Electrochemical Hydrogen Storage Systems

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Overview

Timeline

- Project start date: 3/1/05
- Project end date: 2/28/10
- Percent complete: 70%

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
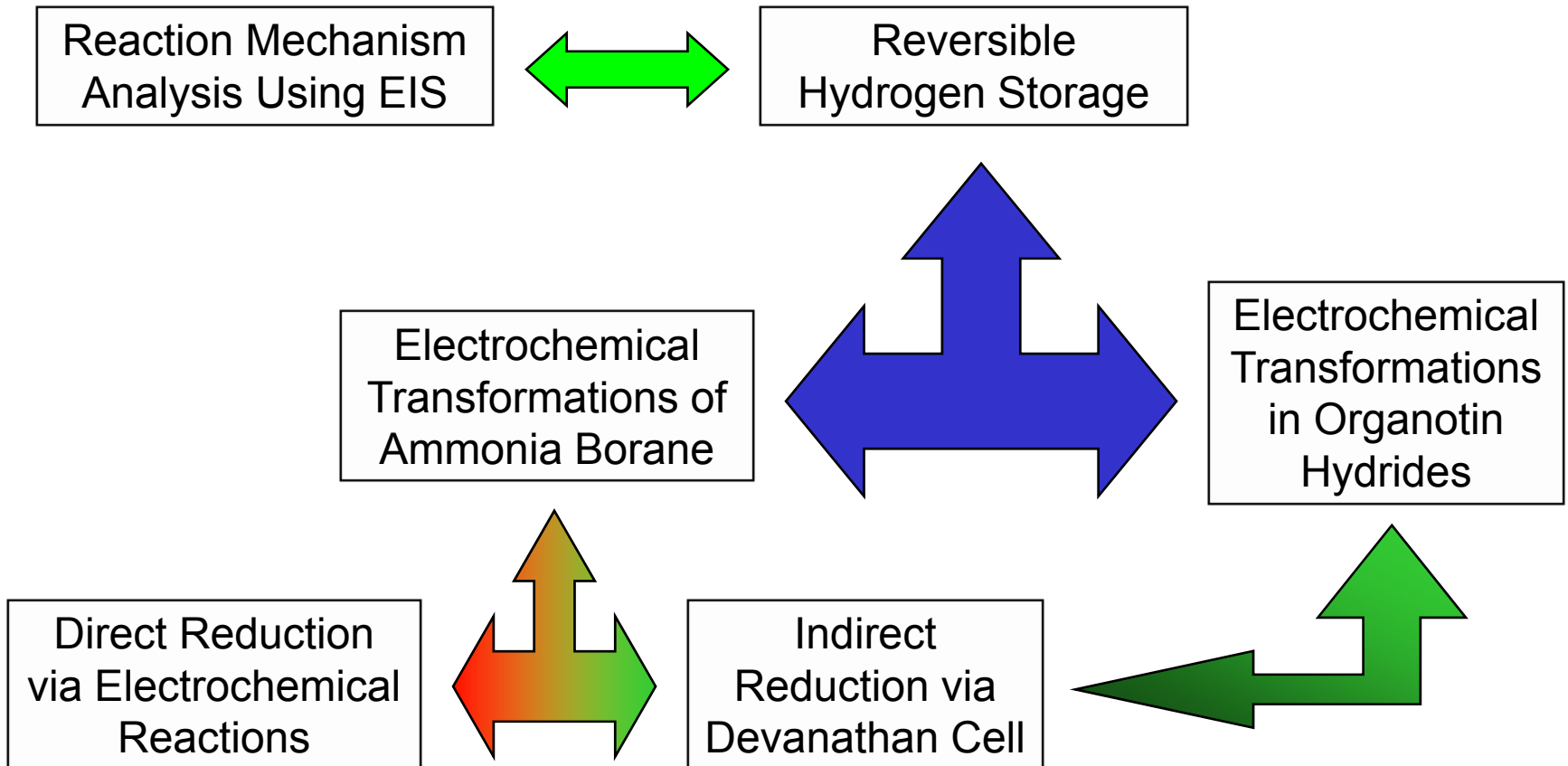- Funding for FY09: $280,000

