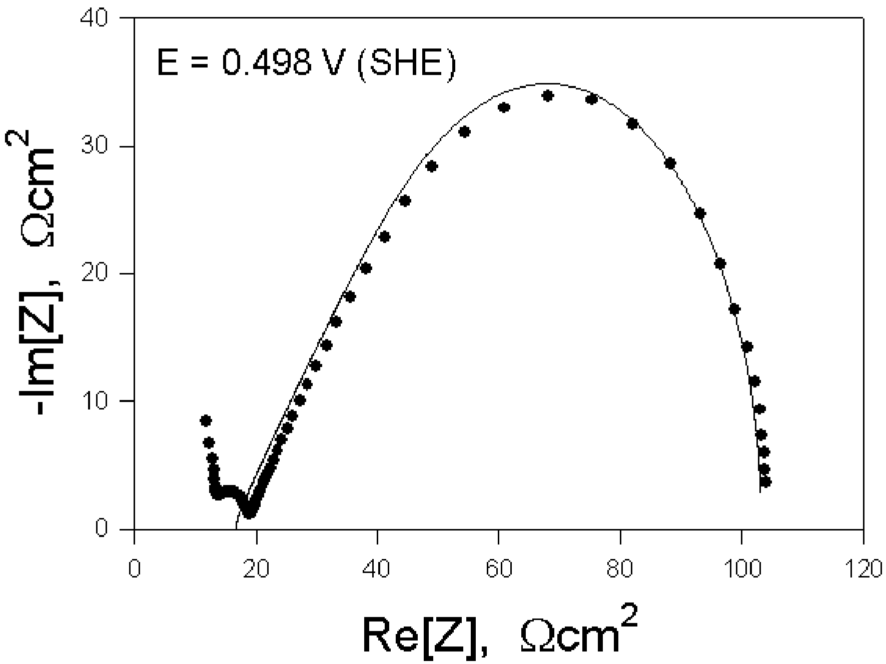
- **Nyquist and Bode plots for the simulated ECE mechanism show a clear influence for various changes in the rate parameters.**

- **The calculation speed is very fast on a common desktop PC – a typical execution of the modeling program takes under 20 seconds to complete a full set of theoretical data, even for more complicated mechanisms.**

- **Unlike other EIS modeling programs that utilize equivalent circuit analysis, our model is strictly generalized to chemical and electrochemical steps.**

Validation of EIS Model: Ferricyanide

- The reduction of the ferricyanide anion has been studied in depth and has been established to be a single-electron electrochemical reaction: $Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$
- Our computer code inputs experimental results and fits theoretical data to it on a best-fit basis.



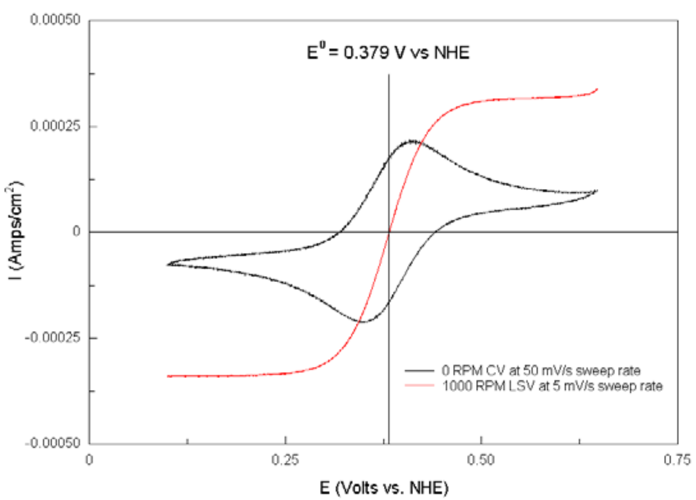
The model fits nicely, except for at high frequencies (data closest to the origin).

We are addressing this currently by modifying the model and code.

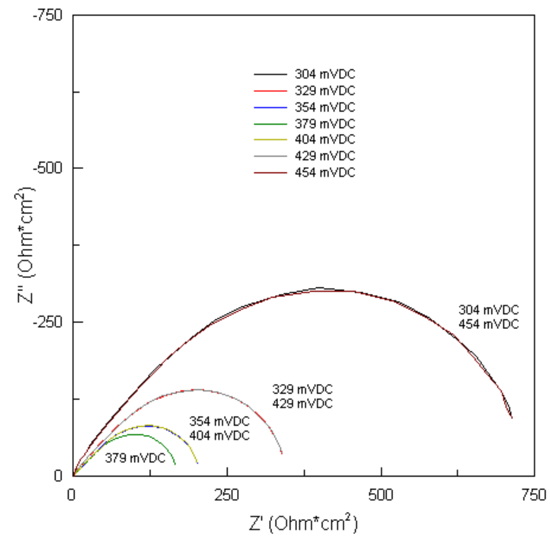
The dots are experimental data and the line is the best-fit theoretical data.

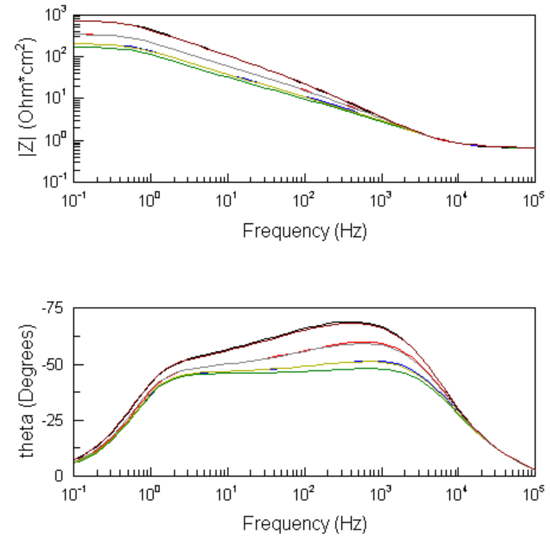
Experimental and Model Results Compared

- **Experimental EIS data for a redox couple (E mechanism):** $$Fe(CN)_6^{-3} + e \Leftrightarrow Fe(CN)_6^{-4}$$



Cyclic voltammogram and RDE linear sweep voltammogram for 1 mM potassium ferricyanide + 1 mM potassium ferrocyanide + 2 M NaOH at a 5 mm diameter platinum working electrode. A platinum wire counter electrode and Hg/HgO reference electrode were used.





