

# Durability Improvements Through Degradation Mechanism Studies

## DOE 2011 Annual Merit Review Meeting

May 14 - 18, 2012

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

# Organizations / Partners / Collaborators

- **Los Alamos National Lab (LANL)**

- R. Mukundan, J. Davey, Bo Li, D. Spornjak, J. Fairweather, K. Rau, R. Lujan, D. Langlois, J. Chlistinoff; [Applied Science Task](#); Christina Johnston, Yu Seung Kim, Nate Mack



- **Argonne National Laboratory (ANL)**

- Rajesh Ahluwalia, Xiaohua Wang



- **Lawrence Berkeley National Laboratory (LBNL)**

- Adam Weber, Ahmet Kusoglu



- **Oak Ridge National Laboratory (ORNL)**

- Karren More, Mike Brady



- **Ballard Power Systems (BPS)**

- Paul Beattie, Sylvia Wessel, G. James, D. Ramrus, S. Loif, W. Williams



- **Ion Power**

- Steve Grot, Walter Grot



- **University of New Mexico (UNM)**

- Kateryna Artyushkova, Plamen Atanassov, Anant Patel



- **University of Nancy, Lorraine France**

- Gaël Maranzana, Adrien Lamibrac, Jérôme Dillet, Sophie Didierjean, Olivier Lottin



- **Nuvera, Ballard, ANL, LANL-AST, UTC-AST Durability projects**

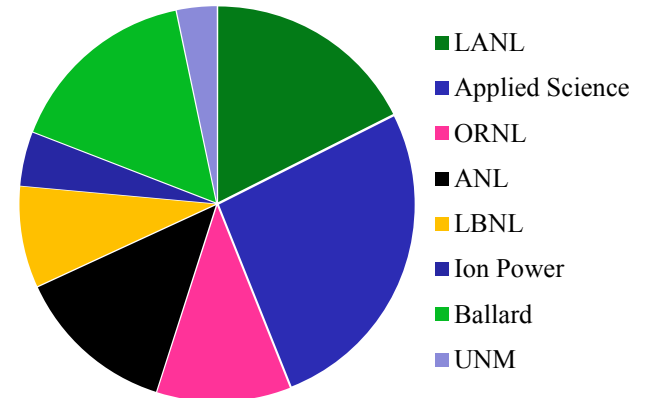
# Budget

| 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    |

Approximately 2/3 through project: 18 months left

| Participant  | FY11 (Year 2) |
|--|---------------|
| LANL   | \$1000k       |
| Industrial + Univ. Partners<br>(Ballard, Ion Power, UNM) | \$425k        |
| Other National Labs<br>(ANL, LBNL, ORNL)                 | \$850k        |



# Relevance and Objectives

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- **Relevance**

- Increase fuel cell durability; not at the expense of component cost

- **Objectives**

- Identify and Quantify Degradation Mechanisms

- Degradation measurements of components and component interfaces
- Elucidation of component interactions, interfaces, operating conditions leading to degradation
- Development of advanced in situ and ex situ characterization techniques
- Quantify the influence of inter-relational operating environment between different components
- Identification and delineation of individual component degradation mechanisms

- Understand Electrode Structure Impact - Applied Science Subtask

- Better understand the electrode structural and chemical reasons for differences in durability
- Understand impact of electrode structure on durability and performance
- Correlate different electrode structures to fuel cell tests and durability
- Define different fabrication effects (esp. solvents) on electrode structure

- Develop Models Relating Components and Operation to Fuel Cell Durability

- Individual degradation models of individual fuel cell components
- Development and public dissemination of an integrated comprehensive model of cell degradation


- Methods to mitigate degradation of components

- New components/properties, designs, operating conditions

# Technical Targets/Barriers

**Table 3.4.3 Technical Targets for Automotive Applications:  
80-kW<sub>e</sub> (net) Integrated Transportation Fuel Cell Power Systems Operating on Direct Hydrogen<sup>a</sup>**

| Characteristic                                      | Units                | 2011 Status        | 2017 Targets       | 2020 Targets       |
|---|----------------------|--------------------|--------------------|--------------------|
| Energy efficiency <sup>b</sup> @ 25% of rated power | %                    | 59                 | 60                 | 60                 |
| Power density                                       | W / L                | 400 <sup>c</sup>   | 650                | 850                |
| Specific power                                      | W / kg               | 400 <sup>c</sup>   | 650                | 650                |
| Cost <sup>d</sup>                                   | \$ / kW <sub>e</sub> | 49 <sup>e</sup>    | 30                 | 30                 |
| Durability in automotive drive cycle                | hours                | 2,500 <sup>h</sup> | 5,000 <sup>i</sup> | 5,000 <sup>i</sup> |
| Assisted start from low temperatures <sup>j</sup>   | °C                   | -                  | -40                | -40                |
| Unassisted start from low temperatures <sup>j</sup> | °C                   | -20 <sup>f</sup>   | -30                | -30                |



**Table 3.4.5 Technical Targets: 1–10 kW<sub>e</sub> Residential Combined Heat and Power and  
Distributed Generation Fuel Cell Systems Operating on Natural Gas<sup>a</sup>**

| Characteristic                        | 2011 Status | 2015 Targets | 2020 Targets |
|---------------------------------------|-------------|--------------|--------------|
| Degradation with cycling <sup>h</sup> | <2%/1,000 h | 0.5%/1,000 h | 0.3%/1,000 h |
| Operating lifetime <sup>i</sup>       | 12,000 h    | 40,000 h     | 60,000 h     |

# Approach

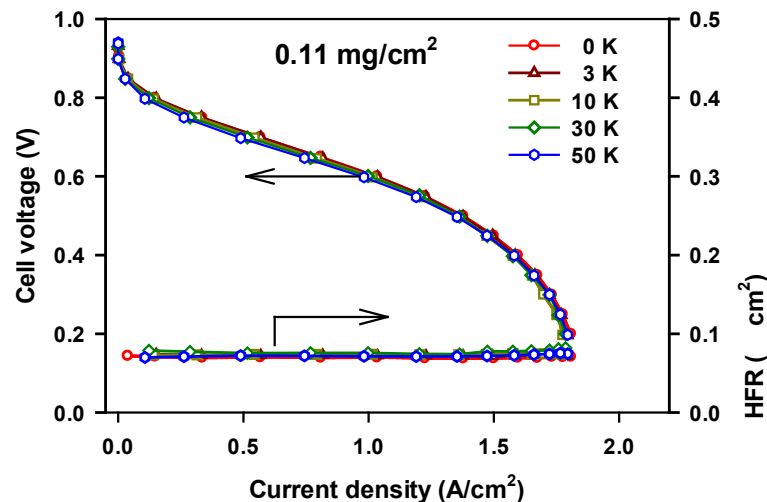
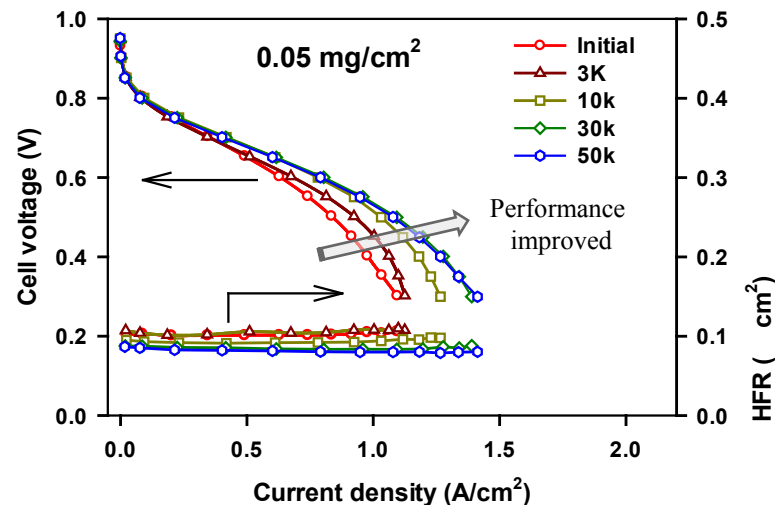
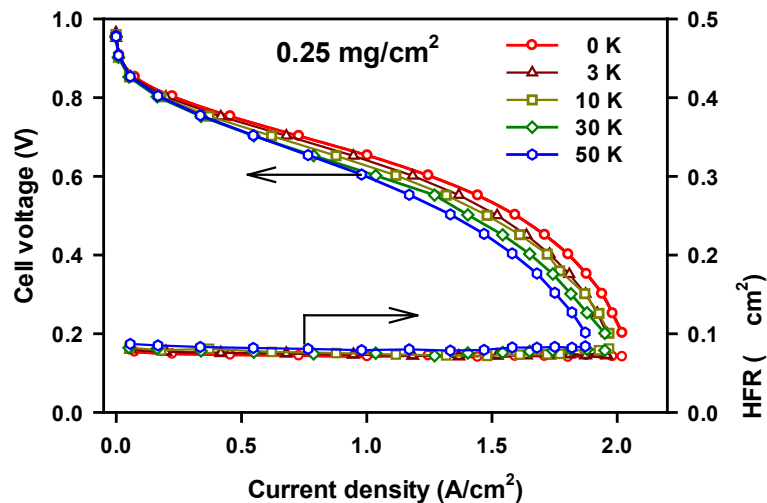
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- **Understand Degradation Mechanisms**
  - Measurements of degradation ex situ and in situ
  - Analysis to define individual component contributions to loss in performance
- **Characterization of Component Degradation**
- **Understand and Correlate Electrode Structure to Durability**
  - Understand connection between structure and performance/durability
    - Vary the ionomer and catalyst with different solvents to assess impact
- **Modeling**
  - Fundamental degradation mechanisms (LBNL)
  - Integrated degradation model – kinetic/rate based (ANL)
  - Coordinate activities with other efforts via DOE Modeling Working Group
- **Coordinate activities with other durability projects**
  - DOE Durability Working Group
  - Current coordination includes: ANL, Nuvera, Ballard, UTC-AST, LANL-AST
    - Data from ANL on Pt dissolution used for modeling effort
    - Joint material testing with AST projects (esp. LANL)
    - Extend characterization (Neutron Imaging) to benefit Ballard

# Approach - FY2012 Milestones

| Mon Yr    | Milestone  |   |
|-----------|--|---|
| Nov 2011  | Complete OCV tests for 200 hr on improved LANL cathodes and compare the performance drop to LANL standard and commercial MEAs  | Experiments complete  |
| Dec 2011  | Compare carbon corrosion due with GDL variations (SGL 24BC-24BC and 24BC-24BA cells) by measuring performance in 10x10 segmented cell during carbon corrosion AST  | Experiments complete  |
| Jan 2012  | Calculate a relative activation energy for metal plate corrosion comparing FE-20Cr-4V and 904L metals by measuring relative corrosion rates between 20C and 80C  | Experiments complete  |
| Feb 2012  | Compare water bonding with new (stabilized, non-stabilized) and aged ionomer by DSC (Differential Scanning Calorimetry) to identify changes in water bonding with age.   | Incomplete; Lost Student  |
| Mar 2012  | Determine the impact of catalyst loading over the range 0.05 mg/cm <sup>2</sup> to 0.20 mg/cm <sup>2</sup> on the durability of improved LANL cathodes to potential cycling tests from 0.60-1.0 V for 30,000 cycles at 50 mV/s | Experiments complete  |
| May 2012  | Complete microscopy on improved LANL cathodes and compare to durability results from potential cycling (0.60-1.0 V, 30,000 cycles) and OCV tests (200 hr)  | On-going; microscopy complete on baseline                       |
| June 2012 | Measure and compare changes in catalyst layer and GDL surface energies/hydrophobicity due to operation with shutdown/startup (using durability working group protocol)   | SD/SU Experiments complete<br>Characterization underway         |
| Sept 2012 | Compare cathode catalyst loading effect on catalyst electrode layer durability examining loadings of 0.15, 0.2, 0.25, 0.4 and 0.5 mg/cm <sup>2</sup>   | Partially complete, MEAs received<br>Testing partially complete |

# Durability of Low Loading Pt/C Cathode during Potential Cycling



ECDSA change\*

| Pt (mg/cm <sup>2</sup> ) | 0 K | 10 K | 30 K | 50 K | % change |
|--------------------------|-----|------|------|------|----------|
| <b>0.25</b>              | 50  | 35   | 28   | 22   | -55      |
| <b>0.11</b>              | 49  | 28   | 24   | 22   | -56      |
| <b>0.05</b>              | 52  | 29   | 21   | 14** | -74**    |

\* Determined by the H<sub>2</sub> desorption of CV; \*\*very low surface areas with higher error

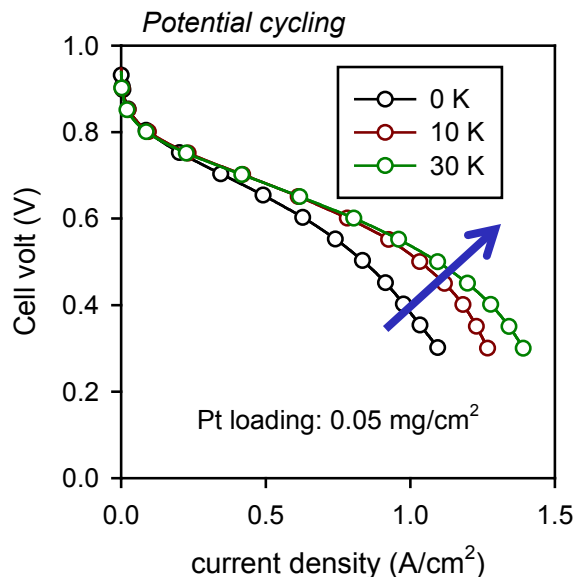
Anode: 0.2 mg cm<sup>-2</sup> Pt/C (BASF), Cathode: 0.06-0.25 mg cm<sup>-2</sup> Pt/C (BASF); Membrane: Nafion<sup>®</sup> 212; Cell: 80°C, 30 psig backpressure, Potential cycling: 0.6 – 1.0 V under H<sub>2</sub>/N<sub>2</sub>  
 Typical LANL decal process using water/alcohol/glycerol mixture in the ink was used.

- Performance of ultra-low loading cathode (0.05 mg/cm<sup>2</sup>) increased with potential cycling
- Performance of MEA with “high” loading decreased; with “low” loading stayed the same
- ECDSA decreased with potential cycling for all MEAs; does not correlate with performance change

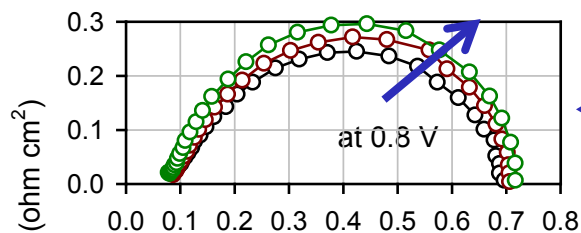
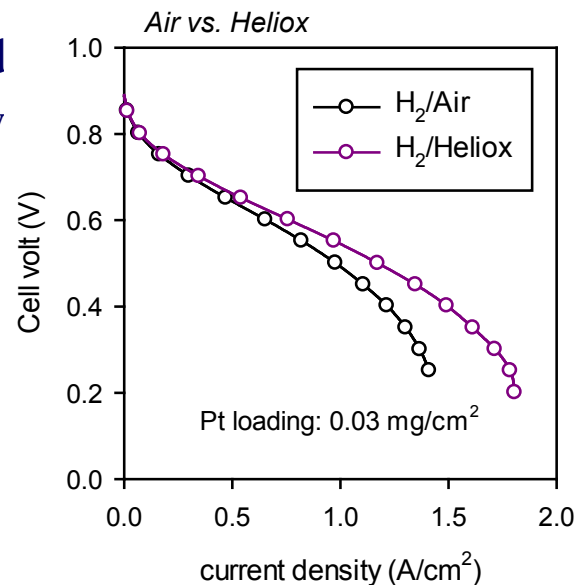
*Electrode milestone (Determine the impact of catalyst loading on the durability of LANL cathodes to potential cycling tests) - Achieved*



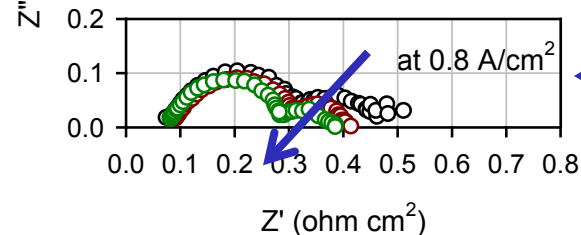
# Electrode Structural Change during Potential Cycling



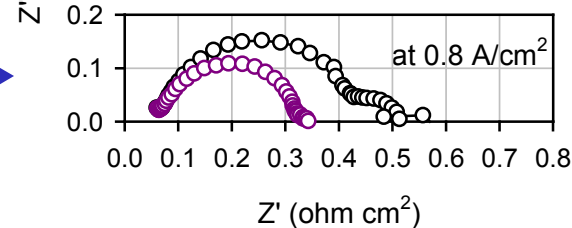
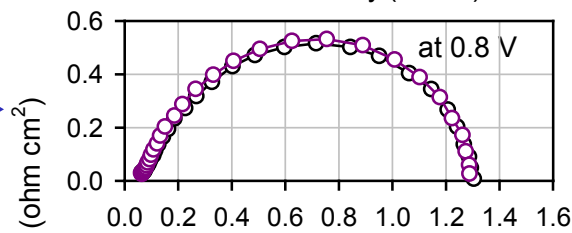
- Enhanced performance and impedance behavior of low loading cathode with potential cycling have similarity with performance improvement with heliox (or air flow increase)



