Durability Improvements Through Degradation Mechanism Studies

Includes: Applied Science for Electrode Cost, Performance, and Durability

DOE 2010 Annual Merit Review Meeting

June 7 - 11, 2010

Presented by: Rod Borup

National Labs: Los Alamos National Lab (LANL), Argonne National Lab (ANL), Oak Ridge National Lab (ORNL), Lawrence Berkeley National Lab (LBNL)
Industry: Ballard Fuel Cells, Ion Power
University: University of New Mexico

FC013

This presentation does not contain any proprietary or confidential information

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Organizations / Partners

- Los Alamos National Lab (LANL) – Degradation Mechanisms
  - Lead: durability testing and fundamental characterization
  - Rangachary Mukundan, John Davey, Cynthia Welch, Roger Lujan, Bo Li, Dusan Spernjak, Joe Fairweather, Andrea Labouriau
- Los Alamos National Lab (LANL) – Applied Science Task
  - Fundamental understanding of electrode structure
  - Christina Johnston, Yu Seung Kim, Cynthia Welch, Rex Hjelm, Bruce Orler, Marilyn Hawley, Nathan Mack, Zhongfen Ding, Baeck Choi
- Argonne National Laboratory (ANL)
  - Integrated comprehensive degradation model and model distribution
  - Rajesh Ahluwalia, Xiaohua Wang
- Ballard Power Systems (BPS)
  - Fuel cell system testing, stack integration, component interactions, and stack materials
  - Sylvia Wessel, Paul Beattie, Greg James, Daniel Ramrus, Svetlana Loif, Warren Williams
- Ion Power
  - Specialized membranes, Ionomer and MEAs
  - Steve Grot, Walter Grot
- Lawrence Berkeley National Laboratory (LBNL)
  - Fundamental modeling
  - Adam Weber, Ahmet Kusoglu
- Oak Ridge National Laboratory (ORNL)
  - Characterization (TEM) and metal bipolar plates
  - Karren More, Mike Brady
- University of New Mexico (UNM)
  - Characterization (XPS) and carbon corrosion measurements
  - Kateryna Artyushkova, Plamen Atanassov, Anant Patel

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Budget

DOE Cost Share	Recipient Cost Share	Total
$8,225k	$501k	$8,726k
94%	6%	100%

Yr 1	Yr 2	Yr 3	Yr 4	Cumulative
$2000k	$2000k	$2175k	$2050k	$8225k

Participant	FY10 (Year 1)
LANL	$1245k
Industrial + Univ. Partners (Ballard, Ion Power, UNM)	$425k
Other National Labs (ANL, LBNL, ORNL)	$850k

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Objectives

- Identification and delineation of individual component degradation mechanisms
- Development of advanced in situ and ex situ characterization techniques for analysis of fuel cell component degradation
- Quantify the influence of inter-relational operating environment between different fuel cell components
- Degradation measurements of components and component interfaces
- Elucidation of component interactions, interfaces, operating conditions leading to cell degradation
- Individual degradation models of all fuel cell components
- Development and public dissemination of an integrated comprehensive model of cell degradation
- Methods to mitigate degradation of components

Applied Science Task:

- Explore Nafion® structure using SANS and NMR, and correlate different electrode structure to fuel cell tests
- Define different production methods (esp. solvents) on electrode structure
- Understand impact of structure electrode on durability and performance
- Better understand the electrode structural and chemical reasons for differences in durability

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Technical Targets/Barriers

Table 3.4.3 Technical Targets: 80-kW_e (net) Transportation Fuel Cell Stacks Operating on Direct Hydrogen [a]					
Characteristic	**Units**	**2003 Status**	**2005 Status**	**2010**	**2015**
Durability with cycling	hours	N/A	2,000 [g]	5,000 [h]	5,000 [h]
Transient response (time for 10% to 90% of rated power)	seconds	<3	1	1	1
Unassisted start from low temperature [j]	°C	N/A	-20	-40	-40

Table 3.4.5 Technical Targets: Stationary PEM Fuel Cell Stack Systems (5-250 kW) Operating on Reformate [a]			
Characteristic	**Units**	**2005 Status [b]**	**2011**
Durability	hours	20,000	40,000
Survivability	°C	-25	-35
(min and max ambient temperature)	°C	+40	+40

Durability	**Hours**	**5,000**
	Start /Stop Cycles	**17,000**
	Frozen	**1,650**
	Load Cycles	**1,200,000**

From: S. Motupally, UTC, Durability Workshop, 2007

Degradation Mechanism Studies Approach

- **Fuel cell testing**
  - Individual component testing
    - (including controlled environmental aging)
  - Measurements of degradation
    - Life testing: Drive cycle, Accelerated Stress Tests (ASTs), Shut-down/start-up, freeze
  - Examination of performance losses, analysis to define individual component contributions to loss in performance

- **Applied Science for Electrode Cost, Performance, and Durability**
  - Explore effect of electrode composition and processing on utilization, performance, and durability
  - Combine multiple techniques to understand links between electrode structure and performance and durability
    - Evaluate structure and local chemical environment of Nafion® dispersed in different solvents and solvent mixtures
    - Structural characterization used to examine electrode structures before and after durability testing

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Degradation Mechanism Studies Approach (cont.)

- **Characterization**
  - Chemical characterization of components
    - Understand and quantitate the changes in surface species of component materials
  - Morphological evaluation of components
  - Physical characterization using porosimetry, surface energy analysis, contact angle, surface area, pore size, pore volume, etc.
    - (see list of characterization techniques planned)

- **Modeling**
  - Fundamental degradation mechanisms (LBNL)
  - Individual degradation models – kinetic/rate based (ANL)
  - Integrated comprehensive model (ANL)

- **DOE Durability Working Group**
  - Coordinate activities with other durability projects
    - ANL, Nuvera, Ballard, UTC-AST, LANL-AST
  - Share data, develop more comprehensive models

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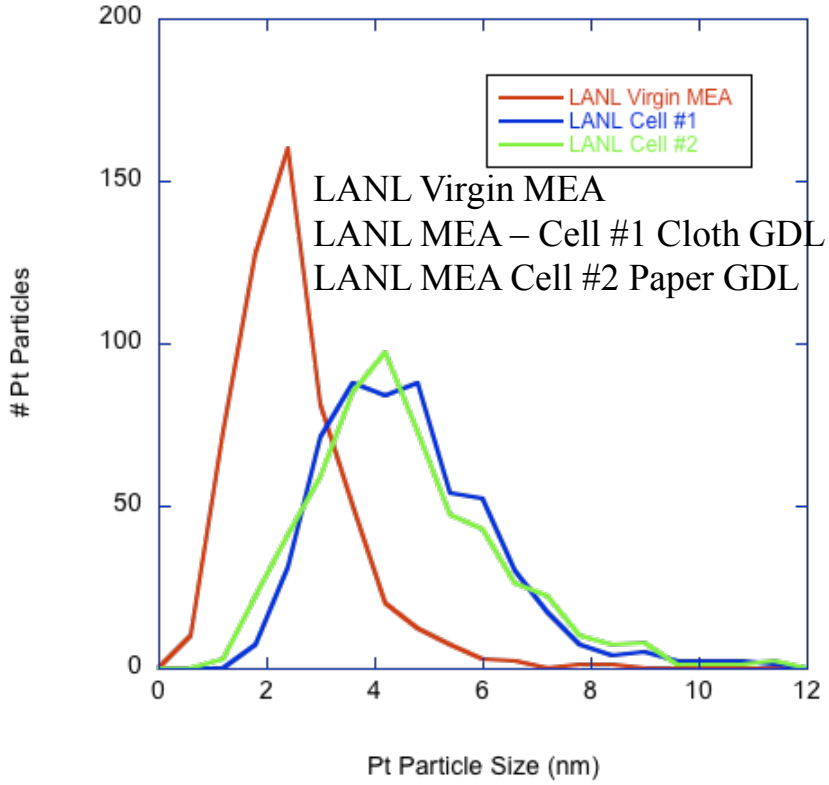
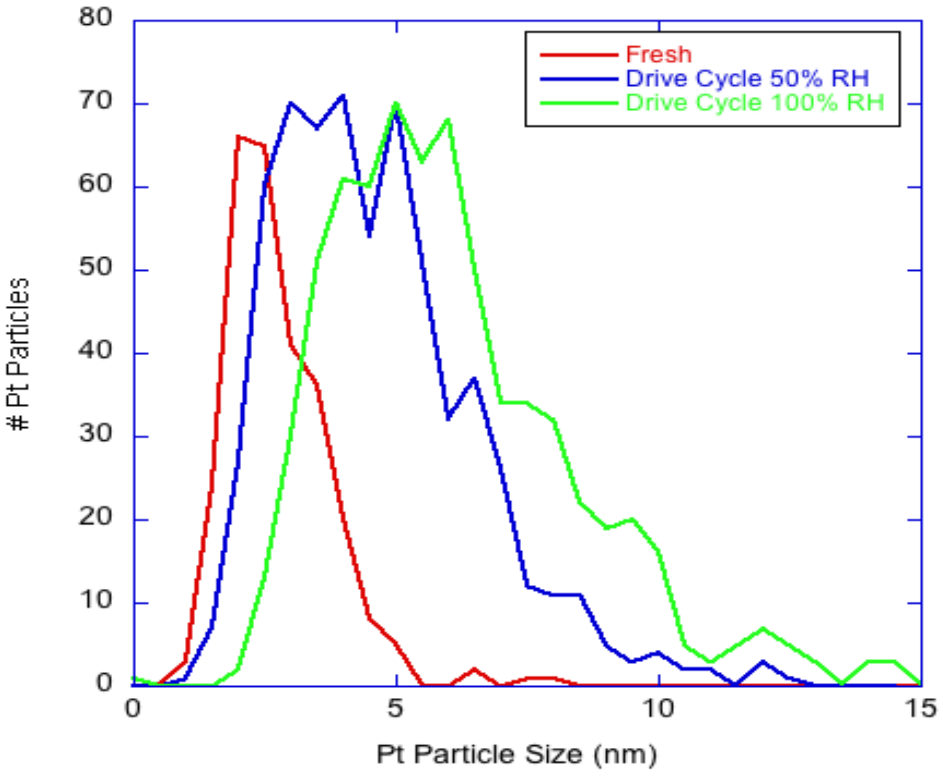
Particle Size Distributions

After Freeze Starts

5 starts @ -10°C, 5 starts @ -20°C, 3 starts @ -40°C



After 2000 Hours Drive Cycle Operation



- Cathode catalyst coarsening observed over 2000 hours of drive cycle operation similar to over a short period of operation with freeze cycles
- During freeze operation, significant coarsening of Pt on cathode was observed (from ~2.2 nm to ~4.2 nm) for both tested cells, no difference was observed in the Pt sizes and distributions between the two cells

