

Applied Science for Electrode Cost, Performance, and Durability

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This presentation does not contain any proprietary or confidential information

Overview

Time Line

- Start: FY 05
- Status: ongoing

Barriers Addressed

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

Funding

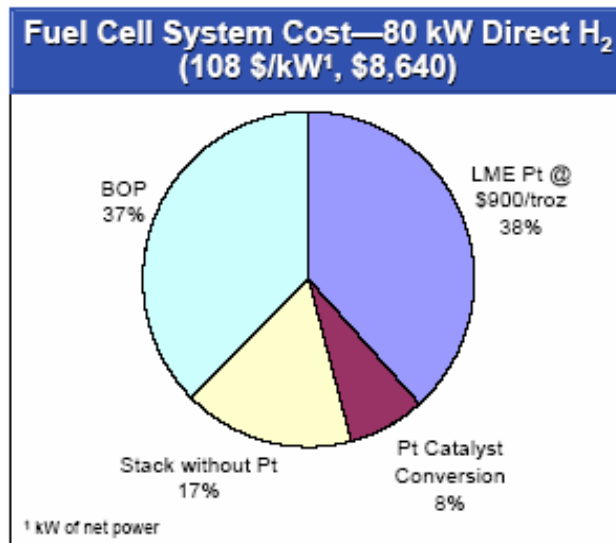
- Funding in FY06: \$600 K
- Funding for FY07: \$600 K
- Non-cost shared

Collaborators

- Brookhaven National Laboratory
- Case Western Reserve University
- Oak Ridge National Laboratory

Objectives

- **To assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program in meeting cost, durability and performance targets by addressing issues directly associated with electrodes (electrode science not specifically called out in latest call).**



Pt is primary limitation
on commercialization

http://www.hydrogen.energy.gov/pdfs/review06/fcp_36_carlson.pdf

Approach

2006

Model membrane-electrode delamination. (complete)

Model hydrogen oxidation reaction (HOR) and ORR.

Investigate the effect of the platinum-ionomer interface on ORR.

2007

Model ORR using reactive adsorption mechanism.

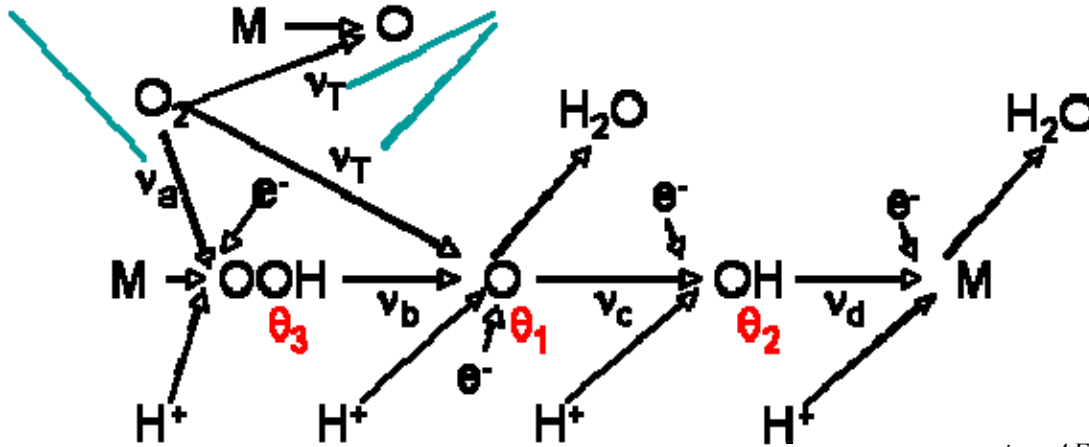
Use micro-electrodes and interdigitated micro arrays to study ORR and peroxide generation.

Elucidating catalyst utilization and durability of electrodes.

ORR using reactive intermediates

REDUCTIVE ADSORPTION

DISSOCIATIVE ADSORPTION



Comparisons of rate limiting step and isotherms suggest PtOH is dominant surface species.

Collaboration with Brookhaven National Lab.

$$j_{oT} = 4F\kappa_T; j_{oH} = 4F\kappa_H; j_{oV} = 4F\kappa_V; j_k = 2F(v_H + v_V) = 4F(v_H + v_T)$$

$$4Fv_T = j_{oT}c_r \left[(1-\theta_1)^2 - \left(\frac{1-\theta_1^0}{L_1(\theta_1^0)\theta_1^0} \right)^2 (L_1(\theta_1)\theta_1)^2 \right]$$

$$4Fv_H = j_{oH}c_r \left[(1-\theta_1)e^{\frac{-\eta F}{2RT}} - \frac{1-\theta_1^0}{L_1(\theta_1^0)\theta_1^0} L_1(\theta_1)\theta_1 e^{\frac{3\eta F}{2RT}} \right]$$

$$4Fv_V = j_{oV} \left[L_1(\theta_1)\theta_1 e^{\frac{-\eta F}{2RT}} - \frac{L_1(\theta_1^0)\theta_1^0}{1-\theta_1^0} (1-\theta_1) e^{\frac{3\eta F}{2RT}} \right] \quad (13)$$

$$j_k = j_{oT}c_r \left[(1-\theta_1)^2 - \left(\frac{1-\theta_1^0}{L_1(\theta_1^0)\theta_1^0} \right)^2 (L_1(\theta_1)\theta_1)^2 \right] + j_{oH}c_r \left[(1-\theta_1)e^{\frac{-\eta F}{2RT}} - \frac{1-\theta_1^0}{L_1(\theta_1^0)\theta_1^0} L_1(\theta_1)\theta_1 e^{\frac{3\eta F}{2RT}} \right]$$

$$j_{oT} = 4F\kappa_T; j_{oH} = 4F\kappa_H; j_{oV} = 4F\kappa_V; j_k = 2F(v_H + v_V) = 4F(v_H + v_T)$$

$$4Fv_T = j_{oT}c_r \left[(1-\theta_2)^2 - \left(\frac{1-\theta_2^0}{L_2(\theta_2^0)\theta_2^0} \right)^2 (L_2(\theta_2)\theta_2)^2 e^{\frac{4\eta F}{2RT}} \right]$$

$$4Fv_H = j_{oH}c_r \left[(1-\theta_2)e^{\frac{-\eta F}{2RT}} - \frac{1-\theta_2^0}{L_2(\theta_2^0)\theta_2^0} L_2(\theta_2)\theta_2 e^{\frac{5\eta F}{2RT}} \right]$$

$$4Fv_V = j_{oV} \left[L_2(\theta_2)\theta_2 e^{\frac{-\eta F}{2RT}} - \frac{L_2(\theta_2^0)\theta_2^0}{1-\theta_2^0} (1-\theta_2) e^{\frac{\eta F}{2RT}} \right]$$

$$j_k = j_{oT}c_r \left[(1-\theta_2)^2 - \left(\frac{1-\theta_2^0}{L_2(\theta_2^0)\theta_2^0} \right)^2 (L_2(\theta_2)\theta_2)^2 e^{\frac{4\eta F}{2RT}} \right]$$

