Project ID # FC22

# Applied Science for Performance, Cost, and Durability


**Jerzy Chlistunoff**
**Fernando Garzon**
**Christina Johnston**
**Yu Seung Kim**
**Bryan Pivovar (Point of Contact)**
**Tom Springer**
**Francisco Uribe**

Los Alamos National Laboratory
Institute for Hydrogen and Fuel Cell Research


May 17, 2006

This presentation does not contain any proprietary or confidential information

# Overview

### ***Time Line***

- Start: FY 05
- Status: ongoing

### ***Funding***

- Funding in FY05: $600 K
- Funding for FY06: $600 K
- Non-cost shared

### ***Barriers Addressed***

- **A. Durability**
- **B. Cost**
- **C. Electrode Performance**

### ***Collaborators***

- Brookhaven National Laboratory (HOR)
- Virginia Polytechnic and State University (Delamination)
- Lawrence Berkeley National Laboratory (Delamination)
- Other LANL investigators/projects and their respective collaborators (Impurities, FC 24; Non Nafion MEAs, FC 3)

# Objectives

- **To assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program in meeting cost, durability and performance targets by developing the fundamental understanding and the technical underpinnings of new, potentially enabling technologies .**

2005

**Develop/model reliable reference electrodes. (complete)**

**Model membrane-electrode delamination.**

**Investigate low humidity oxygen reduction reaction (ORR). (expanded)**

**Investigate high pH electrolytes. (abandoned)**

2006

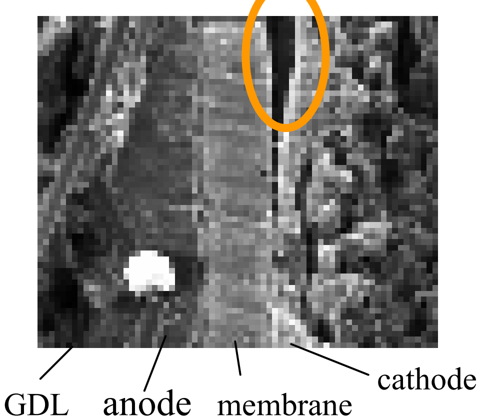
**Model membrane-electrode delamination.**

**Model hydrogen oxidation reaction (HOR) and ORR.**

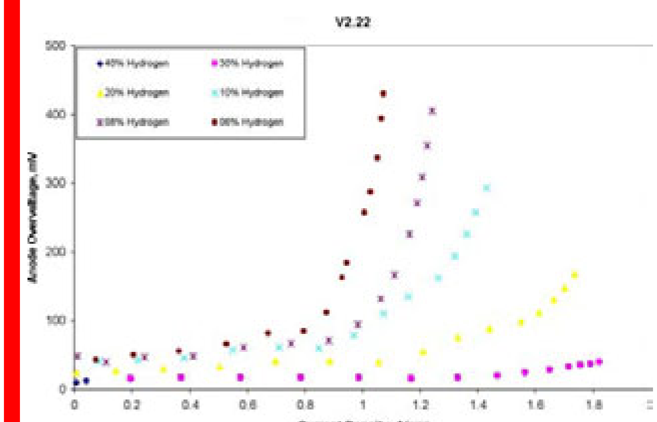
**Investigate the effect of the platinum-iomomer interface on ORR.**

# Approach (3 Thrusts)

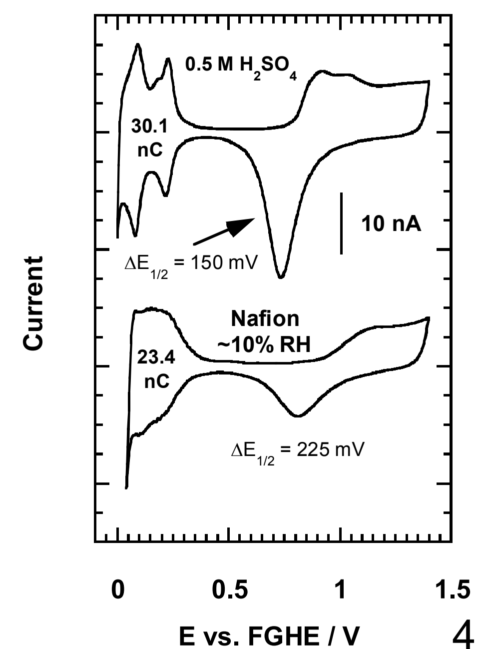
- **Membrane-Electrode Interfacial Delamination Model**
  - Refine a phenomenological and CFD model to explain observed membrane-electrode resistance based on electrode delamination.
  - Validate model using experimental results.




- **Refined Kinetic Models**
  - Develop models of the hydrogen oxidation reaction, that can be applied to loading (cost) and performance.
  - Validate model using experimental results.



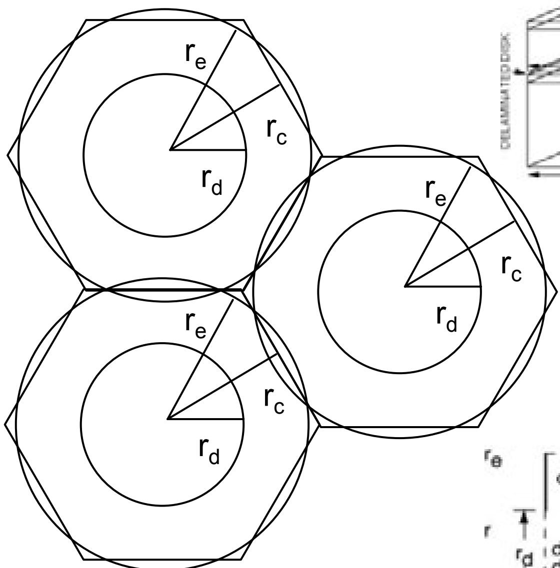

- **Effect of platinum-ionomer interface on ORR**
  - Investigate ORR as a function of relative humidity and ionomer type.
  - Use platinum micro-electrode and rotating ring disc electrode studies.

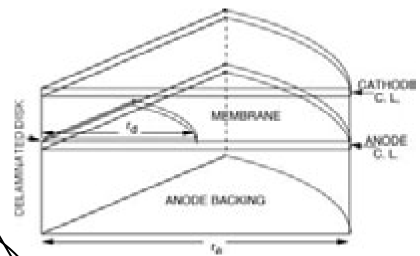


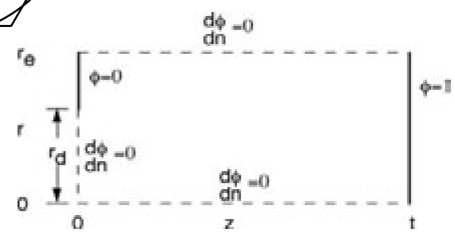
# Membrane-Electrode Delamination

(Springer, Kim, Pivovar)

We have correlated performance loss and durability to membrane-electrode delamination (see 2005 HFCIT Program Review).



