PEM Fuel Cell Durability

2006 DOE Hydrogen Program Review

Thursday May 18, 2006

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Project #: FC28

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 PEM H_2 Durability

Barriers

- Durability (Barrier A)
- Cost (Barrier B)
- Electrode Performance (Barrier C)

Budget

- FY04: $900k
- FY05: $950k
- FY06: $1000k

Collaborators

- **Analysis:**
  - ORNL, Univ. New Mexico, Augustine Scientific, Porous Materials Inc., Surface Measurement Systems NA
- **Materials:**
  - Gore, SGL, Toray, 3M, ETEK, Cabot-SMP

Objectives:

Quantify and Improve PEM Fuel Cell Durability

2010 Technical Target: Durability with cycling 5000: hours

- Define degradation mechanisms
- Design materials with improved durability

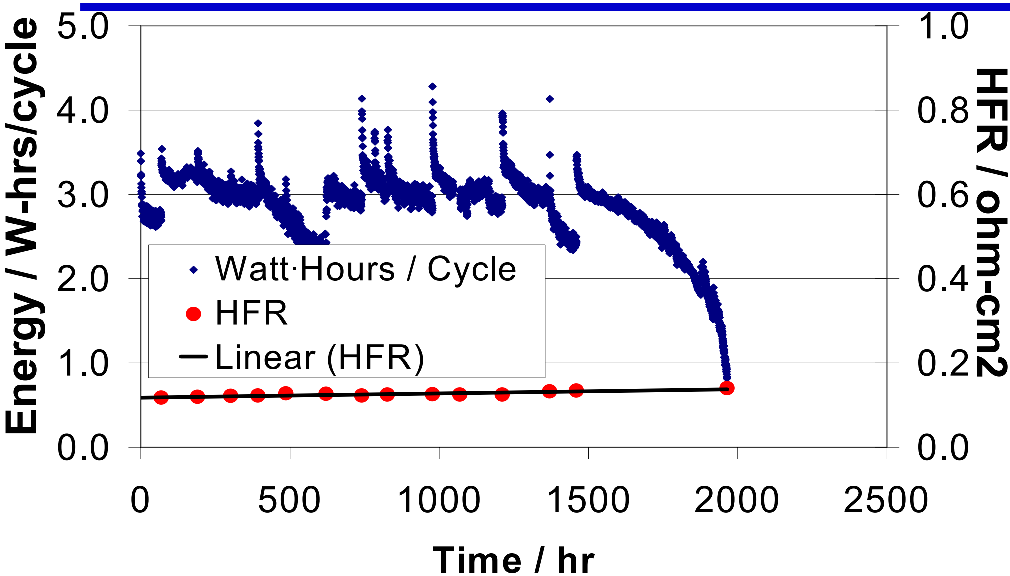
- Identify and quantify factors that limit PEMFC Durability
  - Measure property changes in fuel cell components during life testing
    - Life testing of materials
      - Examine testing conditions, esp. drive cycle
    - Membrane-electrode durability
    - Electrocatalyst activity and stability
 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

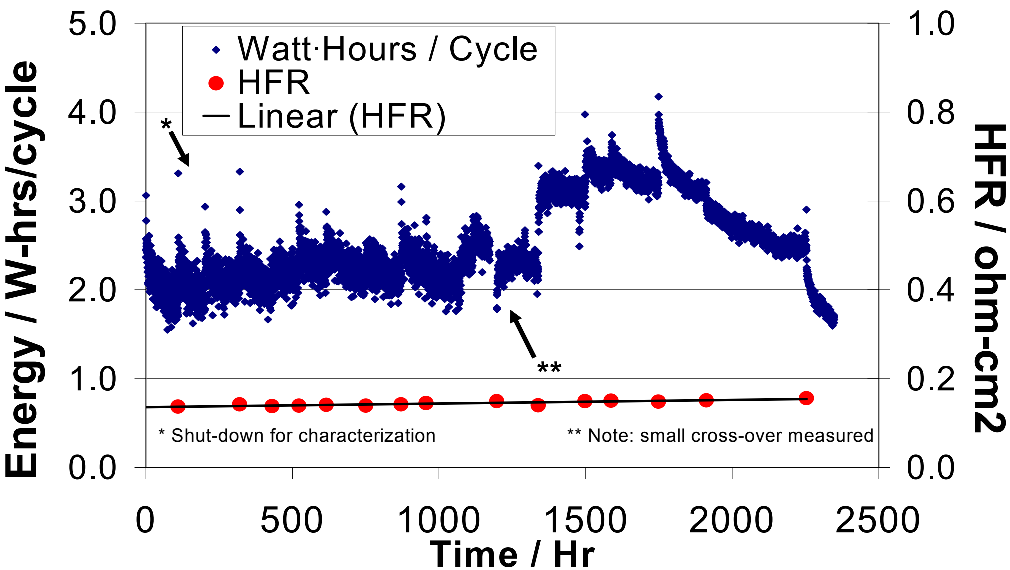
Approach to Durability Studies

- Fuel Cell MEA Durability Testing and Study
  - Constant voltage/current/power and power cycling (drive cycle)
    - VIR / cell impedance
    - Catalyst active area
    - Effluent water analysis
- *in situ* and post-characterization of MEAs, catalysts, GDLs
  - SEM / XRF / XRD (*ex situ* and *in situ*) / TEM / ICP-MS / neutron scattering / H_2 adsorption / Inverse Gas Chromatography / Contact Angle / total porosity / hydrophillic vs. hydrophobic porosity
- Develop and test with off-line and accelerated testing techniques
  - Potential cycling
  - Environmental component aging, testing and characterization
  - Component interfacial durability property measurements

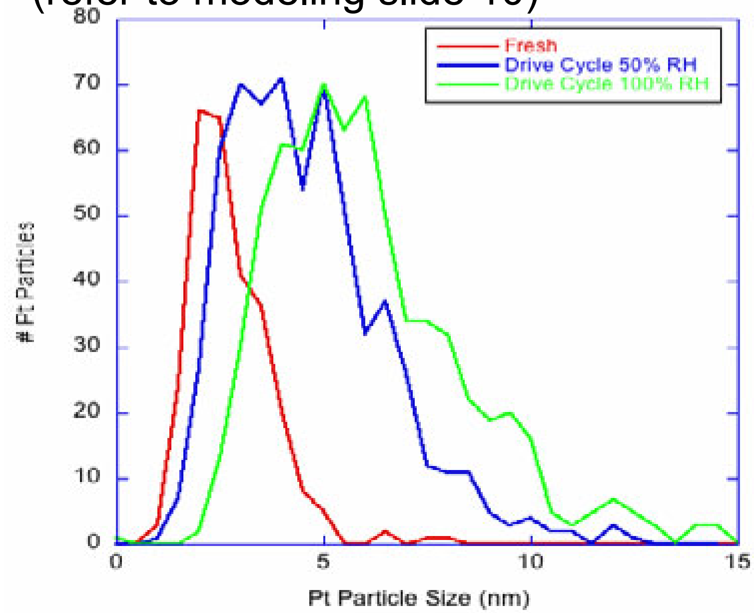
•Slight increase in HFR (linear)

US06 Drive Cycle Testing





TEM and XRD show 'bimodal' distribution (refer to modeling slide 10)



100 % RH Operation

- Little decay till 1500 hrs (VIRs also)
- Rapid decay after cross-over formed
- 4.1 (5.5 / 5.0) nm particle size (2000 hrs)

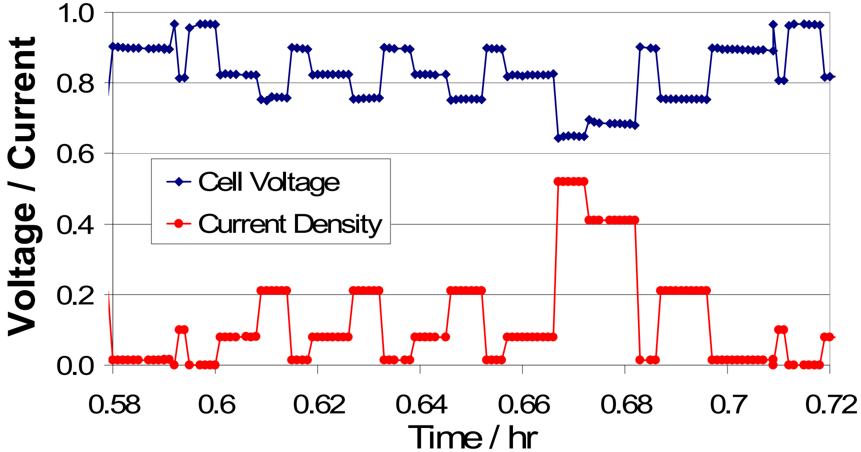
50 % RH Operation

- Increase for 2000 hrs (VIRs also)
- Increased after small cross-over formed
- 3.4 (4.5 / 4.2) nm particle size (2400 hrs)