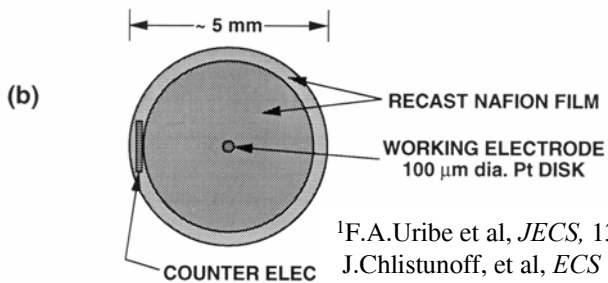
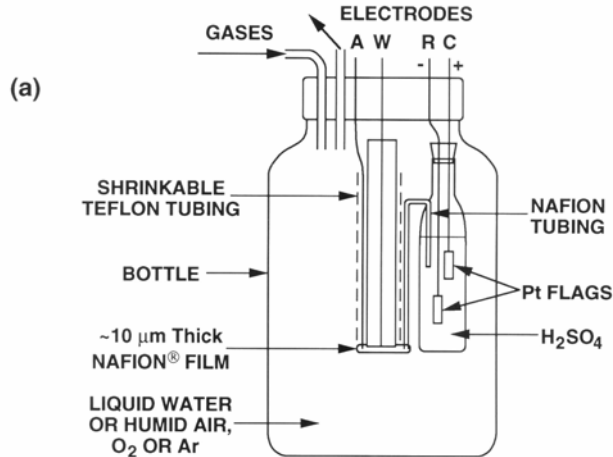
$$+ j_{oH}c_r \left[(1-\theta_2)e^{\frac{-\eta F}{2RT}} - \frac{1-\theta_2^0}{L_2(\theta_2^0)\theta_2^0} L_2(\theta_2)\theta_2 e^{\frac{5\eta F}{2RT}} \right]$$

PtO

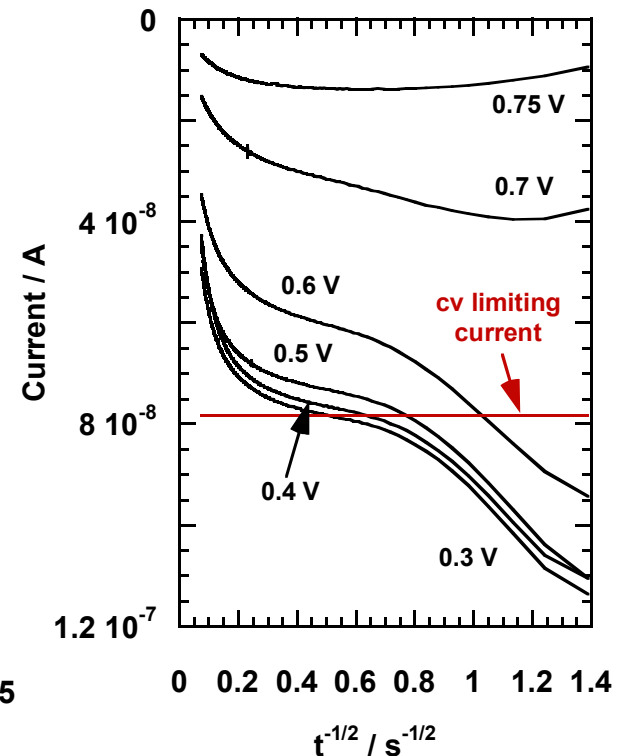
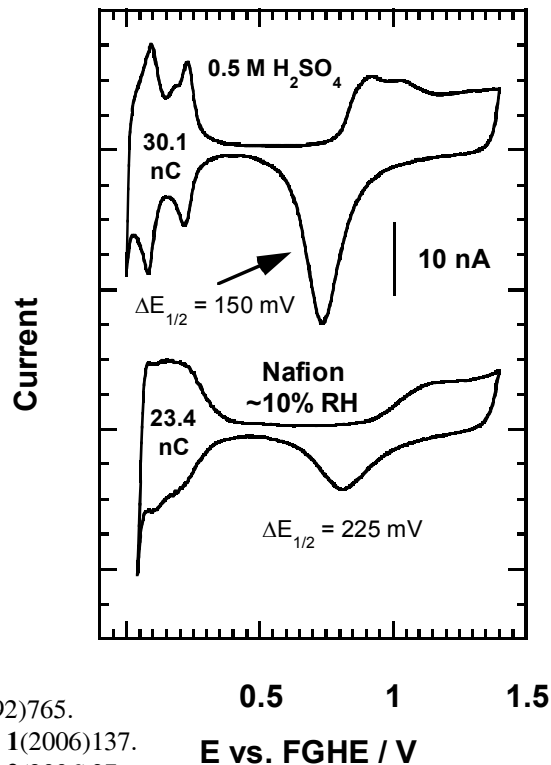
PtOH

