PEM Fuel Cell Durability

2005 DOE Hydrogen Program Review

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Project #:
FC40

This presentation does not contain any proprietary or confidential information.

Overview

Timeline

2001: Project started as Fuel Cell Stack Durability on Gasoline Reformate

2004: Changed focus to concentration on PEM H_2 Durability

Barriers

- Durability (Barrier P)
- Electrode Performance (Barrier Q)
- Stack Material & Manf. Cost (Barrier O)

Budget

- FY04: $900 k
- FY05: $950 k

DOE Technical Targets (2010)

- Durability 5000 hours
- Precious metal loading (0.2 g/rated kW)
- Survivability (includes thermal cycling and realistic driving cycles)

Technical Objectives:
Quantify and Improve PEM Fuel Cell Durability

- Define degradation mechanisms
- Design materials with improved durability

- Identify and quantify factors that limit PEMFC Durability
  - Measure property changes in fuel cell components during life testing
    - Life testing of materials
      - Examine testing conditions, esp. drive cycle
    - Membrane-electrode durability
    - Electrocatalyst activity and stability
    - Electrocatalyst and GDL carbon corrosion
    - Gas diffusion media hydrophobicity
    - Bipolar plate materials and corrosion products
  - Develop and apply methods for accelerated and off-line testing
- Improve durability

Approach to Durability Studies

- Fuel Cell MEA Durability Testing and Study
  - Constant roltage/current/power and power cycling (drive cycle)
    - 5 cm^2, 50 cm^2 and full-size active area (200 cm^2) stack
    - VIR / cell impedance
    - catalyst active area
    - effluent water analysis
- *in situ* and post-characterization of membranes, catalysts, GDLs
  - SEM / XRF / XRD / TEM / ICP-MS / neutron scattering / H_2 adsorption
- Develop and test with off-line and accelerated testing techniques
  - Potential sweep methods
  - Environmental component testing and characterization (GDL)
  - *in situ* XRD
  - Component interfacial durability property measurements
  - Membrane thinning and analysis

DOE Review Meeting
Reviewer Comments

FY2004 Reviewer Comments (Scores of 4 Outstanding and 1 Good)

- The team seems to have the big picture well understood, which consequently elevated its capability to do this analytical focused project

Strengths

- Important work about durability
- Excellent project execution with comprehensive set of tasks

Weaknesses

- Did not show any collaboration outcome even with LANL group

FY2003 Reviewer comments:

- The durability objective of this project is very important and I hope it will be actively addressed.
- I especially like the proposal of operating the system in a duty cycle operating mode.
- Introduction of drive cycle dynamics and start-up for next year is a plus …
- **Need more fundamental work.**

Interactions/Collaborations

- Fuel Cell Materials
  - MEAs (3M, Gore, LANL)
  - GDLs (Spectracorp, Toray, SGL, ETEK)
  - Catalysts (ETEK, SMP)
- Supporting measurements/interactions

  Augustine Scientific (Chris Rulison – Contact angle)

  Oak Ridge National Laboratory (Karren More– TEM / SEM/EDS)

  Celanese Ticona (Rong Chen - SEM)

  LANL - NMT Division (Dave Wayne ICP/MS, Laser Ablation)

  LANL - LANSCE (Jaroslaw Majewski, Eric Watkins - Neutron Reflectivity)

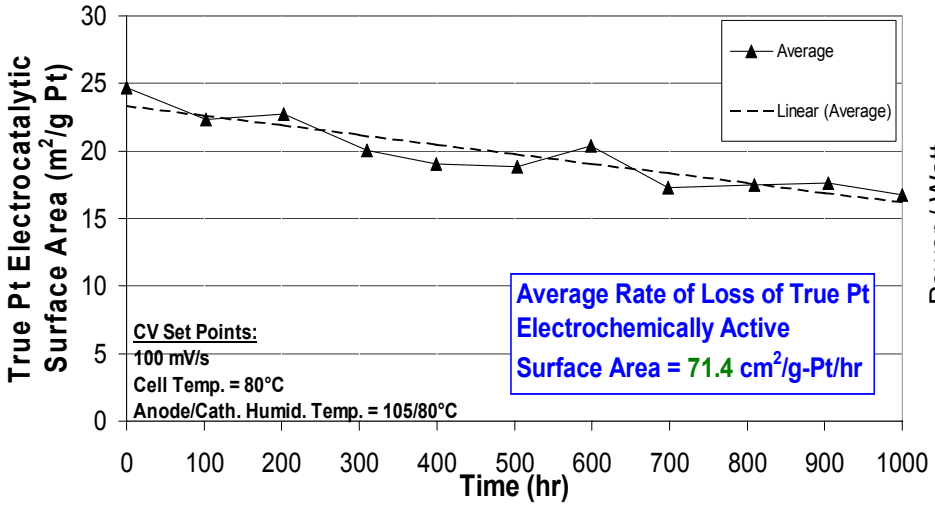
  UNM (Plamen Atanassov – ICP/MS, Ion chromatography, Washburn Adsorption)

  NREL (Tony Markel – Fuel Cell Vehicle Drive Cycle)
- Stack: Teledyne Energy Systems

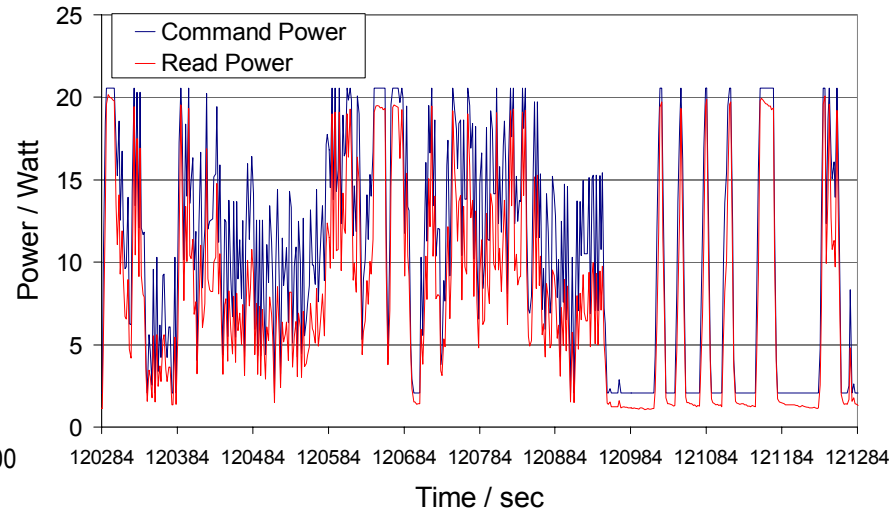
Electrocatalyst Durability

Durability testing shows loss of active Pt surface area

Catalyst Surface Area During Constant Power Operation



Drive cycle 'controls' power



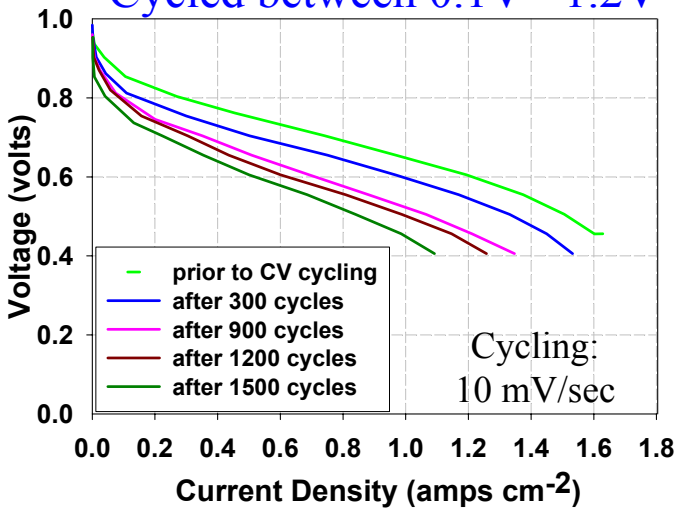
- Catalyst surface area decreases during testing
  - Pt Particles increase in size

- Drive Cycle testing shows faster degradation than steady-state testing
  - Greater Pt Surface Area Loss
  - Larger Pt Particle

