Expanding Clean Energy Research and Education Program at the University of South Carolina

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Project ID # **STP20**

Overview of Projects

Project I: Low Temperature Electrolytic Hydrogen Production (Dr. John Weidner). Purpose: to lower the cost and improve the efficiency of methods for producing hydrogen from thermal and electrical energy.

Project II: Development of Complex Metal Hydride Hydrogen Storage Materials (Dr. James Ritter). Purpose: to carry out a systematic study on the preparation, characterization and testing of new metal doped complex hydrides for reversible hydrogen storage using conventional and proprietary physiochemical processing routes.

Project III: Hydrogen Storage Using Chemical Hydrides (Dr. Michael Matthews). Purpose: to use fundamental kinetic, chemical and thermodynamic reaction data on the novel steam + chemical hydride reaction to evaluate this technology as a means to deliver hydrogen for automotive fuel cells.

Project IV: Understanding Internal Air Bleed Effect on CO Poisoning in a PEMFC (Dr. John Van Zee). Purpose: to characterize and quantify the effect of internal O_2 on CO poisoning (internal air bleed, to examine the effect of MEA thickness on internal air bleed, and to develop a model to explain the effect of internal air bleed and predict the anode over-potential.

Project V: Using EIS and RDE to Study Pt Catalyst Aging (Dr. Ralph White). Purpose: to use the electrochemical impedance spectroscopy (EIS) and the rotating disk electrode (RDE) to characterize the aging of Pt catalyst for the oxygen reduction reaction (ORR) in a polymer electrolyte membrane (PEM) fuel cell.

Project VI: Molecular Simulation of Hydrogen Storage Materials (Dr. Jerome Delhommelle). Purpose: to use molecular modeling to characterize the properties of new hydrogen storage materials (metal-organic frameworks, clathrate hydrates and doped complex hydrides) and to provide leads to improve them.

2005-2007 Total Project Budget

- Total Funding (18 mo Period Beginning 11/05)
  - $1,984,000
- Personnel
  - 6 co-PIs (White, Weidner, Matthews, Ritter, Van Zee and Delhommelle)
  - 2 Research Professors (Ebner and Davis)
  - 11 PhD Students
- Travel
- Equipment
  - XPS System and 32 Node 64 Processor Cluster
- Materials and Supplies

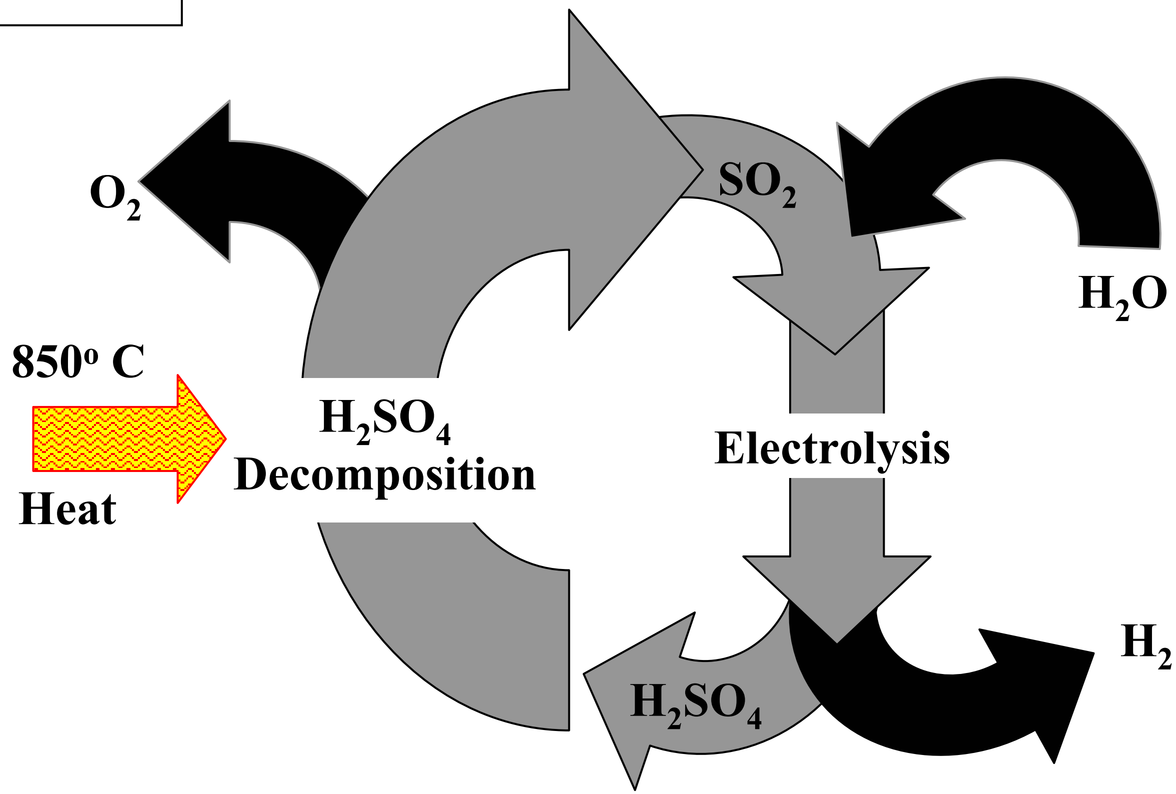
Project I: Low Temperature Electrolytic Hydrogen Production

Hybrid Sulfur Cycle

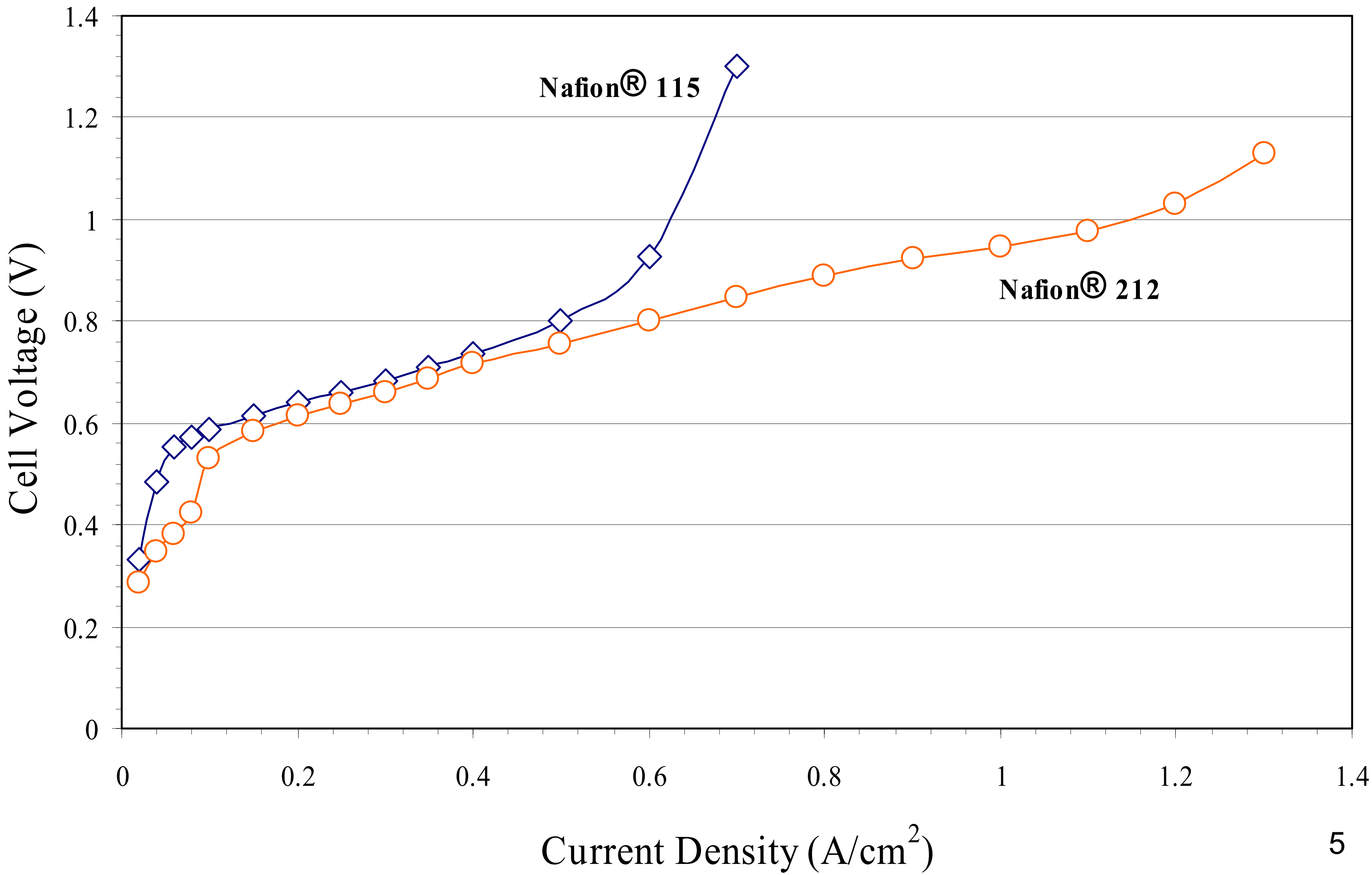
Anode: $SO_2(g) + 2H_2O \rightarrow H_2SO_4 + 2\,H^+(aq) + 2\,e^-$