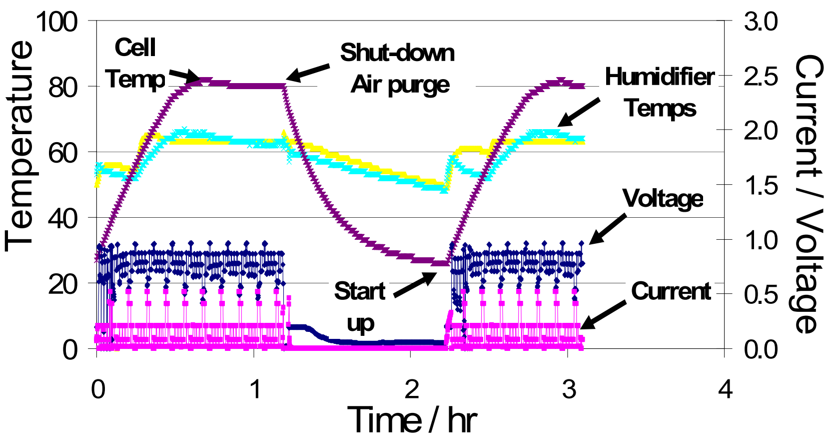
Blue = XRD : Green = TEM

Operation with DOE Drive Cycle Protocol - Start-Stop

DOE Drive Cycle



Transients During Shut-down / Start-up

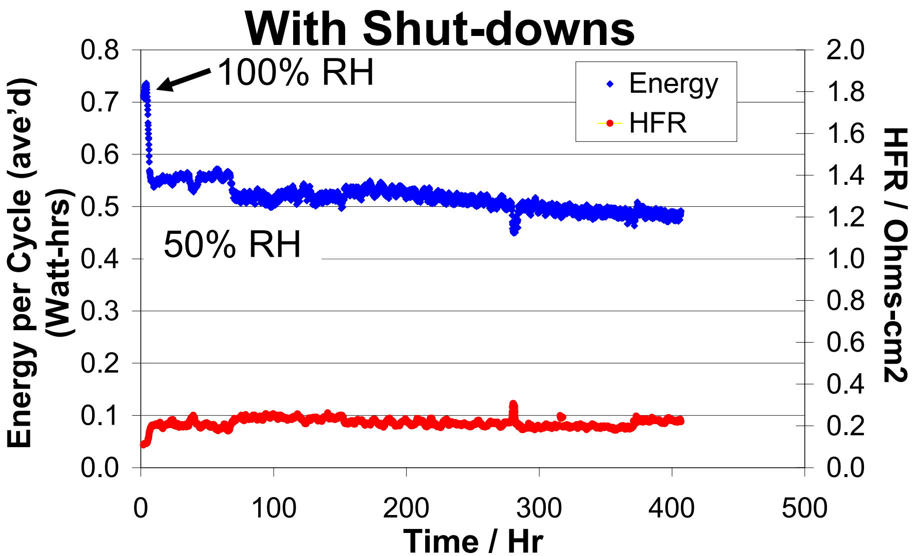


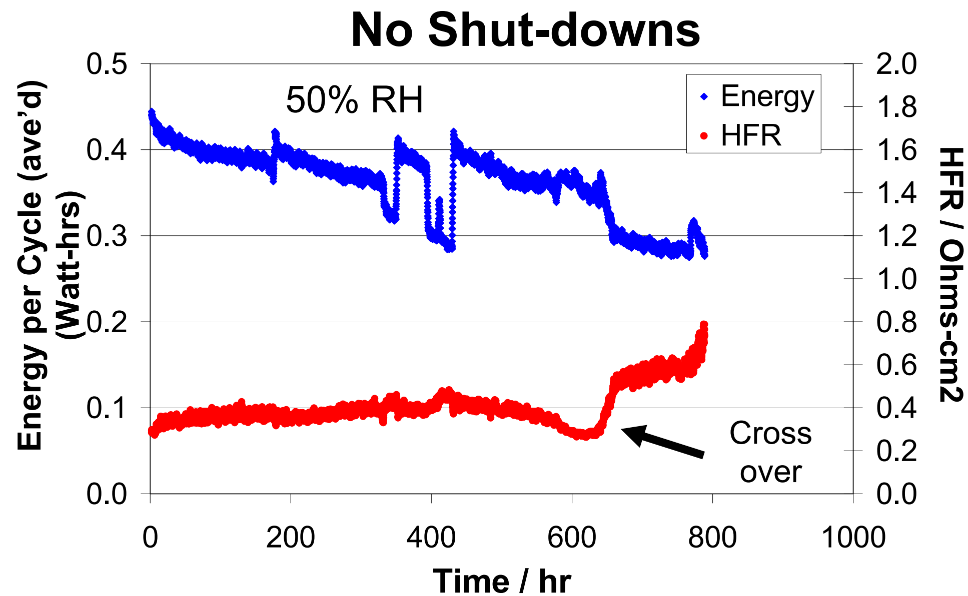
<u>**Operation with DOE Drive Cycle Protocol**</u>

- Constant Stoich - Fows lead current (4 sec.)
- Modified for use incorporating shut-down
  - 10 Drive Cycles followed by stop / restart
  - Shut-down purges with dry air (2 min)
  - Air purge removes potential within < 3 sec
  - Cell Voltage < 0.2 V during shut-down
  - Cell cool-down to T_{room} (1 hr)
- **Shut-down/startup operation show large transients**
  - **Shut-down/purge effect on HFR**

start-up

Drive Cycle Operation With/Without Shut-down/Start-up





- Parallel, same drive cycle with / without shutdown cycles
  - Drive Cycle Shut-down Cell
    - 400 hrs, 375 shutdown cycles, 3570 drive cycles
    - 0.20 mW/hr-cycle loss – 36% in 1000 hrs
    - On-going
  - Drive Cycle No - Shut-down Cell
    - 800 hrs, 7280 drive cycles
    - 0.18 mW/hr-cycle loss – 43% in 1000 hrs
    - Test ended - voltage not maintained at high currents

N1135
Constant Stoich 1.1 / 2.0
Constant P = 20 psig
$T_{(max)}$ = 80
50% $RH_{(inlet)}$

Pt Particle Growth

- MEAs lose catalyst surface area during operation
  - Catalyst surface area loss is due to growth in platinum particle size.
    - Particle size growth is exacerbated by potential cycling
    - Pt particles are not strongly bonded to carbon substrate
- Evaluation of Pt particle size during testing and potential cycling
  - *in situ* surface area, XRD (*in situ* and *ex situ*) and TEM

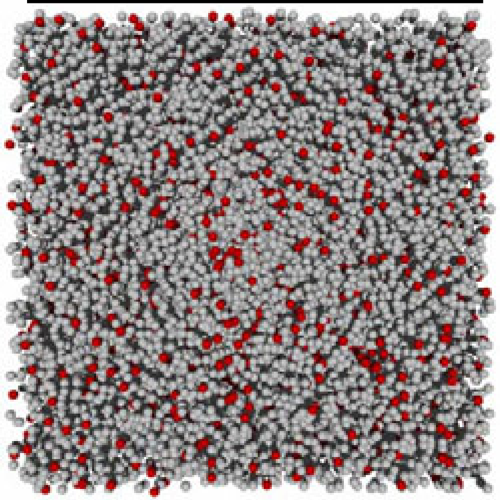
- **Pt Particle Growth Modeling: 3 Modeling simulations**
- Kinetic model
  - Initial distribution, particle growth rate, coalescence rate
- Convection/diffusion
  - Diffusion inverse with particle size (exponential decay with time)
- Brownian dynamics (Molecular Dynamics++)
  - Stoichastic thermal forces, electric field, and electro-osmotic drag
    - Simulates ionomer tortuosity as a static gel

