

Electrochemical Hydrogen Storage Systems

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Project ID #
194 ST-P 4

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

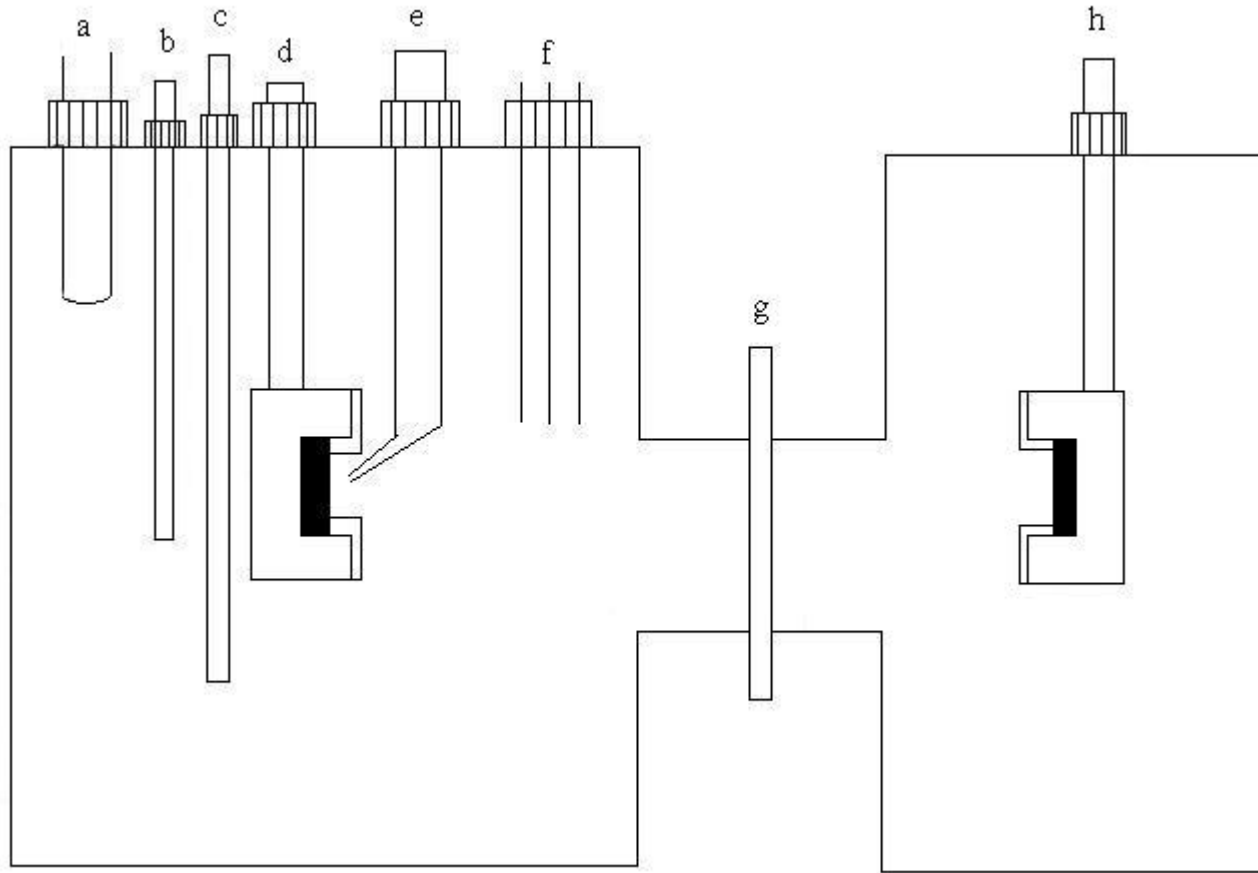
Tier 1 Technical Approach

- 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

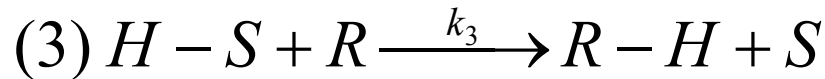
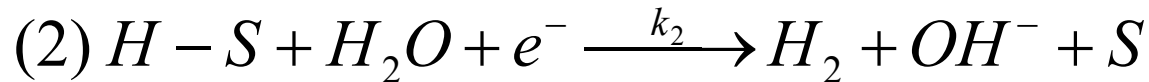
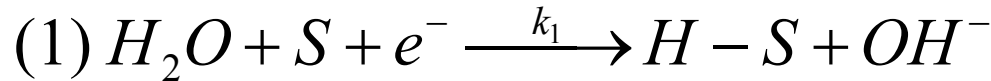
Basic Cell Design



Legend

- a: Pd/Ag thimble for H₂ monitoring
- b: For monitoring production of B₂H₆
- c: N₂ input
- d: Working electrode
- e: Luggin capillary/ reference electrode
- f: CV probe for monitoring of BH₄⁻
- g: Nafion 117 membrane
- h: Counter electrode

Primitive Hydrogenation Model



Fraction of unoccupied sites : $1 - \theta$

Fraction of sites occupied by adsorbed H : θ

Surface concentration of sites : Γ (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:

$$\eta = \frac{d[RH]/dt}{(d[RH]/dt + d[H_2]/dt)} = \frac{k_3^o [R]}{k_3^o [R] + k_2^o e^{-E/b_2}} \leq 1$$

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: $Z = E / I$
- 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 (θ), 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

Major Milestones/ Deliverables	3/05	3/06	3/07	3/08	1/09
Demonstration of Electrochemical Transformations	→				
Practically Useful Oxidation State		→			
Change Demonstration of Reversible H ₂ storage			→		
Specification of Optimal System				→	
Task Completion					→



Electrochemical Reduction of *B-O* to *B-H*

Major Milestones/ Deliverables	3/05	3/06	3/07	3/08	1/09
Demonstration of <i>B-O</i> to <i>B-H</i>	→				
Reaction Mechanism		→			
Reaction Kinetics			→		
Specification of Optimal System				→	
Task Completion					→

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 B_2H_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