Nyquist and Bode plots for 1 mM potassium ferricyanide + 1 mM potassium ferrocyanide + 2 M NaOH at a 5 mm diameter platinum RDE (1000 RPM). The frequency range was 100,000 Hz to 0.1 Hz and the AC potential amplitude was 20 mV.

Fitting Parameters From Experimental Data

Experimentally measured impedance is: $Z = R_e + \frac{Z_c Z_f}{Z_c + Z_f}$

$Z_c = \frac{1}{j\omega C_d}$ **is the resistance of the double layer with the capacitance C_d**

R_e **is the resistance of electrolyte**

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

Fitted parameters: k_O, k_R, β, D_O, D_R, R_e, C_d

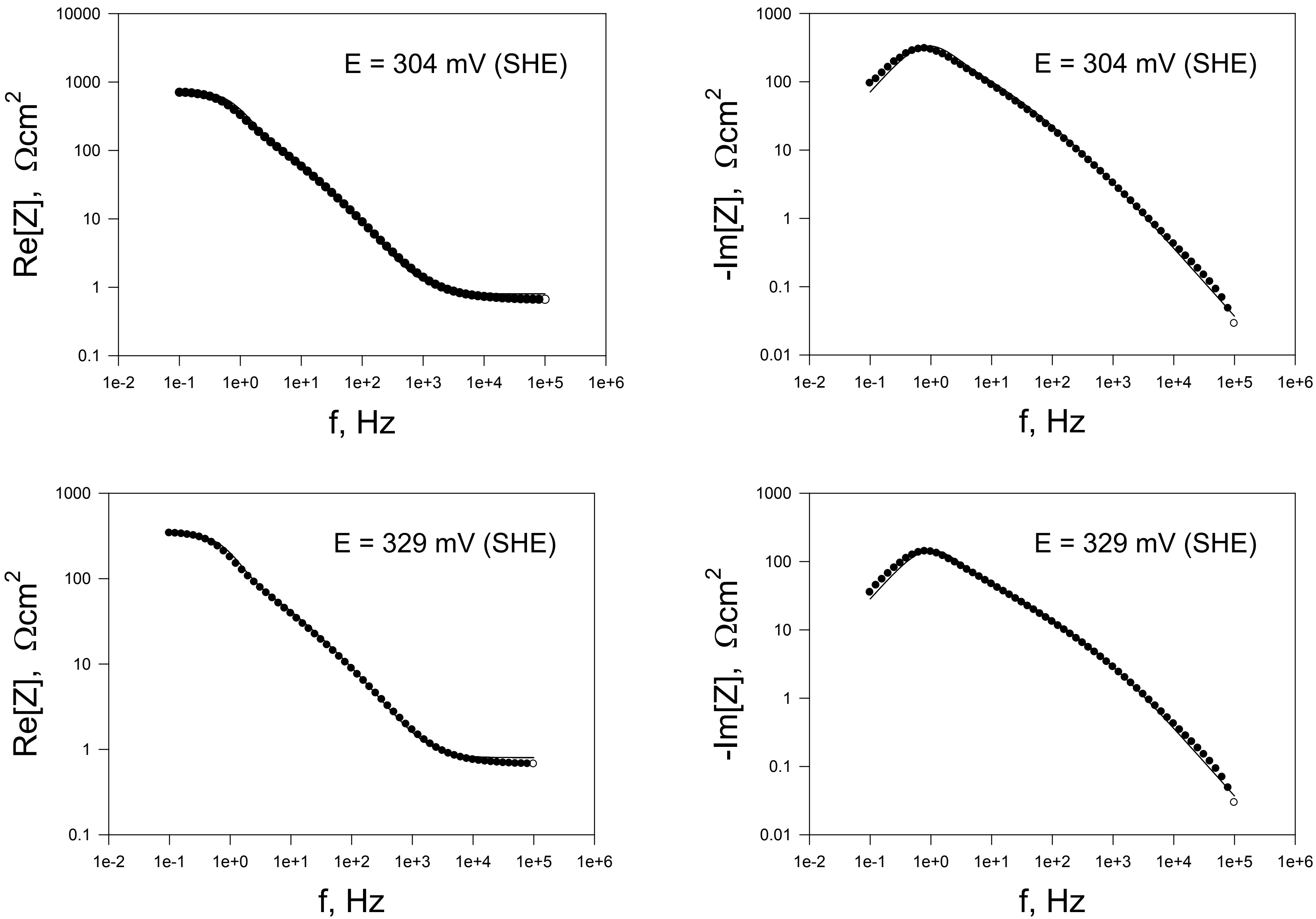
Results of fitting: $k_R/k_O = 3.55e\text{-}7$ [for $E_0 = 0.379$ V (SHE)], $\beta = 0.5$,