Higher Kinetic Resistance

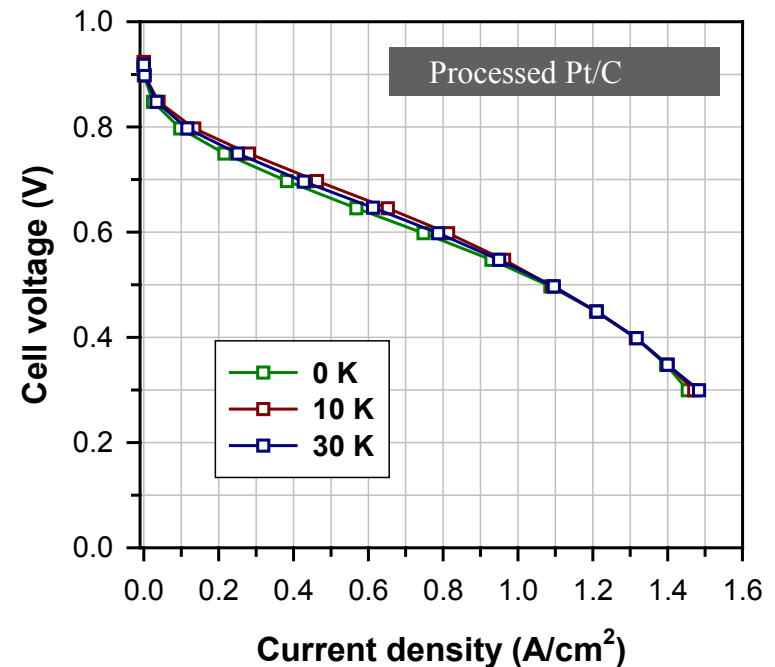
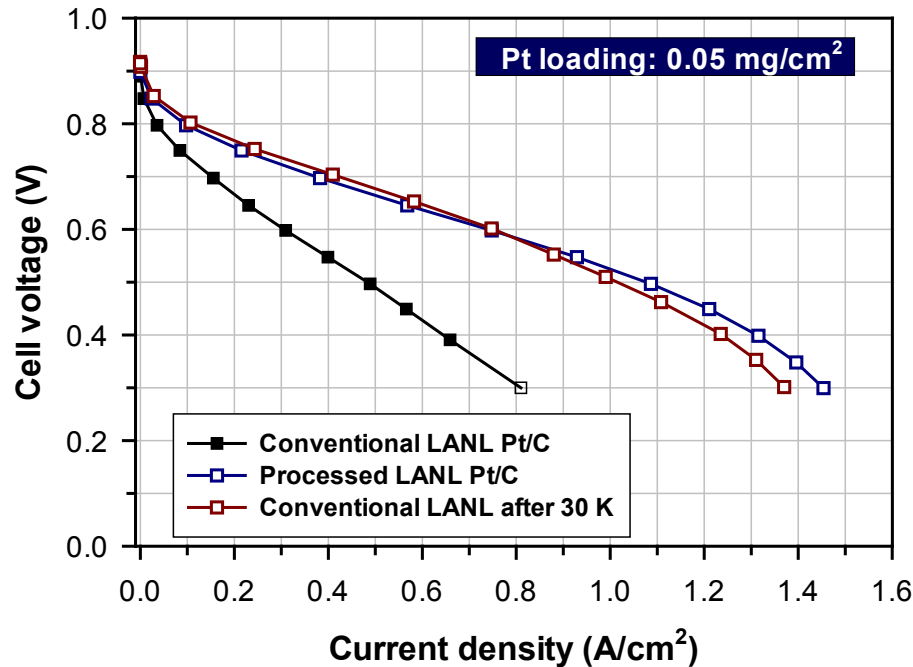


Lower MT Resistance



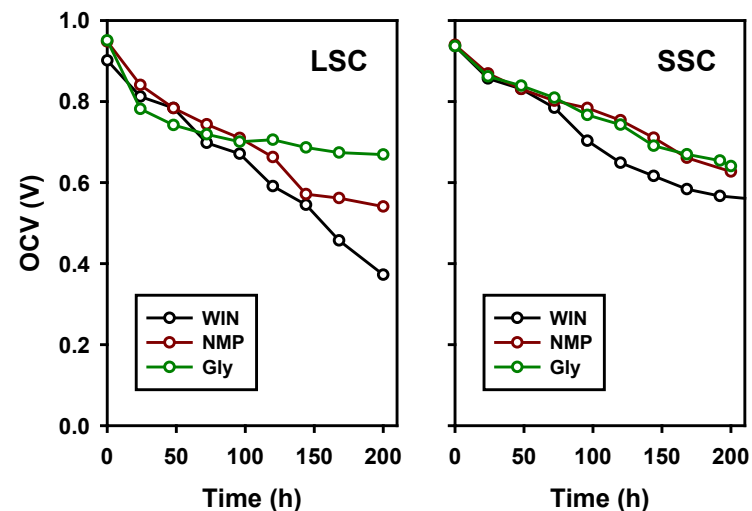
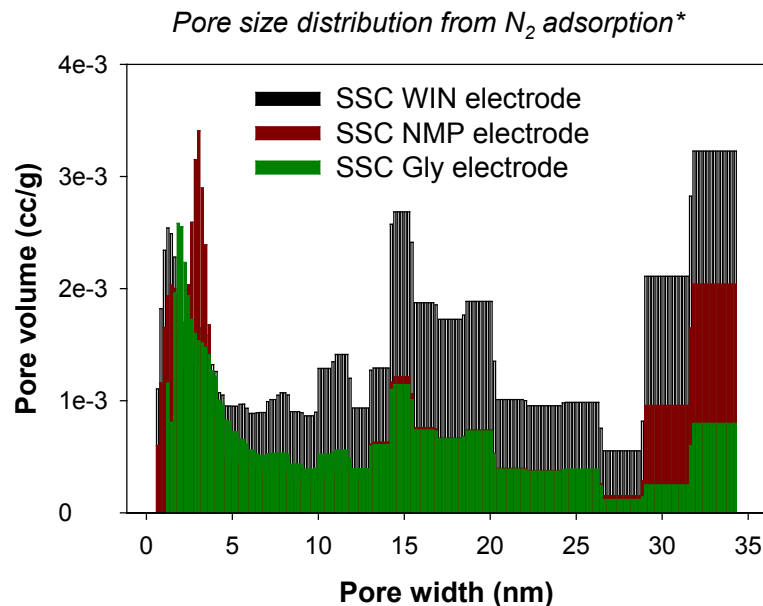
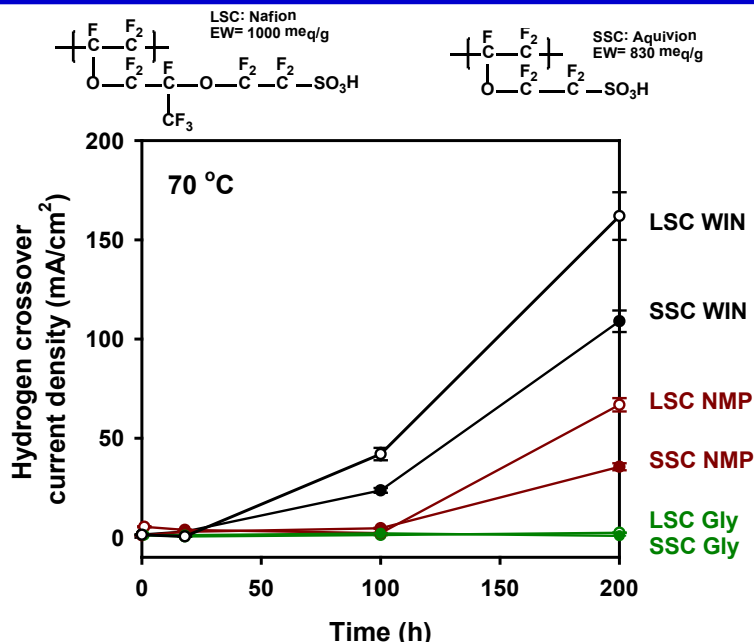
Electrode structural change that occurs during potential cycling in favor of oxygen diffusion, lower Mass Transport Resistance

# Electrode Performance and Durability of Processed Low Loading Cathode



- **Highlight:** Introduce new electrode processing technologies that generate better electrode structure for low loading Pt/C cathode -- **Electrode processing time reduced from 5.5 days, ca. 30,000 cycles to 2 h**
- **Highlight:** High power density achieved with low Pt loading and pre-processed Pt/C (i.e.  $P_{0.5V} = 540 \text{ mW/cm}^2$  for  $0.05 \text{ mg/cm}^2$  vs.  $P_{0.5V} = 840 \text{ mW/cm}^2$  for  $0.25 \text{ mg/cm}^2$ )
  - Not yet optimized for CL ionomer and membrane
- Processed electrode shows excellent stability with potential cycling from 0.6-1.0 V; cell performance was slightly improved after first 10,000 cycles then remained same after further 20,000 cycles
- ECSA decreased from 58.5 to 35.8 m<sup>2</sup>/g<sub>Pt</sub> after 30,000 cycles; the reduction of ECSA does not impact fuel cell performance

# Impact of Cathode Structure on Membrane Degradation



\*Slit pore QSDFT model used assuming carbon surfaces; results provide qualitative comparison

- Durability of MEAs to OCV test depends both on electrode ionomer choice and solvent used in inks
- OCV durability ranking:
  - WIN < NMP < Gly
  - LSC < SSC
- Hydrogen crossover after OCV test affected by cathode electrode structure; implies membrane is indirectly affected by the electrode
- Hydrogen crossover after OCV test correlates well with electrode porosity; perhaps oxygen diffuses into membrane faster and accelerates its degradation when the electrode is more porous

**Anode:** 0.2 mg cm<sup>-2</sup> Pt/C (BASF) LANL standard processing, **Cathode:** 0.2 mg cm<sup>-2</sup> Pt/C (BASF) processed with different dispersing solvent; **Membrane:** Nafion® 212; **Cell:** 80°C, 30 psig backpressure; **OCV test:** H<sub>2</sub>/Air at 90°C, 30% RH, no backpressure; H<sub>2</sub> crossover measured at 70°C, 50/50 sccm of H<sub>2</sub>/N<sub>2</sub>

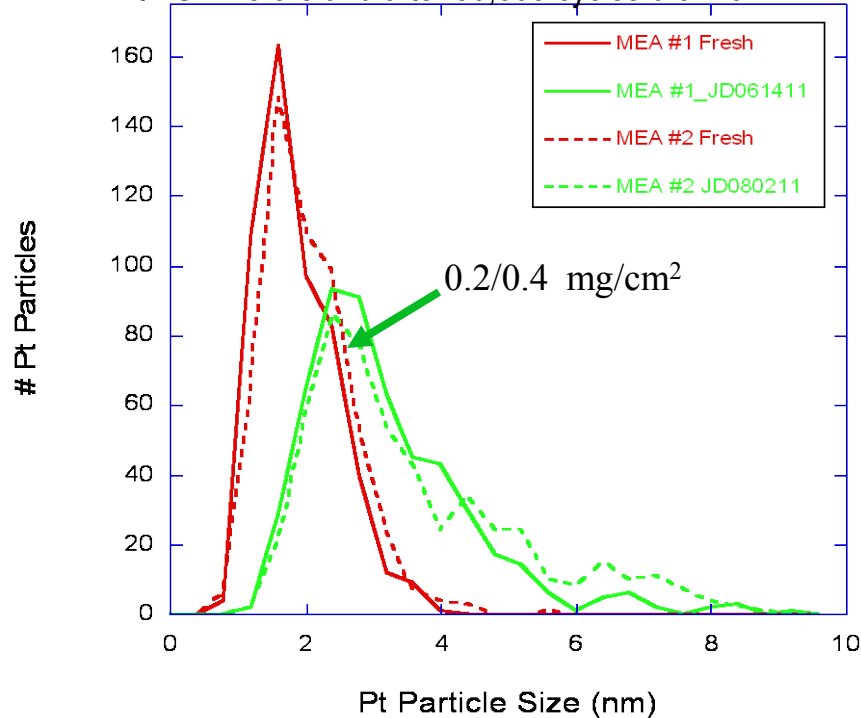
# Rate of Platinum Agglomeration Depends → Loading & Mechanism

## Catalyst Degradation Comparison for Catalyst Layers with Similar Carbon Loadings

Loadings of 0.2 mg/cm<sup>2</sup> (20 wt%Pt) and 0.4 mg/cm<sup>2</sup> (40wt%Pt)

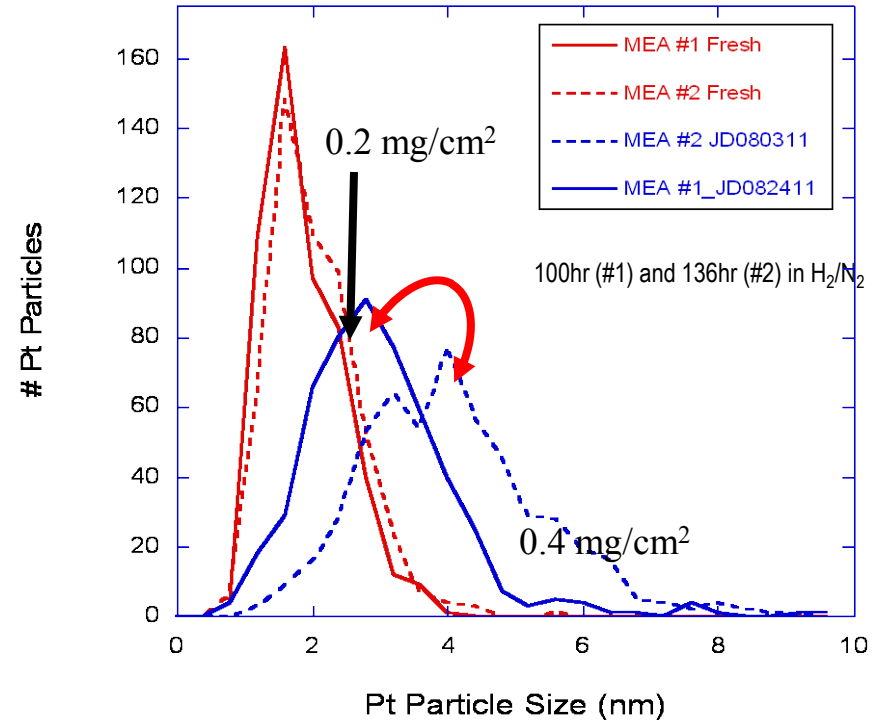
### Catalyst Cycling AST

Pt PSD Before and after 30,000 cycles 0.6-1.0V



### Catalyst Support AST

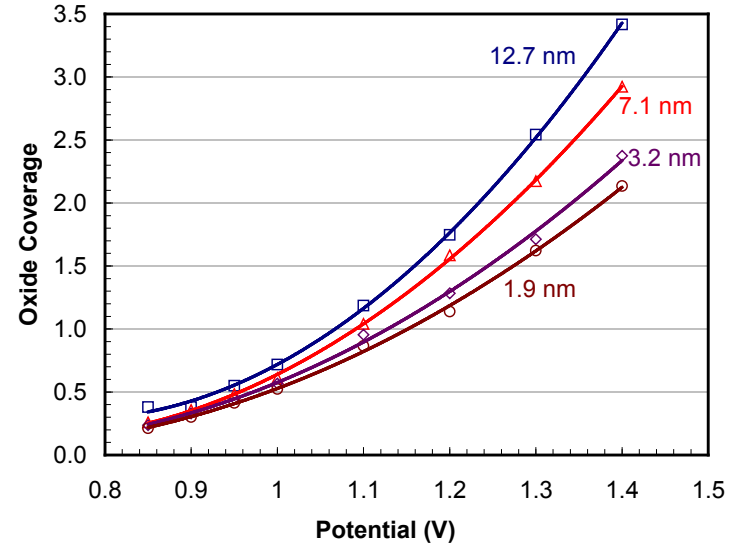
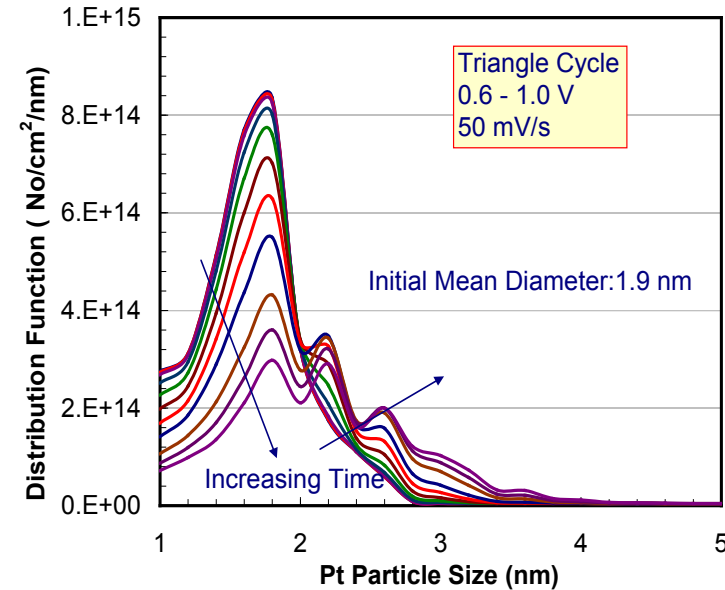
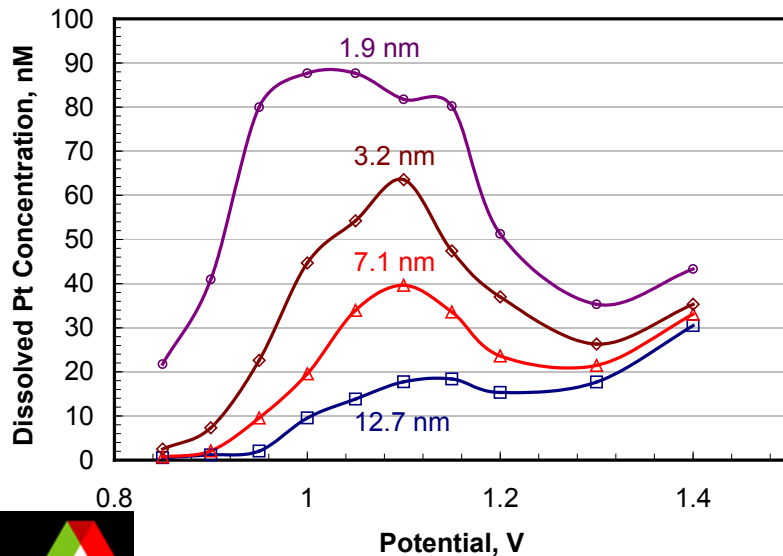
Pt PSD Before/After 1.2V Hold