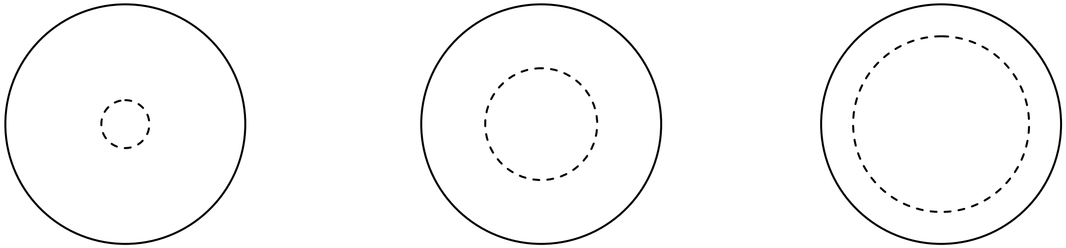



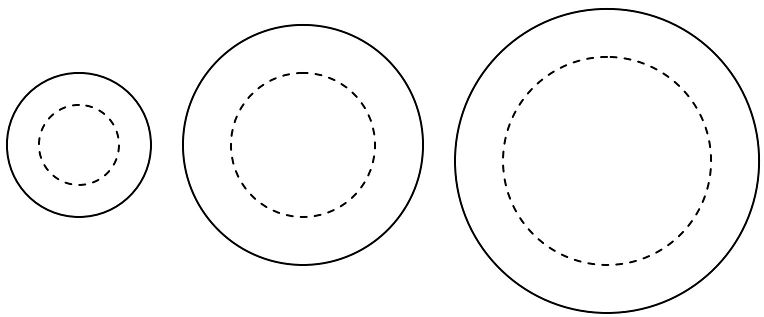
- Model uses cylindrical coordinates, based on hexagonal geometry.
- Two independent variables for calculations, the size of the delaminated area ($r_d$) and the distance between representative hexagons ($r_e$).
- Includes catalyst layer, backing and membrane.

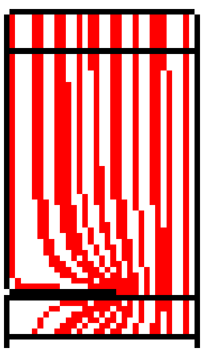
- Model verification will let us better understand the impact and time frame of interfacial resistance and develop strategies to mitigate these performance losses.

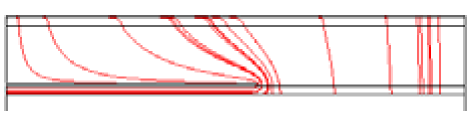
# Delamination Size and Fraction Delaminated



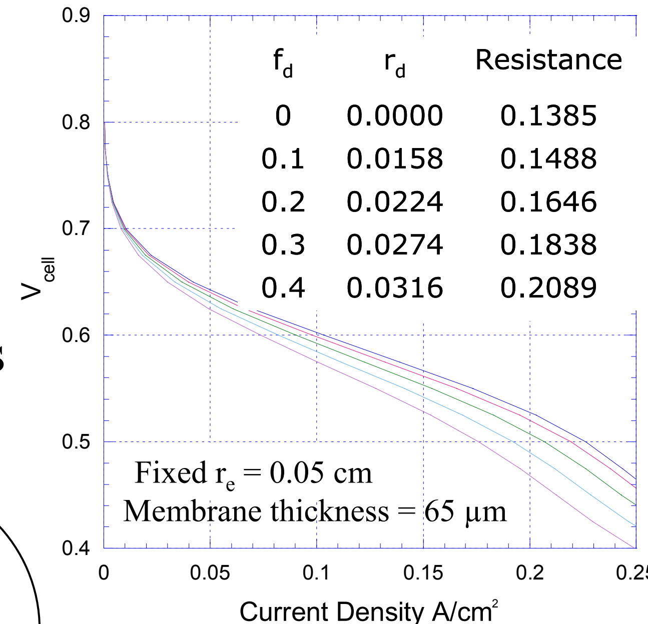
Increasing fraction delaminated (fixed spacing) leads to decreased performance and increased resistance.