$D_O = 4.06e\text{-}5$ cm^2/s, $D_R = 4.66e\text{-}5$ cm^2/s,

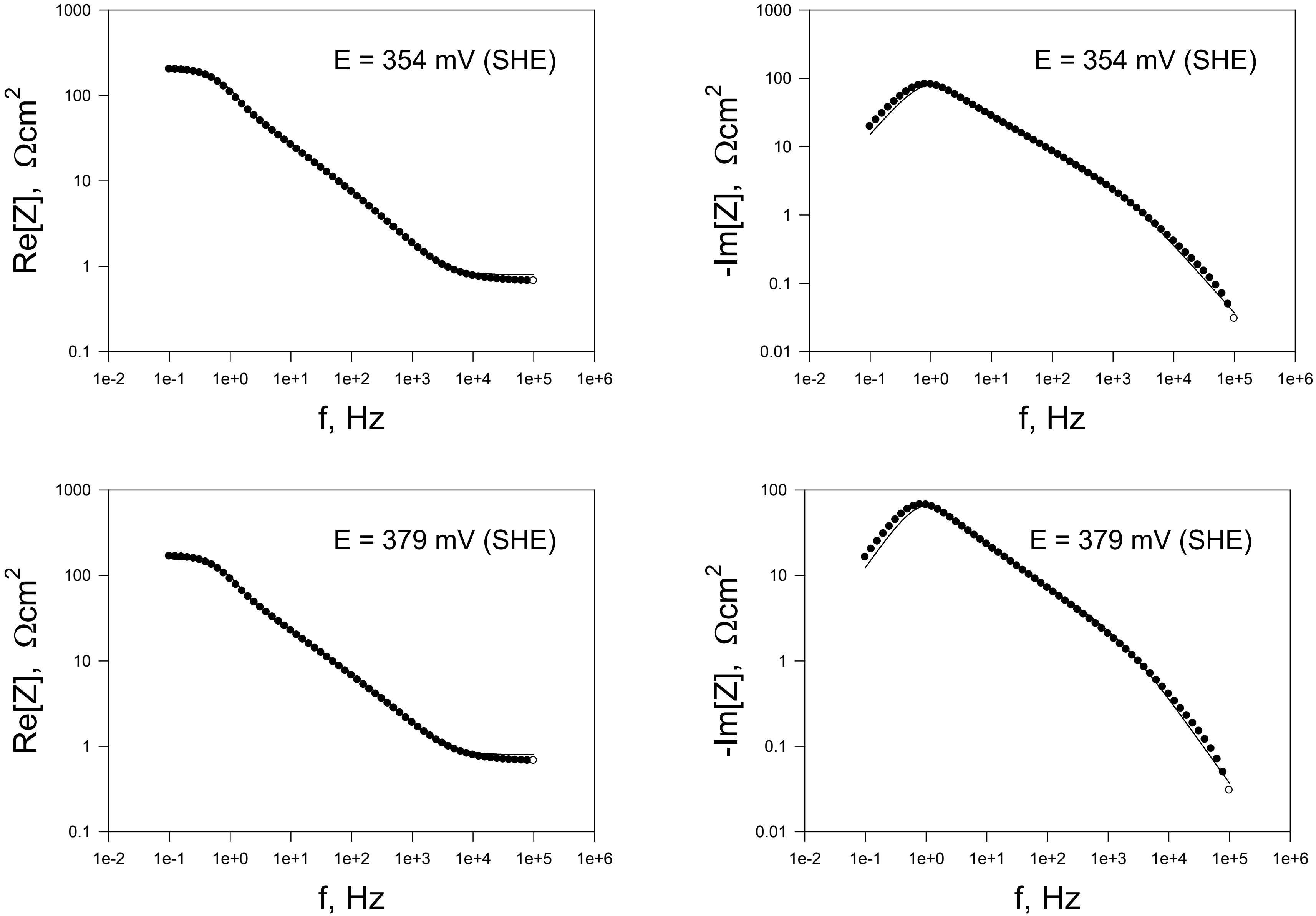
$R_e = 0.8$ Ωcm^2 and $C_d = 43$ μF/cm^2.

Experimental Data: $R_e = 0.76$ Ωcm^2 and $C_d = 46$ μF/cm^2.