Partners

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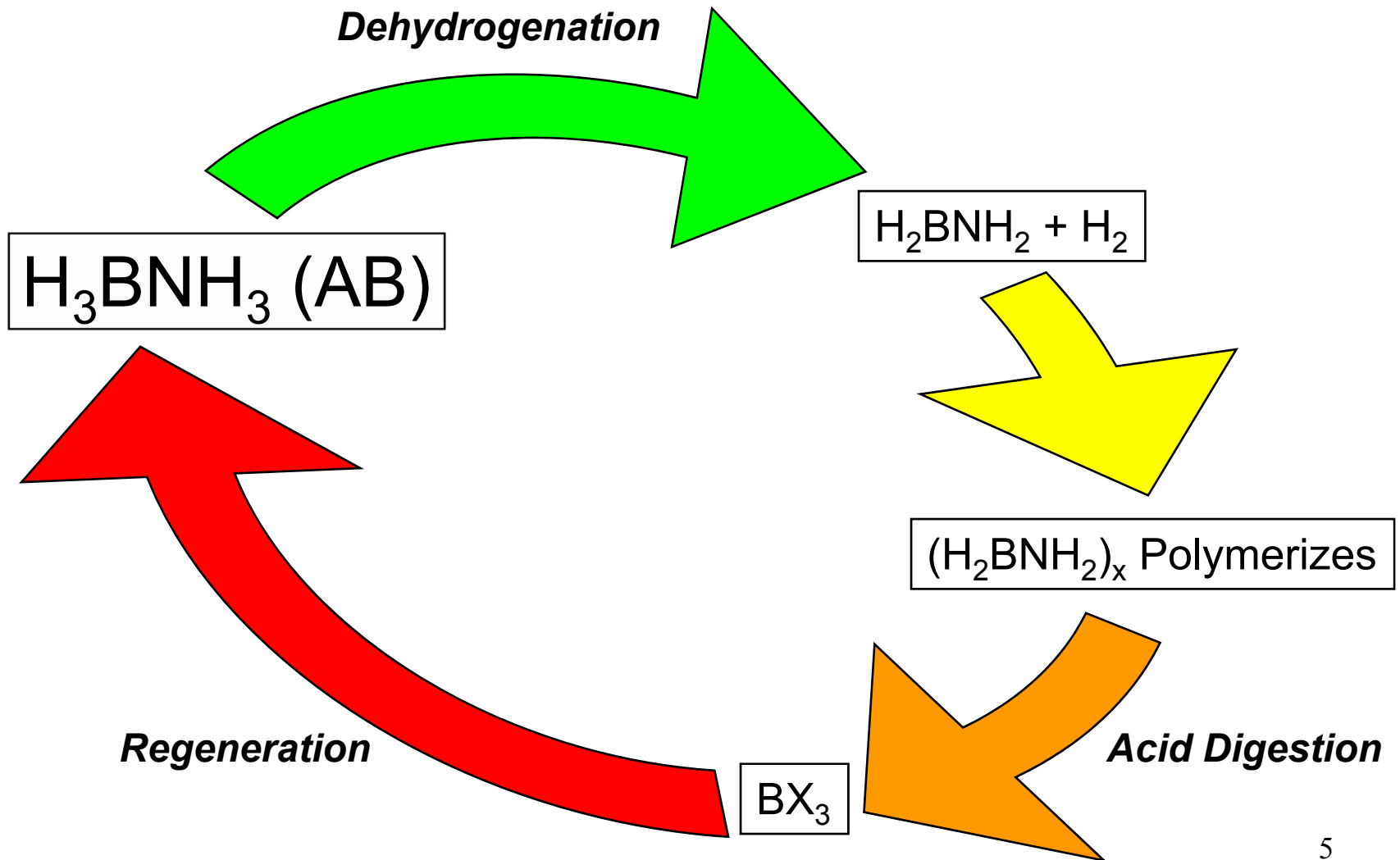- University of Missouri

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.
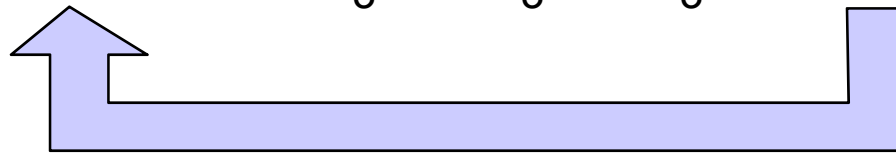
Technical Approach

Reaction Mechanism Analysis Using EIS
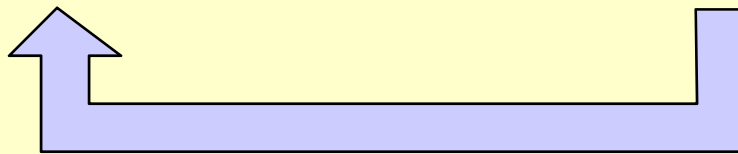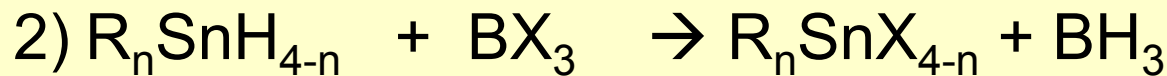
Reversible Hydrogen Storage

Electrochemical Transformations of Ammonia Borane

Electrochemical Transformations in Organotin Hydrides

Direct Reduction via Electrochemical Reactions

Indirect Reduction via Devanathan Cell

Ammonia Borane (AB) Lifecycle

Dehydrogenation

H_3BNH_3 (AB)