- Pt PSD shows no difference after potential cycling
- Dissolution/re-precipitation kinetics/particle growth kinetic unaffected by Pt particle concentration
- Greater Pt coarsening for cathode with higher Pt loading
- Higher concentration of Pt particles led to higher agglomeration

# Pt Dissolution Model

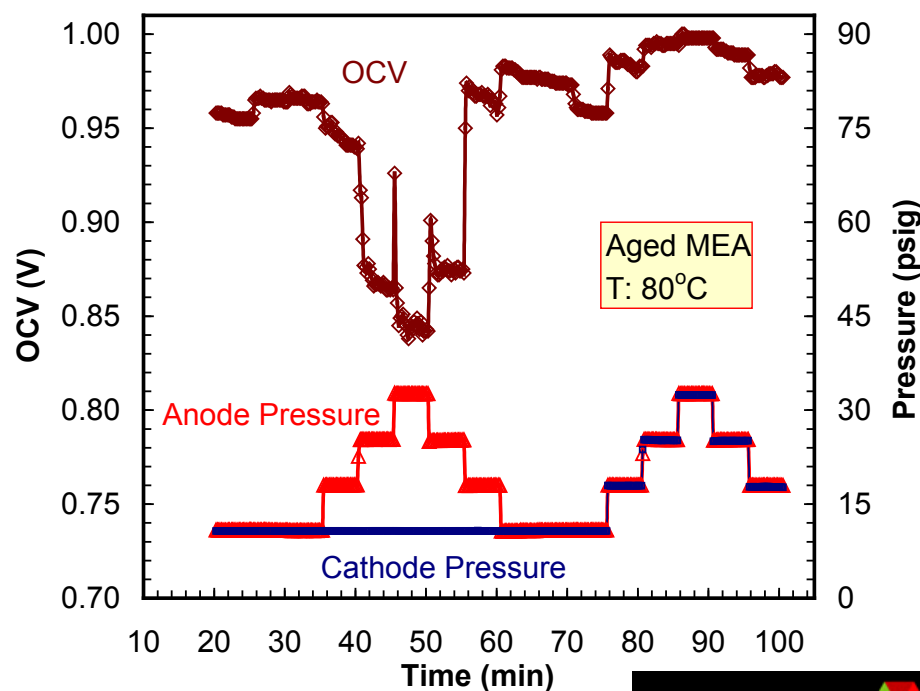
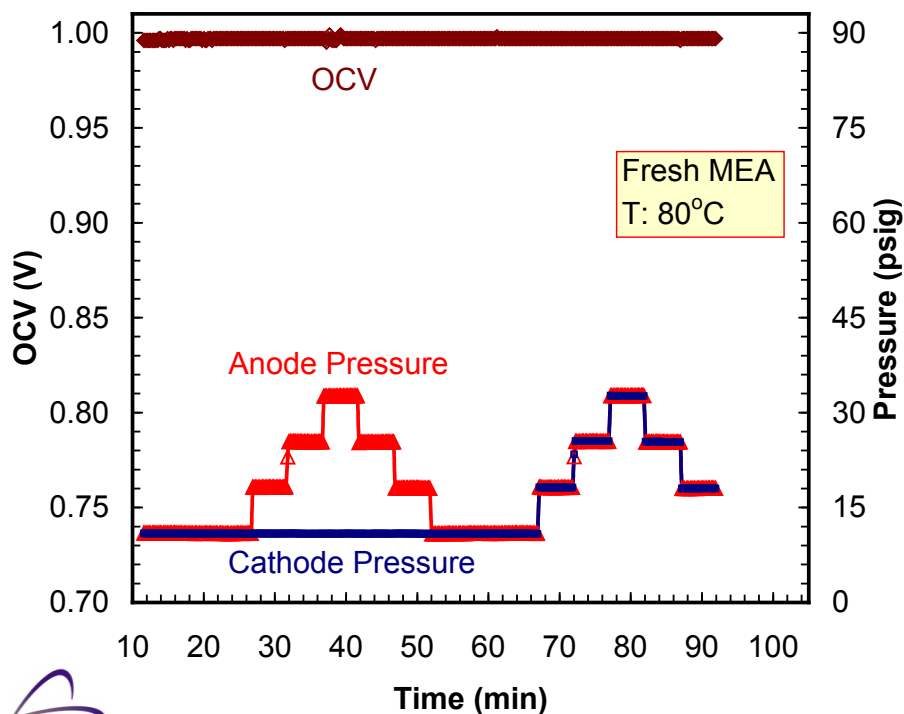
- Completed initial development of Pt dissolution model
  - Dissolution thermodynamics from aqueous potentiostatic data
  - Oxide growth thermodynamics from the measured reduction charge after long hold at different CV potentials
  - Oxide growth kinetics from CV oxidation and reduction scans
  - Dissolution kinetics from constant potential and potential cycling data
  - Size evolution driven by dissolution of small Pt particles and growth of large particles through re-deposition and coalescence (primary)
  - Growth in average size more significant for initial distributions with small mean diameter and potential cycles with higher UPL (more dissolution), lower LPL (more re-deposition), and **faster** scan rates



Collaboration with ANL (D. Myers) and Nuvera durability projects **Discussed Earlier by (D. Myers)**

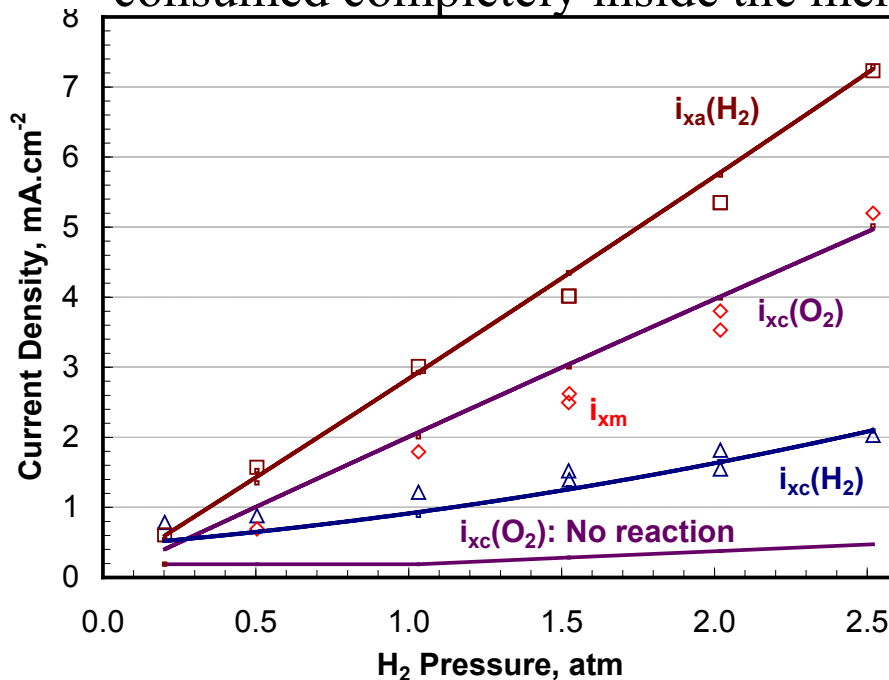
# Understanding Changes to Hydrogen Crossover During MEA Aging

- Measuring OCV as a function of H<sub>2</sub> pressure and relating OCV to H<sub>2</sub> crossover to cathode
- Cell aged for more than 1500 h using DOE Drive Cycle Protocol:
  - Deposits Pt particles inside the membrane
- Measured OCV is less than the Nernst potential and close to mixed potential typical of ORR and HOR
  - Suggests H<sub>2</sub> crossing from anode does not completely react inside membrane
  - Data for unequal anode and cathode pressures not meaningful because of H<sub>2</sub> leaks around the seals and gaskets in aged MEA



# Pt Particles Deposited in Membrane Promote Reaction Between Crossing $H_2$ and $O_2$

- Our OCV data show that the Pt particles deposited in an aged membrane promote reaction between  $H_2$  crossing over from the anode ( $i_{xa}$ ) and  $O_2$  crossing over from the cathode ( $i_{xc}$ )
- Only a fraction of the  $H_2$  that crosses over from the anode reacts in the membrane ( $i_{xm}$ ), and this fraction decreases as  $P(H_2)$  is reduced
- $H_2$  crossover from anode is weakly affected by  $H_2$  reaction in the membrane ( $i_{xa}$ ), but  $O_2$  crossover from cathode ( $i_{xc}$ ) can increase markedly and be consumed completely inside the membrane.



$i_{xa}(H_2)$ :  $H_2$  crossover from anode

$i_{xc}(H_2)$ :  $H_2$  crossover to cathode

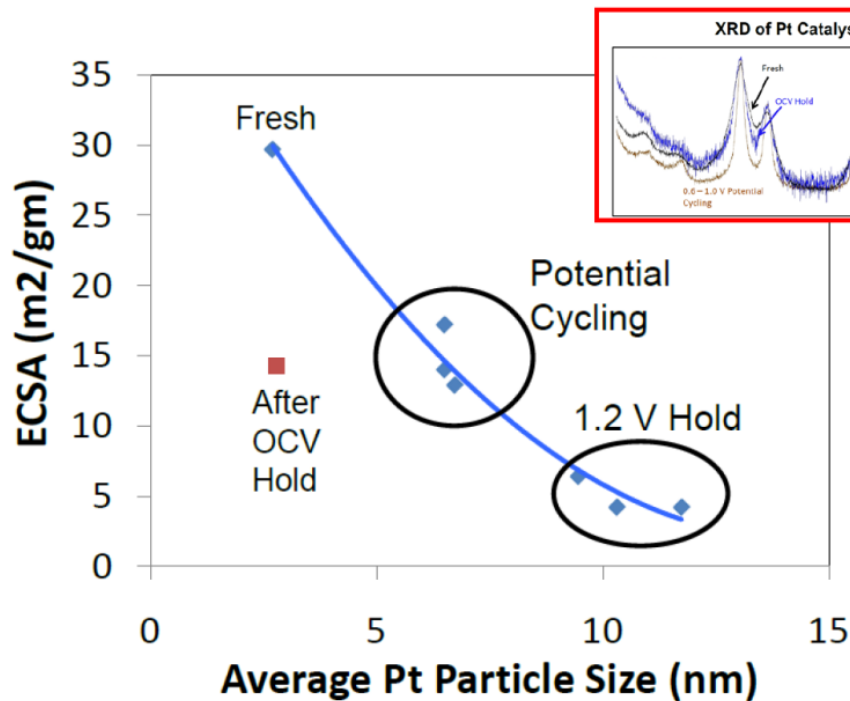
$i_{xc}(O_2)$ :  $O_2$  crossover from cathode

$i_{xm}(H_2)$ : Reaction between  $H_2$  and

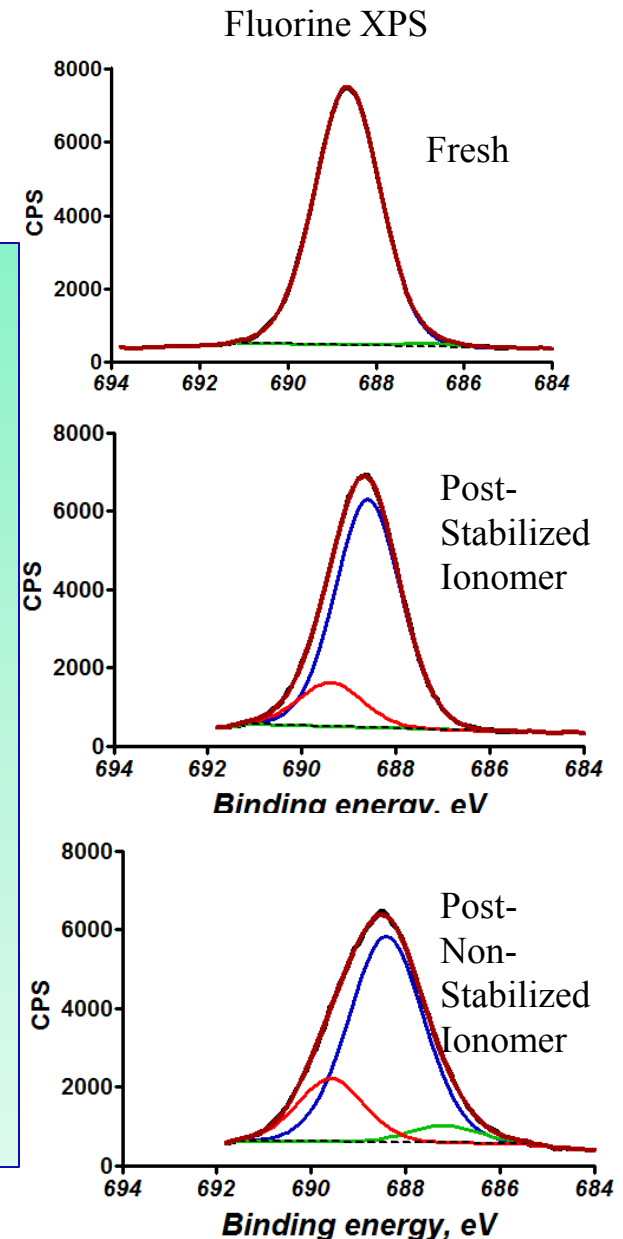
$O_2$  inside membrane

# Evidence of Ionomer Electrode Degradation

## XPS Chemical Analysis shows Changes in Fluorine, Carbon, Oxygen



- New Fluorine Binding Energy species detected after testing
- Twice as much for nonstabilized system vs stabilized
- Carbon changes → more pronounced for nonstabilized system
- Increase in Oxygen high BE component due to oxygen connected to teflon