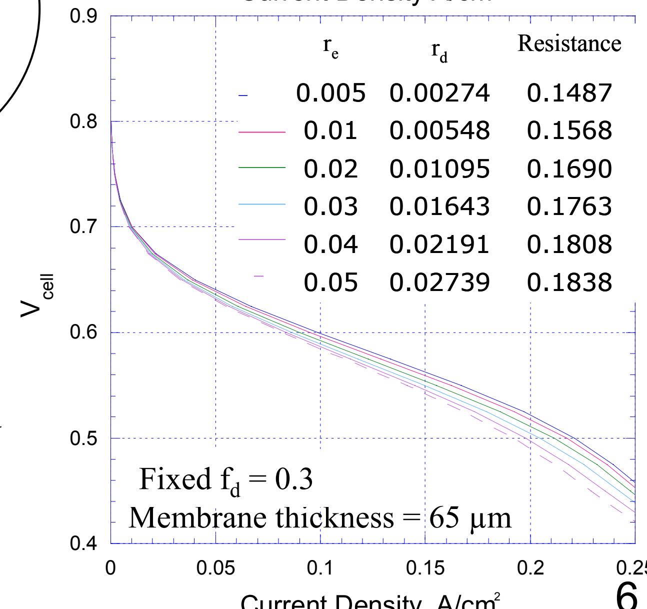




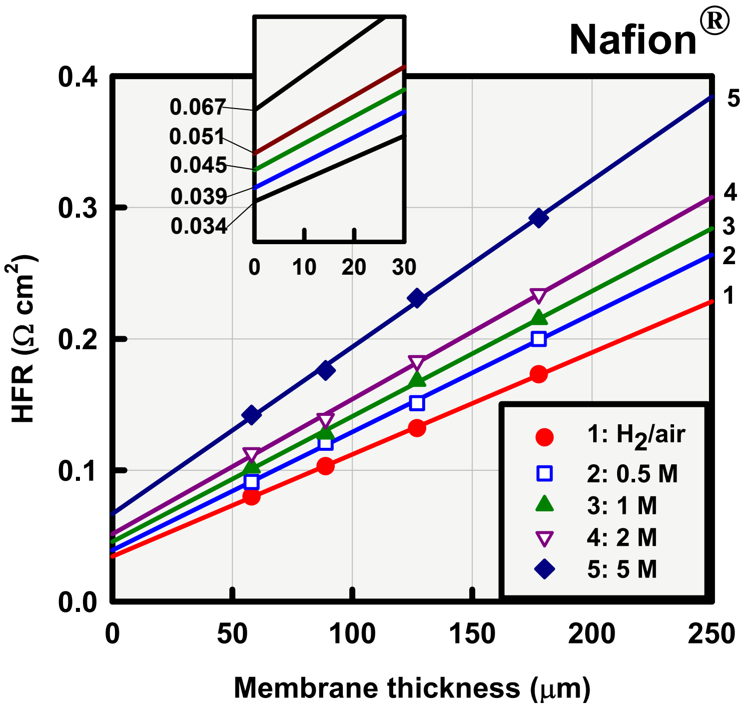


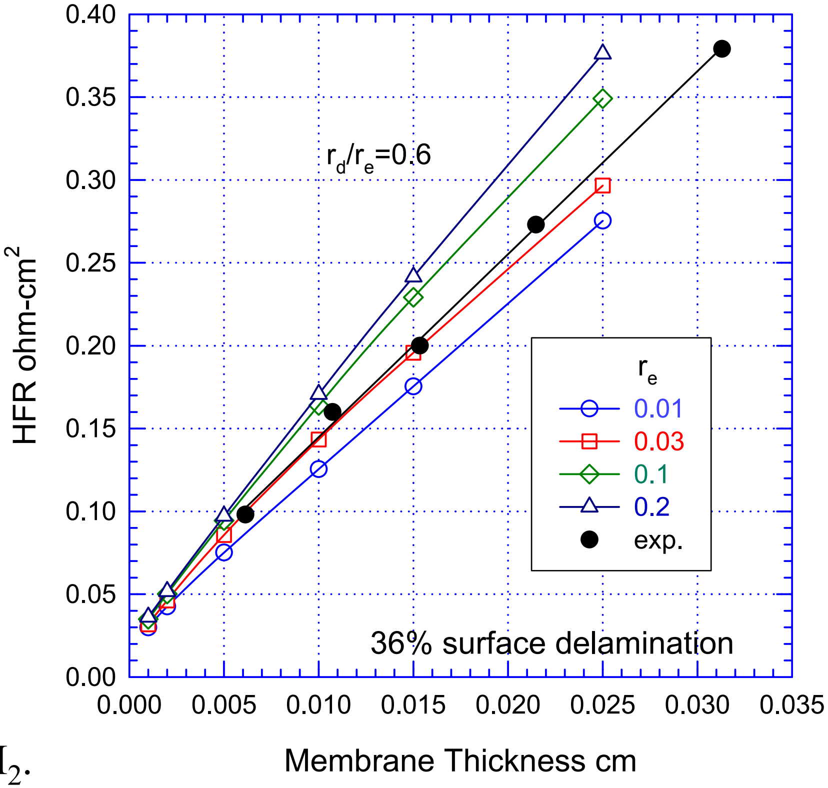
Increasing delamination size (fixed fraction delaminated) leads to decreased performance and increased resistance.



# Delamination Size and Fraction Delaminated



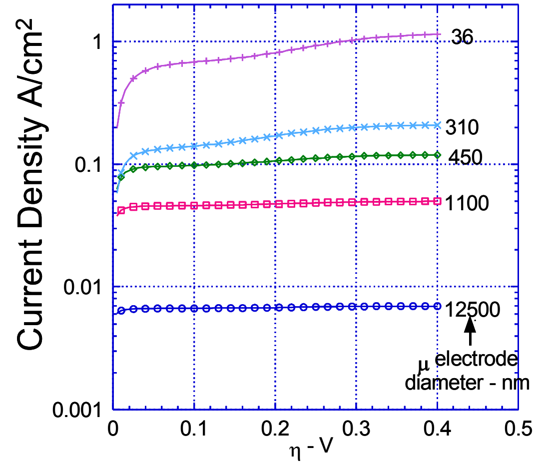

Experimental data show appreciable interfacial resistance (5 mΩ cm$^2$) of Nafion 1100 MEAs on $H_2$. Methanol has been found to accelerate delamination.

Delamination model can be used to estimate fraction of the surface delaminated and average (weighted) delamination size.

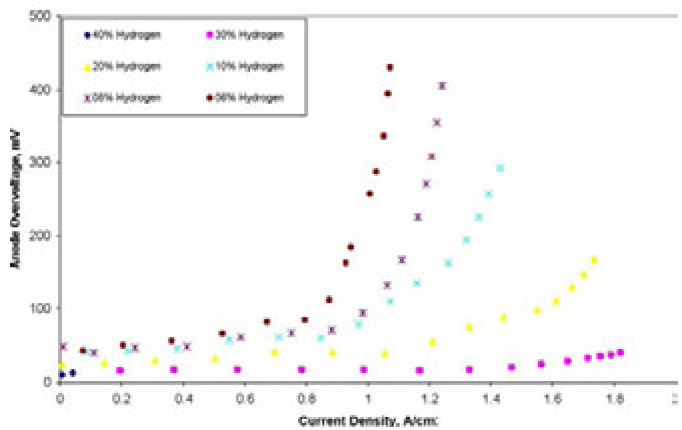
# $H_2$ REACTION KINETICS MODELING

(Springer, Garzon, Pivovar)

- Most fuel cell models use Butler-Volmer kinetics at the anode.
- These models cannot explain anode behavior at high overpotential of concern for low loadings, in dilute $H_2$ streams, and in the presence of impurities.
- In collaboration with Brookhaven National Lab we have helped elucidate anode kinetics by using Tafel-Volmer at low- and Heyrovsky-Volmer models at high-potential.

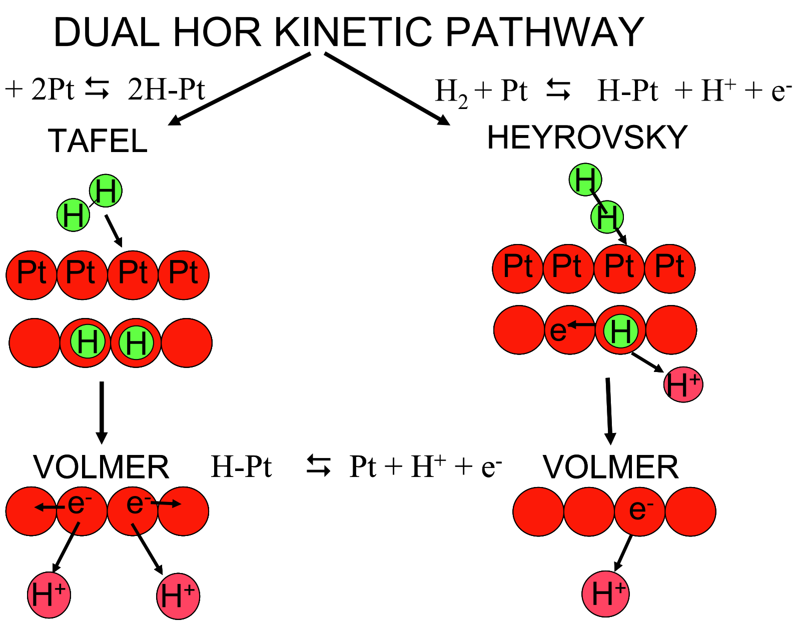



Chen and Kucernak, *J Phys Chem B*, **108**, 2004.