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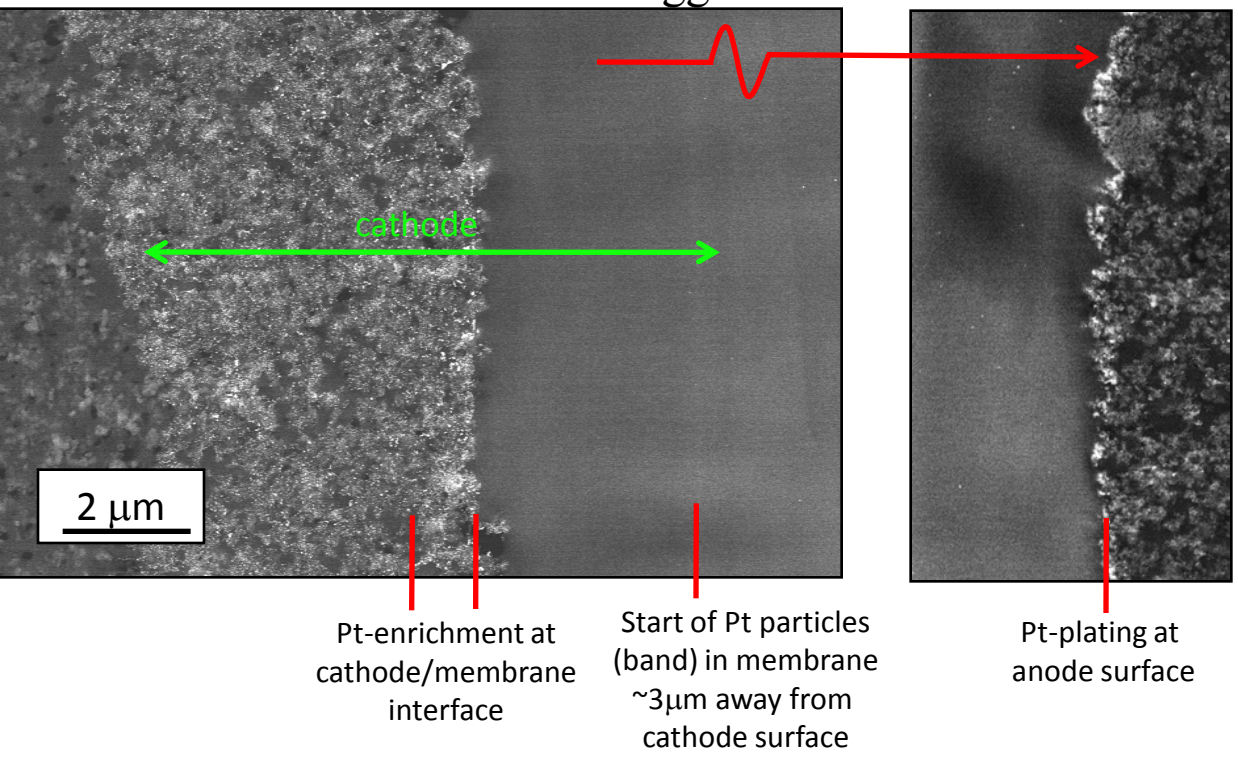
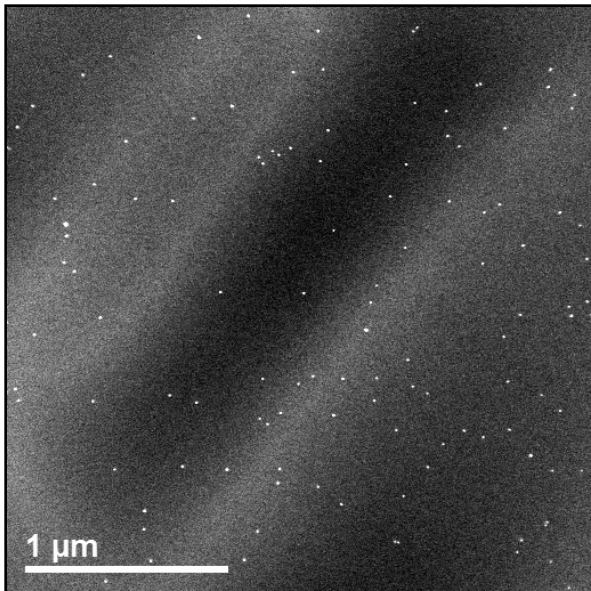
Catalyst Degradation Due to Freeze Cycles

Clear movement of Pt from cathode to cathode/membrane interface.
Increased Pt agglomeration observed near interface (0.2-0.4 µm).



Distribution of Pt particles in center of membrane



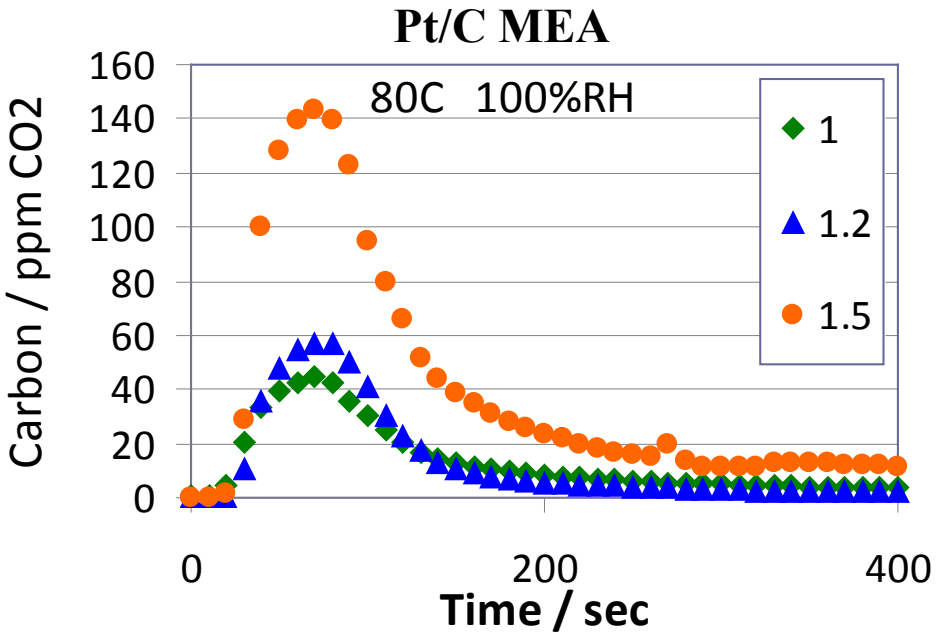
Distribution of Pt particles in center of membrane – note that Pt particles are observed continuously/homogeneously across the membrane starting ~3 mm from cathode.
Nominal Pt particle size ~15 nm diameter.
Pt particles are found across membrane up to anode/membrane interface, where the Pt "plates" the anode surface.

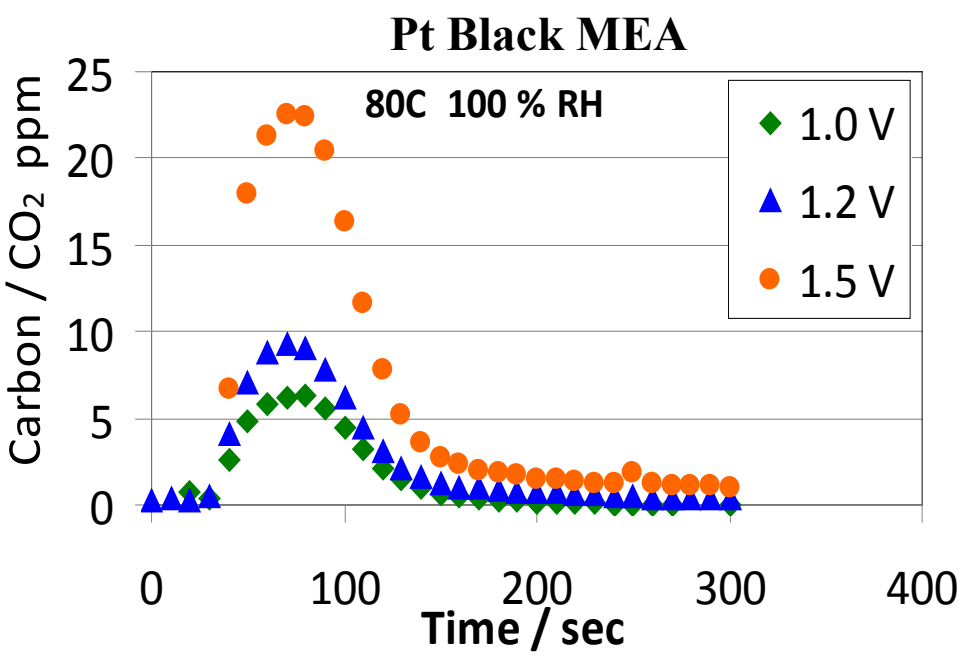
LANL MEA – Cloth GDL
5 starts @ -10°C; 5 starts @ -20°C; 3 starts @ -40°C

Carbon Corrosion From Catalyst and MPL

Start-Stop accelerating mechanism for carbon corrosion

- Estimate 30,000 start-stops
- Could expect 10 sec at air/air potential (~1.2V) for mitigated start-stop
  - 30,000 start-stops x 10 sec at 1.2V / start-stop ~ 100 hrs at 1.2V





- Measured carbon corrosion of catalyst support, MPL carbon, GDL substrate in situ
  - Direct CO_2 measurement by CO_2 NDIR
- Separate Catalyst support corrosion from GDL
  - CO_2 from standard MEA with GDL/MPL
  - CO_2 from Pt MEA with GDL/MPL
  - CO_2 from Pt Black MEA with GDL substrate only

- **At 80C 100%RH potential spike:**
  - **1.1% catalyst carbon corroded**
  - **0.052% of MPL carbon corroded**

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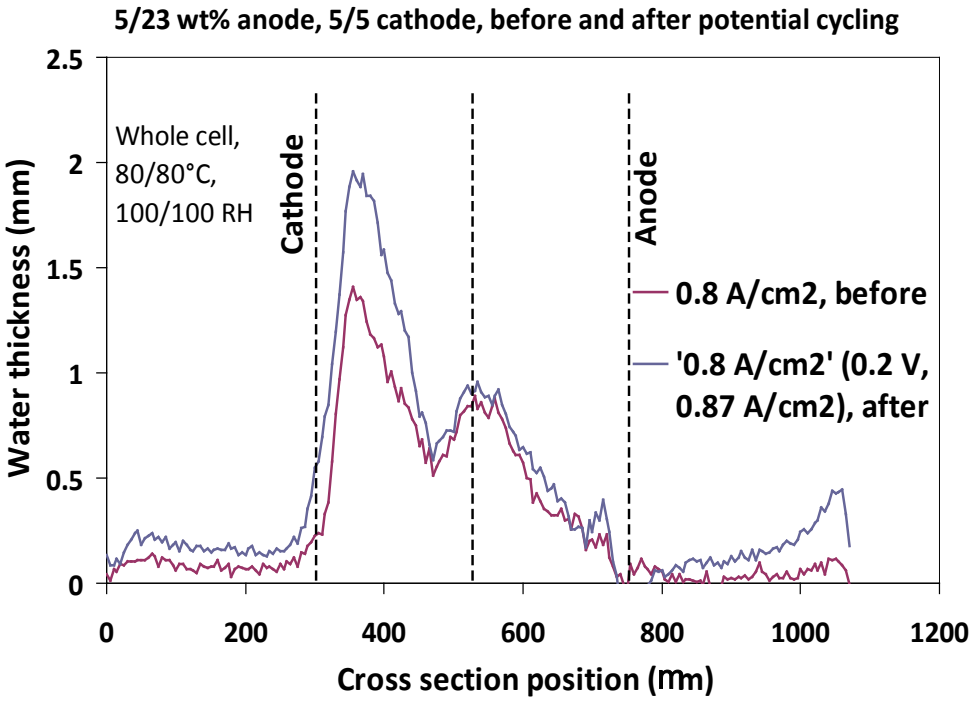
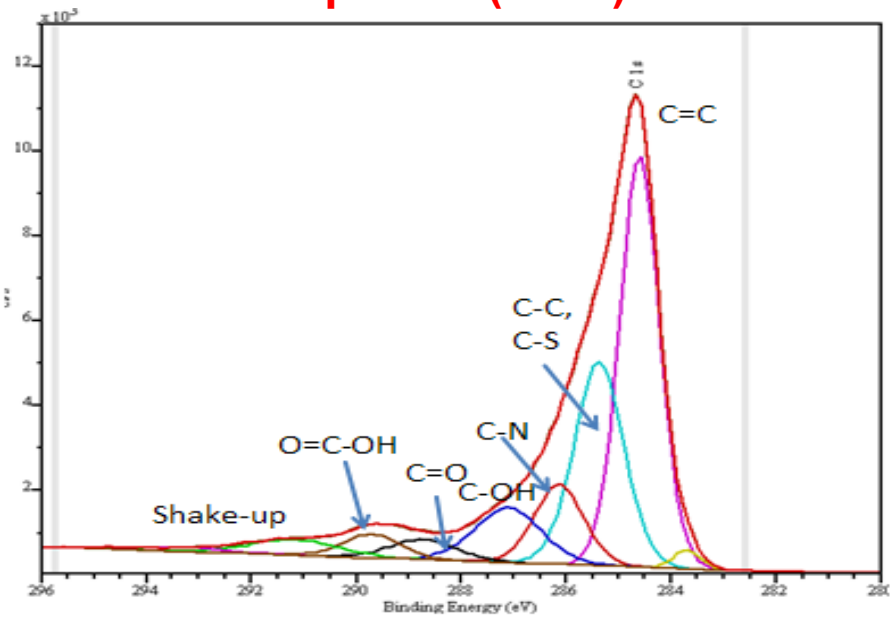
Carbon Corrosion Changes MEA Properties