$H_2BNH_2 + H_2$

$(H_2BNH_2)_x$ Polymerizes

Regeneration

BX_3

Acid Digestion

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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) $R_nSnH_{4-n} + BX_3 \rightarrow R_nSnX_{4-n} + BH_3$
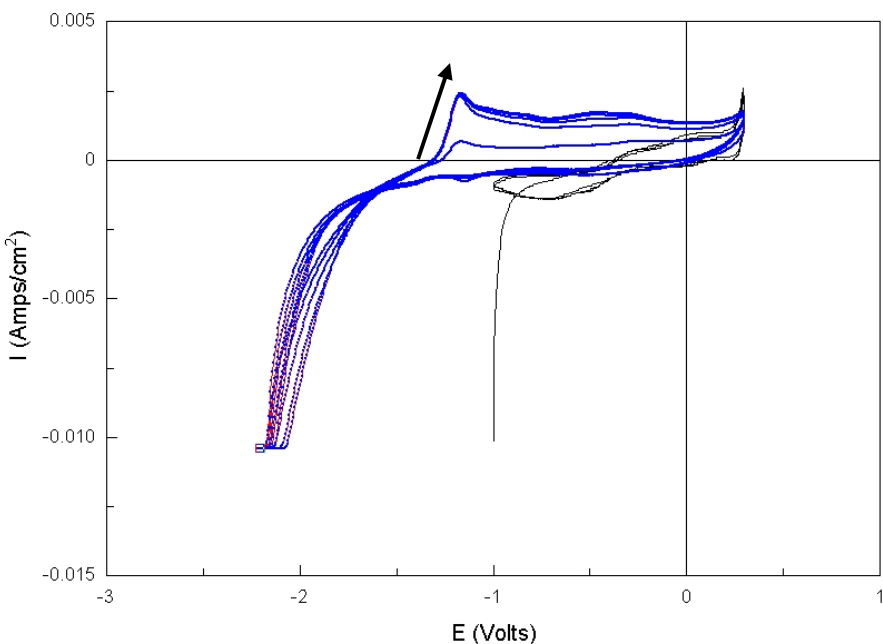
R_nSnH_{4-n} regeneration
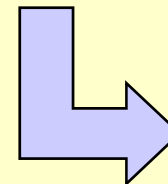
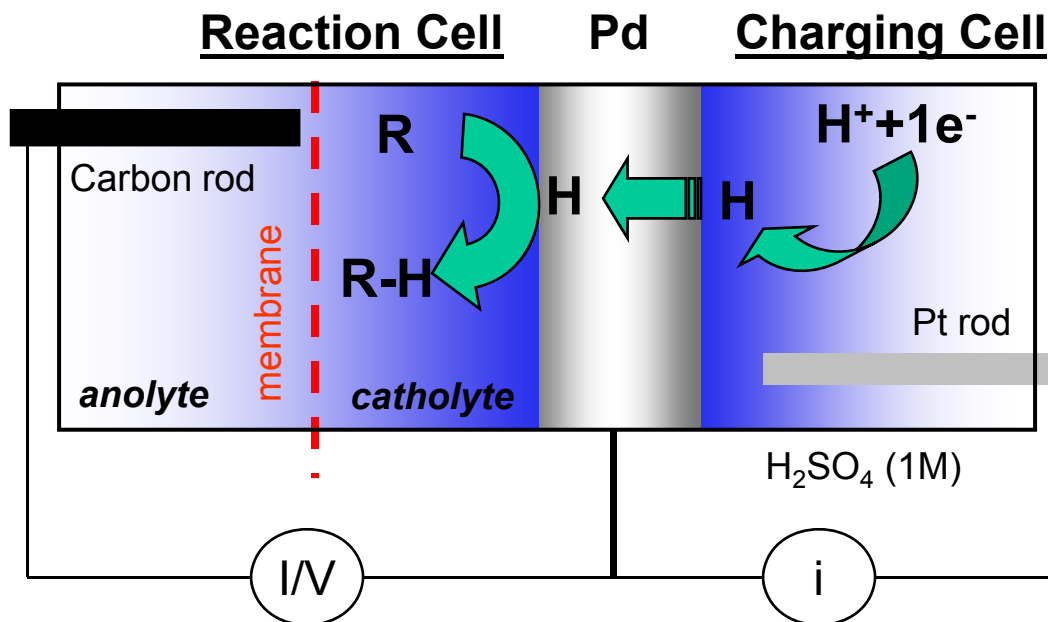H_3BNH_3

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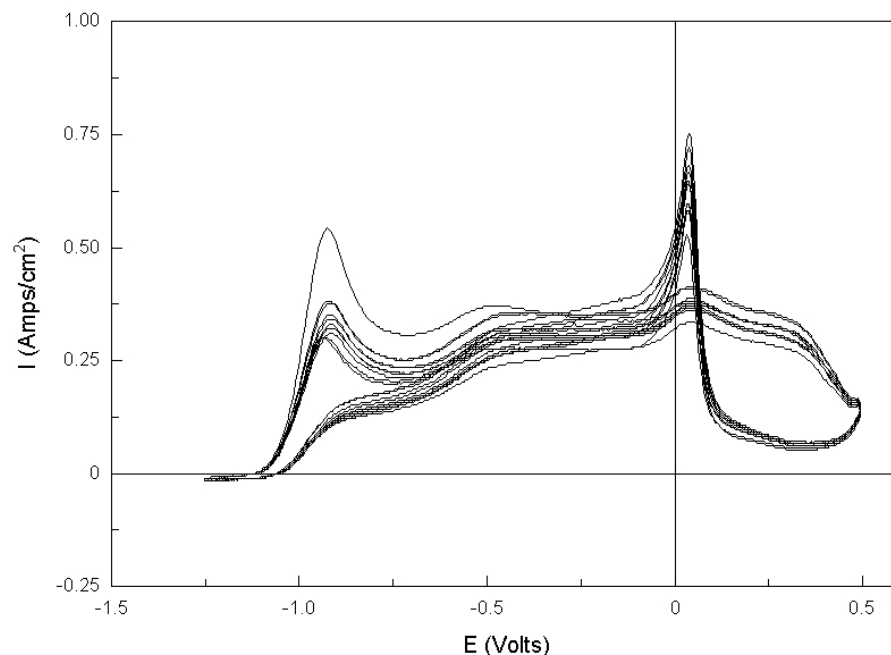
CV of 10 mM ammonia borane (AB) in 2 M NaOH. WE = 5 mm Au disk, CE = Pt mesh, RE = SCE. Scan rate = 50 mV/s.

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.

