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

FC013

This presentation does not contain any proprietary or confidential information

Organizations / Partners /Collaborators

- **Los Alamos National Lab (LANL)**
  - R. Mukundan, J. Davey, Bo Li, D. Spernjak, 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**

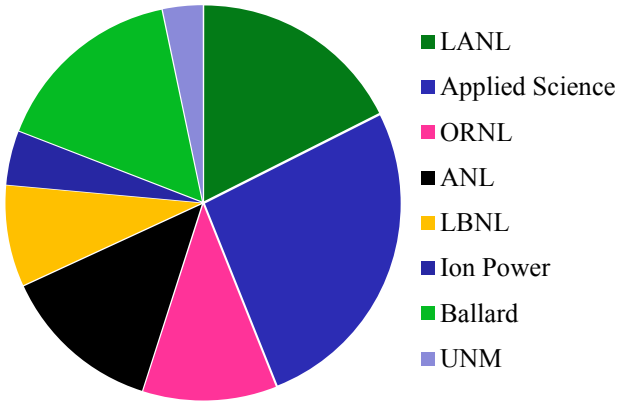
Budget

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 (Ballard, Ion Power, UNM)	$425k
Other National Labs (ANL, LBNL, ORNL)	$850k



Relevance and Objectives

- **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_e (net) Integrated Transportation Fuel Cell Power Systems Operating on Direct Hydrogen [a]				
Characteristic	Units	2011 Status	2017 Targets	2020 Targets
Energy efficiency[b] @ 25% of rated power	%	59	60	60
Power density	W / L	400[c]	650	850
Specific power	W / kg	400[c]	650	650
Cost[d]	$ / kW_e	49[e]	30	30
Durability in automotive drive cycle	hours	2,500[h]	5,000[i]	5,000[i]
Assisted start from low temperatures[j]	°C	–	-40	-40
Unassisted start from low temperatures[j]	°C	-20[f]	-30	-30

Table 3.4.5 Technical Targets: 1–10 kW_e Residential Combined Heat and Power and Distributed Generation Fuel Cell Systems Operating on Natural Gas[a]			
Characteristic	2011 Status	2015 Targets	2020 Targets
Degradation with cycling[h]	<2%/1,000 h	0.5%/1,000 h	0.3%/1,000 h
Operating lifetime[i]	12,000 h	40,000 h	60,000 h

Approach

- **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

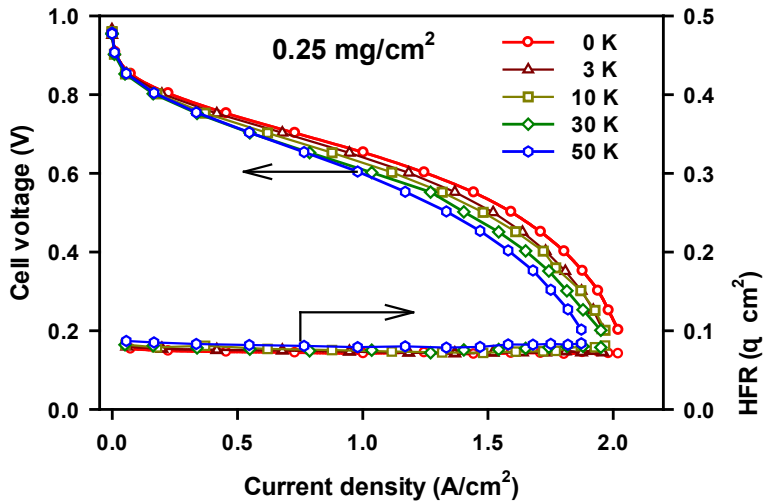
- **Modeling**
  - Fundamental degradation mechanisms (LBNL)
  - Integrated degradation model – kinetic/rate based (ANL)
  - Coordinate activities with other efforts via DOE Modeling Working Group

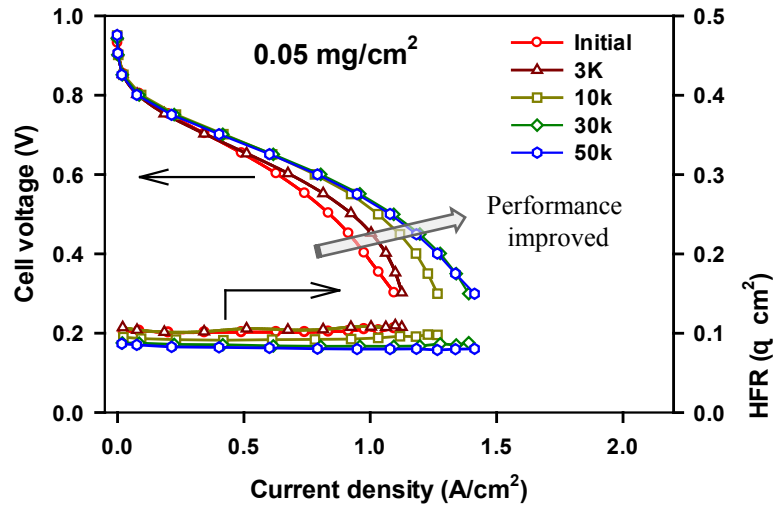
- **Coordinate activities with other durability projects**
  - DOE Durability Working Group
  - Current coordination includes: ANL, Nuvera, Ballard, UTC-AST, LANL-AST
    - Data from ANL on Pt dissolution used for modeling effort
    - Joint material testing with AST projects (esp. LANL)
    - Extend characterization (Neutron Imaging) to benefit Ballard

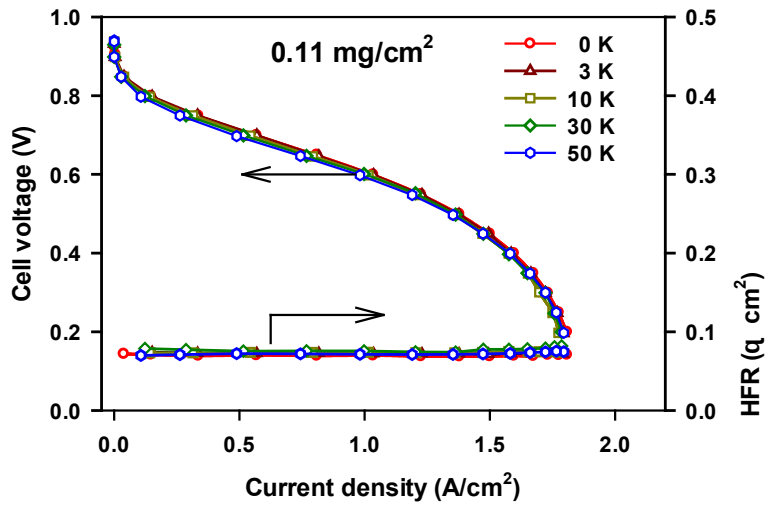
Approach - FY2012 Milestones

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^2 to 0.20 mg/cm^2 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 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^2	Partially complete, MEAs received Testing partially complete

Durability of Low Loading Pt/C Cathode during Potential Cycling







*ECSA change**

Pt (mg/cm²)	0 K	10 K	30 K	50 K	% change
0.25	50	35	28	22	-55
0.11	49	28	24	22	-56
0.05	52	29	21	14**	-74**

* Determined by the H_2 desorption of CV; **very low surface areas with higher error

__Anode:__ 0.2 mg cm^{-2} Pt/C (BASF), __Cathode:__ 0.06-0.25 mg cm^{-2} Pt/C (BASF); Membrane: Nafion® 212; __Cell:__ 80°C, 30 psig backpressure, Potential cycling: 0.6 – 1.0 V under H_2/N_2

Typical LANL decal process using water/alcohol/glycerol mixture in the ink was used.

- Performance of ultra-low loading cathode (0.05 mg/cm²) increased with potential cycling
- Performance of MEA with "*high*" loading decreased; with "*low*" loading stayed the same
- ECSA 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

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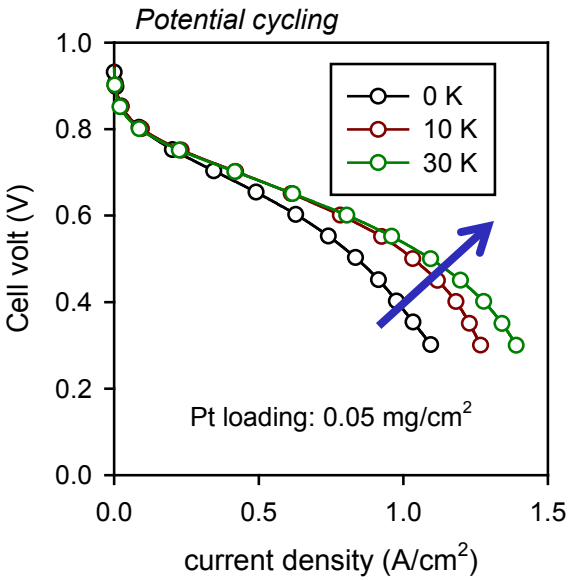
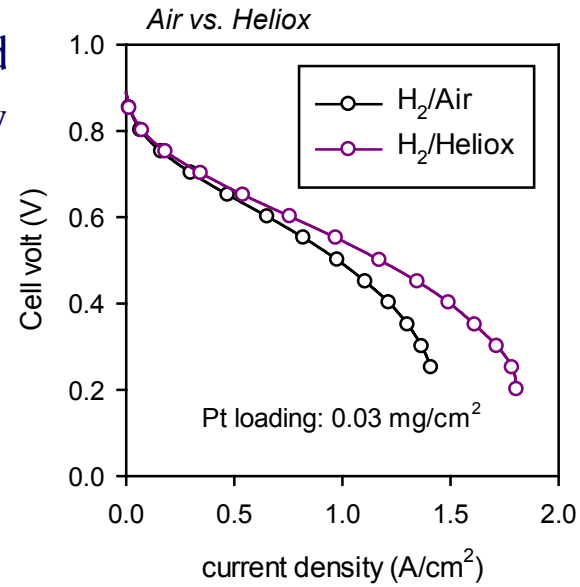
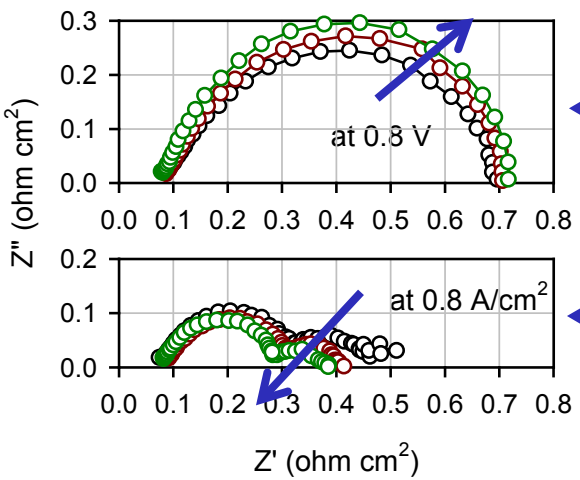
Electrode Structural Change during Potential Cycling