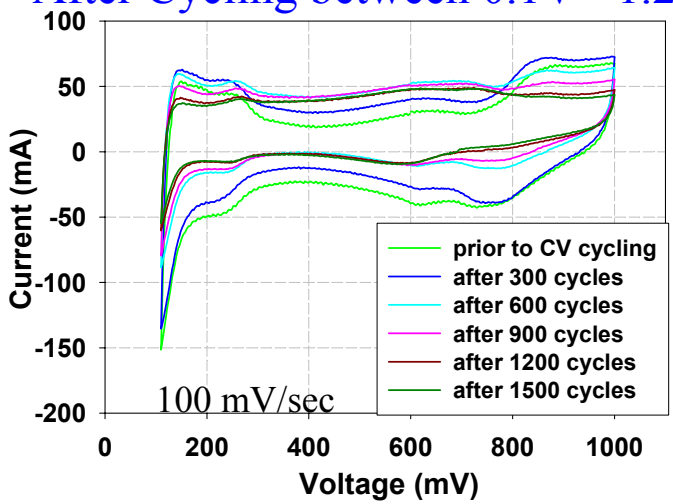
Fuel cells in automotive applications cycle in power

Electrocatalyst Durability
Potential Cycling Measurements

Polarization Curves For Fuel Cell Cycled between 0.1V - 1.2V



Characterization CVs After Cycling between 0.1V - 1.2V

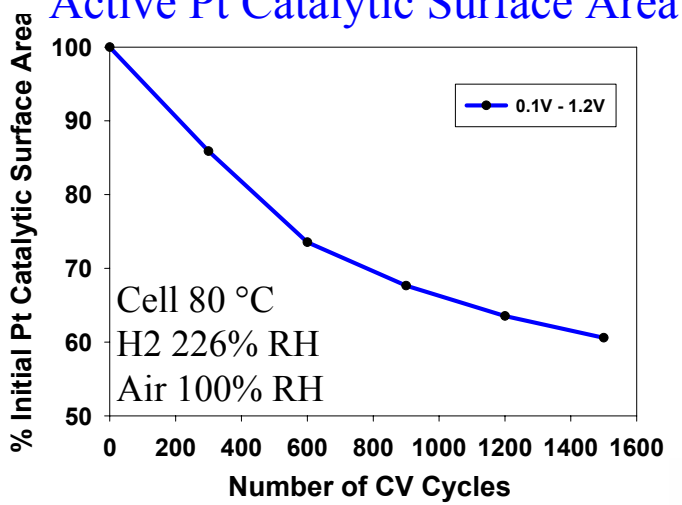


- Potential cycling:
  - Simulates drive cycle
  - Accelerated catalyst aging

Variables Examined:

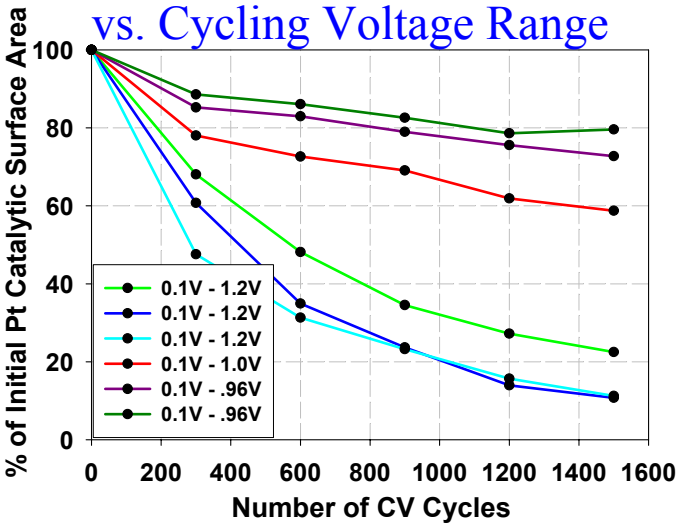
Potential Range
Temperature
Cycles vs. Time (Scan Rate)
Relative Humidity
Catalyst Loading

Active Pt Catalytic Surface Area

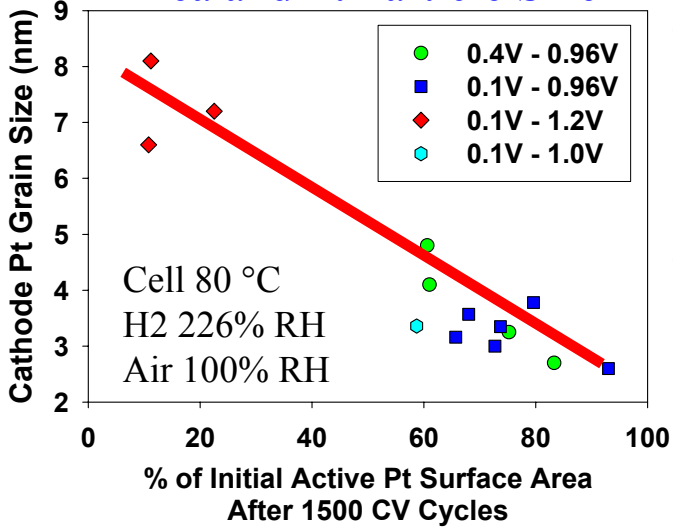


Potential & Temperature Effect on Catalyst Growth

Active Pt Catalytic Surface Area vs. Cycling Voltage Range

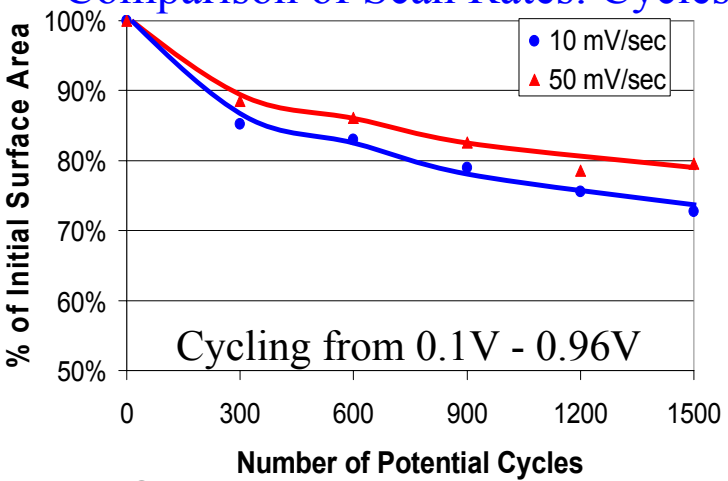


Correlation Between Pt Surface Area and Pt Particle Size

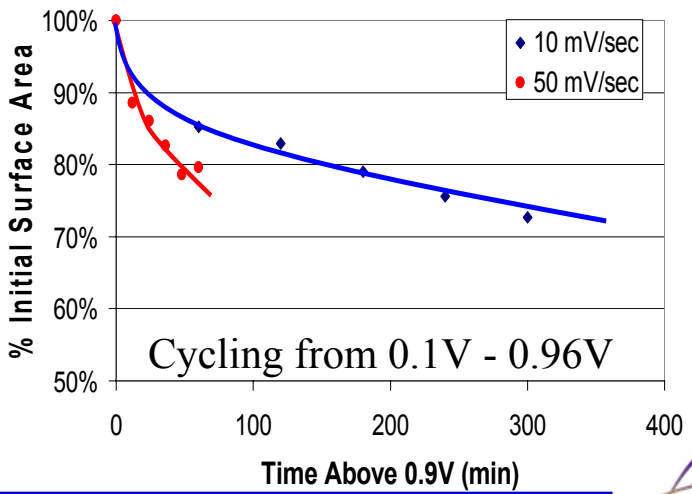


- Peak potential has large effect on particle growth
- Direct relation between XRD particle size and surface area

Comparison of Scan Rates: Cycles



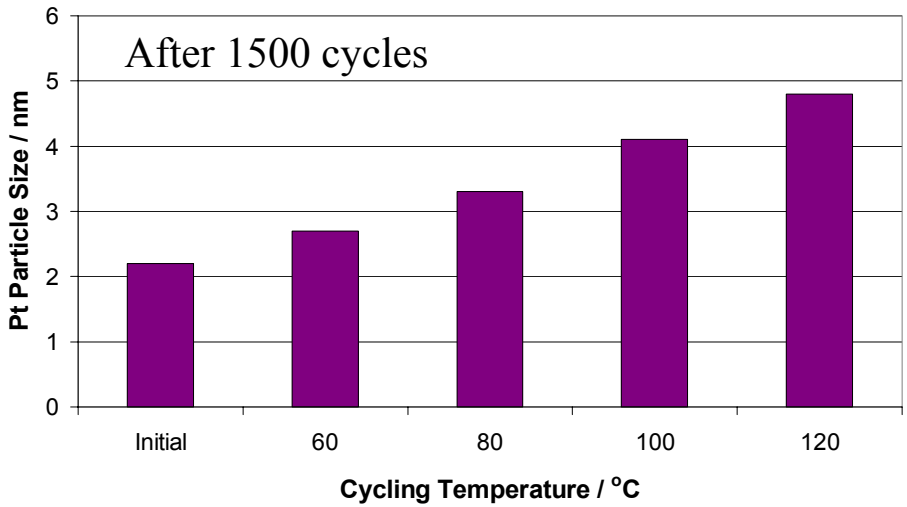
Comparison of Scan Rates: Time



- Pt Sintering correlates with # of cycles
- Time at peak potential has lower correlation