Cathode: $2H^+(aq) + 2\,e^- \rightarrow H_2(g)$

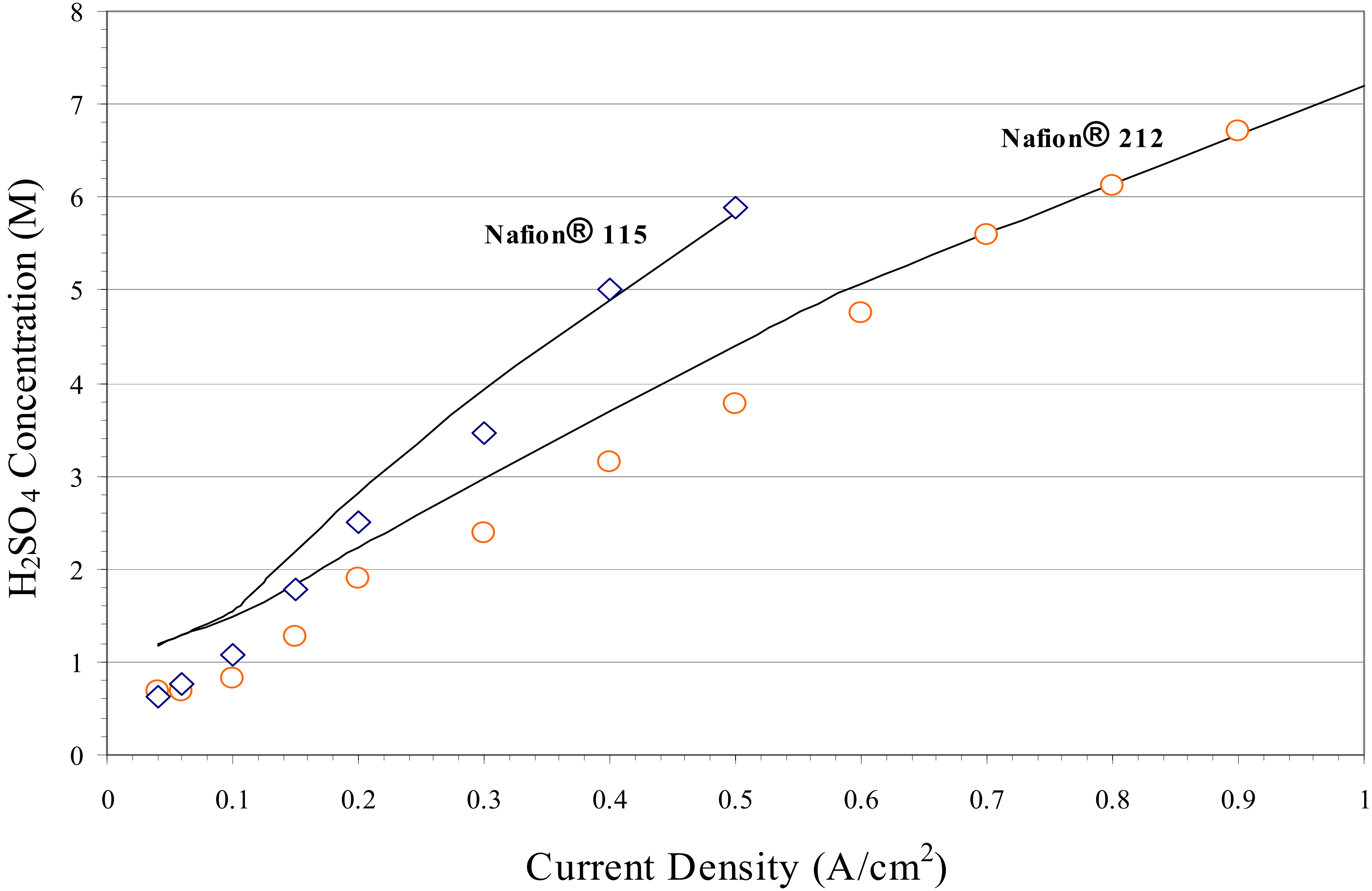
Overall: $SO_2(g) + 2H_2O \rightarrow H_2(g) + H_2SO_4 \quad E^\circ = 0.18\ V$



Hybrid Sulfur Electrolyzer Performance



Exiting H_2SO_4 Concentrations and Model Predictions



Project II: Development of Complex Metal Hydride Hydrogen Storage Materials

Objective

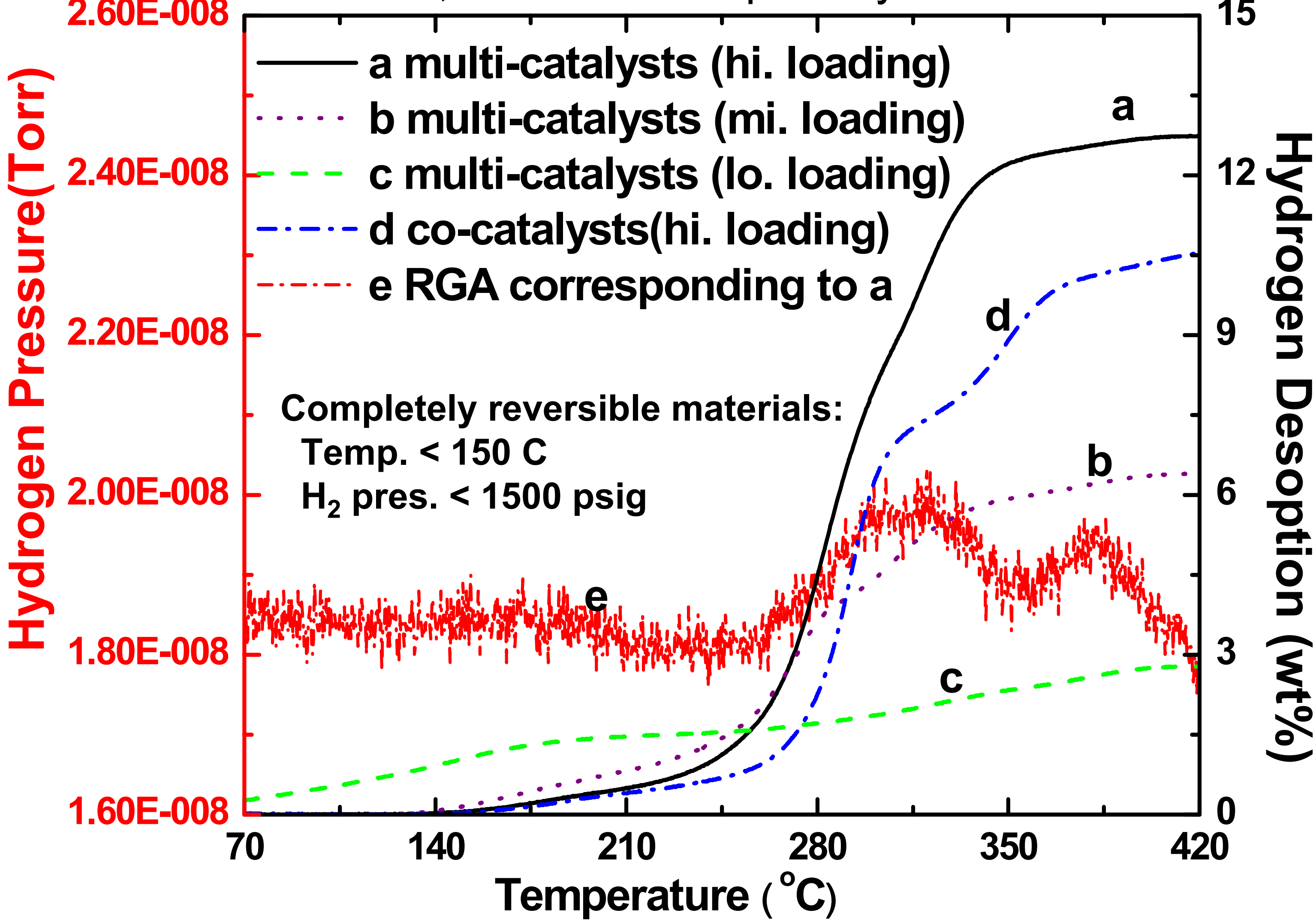
- introduce new class of reversible H_2 storage materials with high capacity at relatively high but still engineering temperatures based on Physiochemical Pathway and *Thermal Hydrogenation Approaches*