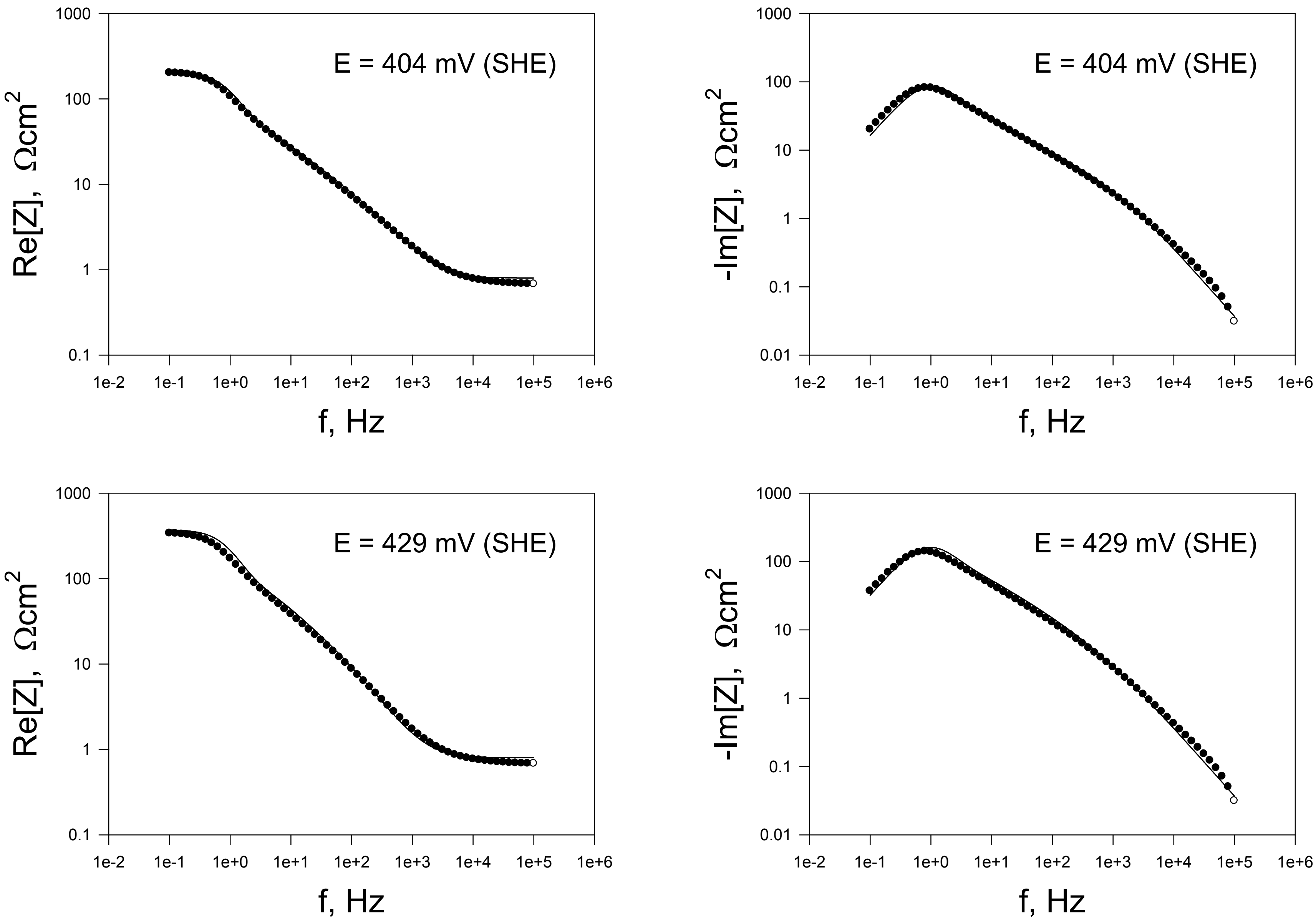
Experimental and Model Results Compared



Experimental and Model Results Compared

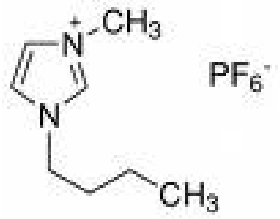


Experimental and Model Results Compared



Direct Electrochemical Hydrogenation

- Indirect hydrogenation has been demonstrated above using a Devanathan cell for hydrogenating easily hydrogenated materials, such as styrene to produce ethyl benzene.
- This technique was found not to work for reducing metaborate to borohydride and it was theorized that the reason was that the activity of H on the surface was too low or that the species that needed to be formed was H^- rather than H.
- We then decided to employ an aprotic solvent and H_2 as a hydrogen source so as to inhibit massive hydrogen evolution at the cathode as the potential was displaced to very negative values.
- The aprotic solvents employed were acetonitrile and an ionic liquid, 1-butyl 3-methyl immidazolium hexafluorophosphate (BMIM-PF_6)



Electrochemical Reduction of CO_2

- **The present investigation involves the electrochemical conversion of CO_2 to methanol via electrochemical hydrogenation in ionic liquid [1-butyl 3-methyl Immidazolium Hexafluorophosphate (BMIM-PF_6)] or in aqueous solutions of the ionic liquid.**
- **Ionic liquids are characterized by a wide electrochemical window of stability, a reasonable ionic conductivity and a very low vapor pressure [2,3]. Carbon dioxide has a high solubility in ionic liquids, which makes the electrochemical hydrogenation of CO_2 more prospective in ionic liquid. Ionic liquids that possess the bis-trifluoromethanesulphonyl-imide anion have a strong affinity for carbon dioxide.**
- **The technique used to monitor the hydrogenation of CO_2 process was cyclic voltammetry; this was carried out with a computerized electrochemical workstation (Gamry Instruments). To analyze the reaction product, Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) spectroscopy has been employed.**
- **Initial experiments were carried out in 0.01M 1-butyl 3-methyl Immidazolium Hexafluorophosphate aqueous solution. A platinum metal plate (99.9% metal basis) was employed as a working electrode. The surface of the electrode was etched by hot concentrated sulfuric acid. The electrode potential of the cathode was measured with respect to Ag/AgCl (sat. KCl) reference electrode. A platinum wire was used as counter electrode. Pure N_2 gas was bubbled into the solution for an hour to remove dissolved oxygen. The electrolysis was carried out in a closed U-cell and the solvent was saturated with CO_2 for 120 minutes. The cell was usually operated at room temperature under H_2 atmosphere.**

Electrochemical Reduction of CO_2 (cont)

- **The cyclic voltammetry responses for platinum plate in CO_2 saturated ionic liquid solution are shown in Figure 1, Curve (a), and N_2 saturated solution are shown in Figure 4, Curve (b). The cyclic voltammetric response in CO_2 saturated solution is featureless over the potential region between 0.5 V to -0.3 V. In Curve (b), the reduction current starts at more positive potential (-0.1 V) compared to Curve (a) and the current gradually increases as the potential goes to more negative values. It has been assumed that this reduction response is due either to CO_2 reduction or hydrogen evolution reaction.**
- **Similar observations were reported by Y. Tomita and Y. Hori in earlier work [4]. They noted that the reducing current in CO_2 saturated solution starts at more positive potential than in argon saturated solution. In their work they used argon instead of nitrogen gas to deaerate the cell.**
- **Cyclic voltammetry was used as an *in situ* probe for determining CO_2 reduction, because it is relatively inexpensive and is an easily implemented method. Infrared spectroscopy has also been used to analyze for the presence of reaction product in the solvent. Figure 2 shows the FTIR-ATR spectra for ionic liquid solvents for both prior and post experimental conditions. It has been shown that both the Pre-(red) and Post-(blue) samples appeared similar to that which would be expected for water. The possible reasons for this Infrared spectrum result are either (1) no methanol was produced or (2) due to the low concentration of the ionic liquid the product concentration was below the detection limit.**