Water Profile by Neutron Imaging After Potential Cycling



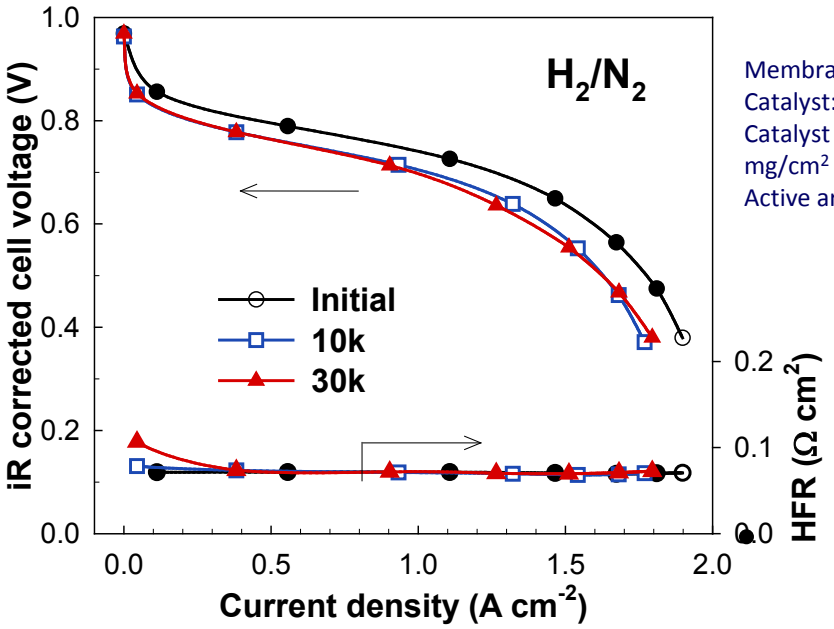
- After electrochemical potential cycling, increased cathode water is observed
  - Higher mass transport resistance

XPS of Carbon Surface Species (UNM)

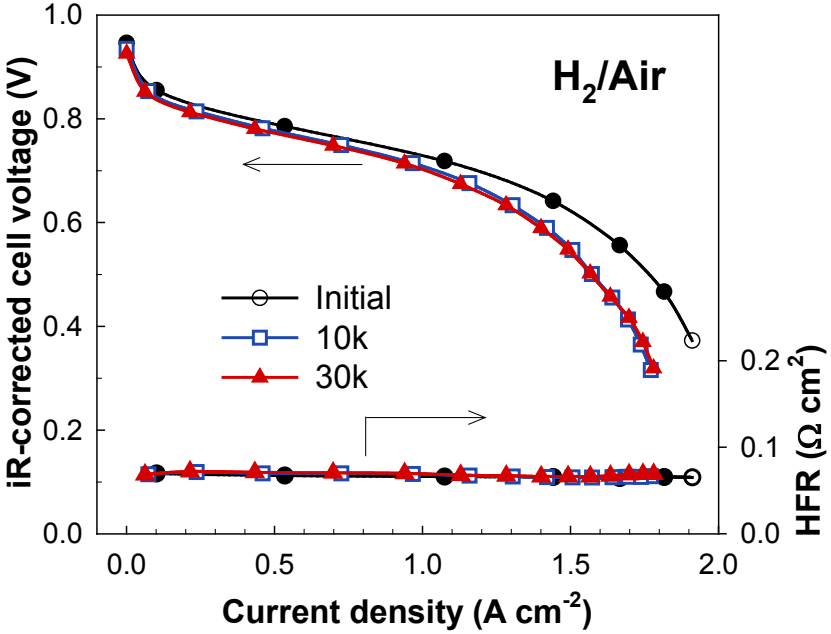


- Definition of surface carbon species by chemical shift of Carbon by XPS

Discrepancy between Observed Durability and ECSA Measurements



Membrane: Nafion® 212
Catalyst: ETEK 20% Pt/C
Catalyst loading: ~ 0.20 mg/cm²
Active area: 5 cm²



	After DOE Cycling Protocol in N_2			After LANL Cycling Protocol in Air		
Potential cycles	Initial	10k	30k	Initial	10k	30k
ECSA/CV (m^2/g)	35	17	13	36	30	28
ECSA loss (%)	0	50	63	0	18	22
Cell voltage at 0.8 A/cm²	0.765	0.743	0.733	0.756	0.741	0.734
Voltage loss (mV) at 0.8 A/cm²	0	22	32	0	15	22

Cathodes on this slide derived from glycerol-based ink (not optimized)

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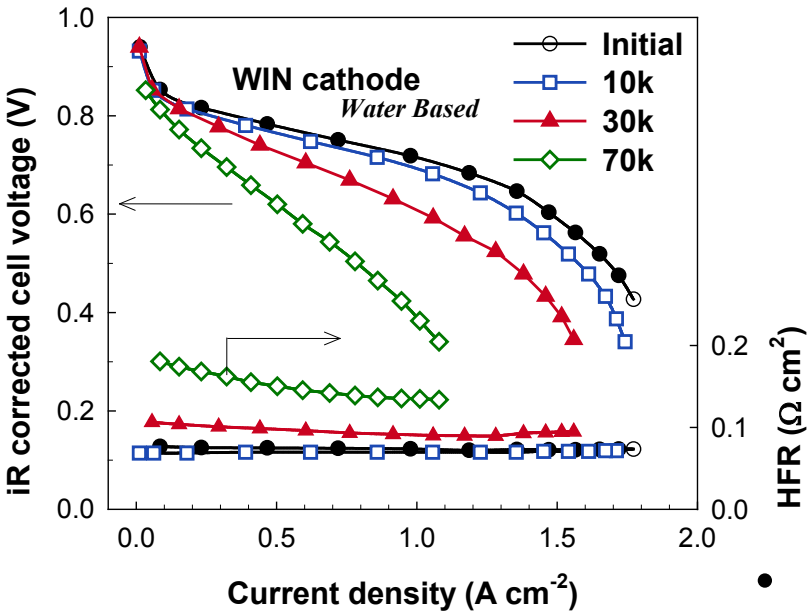
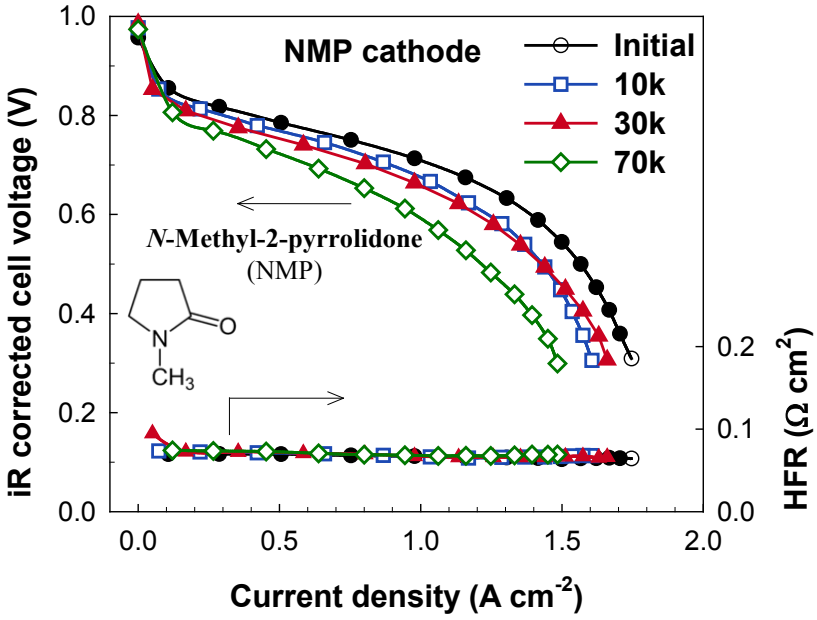
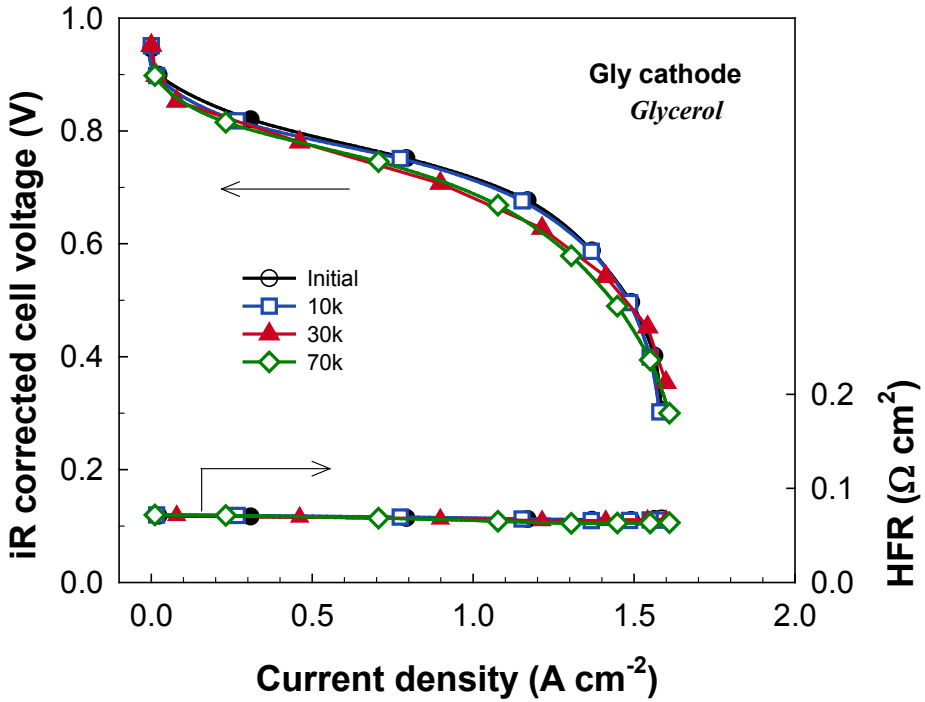
Performance Durability of Electrodes made with Varying Solvent Technology