Approach

- prepare samples of materials based on Al and B complex hydride chemistry.
- characterize prepared samples in terms of their dehydrogenation and hydrogenation kinetics, capacity and reversibility

Physiochemical Pathway Approach

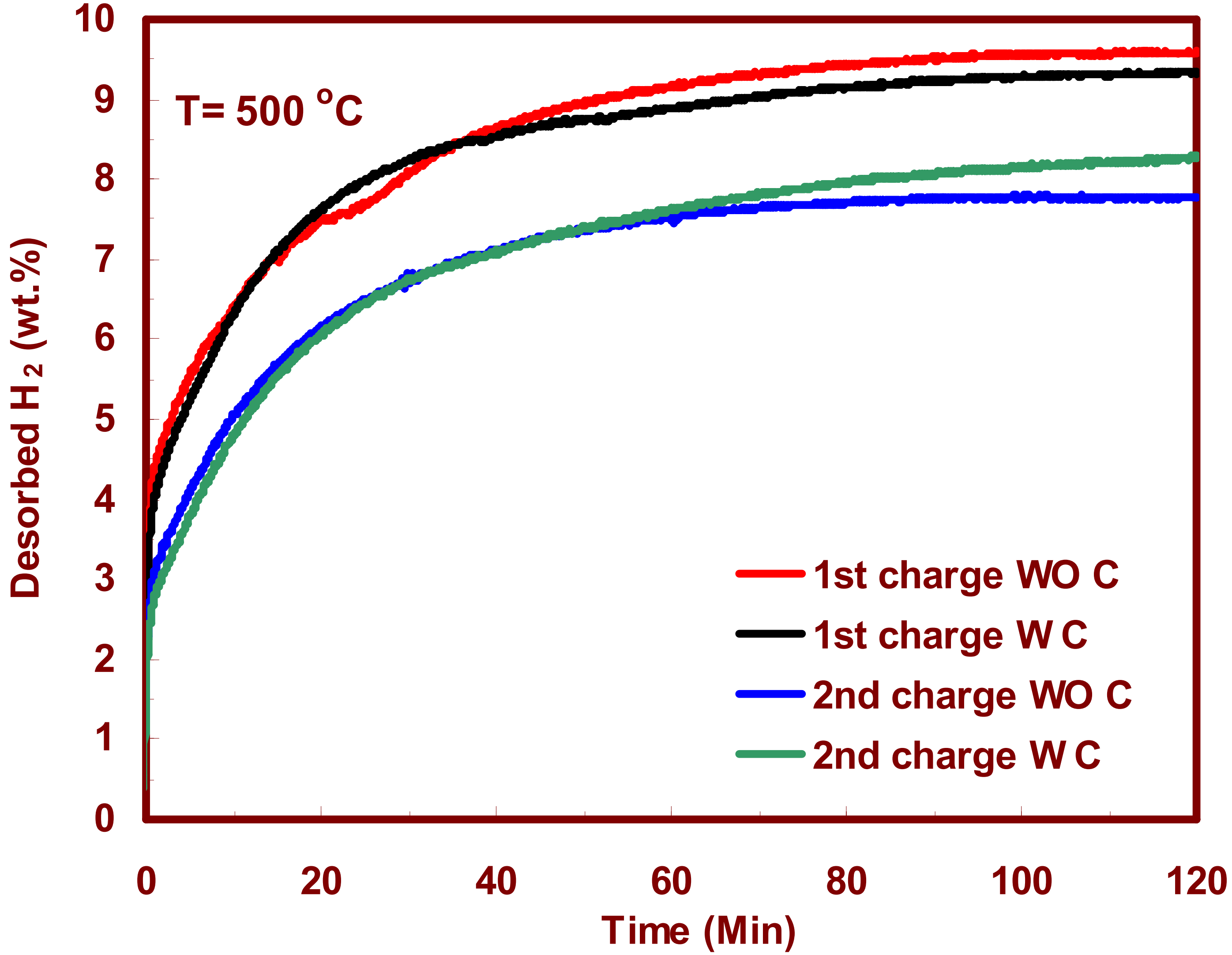
New Reversible H_2 Storage Materials with High Capacity based on Li, Al and B Complex Hydride