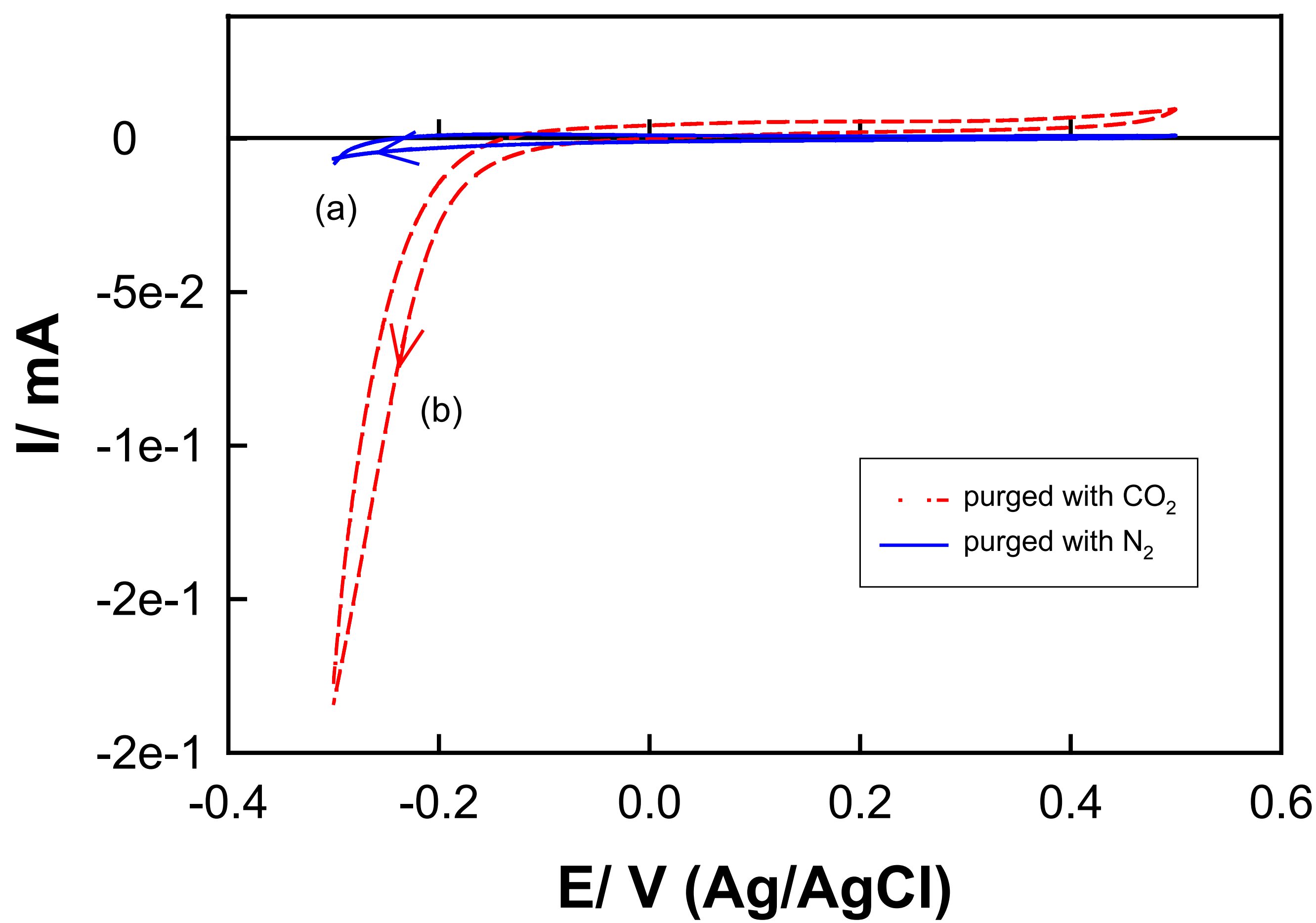


Figure 1: Cyclic voltammetry responses for Pt electrode (0.50 to -0.30 V, 10 mV s^{-1}) in ionic liquid aqueous solution at room temperature; (a) solvent saturated with nitrogen and (b) saturated with CO_2.