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Devanathan-Stachurski Cell

Reaction Cell | **Pd** | **Charging Cell**

Carbon rod

membrane

R

$R\text{-}H$

H ← H

$H^+ + 1e^-$

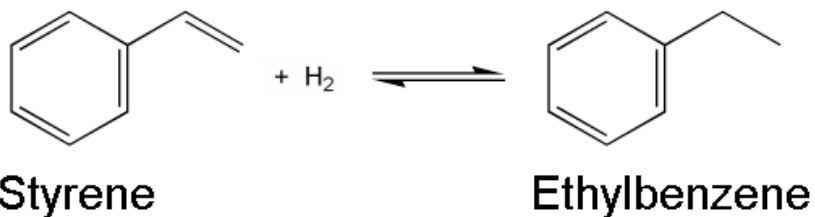Pt rod

anolite | *catholyte*

H_2SO_4 (1M)

I/V

i

➢ 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.

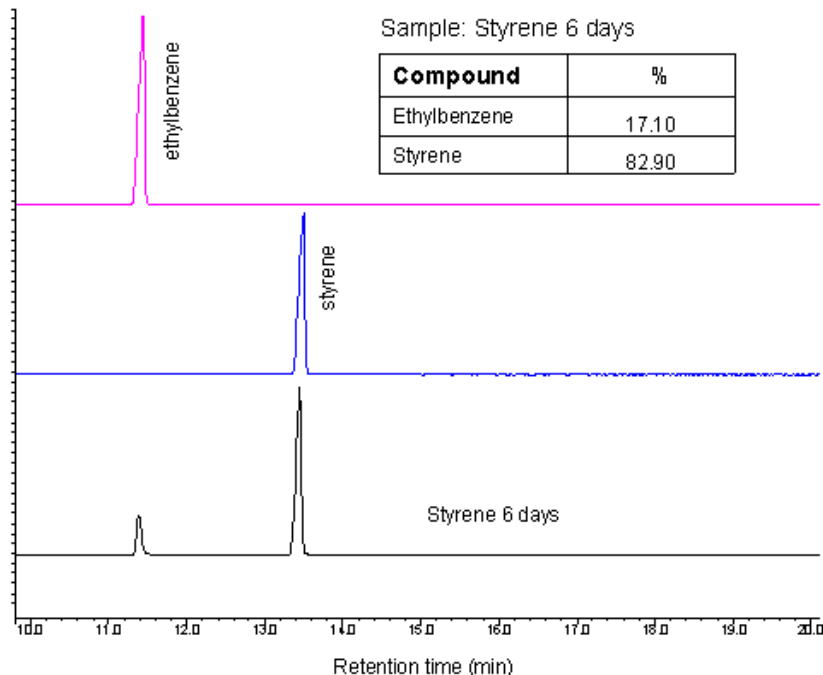➢ The use of the Devanathan cell will be explored to:

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).

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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   + H_2 ⇌   Ethylbenzene

Sample: Styrene 6 days

| Compound	%
Ethylbenzene	17.10
Styrene	82.90

Retention time (min)

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%.

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

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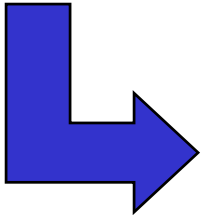
Both hydride-forming materials may be employed as intermediates in hydrogenating other species in regeneration schemes.

➢ 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 will examine hydride transfer reagents:

$$BX_3 \ + \ 3 \cdot MH \ + \ NH_3 \rightarrow H_3BNH_3 \ + \ 3 \ MX$$
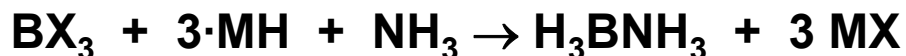
The current thinking is the use of tin hydrides (reactions not balanced):

$$R_nSnH_{4-n} \ + \ BX_3 \ \rightarrow \ BH_3 \ + \ R_nSnX_{4-n}$$
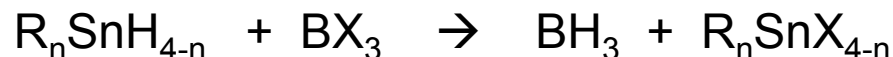
X is probably sulfide R-S

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!)

$$R_nSn(CO_2H)_{4-n} \ \rightarrow \ R_nSnH_{4-n} \ + CO_2$$
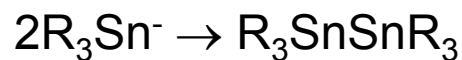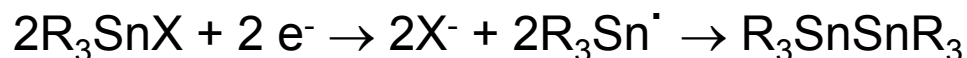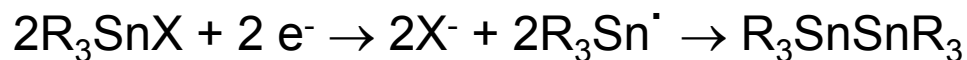
These hydride transfer reagents can facilitate the conversion of electrode-based hydrides to active solution-based hydride transfer reagents.
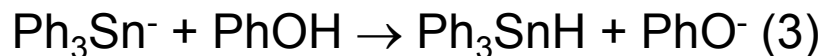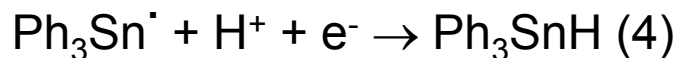
R₃SnH Regeneration

➤ Polarographic studies in protic solvents (MeOH/LiClO$_4$) (1,2)

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

$$\downarrow\ 2e^-$$

$$2R_3Sn^- \rightarrow R_3SnSnR_3$$

➤ Polarographic studies in acetonitrile (3)