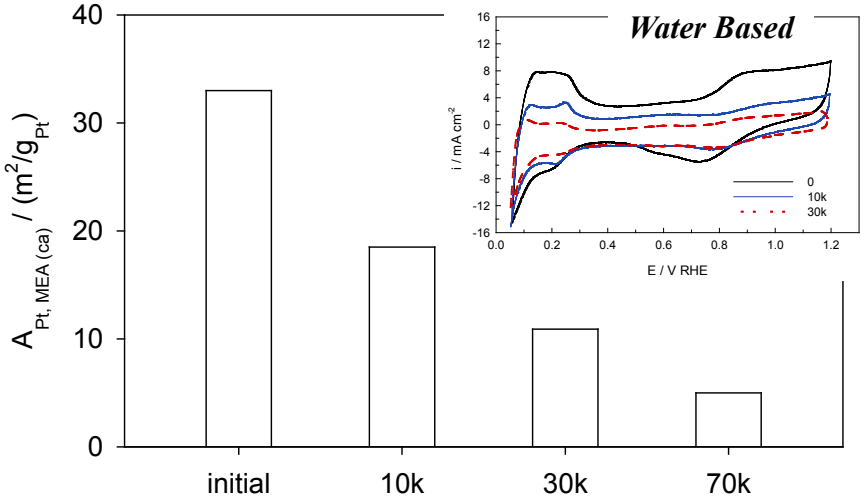


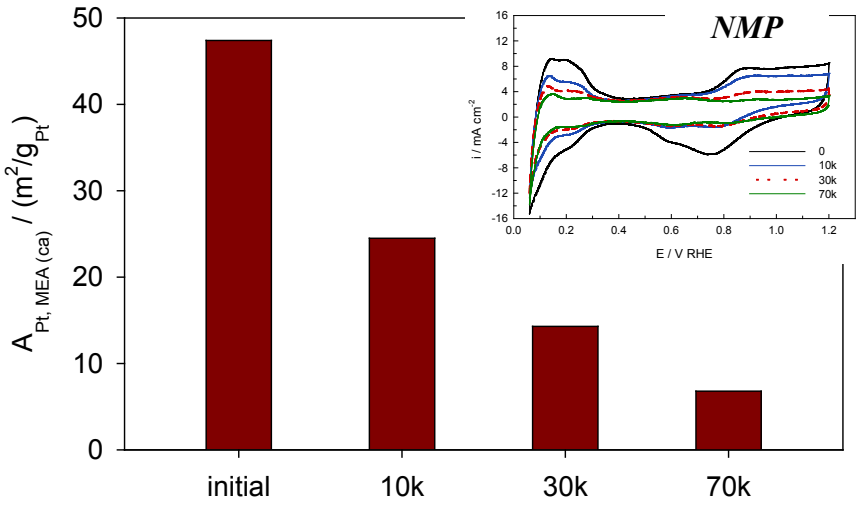


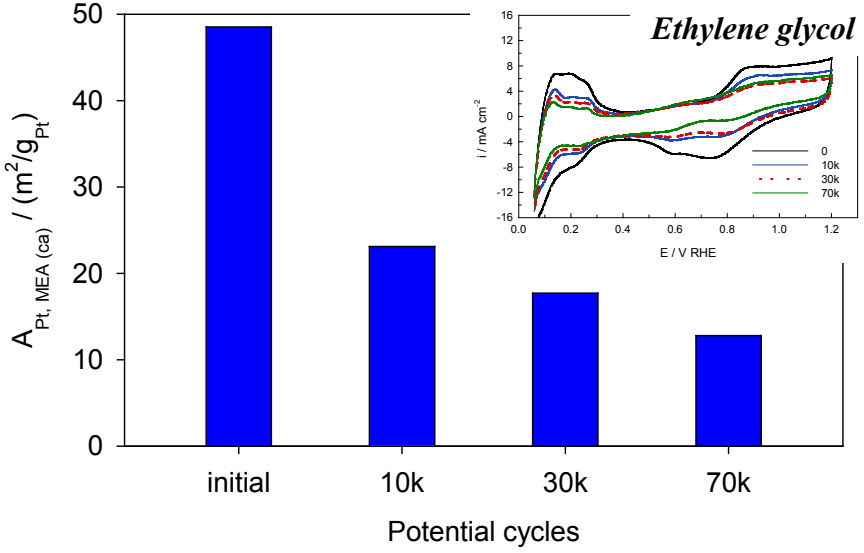
- Win cathode showed the worst durability
- NMP cathode showed significant performance loss
- Gly cathode showed an excellent durability (~ 20 mV loss at 0.8 A/cm^2 after 70k cycle)

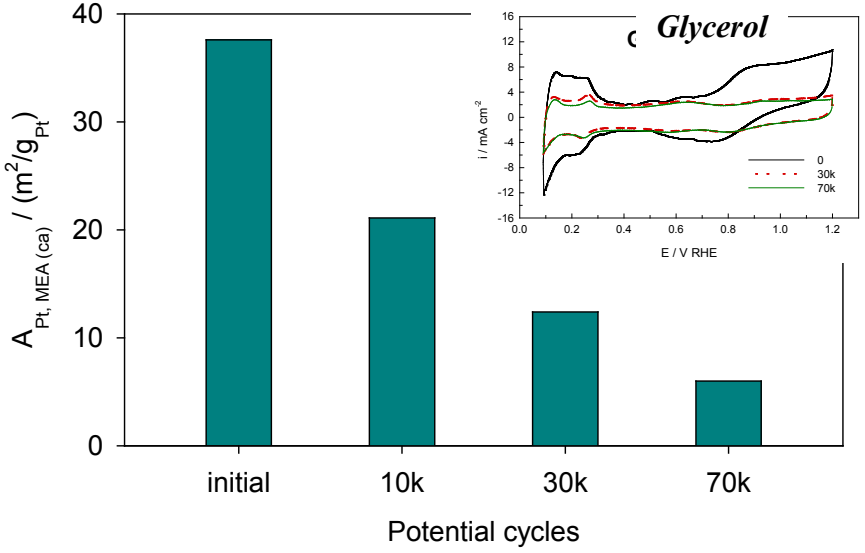
DOE durability target (30 mV loss after 30k cycle) has been achieved – up to 70K cycles!!

ECSA Change during Potential Cycling



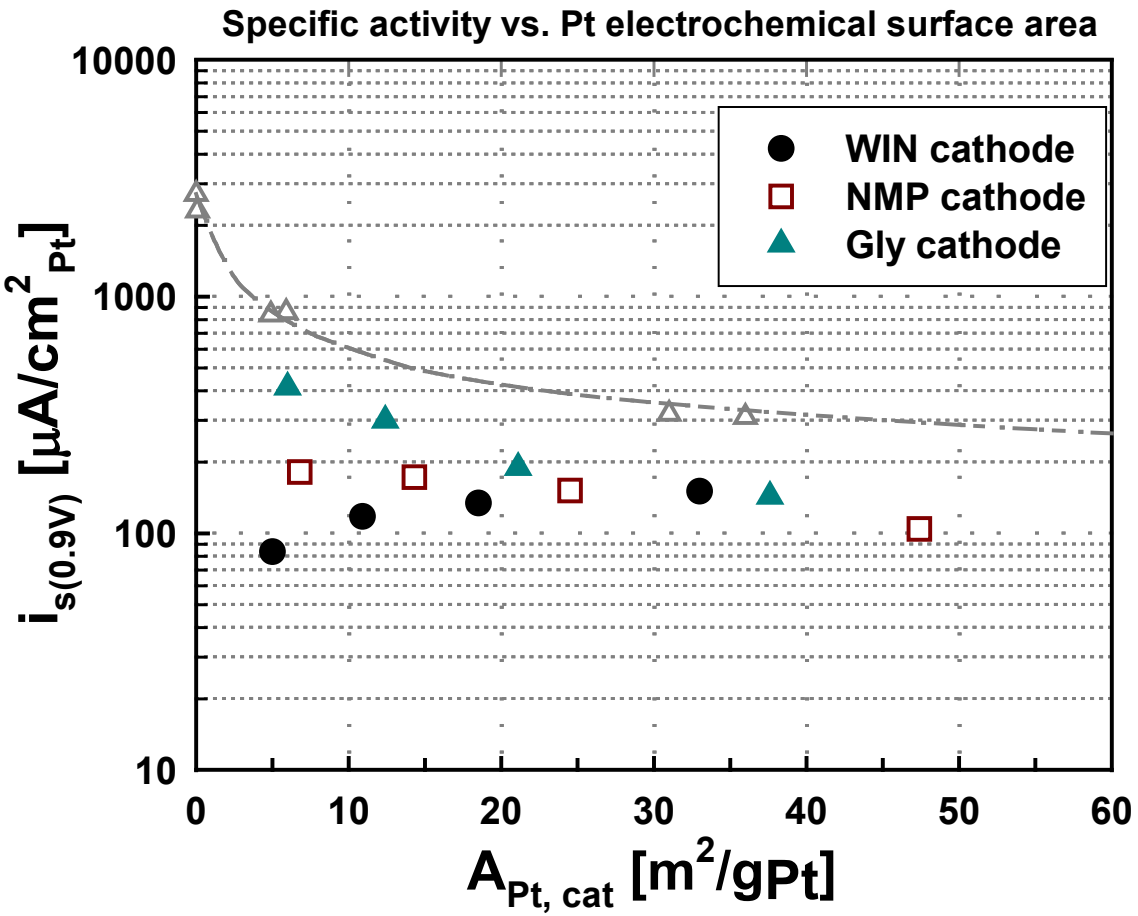






Although differences in durability are large, differences in ECSA values after cycling are much smaller

Catalyst Activity Change during Potential Cycling



* Gasteiger et al. Appl. Cat. B: Environ. 2005, 56, 9-35: ORR activities of Pt was determined via RDE-measurements in O_2 saturated 0.1 M $HClO_4$.

- **As Pt particle size increases, Pt specific activity for ORR should also increase, based on RDE measurements.**
- **Usually, this trend is not observed in fuel cells as particle size increases during durability testing, because other aspects besides the catalyst are degrading as well as well – probably the ionomer structure**
- **Modification of ionomer structure allowed expected trend to be observed**

Comparison between WIN and Gly cathode demonstrates impact of electrode structure on specific activity after durability tests---same trend can be observed in MEA as in aqueous electrolyte!!!