Brownian/MD Modeling

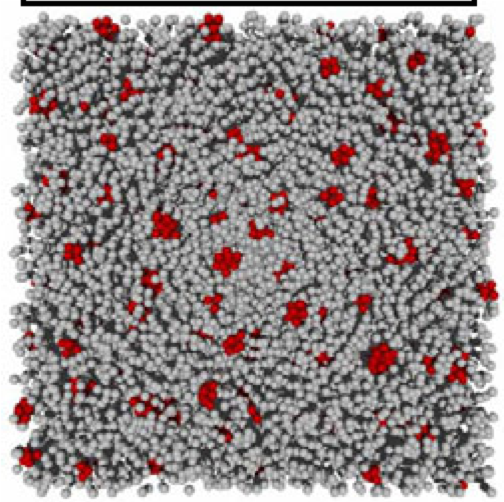
Simulates Pt particles agglomeration in ionomer matrix

TEM of 2400 hr Drive cycle
Karren More, ORNL

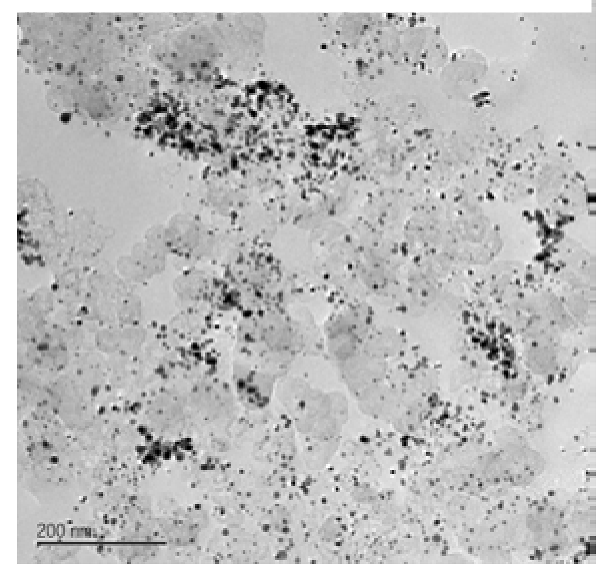
Initial Distribution

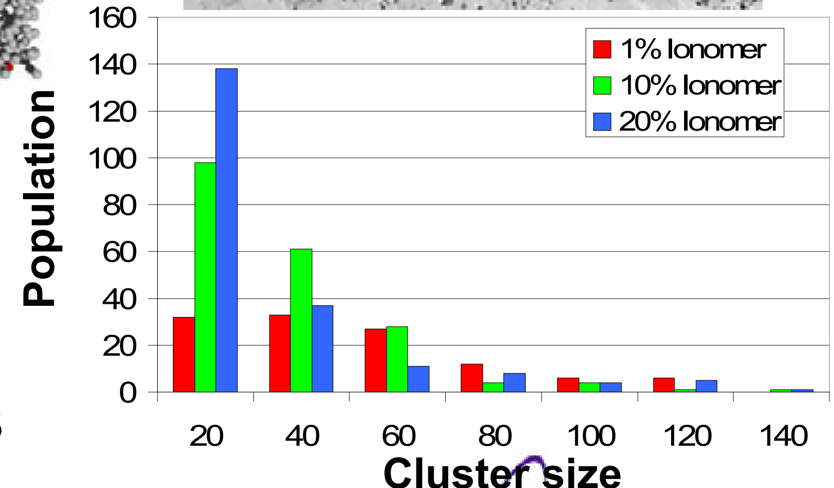


Aged Distribution



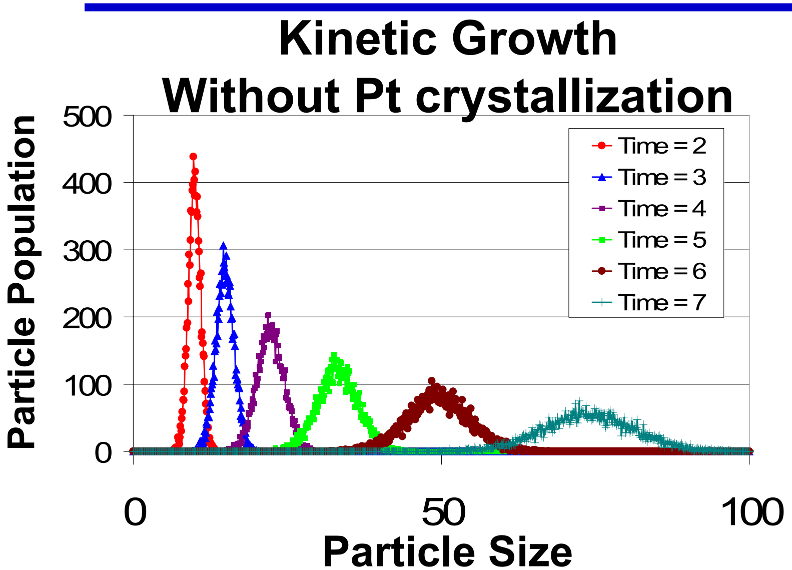
Grey = ionomer **Red = Pt Clusters**

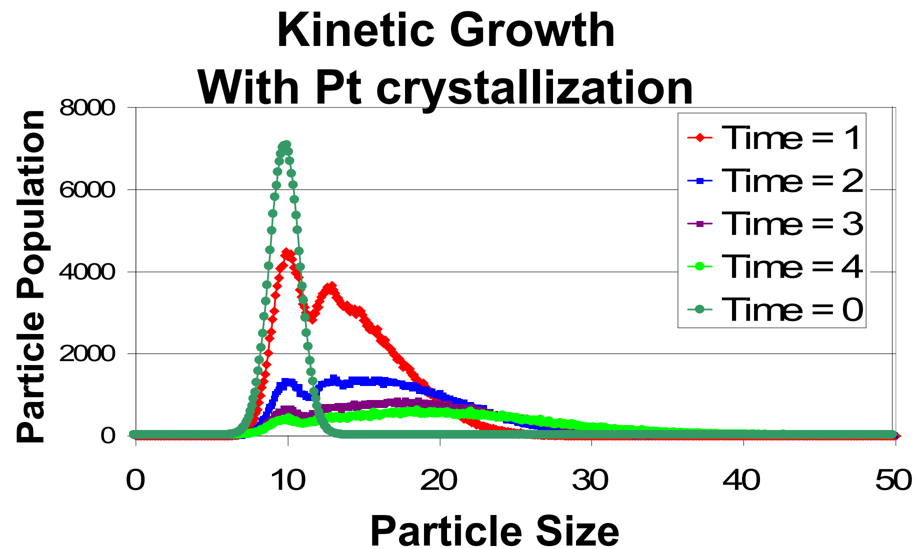




- Random initial distribution
- Monitor cluster size distribution during aging
- Add: Convection/diffusion rate laws

