Electrochemical Hydrogen Storage Systems

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This presentation does not contain any proprietary or confidential information
Overview

Timeline
Start Date: FY 2005
End Date: FY 2009
New Start

Barriers
Low-cost, energy efficient regeneration processes have not been established.

Budget
DOE: $1,215,637
PSU: $303,909
FY2004: n/a
FY2005: $202,000 (requested)
$165,000 (advanced)

Partners
DOE Center for Excellence in Chemical Hydrogen Storage
Tier 1 Objectives

• To assist our partners, Rohm & Haas and Millenium Cell, in answering this question: Can the electrochemical reduction of metaborate ion to borohydride ion be achieved?
• We will study the fundamental mechanism of this reaction; i.e. determine what each elementary step is in the reaction.
• With the mechanism, we can determine if catalysis may be used to minimize overpotential (energy consumption) and maximize efficiency of borohydride production.
Center Collaborations

• LANL
  • New electrode fabrication
  • Complexation of borate to adjust electrochemical properties
  • Electrocatalyst development
  • Stoichiometric chemical reduction

• PNNL/Alabama
  • Computation of reaction intermediates and energetics

• Rohm & Haas
  • Access to proprietary information on borate electrochemistry
  • Engineering assessment
    • Data mining results
    • PSU electrochemical results

• Millennium Cell
  • Data mining and background information

• UCLA
  • Synthesis and characterization of polyboranes
  • Expertise on chemical reactivity and properties of polyboranes
Tier 1 Technical Approach

• Define reaction mechanism in terms of **elementary** reaction steps
• Determine values for the rate constants and Tafel constants for these reactions. This will be done by optimizing the model on impedance data.
• Manipulate the kinetics of individual steps to enhance the efficiency of borohydride production while minimizing the overpotential.
Tier 1 Background

• Patent literature suggests methods for electrochemical reduction of metaborate (see, for example: Cooper, US Patent 3,734,842, and Amendola, US Patent 6,497,973)

• One open literature article found that patent results could not be reproduced (Gyenge & Oloman, J. Applied Electrochem., 28 (1998), 1147-1151)

• No studies found in any literature on the true mechanism of this reaction
Basic Cell Design
Legend

- **a**: Pd/Ag thimble for $\text{H}_2$ monitoring
- **b**: For monitoring production of $\text{B}_2\text{H}_6$
- **c**: $\text{N}_2$ input
- **d**: Working electrode
- **e**: Luggin capillary/ reference electrode
- **f**: CV probe for monitoring of $\text{BH}_4^-$
- **g**: Nafion 117 membrane
- **h**: Counter electrode
Primitive Hydrogenation Model

(1) $H_2O + S + e^- \overset{k_1}{\rightarrow} H - S + OH^-$

(2) $H - S + H_2O + e^- \overset{k_2}{\rightarrow} H_2 + OH^- + S$

(3) $H - S + R \overset{k_3}{\rightarrow} R - H + S$

Fraction of unoccupied sites: $1 - \theta$

Fraction of sites occupied by adsorbed H: $\theta$

Surface concentration of sites: $\Gamma$ (mol/cm$^2$)
Assumptions and Definitions

- Reaction (3) is one step in the hydrogenation of the B-O or B-H-O substrate – the actual system will be much more complicated and involve a multistep mechanism.
- Reactions (2) and (3) occur in competition.
- Reactions (1) and (2) are electrochemical, so the rate constants may be expressed as: 
  \[ k = k^o e^{-E/b} \]
- Efficiency for borohydride production may be expressed as:
  \[ \eta = \frac{\frac{d[RH]}{dt}}{\left(\frac{d[RH]}{dt} + \frac{d[H_2]}{dt}\right)} = \frac{k_3^o [R]}{k_3^o R + k_2^o e^{-E/b_2}} \leq 1 \]
The Impedance Model: Definitions

- We will make extensive use of Electrochemical Impedance Spectroscopy to study the mechanism.
- Impedance is defined in terms of current and voltage by Ohm’s Law: \[ Z = \frac{E}{I} \]
- Admittance is the reciprocal of impedance.
- “Specific” refers to the quantity being normalized to the surface area of the electrode, hence, current density, and not current, will appear in the expression.
- “Faradaic” indicates a process where the current flowing causes a reaction to occur; “non-Faradaic” indicates that the current flowing increases the charge on the electrical double layer. The total impedance (or admittance) will contain terms from both Faradaic and non-Faradaic processes.
Definitions, continued

- Current density: \[ |i| = \frac{Fk_1\Gamma(2k_2 + k_3[R])}{k_1 + k_2 + k_3[R]} \]