J. A. Ritter, T. Wang, A. D. Ebner, J. Wang and C. E. Holland, Provisional Patent Application, filed May (2006).

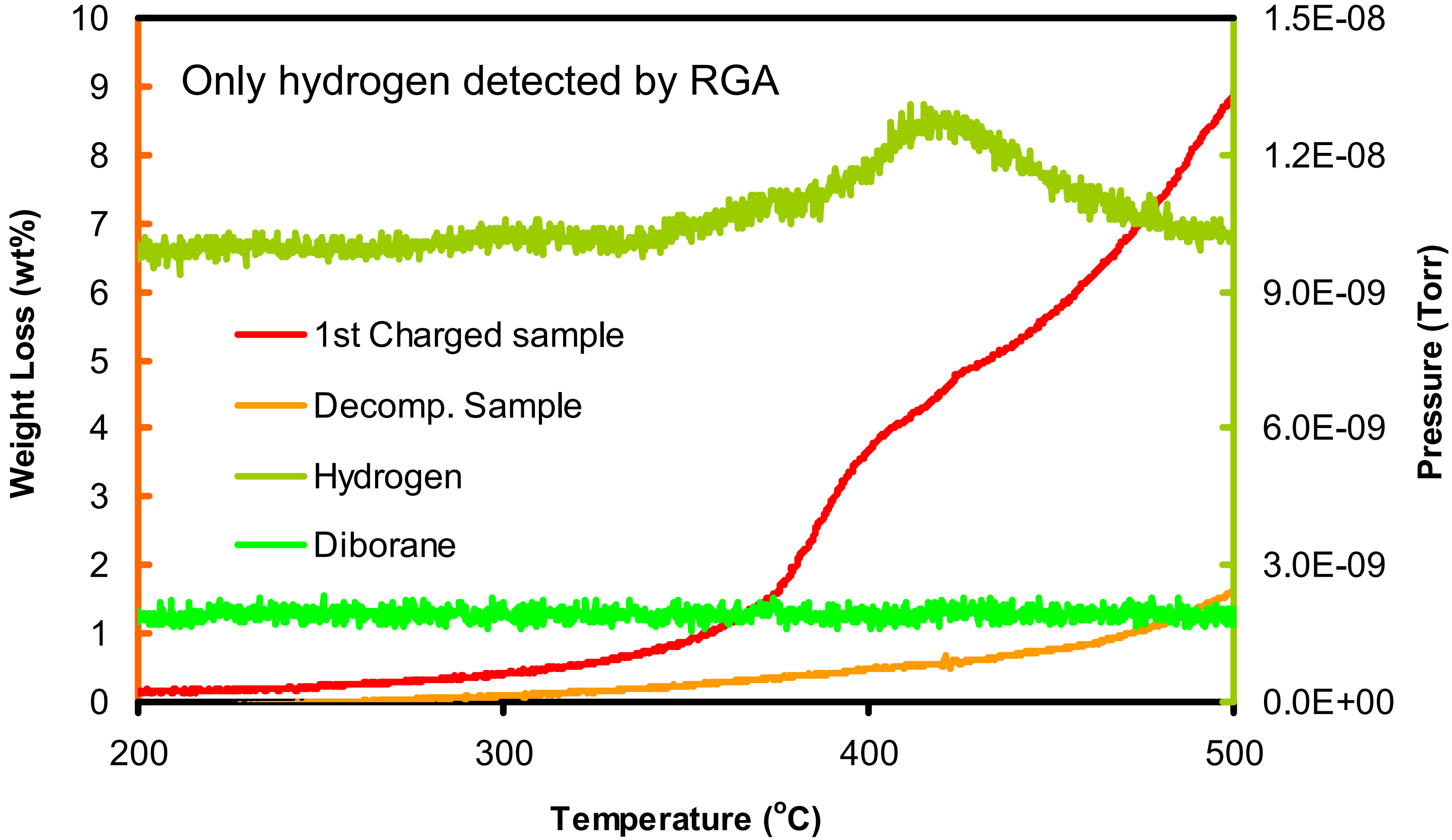
Thermal Hydrogenation Approach

$LiBH_4$ with Al Weight Ratio of 7:3 with 4 mol% Ti and 0 or 5 wt% MWNT

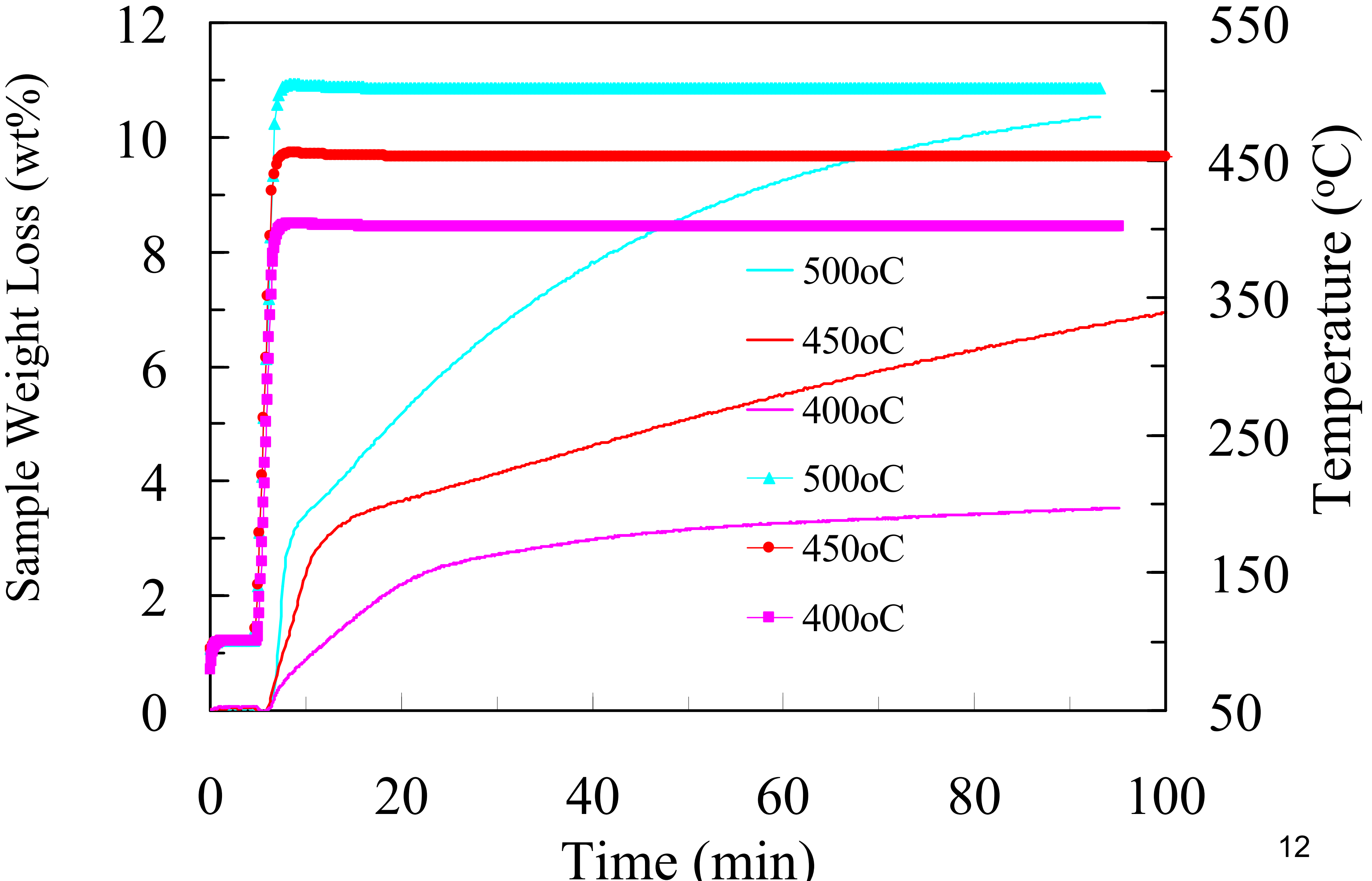


Thermal Hydrogenation Approach

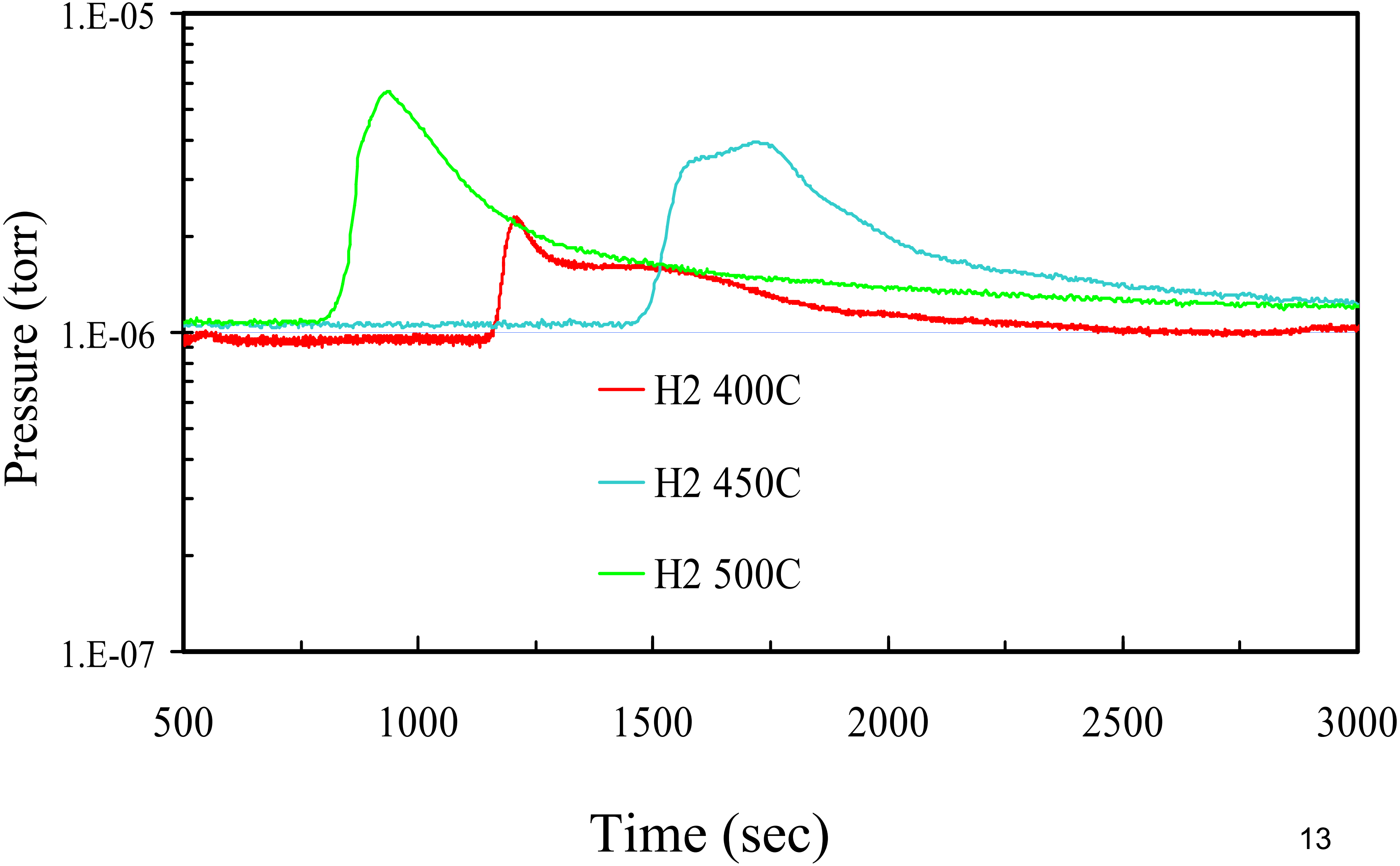
$LiBH_4$ with Al wt Ratio 6:4 with 4 mol% Ti and 5 wt% MWNT