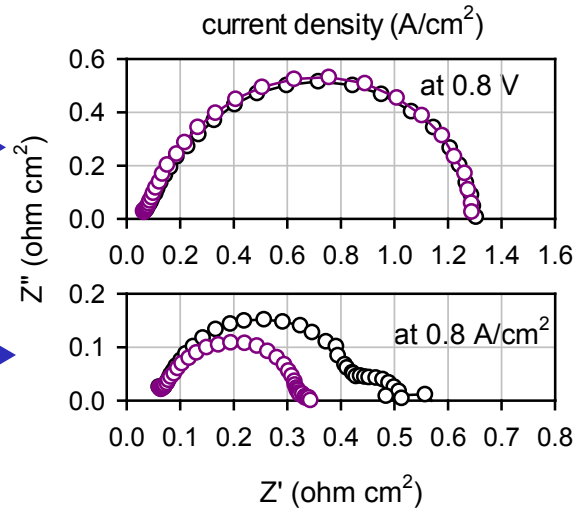
- Enhanced performance and impedance behavior of low loading cathode with potential cycling have similarity with performance improvement with heliox (or air flow increase)





Higher Kinetic Resistance

Lower MT Resistance



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

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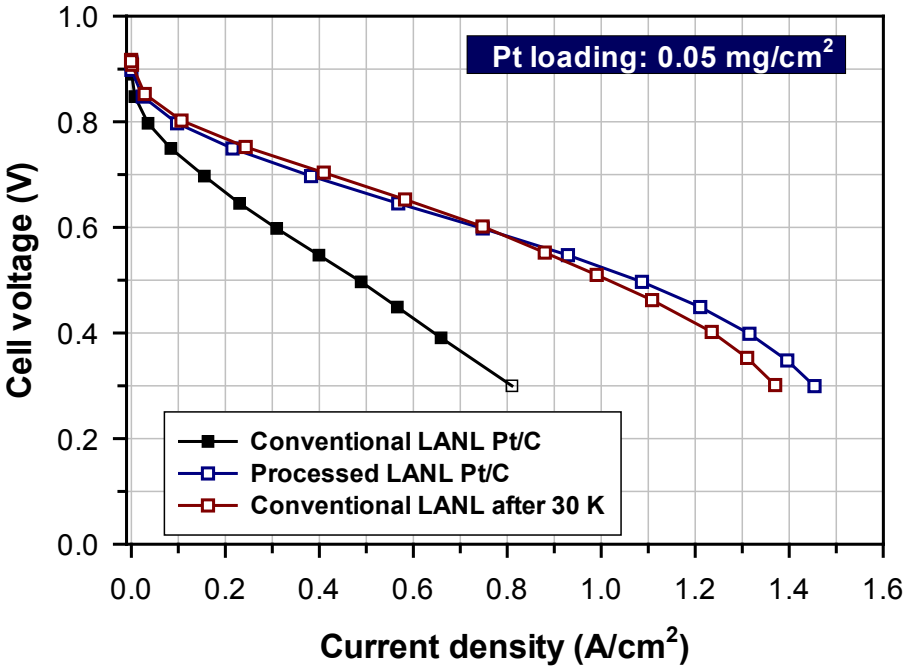
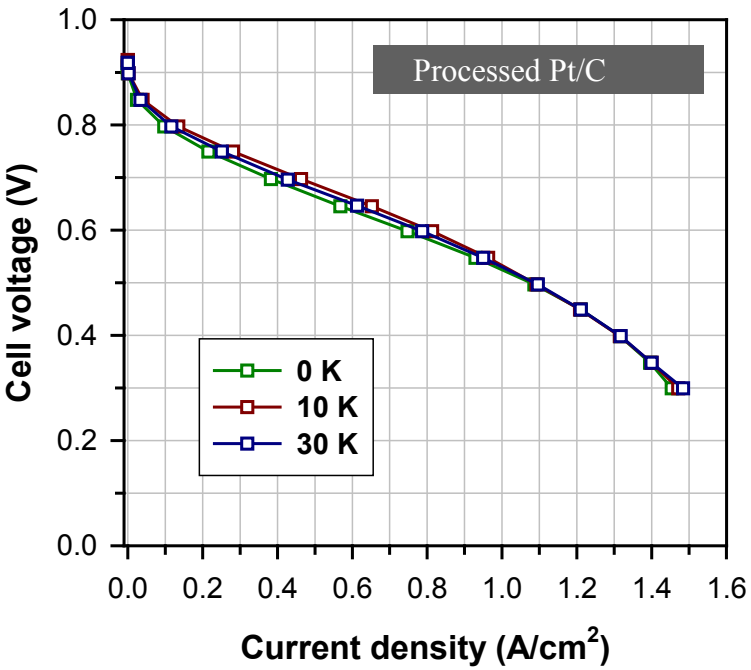
Electrode Performance and Durability of Processed Low Loading Cathode





- 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 mW/cm^2 for 0.05 mg/cm^2 vs. $P_{0.5V}$ = 840 mW/cm^2 for 0.25 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^2/g$_{Pt}$ after 30,000 cycles; the reduction of ECSA does not impact fuel cell performance

Anode: *0.2 mg cm^{-2} Pt/C (BASF),* ***Cathode:*** *0.05 mg cm^{-2} Pt/C (Commercially available), ionomer: Nafion® 1100; Membrane: Nafion® 212;* ***Cell:*** *80°C, H_2/air under 30 psig backpressure, Potential cycling: 0.6 – 1.0 V under H_2/N_2 condition*

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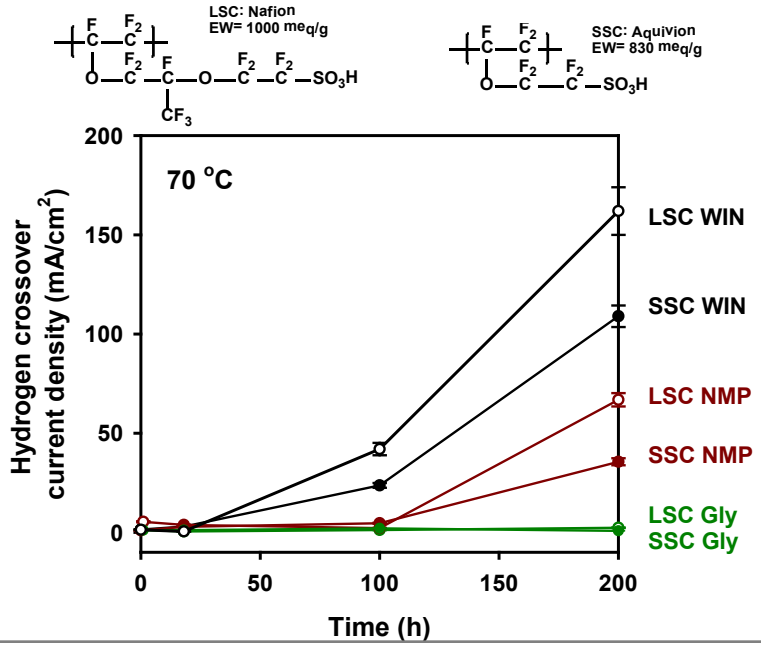
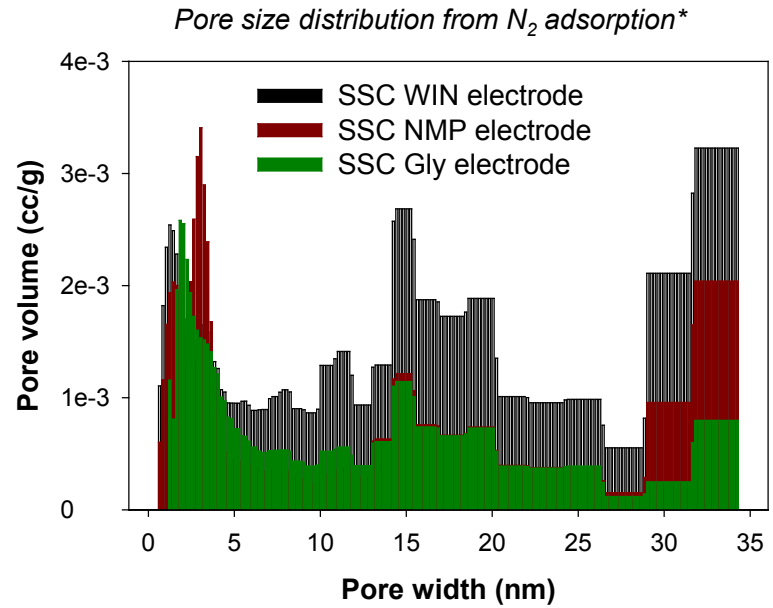
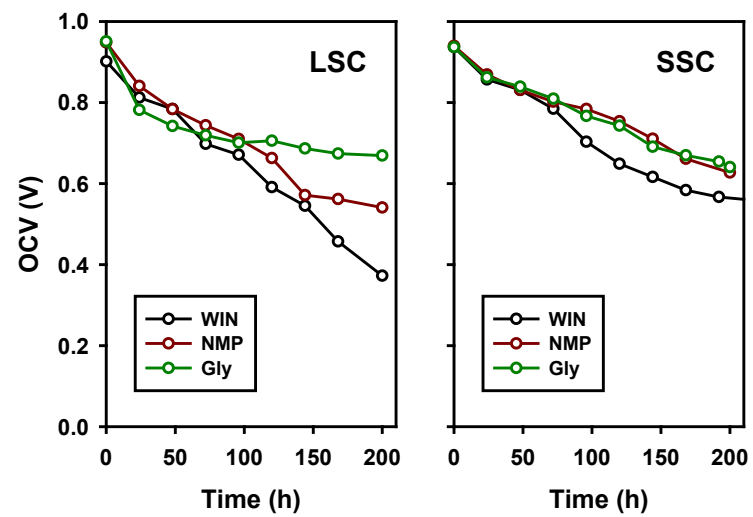
Impact of Cathode Structure on Membrane Degradation