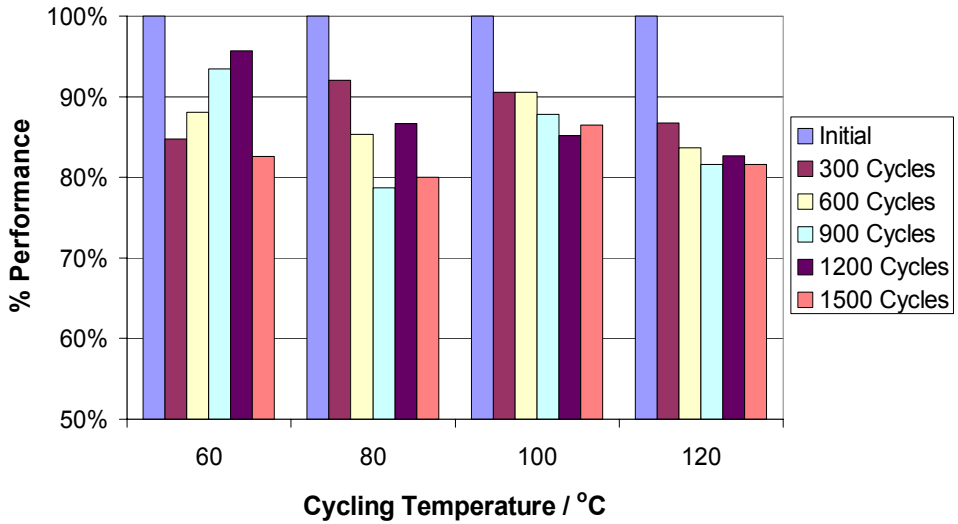
Temperature Effect on Catalyst Growth

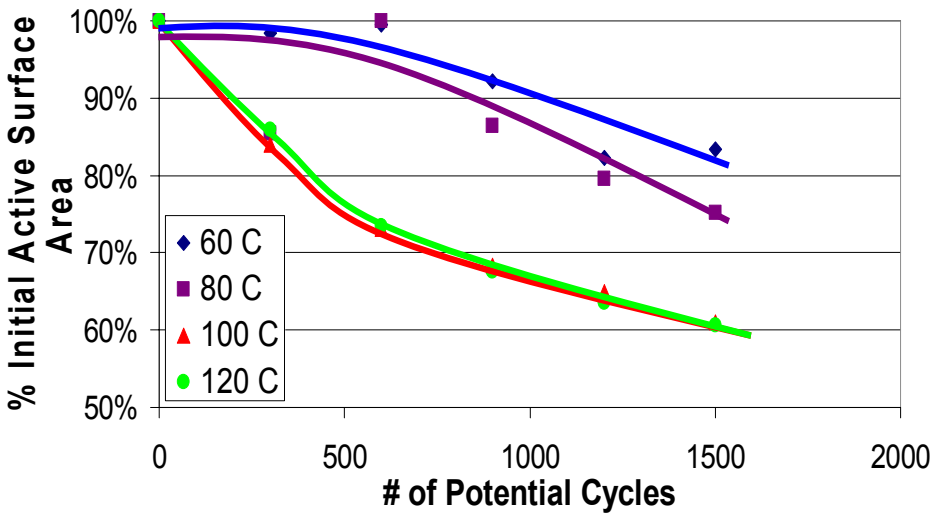
Pt particle size



Normalized performance decay

based on polarization curve current density at standard conditions: comparison at 0.65 V, 80 °C, 100 % RH

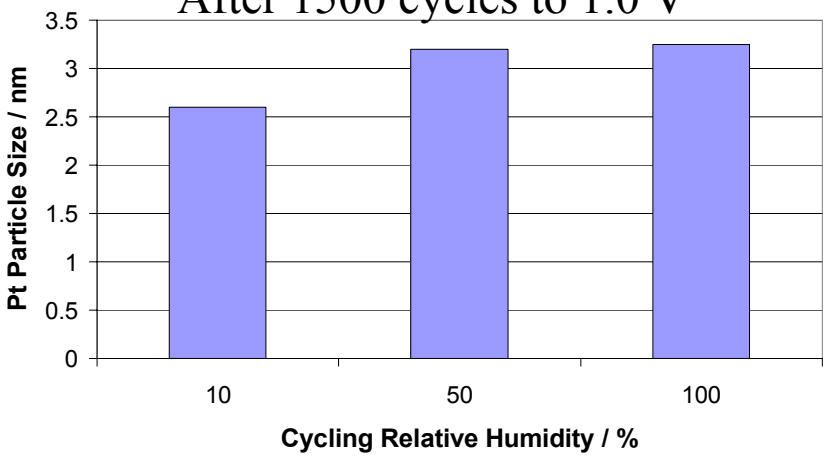




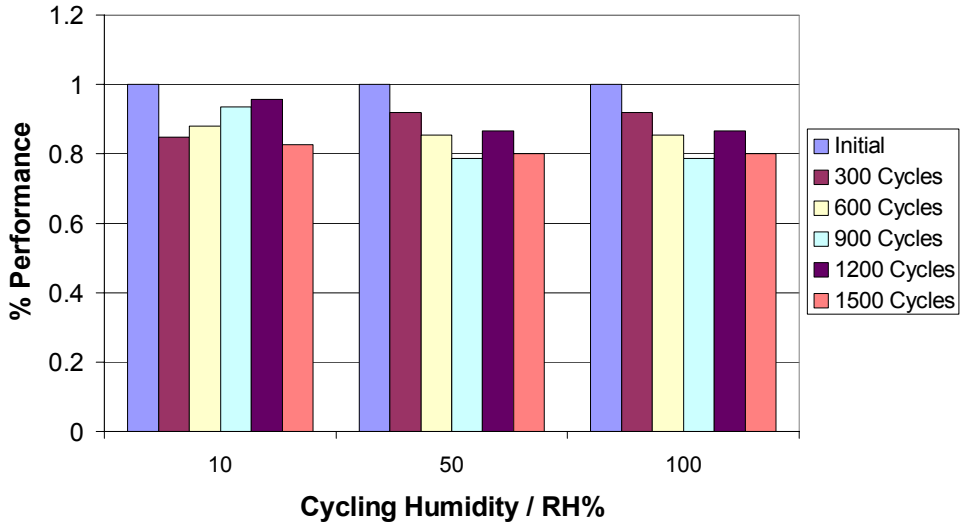
Increasing temperature leads to increased catalyst sintering

Humidity Effect on Catalyst Growth

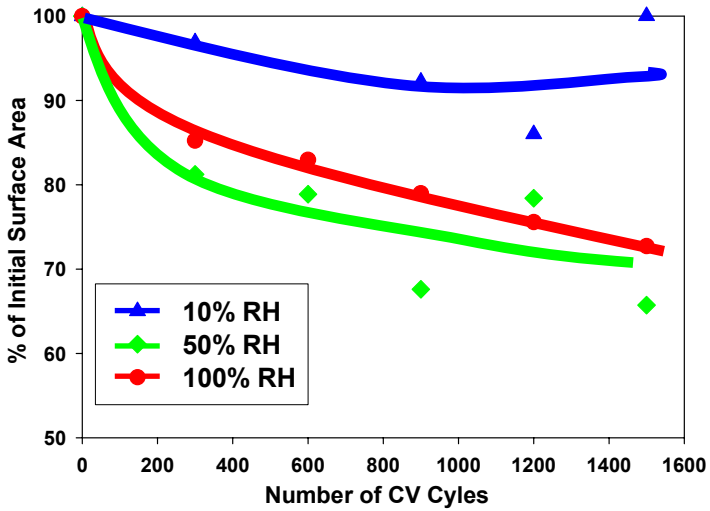
Pt particle size
After 1500 cycles to 1.0 V



Normalized performance decay
based on polarization curve current density at standard conditions: comparison at 0.65 V, 80 °C, 100 % RH