Kinetic Modeling of Pt Particle Growth

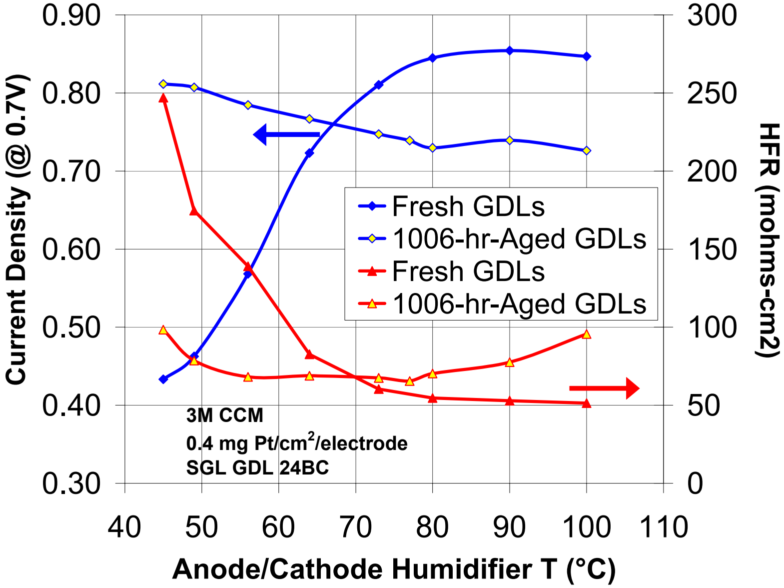


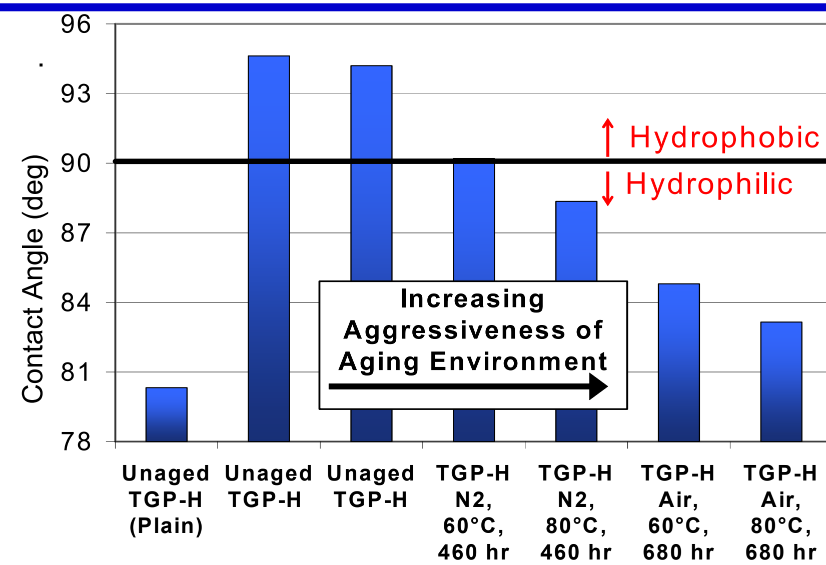


- Pt Particles show change in diameter and distribution form
  - Start with initial distribution and particle growth rate
    - Fig. 1 - $R_{growth} = k^*(Pt_{SA})\ dPt_{SA}/dt = k * Pt_{SA}$
    - Fig. 2 – Adds Nuclie Coalescence to growth rate
  - Kinetic modeling of particle growth without coalesence
    - Growth in particle size occurs, distribution form does not change
  - With coalesence:
    - Particle size distribution form changes – bimodal distribution
      - (refer to TEM slide 9, slide 5 US06 drive cycle particle distribution)

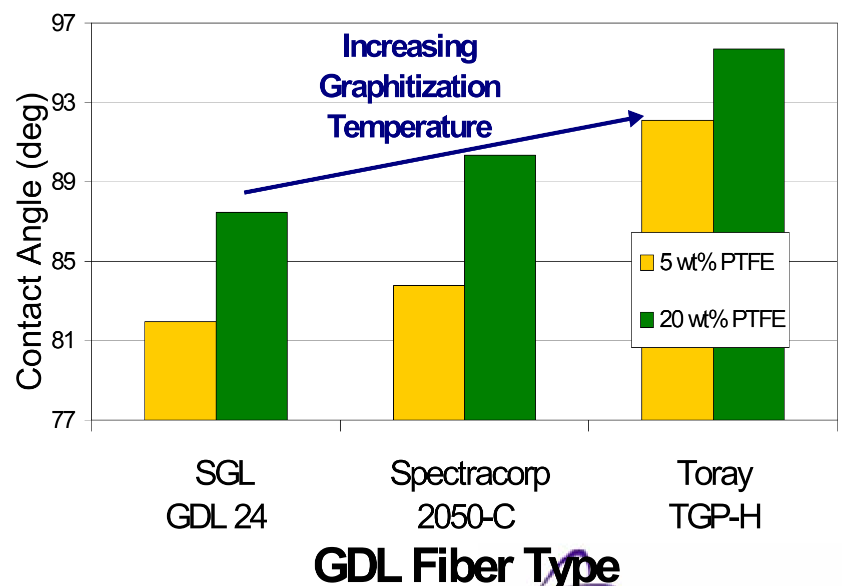
Gas Diffusion Layer Durability

GDL Performance varies with time



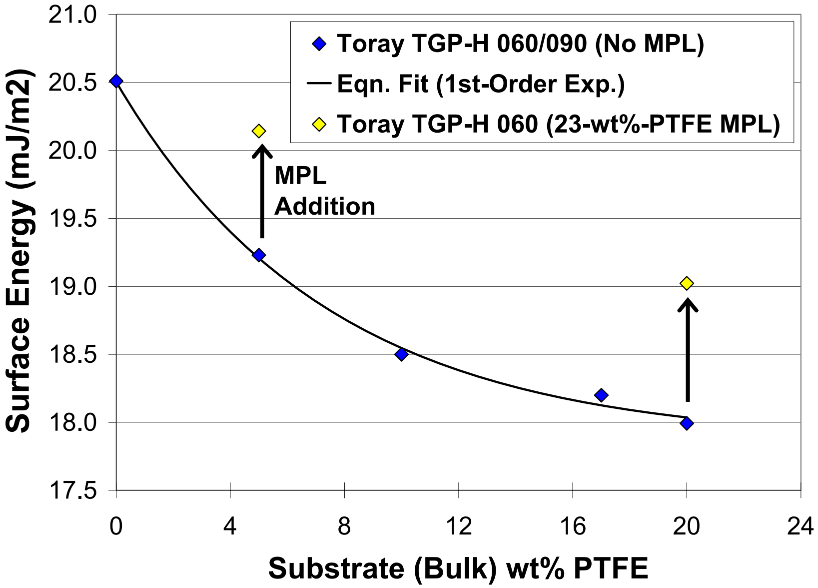


- RH sensitivity scan shows GDL aging effect on cell performance as f(RH)
- Increasing aggressiveness of again environment increases loss of GDL hydrophobic properties
- Fiber graphitization can increase single-fiber contact angle ~ 10°
- Both graphitization T and PTFE loading change hydrophobic properties

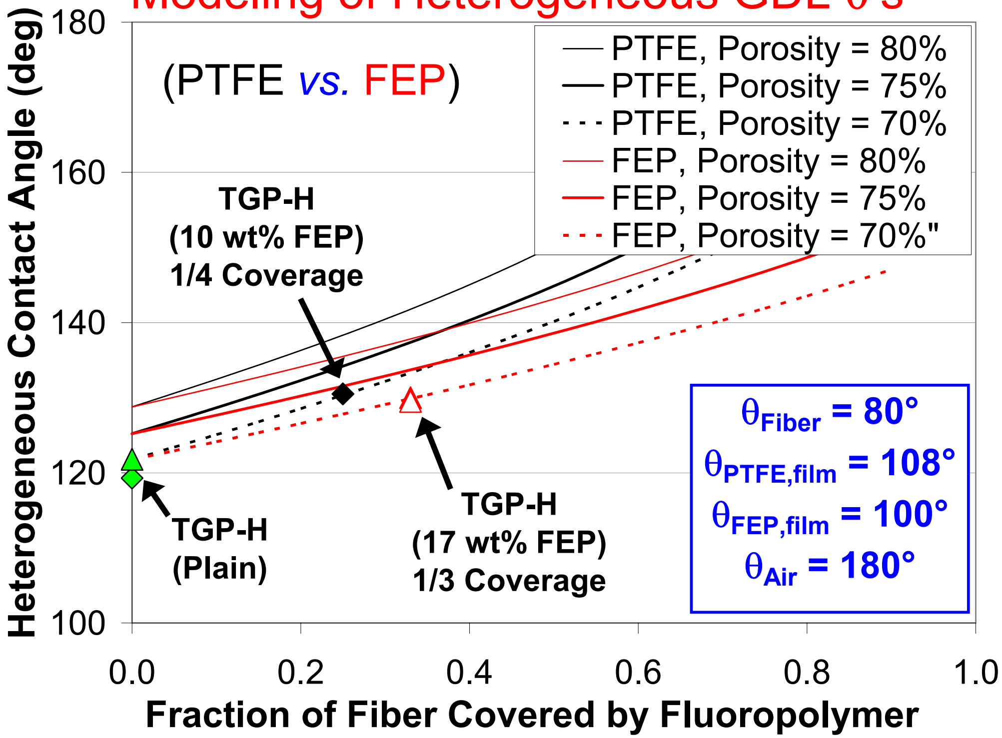


Modeling of Heterogeneous GDL θ's

Surface Energy is the Fundamental Property Defining GLD Hydrophobicity



Modeling of Heterogeneous GDL θ's



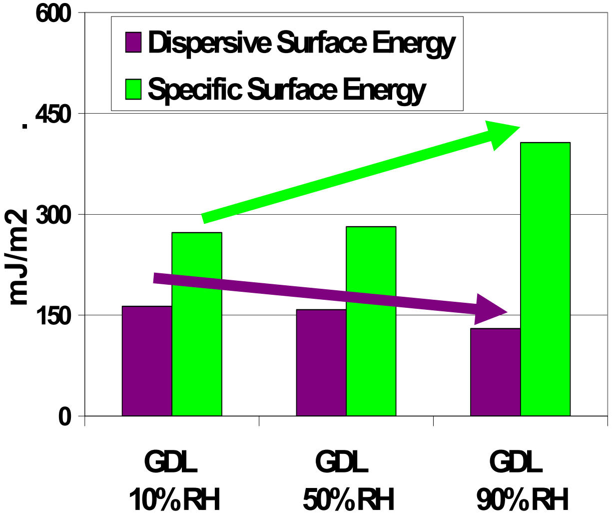
- GDL surface-energy decreases with increasing PTFE content.
  (more hydrophobic)
- Microporous Layer (MPL) increases GDL surface energy.
- Hydrophobicity should be maintained over lifetime