Micro-electrode studies

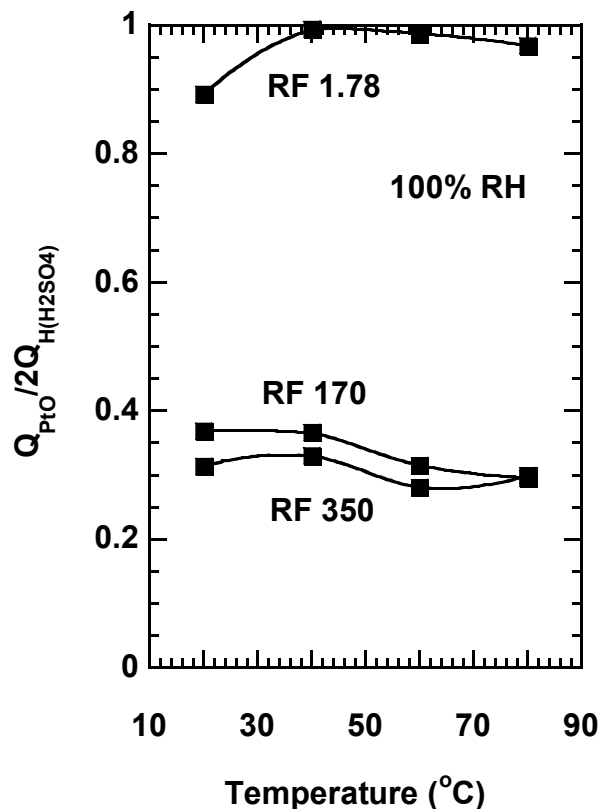
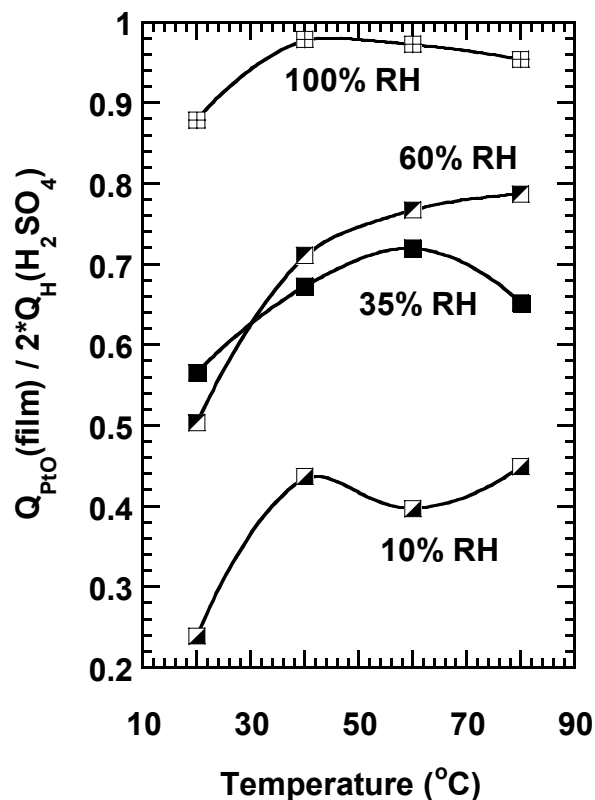
- We undertook micro-electrode studies to try to better understand the platinum-ionomer interface.
- The platinum-ionomer interface is much more complex/dynamic (temperature, humidity, ionomer) than is traditionally considered.



¹F.A.Urbe et al, *J ECS*, 139(1992)765.
 J.Chlistunoff, et al, *ECS Trans.* 1(2006)137.
 J.Chlistunoff, et al, *ECS Trans.* 2(2006)37.



Pt Accessible Catalyst Surface Area



- At 100% RH on smooth Pt surface, nearly all of the surface is accessible.

- Decreases in RH make significantly less of the surface available.

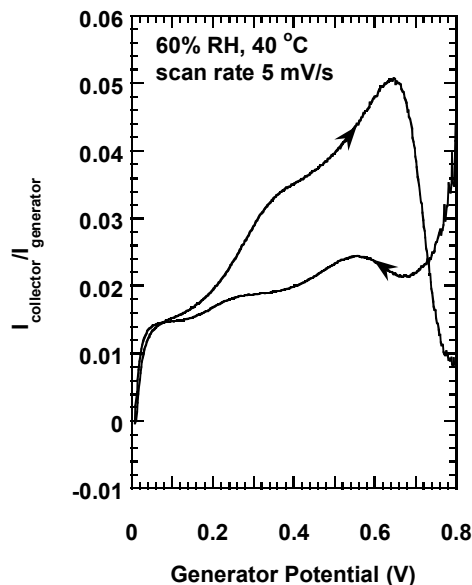
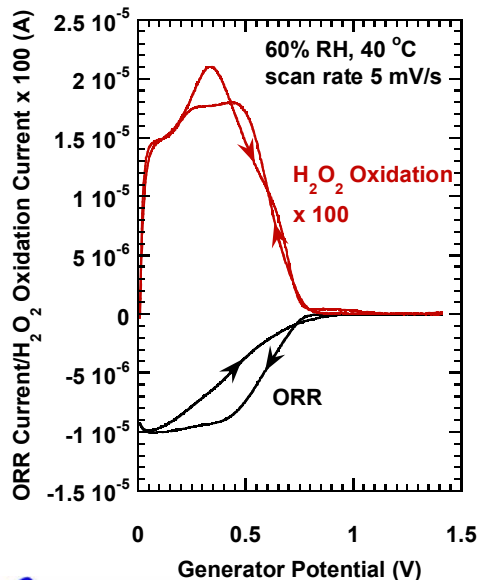
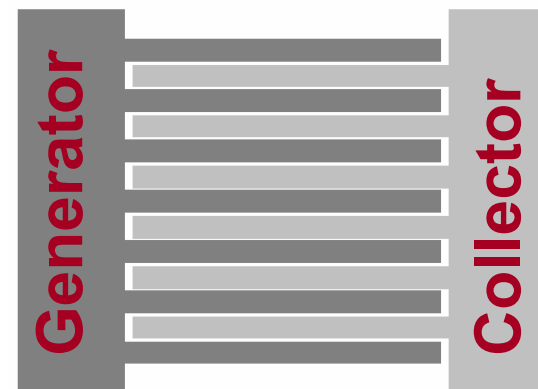
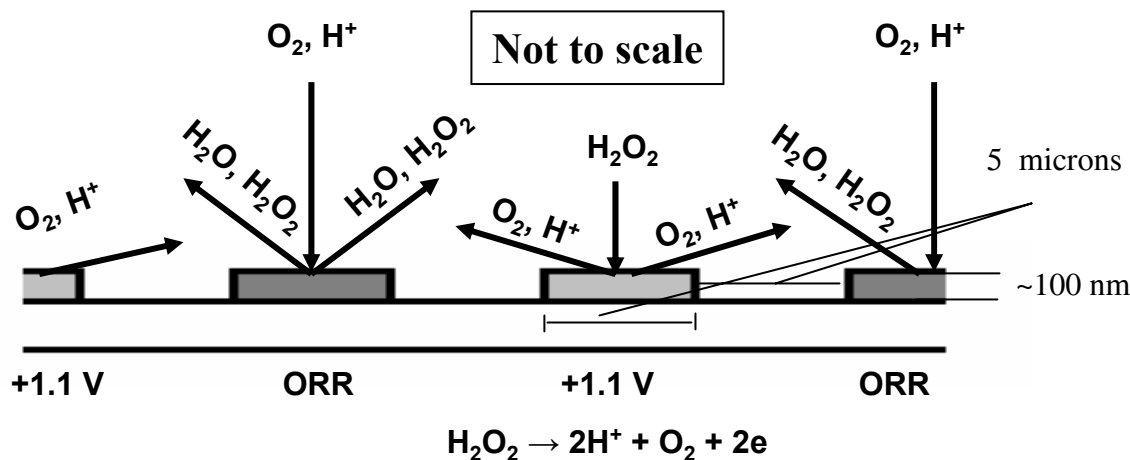
- Platinized (rough) surfaces show much lower available surface area, even at high RH.