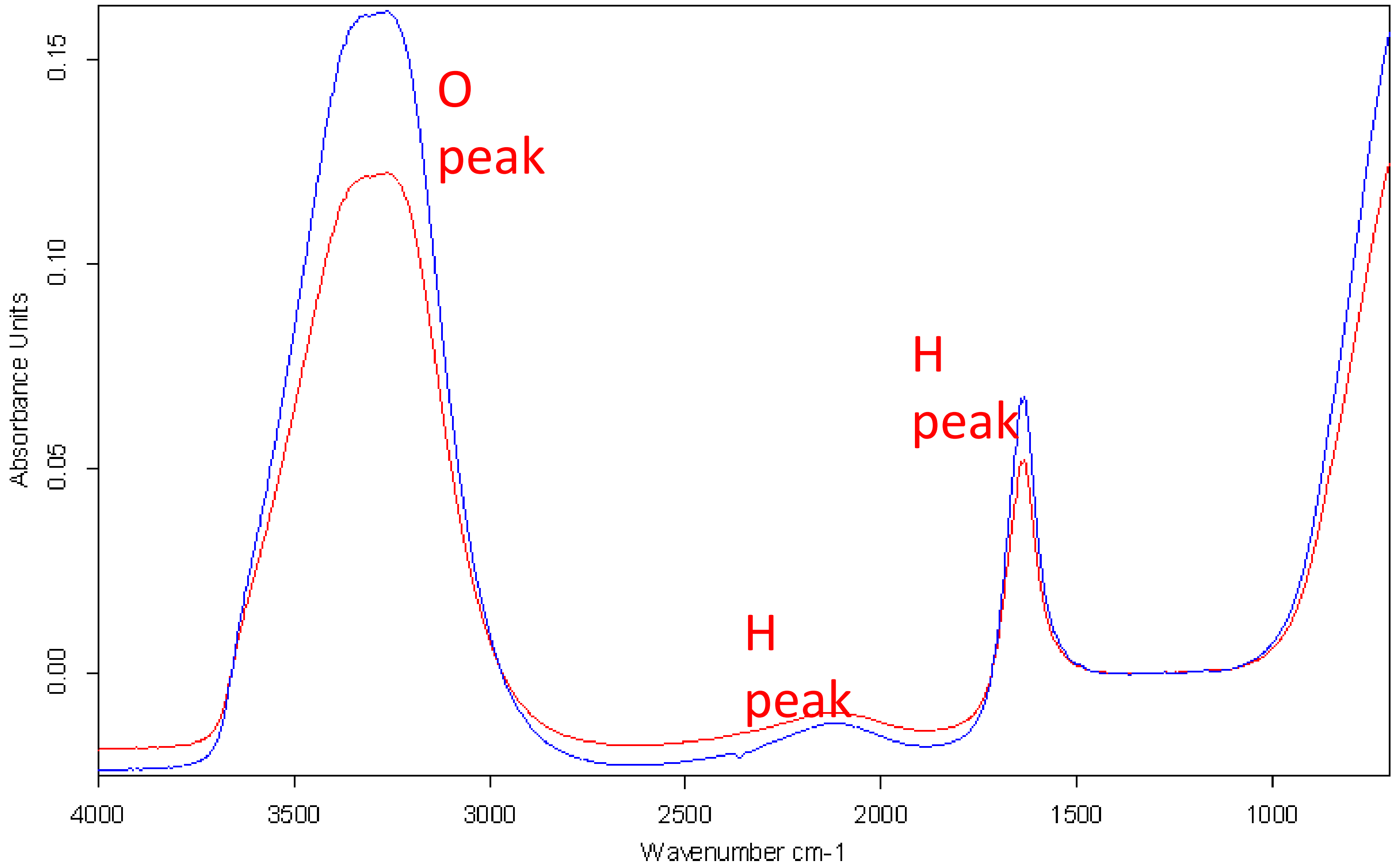


Figure 2: Fourier Transform Infrared - Attenuated Total Reflectance spectra for ionic liquid aqueous solution. Red line for prior-experiment and blue line for post-experiment.

Hydrogenation of CO_2 to methanol in pure ionic liquid (1butyl-3methyl-immidazolium-hexafluorophosphate)

- **The technique used to monitor the hydrogenation of CO_2 process was potentiostatic polarization; this was carried out with a computerized electrochemical workstation (EG&G Instrument). To analyze the reaction product, Gas Chromatography (LECO TrueToF HT, HP Agilent Technologies 7890A GC system) has been employed. Experiments were carried out in non-aqueous ionic liquid (1-butyl 3-methyl immidazolium hexafluorophosphate). A copper mesh (99.9% metal basis) was employed as a working electrode. The surface of the electrode was etched by nitric acid. The electrode potential of the cathode was measured with respect to a Ag/AgCl (sat. KCl) reference electrode. A copper mesh was also used as counter electrode. Pure N_2 gas was bubbled into the solution for an hour to remove dissolved oxygen. The electrolysis was carried out in a closed cell and the solvent was saturated with CO_2 for 120 minutes. The electrode was held at -0.2 V (Ag/AgCl) for 3 hrs, shown in Fig. 1. The cell was usually operated at room temperature under H_2 atmosphere.**
- **During the running of an experiment, the gaseous product was transferred through Teflon® tubing to a closed vial of Ethylene glycol diethyl ether (EGDE, 98%) solvent. Methyl alcohol is soluble in EGDE. This EGDE containing vial was held in an ice bath to control the temperature. Later both methanol saturated EGDE and blank EGDE were manually injected to GC to analyze the reaction products. The GC analyses were performed on a 30-m × 0.25-mm i.d. capillary column coated with 95% methyl/ 5% phenol silicon.**