- 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



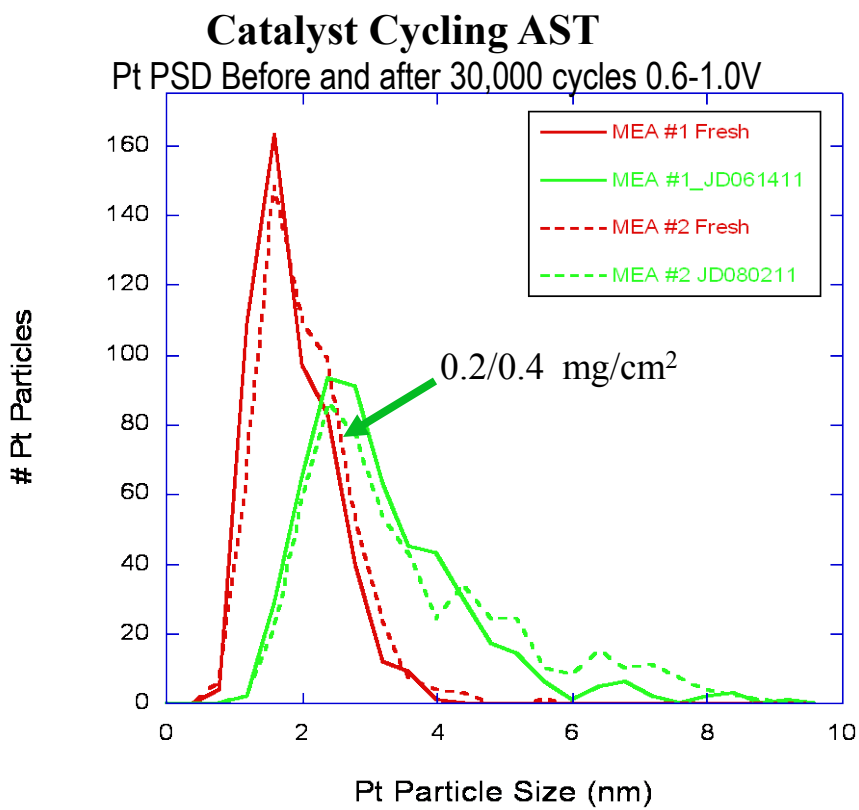
*Slit pore QSDFT model used assuming carbon surfaces; results provide qualitative comparison

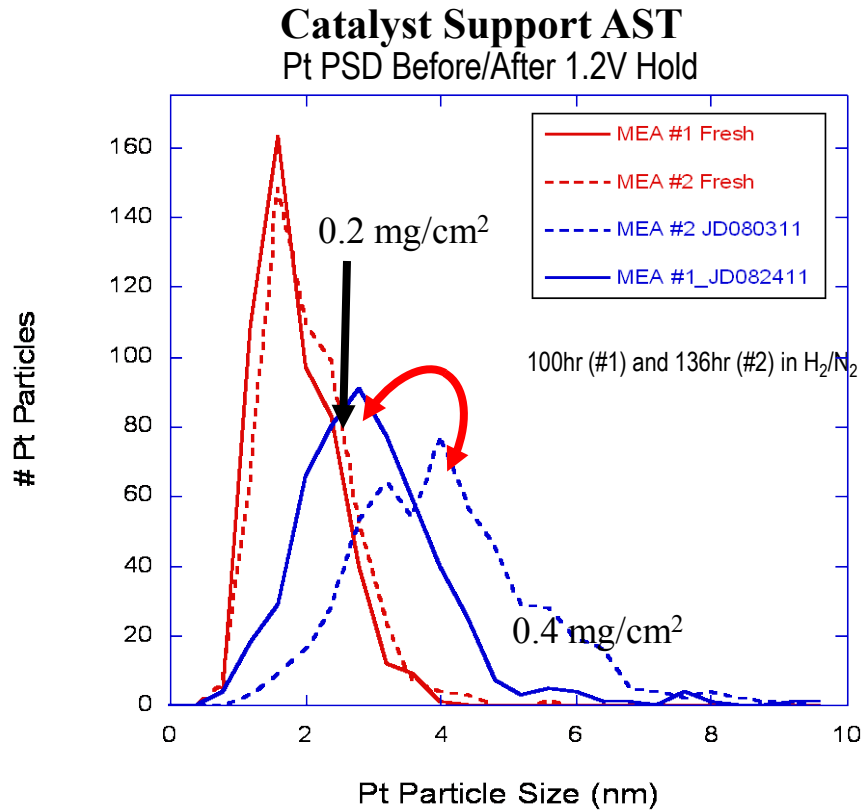
Anode: *0.2 mg cm^{-2} Pt/C (BASF) LANL standard processing,* ***Cathode:*** *0.2 mg cm^{-2} Pt/C (BASF) processed with different dispersing solvent; Membrane: Nafion® 212;* ***Cell:*** *80°C, 30 psig backpressure; OCV test: H_2/Air at 90°C, 30% RH, no backpressure; H_2 crossover measured at 70°C, 50/50 sccm of H_2/N_2*

Rate of Platinum Agglomeration Depends → Loading & Mechanism

Catalyst Degradation Comparison for Catalyst Layers with Similar Carbon Loadings

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





- 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

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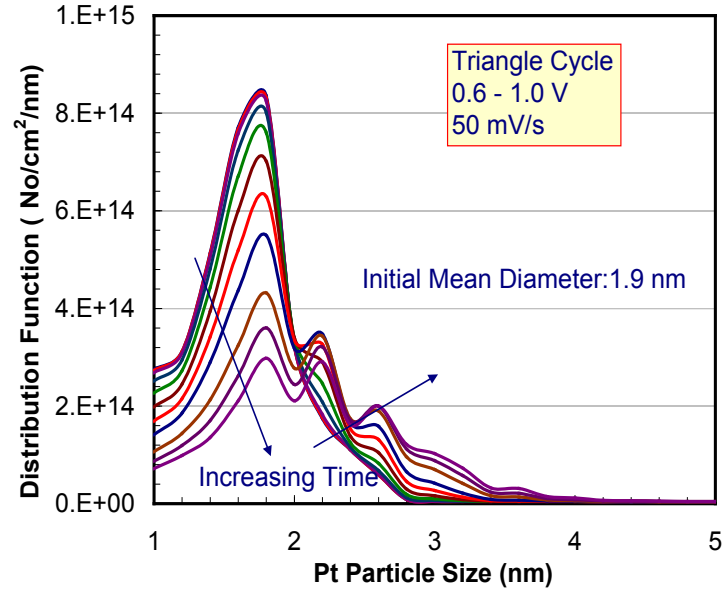
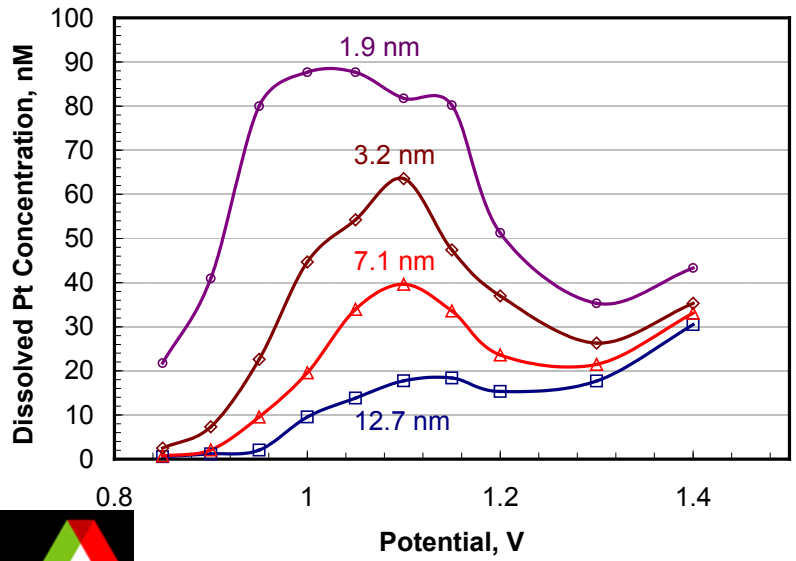
Ion Power, Inc