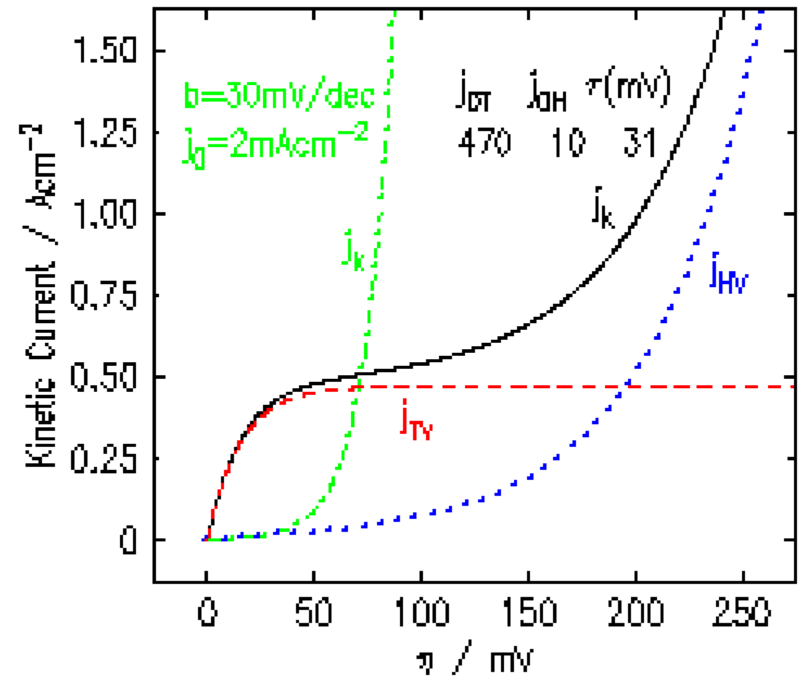

Unpublished LANL data

# Tafel-Heyrovsky Kinetics




$$j_{kinetic} = j_{0T}\left(1 - e^{-\frac{2F\eta}{\beta RT}}\right) + j_{0H}e^{\frac{F\eta}{2RT}};\ \beta \approx 1.2$$

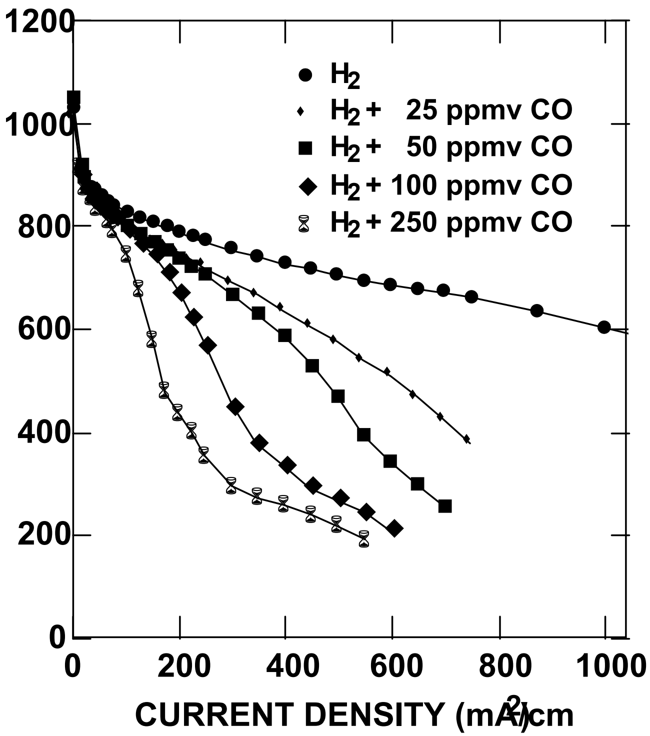
- Two exchange currents $j_{0T}$ (0.47 A/cm²) and $j_{0H}$ (0.01 A/cm²)

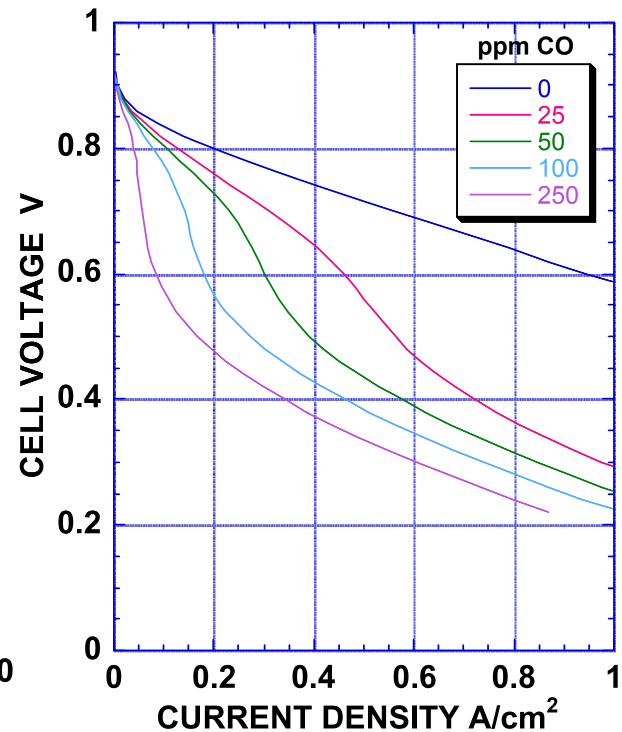



Wang, Springer, Adzic, *J. Electrochem. Soc*. (2006) in press.

Tafel-Heyrovsky kinetics can explain both low and high overpotential anode performance.

# CO Poisoning Effects




Complex polarization curves show good qualitative between model and experiment.

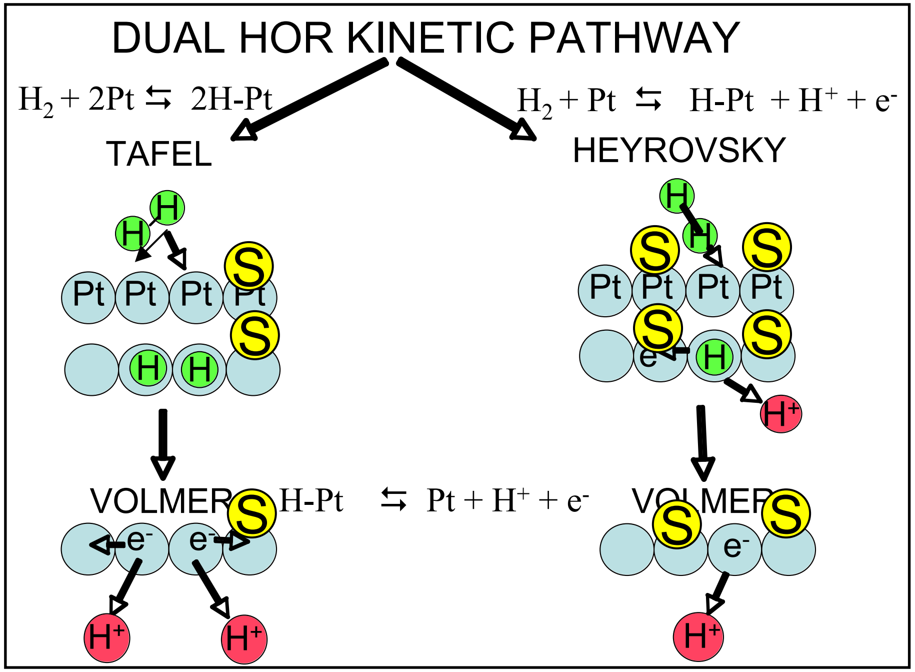
Relevant at low poisoning concentrations.