# Local currents during Shut-down /

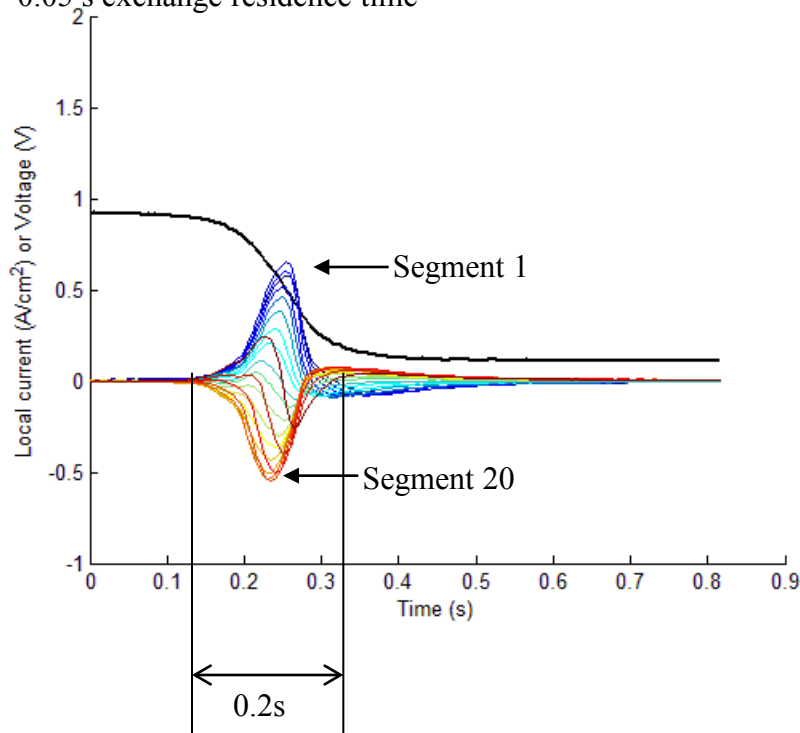
## Start-up Transients

University of Nancy Collaboration

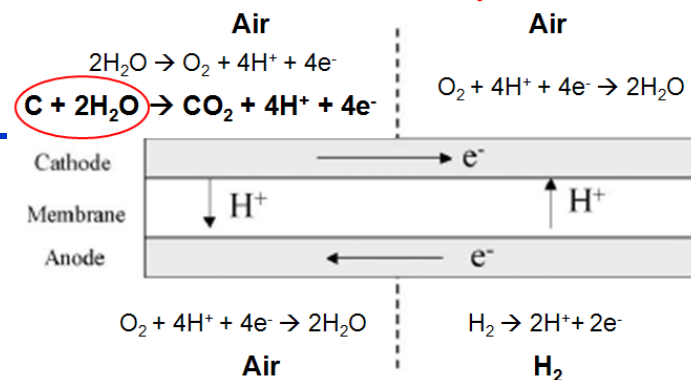
Measure carbon corrosion by linear series segments and CO<sub>2</sub> by NDIR

### Shut-down

Anode purge with air  
 ~ 0.05 s exchange residence time

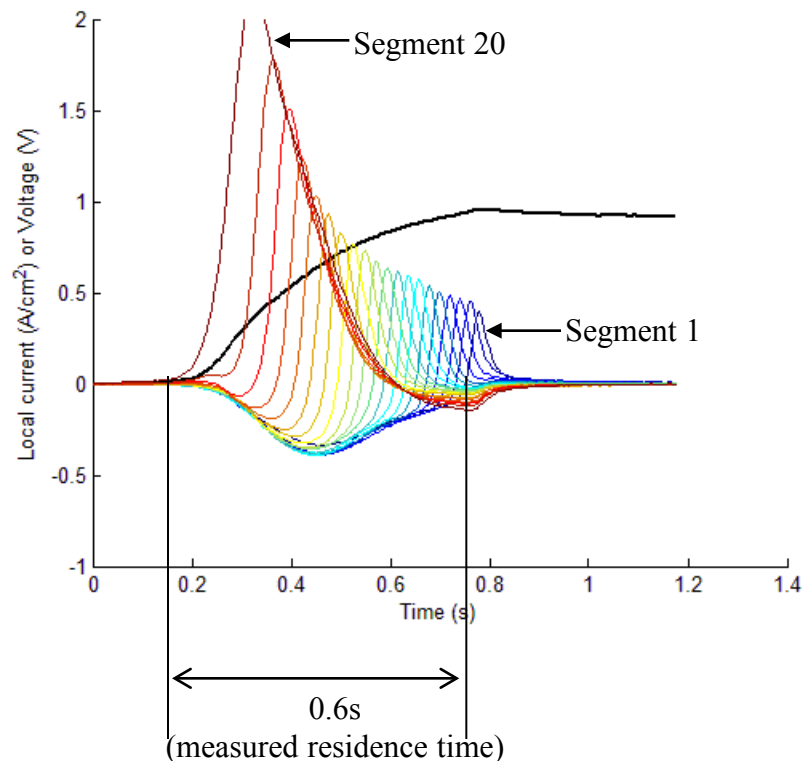


Regional reversals raise potentials dramatically



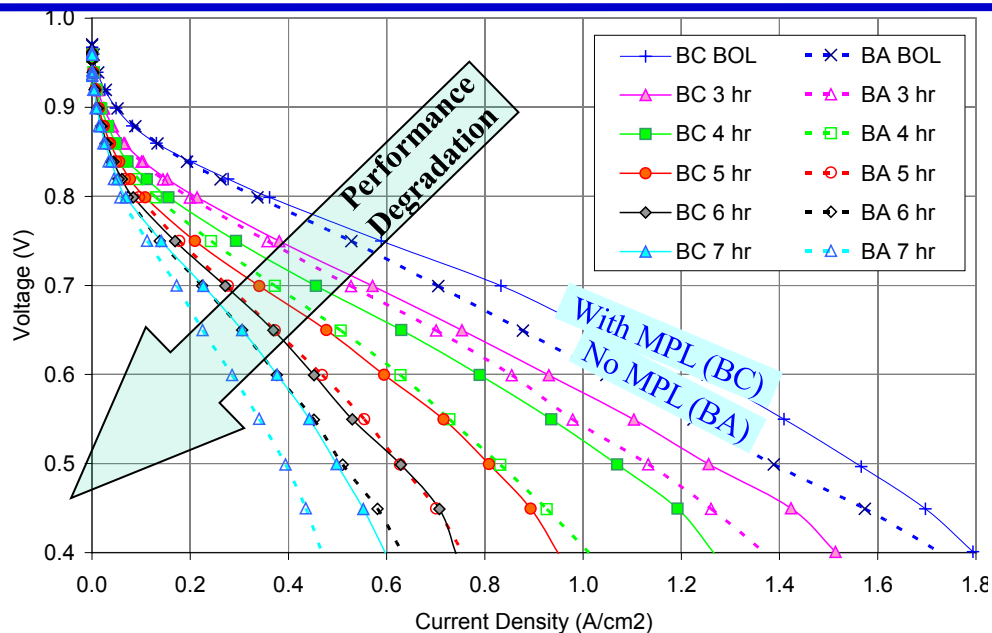
### Start-up

Anode H<sub>2</sub> feed  
 ~ 0.2 s exchange residence time

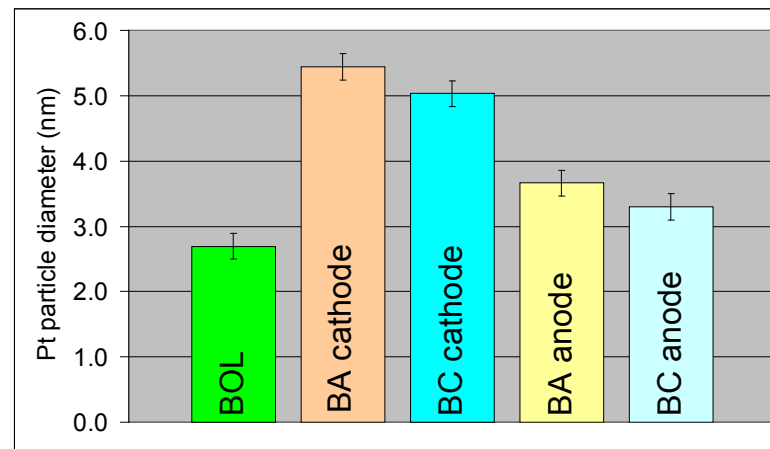


# GDLs Effect Localized Performance Degradation:

## GDLs with and without MPL



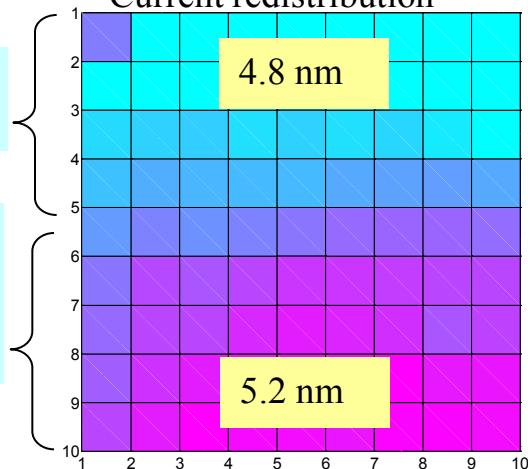
XRD: Pt particle size diameter (nm)



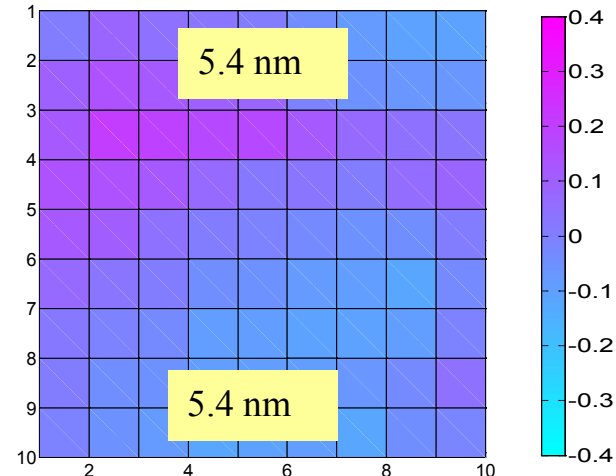
- Current density at 0.4 V reduced by:
 

|   |
|---|
| factor of 3 for the MPL case (BC cell)  |
| factor of 3.7 without the MPL (BA cell) |

BC cell (with MPL)  
Current redistribution



BA cell (no MPL)  
Current distribution ~ same

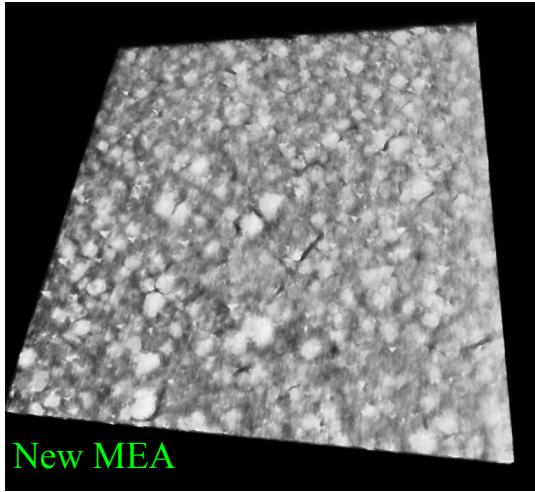


Top portion (upstream):  
Current increased (negative difference).

Bottom portion (downstream):  
Current decreased (positive difference).  
Small portions of the central lower region decreased more.

# Ex Situ Characterization Post-Carbon Corrosion Shows Non-Uniform Carbon Corrosion Due to GDL / Water Content

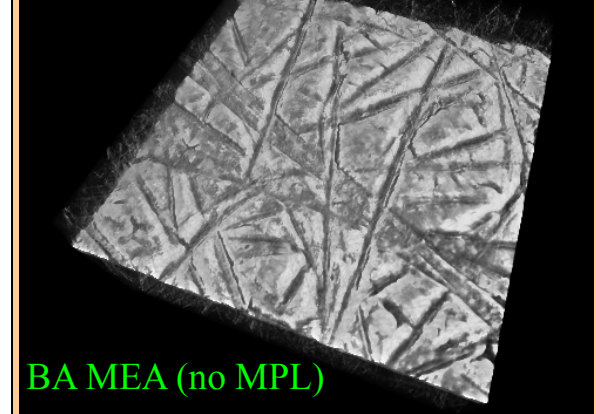
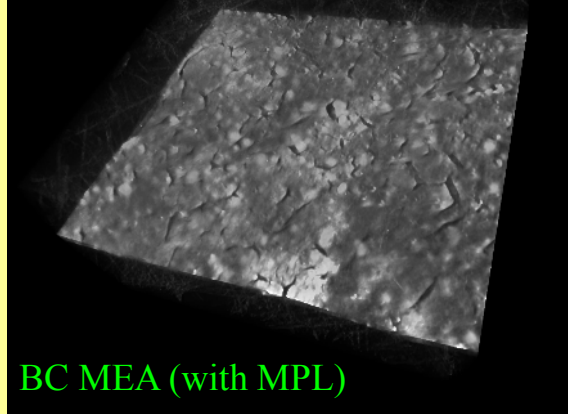
New MEA (without GDL)



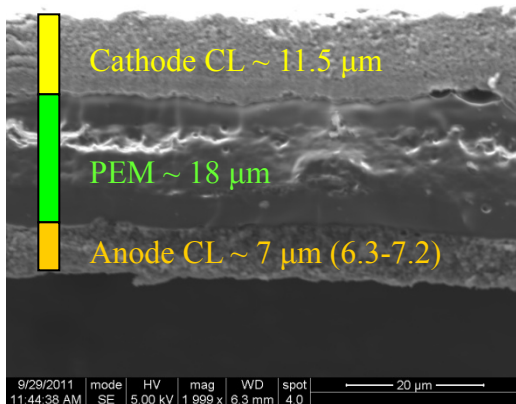
MEAs corroded for 7 hours (with GDL, cathode on top)

Area ~ 1 x 1 mm

X-Ray Computed Tomography

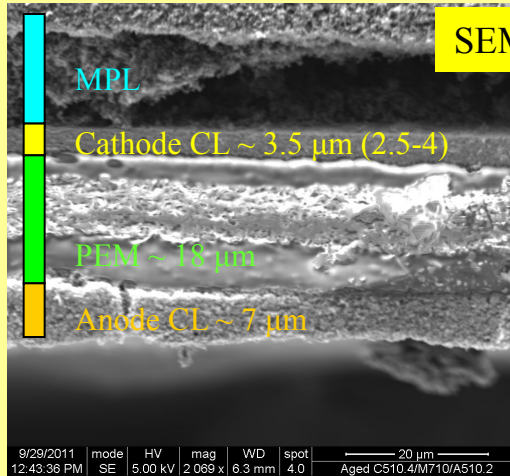


New MEA

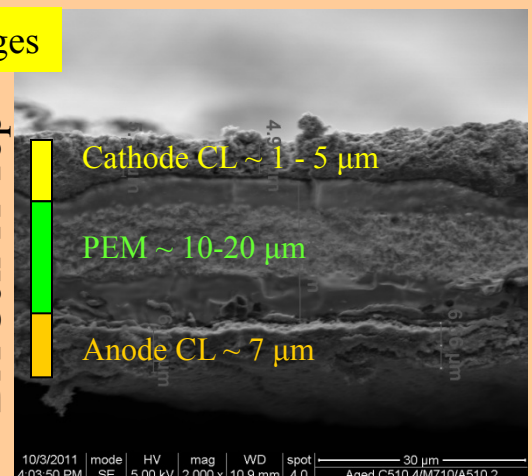


SEM Images

BC Cell 10 Bottom



BA Cell 11 Top



Uniform cathode thinning  
 (~30% remains)

Anode thickness unchanged

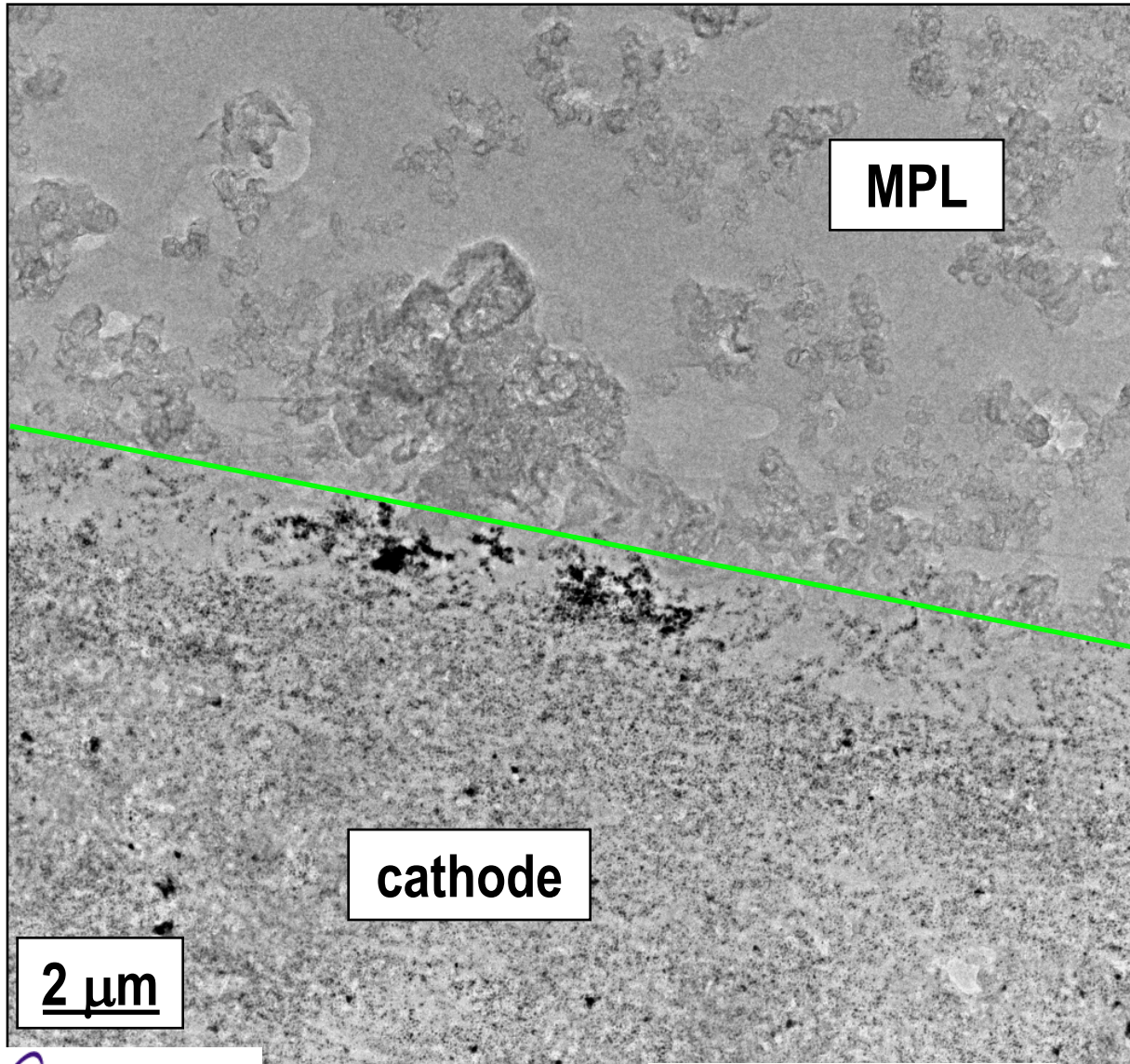
Nonuniform cathode thinning  
 Membrane 'flows' under pressure  
 Anode thickness unchanged