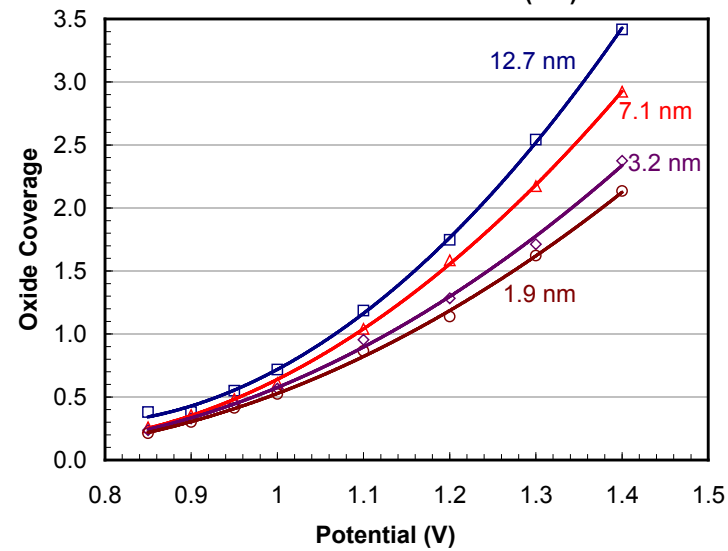
Oak Ridge National Laboratory

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)**

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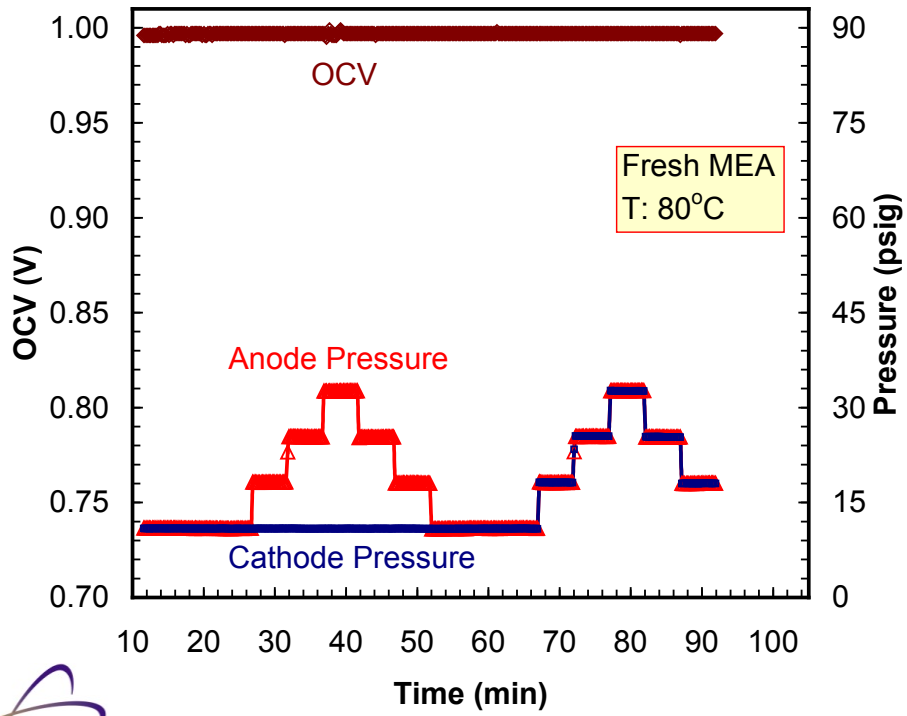
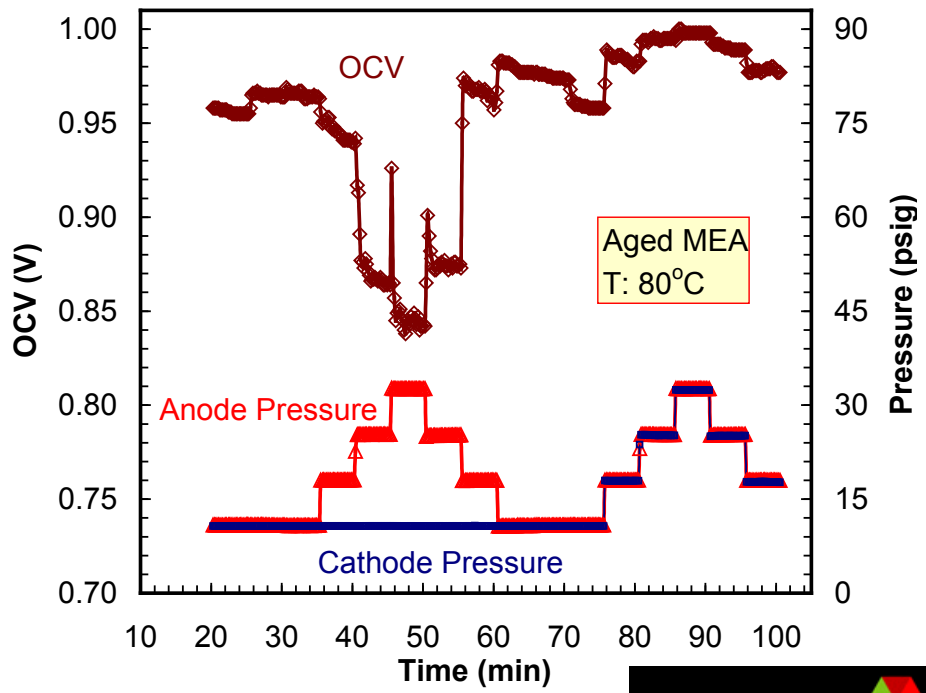
Understanding Changes to Hydrogen Crossover During MEA Aging

- Measuring OCV as a function of H_2 pressure and relating OCV to H_2 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_2 crossing from anode does not completely react inside membrane
  - Data for unequal anode and cathode pressures not meaningful because of H_2 leaks around the seals and gaskets in aged MEA





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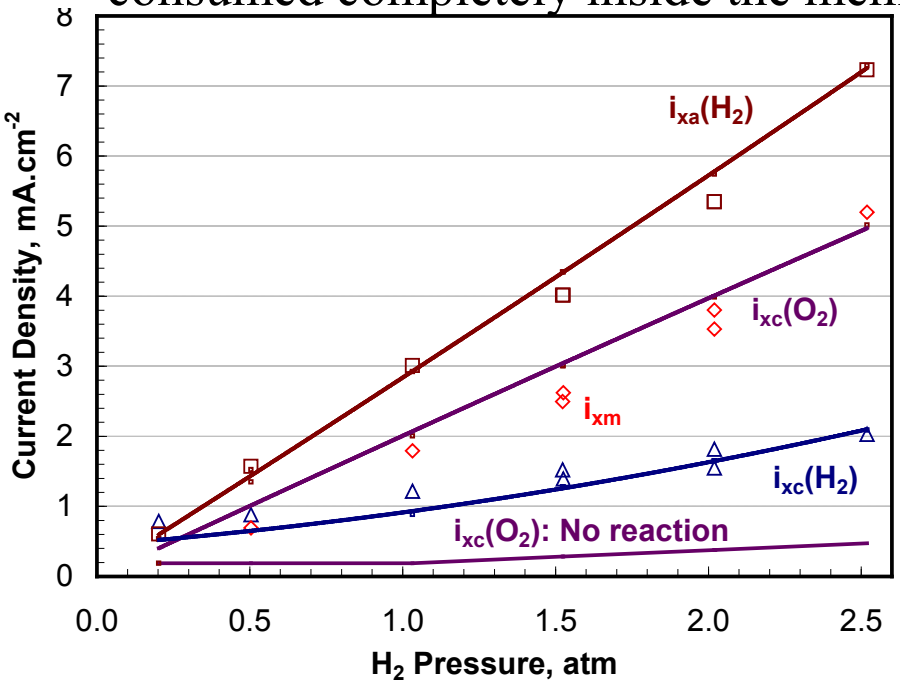
Pt Particles Deposited in Membrane Promote Reaction Between Crossing H_2 and O_2

- 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

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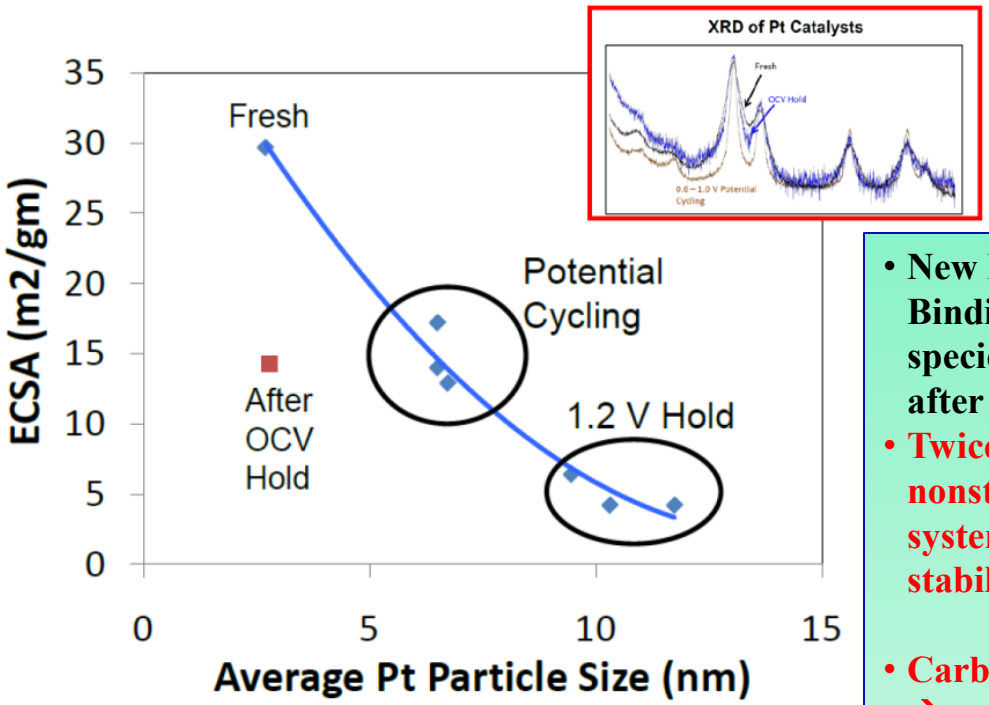
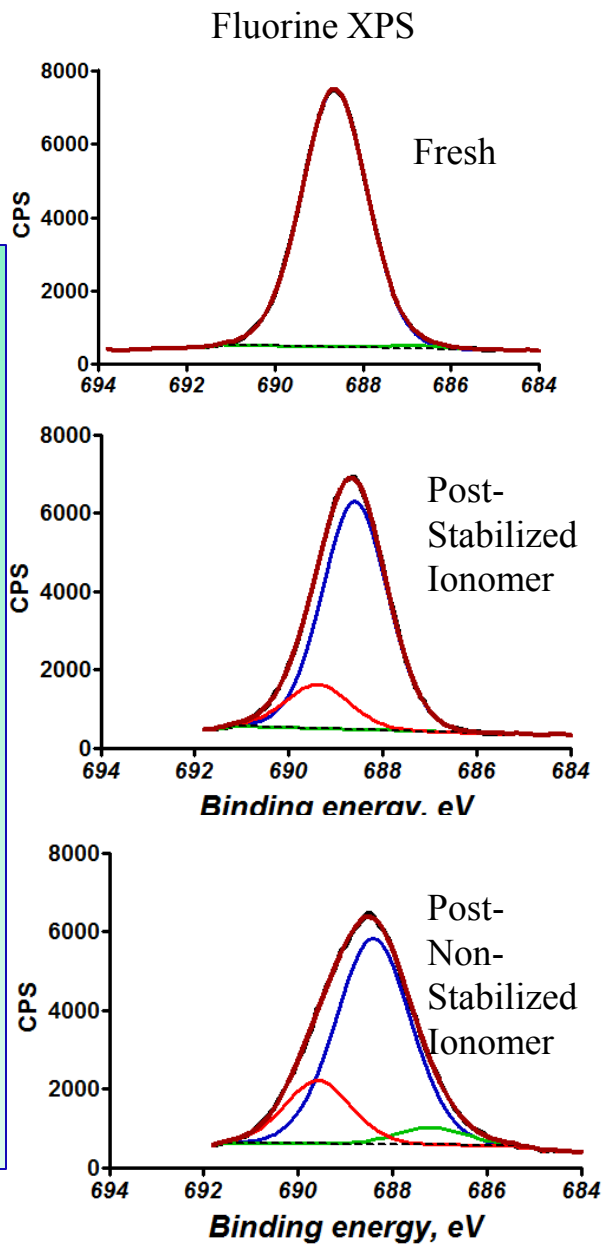
Evidence of Ionomer Electrode Degradation