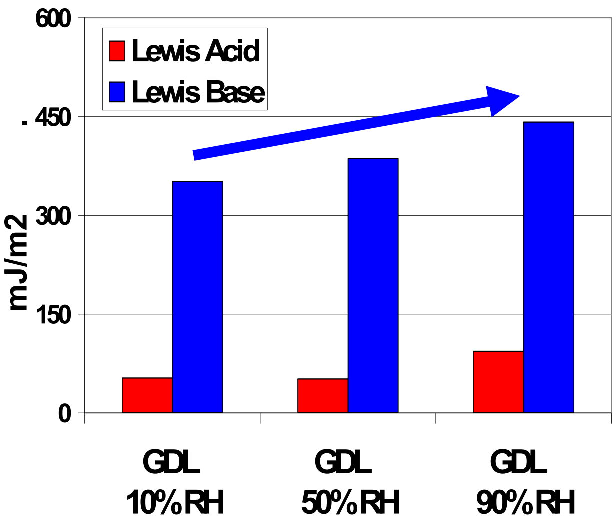
- Measured θ-reduction :
  130.0° to 123.3° (680 hr aging at 80°C and Air)
- Model predicts:
  - θ-decrease from 130° to 122° from aging
  from (graphite powder θ-decrease 57° – 32°) aged in 92%O_2/8% O_3(7 hrs)

RH Effect on GDL Surface Energy

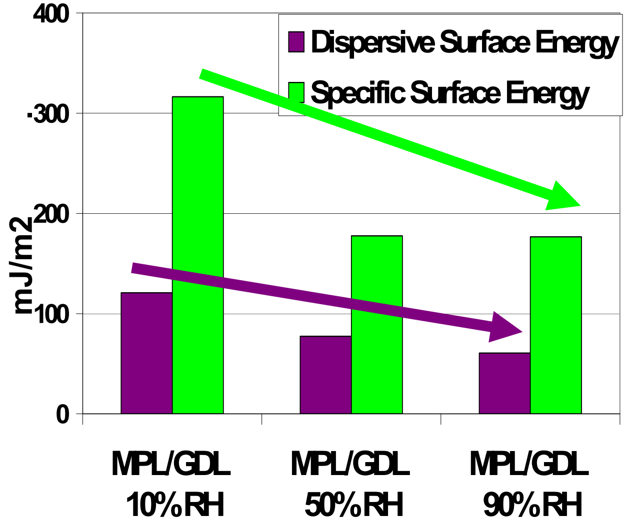
Inverse Chromatograph Analysis (IGC)**

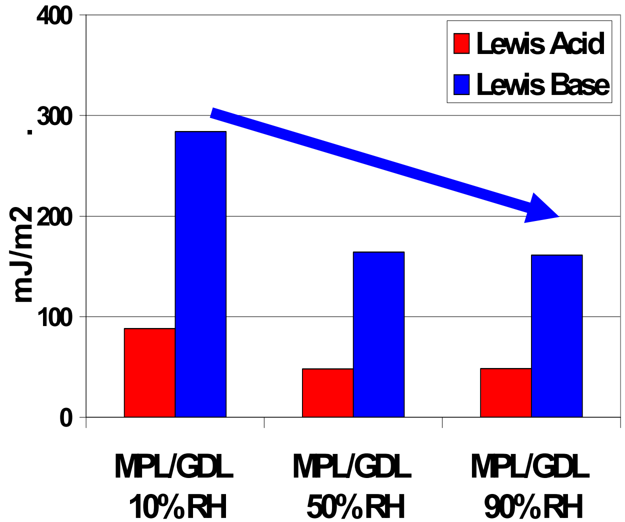
GDL





MPL / GDL





- **RH (water adsorption) effects surface properties**
- **Inverse effects on GDL and MPL acid/base surface energies**
- **RH (water) reduces dispersive surface energy**

Dispersive Surface Energy: (non-polar) interactions

Specific Energy: (polar) interactions

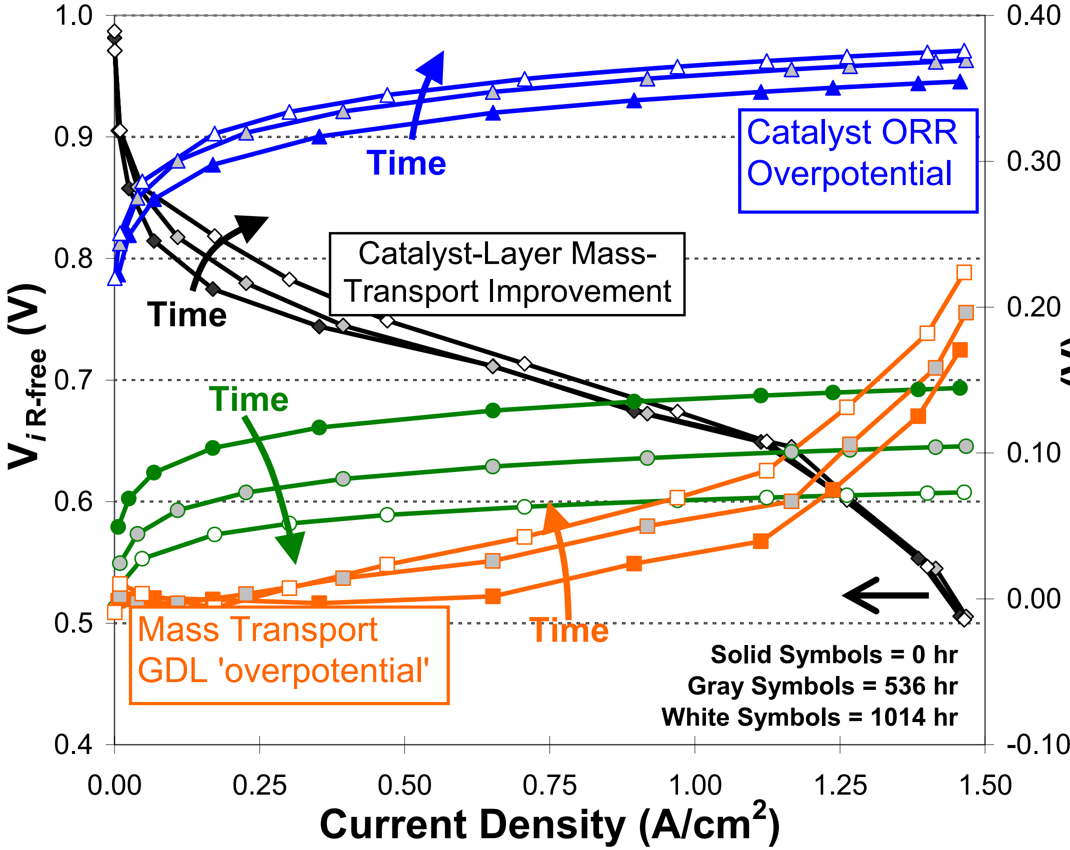
GDL 5% PTFE Loading
MPL 23% PTFE Loading