CTD of 77%LiBH4:23%Al Sample at 400, 450, 500 ^oC



RGA of Pressure vs. Time of CTD Effluent at 400, 450, and 500°C



Project III: Hydrogen Storage Using Chemical Hydrides

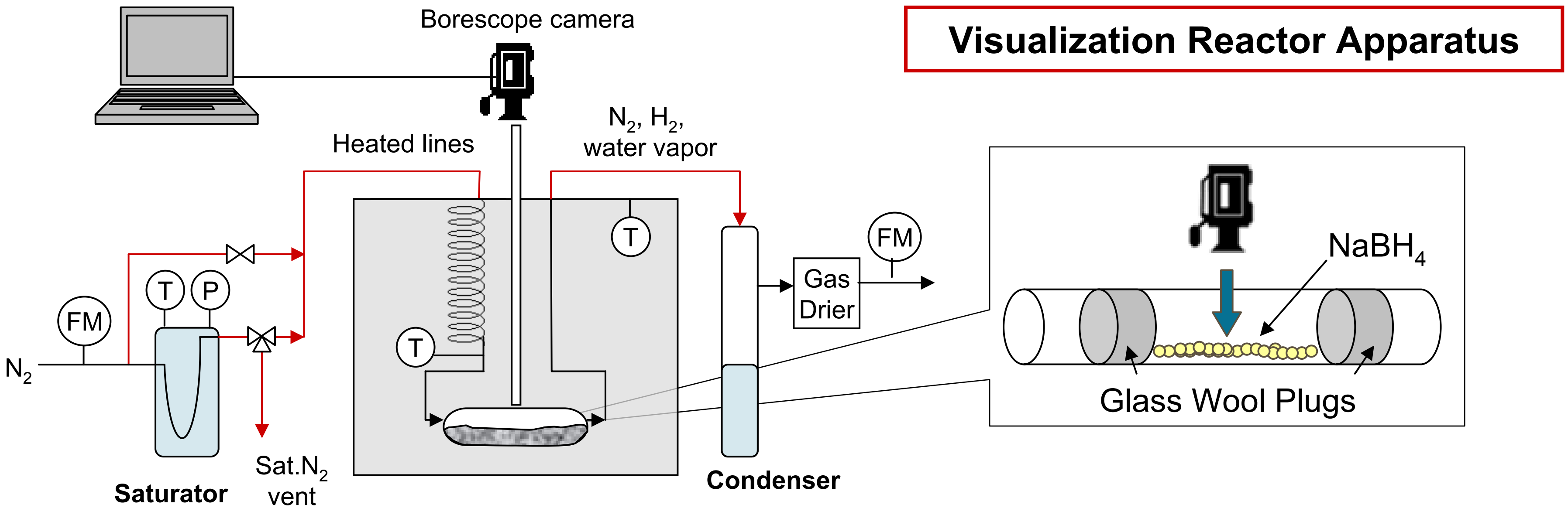
Objectives and Approach

- Develop hydrogen storage and delivery technology based on steam hydrolysis of chemical hydrides for automotive fuel cell applications

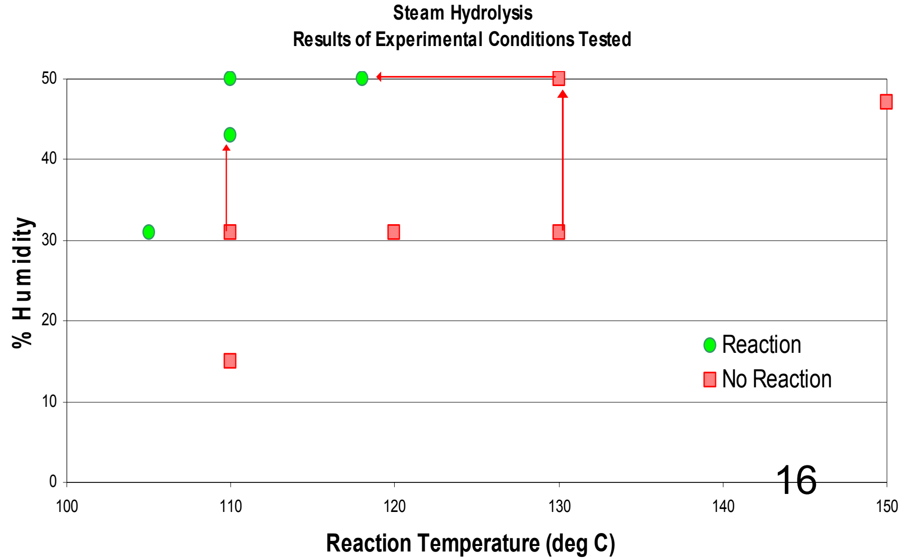
$$NaBH_4 + (2+x)H_2O \rightarrow 4H_2\,(g) + NaBO_2 \cdot x\, H_2O + \Delta H_{rxn}$$

- Quantify/optimize steam + solid chemical hydride reaction kinetics as the basis for production of hydrogen
- Operate reactor at low temperatures (100 –150^{O}C) and pressures (~ atmospheric)
- Conduct basic research to minimize water utilization and maximize H_2 delivery rate
- Understand the mechanism of steam hydrolysis and how it differs from aqueous hydrolysis
- Understand the role of water adsorption in the hydrolysis reaction

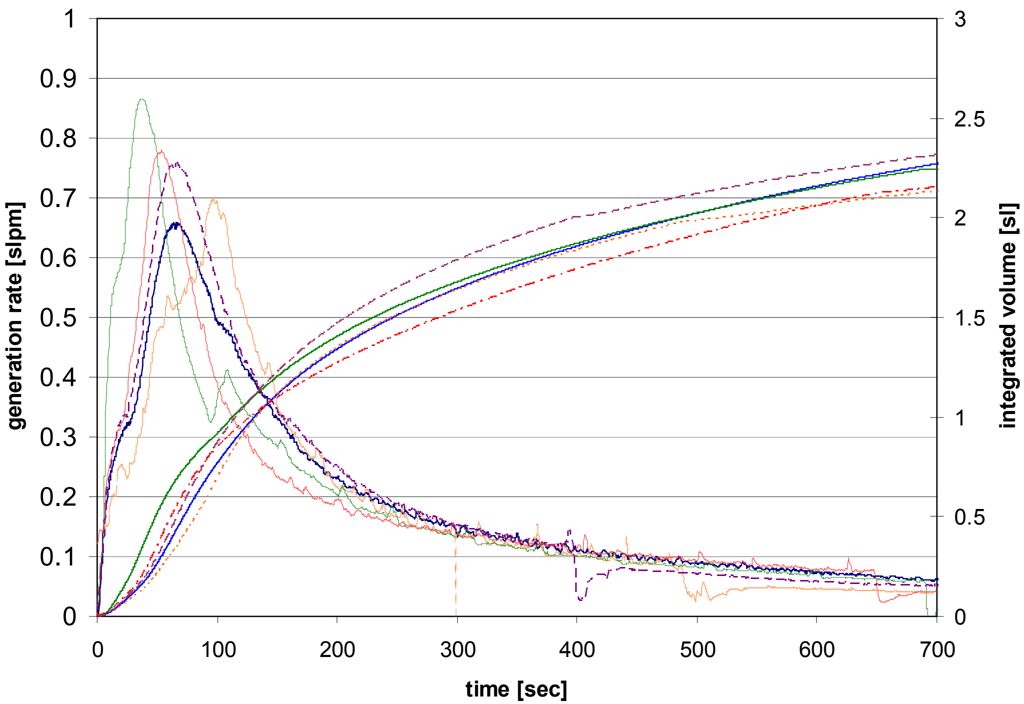
Conditions Required for Initiation of Steam Hydrolysis of $NaBH_4$

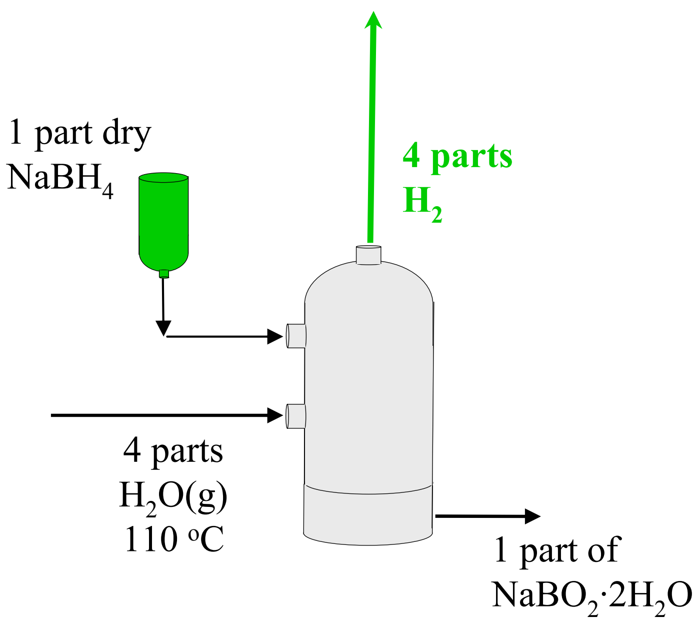


- **Reaction only occurs at low temperatures and high humidities**
- **The reaction does not initiate above 118°C at 50% humidity**



Hydrogen Storage Prototype Performance Data





- T_{rxr} = 110 °C
- Avg. H_2 yield = 91 %
- Initial H_2 generation rate = 0.38 g/s/kg $NaBH_4$
- Much higher H_2 generation rates than seen in screening reactor (0.03 g/s/kg $NaBH_4$)