XPS Chemical Analysis shows Changes in Fluorine, Carbon, Oxygen



- Correlation between ECSA and particle size normally observed
- Not for tests using OCV hold (AST) designed to accelerate membrane degradation through formation of radicals
  - No effect on catalyst particle size (XRD)
  - Reduced ECSA measured

- **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 telfon**



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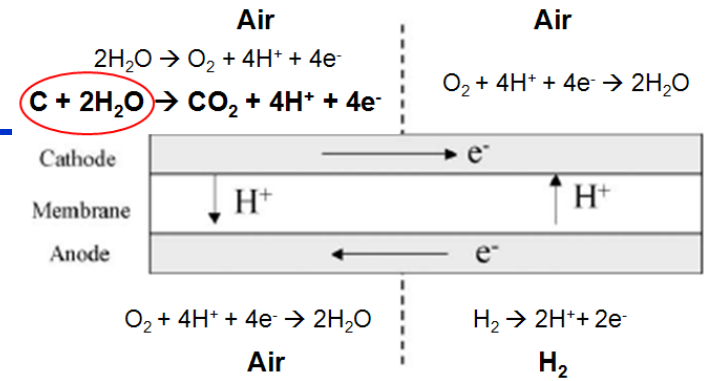
THE UNIVERSITY of NEW MEXICO

Local currents during Shut-down / Start-up Transients

University of Nancy Collaboration

Regional reversals raise potentials dramatically

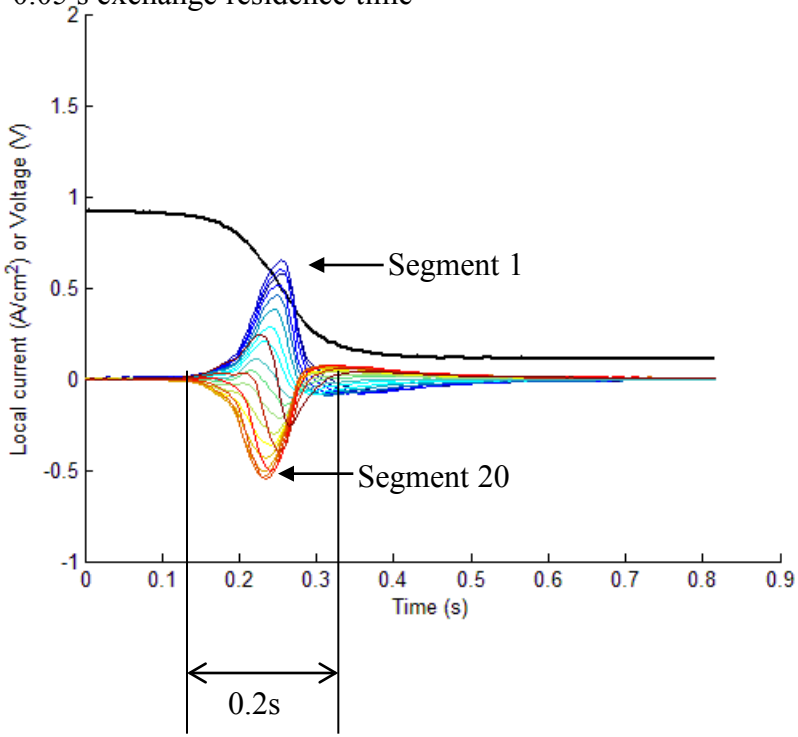


Measure carbon corrosion by linear series segments and CO_2 by NDIR

Shut-down

Anode purge with air

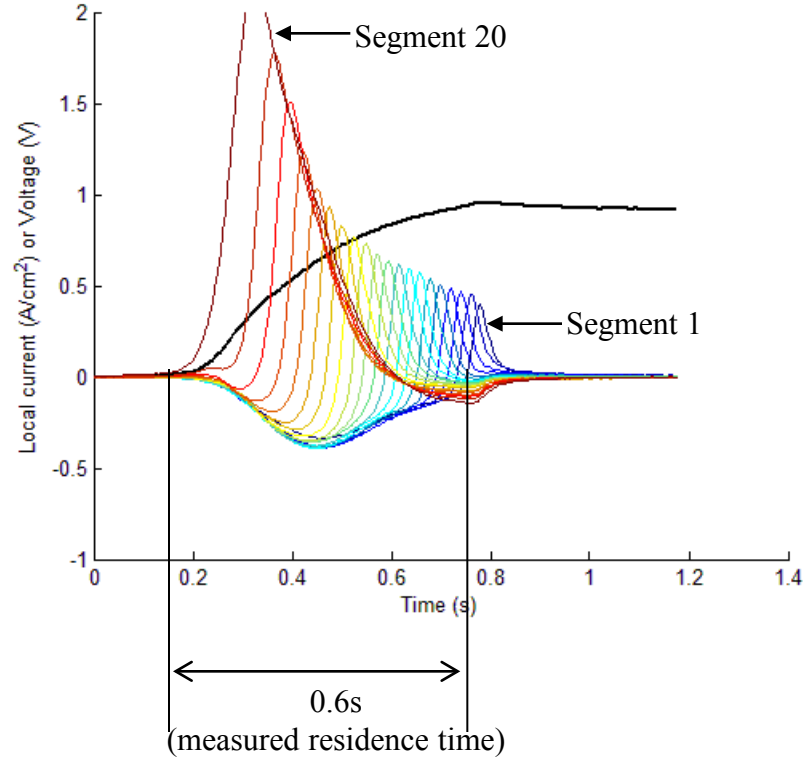
~ 0.05 s exchange residence time



Start-up

Anode H_2 feed

~ 0.2 s exchange residence time

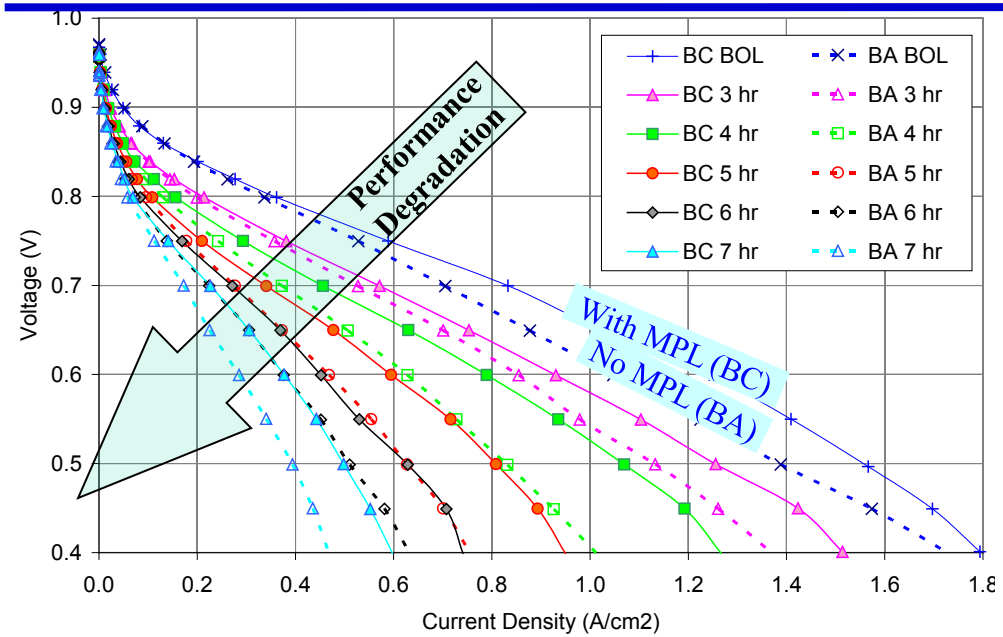


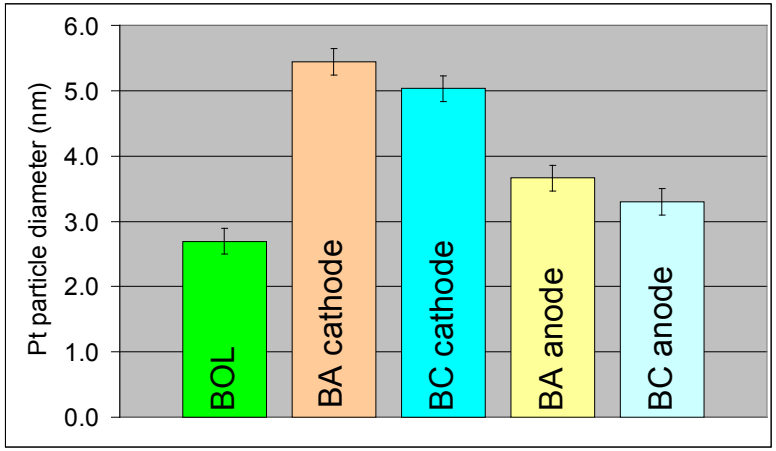
Nancy-Université

The difference between the calculated residence time and the measured residence time (from internal currents) is due to the GDL volume and diffusion times