CO handled strictly by adsorption isotherm (no electrochemical oxidation).

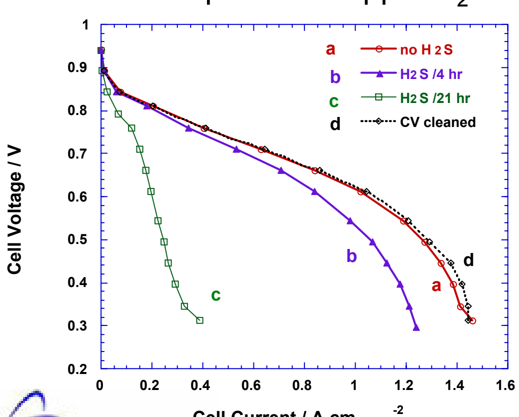
Isotherms/electrochemical oxidation need further study.

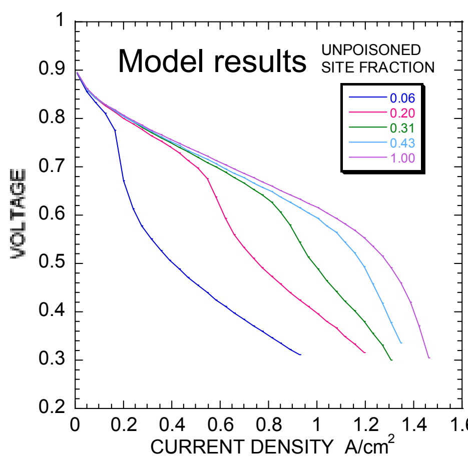
These types of analysis are critical for determining performance as a function of cost factors (loading and hydrogen purity).

# $H_2S$ Poisoning Effects




Cell exposed to 1 ppm $H_2S$




$H_2S$ handled by non-reactive surface coverage accumulating over time rather than equilibrium adsorption.

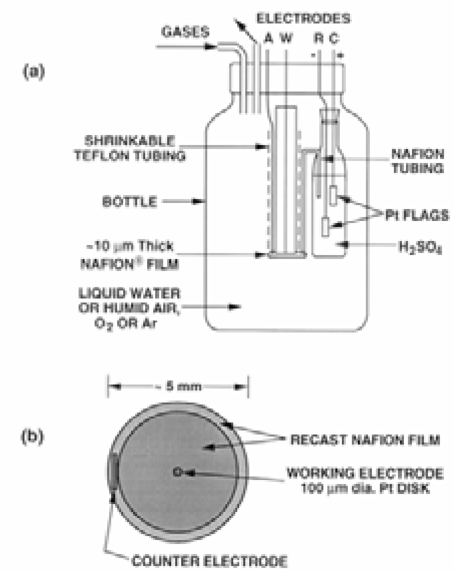
Complex polarization curves again show qualitative agreement between model and experiment.

Relevant at low poisoning concentrations, but dependent also on time.

Intermediate (experimentally obtained) surface coverage and correlation with (modeled) surface adsorbed sulfur are being pursued.

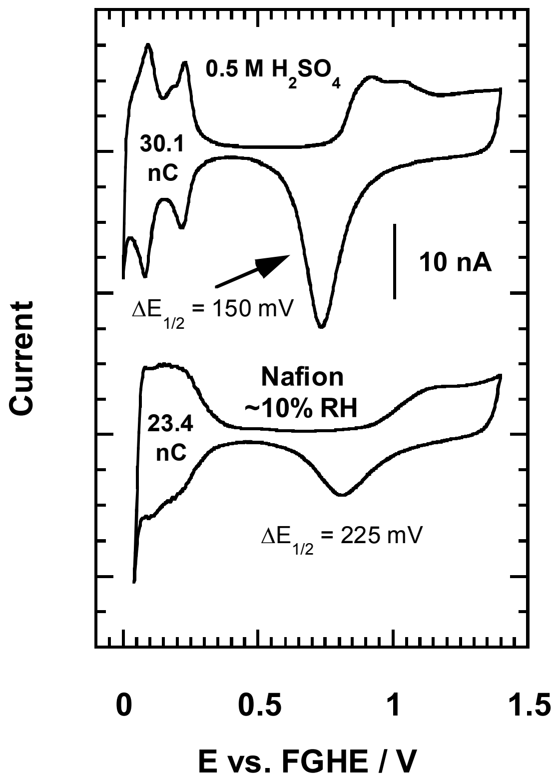
# Platinum-Ionomer Interface
## (Chlistunoff, Johnston, Kim, Uribe, Pivovar)

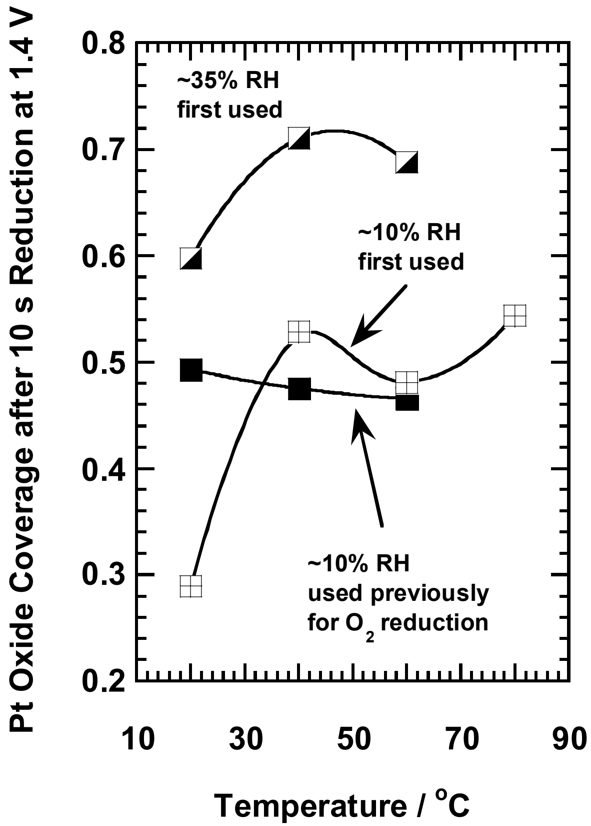
- Our[1] and other researchers[2] recent and historic evidence suggest ORR might be influenced by water availability and/or activity.
- This has significant implications when it comes to low humidity operation of fuel cells and the development of higher conductivity low RH membranes.
- When we began these studies, we found the platinum-ionomer interface is much more complex (temperature, humidity, ionomer) than is traditionally considered.
- We are using micro-electrodes and rotating ring disc electrodes to study the platinum-ionomer interface and its impact on ORR.




[1]F.A.Uribe et al, *J.Electrochem.Soc*. 139(1992)765.
J.Chlistunoff, et al, accepted for publication in *Transactions of the Electrochemical Society*
[2]H. Saffarian et al., *J. Electrochem. Soc*, 139 (1992) 2391.
M. Enayetullah et al., *J. Appl Electrochem*, 18 (1988) 763.
K. Neyerlin et. al., *J. Electrochem. Soc.*, 152 (2005) A1073.
H. Xu et al, *J.Electrochem. Soc.,* 152 (2005) A1828.