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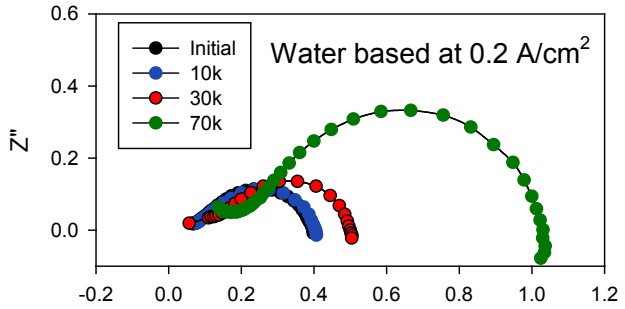
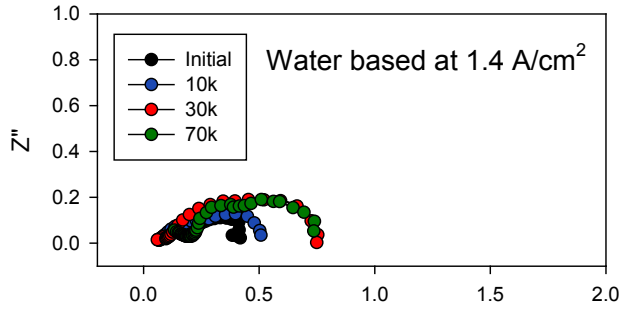
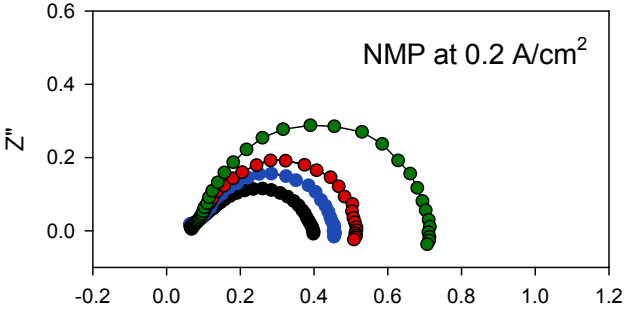
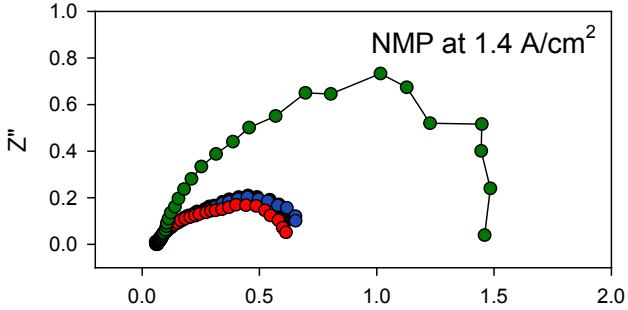
Impedance Analysis during Potential Cycling

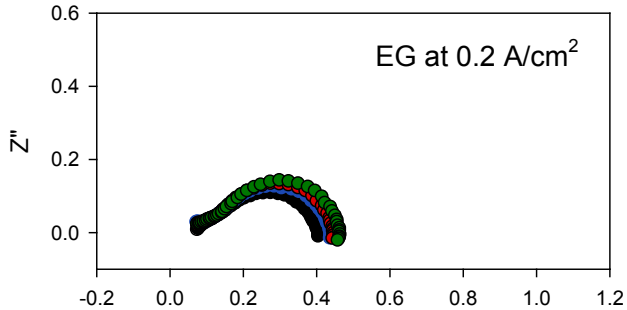
- **WIN electrode properties change greatly at both high and low current densities**
- **Glycerol electrode changes very little with cycling; NMP and EG electrode shows intermediate properties**

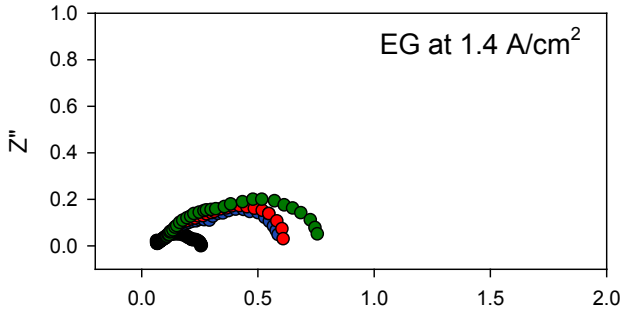


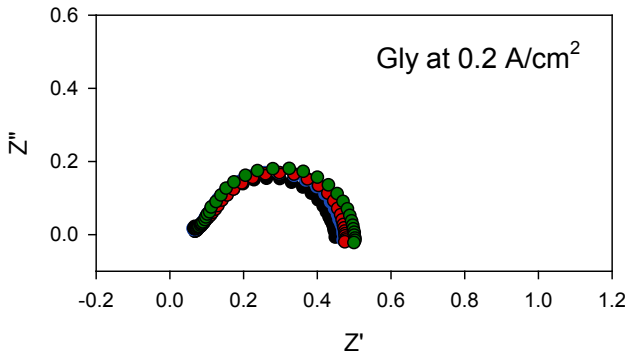


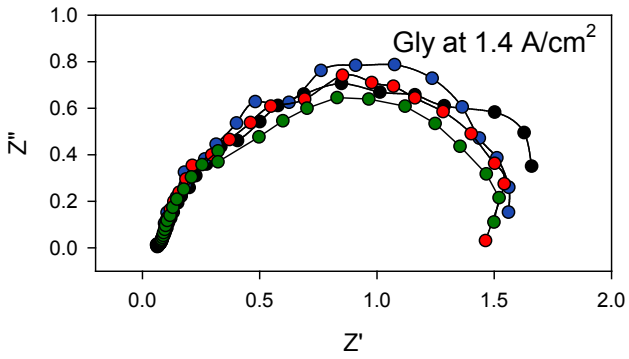








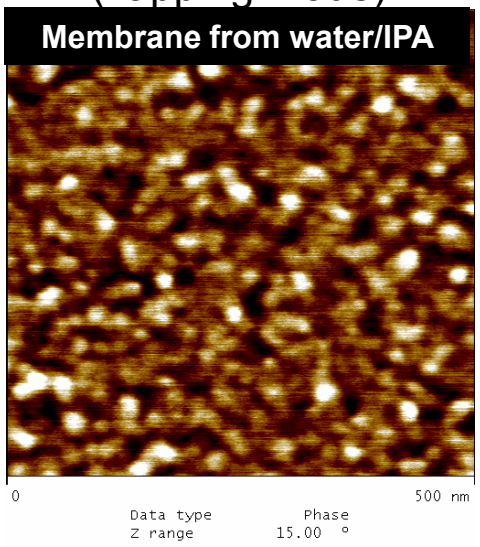


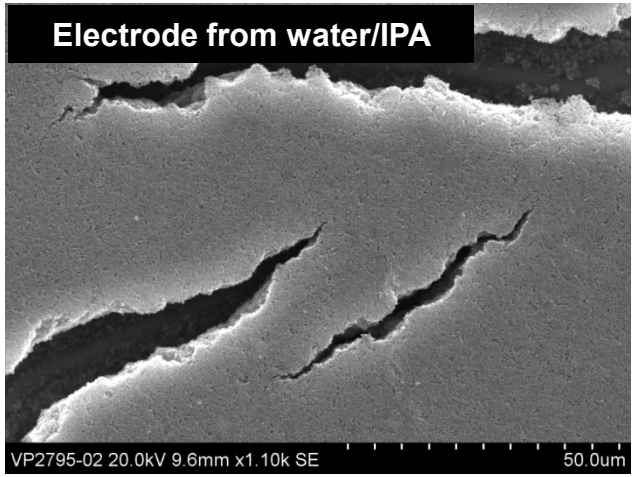


Microscopic results show different morphologies of films and electrode from water based and single solvent evaporation

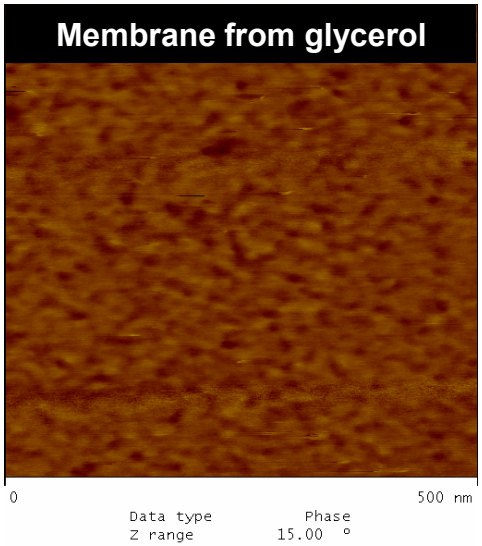
Atomic Force Microscopy
(Tapping mode)

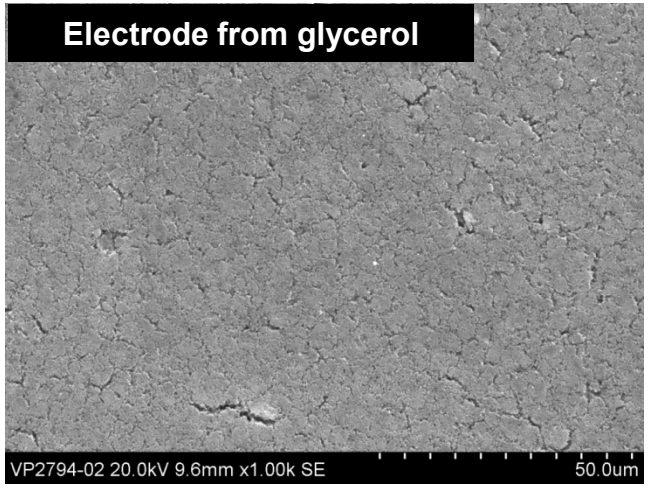
SEM





- **Complex morphology possibly created by multi-layer depositions**
- **Bright, hard domains are NOT crystalline structure**
- **<u>Produce poor film-forming properties and cracked electrode</u>**





- **Uniform morphology**
- **<u>Produce good film-forming properties and more dense electrode</u>**

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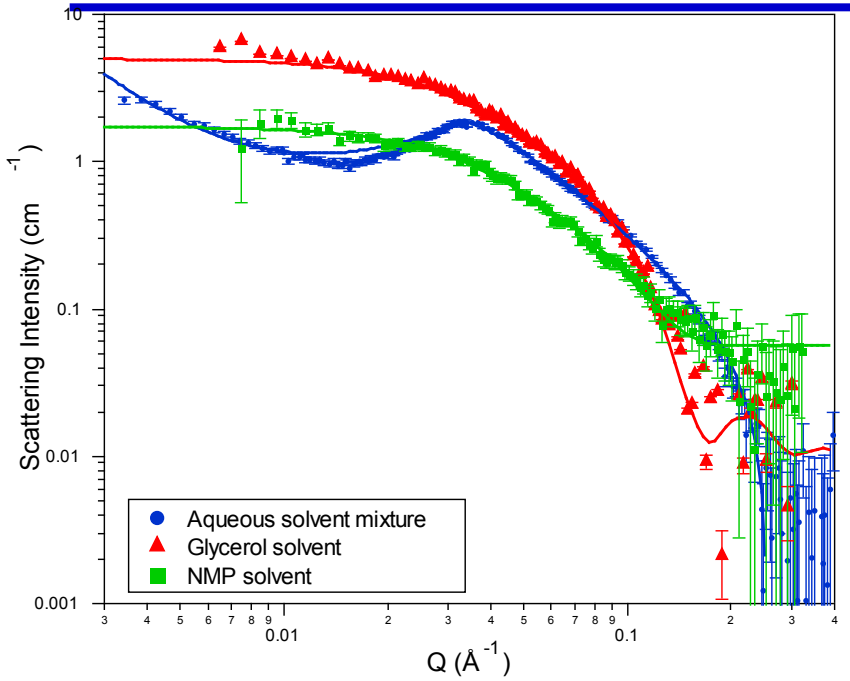
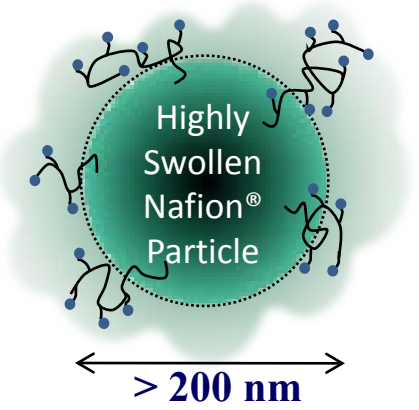
SANS of Diluted Nafion®-212 Dispersion