- Pt reorganization/mobility is key.

*PtO reduction peak taken after 10 s at 1.4V

RF = roughness factor = Pt surface area/geometric area

Interdigitated Micro-Arrays for Peroxide Generation

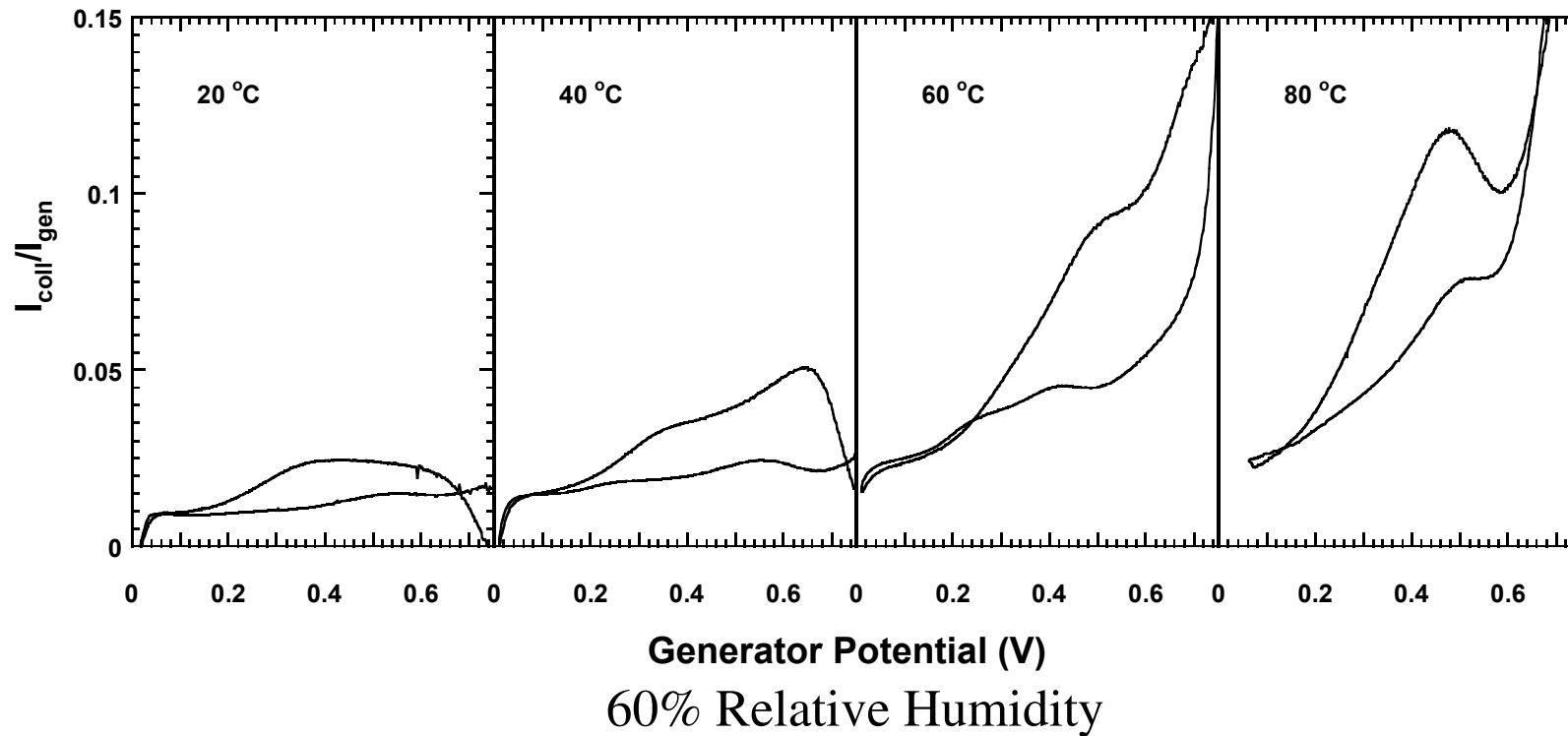


Restructuring of Nafion at the interface with smooth Pt results in increased peroxide generation in reverse scan.

Little exists in literature quantifying *in-situ* peroxide generation for fuel cells.

Temperature and RH effect on peroxide generation

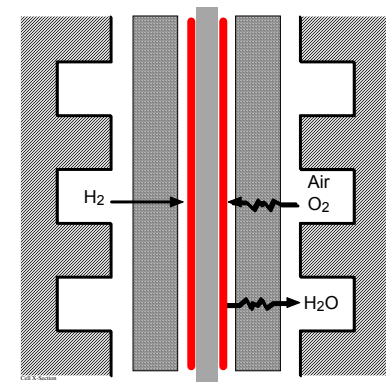
- Increasing temperature and relative humidity (not shown) lead to increasing relative peroxide generation, concordant with increased Nafion reorganization witnessed on micro-electrodes.