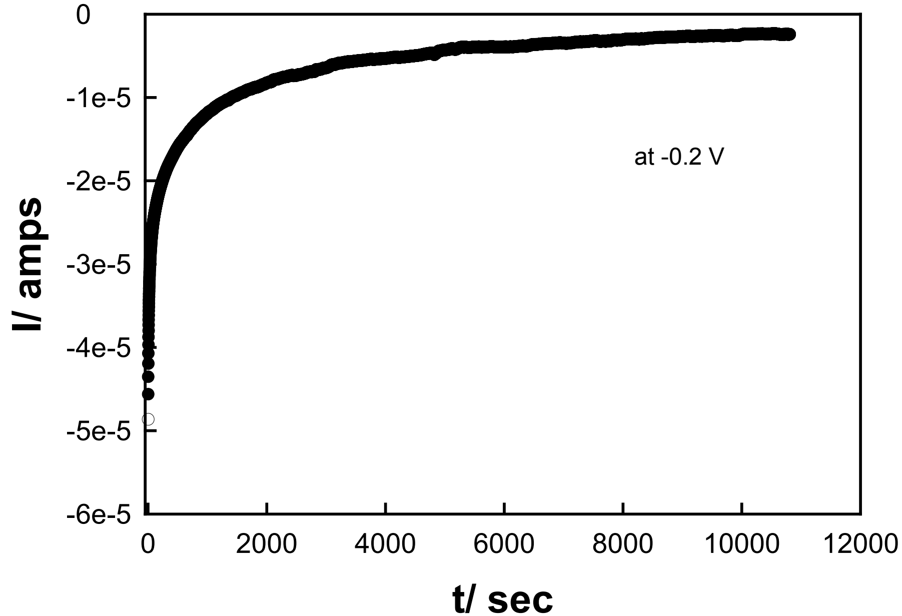
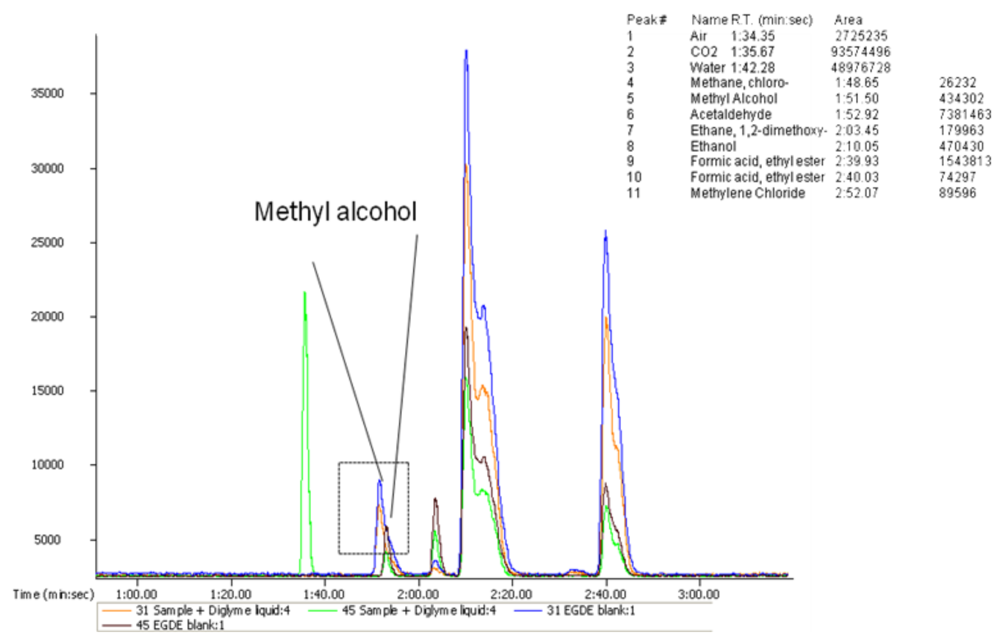


Fig.1: i-t diagram for Cu mesh in ionic liquid at -0.2V (Ag/AgCl), at room temperature condion.



Peak#	Name	R.T. (min:sec)	Area
1	Air	1:34.35	2725235
2	CO2	1:35.67	93574496
3	Water	1:42.28	48976728
4	Methane, chloro-	1:48.65	26232
5	Methyl Alcohol	1:51.50	434302
6	Acetaldehyde	1:52.92	7381463
7	Ethane, 1,2-dimethoxy-	2:03.45	179963
8	Ethanol	2:10.05	470430
9	Formic acid, ethyl ester	2:39.93	1543813
10	Formic acid, ethyl ester	2:40.03	74297
11	Methylene Chloride	2:52.07	89596

Fig. 2: GC/MS results of collected sample and EFDE.

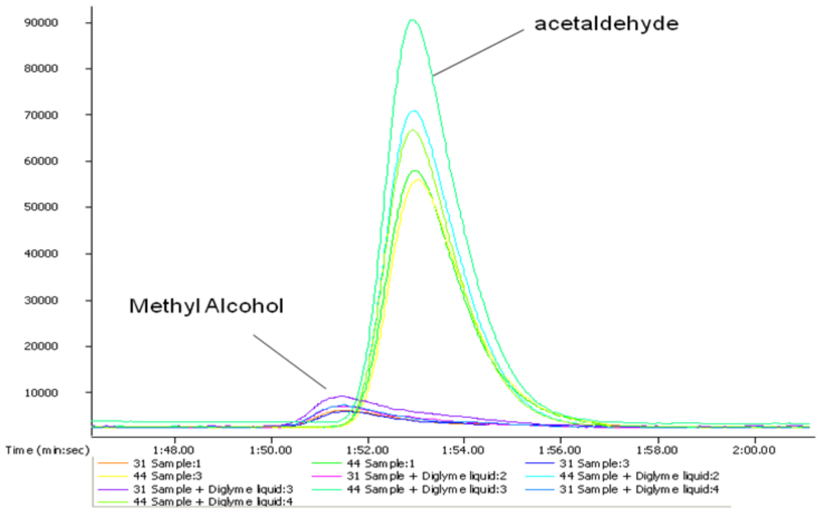


Fig. 3: GC/MS results of collected sample and EFDE. Explore the marked area (dotted line) shown in Fig.1.

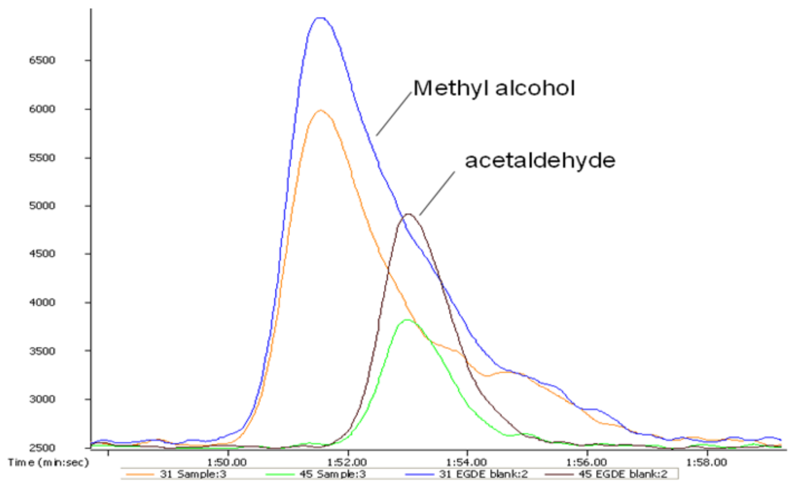


Fig. 4: GC/MS results of collected sample and EFDE. Blow-up the mass number 31 and 45 shown in Fig.2.