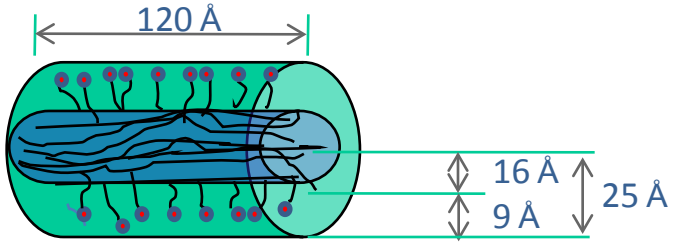
WIN dispersion: **Highly Swollen Large Particle**

*Structures are visual aids reflecting current understanding



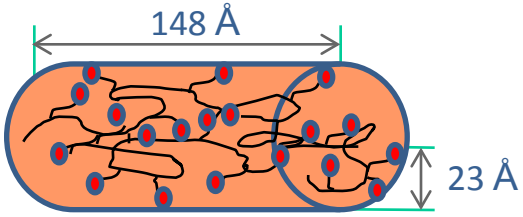
- Can not be fit to any particle shape form factor
- Data fits well to clustering / solvation model
- Well penetrated by solvent (Porod exponent n ≈ 2)

NMP dispersion: **Core-Shell Cylinder**



- Sharp interface between core and shell
- SLD* of core = ~calculated Nafion® backbone
- SLD of shell = ~solvent
- No solvent penetration into the core
- Solvent penetrates side chains (low slope)

Glycerol dispersion: **Cylinder Model**



- Less phase separation
- Scattering length density of cylinder (from SANS fit) is consistent with that calculated for Nafion® backbone, indicating little or no solvent penetration

Future Work

Degradation Mechanisms

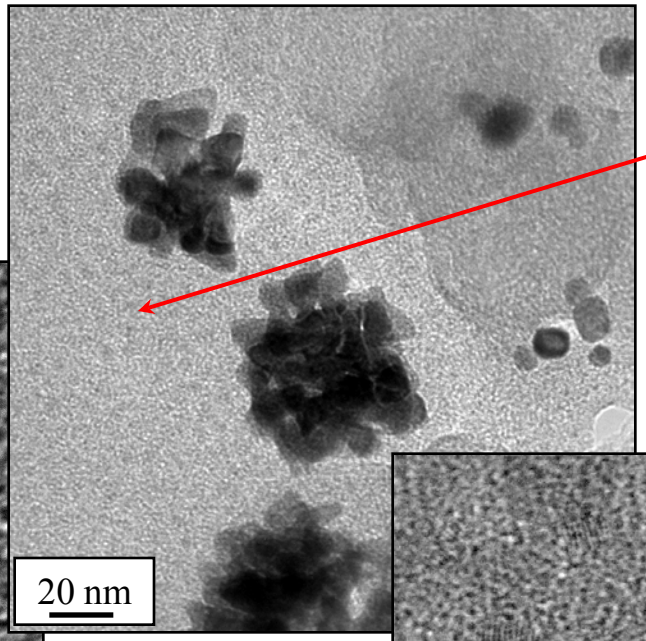
(New project, ~ ½ year old, subcontracts recently finished)

- Elucidation of Single Component Degradation Mechanisms
  - Electrocatalyst, Catalyst Support, Membrane, Ionomer, MEA, GDL, Metal Bipolar Plate, Carbon Bipolar Plate, Seals
- Elucidation of Multi-component Degradation Mechanisms
  - Above component interactions and interfacial changes
- Parametric Aging Studies
  - Temperature, RH, Transients (potential cycling), Shut-down/Start-up
- Science-Based Degradation Models
- Comprehensive Cell Degradation Models
- Development of *in situ* Analytical Techniques and Mitigation Strategies

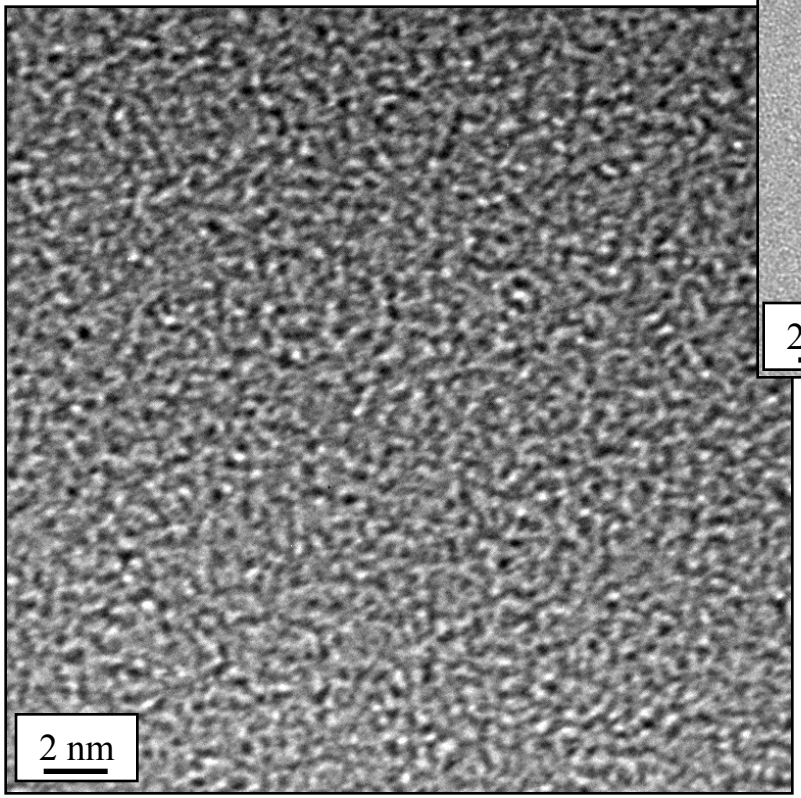
Applied Science

- Evaluation of water/Nafion® dispersions tendency to create weaker electrode structures
- Effect of film-forming properties on the electrode/membrane interface by X-ray tomography and SEM
- SANS of electrode layers
- Development of models for AC impedance data; heliox and 100% O_2 experiments
- Validation of durability results with state-of-the-art catalyst
- Extension of durability work to other pure solvents

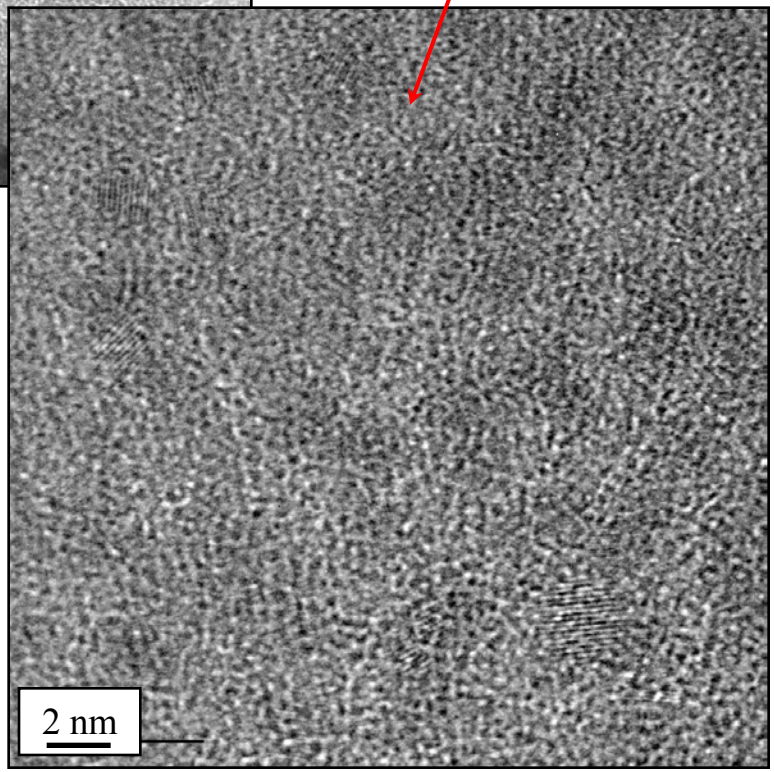
Nafion® Membrane "Structure" Changes During Potential Cycling



Membrane is nano-crystalline after 60°C cycling to 1.2 V

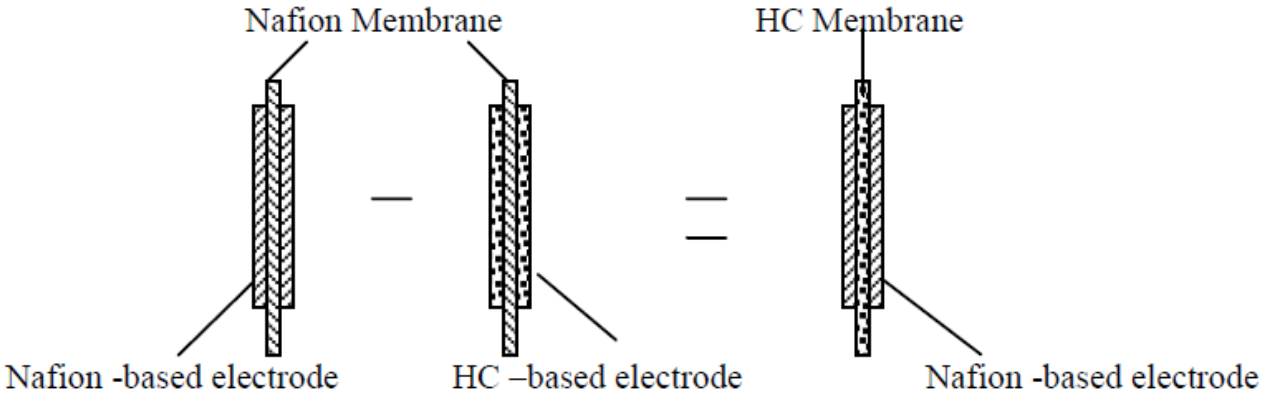


Amorphous structure of membrane In fresh MEA



Future Work: Study of Ionomer Degradation with Mixed MEAs

- Prior indications of Nafion® structural changes in electrode during operation
  - XRD & TEM: Higher crystallinity in aged electrodes
  - NR: Swelling of Nafion® films on carbon substrates
- Study of electrode layer Nafion® chemical and morphological structure aging
  - Fuel cell testing on mixed MEAs
  - Analysis of Nafion® extracted from mixed MEAs
  - Characterization of Nafion® within aged electrode films
  - Basic science studies of Nafion® structural changes under aging conditions
  - Fluoride ion evolution will be monitored during OCV tests of MEAs
- Differences between three types of MEAs will allow us to determine fluoride ion concentration due to degradation of Nafion® ionomer in electrode



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Future Work: Solid-State NMR

- Use NMR spectroscopy to characterize aging of fuel cell components (membrane, catalyst and GDL) since degradation mechanisms not fully understood. Examples:
  - Membranes show degradation dependent upon operation. Probe chemical changes by ^{19}F NMR.
  - Catalyst particles not strongly anchored to carbon support. Probe changes in carbon support by solid-state ^{13}C NMR.
  - NMR characterization of GDL material before and after fuel cell use.
  - Probe the state of water in these materials (amount of free and bound water as well as their exchange rates) by ^{1}H-NMR and NMR relaxation times.

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Future Work: Combined Chemical-Mechanical Degradation

- Effect of Mechanical Loads on Chemical Degradation
  - In-situ
    - How does the clamping loads alter the in-situ degradation of MEAs?
  - Ex-situ
    - Does applying tensile load to the membrane affect the material loss?

