Electrochemical Hydrogen Storage Systems

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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
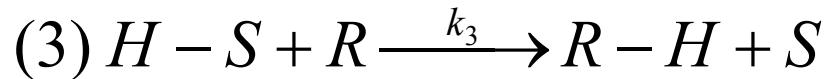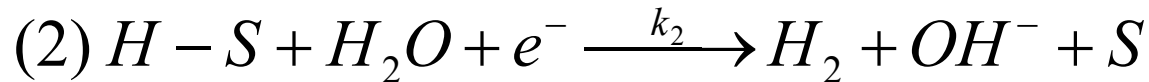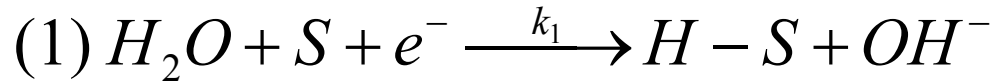
Basic Cell Design
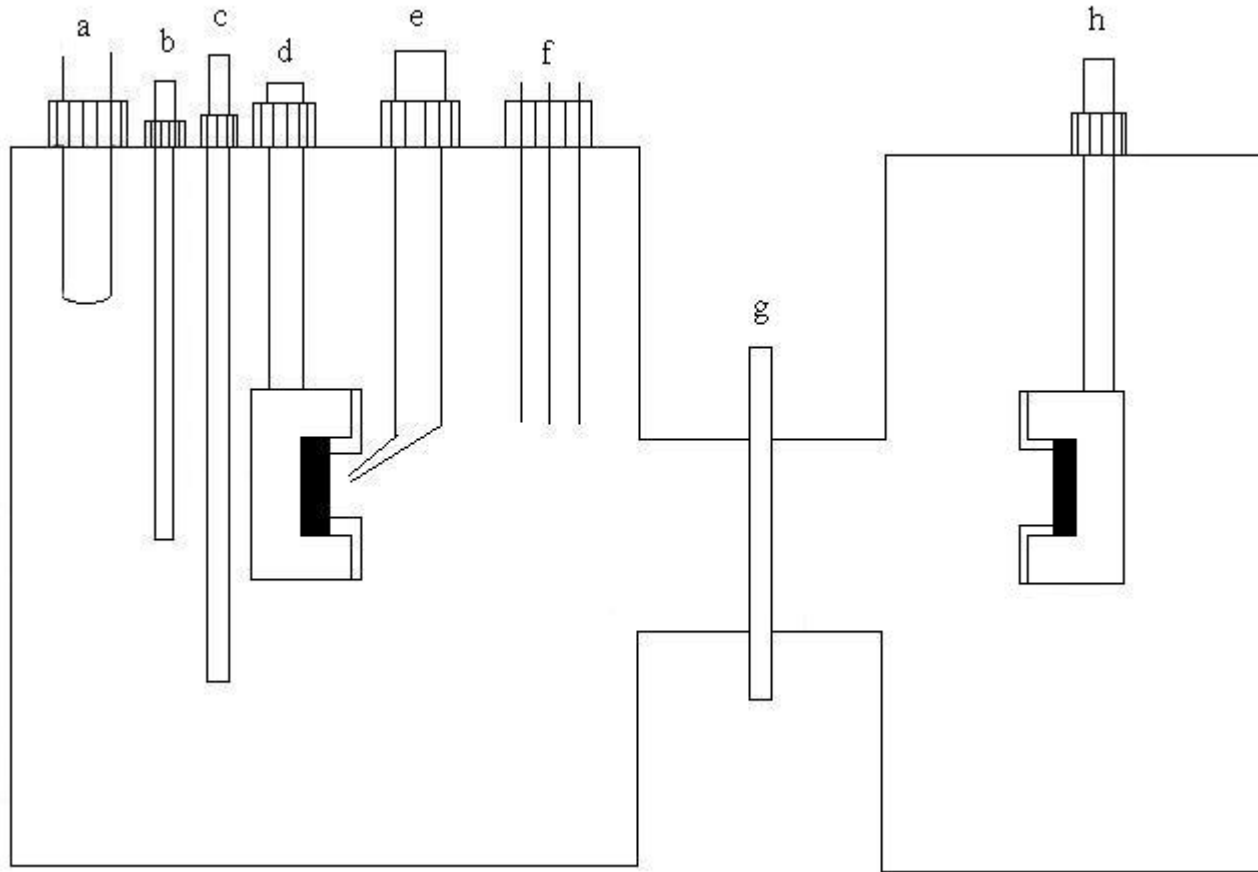
Legend

- a: Pd/Ag thimble for H_2 monitoring
- b: For monitoring production of B_2H_6
- c: N_2 input
- d: Working electrode
- e: Luggin capillary/ reference electrode
- f: CV probe for monitoring of BH_4^-
- g: Nafion 117 membrane
- h: Counter electrode

Primitive Hydrogenation Model

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

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

(3) $H - S + R \xrightarrow{\quad k_3 \quad} R - H + S$

Fraction of unoccupied sites : $1\text{-}\theta$

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:

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

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:

$$|i| = \frac{F k_1 \Gamma (2k_2 + k_3[R])}{k_1 + k_2 + k_3[R]}$$

- 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 *B-O* to *B-H*	———→				
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