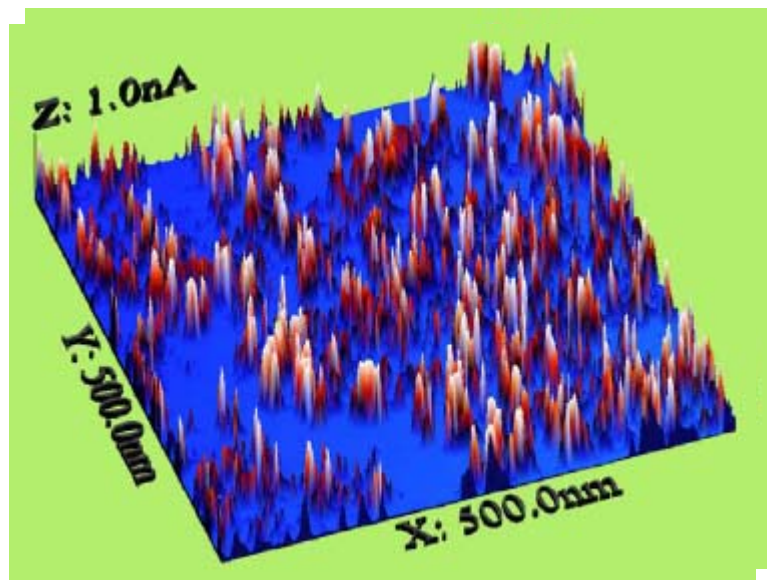
Electrode History

- ‘GE’ style electrode: Pt black steam-bonded to membrane with Teflon binder
- 1986: Raistrick (LANL): Impregnated catalyzed Prototech electrode (ELAT)
- 1990: Wilson (LANL): Intimately mixed ionomer/catalyst ink applied to membrane
- Mid 90’s – Present: Nanostructured electrodes (3M, carbon nanotubes)

Catalyst compositions often “empirically” optimized for best initial performance. New studies (microscopy, microelectrodes) have allowed further insight into microstructure.



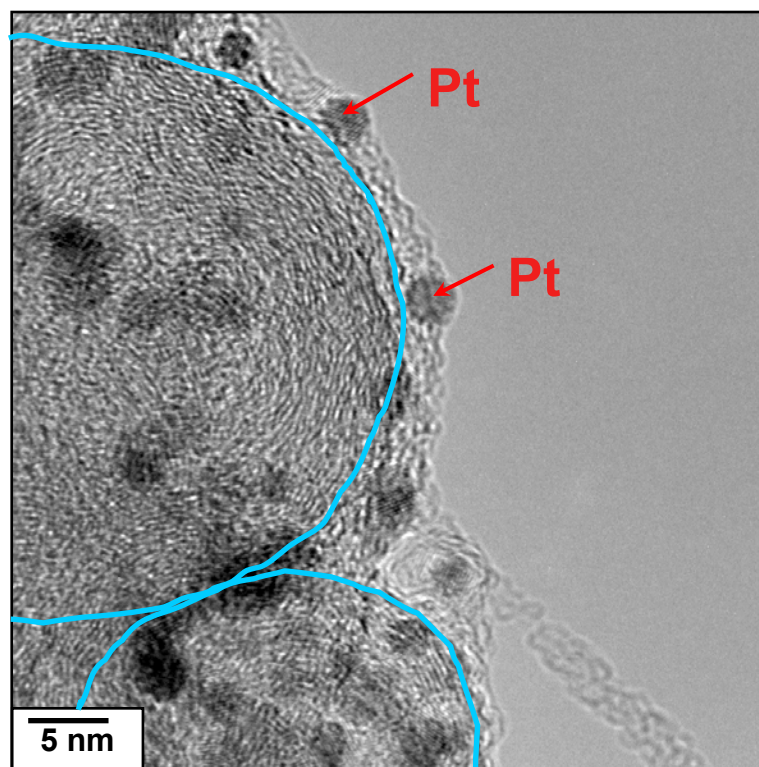
Microscopy



- Electrochemical AFM of a Nafion surface shows large dead domains to proton conductivity (changes with RH qualitatively agree with our microelectrode studies).

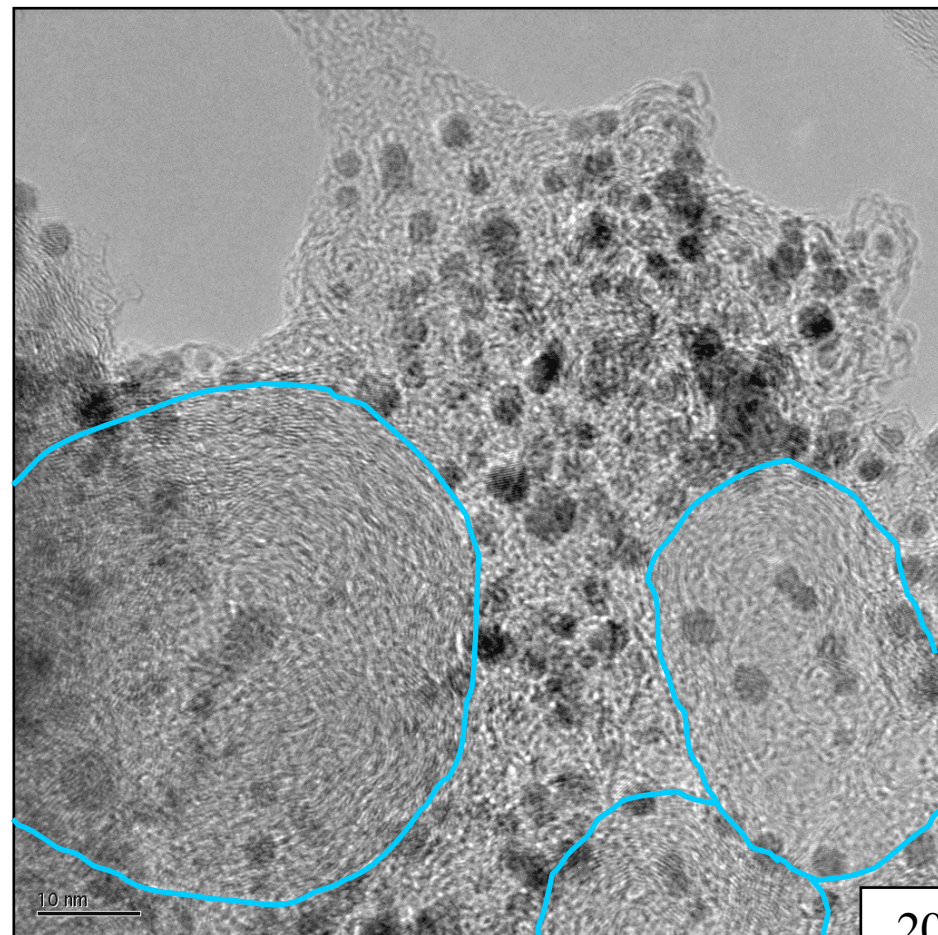
Emil Roduner, University of Stuttgart, Advances in materials for proton exchange membrane fuel cell systems Asilomar, CA, February 19 –22, 2007

- HR-TEMs have been able to show carbon, platinum, ionomer and pore space. Appearance of polymer doesn't guarantee ionic contact.