Fuel Cell Program

**Surface Measurement Systems NA

Los Alamos

Durability Performance Modeling
Durability of iR-Corrected Overpotentials

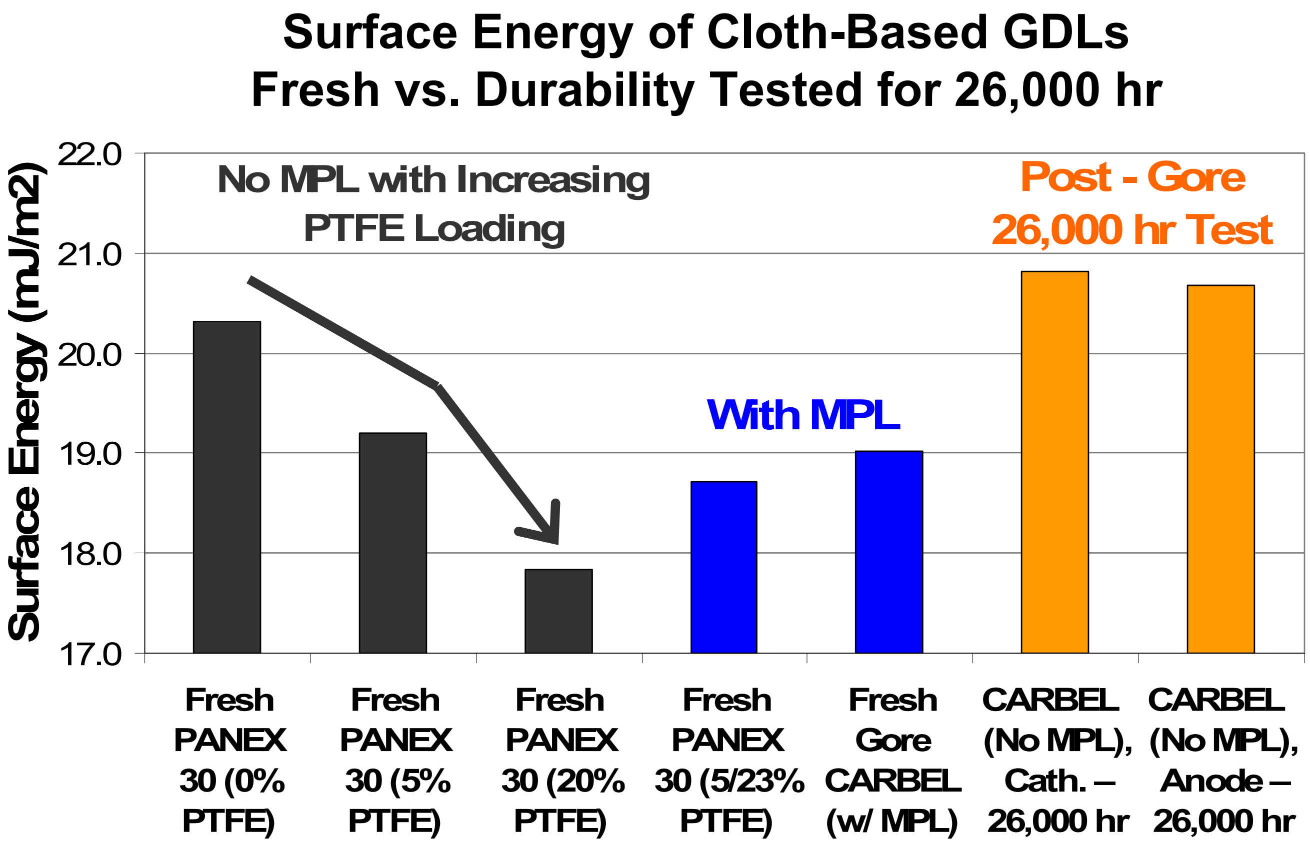


- Provides method for quantization of Mass-transport resistance and GDL durability
- Publication on methodology

MEA: Gore-Select 5620
CC = 0.9 A/cm²
GDL: SGL 24BC
Decay: 12 μV / hr
T_{cell} = 80°C
Gas Press. = 15 / 15 psig
RH = 75% / 75%
Flow Rates = 1.2 / 2.0 (A/C) × 1.5 A/cm2 equiv.

- Modeling of mass-transport losses extrapolated to 'over-potential'
  - Method for analyzing performance losses (iR, ORR, MT)
- Better understanding of ***long-term*** fuel cell test data
  - Definition of components leading to performance degradation

Surface Energy of Cloth-Based GDLs



Gore 26,000 hr Test:
T_{Cell} = 70°C
T_{sat} (A/C) = 70/70°C
P_{gas}= 1 atm abs.
i = 0.8 A/cm2
A/C Stoich. = 1.2 / 2.0

- Cloth GDLs show hydrophobicity loss with aging
  - PTFE loading increase hydrophobicity
  - MPL reduces overall hydrophobicity
  - Post 26,000 hr test, more hydrophillic than untreated fresh GLD Cloth

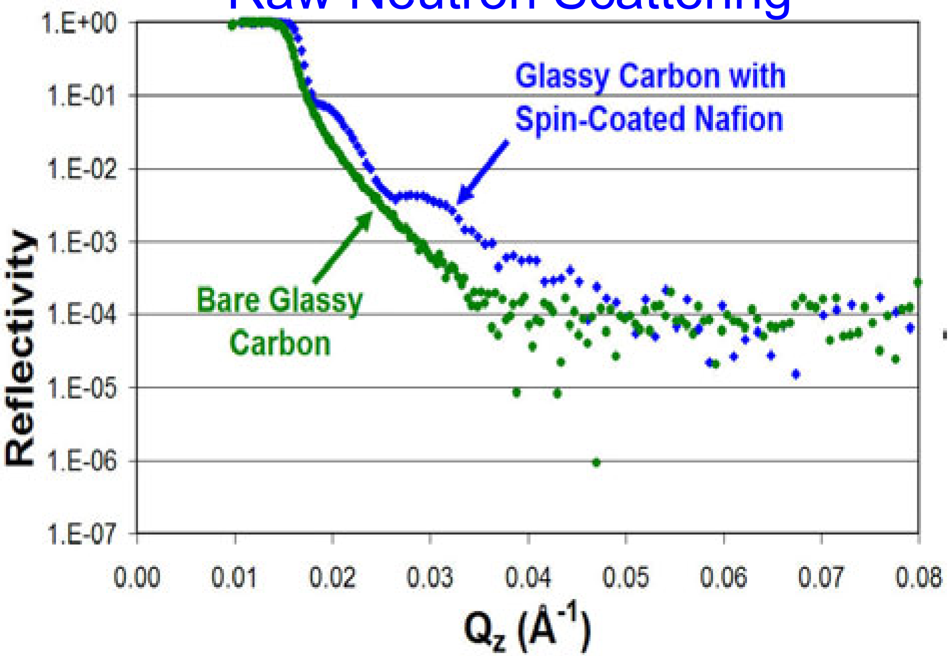
Neutron Reflectometry

SPEAR (Surface Profile Analysis Reflectometer)

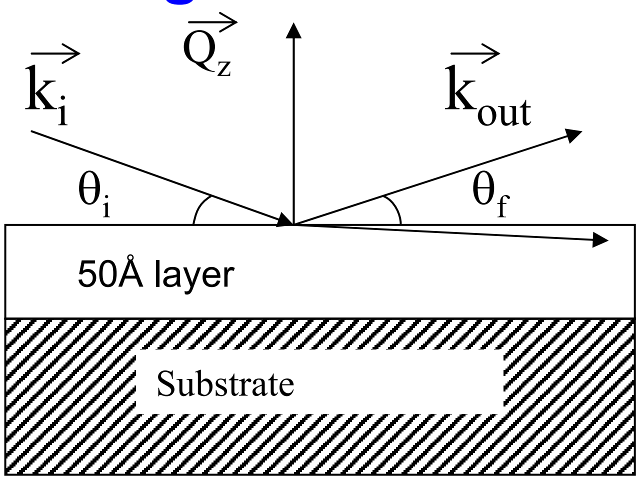
SPEAR:

Film thickness
Interfacial Roughness
Coverage
Molecular properties changes

Thin-Film Nafion/Glassy-C
Raw Neutron Scattering



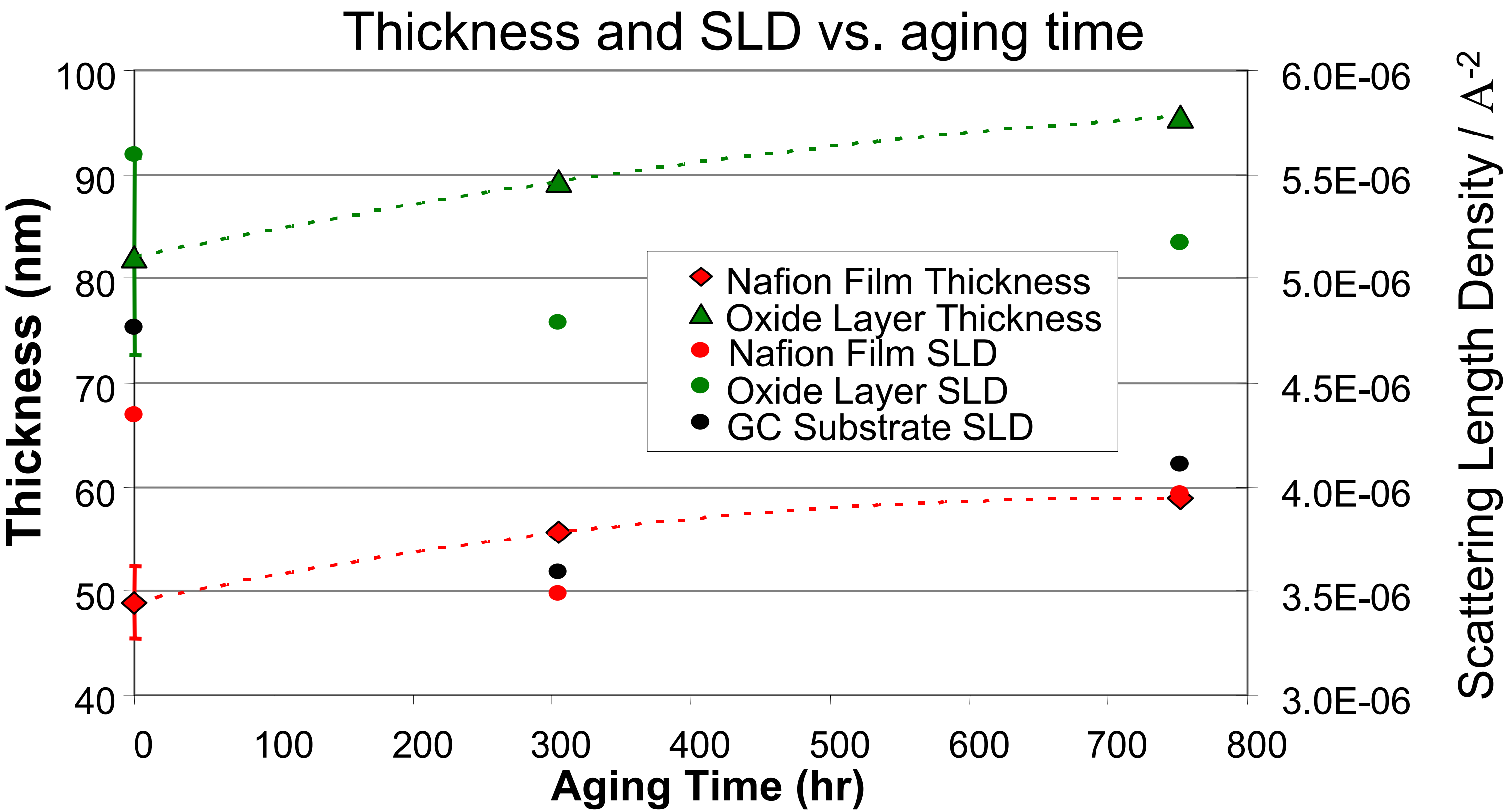
Scattering Vector Schematic



- For good scattering results, ~ atomically smooth surfaces required
- Glassy Carbon acceptable surface

Carbon Substrate Roughness = 183 Å
Carbon Surface-Oxide Thickness / Roughness = 88.7 nm / 58.9 Å
Nafion Film Thickness / Roughness = 45.3 nm / 27.1 Å

Neutron Reflectivity of Nafion on Carbon

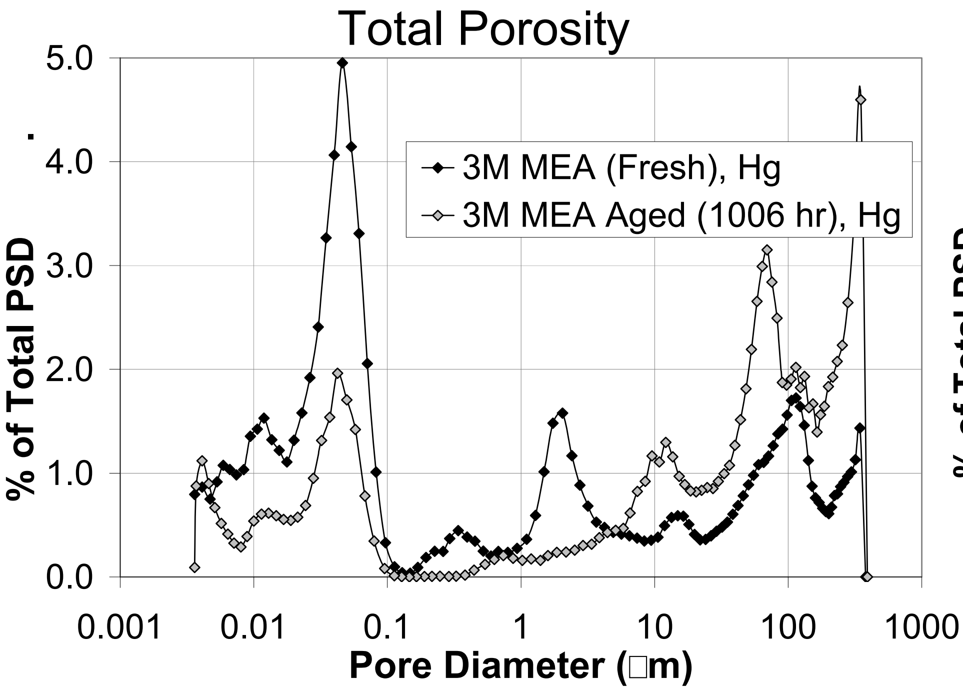


- Increasing thickness of Nafion film and Carbon-oxide layer
- SLDs of substrate, oxide layer, and Nafion film decrease during aging
  - Swelling of Nafion and/or loss of Nafion mass
  - Changes in distribution and/or composition of the of Carbon-oxide layer

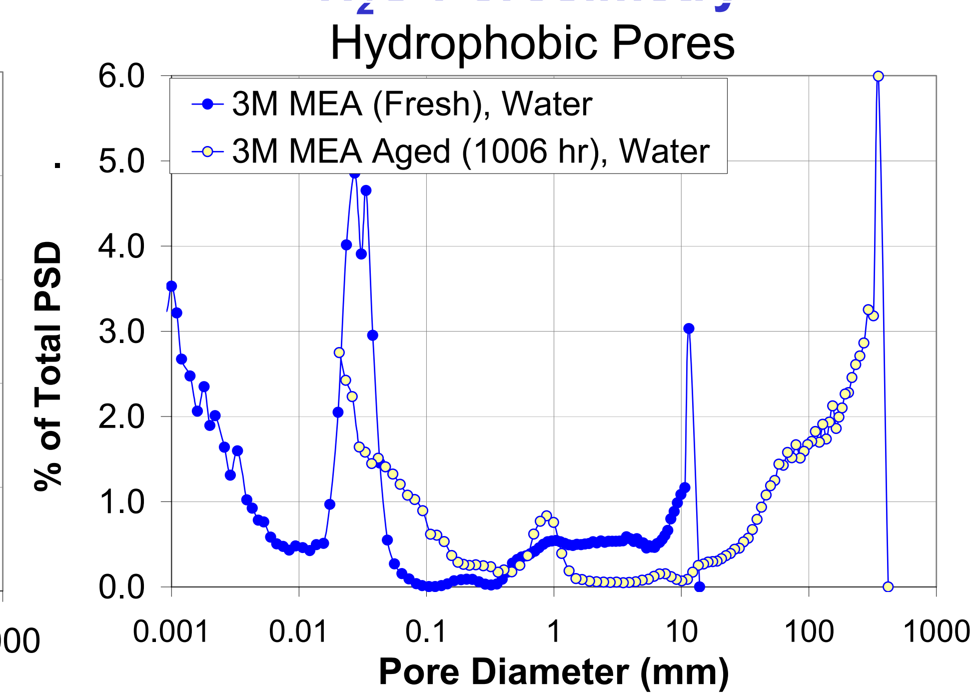
SLD - the effective scattering in terms of coherent path length of a molecule/atom within the volume it occupies