Project IV: Understanding Internal Air Bleed Effect on CO Poisoning in a PEMFC

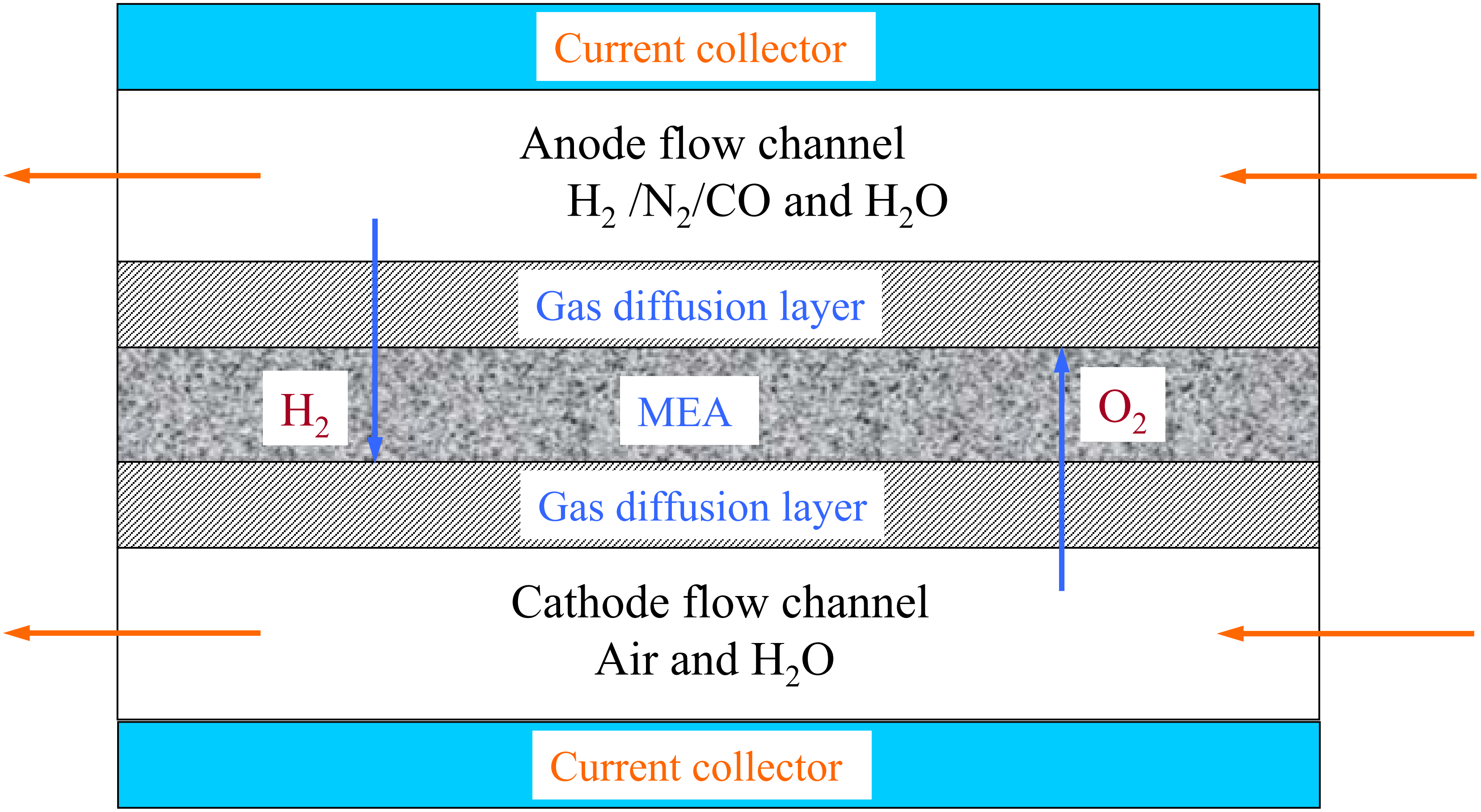
Objectives

- Characterize and quantify the effect of internal O_2 on CO poisoning (internal air bleed)
- Examine the effect of MEA thickness on internal air bleed
- Develop a model to explain the effect internal air bleed and predict the anode over-potential

Conclusions

- Anode polarization is decreased when the cathode back pressure is increased or a thinner MEA is used.
- The diffused oxygen (internal air bleed) shows promise to combat CO poisoning only when thin MEA are used.
- A model with internal air bleed term is developed to explain the observed effect of cathode back pressure and to help quantify the effects on isotherms.
- The model predictions of anode overpotential agree very well with the experimental data.
- The air-bleed effect is limited by the adsorption of O_2 on Pt.

Internal Diffusion through MEA = f (P_{air}, P_{CO}, thickness)