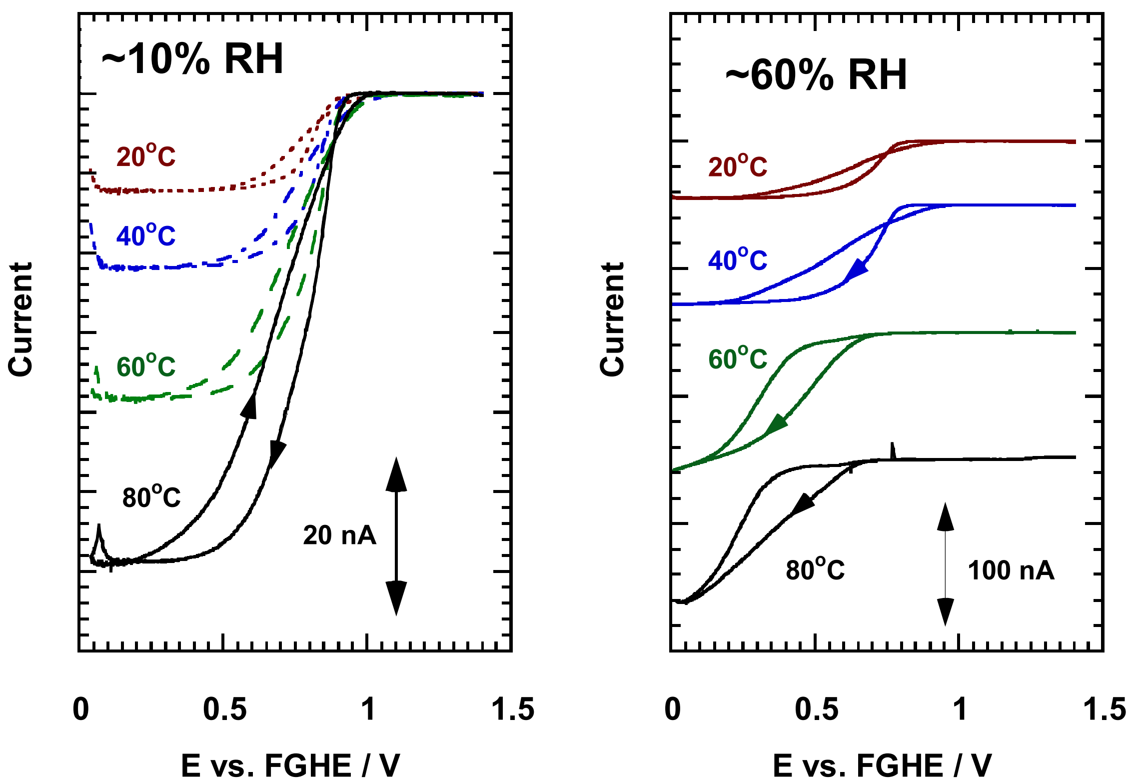
# Pt Accessible Catalyst Surface Area
## ($H_2SO_4$ vs. Nafion 1100 EW)



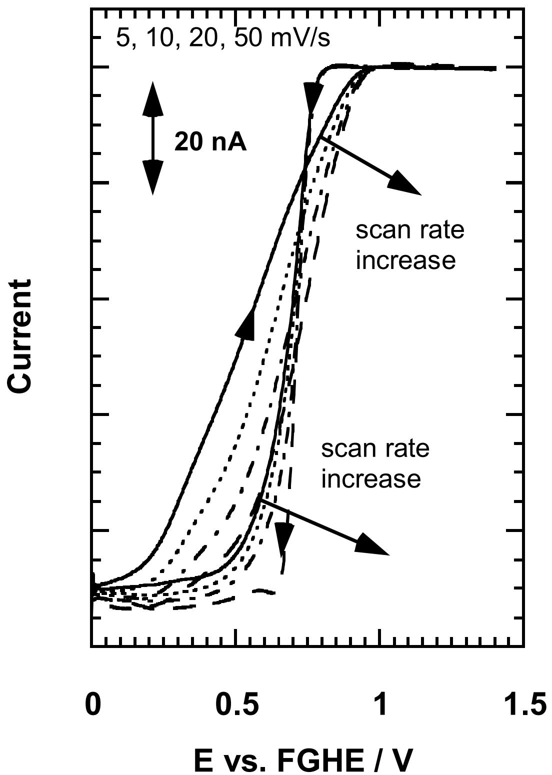

- **Cyclic Voltammetry (CV) highly dependent on electrolyte and reveals less Pt accessible in Nafion covered samples ($H_2$ adsorption/ desorption and Pt/PtO peaks)**
- **Trend for decreasing Pt access with decreasing RH.**

# RH and Temperature Effects on ORR
## (Nafion 1100 EW)

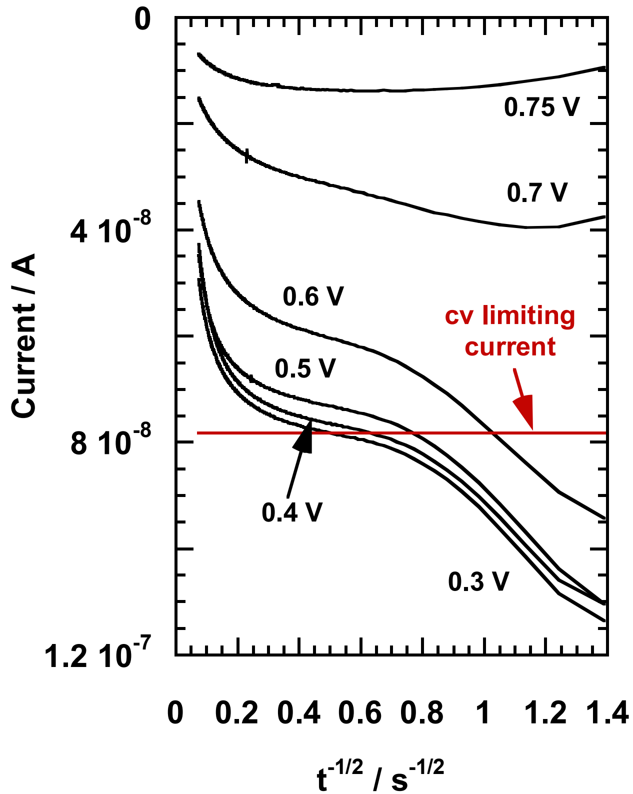



- **Ionomer reorganization (kinetic limitations) manifested by large hysteresis between forward and reverse scans and departures from symmetric sigmoidal shape**
- **Kinetic limitations increase with temperature and relative humidity**
- **RH studied: ~10%, ~35%, ~60%, and 100%.**