No published data in available literature

- Effect of Chemical Degradation on Mechanical Properties
  - In-situ
    - Mechanical properties degrade when the membranes tested in a fuel cell
  - Ex-situ
    - Aging of a membrane in H_2O_2 or Fe agent alter its Young's modulus
- Correlate experimental data with detailed membrane modeling to allow prediction of synergistic effects and examination of mitigation strategies

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Thanks to

- U.S. DOE -EERE Fuel Cell Technologies Program for financial support of this work
  - Technology Development Manager: Nancy Garland

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Supplemental Slides

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FY2010 Milestones

Mon/Yr	Milestone
Dec 2009	Measure ECSA changes in situ with variable water content to determine the effect of water and cell location on ECSA by segmented cell operation
June 2010	Effect of temperature on metal bipolar plate corrosion of Nitrided Materials
June 2010	Plate Resin analysis depending upon execution of acceptable legal agreement.
Sept 2010	Definition of component impurities from seal materials for secondary exposure studies
Sept 2010	Definition of component impurities from carbon bipolar plate materials for secondary exposure studies

☑

Applied Science

Mon/Yr	Milestone
Sept 09	Fabricate an MEA with a layered structure and evaluate the approach in terms of ESA versus performance (completed)
Jan 2010	Characterize ionomer dispersions in five dispersing solvent systems by neutron scattering, NMR, and microscopy (measurements complete – analysis ongoing)
May 2010	Complete durability test for the electrode using the five dispersing solvent systems according to DOE durability protocol (ongoing)

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80%

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Approach: Characterization Methods to Delineate Degradation Mechanisms

- TEM (Transmission Electron Microscopy)
  - Catalysts, catalyst layer structure, membrane
- SANS (Small Angle Neutron Scattering)
  - Electrode structure
- X-ray Tomography – MicroXCT
  - 3-D imaging of MEAs, catalyst layer delamination
- FTIR (ATR, Transmission, DRIFTS)
  - Surface structure changes, ionomer/membrane functional changes
- XPS – (X-ray Photoelectron Spectroscopy)
  - Carbon corrosion, surface oxidation
- NMR (Solid-state and solution)
  - Ionomer and membrane chemical changes, carbon surface
- IGC - (Inverse Gas Chromatography)
  - Surface Energies
- Hg and H_2O porosimetry
  - Electrode and GDL pore size distributions and hydrophobic vs. hydrophillic pores
- SEM/ESEM (Environmental Scanning Electron Microscopy)
  - MEA structural and elemental analysis
- TGA/DSC & MS (Thermogravimetric Analysis / Differential Scanning Calorimetry)
  - Component chemical analysis
- Powder XRD (x-ray diffraction)
  - Catalyst particle size distribution
- Laser Ablation ICP-MS
  - Impurities analysis
- Fuel Cell Testing: AC Impedance
  - Mass Transport limitations

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Oak Ridge Metal Bipolar Plates

LANL Effort Plan

Three Nitrided Alloys Representing Range of Nitrided Structures and Behavior

- Model Ni-50Cr: forms dense Cr_xN surface
- Commercial Ni-35Cr alloy Hastelloy G-35: forms primarily Cr_xN surface, some local regions of mixed Mo, Ni nitride/oxide structures
- ORNL Developmental Fe-20Cr-4V Alloy: $V_xN + Cr_2O_3$ Surface

Correlate ex-situ corrosion and ICR behavior with single-cell results

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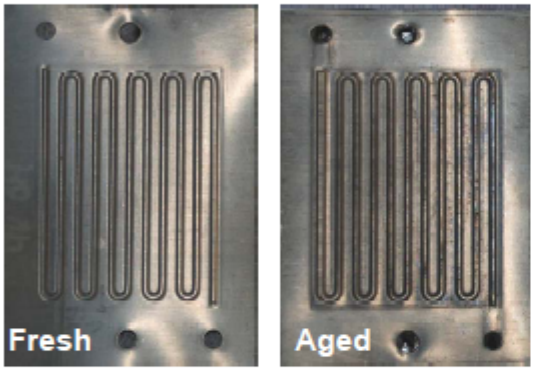
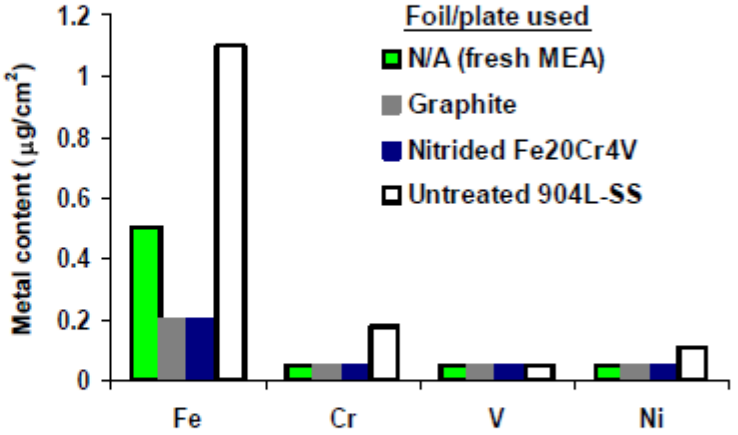
Pre-Oxidized/Nitrided Surface on Fe-20Cr-4V Protected MEA from Metal Contamination

Nitrided Fe-20Cr-4V Plates



X-ray Fluorescence (XRF) of MEAs



- No visible attack of nitrided Fe-20Cr-4V plates (slight staining-GDL contact)
- XRF found MEAs from graphite and nitrided Fe-20Cr-4V plates "clean"
- Small (0.2 to 1 μg/cm^2) level of metal ion contamination with 904 L

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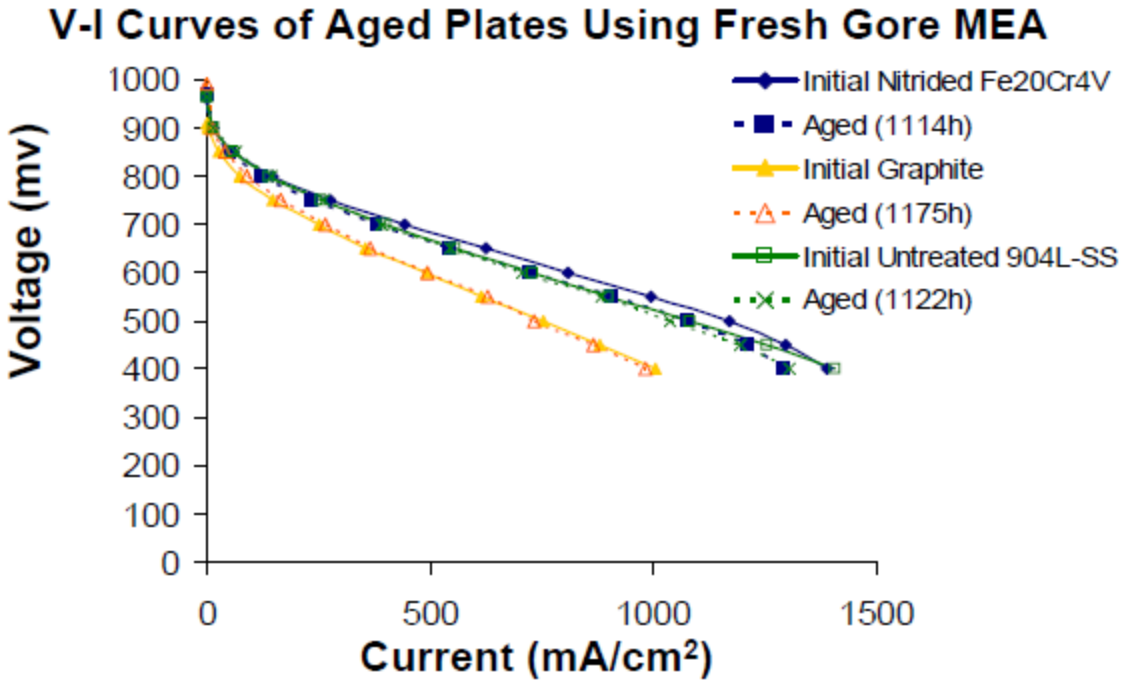
1000 h Aged Nitrided Fe-20Cr-4V, 904L, and Graphite Plates All Showed Good Durability



- Slight decline in nitrided Fe-20Cr-4V data likely within fuel cell build-to-build variation (< 5-10% variation of peak power output)

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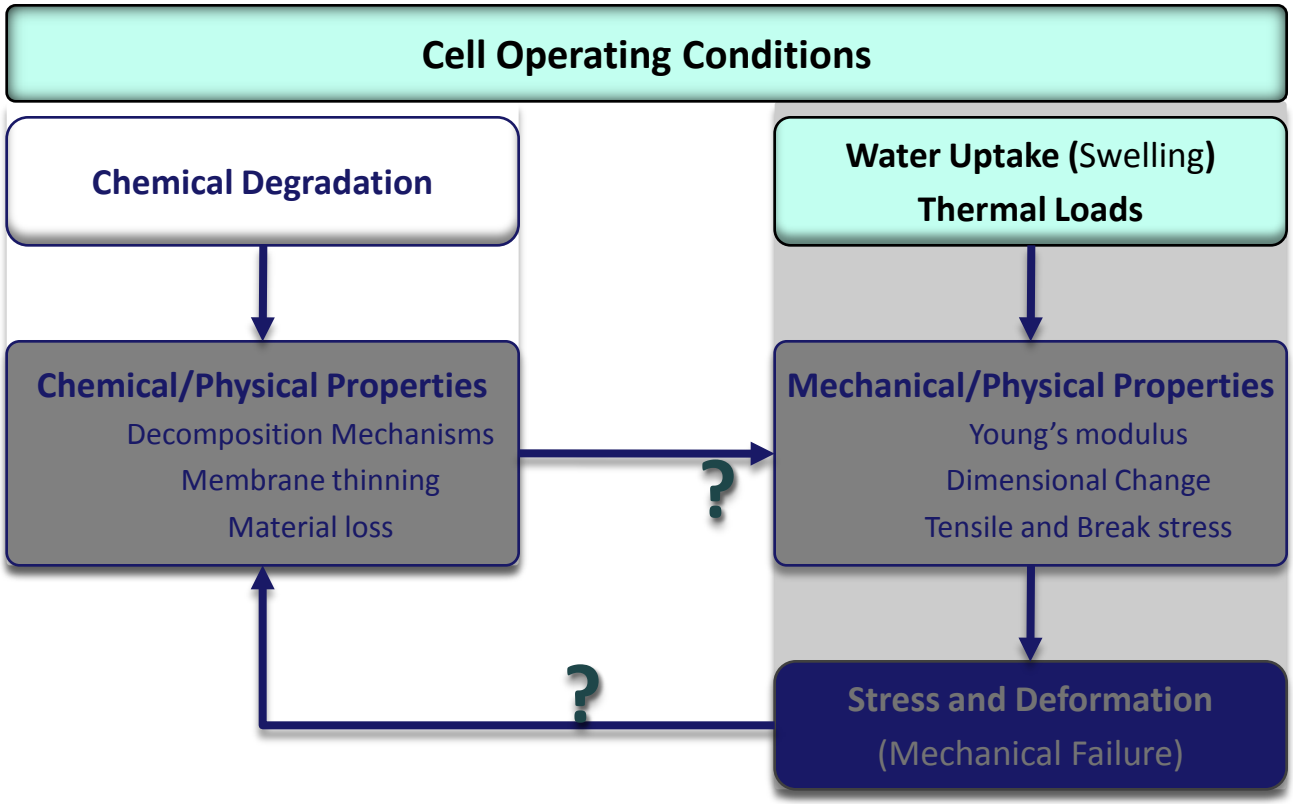
Chemical – Mechanical Degradation



Are there correlations or synergistic effects between chemical and mechanical degradation?