CO Poisoning & Air Bleed Effect

Reactions Used in Model

Adsorption and Desorption

⇩

$$Pt + H_2 \Leftrightarrow Pt\text{-}H_2 \qquad k_{fh}, b_{fh}$$

$$Pt + CO \Leftrightarrow Pt\text{-}CO \qquad k_{fc}, b_{fc}$$

Electrochemical Reaction

⇩

$$Pt\text{-}H_2 \rightarrow Pt + 2H^+ + 2e^- \qquad k_{ec}$$

Chemical Reactions

⇩

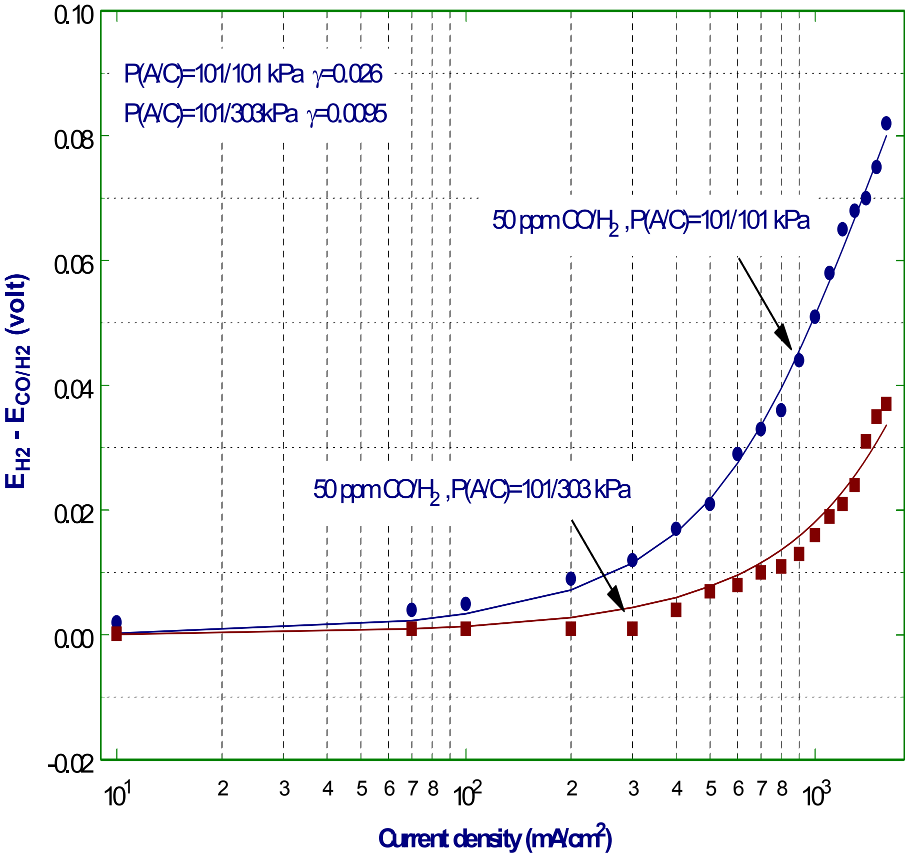
$$O_2 + 2CO \rightarrow 2CO_2$$

$$O_2 + 2H_2 \rightarrow 2H_2O$$

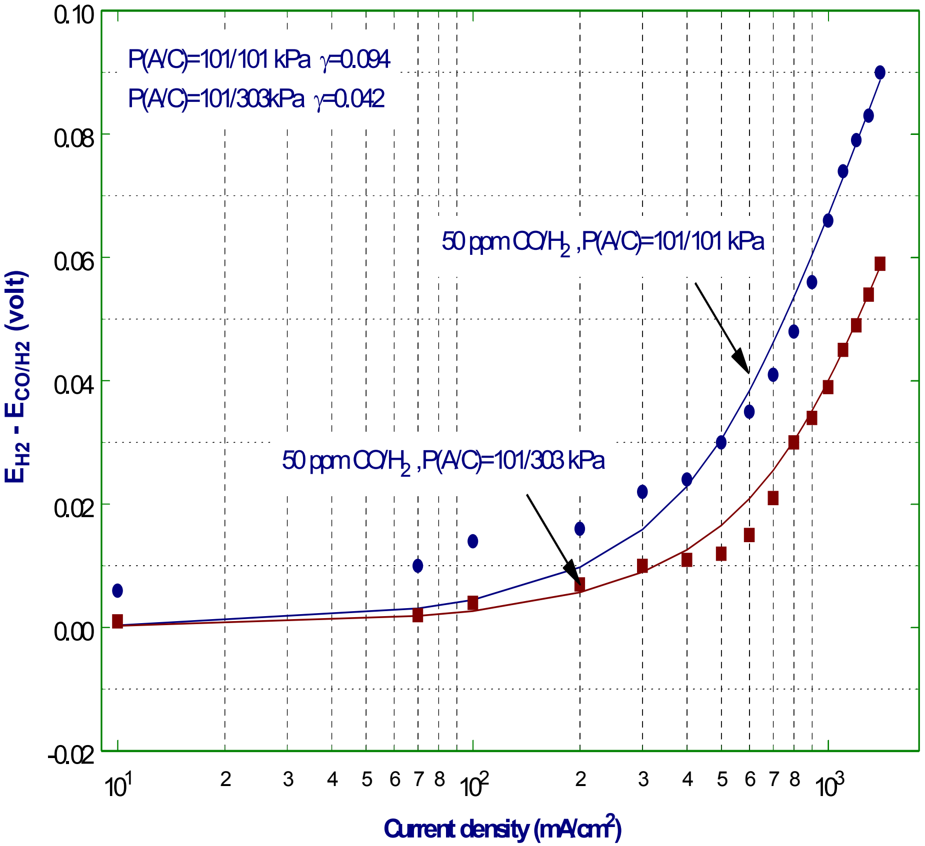
Internal Air Bleed Effect

Comparison Between Model Predictions and Experimental Data with <u>50 ppm</u> CO/H_2

5 mm MEA ⇩



25 mm MEA ⇩



Internal Air Bleed Effect

Overall Reactions

$$O_2 + 2H_2 \rightarrow 2H_2O$$

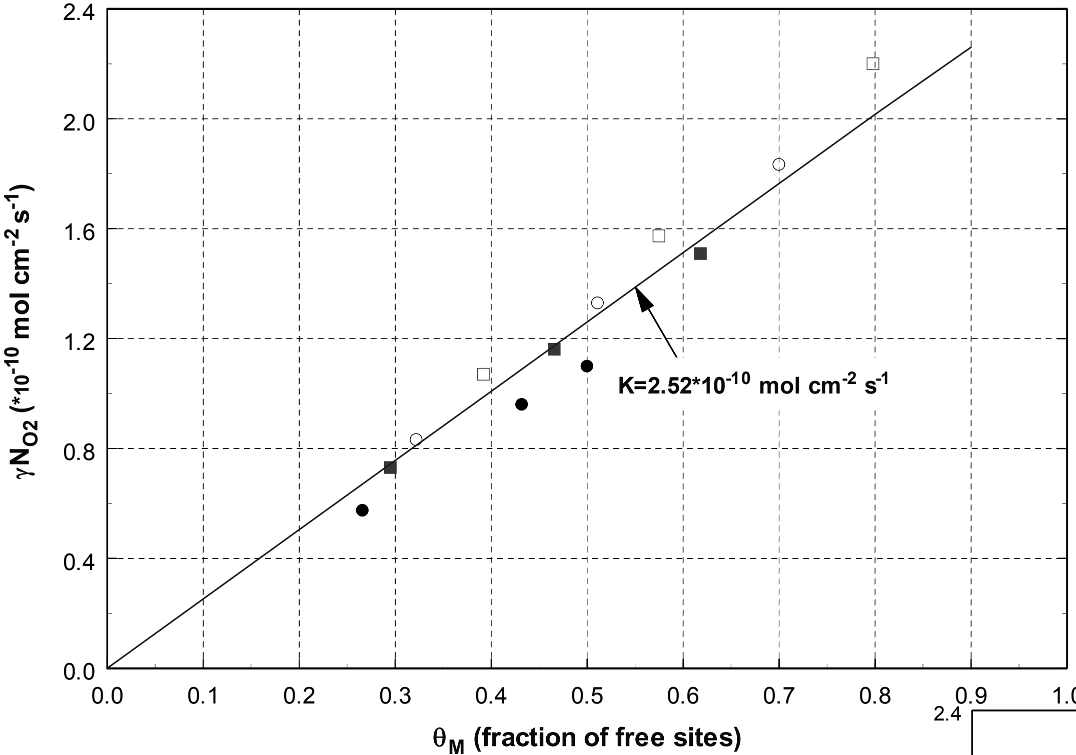
$$\tfrac{1}{2}\, O_2 + CO \rightarrow CO_2$$

Surface Reactions

(1) $Pt + CO \Leftrightarrow Pt\text{-}CO \qquad r_1 = k_{f1}\ \theta_M\, P_{co} - k_{b1}\, \theta_{co}$

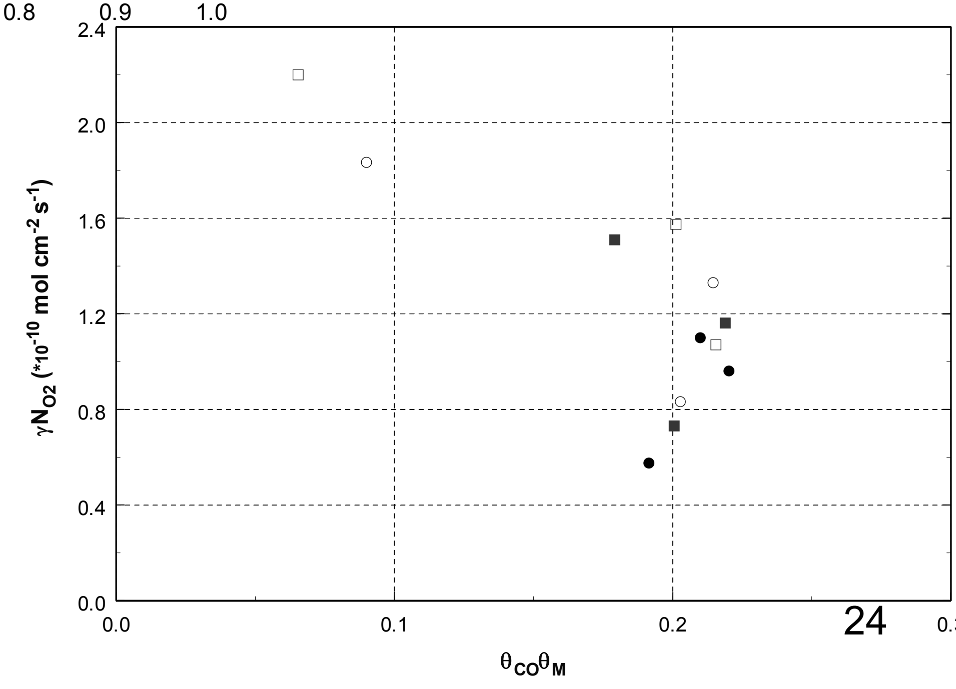
(2) $Pt + \tfrac{1}{2}\, O_2 \Leftrightarrow Pt\text{-}O \qquad r_2 = k_{f2}\ \theta_M\, (P_{o2})^{1/2} - k_{b2}\, \theta_o$

(3) $Pt\text{-}CO + Pt\text{-}O \rightarrow 2Pt + CO_2 \qquad r_3 = k_{f3}\ \theta_{co}\, \theta_o$



Oxygen adsorption is rate limiting for CO oxidation during Internal Air Bleed

- ● 25 μm MEA P(A/C)=101/101 kPa,
- ○ 25 μ m MEA P(A/C)=101/303 kPa,
- ■ 5 μ m MEA P(A/C)=101/101 kPa,
- □ 5 μ m MEA P(A/C)=101/303 kPa.