# Scan Rate Dependence and Chronoamperometry (Nafion 1100 EW)



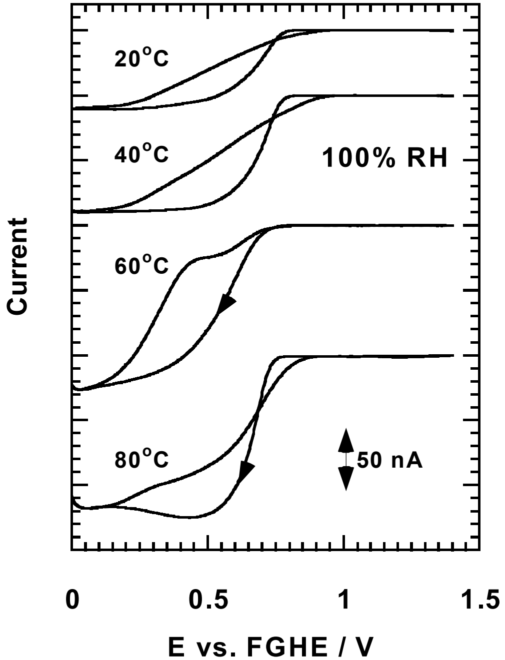

100% RH, 40°C
Voltammetry



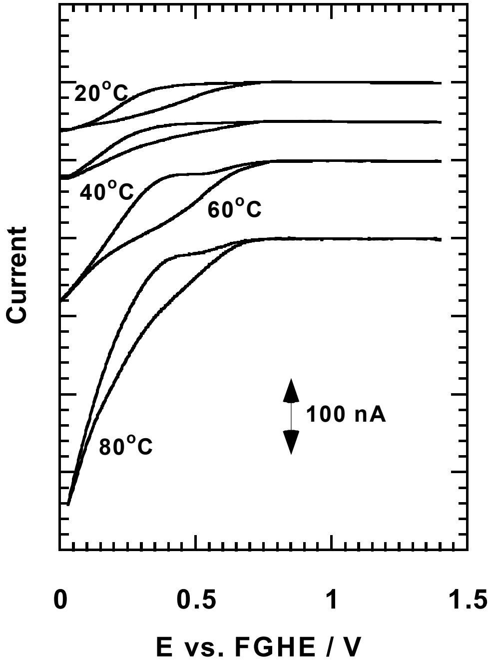

60% RH, 40°C
Chronoamperometry

- **CVs show scan rate dependence, although limiting current essentially unchanged.**
- **Chronoamperometry shows unsteady state performance near CV limiting current, but transient response with lower limiting current.**
- **Unsteady state performance also witnessed at higher overpotentials.**
- **Ionomer reorganization appears to be related to potential.**

# Ionomer Equivalent Weight Effects




Nafion® (EW 1100)
13.5 μm film



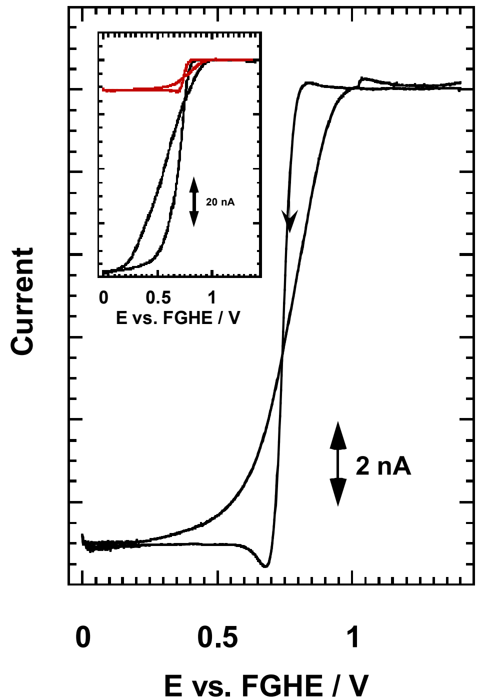

Nafion® (EW 950)
25.8 μm film

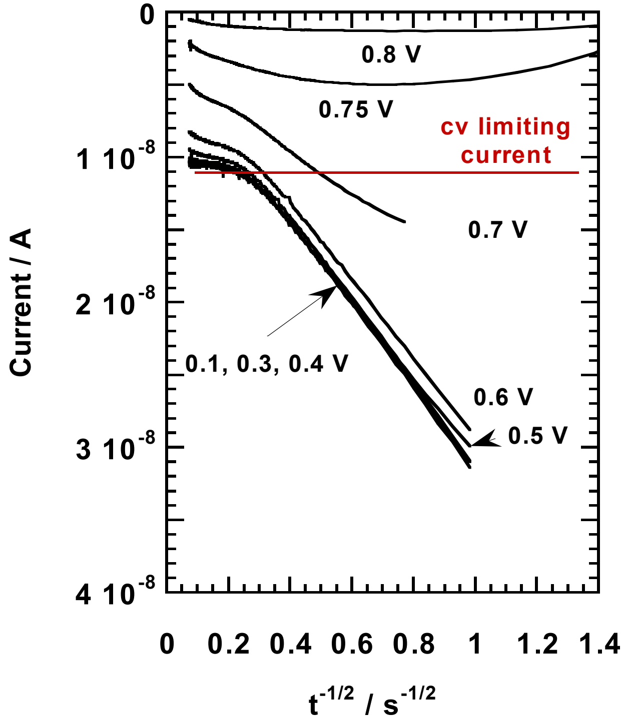
- **Higher ORR currents for the thicker Nafion® (EW 950) film indicate its higher permeability to oxygen**

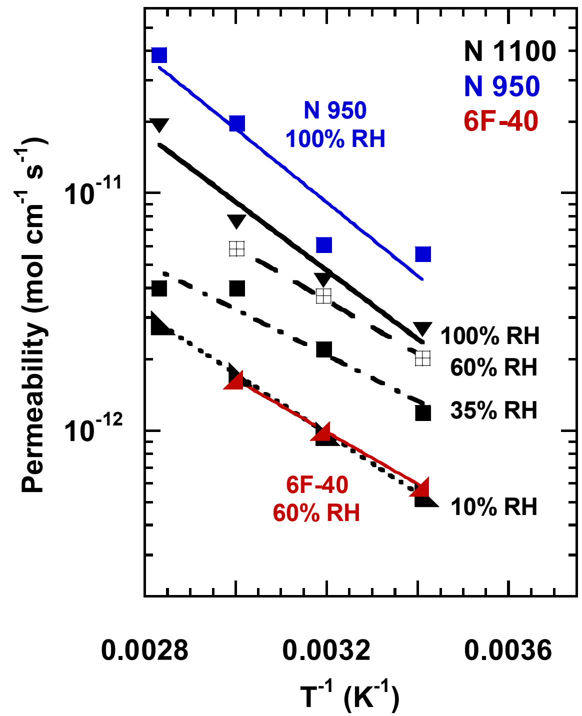
- **More severe distortions of voltammograms for Nafion® (EW 950) indicate its higher tendency to undergo restructuring.**

# Alternative Polymer Performance

60% RH, 40°C




- Lower ORR currents for the 6F-40 film indicate its lower permeability to oxygen
- Reduced surface restructuring from this stiffer wholly aromatic ionomer is evident from CVs and chronoamperometry.