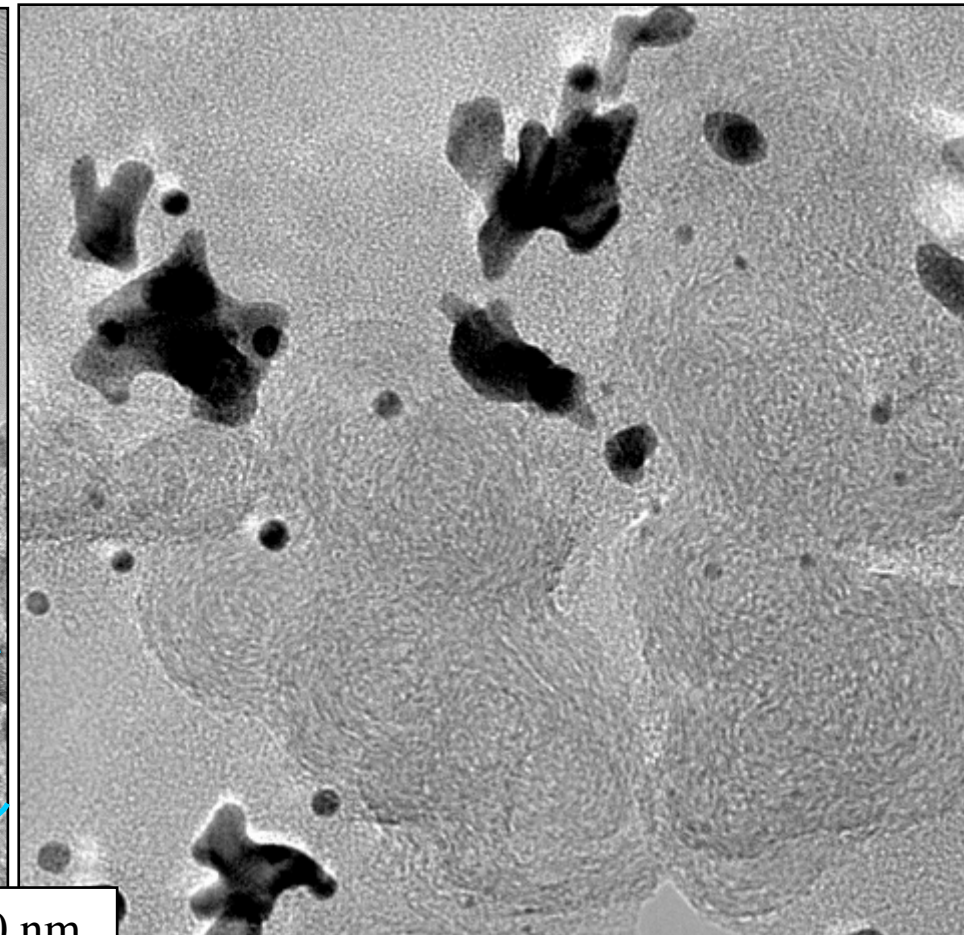


HR-TEMs of LANL MEA courtesy of Karren More, ORNL 11

Ionic/Electronic Conductivity - Durability



Fresh cathode Pt catalyst particles



Pt particles after 60°C cycling to 1.2 V

HR-TEMs courtesy of Karren More, ORNL

Electrode Questions

- How much of the catalyst is electronically or ionically isolated?
- How effectively is the catalyst that can be accessed being utilized?
- These factors impact performance and durability: What role does electrode design/processing play and can it be improved?

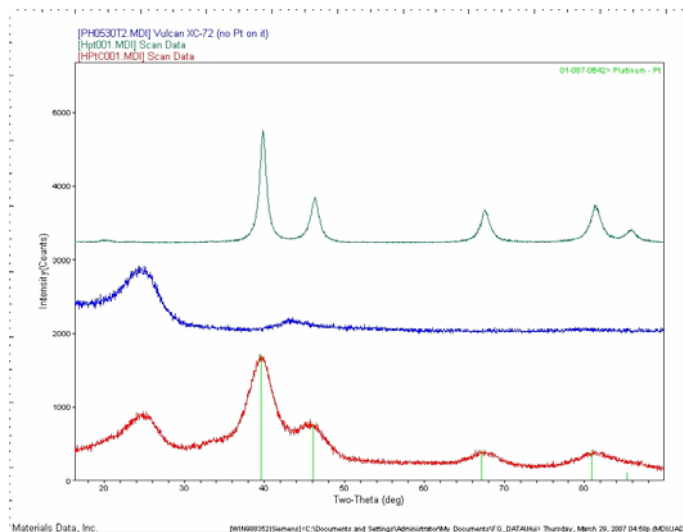
We ultimately care about performance per cost