GDLs Effect Localized Performance Degradation:

GDLs with and without MPL



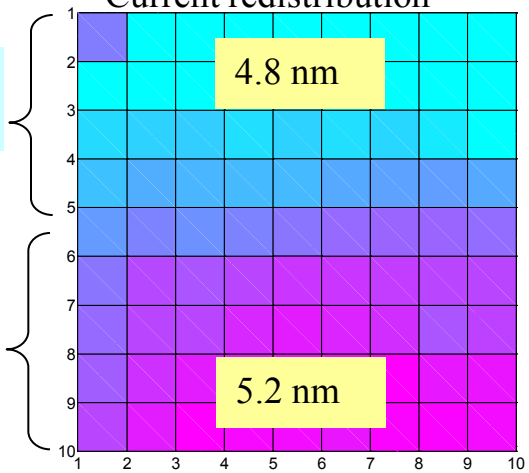


- Current density at 0.4 V reduced by: factor of 3 for the MPL case (BC cell)
  factor of 3.7 without the MPL (BA cell)

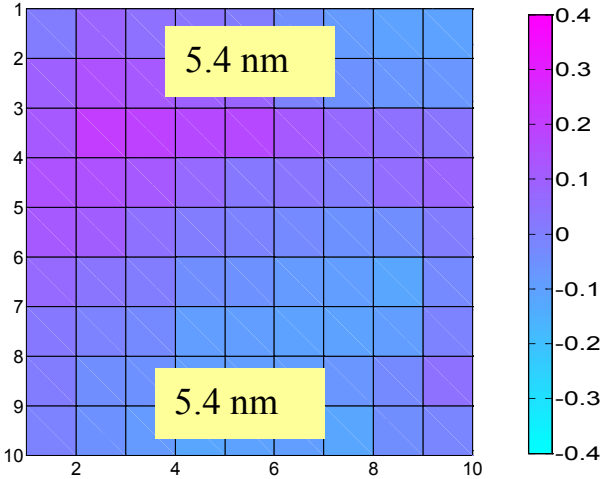
Top portion (upstream):
Current increased (negative difference).

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

BC cell (with MPL)
Current redistribution



BA cell (no MPL)
Current distribution ~ same



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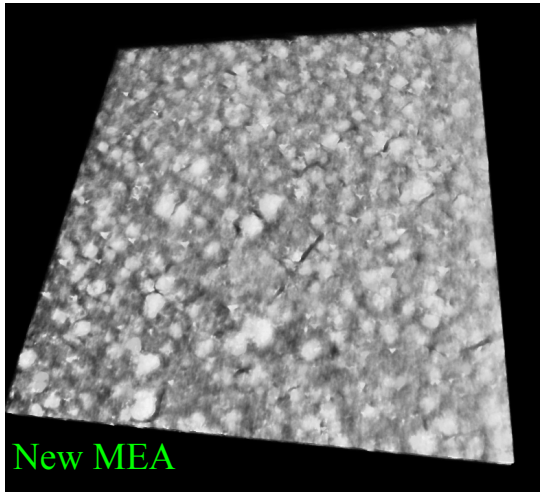
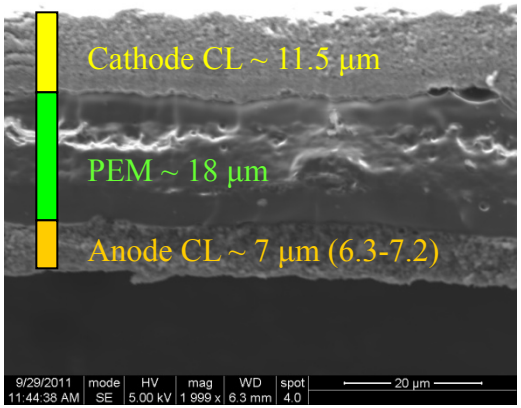
Ex Situ Characterization Post-Carbon Corrosion Shows Non-Uniform Carbon Corrosion Due to GDL / Water Content

New MEA (without GDL)

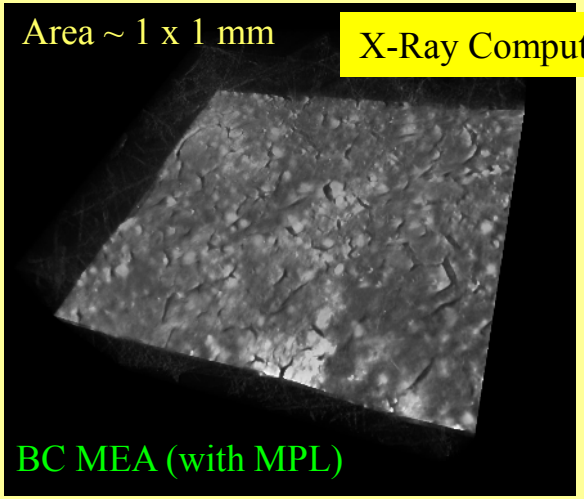


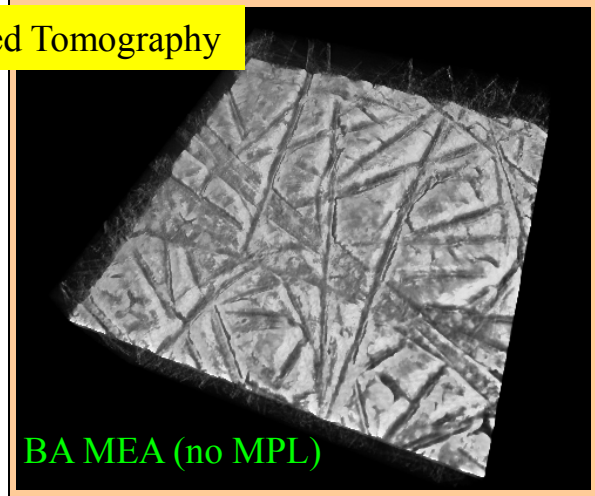
New MEA



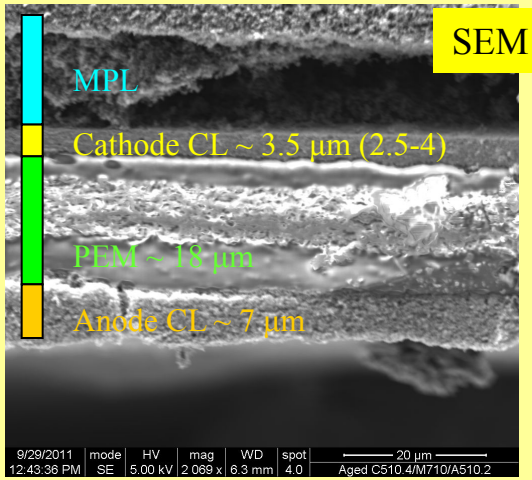
Gore® A510.2/M710.18/C510.4

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





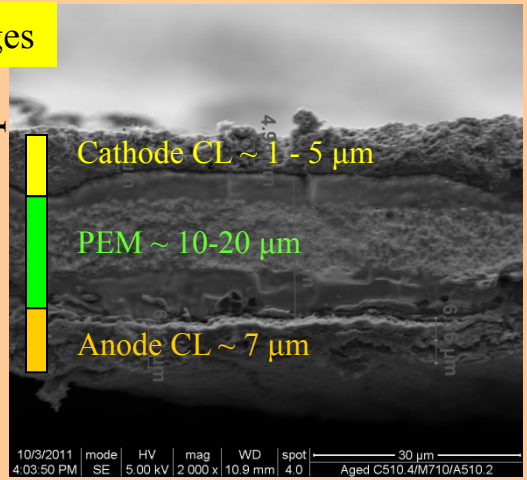
BC Cell 10 Bottom



Uniform cathode thinning (~30% remains)