Gore® A510.2/M710.18/C510.4



# Carbon Structure shows Localized Structure Changes

Loss of meso-graphitic structure in catalyst layer – No structural change in MPL



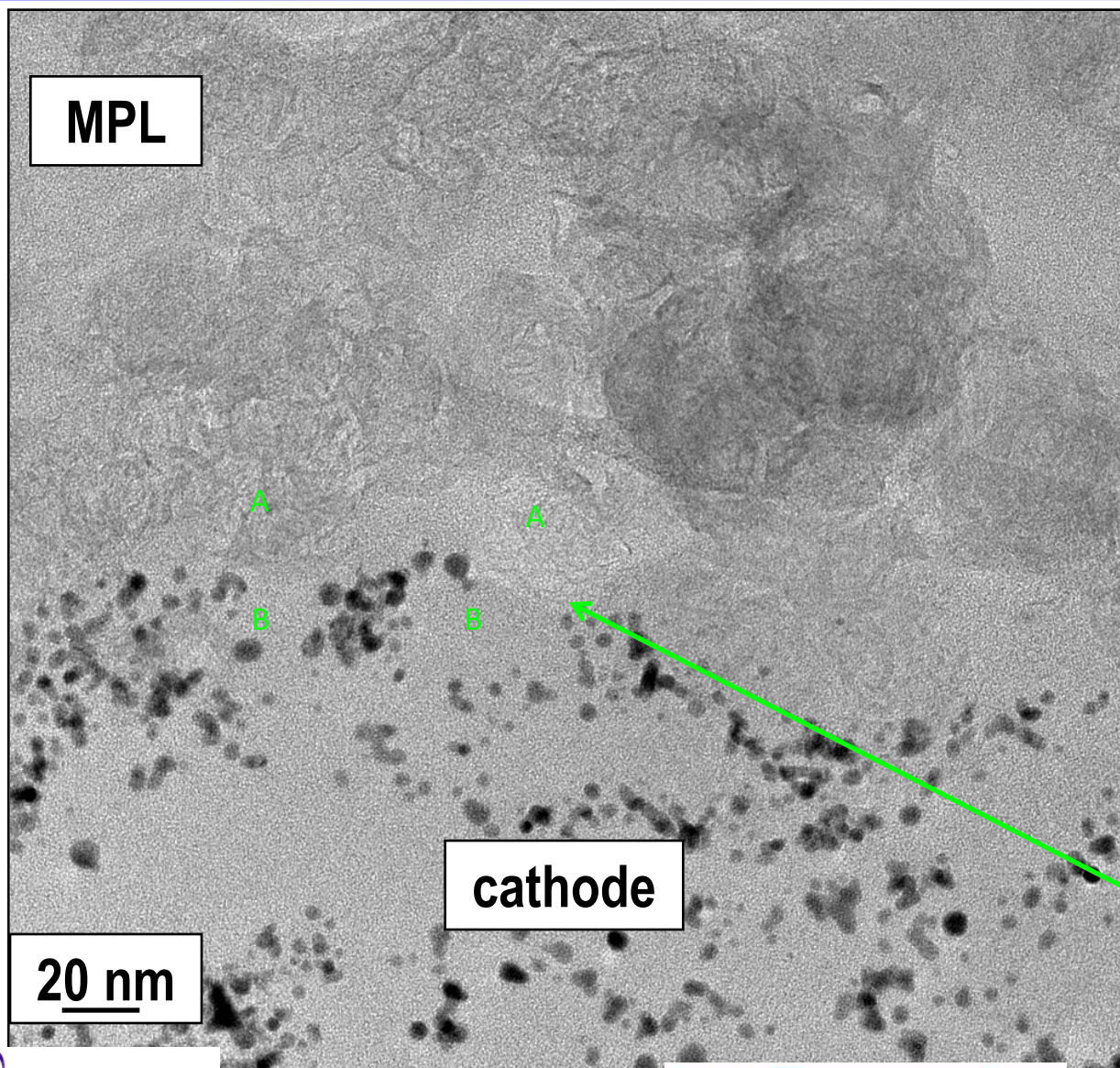
Interface between Pt/High Surface Area Carbon (HSAC) cathode and MPL is distinct – MPL carbon retains its meso-graphitic structure and porous network (even adjacent to the cathode surface) whereas the HSAC directly at the interface is fully oxidized.

AST1.2V hold for 100hr in H<sub>2</sub>/N<sub>2</sub>



# Carbon Structure shows Localized Structure Changes

Loss of meso-graphitic structure in catalyst layer – No structural change in MPL



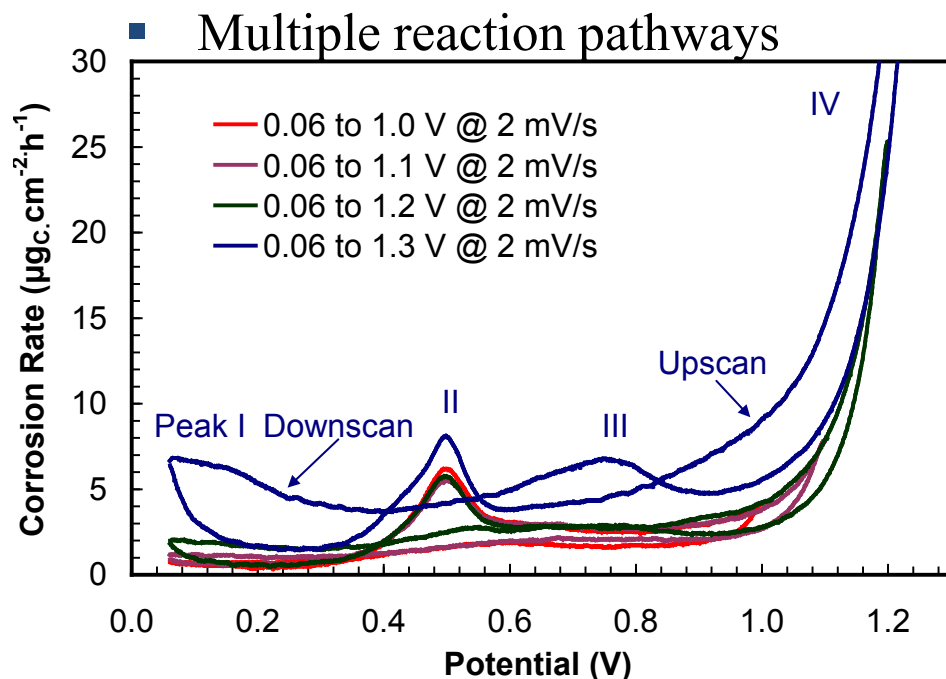
1.2V hold for 100hr in H<sub>2</sub>/N<sub>2</sub>

Interface between Pt/High Surface Area Carbon (HSAC) cathode and MPL is distinct – MPL carbon retains its meso-graphitic structure and porous network (even adjacent to the cathode surface) whereas the HSAC directly at the interface is fully oxidized.

Note distinct interface between meso-graphitic carbon particle in MPL (A) and densified and oxidized Pt/HSAC cathode (B).

# Kinetics of Carbon Corrosion: Model Development

- Carbon corrosion measured shows multiple potentials producing CO<sub>2</sub>



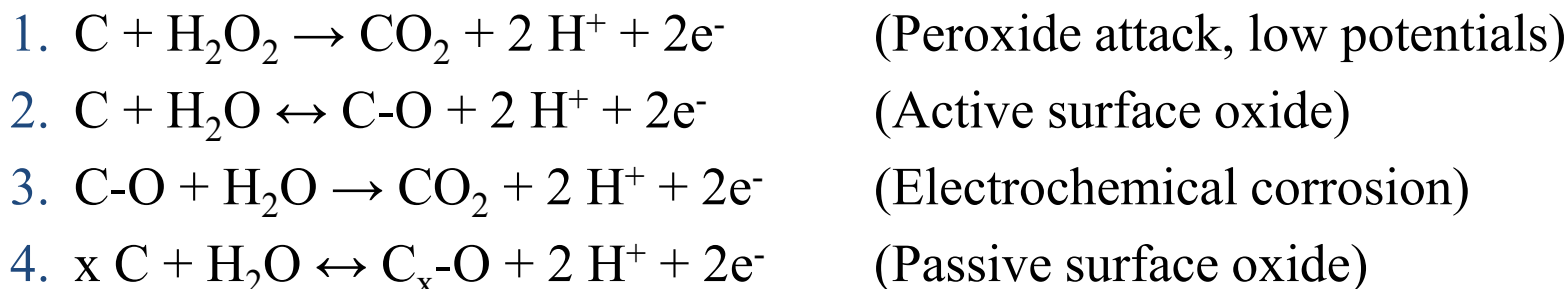
Peak I Peroxide reaction 1  
and CO<sub>2</sub> holdup

Peak II Reactions 2 and 3

Peak III Reactions 3 and 4

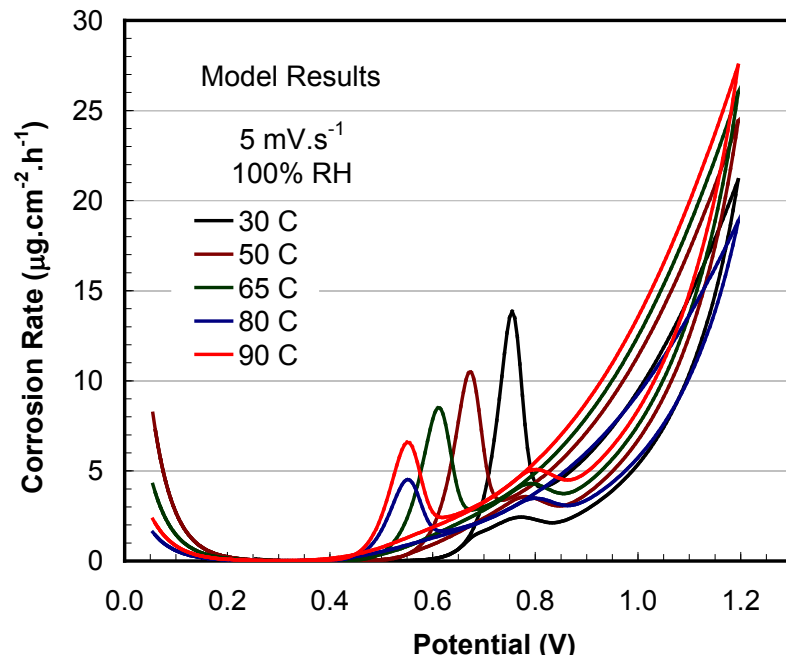
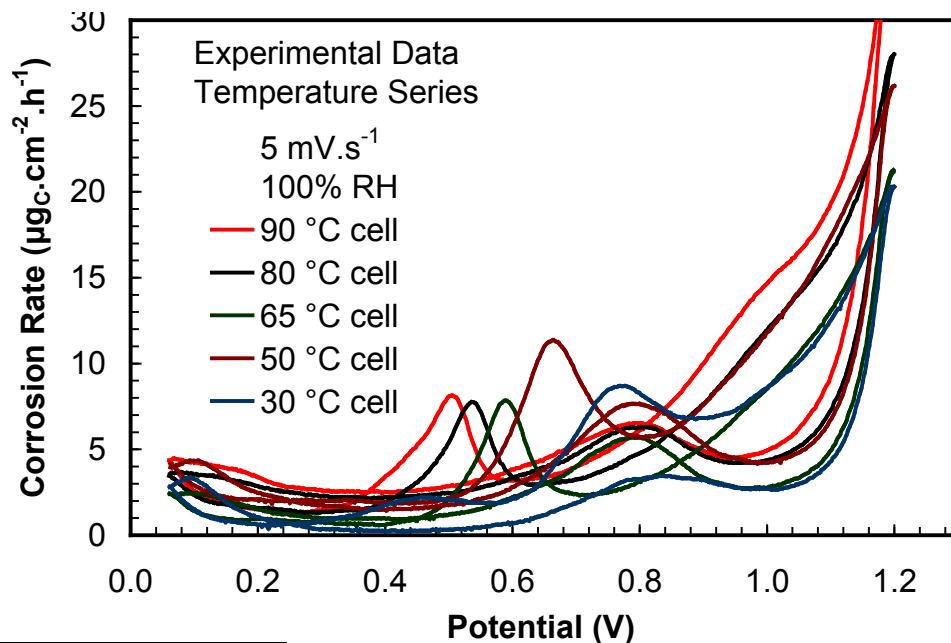
Peak IV Reaction 2

- Initial Model for Corrosion of High-Surface Area Carbon



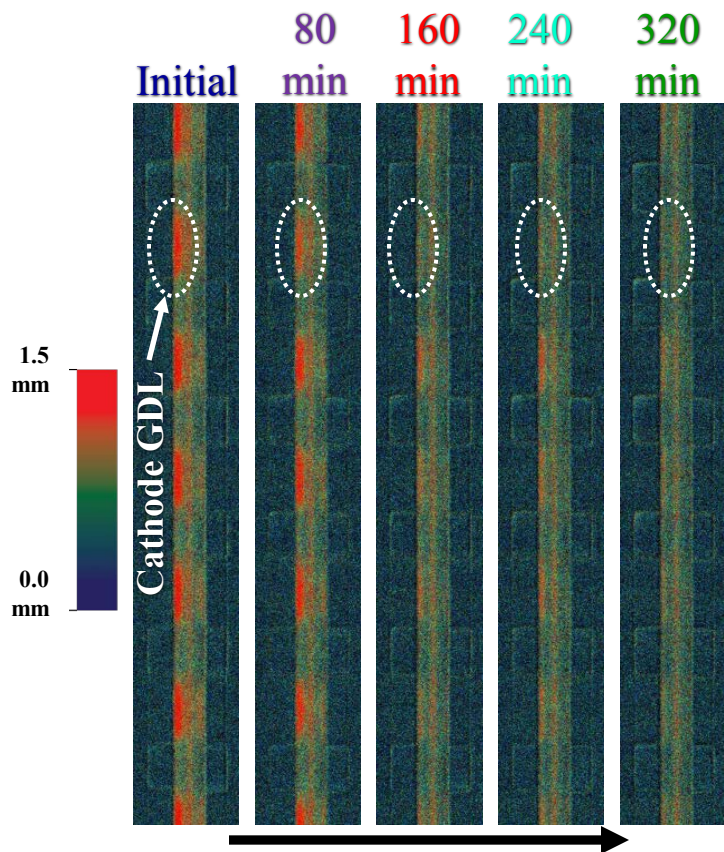
# Parametric Results on Carbon Corrosion

- Effect of cell temperature
  - At higher T, Peak I shifts to lower potentials and decreases in magnitude; Peak IV corrosion rate also increases
- Effect of scan rate
  - At higher scan rates, the corrosion rates are generally higher and the curves lose their fine structure (Peaks II and III disappear)
- Effect of relative humidity
  - At higher RH, the corrosion rates are higher