- Micro-electrode studies also yield permeabilities.

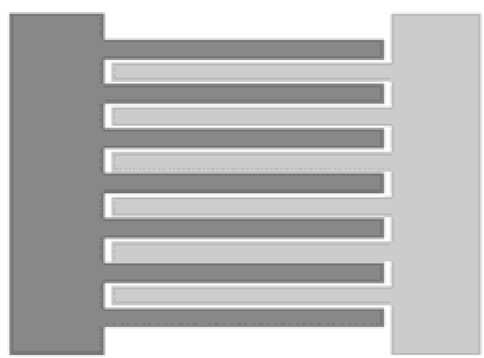
# Peroxide Generation

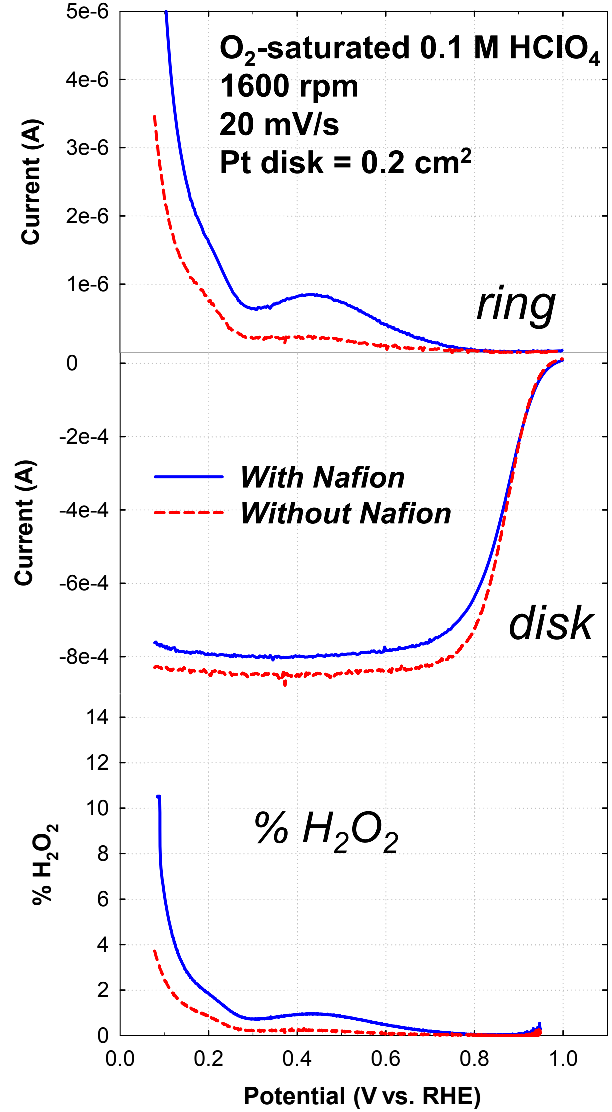
- Our initial attempts to generate micro-electrode arrays have met with limited success.

- We have used RRDEs to study peroxide generation with Nafion and without Nafion on polycrystalline Pt.

- While we have the uncertainty of the added electrolyted (0.1M $HCLO_4$) in these experiments, peroxide generation rates are significantly higher at start at lower overpotentials with the presence of Nafion.

- Future work with interdigitated arrays will allow us to study $H_2O_2$ generation without added electrolyte and at controlled RH.





# Future Work

- Delamination Model
  - Minimal (correlate performance losses with delaminations and prepare publication)
- Catalytic Models
  - Refine anode poisoning models, explore loading level influence, correspond with impurities task for hydrogen purity
  - Investigate cathode kinetics using similar models (explore Pt/PtO, PtO, PtOH, PtOOH intermediates and peroxide generation)
- Platinum-Ionomer Interface
  - Explore peroxide generation (previous slide)
  - Implement non-electrochemical techniques (neutron reflectivity, etc)
  - Extend studies to other polymer systems

# Project Summary

- Developed and validated a delamination model to explain membrane-electrode interfacial resistance, of particular interest for alternative ionomers.
- Developed a model for anode kinetics based on Tafel-Heyrovsky mechanism, applied this model with good qualitative agreement to fuel cells operated with hydrogen impurities.
- Applied micro-electrodes to the study of ORR on polycrystalline Pt, found Pt-ionomer interface depends on potential, RH, ionomer type and temperature.
- These approaches are leading to a better understanding of the effects of impurities, catalyst loading, ORR inefficiencies, and the enablement of novel ionomers that will help meet DOE fuel cell targets.

# Response to Reviewers Comments

- "Consider changing the (project) title"
  - We have changed the project title.
- "Suggest dropping plans for imidazole work."
  - We have abandoned this approach.
- "Strong case for relevance of delamination to practical fuel cell operation would have to be made to justify an extensive program."
  - The effort in this area was modest, and is in the process of concluding.

# Publications and Presentations

- Jia X. Wang, Thomas E. Springer, and Radoslav R. Adzic, "Dual-Pathway Kinetic Equations for the Hydrogen Oxidation Reaction on Pt Electrodes," *J. Electrochem. Soc*. (2006) in press.
- Jia X. Wang, Thomas E. Springer, and Radoslav R. Adzic, "Dual-Pathway Kinetic Equations for the Hydrogen Oxidation Reaction on Pt Electrodes,“ Electrochemical Society Meeting, Denver, CO, May 10, 2006.
- J.Chlistunoff, F.Uribe, B.Pivovar, "Oxygen Reduction at the Pt/Recast-Nafion® Film Interface at Different Temperatures and Relative Humidities" – accepted for publication in *Transactions of the Electrochemical Society.*
- J. Chlistunoff, F.Uribe and B.Pivovar, *Oxygen Reduction at the Pt/Recast-Nafion® Film Interface at Different Temperatures and Relative Humidities*., presentation at the 208th Meeting of the Electrochemical Society, Los Angeles, October 16 – 21, 2005.
- J. Chlistunoff, F.Uribe and B.Pivovar, *Oxygen Reduction at the Pt/Recast-Nafion® Film Interface. Effect of the Polymer Equivalent Weight*., presentation at the 209th Meeting of the Electrochemical Society, Denver, May 7 – 12, 2006.
- B. Pivovar, "LANL Fuel Cell Research: Freeze Studies and Fundamental Catalysis", Lawrence Berkeley National Lab, April 20, 2006.
- B. Pivovar, "Optimizing Alternative Polymer Performance in Fuel Cells," Pacific Polymer Conference IX, Ka'anapali, HI, December 12, 2005.

# Critical Assumptions and Issues

- Membrane-electrode delamination will be important.
  - We have found it to be important in fuel cell systems, although at a limited extent for today's commercial MEAs, still next generation ionomers/MEAs are likely to benefit from this increased understanding.
- Hydrogen quality or catalyst loadings may make anode overpotentials important
  - Hydrogen will likely contain trace impurities and ultra-low loadings may be used for cost savings.
- A better fundamental understanding of the Pt-ionomer interface can result in improved performance, better utilization or better durability.
  - Further improvements in traditional systems are unlikely without increased fundamental understanding.