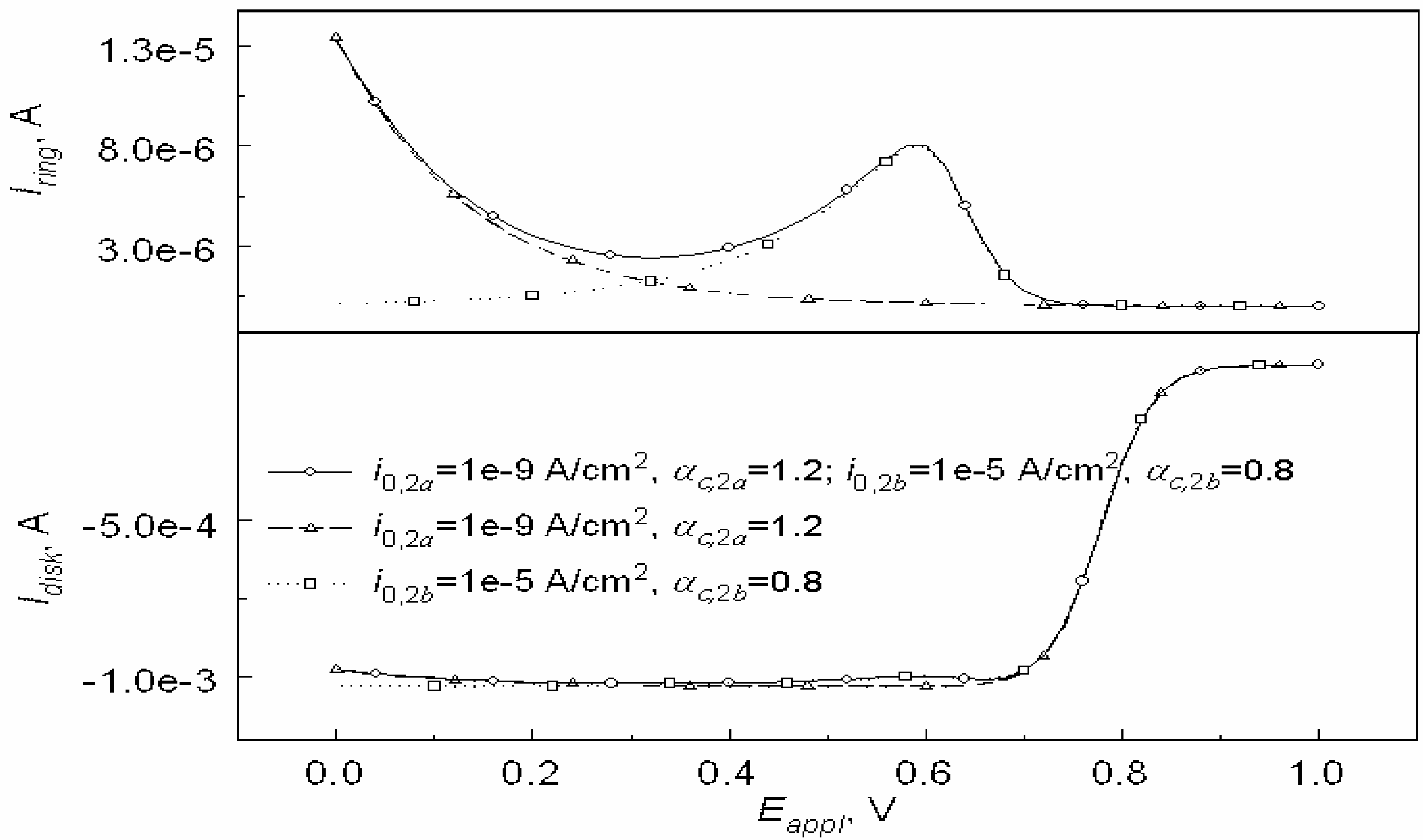


Project V: Using EIS and RDE to Study Pt Catalyst Aging

- This work focuses on the peroxide generation in the ORR system at an RRDE in an acidic environment, as peroxide is an unfavorable side product in the cathode of the PEM fuel cells, and it causes membrane degradation.

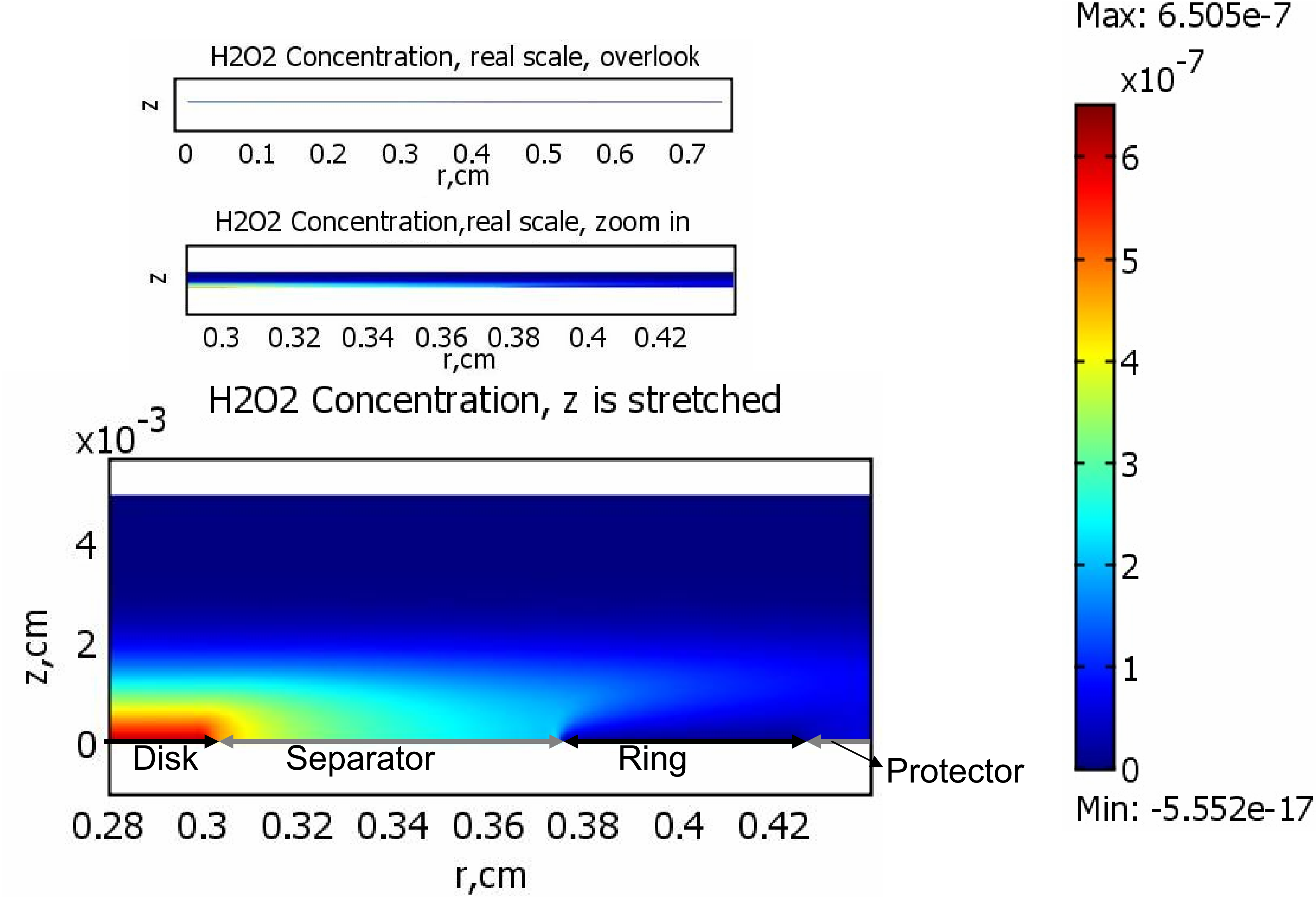
- The phenomena of the humps and the tails shown in the RRDE experimental polarization curves will be captured in terms of the reaction mechanisms.

Peroxide generation on different catalyst materials (a) and (b), with simultaneous 4 e⁻ transfer reaction



$i_{0,1}$=1e-9A/cm^2, α_{c1}=1.0, *no peroxide reduction and decomposition*

Peroxide concentration distribution near an RRDE surface: simulation results with a 2-D model



$i_{0,1}$=1e-9A/cm^2, α_{c1}=1.0, $i_{0,2}$=1e-5A/cm^2, α_{c2}=1.0,$i_{0,3}$=1e-17A/cm^2,α_{c3}=0.35, no peroxide decomposition , E_{appl}=0.5V

Project VI: Investigation of the Formation and Stability of Hydrogen Clathrate

Objectives

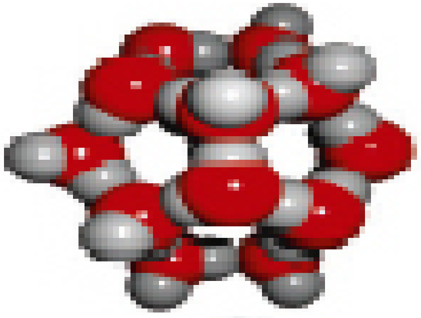
- to understand the mechanism of formation of hydrogen clathrates
- to evaluate the role played by additives (e.g. THF) in the stabilization of hydrogen clathrate

Methods

- molecular dynamics of rare events (umbrella sampling + order parameter)

- Hydrogen can be stored in cavities of structure II clathrates.
- Lee et al. Nature, 434, 743 (2005)

CAGE A



CAGE B

R. Radakrishnan et al. J. Chem. Phys. 117, 1786 (2002)
J. Delhommelle et al. J. Am. Chem. Soc. 126, 12286 (2004)

Project Safety

- The most significant hydrogen hazards associated with this project are:
  - High reactivity of solid chemical hydrides when exposed to humidified air
  - Toxicity: Avoid ingestion or contact with eyes and mucous membranes
- The approach to deal with this hazard is:
  - Handle hydrides in an inert atmosphere within a glove box
  - Use small quantities for laboratory experiments
  - Blanket reactor with inert gas