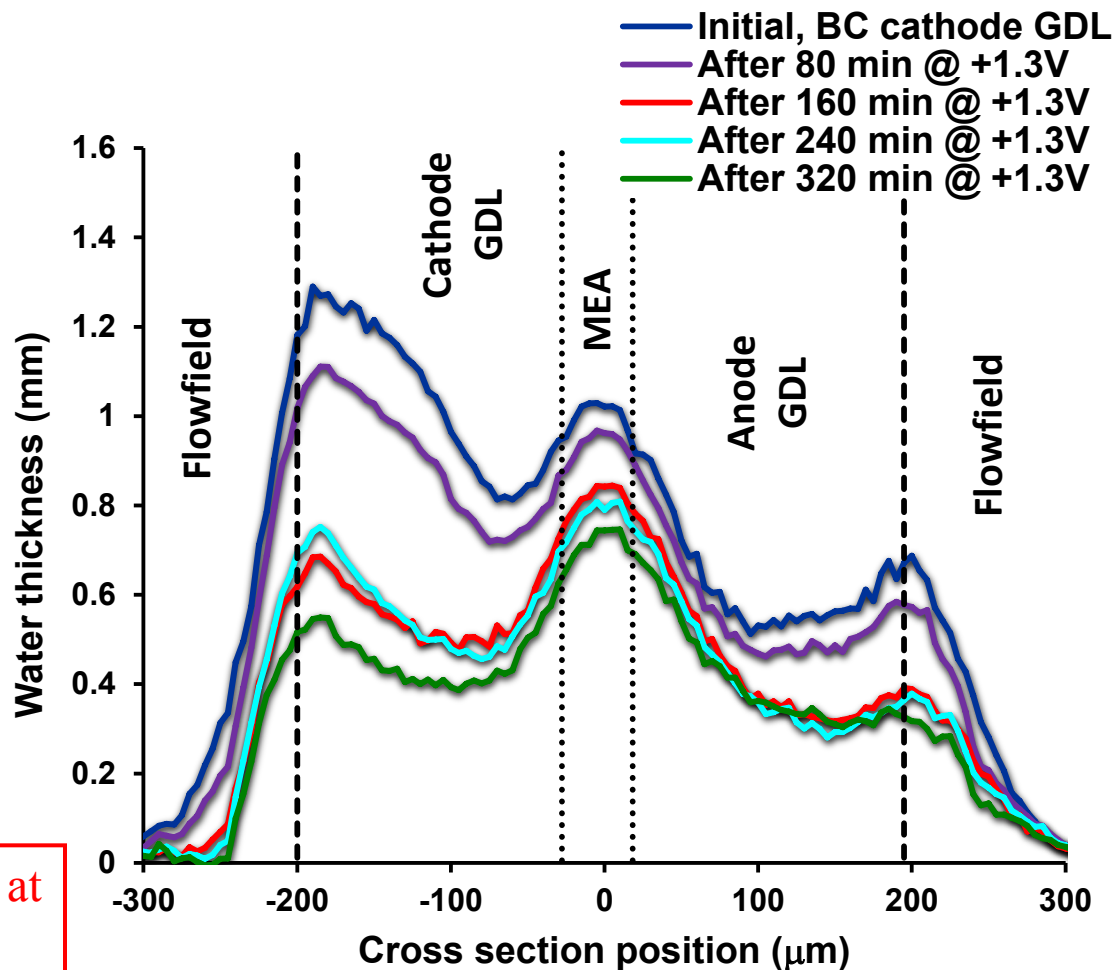


# Water Content is Reduced During Carbon Corrosion AST



Dramatic reduction in water retention at constant current density

0.8 A/cm<sup>2</sup>, 80°C, 100%RH



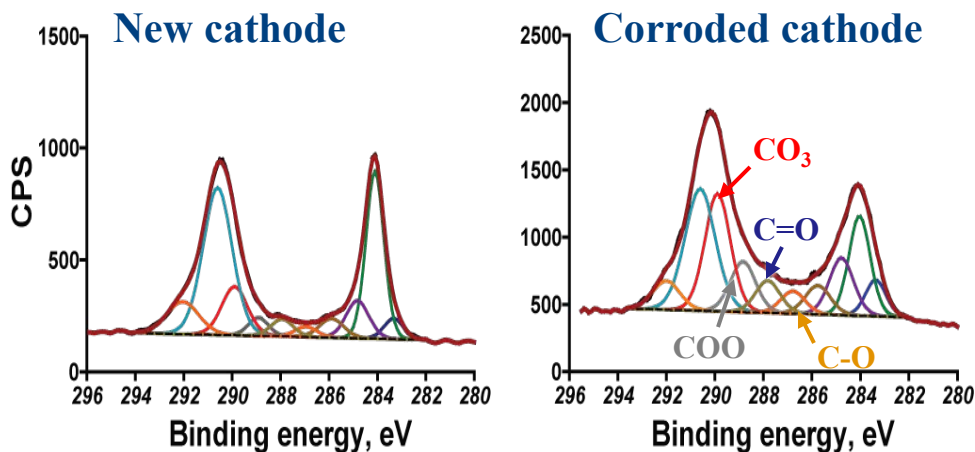
\*x-axis enlarged  
250% to show  
detail



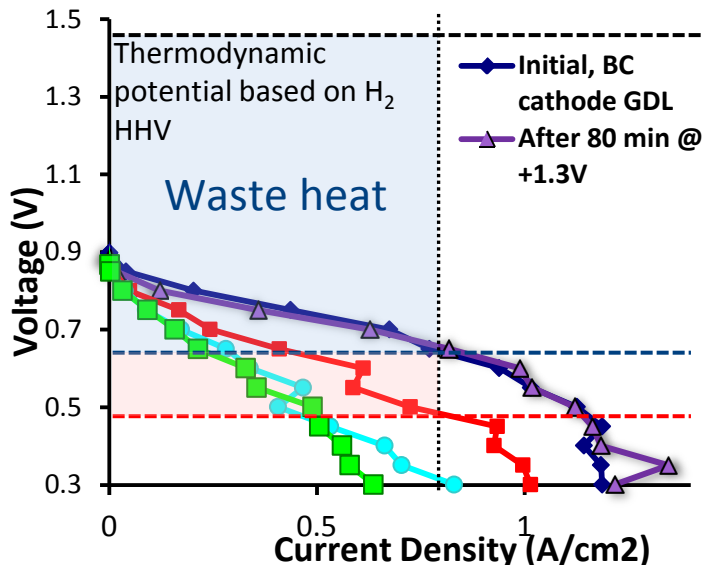
# Post-mortem Characterization: XPS + SEM

Cathode Materials Become More Hydrophilic → Heat Generation dominates

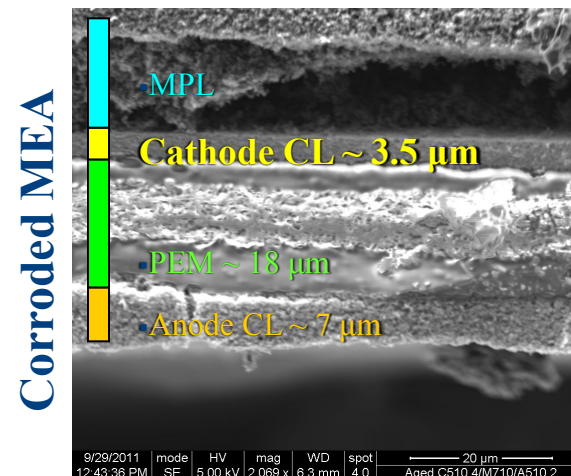
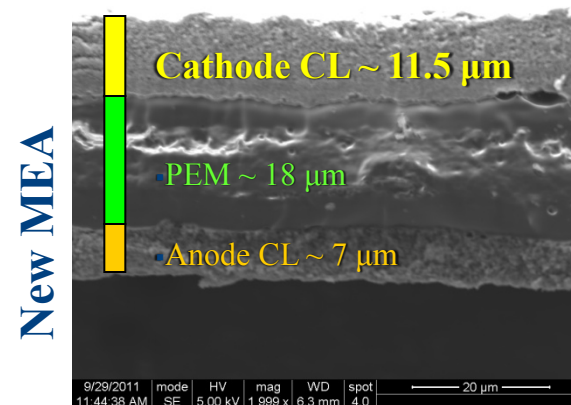
Surface oxides increase → more hydrophilic



| Species:         | C-OH/C-OC | C=O | COOH | C(O) <sub>3</sub> |
|------------------|-----------|-----|------|-------------------|
|                  | %         | %   | %    | %                 |
| New cathode      | 1.9       | 3.7 | 5.2  | 9.6               |
| Corroded cathode | 3.6       | 5.4 | 8.6  | 18.4              |



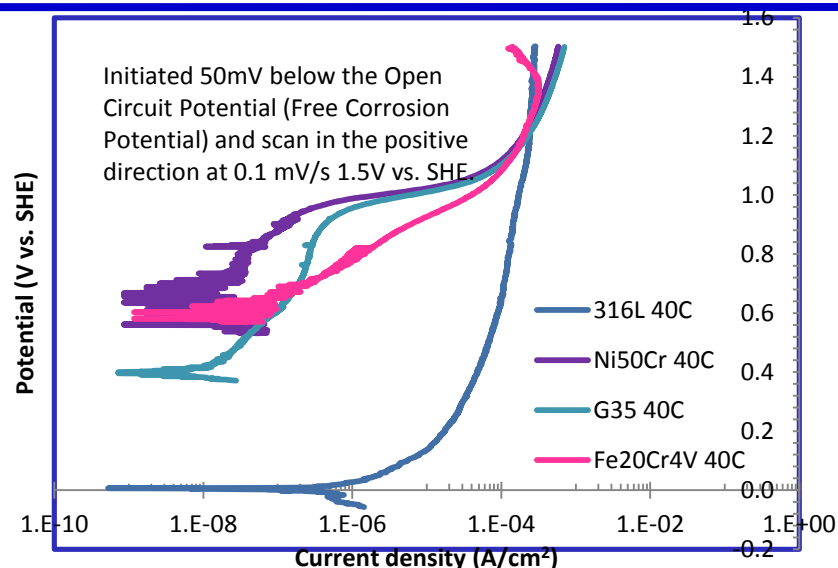
...but bigger change is collapse of cathode layer



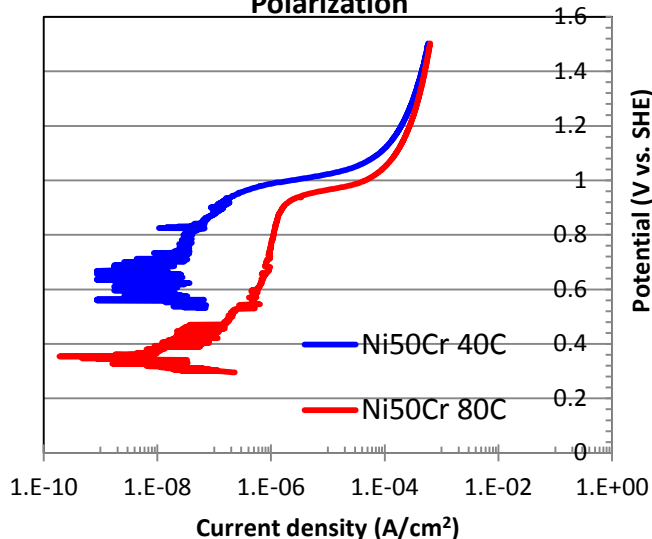
Heat generation dominates changes in hydrophilicity during carbon corrosion AST conditions

# Metal Bipolar Plate Anodic Polarization Corrosion Results

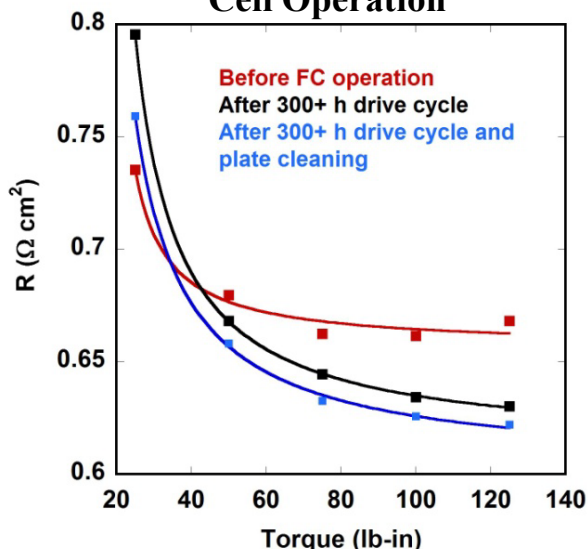
- Examine effects for model development:
  - Different metals (316L S.S., NiCr, Hastelloy)
  - Temperature effect
  - Fluoride anion content effect
  - Contact resistance increase
  - Metal cation poisoning of proton conduction
- Temperature increases corrosion rate
  - Decreases Free Corrosion Potential (OCV)
- Other testing in progress



Temperature Effect on Ni50Cr Polarization



Contact Resistance after Fuel Cell Operation



Post-MEA Analysis

| Component             | Total metal content $\mu\text{g cm}^{-2}$ |
|-----------------------|---|
| Endplate              | $\infty$                                  |
| MEA before FC testing | 0.71                                      |
| MEA after FC testing  | 0.11                                      |
| Cathode GDL           | 0.22                                      |
| Anode GDL             | 0.41                                      |

No Measureable Increase in MEA Metal Cations

Increase in plate contact resistance observed at low contact force

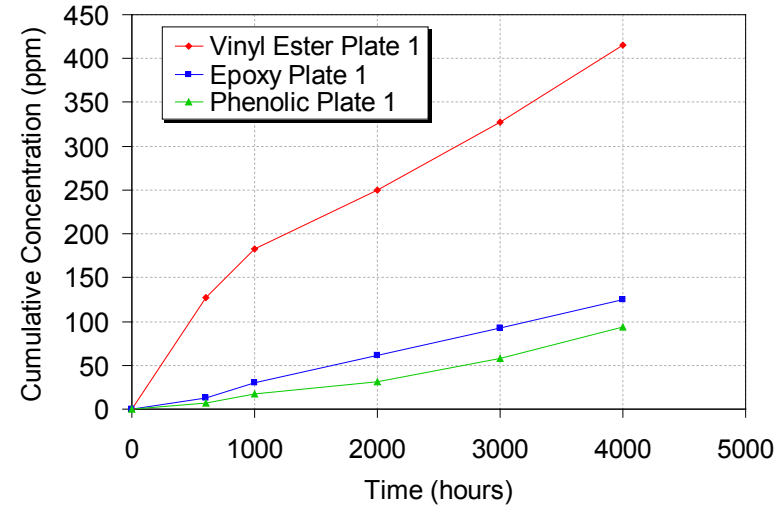
# Carbon Bipolar Plates

## Overview

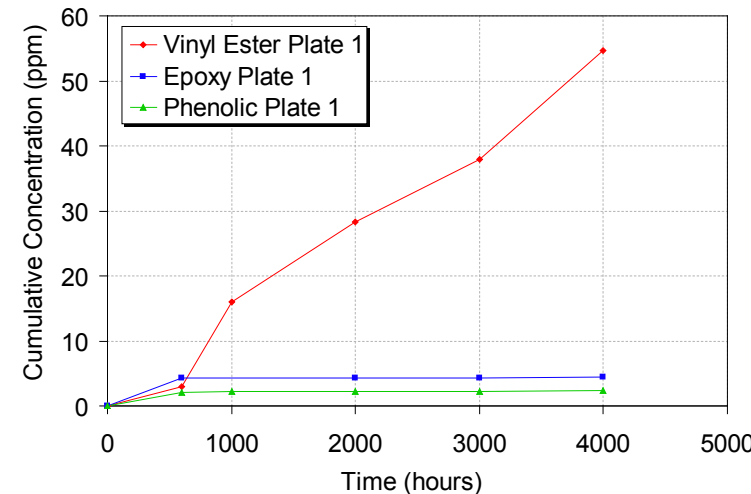
## Contamination

| Group                     | Testing                           | AST Data                                 | Sampling     |
|---------------------------|-----------------------------------|--|--------------|
| Mechanical Change         | Instron                           | Flexural strength                        | To 20K hours |
|                           |                                   | Flexural modulus                         |              |
|                           |                                   | Strain to failure                        |              |
|                           | Dynamic Mechanical Analysis (DMA) | Glass transition temperature             |              |
| Chemical Change           | Thermo-gravimetric Analysis (TGA) | Thermal degradation onset T              | To 20K hours |
|                           |                                   | Isothermal weight loss                   |              |
| Contamination             | Extraction                        | Metals and organics                      | BOL          |
|                           | Leachate Analysis                 | Metals and organics                      | To 4K hours  |
|                           | Rotating Disc Electrode           | Performance vs. concentration (isolated) | BOL          |
| Surface Change            | Tensiometry                       | Advancing / receding forces              | To 1K hours  |
|                           | Goniometry                        | Advancing / receding CA's                |              |
|                           | Laser Microscopy                  | Surface roughness                        |              |
| Intrinsic Property Change | Electrical Conductivity           | Bulk electrical conductivity             | To 1K hours  |
|                           |                                   | Electrical contact resistances           |              |
|                           | Thermal Conductivity              | Bulk thermal conductivity                | BOL, EOL     |