Anode thickness unchanged

BA Cell 11 Top



Nonuniform cathode thinning

Membrane 'flows' under pressure

Anode thickness unchanged

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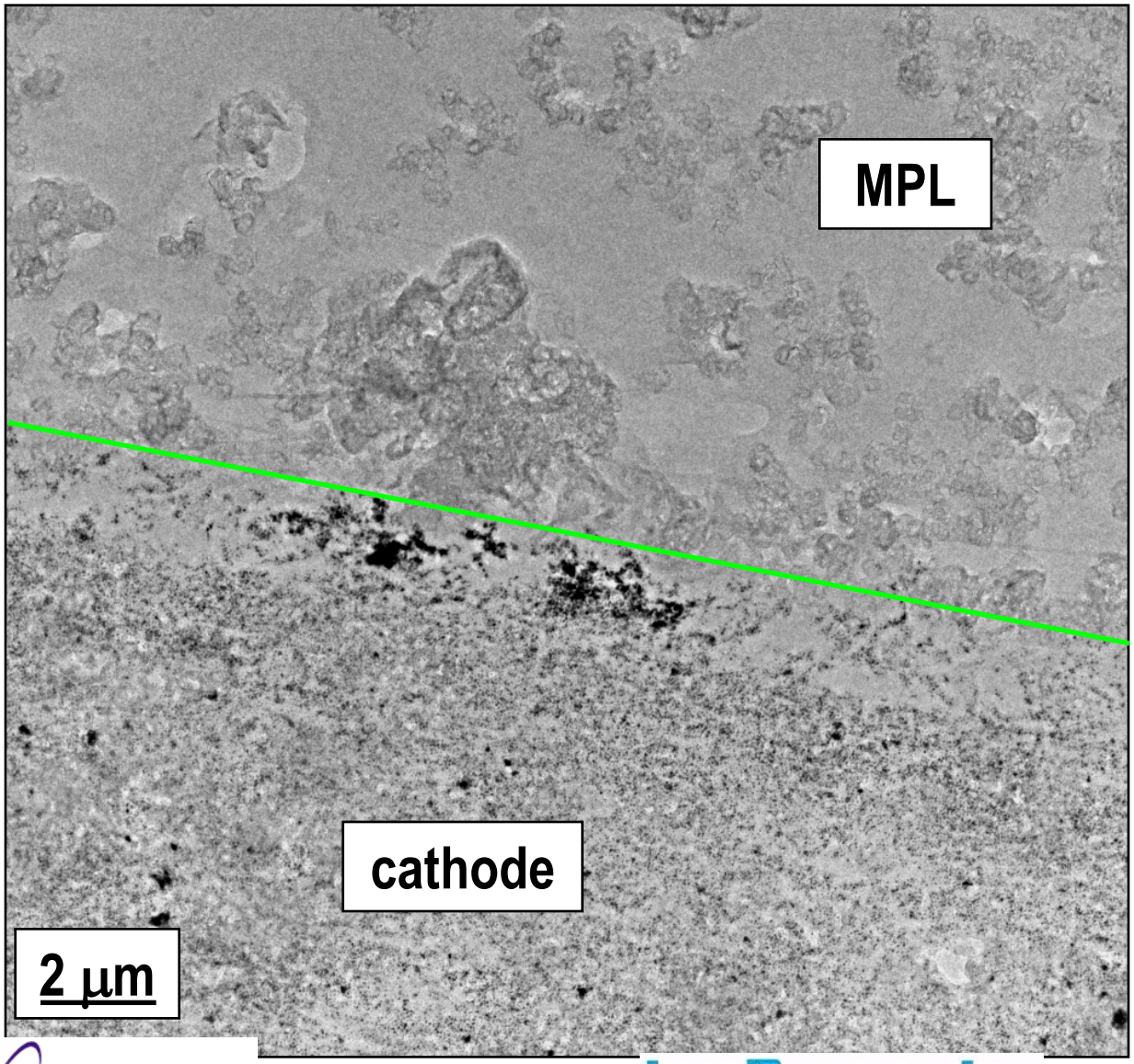
Carbon Structure shows Localized Structure Changes

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_2/N_2

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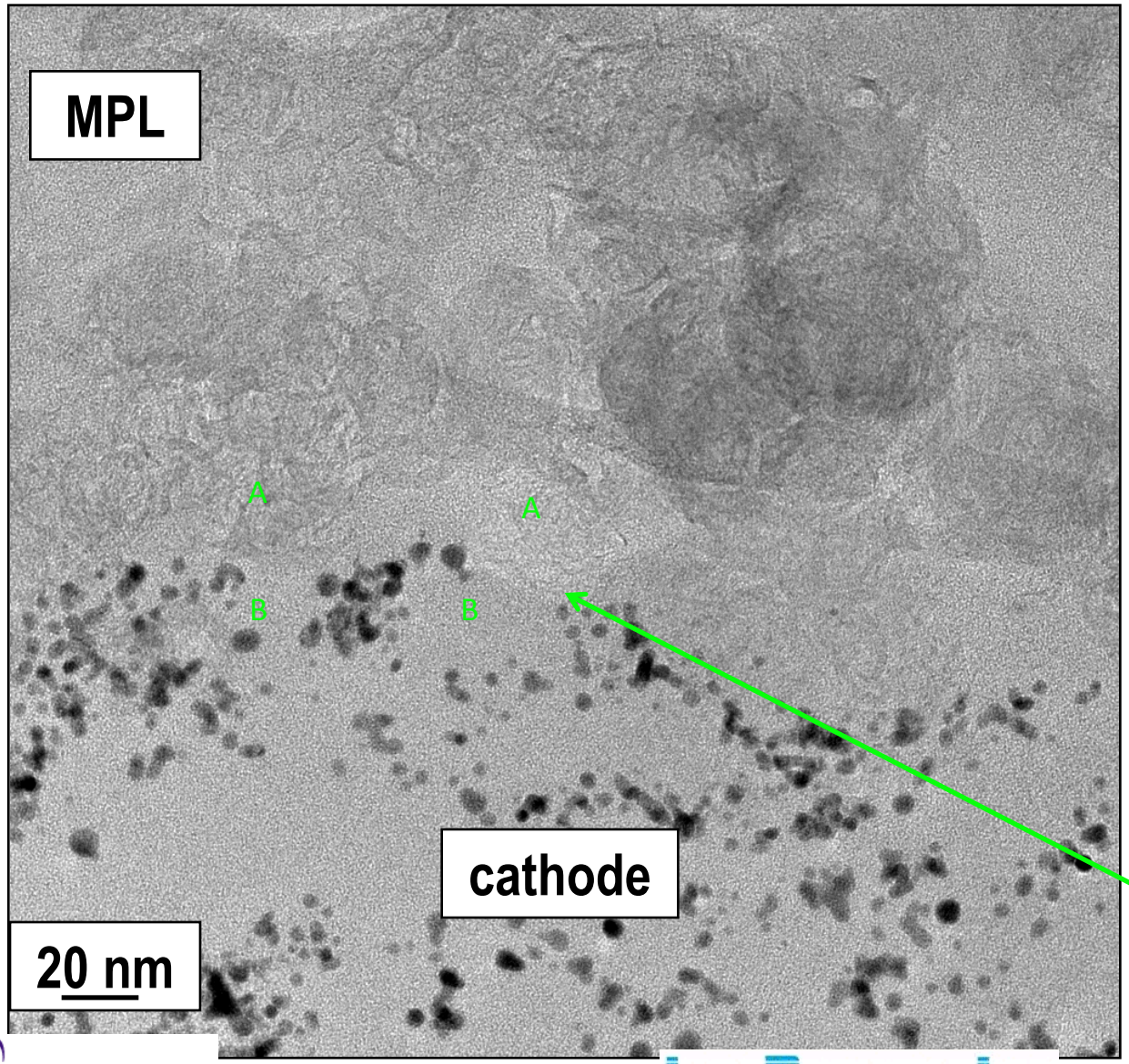
Carbon Structure shows Localized Structure Changes

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



1.2V hold for 100hr in H_2/N_2

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).

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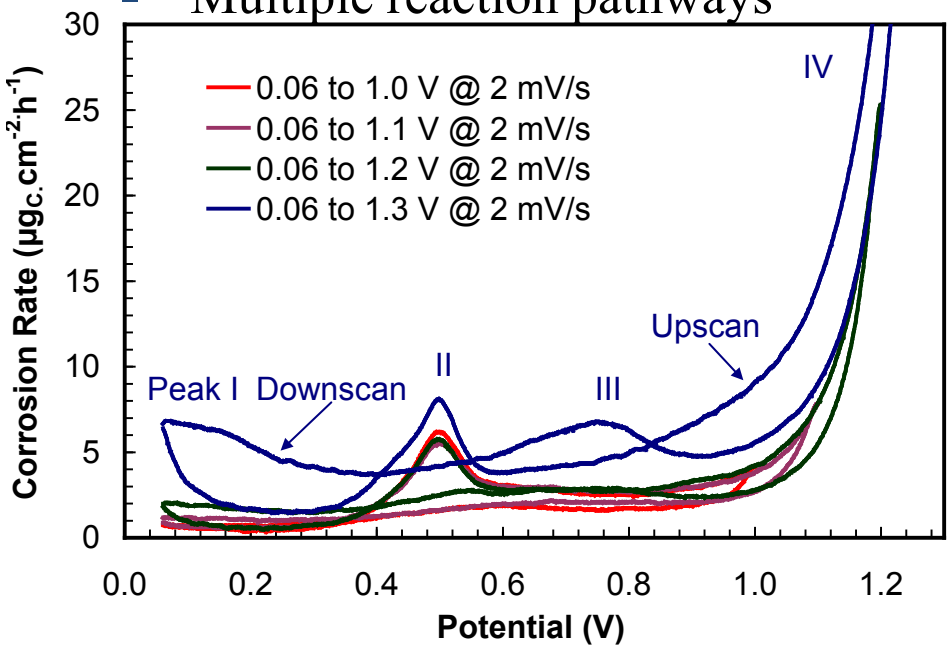
Kinetics of Carbon Corrosion: Model Development

- Carbon corrosion measured shows multiple potentials producing CO_2
  - Multiple reaction pathways