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

$$\downarrow\ 2e^-$$

$$2R_3Sn^-$$

➤ Reactions to consider

$$Ph_3Sn^{\bullet} + H^+ + e^- \rightarrow Ph_3SnH \quad (4)$$

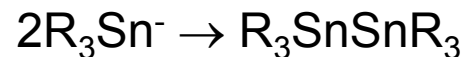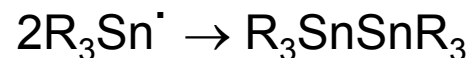$$Ph_3Sn^- + PhOH \rightarrow Ph_3SnH + PhO^- \quad (3)$$

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.
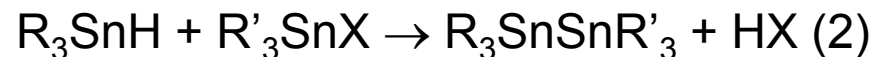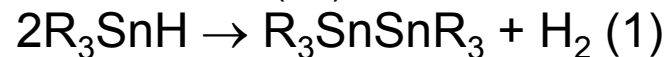
R$_3$SnH Regeneration

➢ Possible side/competing reactions

1. Formation of distannates

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

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

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

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

2. Oligostannanes formation

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

3. Moisture sensitive

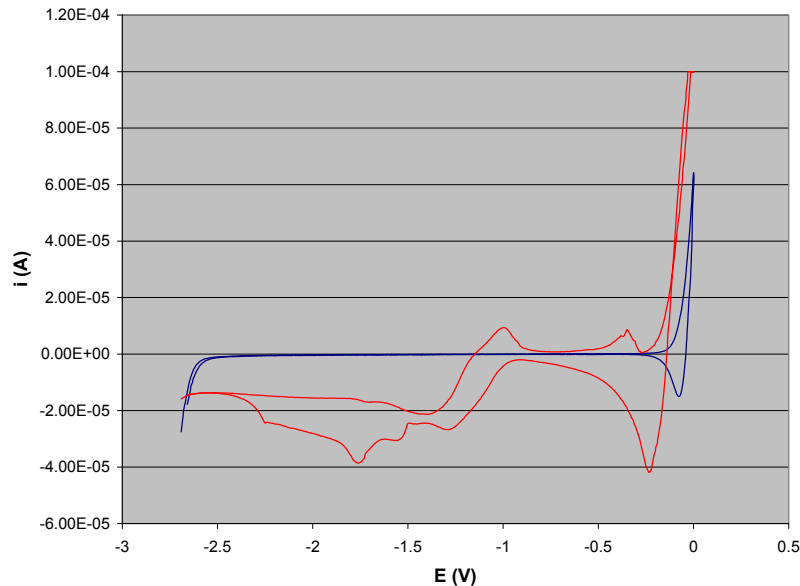$$R_3SnX + H_2O \rightarrow R_3SnOH \rightarrow R_3SnOSnR_3$$

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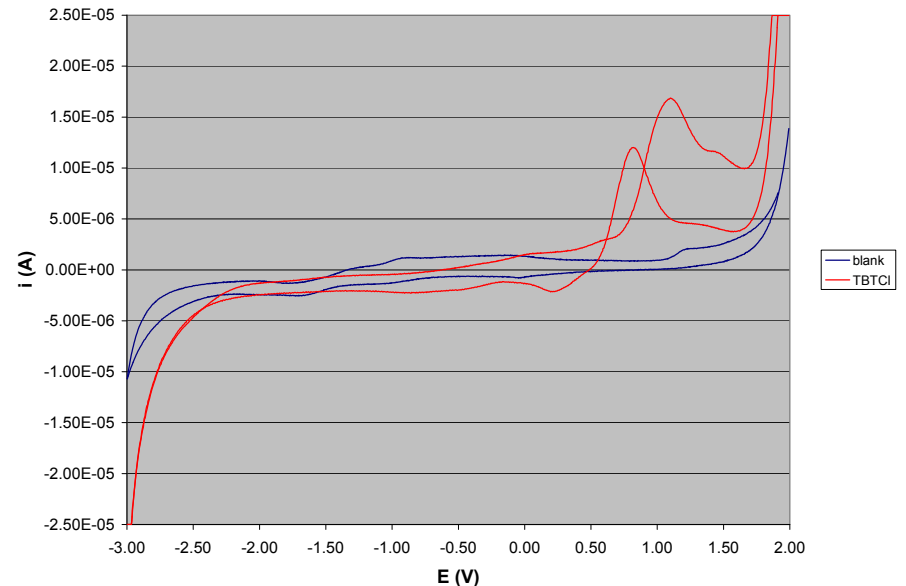2. A. Davies. *Organotin Chemistry*, 2nd ed, 2004, Wiley-VCH
3. A. Savall, G. Lacoste and P. Mazerolles. *Journal of Applied Electrochemistry*, 11 (1981) 61-68.

R₃SnH 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: Pd (1mm disk)

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R₃SnH Regeneration

$$R_3SnH \text{ Regeneration}$$

➤ 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
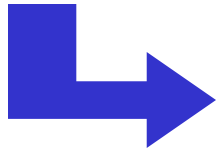
3. Sparging the anode with 10%H_2 ➡ White solid ➡ $(R_2Sn)_x$ (?)

b) Cathode: Cu/Hg flag

Sparging the anode with 10%H_2 ➡ Yellow oil (?) ⟶ to identify [15]

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.

to 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 any reactions (chemical or electrochemical) of arbitrary complexity on small periodic potential perturbations.