Catalyst Utilization

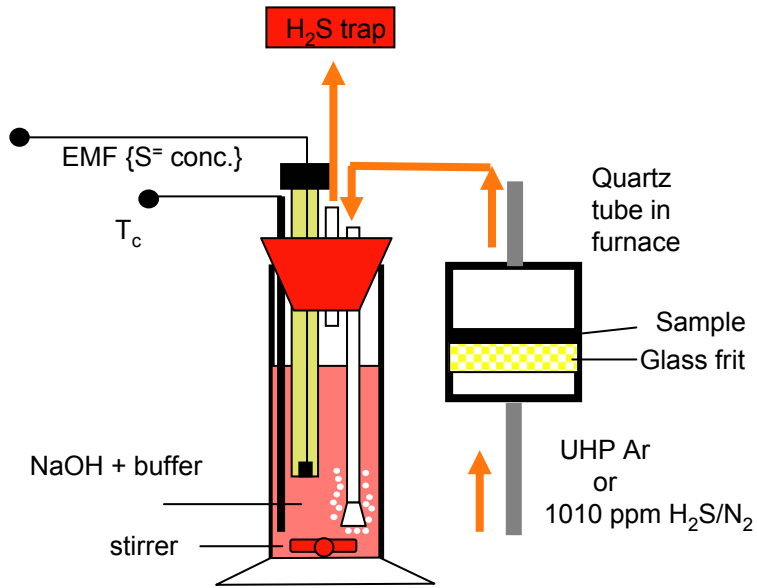
- Means different things to different people
 - Fraction of surface area accessible electrochemically
 - Use of accessible surface area
- Different measurements of surface area
 - X-Ray Diffraction, heterogeneous surface area measurements, half cell electrochemical techniques, fuel cell MEAs

XRD

Pt-carbon (**127 m²/g**)

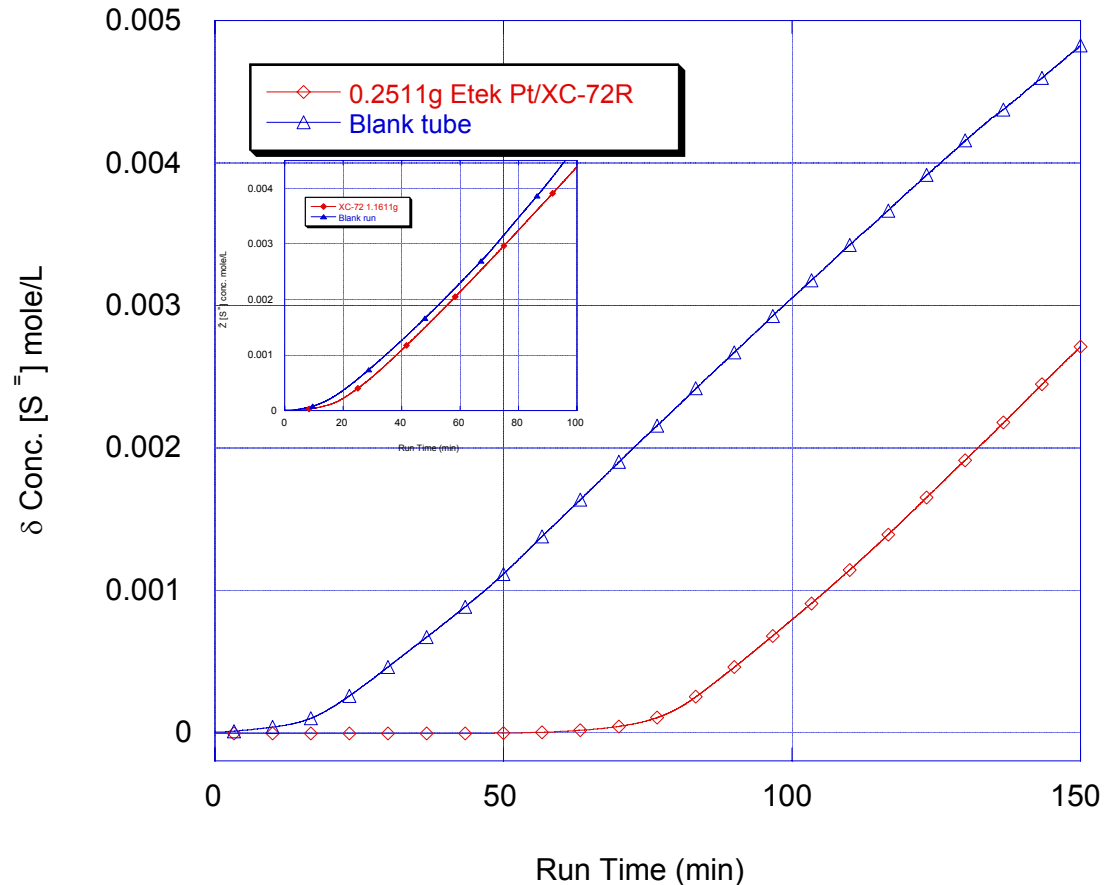


Heterogeneous Surface Area Probe



H₂S adsorption
 Pt-carbon (**110 m²/g**)

H₂S was found to be a good heterogeneous surface area probe.
 CO had difficulty as a probe. Gravimetry is also being explored.



Electrochemical Surface Area Probe

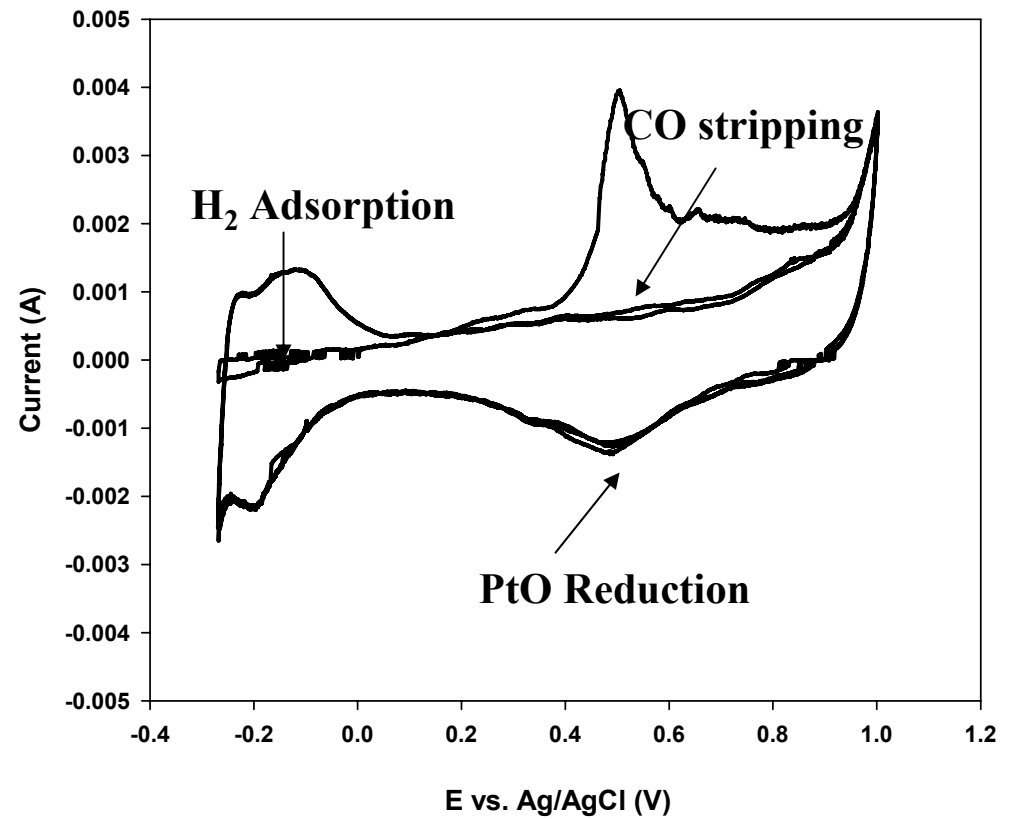
- Cyclic Voltammetry (CV) used to determine electrochemically accessible surface area
 - Wet half cell studies
 - MEA fuel cell studies
 - H₂ adsorption
 - PtO reduction
 - CO stripping
 - Loading
 - Scan rate (kinetics)
 - Processing