- Current density is a function of surface coverage (\( \theta \)), voltage (\( E \)), and concentration of species R (\( C \)), so the total differential of current density is:

\[
\delta i = \left( \frac{\partial i}{\partial \theta} \right)_{E,C} \cdot \delta \theta + \left( \frac{\partial i}{\partial E} \right)_{\theta,C} \cdot \delta E + \left( \frac{\partial i}{\partial C} \right)_{E,\theta} \cdot \delta C
\]

- Specific Faradaic Admittance is defined from Ohm’s Law as:

\[
Y_F = \frac{\delta i}{\delta E}
\]
Specific Faradaic Admittance

Solving for the total differential of $i$, then substituting into the definition of Faradaic Admittance gives:

$$Y_F = \left( \frac{1}{1+a} \right) \left\{ F\Gamma(k_2 - k_1) \cdot \frac{\alpha}{1 + j\tau} - F\Gamma \left[ \frac{k_1}{b_1} (1 - \theta) + \left( \frac{k_2}{b_2} \right) \theta \right] \right\}$$

Where:

$$a = \frac{F\Gamma k_1 k_3 (k_1 - k_2)}{(k_1 + k_2 + k_3[R])^2} \cdot \frac{1}{nFD^{1/2} \omega^{1/2} j^{1/2}}$$

$$\alpha = \frac{\theta(k_2/b_2) - (1-\theta)(k_1/b_1)}{k_1 + k_2 + k_3[R]}$$

$$\tau = \frac{\omega}{(k_1 + k_2 + k_3[R])}$$
Total Specific Admittance and Specific Impedance

\[ Y_T = Y_F + j \omega C_{dl} \]

Where \( C_{dl} \) is the double layer capacitance. The specific impedance then becomes:

\[ Z_T = \frac{1}{Y_T} \]

The double layer capacitance term gives the non-Faradaic contribution to the admittance and impedance expressions.
What do we do with these functions?

• Solve for $i$ as a function of $E$
• Use with constrained optimization of the model on experimental impedance or admittance data to find optimal values for $k$’s and $b$’s
• Use the optimal $k$’s and $b$’s to direct the development of effective and efficient electrodes and electrocatalysts within the Center for:
  – Borate reduction
  – Complexed borate reduction
  – Polyborane redox chemistry
Tier 2 Objectives

• To determine the electrochemistry of complex boranes, and devise a reversible hydrogen storage technology based on the borane system.

• To be able to change the number of B-H bonds on each boron atom electrochemically, since boron has many possible oxidation states. By doing so, we hope to safely store hydrogen in the boron/hydrogen system.
Tier 2 Approach

Borane Electrochemistry

- Explore and define the electrochemistry of polyboranes, polyborane anion molten salts, and non-aqueous solutions in contact with hydrogen gas.
- Determine the identities and structures of the polyboranes.
- Resolve kinetic and mechanistic issues, identify reaction products, determine reaction mechanisms and transport parameters.
- Resolve and characterize the thermal decomposition of the hydrides.
Tier 2 Approach

Borane Hydrogenation

• Explore the feasibility of developing a reversible hydrogen storage technology based on the polyborane system.
• Electrodes will be used to induce changes in the formal oxidation state of boron for a reversible hydrogen storage method.
• Explore the kinetics of the hydrogen/electrode reaction on a variety of electrode materials to maximize the cell efficiency.
Tier 2 Approach

• Develop electrochemical reaction models for hydrogen storage in the polyboranes, polyborane anion molten salts and non-aqueous solutions.

• Develop criteria to confirm that the model agrees with the experimental data.

• Optimize the model on electrochemical experimental data.
Acknowledgements

• Rohm and Haas for providing sodium borohydride

• UCLA and LANL for synthesizing polyboranes

• DOE and PSU for funding

• Penn State University for facilities
# Electrochemistry of Boron-Hydrogen System

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## Electrochemical Reduction of $B-O$ to $B-H$

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Safety: Most Significant Concerns

• Tier 1: Formation of species such as $H_2$ and/or $B_2H_6$ during operation of cell

• Tier 2: Over-pressurization of the reaction vessel
Approaches to Dealing With These Hazards

**Tier 1**

- Cell will be operated in a fume hood
- Cell designed so that $\text{B}_2\text{H}_6$ that may form can be collected and analyzed

**Tier 2**

- Pressure sensor will be built into the cell
- Rupture disks will be built into the cell
- A blast shield will be installed into the glove box as an extra layer of protection in case of rupture