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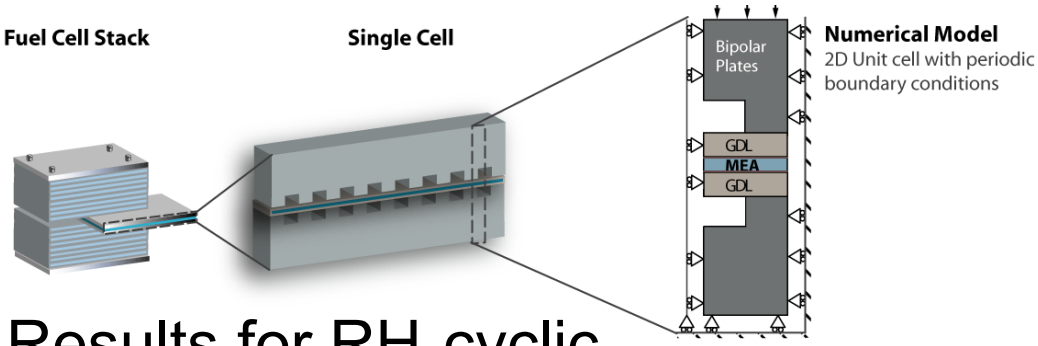
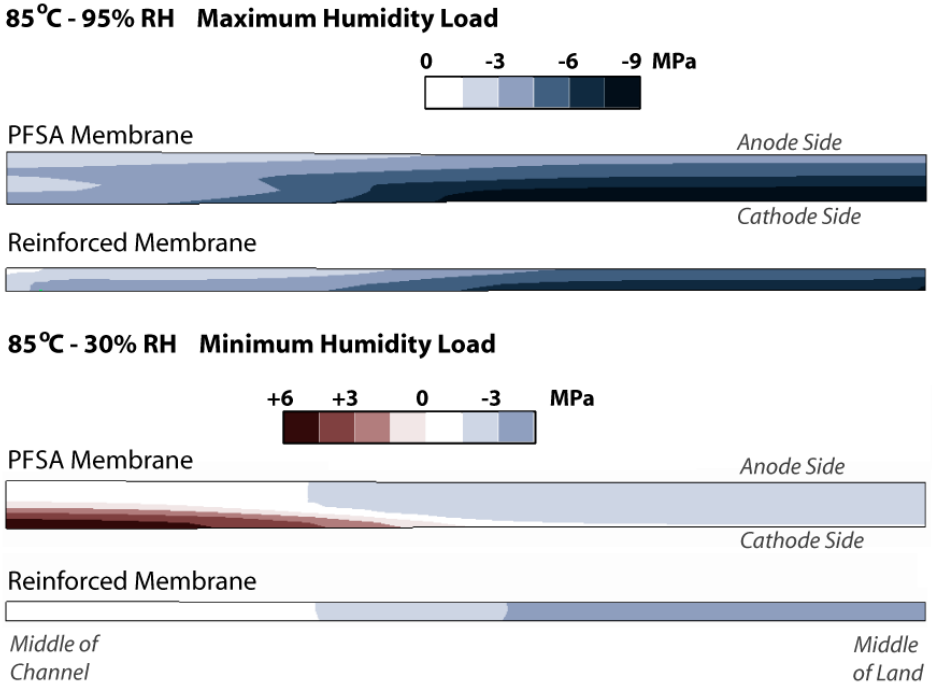
esses in the membrane during RH cyclic

- Numerical Model for Swelling-induced stresses in MEA



- Results for RH-cyclic

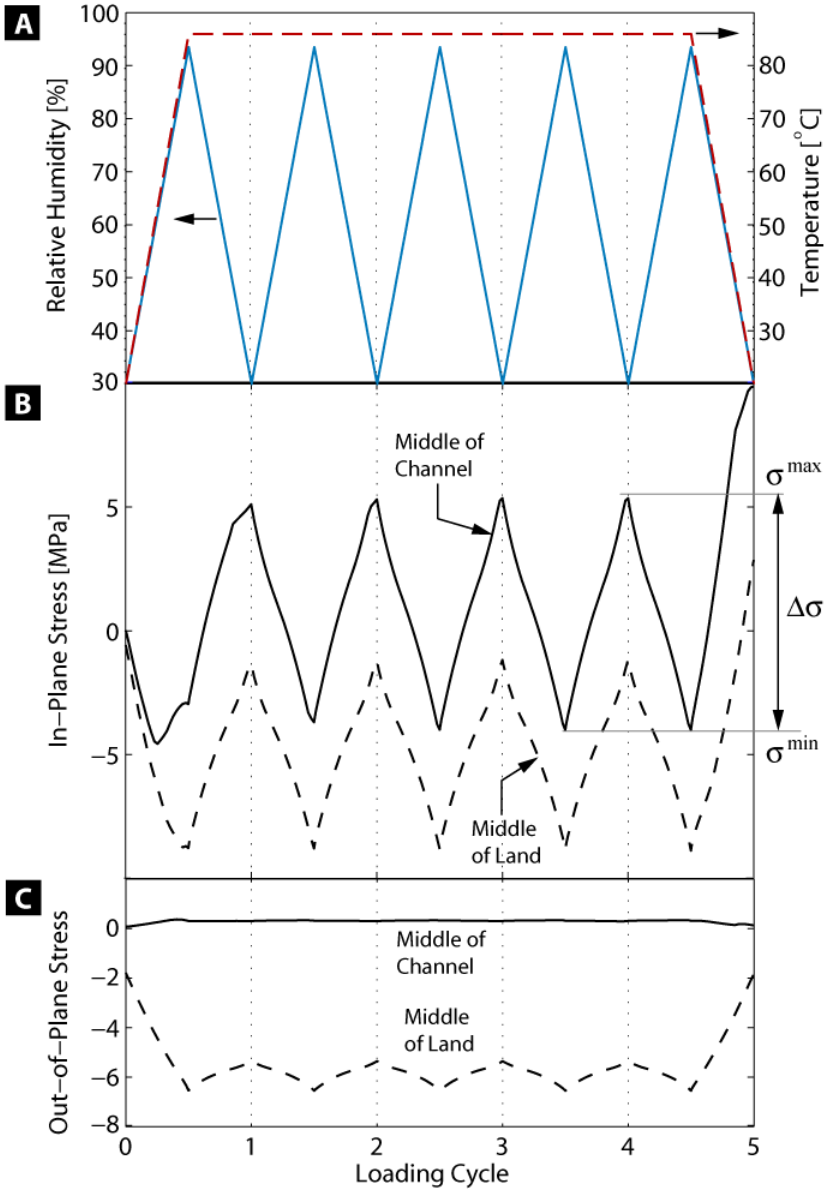


Low swelling of the membrane reduces the stresses in the MEA during RH cyclic and therefore improves the fatigue life.

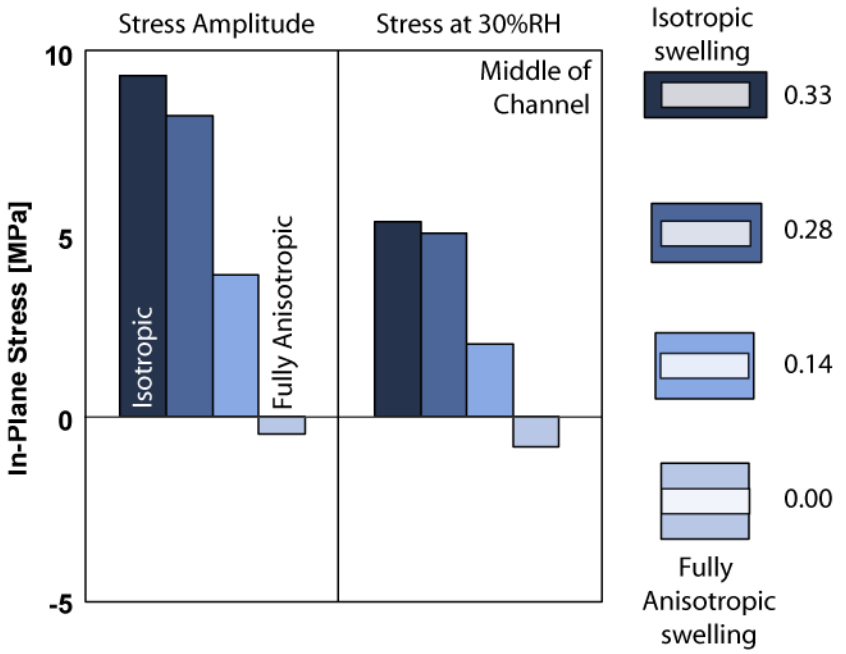
Swelling and degradation of mechanical properties dominate the fatigue response in fuel cells.

Kusoglu et al., *J Power Sources*, 170 (2007)
Tang et al. *J Power Sources*, 175 (2008)

Fatigue Behavior: Effect of Swelling Anisotropy



- **Humidity cycling induces fatigue stress in the membrane.**
- **Fatigue stress decrease with reduced in-plane swelling.**



Kusoglu et al., *J Power Sources*, 170 (2007) 345

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Aging-Induced Changes in Nafion® Structure

- Neutron reflectivity provides Å-level resolution of interfaces between films and Pt and C substrates
  - Expose Nafion® films to peroxide, impurity ions, and elevated temperatures to mimic conditions produced by OCV test
  - Examine how chemical degradation influences Nafion® / Pt / C interfaces
- Small-angle neutron scattering on model electrode films can reveal structural order on the 1 – 100 nm scale
  - Lower Pt / C concentration to obtain better signal from Nafion®
  - Swell films in aqueous mixtures that will allow us to probe long-range Nafion® structure
  - Measure changes in Nafion® structure after exposure to peroxide, impurity ions, and elevated temperature

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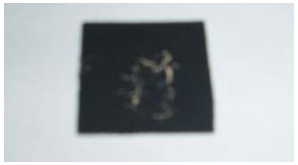
Mixed MEA Fabrication

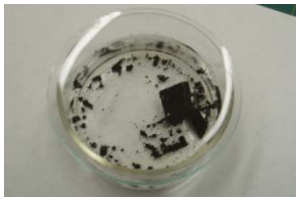
Challenges

- Electrode cracks

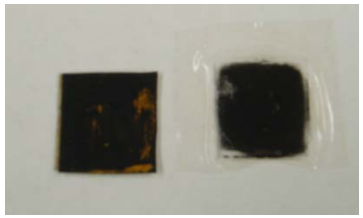


- Wetting issue

- Interface delamination

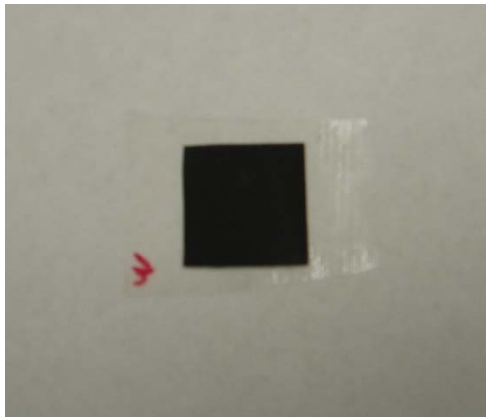


- Transfer issue



Progress

- Crack-free electrode obtained by adjusting ink recipe & homogenization method
- Robust interface obtained when TBA+ form of Nafion® membrane used during hot press



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