Active Pt Catalytic Surface Area

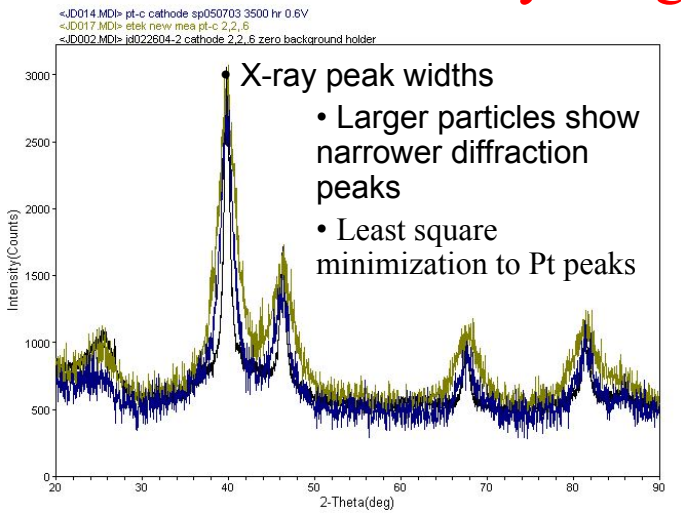


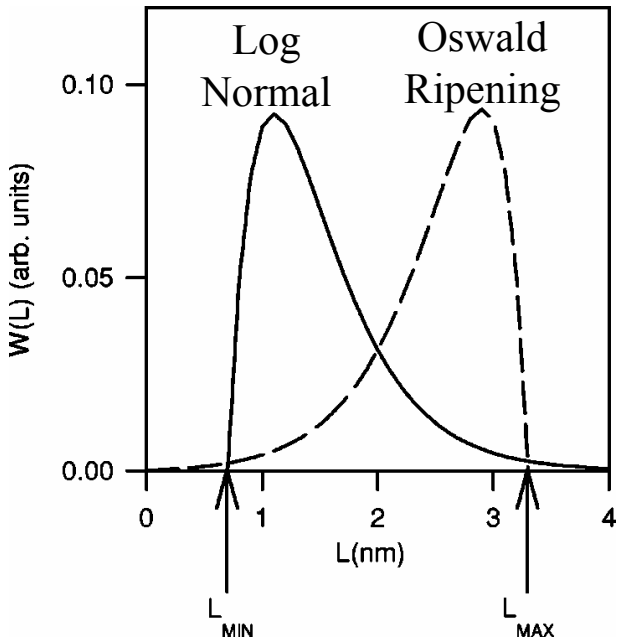
- Pt particle growth rate increases with humidity
- Growth mechanism enhanced by H_2O (Pt mobility?)

(Cell Temp 80 °C, Cycled from 0.1V - 0.96V)

X-ray scattering provides Pt particle size and size distribution

Pt Cathode Catalyst Aging

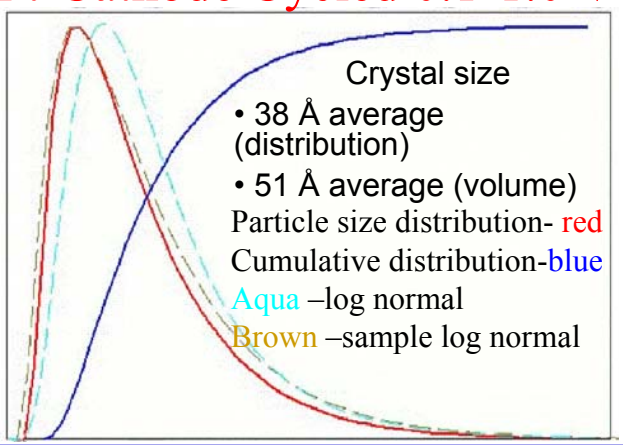




Simulated particle size distribution:
- continuous line log-normal type profile (coalescence growth mechanism)
-- dashed line for an Oswald Ripening profile
Ascarelli, Contini, and Giorgi J. Appl. Phys., Vol. 91, No. 7, 1 April 2002

- Catalysts have non-monotonic size distributions
  - Log normal distribution typical for synthesized particles (J. App. Physics V47 5 1976)
  - Oswald Ripening if catalyst grows by atom migration from small crystals to large ones
  - Coalescence mechanism for particle-particle growth

Pt-Cathode Cycled 0.1-1.0 V

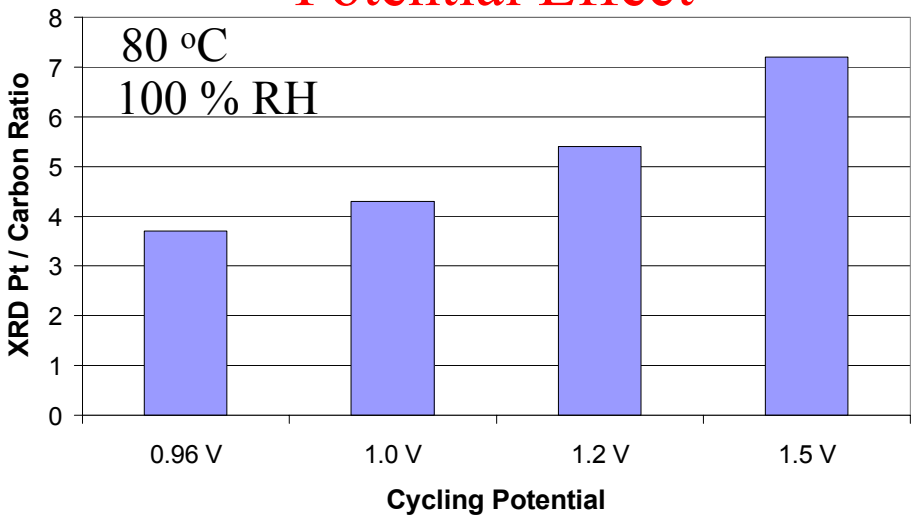


All Samples show Log Normal Distribution (up to 1.5V cycling)

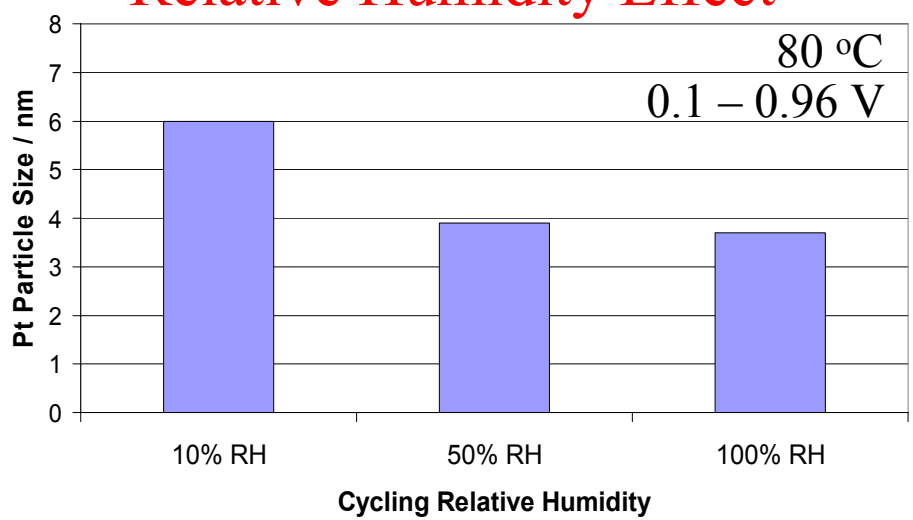
Suggests catalysts grow by particle coalescence for all testing and conditions