Results show that CO_2 can be hydrogenated electrochemically in aqueous solutions of ionic liquids using H_2 as the hydrogen source. The next challenge is to push the hydrogenation all the way to methanol, which is a useful liquid fuel.

Hydrogenation of CO_2 to methanol in pure ionic liquid

- **It is noted from Fig. 2 and Fig. 3 that the peak areas for both methyl alcohol and acetaldehyde are higher for EGDE. Upon the addition of the sample to EGDE the areas decrease by a noticeable amount. Since the peak areas for methyl alcohol and acetaldehyde are lower in the bubbled sample than the solvent blank, it appears that the MeOH and CH_3CHO etc are being stripped from the solvent while being transferred to a closed vial of EGDE. Accordingly, this analysis is ill-defined whether the reaction product was methanol or not. To overcome this interference a new setup has been developed to pursue online-GC. As on-line gas chromatography-mass spectrometry uses for process monitoring using solvent-free sample preparation. However, the Post Doc performing these experiments left the group to take up employment elsewhere and the work remains unfinished.**

References:

1. **M. Buzzeo, R. Evans and G. Compton. *Chem. Phys. Chem.*, 5 (2004) 1106-1120.**
2. **C. Angell, N. Byrne and J. Belieres. *Acc. Chem. Res.*, 40 (2007) 1228-1236.**
3. **Y. Tomita and Y. Hori. In "*Advances in Chemical Conversions for Mitigating Carbon Dioxide: Studies in Surface Science and Catalysis*," edited by T. Inui, M. Anpo, K. Izui, S. Yanagida, and T. Yamaguchi, Vol. 114, pp 581.**
4. **J. Shi, Y. Hu and Y. Hua. *Faming Zhuanli Shenqing Gongkai Shuomingshu*, CN 101328590 A, 2008.**

•

Summary of Important Accomplishments

- Developed a quantitative electrochemical method for BH_4^- analysis in aqueous solution.
- Demonstrated that significant transformation of metaborate to borohydride cannot be affected by electrochemical means as reported in the literature.
- Unable to reproduce any of the patent claims in the literature for significant electrochemical regeneration of borohydride from metaborate.
- However, we did demonstrate electrochemical reduction of B-O to B-H, although at very low concentrations.
- Unable to identify any processes in the polyboranes that might serve as the basis for a reversible electrochemical hydrogen storage technology.
- Discovered BH_4^- catalytic hydrolysis on several metal surfaces.
- Demonstrated multiple redox transitions in ammonia boranes and organotin hydrides.
- Developed a computer algorithm for mechanistic analysis of electrochemical processes using EIS data.
- Demonstrated the indirect electrochemical hydrogenation of styrene using a Devanathan-Stachurski cell.
- Preliminarily demonstrated the direct electrochemical hydrogenation of carbon dioxide in an aqueous solution of an ionic liquid using H_2 as the hydrogen source.

Collaborations

- **PNNL and LANL – Technical guidance specific to ammonia borane and organotin hydride work.**
- **LANL – synthesis of ammonia borane spent fuel.**
- **University of Alabama - valuable advice on the thermodynamics of various reaction schemes for ammonia borane and organotin hydride work.**
- **Rohm and Haas for providing technical support and guidance through internal and external collaboration.**

Suggested Future Work: R_3SnH Regeneration

- Optimize analytical techniques to characterize the products formed during electrolysis (IR, NMR or GC/HPLC).

- Understand the electrochemical activity shown in the CVs.

- Explore the possibility of using different hydrogen sources such as: H_2, PhOH, HCl,etc.

- Develop better reference electrodes for non-aqueous environments in order to run electrochemical experiments.

Suggested Future Work: Ammonia Boranes

- **Key milestones addressed:**
  - **Demonstration of electrochemical transformations in ammonia borane.**
- **Key milestones remaining:**
  - **Demonstration of practically useful oxidation state change (awaiting spent fuel to arrive).**
  - **Demonstration of reversible H_2 storage.**

Suggested Future Work: EIS Modeling

- **Complete model validation on ferricyanide reduction to be sure the model is working properly.**
- **Extend the validation to a more complex, but known, reaction – e.g., the ECE reduction of ortho-bromonitrobenzene.**
- **Once our model has been validated, it should be used to extract kinetic parameters for organotin hydride and ammonia borane dehydrogenation.**
  - **Once the kinetic parameters are known for the dehydrogenation, they should be optimized for efficient hydrogenation schemes.**

Milestones and Current Status

Task Number	Project Milestones	Task Completion Date Originally Planned	Revised Planned	Actual	Percent Complete	Progress Notes
1	Preliminary demonstration of electrochemical transformations in the B/O and B/H systems, in particular B-O to B-H.	4/06		3/08	100	Completed.
2	Demonstration of practically useful oxidation state changes (go/no go decision).	4/08			100	No practically useful oxidation state changes could be found.
3	Definition of reaction kinetics and mechanisms.	4/09			100	Completed.
4	Demonstration of reversible hydrogen storage.	4/09			100	No suitable electrochemical couple could be found in the B/H system.
5	Specification of optimal system.	4/09			100	See Task 4.
6	Task completion.	4/09	6/10	6/10		96%