➢ Model is capable of stationary or rotating disk behavior with varying diffusion layer thicknesses.
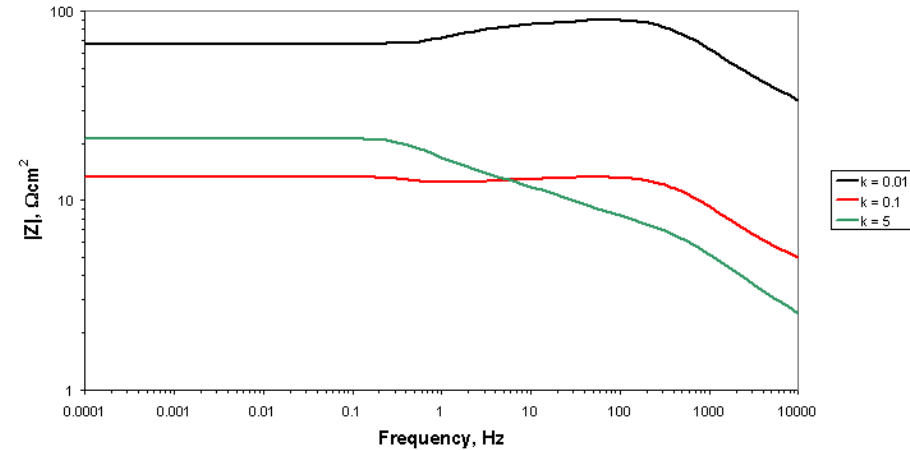
Results for EIS Model: ECE Mechanism

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

$$R \Leftrightarrow 2X$$

$$X + e^- \Leftrightarrow 2Y$$
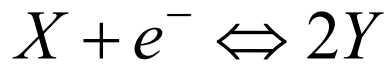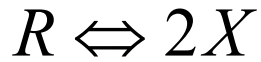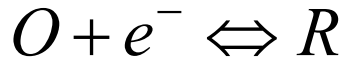
Forward and reverse reaction rates varied for each step to see how each one affected the data.
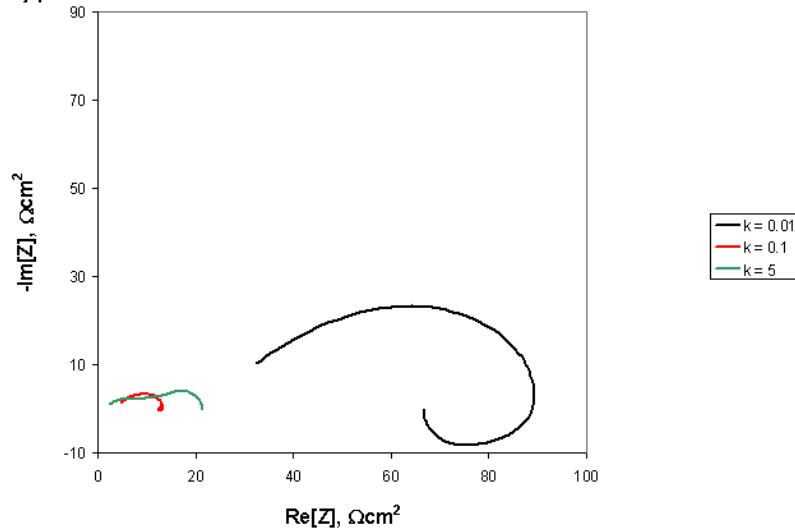
Bode Plot - Affect of First Electrochemical Reaction Forward Rate Coefficient

Nyquist 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.

Bode Plot - Affect of First Electrochemical Reaction Forward Rate Coefficient

Results for EIS Model: ECE Mechanism
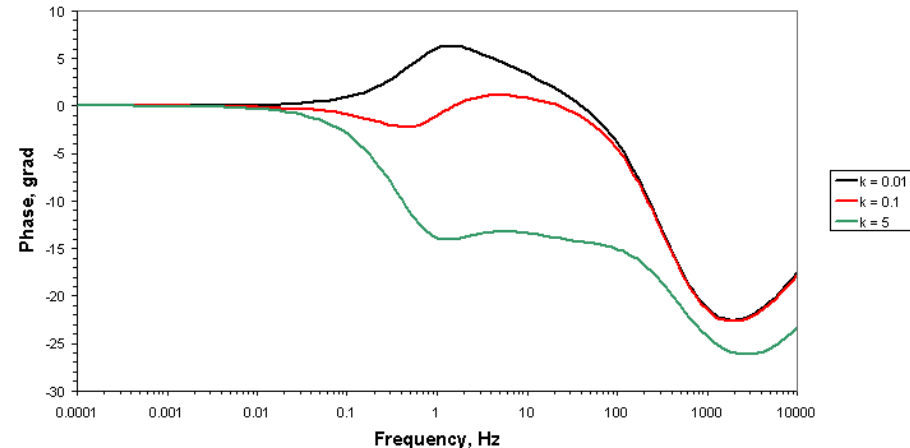
Nyquist Plot - Affect of Middle Chemical Reaction Forward Rate Coefficient