Electrode Carbon Corrosion

Potential Effect



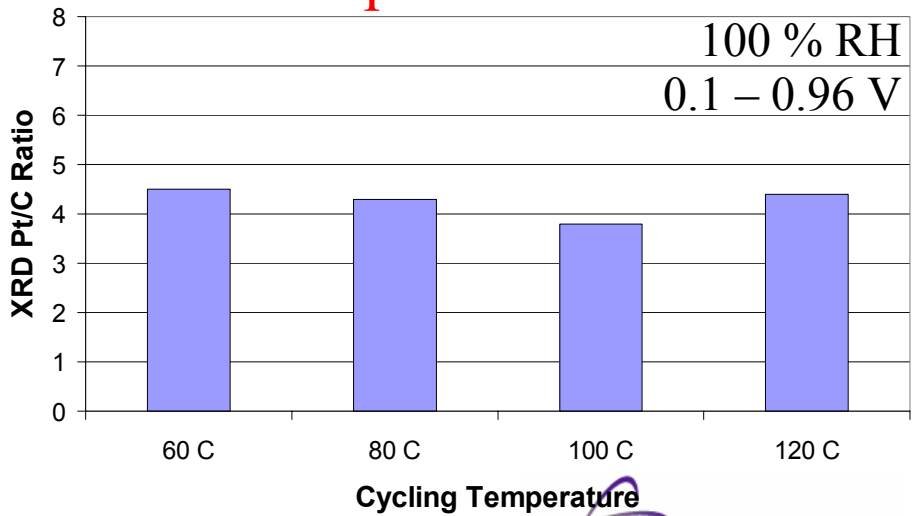
Relative Humidity Effect



Carbon corrosion measured by monitoring XRD Pt/C ratios

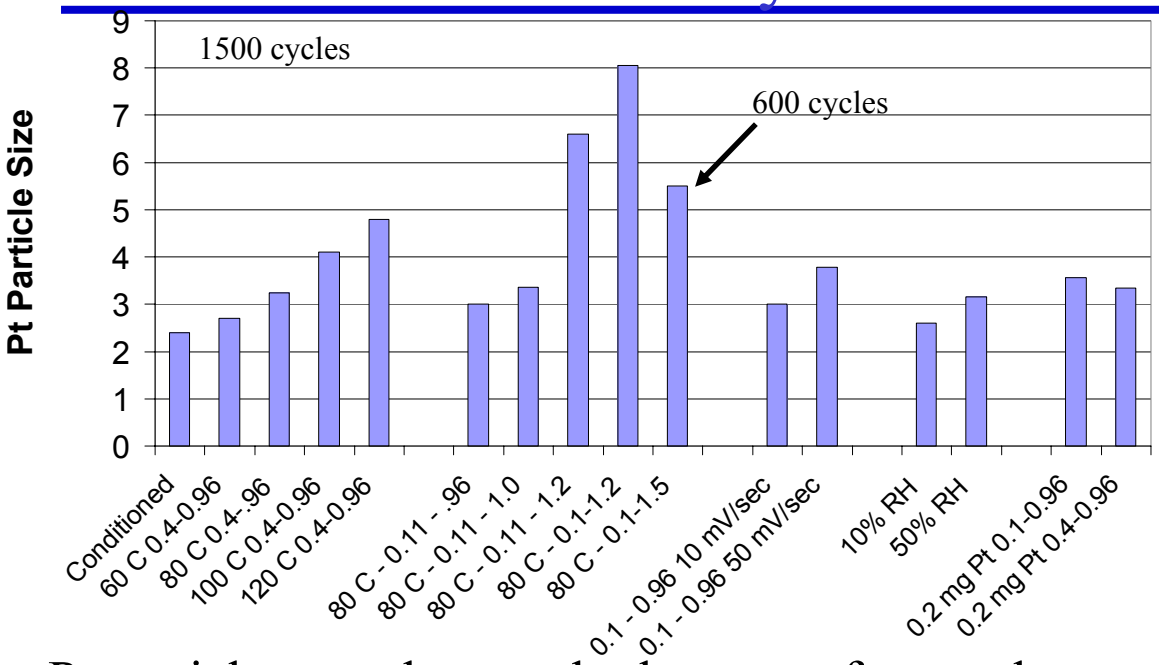
- Carbon corrosion occurs at:
  - High potentials (> 1.0 V)
  - Low Humidity
- Temperature not observed to have an effect at 100 % RH and 1.0 V

Temperature Effect



Electrocatalyst Size Growth

XRD analysis of electrocatalysts

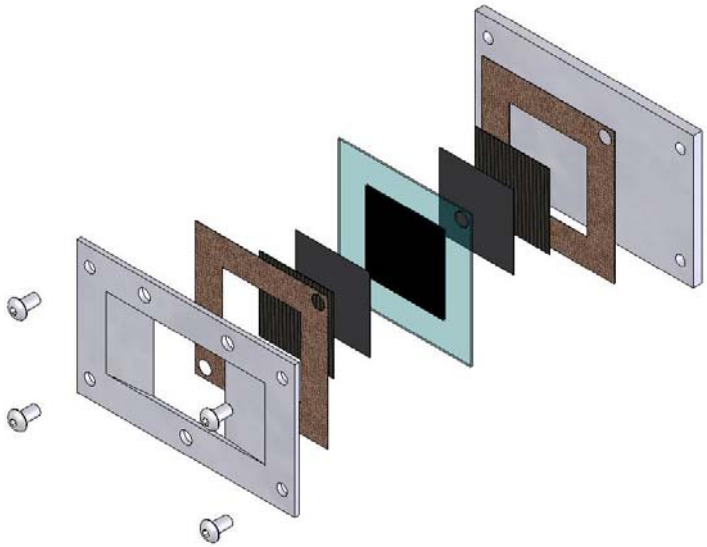


- Cycling increases Pt particle growth rate over steady-state operation
- # cycles has larger effect on catalyst sintering than duration at high potential
- Catalyst grows by particle coalescence regardless of cycling conditions

- Pt particle growth on cathode occurs for steady-state, enhanced with cycling
- No growth in anodes Pt crystallites
- No Oswald ripening mechanism during cycling (potential cycling up to 1.5 V)
- Particle growth increases with temperature
- Particle growth increases with humidification
- Pt loadings (0.2 mg/cm^2 to 0.4 mg/cm^2) did not effect the Pt sintering
- Carbon corrosion is present at high potentials, and low humidification

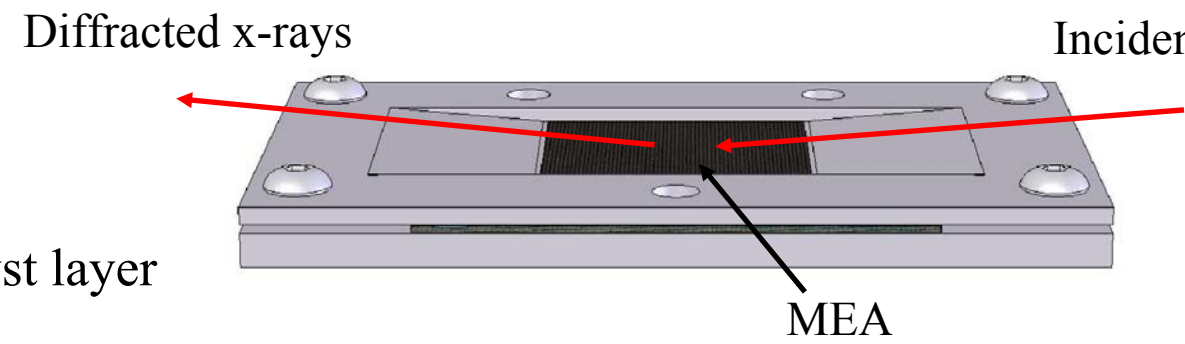
in situ XRD Measurements

non-destructive particle size analysis



Framed MEA for non-destructive testing in XRD
Utilizes 0.022" Nafion to separate electrocatalyst layers

Design for potential controlled *in situ* XRD testing, possible 'real-time' synchrotron particle size analysis



Nafion .022"
Used to separate catalyst layer signals during XRD

Loss of Hydrophobicity in Gas Diffusion Layer (GDL)

MEA (3-Layer)

Aggressive Operating Environment (O_2, H_2, e^- Passage, Voltage, $H_2O_{(l)}$, low Nafion® pH, Electro-oxidation, Electro-reduction, Time)

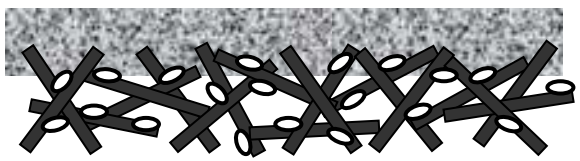
From Membrane → SO_4^{-2}, SO_3^{-2}, F^-

Catalyst → Pt (Co, Cr, *etc.*)

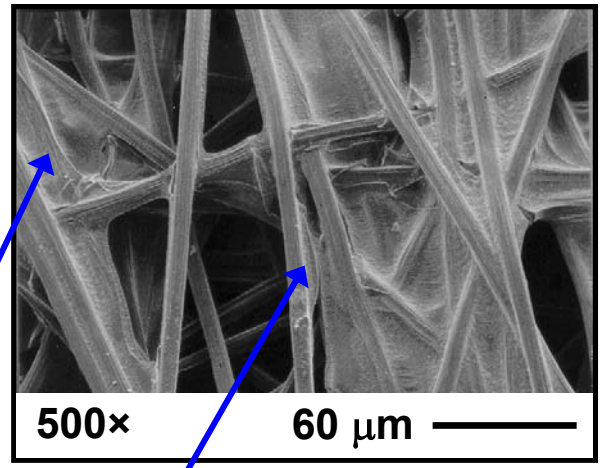
From C-Support → Na^+, Ca^{+2}, Zn^{+2}, Fe^{+3} (10-100 ppm), CO_2 (CO_3^{-2})

Others (Electrocatalytic Byproducts, *etc.*)