### Cumulative Organics



### Cumulative Metals

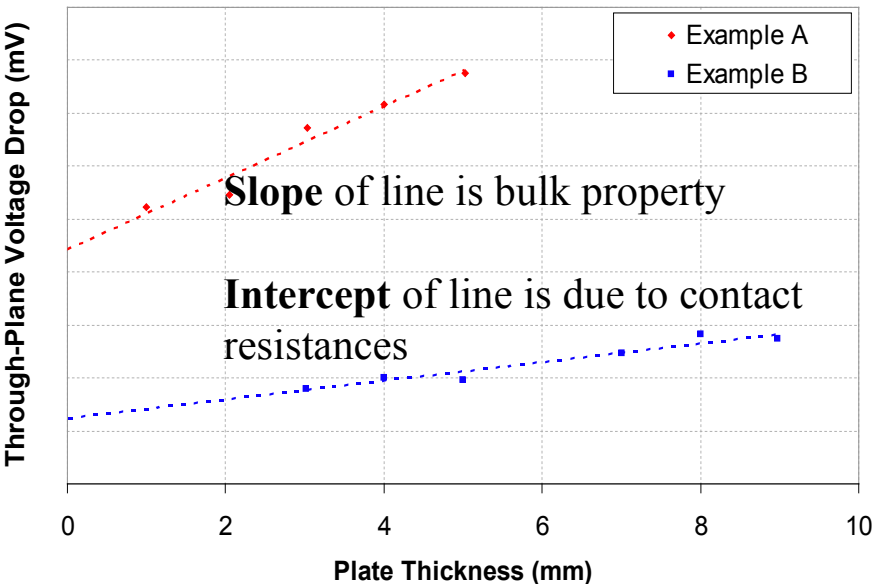


# Carbon Bipolar Plates

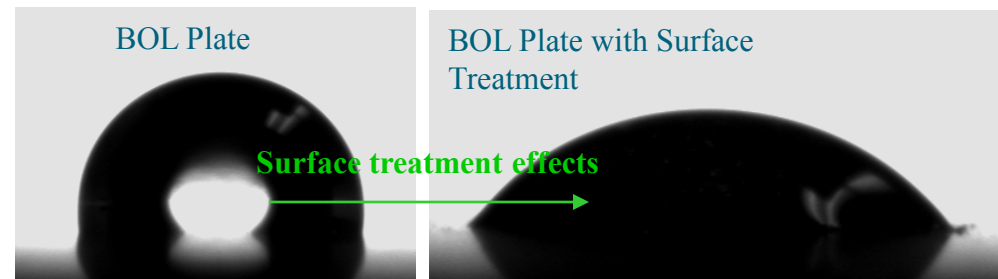
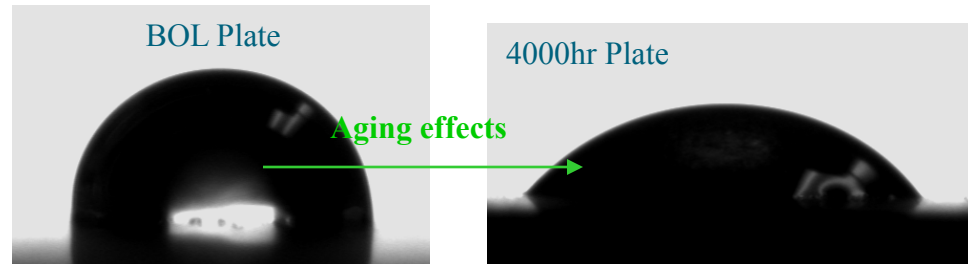
## Electrical Property Change

## Surface Change

- Investigating separation of bulk properties and contact resistances
- Method distinguishes different material types



- Goniometry
  - Dynamic method to capture key properties relating to water management
  - Measureable properties include: advancing / receding contact angle, removal angle (force), droplet size / shape
  - Concentrating on moment of initial water movement



# Summary

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- **Project Goals are to:**
  - **Understand Degradation Mechanisms**
  - **Develop Integrated model of Degradation**
- Material variants include: ionomer, membrane, catalyst, support, electrodes, GDL, metal plates, carbon plates, seal materials
  - > 30 MEA variants, > 6 AST tests, > 3 fuel cell durability tests
- Components
  - Electrode Structure
  - Catalyst
  - Catalyst Support
  - GDL
  - GDL/Catalyst Layer Interface
  - Metal Plates
  - Carbon Plates
  - Seals
- Operational Variables
  - Shut-Down / Start-Up
  - Temperature, RH, etc.

# Selected Technical Conclusions - 1

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- **Catalyst**

- Rate of platinum agglomeration has dependency on loading & mechanism
  - Agglomeration independent of loading for dissolution / reprecipitation
  - Agglomeration dependent on loading during carbon corrosion

- **Electrode structural changes occur**

- During potential cycling favor of oxygen diffusion result in lower MT Resistance
- New electrode processing technologies generate better electrode structure for low loading Pt/C cathode
- Cathode electrode structure effects membrane degradation

- **Catalyst layer ionomer degrades**

- ECSA loss without particle size change, Pt particles agglomerating in ionomer
- Chemical Analysis/Binding Energy changes more pronounced for non-stabilized ionomer, including development of a new fluorine binding energy species

- **Carbon structure shows localized structure changes**

- Loss of meso-graphitic structure in catalyst layer
- No structural change in MPL (meso-graphitic structure remains across interface)
- Rate of carbon oxidation decreases with each potential hold
- Portion of the evolved CO<sub>2</sub> originates from the MPL, not the catalyst layer

# Selected Technical Conclusions - 2

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- **Hydrogen crossover affected by catalyst layer degradation**
  - OCV test affected by cathode electrode structure; implies membrane is indirectly affected by the electrode
  - OCV data show that the Pt particles deposited in an aged membrane promote reaction between H<sub>2</sub> crossing over from the anode ( $i_{xa}$ ) and O<sub>2</sub> crossing over from the cathode ( $i_{xc}$ )
  - Pt particle degradation and migration effects the membrane H<sub>2</sub> crossover
- **GDL effects Catalyst layer Performance Degradation**
  - Surface oxides of carbon of catalyst layer and GDL increase
  - Hydrophilicity increase effect on water transport overwhelmed by overpotential increases
  - Mass transport losses during carbon corrosion are due to collapse of pore space, not increased flooding
- **Bipolar plate primary effect on degrading performance appears to be contact resistance increase**
  - No Measureable Increase in MEA Metal Cations from Metal Plate corrosion,
  - Increases in contact resistance

# Future Work

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## Identify and Quantify Degradation Mechanisms

- Vary MEA materials to better define ionomer degradation
  - Expand mixed hydrocarbon and PFSA materials for unambiguous chemical analysis

## Electrode Structure

- Identify structural change of electrodes during potential cycling and operation
- Identify causes behind ionomer and solvent impact on MEA durability
  - Establish correlation of electrode structure durability to mechanical strength

## Start-up / Shut-down

- Series Segmented Cell SU/SD measurements comparing catalyst support materials
- Compare CO<sub>2</sub> during SU/SD to 1.2V AST holds
- Compare the degradation mechanisms from the SU/SD to the ASTs

## Component Interactions

- Metal bipolar plate evaluation and evaluation of interactions with MEA/GDL
  - Fuel cell testing of metal materials to correlate corrosion rate to metal cation contamination of membrane and proton conduction
- Composite (graphite) bipolar plate evaluation
  - Standardize surface evaluation improving data consistency to evaluate surface properties

## Modeling

- Incorporate parametric studies of components into integrated model
- Water profile modeling during carbon corrosion comparing overpotential and hydrophobicity changes to water transport



# Future Plans: Parametric Studies (on-going)

## Parametric Studies Feed the Final Integrated Model Development

### Membrane Degradation

| Pressure |       | 150 kPa |                  |      | Fuel/Oxidant                         |  | H <sub>2</sub> /air |  |
|----------|-------|---------|------------------|------|--------------------------------------|--|---------------------|--|
| V        | T     | RH      | % O <sub>2</sub> | Time | Measurement Times for F- & TER Rates |  |                     |  |
| OCV      | 90° C | 30%     | 100%             | 80 h | Every 5 h                            |  |                     |  |
| OCV      | 90° C | 30%     | 5%               | 40 h | Every 5 h                            |  |                     |  |
| OCV      | 90° C | 30%     | 50%              | 40 h | Every 5 h                            |  |                     |  |
| OCV      | 90° C | 30%     | 21%              | 40 h | Every 5 h                            |  |                     |  |
| OCV      | 90° C | 30%     | 50%              | 40 h | Every 5 h                            |  |                     |  |
| OCV      | 80° C | 30%     | 50%              | 40 h | Every 5 h                            |  |                     |  |
| OCV      | 65° C | 30%     | 50%              | 40 h | Every 5 h                            |  |                     |  |
| OCV      | 30° C | 30%     | 50%              | 40 h | Every 5 h                            |  |                     |  |
| OCV      | 90° C | 30%     | 50%              | 40 h | Every 5 h                            |  |                     |  |
| OCV      | 90° C | 50%     | 50%              | 40 h | Every 5 h                            |  |                     |  |
| OCV      | 90° C | 75%     | 50%              | 40 h | Every 5 h                            |  |                     |  |
| OCV      | 90° C | 100%    | 50%              | 40 h | Every 5 h                            |  |                     |  |

### Catalyst Support Cycle

| 150 kPa |      | Fuel/Oxidant |      |                       | H <sub>2</sub> /N <sub>2</sub> |  |
|---------|------|--------------|------|-----------------------|--------------------------------|--|
| V       | T    | RH           | Time | Measurement Frequency |                                |  |
| 1.2 V   | 80°C | 100%         | 20 h | after 20 h            |                                |  |
| 1.2 V   | 80°C | 80%          | 20 h | after 20 h            |                                |  |
| 1.2 V   | 80°C | 65%          | 20 h | after 20 h            |                                |  |
| 1.2 V   | 80°C | 45%          | 20 h | after 20 h            |                                |  |
| 1.2 V   | 80°C | 25%          | 20 h | after 20 h            |                                |  |
| 1.2 V   | 90°C | 100%         | 20 h | after 20 h            |                                |  |
| 1.2 V   | 80°C | 100%         | 20 h | after 20 h            |                                |  |
| 1.2 V   | 65°C | 100%         | 20 h | after 20 h            |                                |  |
| 1.2 V   | 50°C | 100%         | 20 h | after 20 h            |                                |  |
| 1.2 V   | 30°C | 100%         | 20 h | after 20 h            |                                |  |
| 1.0 V   | 80°C | 100%         | 20 h | after 20 h            |                                |  |
| 1.1 V   | 80°C | 100%         | 20 h | after 20 h            |                                |  |
| 1.2 V   | 80°C | 100%         | 20 h | after 20 h            |                                |  |
| 1.3 V   | 80°C | 100%         | 20 h | after 20 h            |                                |  |
| 1.4 V   | 80°C | 100%         | 20 h | after 20 h            |                                |  |

Vary Catalyst Loading

Vary Carbon Types: High Surface Area, Low Surface Area, Vulcan Carbon

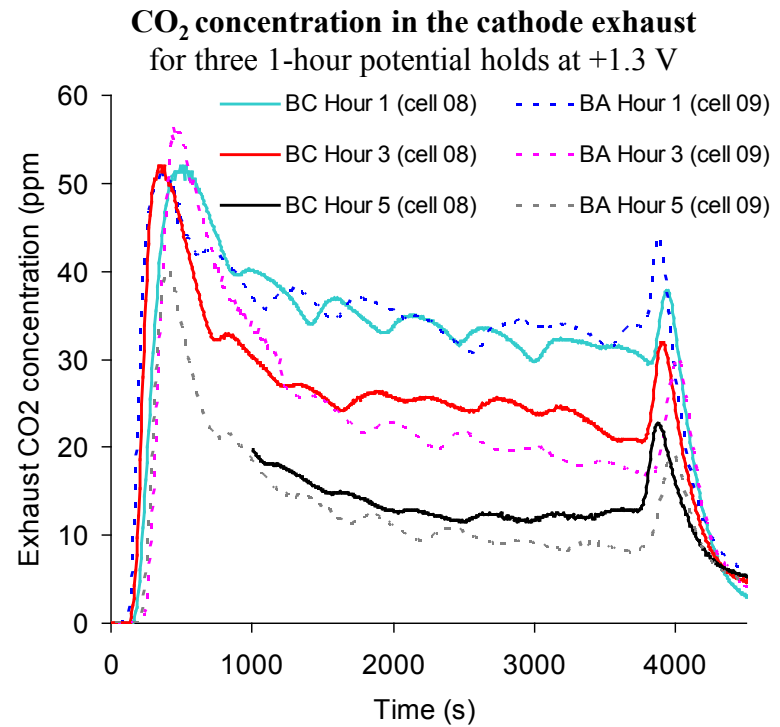
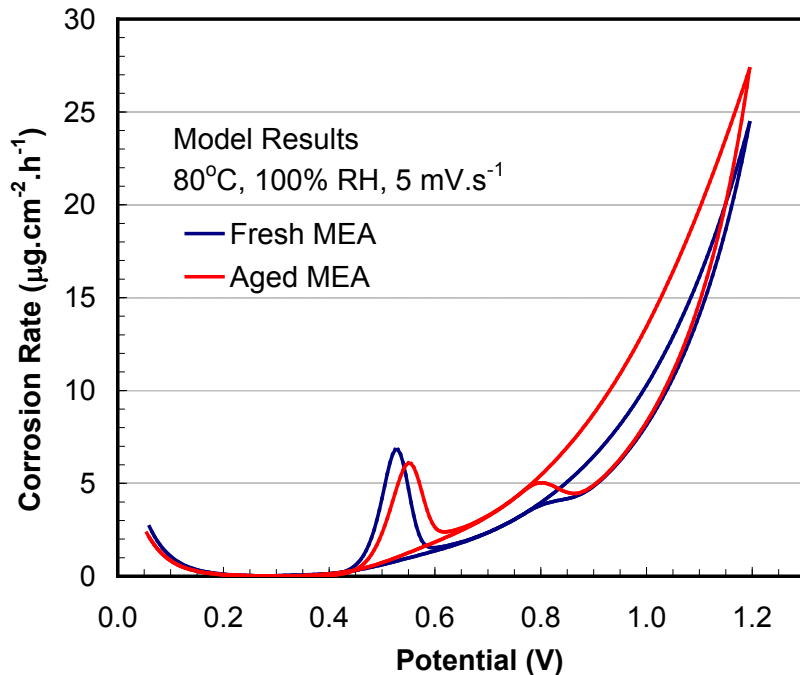
- PO<sub>2</sub>, RH and Temp dependence of membrane degradation

- Carbon corrosion RH, Temp, Loading, Carbon type, V)

- Data for Pt dissolution from ANL study (D. Myers)

# Future Work: Carbon Corrosion

- Characterize corrosion rates of carbon supports with higher degree of graphitization during the aging process
- Measure and model the effect of ageing on carbon corrosion rates
  - Initial observations: ECSA dropped by  $\sim 90\%$ , carbon mass decreased by  $\sim 47\%$ , yet the cell capacitance increased and the carbon corrosion rate did not slow down
- Measure and model the effects of carbon corrosion on growth of Pt particles, loss in ECSA and mass transfer overpotentials



- Define the hysteresis, age effect on the studies (i.e. degradation rates new vs. rates from aged samples)

# Thanks to

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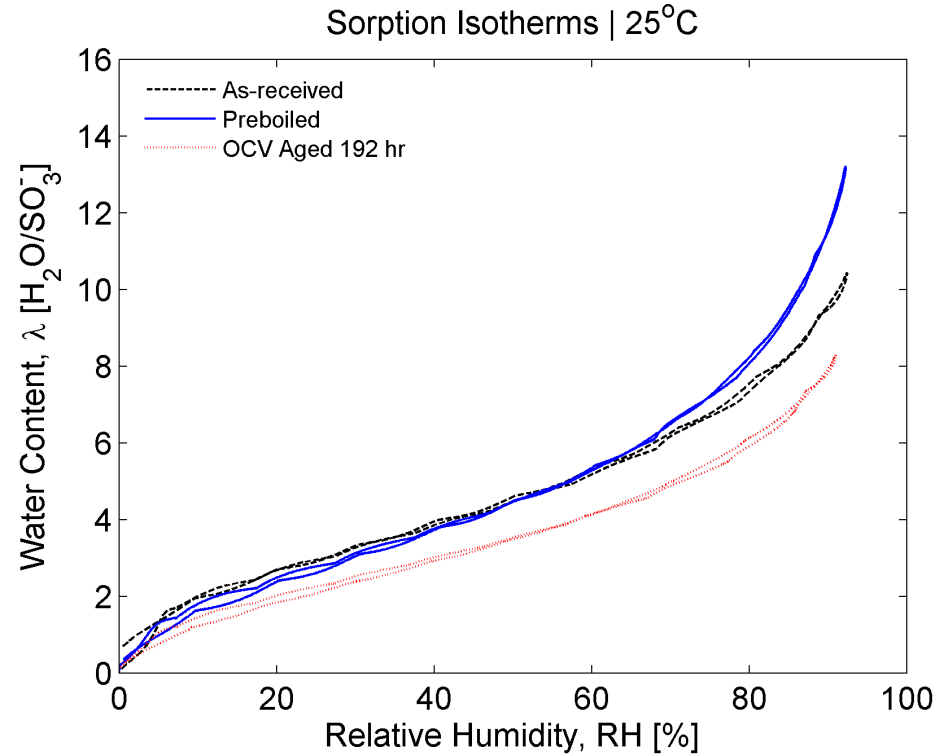
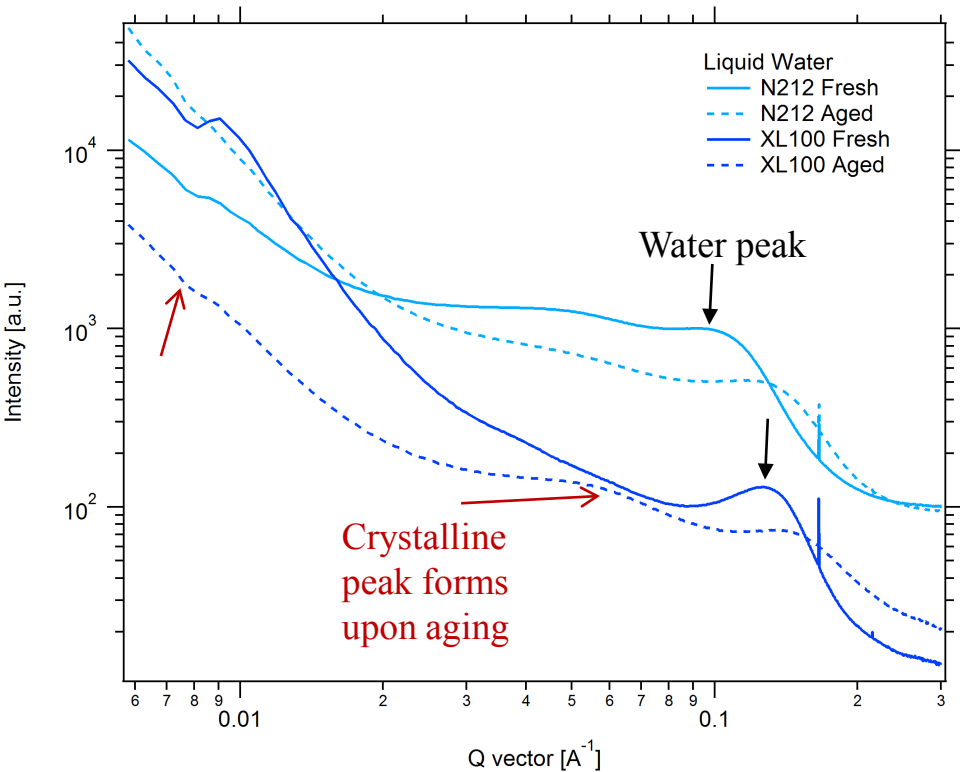
- U.S. DOE -EERE Fuel Cell Technologies Program for financial support of this work
  - Technology Development Manager: Nancy Garland
- All project partners and personnel