Electrode/Membrane Pore-Size Distributions

Hg Porosimetry



H_2O Porosimetry

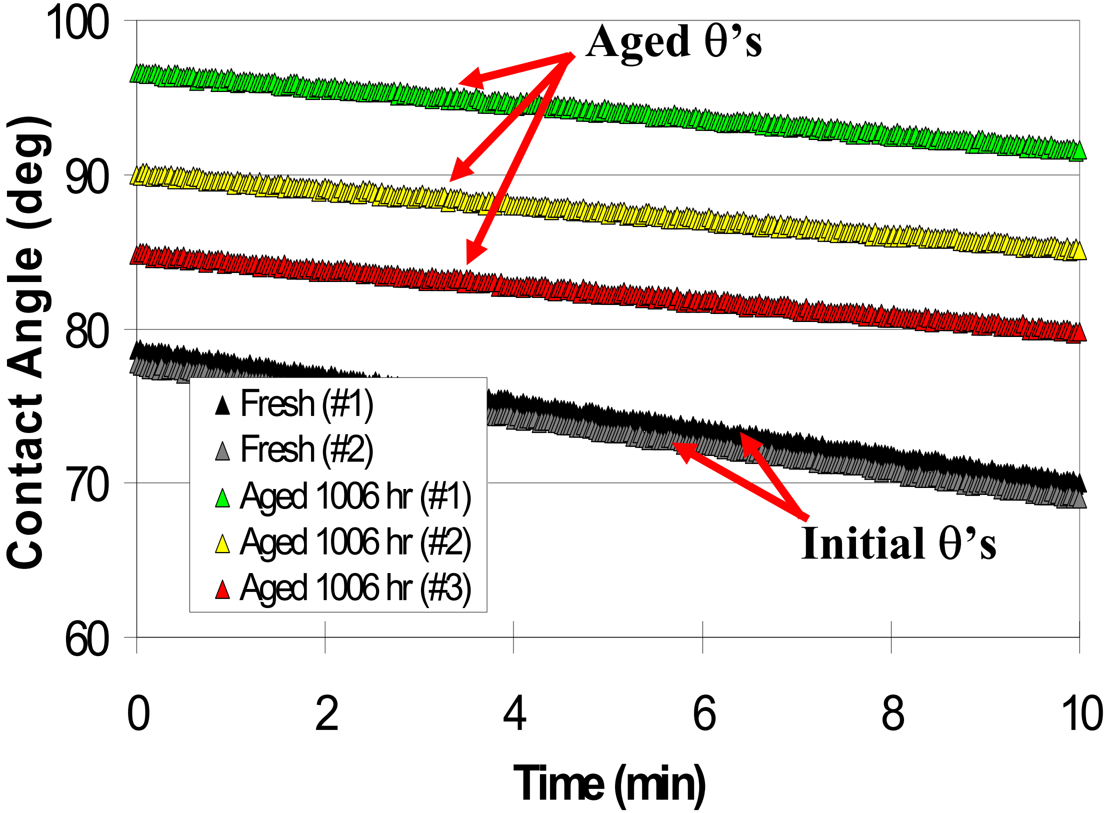


- Membrane / Electrodes show porosity changes after aging
  - Substantial increase in total porosity (Hg) after aging
  - Membrane / Electrode aging shows decrease in catalyst-layer pores (~ 0.05 mm)
  - Membrane / Electrode aging shows increase in large membrane pores (> 20 mm)
  - Collective porosimetry data suggests loss of mass and chemical changes.
  - Increase in large pores size correlates to increasing gas permeability

Loss of Membrane Hydrophilicity

After ~1000 hr Aging (80°C, Air Sparge)

Dynamic Sessile-Drop Contact Angle Measurements



Cast Nafion Membrane

- Initial θ increases after aging – surface becomes more hydrophobic
- Contact-angle slope magnitude decreases after aging (⇒ decreased hydrophilicity) – slower water uptake
- Spread between initial pre-aging θ values increased after aging
- Suggests localized chemical effects (loss of sulphonate sites)

Future Activities

- **MEA Durability Measurements**
  - Drive cycle testing, Shut-down/startup, Operating effects
- **Catalyst Durability / Characterization**
  - Modeling of particle growth to correlate growth conditions
  - Bonding interactions with Pt - develop stable Pt catalysts / supports
  - *in situ* XRD analysis of Pt particle growth period
- **Carbon Corrosion**
  - Evaluate carbon corrosion mechanisms in catalyst 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
    - Changes in hydrophobicity, pore structure
- **Membrane Degradation**
  - Examine conditions leading to membrane thinning and failure
    - Determine conditions leading to peroxide formation

Project Summary
PEM Fuel Cell Durability

- **Durability Testing**
  - Drive Cycle testing, including start-stops
    - *in situ* and *ex situ* characterization
- **Electrocatalyst durability**
  - PEM fuel cell testing, cycling measurements
    - Characterization by HAD, XRD, TEM
    - Fundamental particle growth modeling
- **GDL durability**
  - Measurement and Modeling of Heterogeneous GDL θ's
  - Changes in porosity and hydrophobicity
  - Modeling of degradation due to GDL mass transport losses
    - changes in hydrophobicity, pore structure
- **Membrane durability**
  - Changes in porosity and hydrophilicity
  - Examining thin-film Nafion/Carbon aging by neutron scattering

Back-up Slides

Publications and Presentations

1. 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
2. Durability Study of Polymer Electrolyte Fuel Cells at High Humidity Conditions, Xie et al., *Journal of The Electrochemical Society*, **152** A104-A113 2005
3. 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
4. Long-Term Performance Characterization of Proton Exchange Membrane Fuel Cells, Wood et al., 206th Meeting of The Electrochemical Society, Honolulu, Hawaii, October 5th, 2004
5. Characterization of Nanocrystalline Fuel Cell Catalysts by X-ray Profile Fitting Methods, Garzon et al., 206th Meeting of The Electrochemical Society, Honolulu, Hawaii, October 5th, 2004.
6. Durability Issues of the PEMFC GDL and MEA Under Steady-State and Drive-Cycle Operating Conditions, Borup et al., 2004 Fuel Cell Seminar, San Antonio Texas, Nov. 1-5
7. PEM Electrocatalyst Durability Measurements, Borup et al., The Electrochemical Society, June 12 – 17 2005, Las Vegas NV
8. MASS-TRANSPORT PHENOMENA AND LONG-TERM PERFORMANCE LIMITATIONS IN H2-AIR PEMFC DURABILITY TESTING, Wood et al., Presented at the Fuel Cell Seminar, 2005, Palm Springs, CA, Nov. 14 - 18, 2005
9. Durability of PEM Electrocatalysts and Gas Diffusion Media, Borup et. al, Fuel Cells Durability, December 8, 2005 - Omni Shoreham Hotel, Washington, DC USA
10. PEM Fuel Cell Electrocatalyst Durability Measurements, Borup et. al, Accepted for publication in J. Power Sources, 2006

FY2005 DOE Review Meeting

Reviewer Comments #1 (positive)

FY2005 Reviewer Comments: (Very positive comments received)
(3.9 overall / 4.0 – highest review score of 2005)

- Basic no-nonsense experimental approach combining results from different tests as a means to achieve understanding of impact on durability.
- New tools for understanding degradation are right on target.
- Very relevant work to understanding the issues related to automotive duty cycle operation.
- Solid laboratory approach with excellent analysis of results.
- Good view of the big picture.
- Very comprehensive *in situ* and *ex situ* testing.
- This work is a great beginning.
- Many learnings identified for real world operating conditions: effect on catalyst growth, carbon corrosion, thinning etc.
- Hydrophobicity impact especially important for automotive and stationary systems.
- Investigated many parameters important to durability.
- Important conclusions drawn from well-documented data.
- Good presentation list

FY2005 DOE Review Meeting

Reviewer Comments #2 (Recommendations/Weaknesses)

- ...... Can they now use these tests to develop an understanding of the degradation mechanism and predict materials solutions and lifetimes? ... common approach ... by many industry groups.... emphasize mechanistic understanding and not just materials screening.
    - We have done almost no material screening. We emphasize mechanistic understanding, less materials development. We do not screen materials.
- Authors are also working on many different aspects .... I would rather they focus in one area and gain a deeper understanding.
- Needs more work on GDL and hydrophobicity.
- ... classical "many-variable" problem. ... need to focus on specific problems and work with very well-characterized electrodes.
    - We try to keep a good balance on the various aspect of durability. Some reviewers want more concentration, others desire less.
- Could have more interactions with OEMs.
    - We are always willing to expand interactions. However, for best value, we need interactions outside of NDAs and non-analysis agreements
- Expansion to stationary applications ... (40,000 hours) would be a plus.
    - DOE program managers have indicated desire for us to primarily work on automotive
- Have yet to address ways to improve durability.
    - This projects' approach is define degradation. Other LANL projects are working to improve durability. This project feeds other projects. We proposed many new materials in the DOE National Laboratory Solicitation call based on understanding from this project.

Critical Assumptions and Issues

- LANL durability measurements have limited numbers of samples
  - Time, effort level and equipment limit the numbers of samples
  - Fuel cell stack systems will have ~ 200/250 individual cells
    - Demonstration of individual samples making durability targets is not sufficient proof of stack durability
    - Fuel scale and power stack demonstrations will eventually be required
- Many experiments are limited by membrane failure
  - Failure occurs with ‘catastrophic’ failure - gas crossover
  - MEA failure correlates to hole/pin-hole formation in membrane
- Better automotive OEM description of realistic drive cycle operation is desirable. This includes:
  - RH, Temperature, Pressure, as a function of power level during drive cycle