Attacking Species on PTFE and Graphite Composite Microstructure

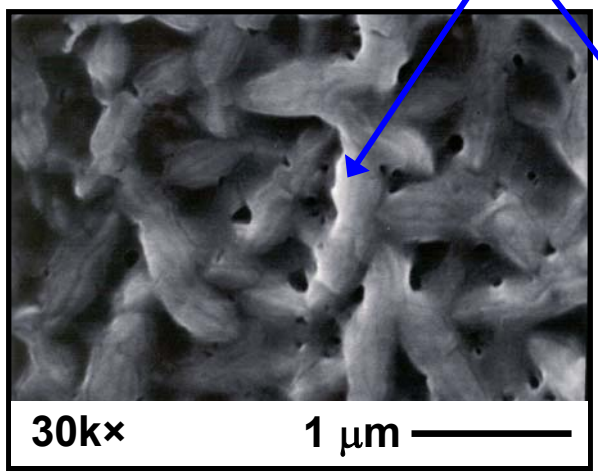


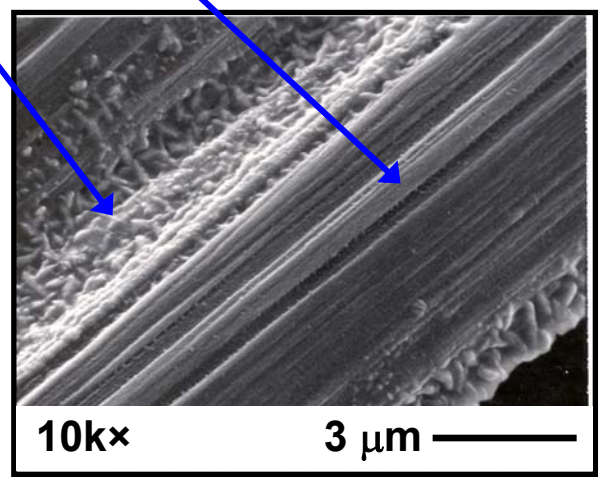
Typical Bilayer GDL



Graphitized Fiber (~10 μm)

Sintered PTFE Nanoparticles (200-500 nm dia.)



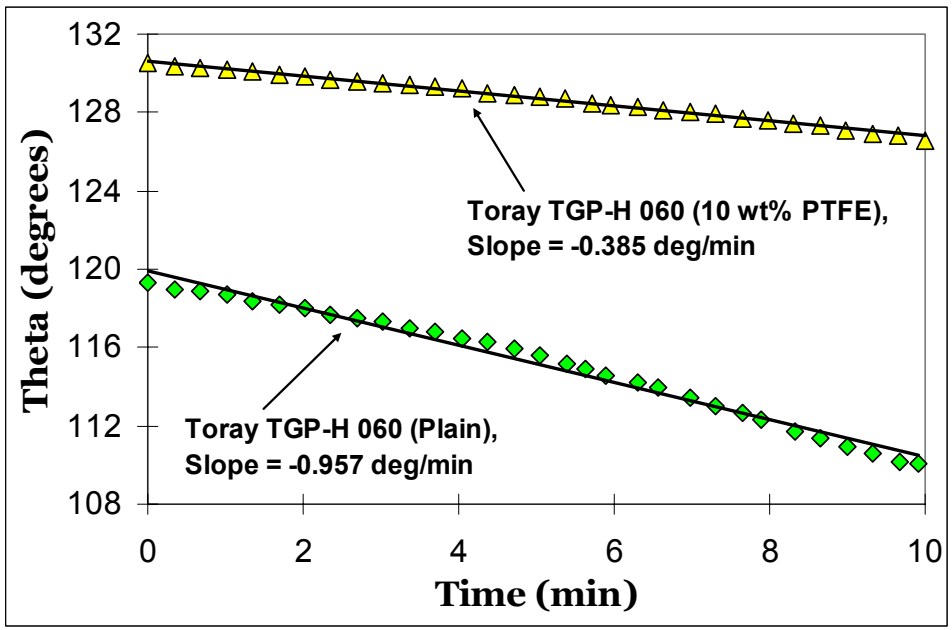


Courtesy SGL Carbon and Celanese Ticona

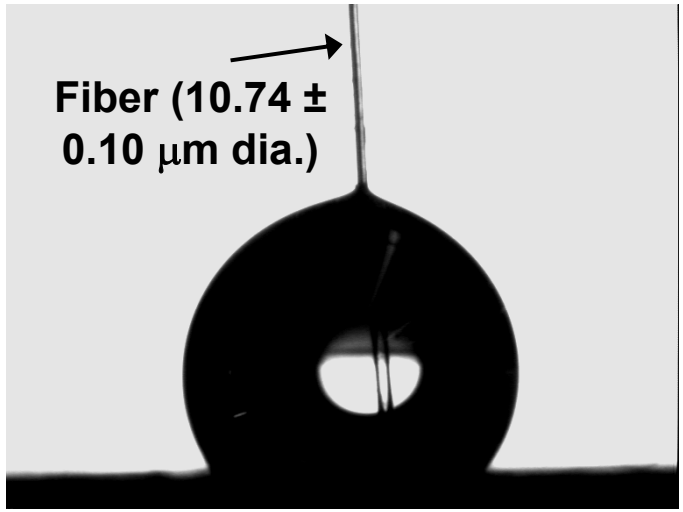
Comparison of Hydrophobicity Measurements
Bulk Material vs. Single Fiber

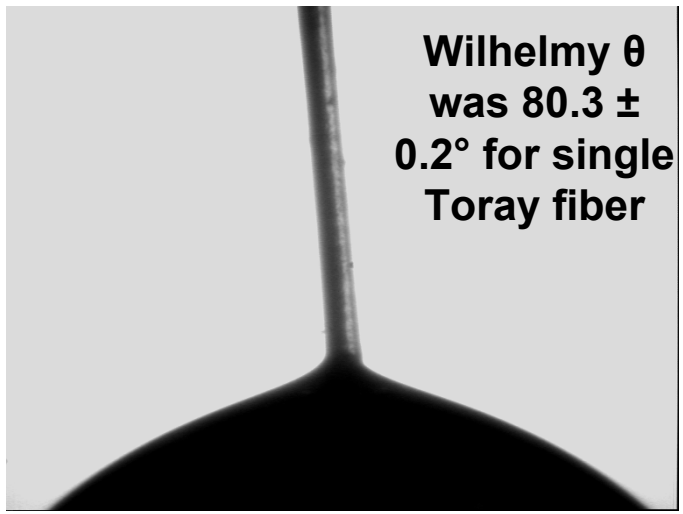
Wilhelmy Plate Contact Angle for Bulk Plain TGP-H 120 was 121.8 ± 0.3°, which is ~41° higher than for a single fiber

Why?

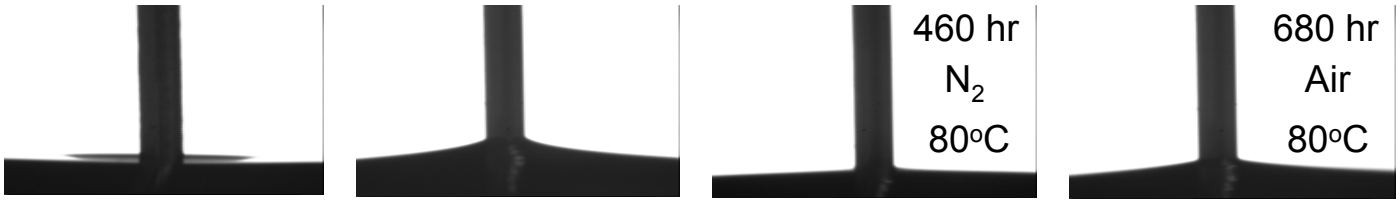


Dynamic Sessile-Drop θ for Toray TGP-H 060





GDL Hydrophobicity Aging

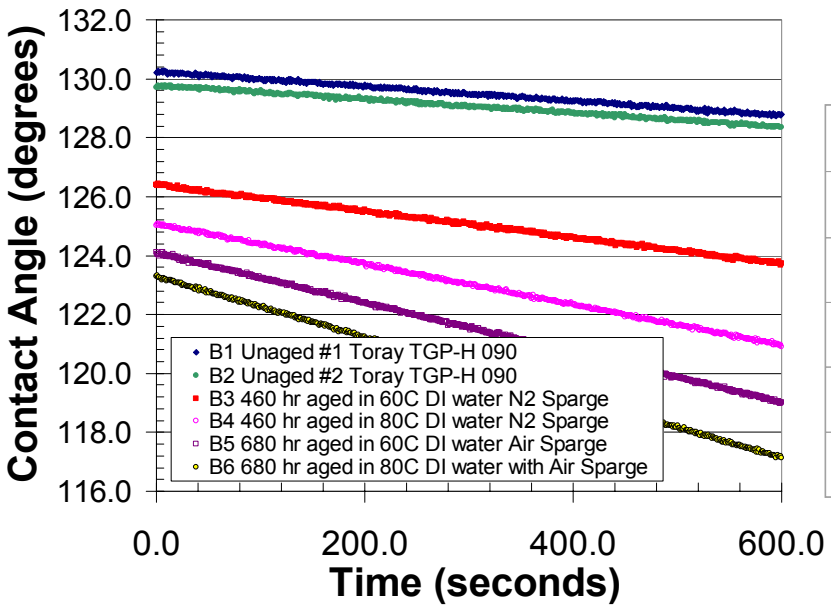


Single Fiber

Untreated Toray Fiber 80.3°	Toray TGP-H090 17.2 wt% FEP 94.6°	Toray TGP-H-090 16.7 wt% FEP 88.4°	Toray TGP-H-060 17.0 wt% FEP 83.2°