Pt-carbon with Nafion

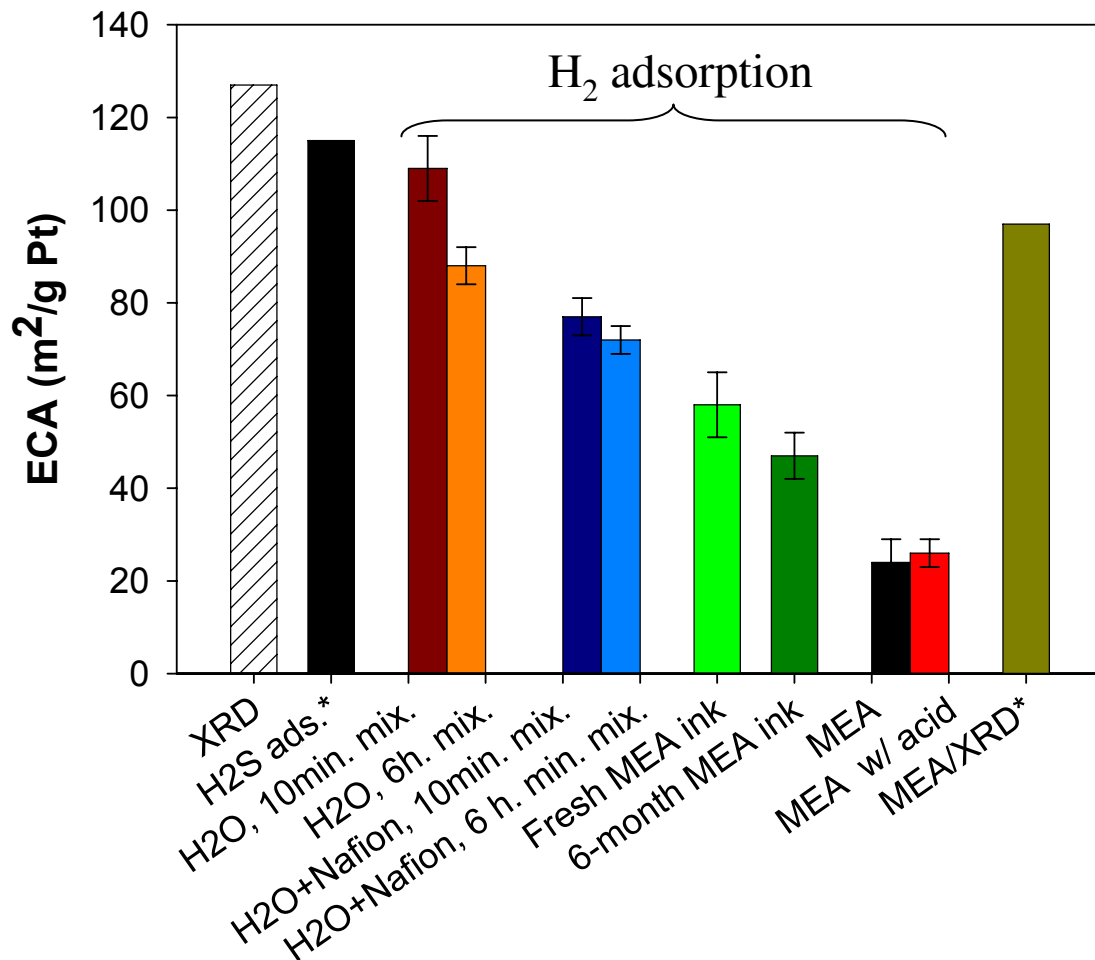
H₂ Adsorption (**75 m²/g**)

PtO Reduction (**86 m²/g**)

CO Stripping (**85 m²/g**)



Surface Area Dependence - Processing



- Here we present H₂ adsorption surface areas, CO stripping shows similar trends but slightly increased surface areas, PtO reduction is more complex.

- Measured surface area decreases as processing increases.

- MEAs have up to 4x lower surface area than those obtained by other techniques, suggesting loadings could be significantly reduced with improved design.

MEA composition in Wilson et al., *Electrochimica Acta*, 40, 1995, 355.

*Data taken from separate catalyst batch

Future Work

- Kinetic Studies
 - Discerning activity within accessible Pt (not all sites are equal), can accessible sites be made more active?
- Electrode Design/Processing Studies
 - Differences in processing of electrodes
 - Coupling performance and durability with structure
- Tool Development
 - AFM (phase mode plus conductivity/reaction)
 - Ionic/Electronic conductivity decoupling

Project Summary

- Micro-electrodes studies have shown the importance of the Pt-ionomer interface and ionomer reorganization on accessible catalyst surface area and peroxide generation.
- Roughened surfaces (perhaps more fuel cell like) have shown decreased ability of the ionomer to reorganize.
- We have characterized platinum surface area as a function of processing and shown significant decreases in surface area with composition and steps.
- Significant reduction in loading ($>4x$) might be achievable with little impact on performance and durability if the platinum in the electrodes could be utilized more efficiently.