Bode Plot - Affect of Middle Chemical Reaction Forward Rate Coefficient

Bode Plot - Affect of Middle Chemical Reaction Forward Rate Coefficient

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

Results for EIS Model: ECE Mechanism

Nyquist Plot - Affect of Final Electrochemical Reaction Forward Rate Coefficient
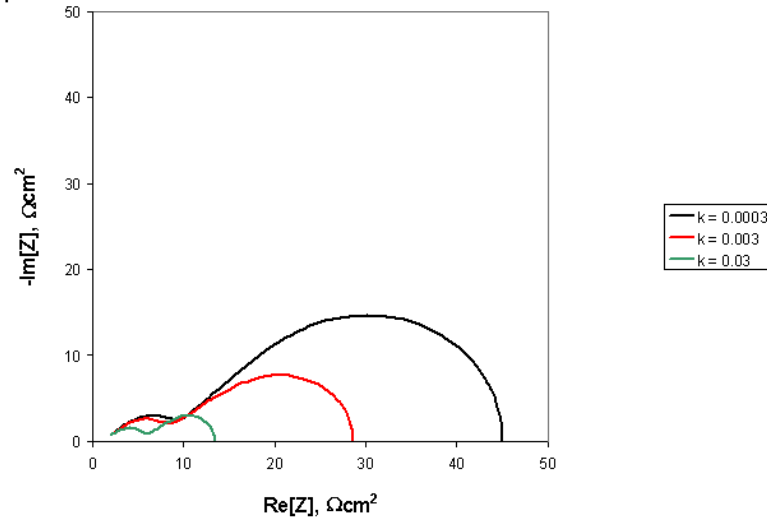
Bode Plot - Affect of Final Electrochemical Reaction Forward Rate Coefficient
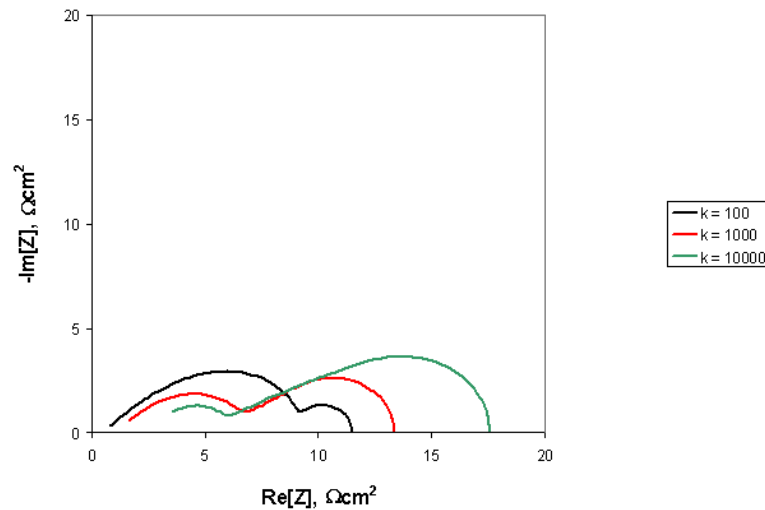
Bode Plot - Affect of Final Electrochemical Reaction Forward Rate Coefficient
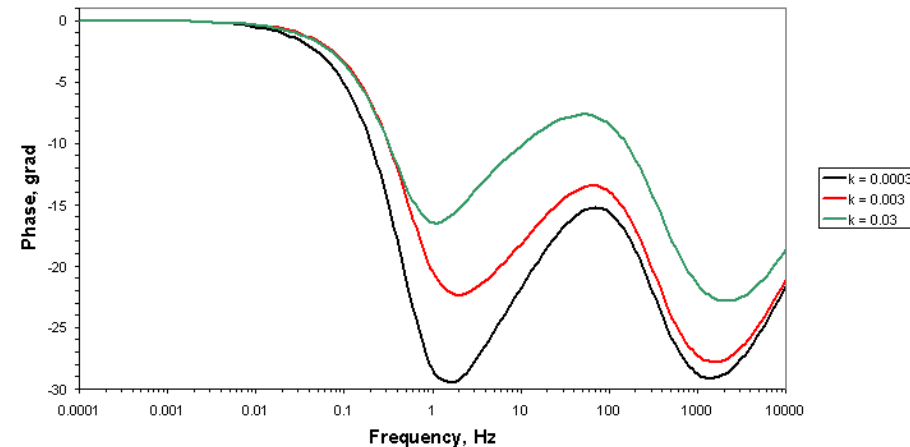
Nyquist and Bode plots for simulated ECE mechanism showing the affect of the last electrochemical reaction's forward rate coefficient.
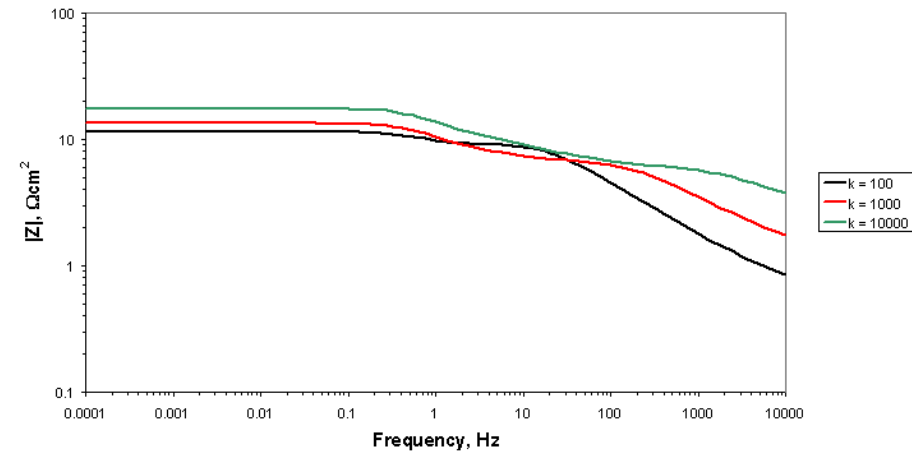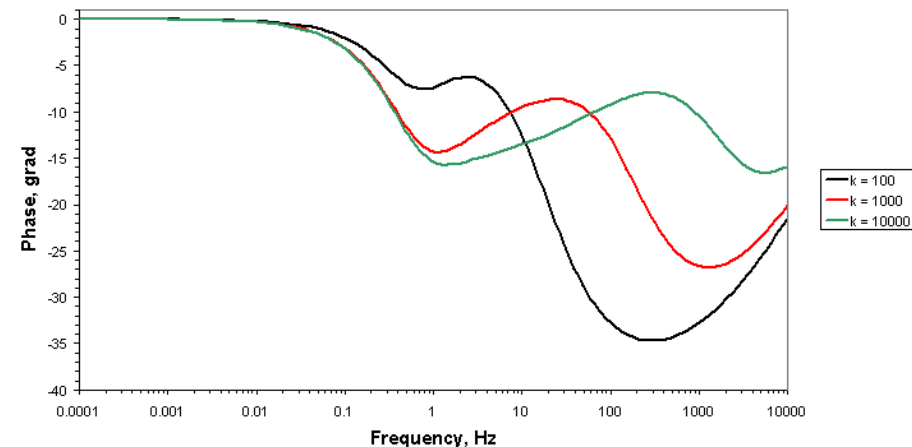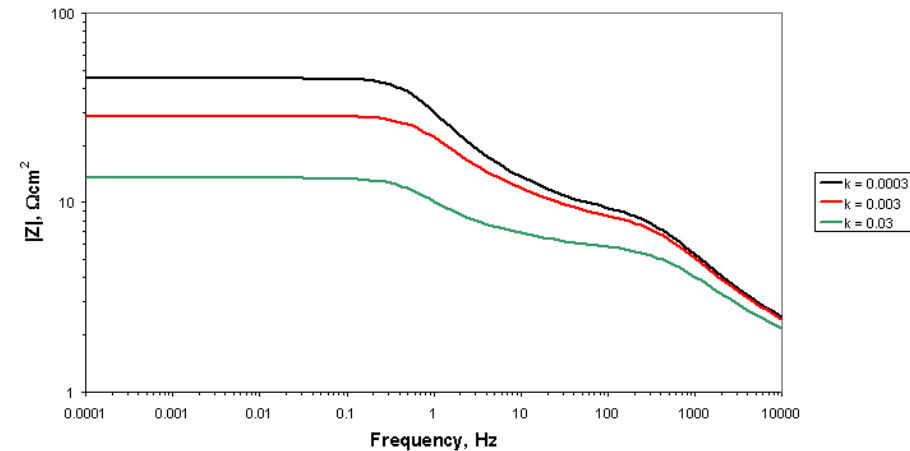
Results for EIS Model: ECE Mechanism