Sessile

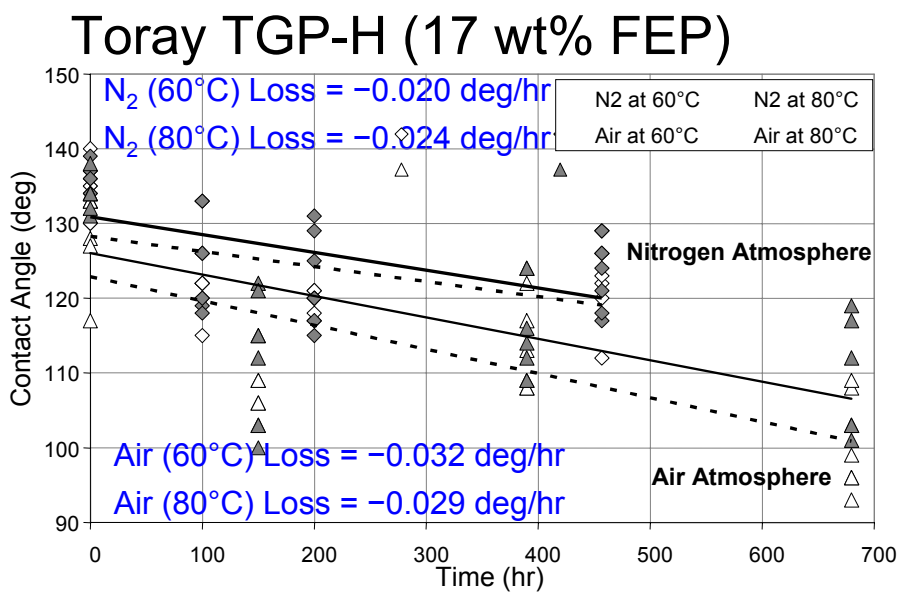
Drop Spreading Contact Angle

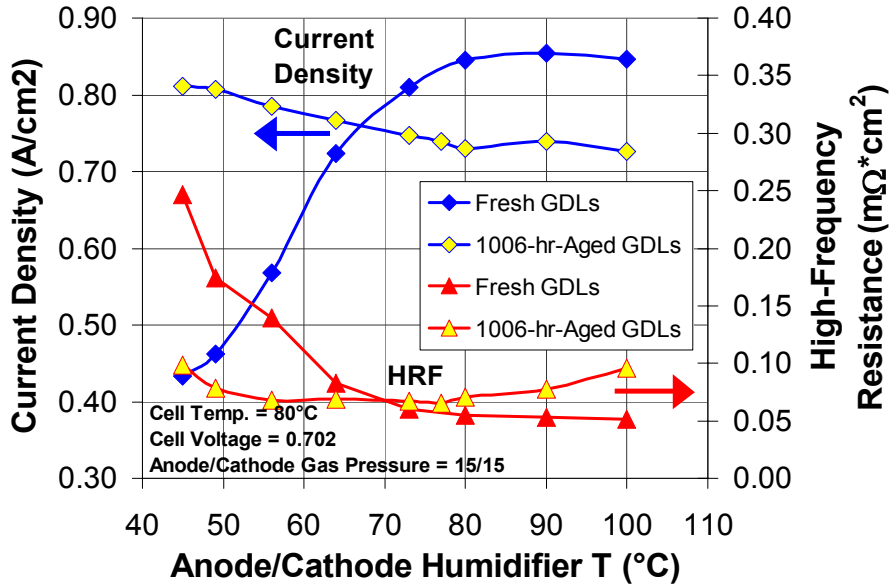


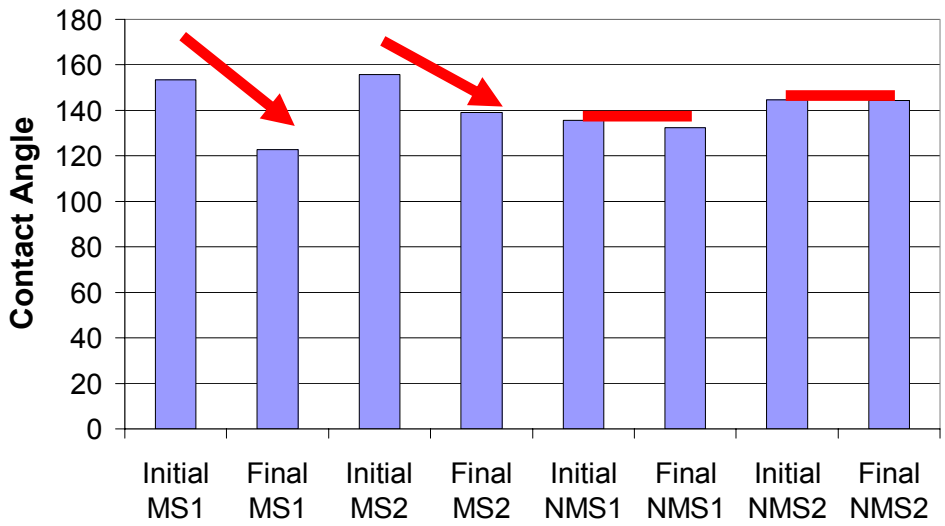
Loss of hydrophobicity increases with temperature and oxidation

- Unaged #1 Toray TGP-H 090
- Unaged #2 Toray TGP-H 090
- 460 hr aged in 60°C DI Water with N2 Toray TGP-H 060
- 460 hr aged in 80°C DI Water with N2 Toray TGP-H 090
- 680 hr aged in 60°C DI Water with Air Toray TGP-H 060
- 680 hr aged in 80°C DI Water with Air Toray TGP-H 060

Decrease in Hydrophobicity of FEP-treated Toray GDL







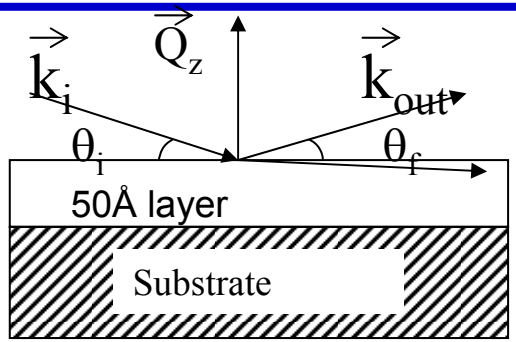
- Hydrophobicity loss on microporous layer
- No loss in hydrophobicity of non-microporous layer

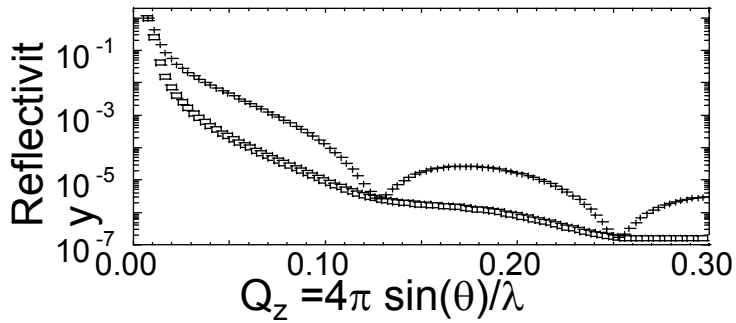
MS = Microporous layer
NMS = non-microporous layer