## Other Acknowledgments:

- SANS beam time provided by
  - Los Alamos Neutron Science Center: LQD beam line
  - NIST: NG3, NG7 beam lines
- Neutron imaging beam time provided by
  - National Institute of Standards and Technology: BT-2
- Other materials provided by:
  - W.L. Gore
  - Solvay
  - SGL Carbon GmbH

# Technical Backup Slides

# Morphology of Aged Ionomeric Membranes

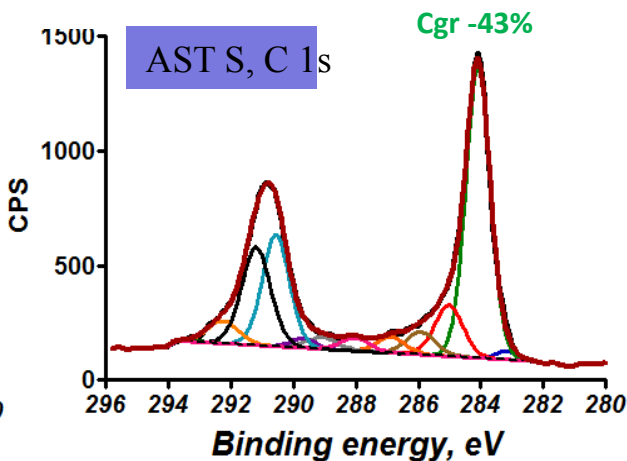
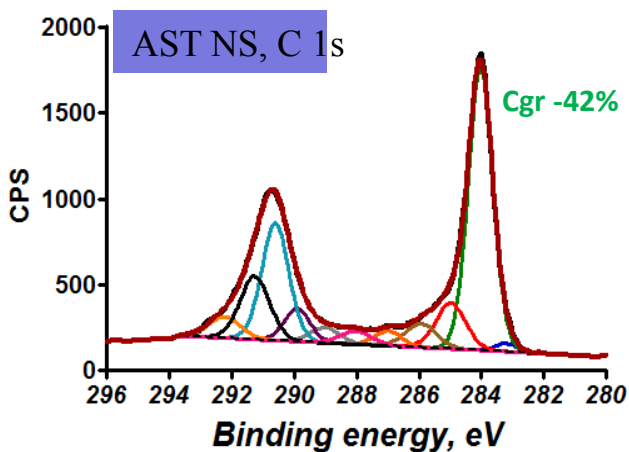
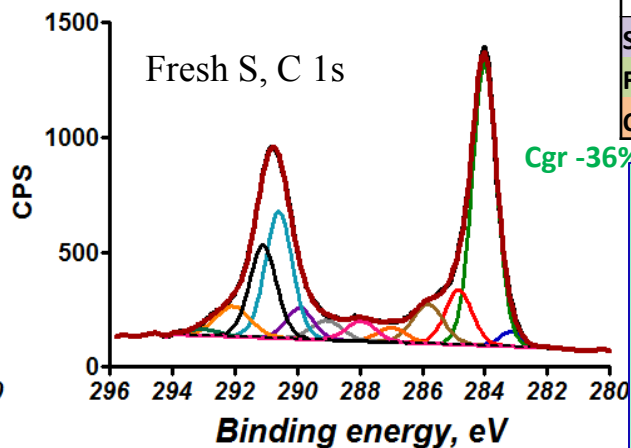
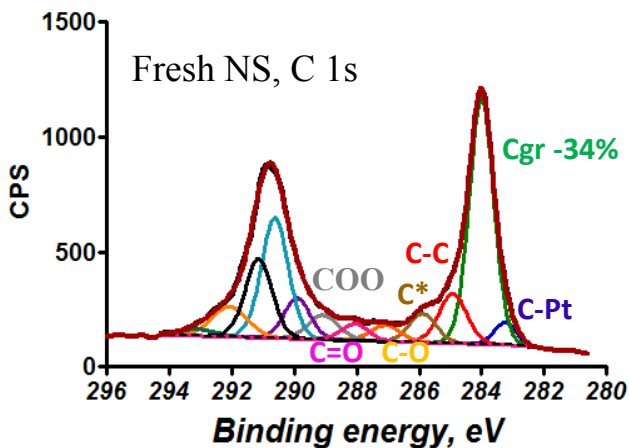


- Morphology changes upon aging (OCV Test)
  - Water domain spacing reduces when membrane is equilibrated in water
  - Crystalline peak formation is observed for XL100 at  $\sim 0.06 \text{\AA}^{-1}$
  - Aging results in a similar domain region for both XL and N212
  - Initial slope also suggests change in morphology, where aged sample reach similar structure

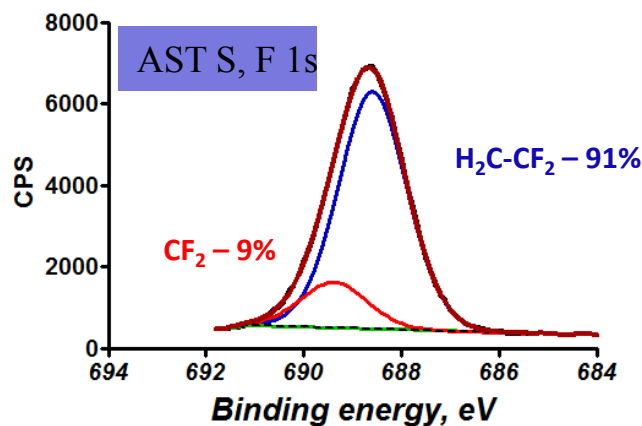
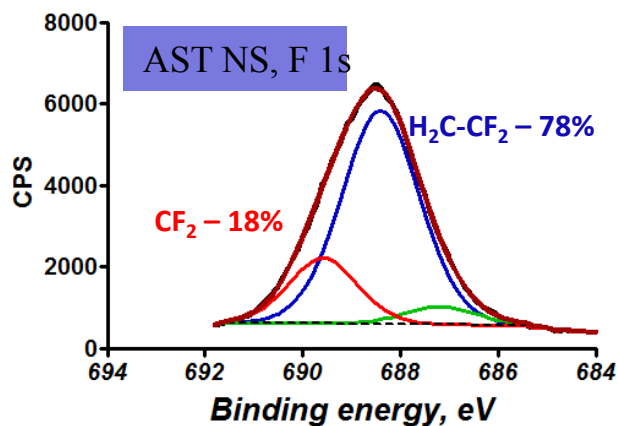
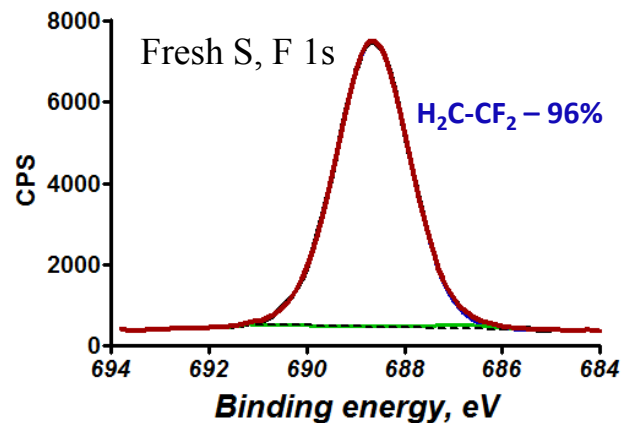
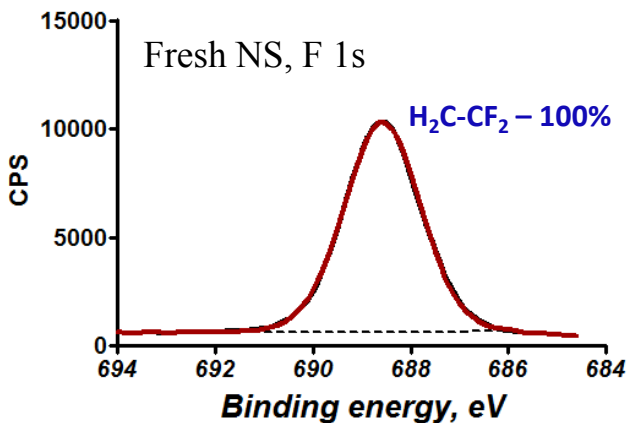
# Chemical Analysis of Ionomer Degradation: Carbon 1s

|                    | COOH  | CO3   | catalyst ionomer |         |
|--------------------|-------|-------|------------------|---------|
|                    | 289.0 | 289.8 | <288 eV          | >288 eV |
| NS IONOMER         | 1.7   | 4.5   | 11.3             | 88.7    |
| Fresh NS cathode   | 5.1   | 6.3   | 55.1             | 44.9    |
| OCV AST NS cathode | 3.7   | 4.7   | 60.0             | 40.0    |
| S IONOMER          | 0.9   | 2.1   | 8.7              | 91.3    |
| Fresh S cathode    | 4.8   | 5.7   | 58.5             | 41.5    |
| OCV AST S cathode  | 2.8   | 2.6   | 60.4             | 39.6    |

- Stabilized ionomer has more of CF<sub>2</sub> ends/no CO
- Increase in graphitic C is detected for both nonstabilized and stabilized
  - Larger graphitic C increase for NS system
  - Amount of C<sub>x</sub>O<sub>y</sub> species decreased after testing
- CF<sub>x</sub> species is unchanged
- Overall trend during testing
  - Decrease in high BE C
  - Increase in low BE C
  - More pronounced for nonstabilized system



# Chemical Analysis of Ionomer Degradation: Fluorine 1s



- New F BE species detected after testing
- BE similar to Teflon<sup>®</sup>-like species.
- Twice as much for nonstabilized system vs stabilized
- Analysis of Teflon<sup>®</sup>-less GDL MEA is planned to rule out migration from these species from GDL



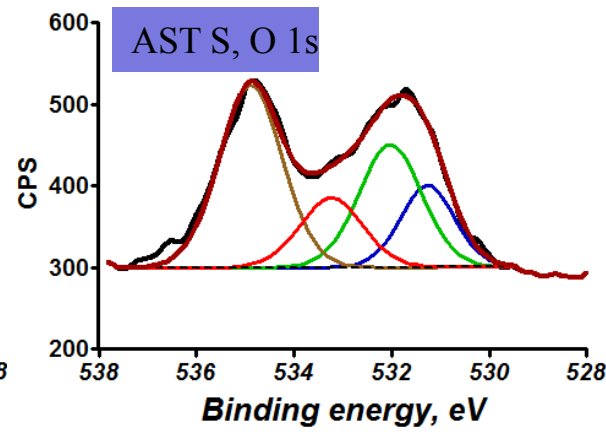
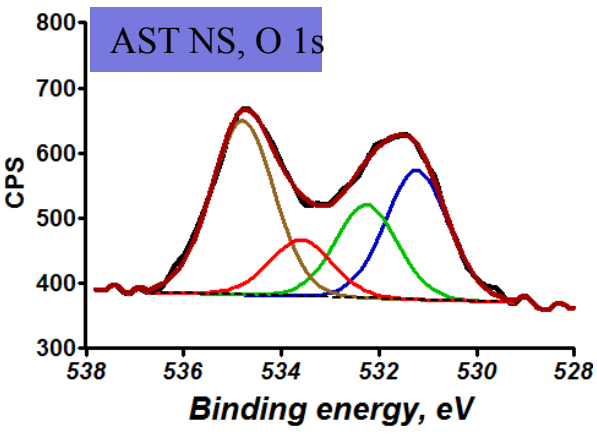
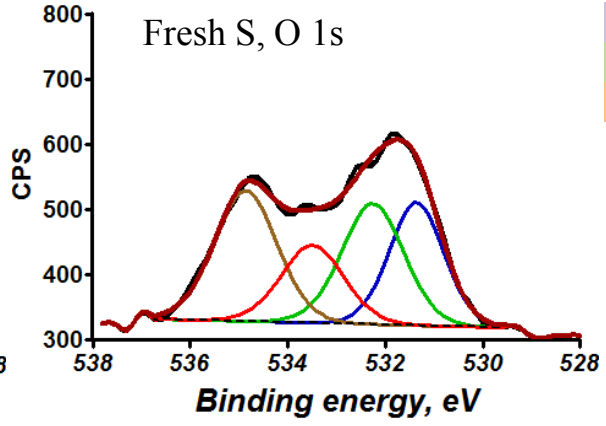
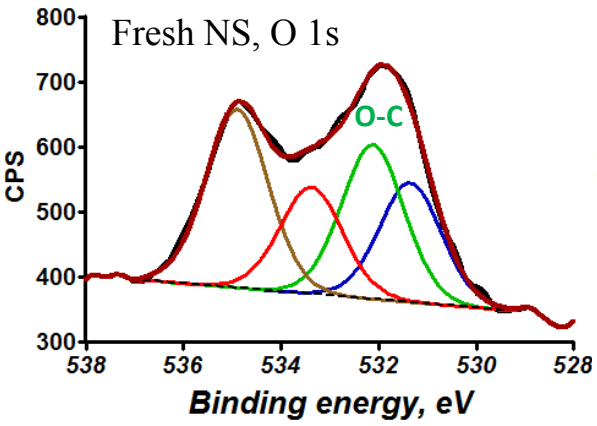
# Chemical Analysis of Ionomer Degradation: Oxygen 1s

O=Car    O-  
CO\*CF    O\*-COCF    O-CF2

|                  | 531  | 532.5 | 533.4 | 535.0 |
|------------------|------|-------|-------|-------|
| NS IONOMER       |      | 17.4  | 9.3   | 73.3  |
| Fresh NS cathode | 29.1 | 24.3  | 17.9  | 28.7  |
| AST NS cathode   | 30.4 | 18.9  | 12.8  | 37.9  |

|                 | 27.4 | 12.4 | 60.2 |
|-----------------|------|------|------|
| S IONOMER       |      |      |      |
| Fresh S cathode | 25.6 | 23.2 | 22.9 |
| AST S cathode   | 21.4 | 25.3 | 17.1 |

- Fresh NS and S systems have similar O 1s speciation
- Decrease in CO\*CF / COCF species from testing
- Increase in high BE component due to oxygens connected to Telfon<sup>®</sup>-like species detected for both
  - Slightly bigger increase for NS





# FC Tech Team Action items

- NREL Contamination

- Contacted Huyen Dinh
- Gave general input on their approach
- Provided specific input on durability testing
- Suggested material types for their investigations
- Will establish regular dialogue

- Thermal conductivity plan

- Investigated off-site measurement tool
- ASTM E1530 – Guarded Heat Flow Meter Technique
- Testing planned for later this year on BOL and EOL samples

- Normalized water management noise signal

- Internal group measured pressure drop in a channel with various geometries and surface treatments
- As water was produced and moved through the channel, the pressure drop signal fluctuated
- This was called a “water management noise signal”
- The uncoated plate showed a 4:1 ratio in this signal compared to the hydrophilic plate, meaning it fluctuated 4x as much.

- Hydrogen permeance

- No plan to investigate at this time