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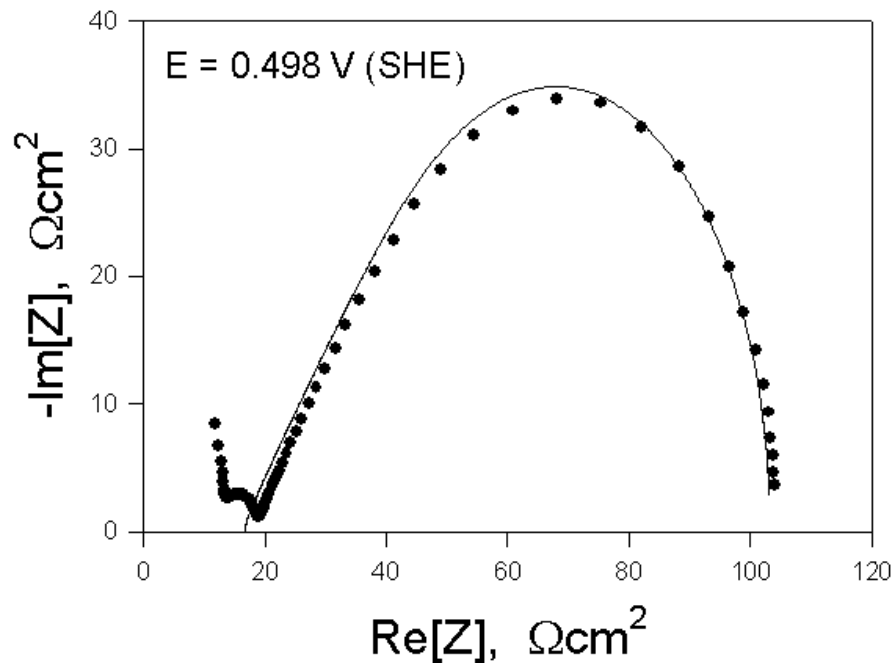
The model fits nicely, except for at high frequencies (data closest to the origin).

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.

Collaboration

➢ 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.

Future Work: R_3SnH Regeneration

➢ It is required to 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 reference electrodes for non-aqueous environments to run potentiostatic experiments.

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.

Future Work: EIS Modeling

➢ Finish model validation on ferrocyanide reduction to be sure the model is working properly.

➢ Extend the validation to a more complex, but known, reaction – the ECE reduction of ortho-bromonitrobenzene.

➢ Once our model has been validated, we will use it to extract kinetic parameters for organotin hydride and ammonia borane dehydrogenation.

- ▪ Once the kinetic parameters are known for the dehydrogenation, we plan to exploit them for optimal hydrogenation schemes.

Summary of Important Accomplishments to Date

➤ Developed a quantitative method for BH_4^- analysis in aqueous solution.

➤ Demonstrated electrochemical reduction of B-O to B-H, although at very low concentrations.

➤ Discovered BH_4^- 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.

Milestones and Current Status

Task Schedule

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
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			70%	On-Track
3	Definition of reaction kinetics and mechanisms	4/09			75%	On-Track
4	Demonstration of reversible hydrogen storage	4/09			0%	Not started
5	Specification of optimal system	4/09			0%	Not started
6	Task completion	4/09			0%	In progress