Neutron Reflectometry

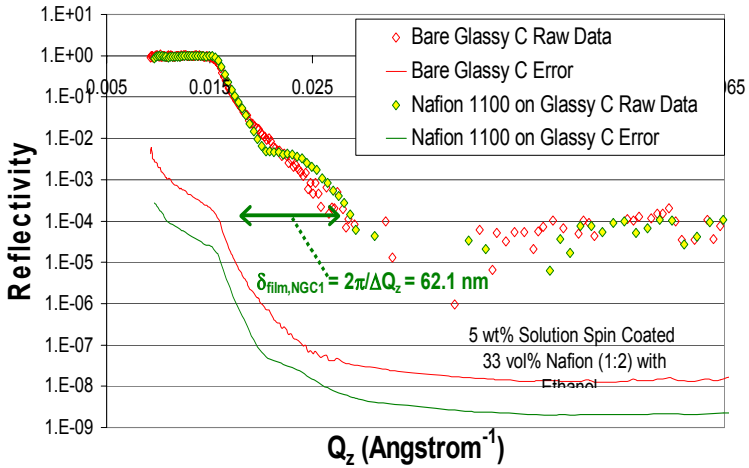
SPEAR (Surface Profile Analysis Reflectometer)

SPEAR:
Film thickness
Roughness
Coverage





Thin-Film Nafion1100EW/Glassy-C

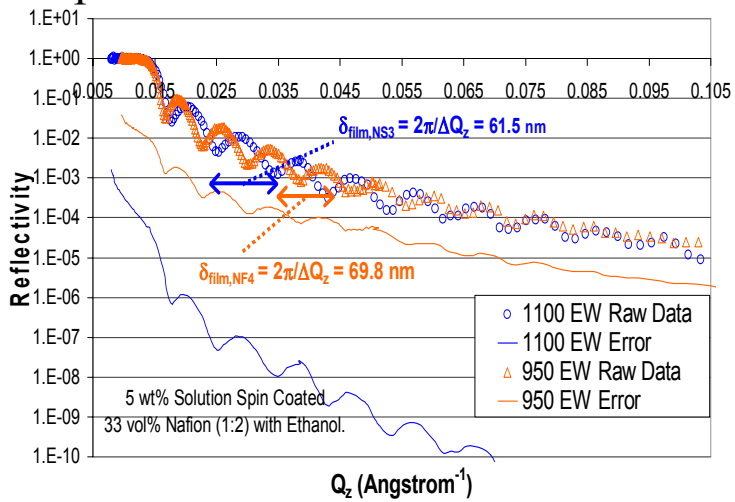


Calculated Scattering Length Density (SLD) for Glassy C = 5.10×10^{-6}, Surface Roughness = 79.7 Å

Glassy Carbon (~ only) acceptable surface to study PEM Fuel cell polymer/carbon interactions

Thin-Film Nafion/Si

(Comparison between 1100 and 950 EW)

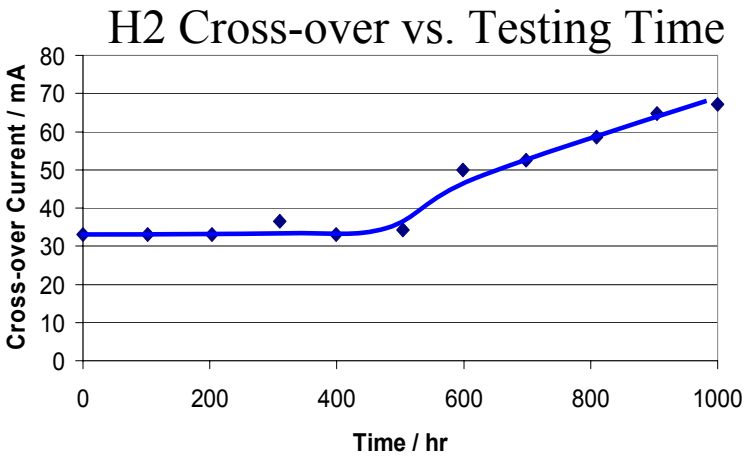


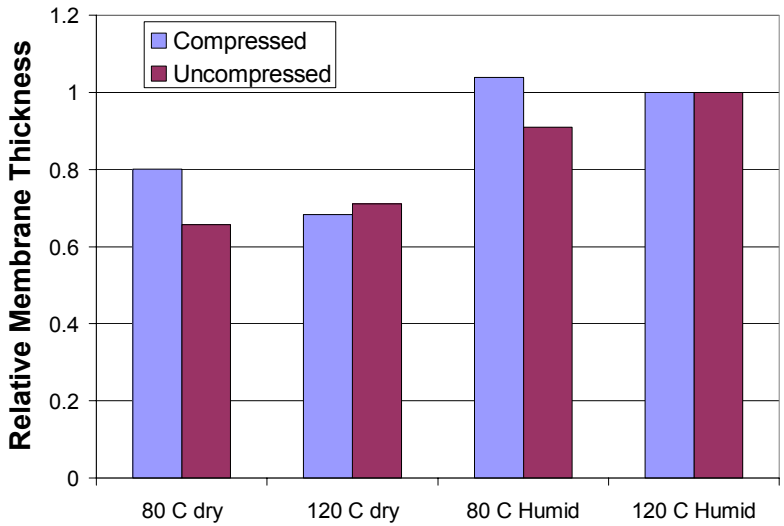
Nafion 1100EW / 950EW Scattering Length Densities (SLDs) = 4.23×10^{-6} / 3.95×10^{-6}

Membrane Thinning

- Membrane degradation exemplified by cross-over, and hole formation
- Post analysis shows membrane 'thins'
- Peroxide formation a key to membrane degradation

Post-characterization of membrane





- Examining membrane properties:
  - H form of membrane compressed in flowfield exposed to inert gas and temperature.
  - No backing layers, catalyst layer, proton conduction, etc.

Regardless of compression, membrane showed thinning with exposure to dry gases

Future Plans

- **Catalyst Durability / Characterization**
  - *in situ* XRD analysis of Pt particle growth period
  - Modeling of particle growth to correlate growth conditions
  - Pt equilibrium diagram with PEM fuel cell conditions with F-, sulfates, etc.
  - Carbon bonding interaction with Pt - develop stable Pt/C catalysts
  - Pt alloys with higher stability
  - Examine non-carbon electrocatalyst supports for durability
- **Carbon Corrosion**
  - Further examine carbon corrosion in electrocatalyst layers and GDL materials
- **Component Interfacial Durability Property Measurements**
  - GDL material interfacial contact with the MEA catalyst layer
  - examine Nafion / PTFE degradation and carbon bonding via neutron scattering
- **Membrane Degradation**
  - examine conditions leading to membrane thinning
  - examine conditions leading to membrane failure

Publications and Presentations

Microstructural Changes of Membrane Electrode Assemblies during PEFC Durability Testing at High Humidity Conditions, Xie et al., *Journal of The Electrochemical Society,* **152** 5 A1011-A1020 2005

Durability Study of Polymer Electrolyte Fuel Cells at High Humidity Conditions, Xie et al., *Journal of The Electrochemical Society*, **152** A104-A113 2005

Effects of Long-Term PEMFC Operation on Gas Diffusion Layer and Membrane Electrode Assembly Physical Properties, Wood et al., 206th Meeting of The Electrochemical Society, Honolulu, Hawaii, October 5th, 2004

Long-Term Performance Characterization of Proton Exchange Membrane Fuel Cells, Wood et al., 206th Meeting of The Electrochemical Society, Honolulu, Hawaii, October 5th, 2004

PEM FUEL CELL DURABILITY, Borup et al., FY 2004 DOE EERE Hydrogen Program Annual Report

DURABILITY ISSUES OF THE PEMFC GDL and MEA UNDER STEADY-STATE AND DRIVE-CYCLE OPERATING CONDITIONS, Wood et al., 2004 Fuel Cell Seminar, San Antonio Texas, Nov. 1-5

PEM Electrocatalyst Durability Measurements, Borup et al., To be presented at the Electrochemical Society, June 12 – 17 2005, Las Vegas NV

PEM Electrocatalyst Durability Measurements, Davey et al., To be presented at the Fuel Cell Seminar, 2005, Palm Springs, CA, Nov. 14 - 18, 2005

MASS-TRANSPORT PHENOMENA AND LONG-TERM PERFORMANCE LIMITATIONS IN H2-AIR PEMFC DURABILITY TESTING, Wood et al., To be presented at the Fuel Cell Seminar, 2005, Palm Springs, CA, Nov. 14 - 18, 2005

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Hydrogen leak in the hydrogen supply coupled with ignition leading to a significant hydrogen fire.

Hydrogen Safety

Our approach to deal with this hazard is:

Hydrogen and carbon monoxide room sensors are electrically and computer interlocked with the test stand power and the gas supplies.

H2 sets off the H2 sensors (set at 10% of LFL)

H2 also sets off the CO sensors, (set at 30 ppm)

Limits H2 far from the flammable or explosive limit

Work has been reviewed through Los Alamos National Lab's safety programs:

Hazard Control Plan (HCP) - Hazard based safety review

Integrated Work Document (IWD) - Task based safety review

Integrated Safety Management (ISM)