Peak I Peroxide reaction 1 and CO_2 holdup

Peak II Reactions 2 and 3

Peak III Reactions 3 and 4

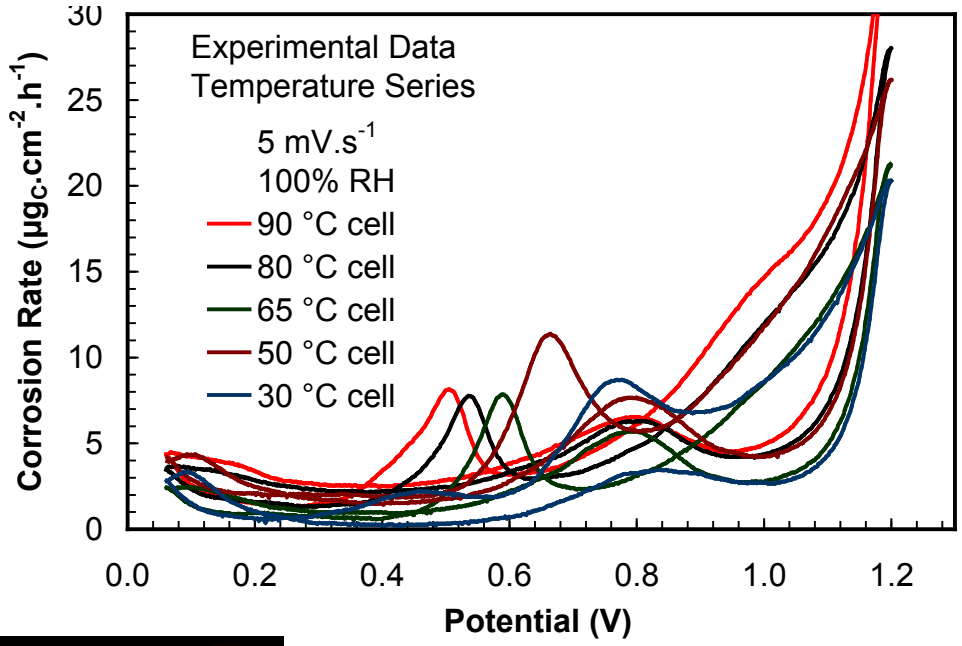
Peak IV Reaction 2

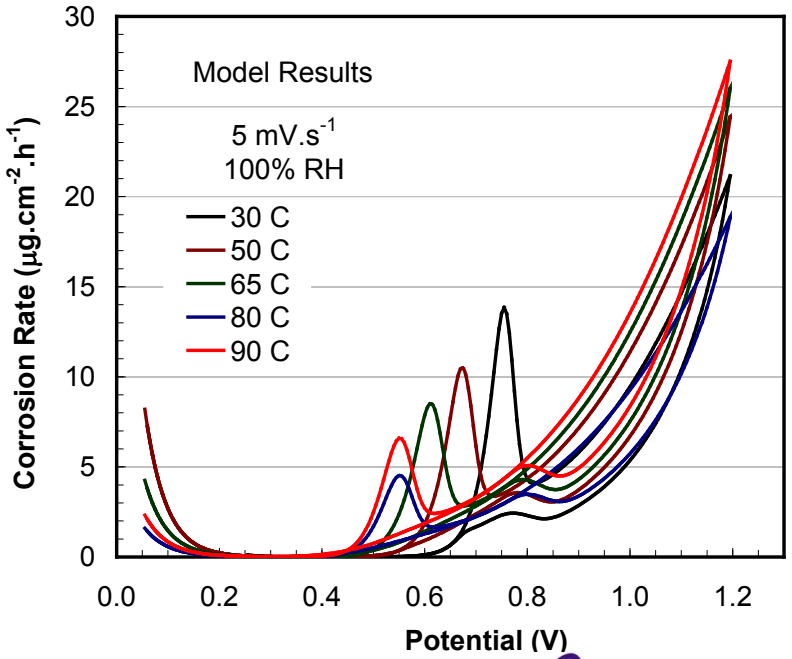
- Initial Model for Corrosion of High-Surface Area Carbon
  1. $C + H_2O_2 \rightarrow CO_2 + 2\,H^+ + 2e^-$ (Peroxide attack, low potentials)
  2. $C + H_2O \leftrightarrow C\text{-}O + 2\,H^+ + 2e^-$ (Active surface oxide)
  3. $C\text{-}O + H_2O \rightarrow CO_2 + 2\,H^+ + 2e^-$ (Electrochemical corrosion)
  4. $x\,C + H_2O \leftrightarrow C_x\text{-}O + 2\,H^+ + 2e^-$ (Passive surface oxide)

Current is not a good indication of CO_2 production; measured by NDIR

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





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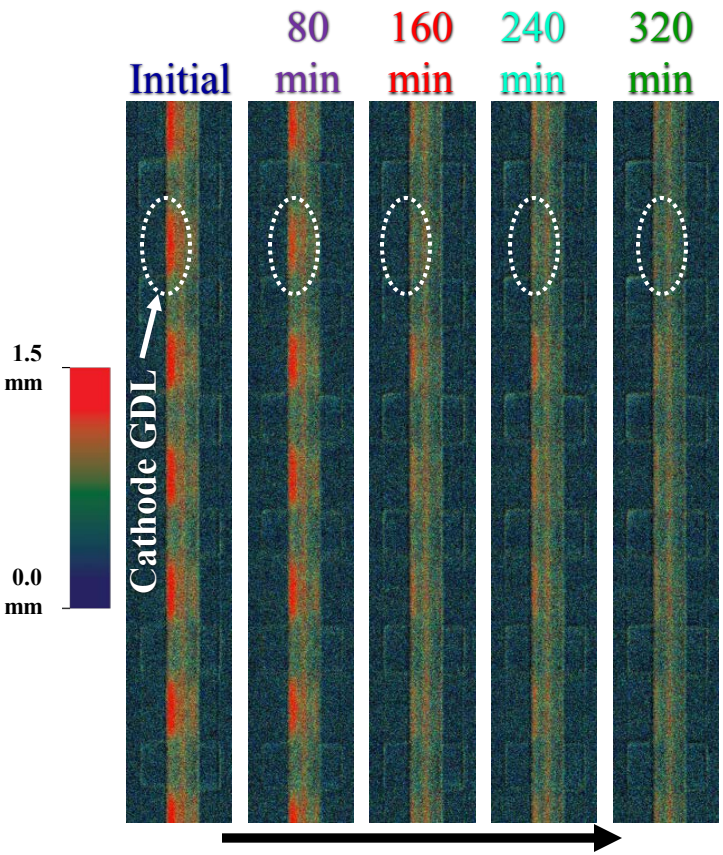
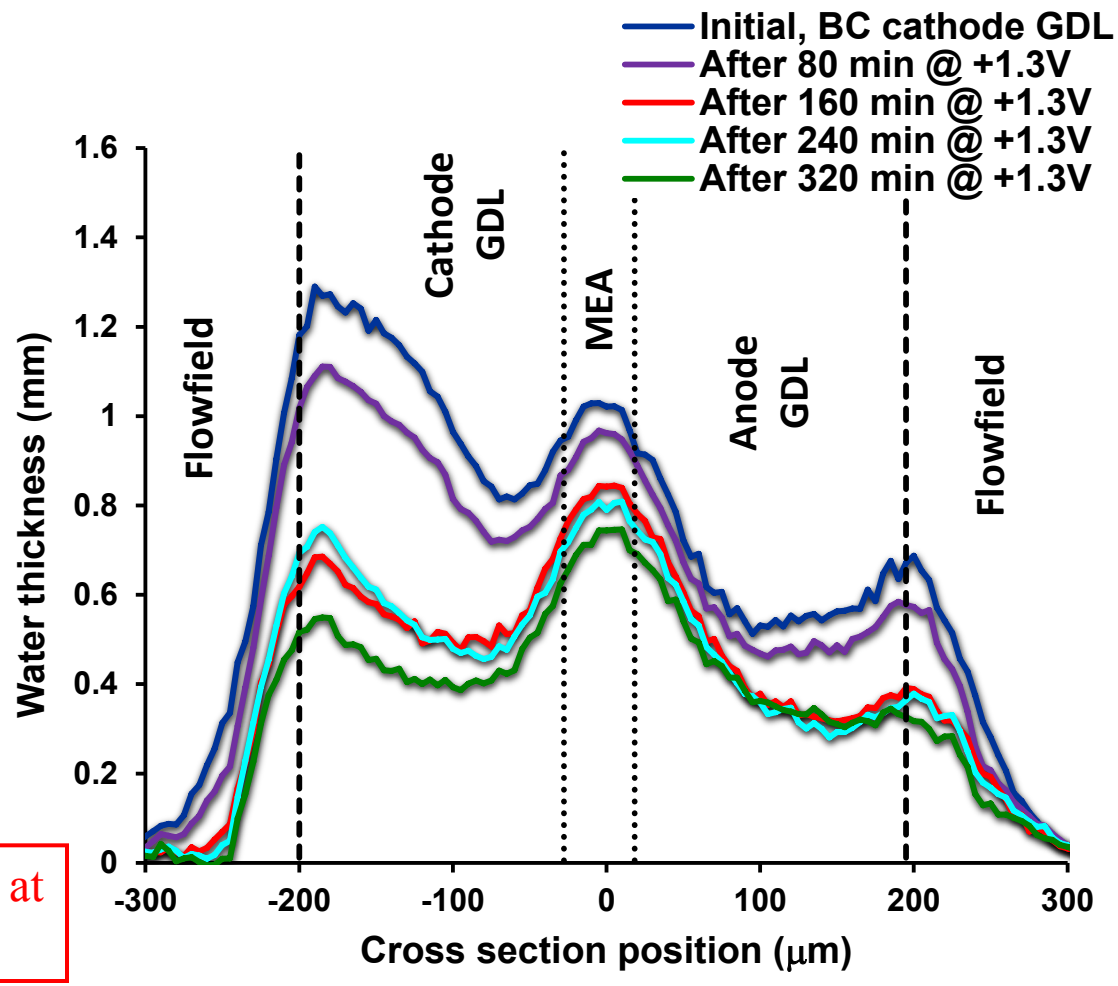
Water Content is Reduced During Carbon Corrosion AST





Dramatic reduction in water retention at constant current density

0.8 A/cm^2, 80°C, 100%RH

*x-axis enlarged 250% to show detail

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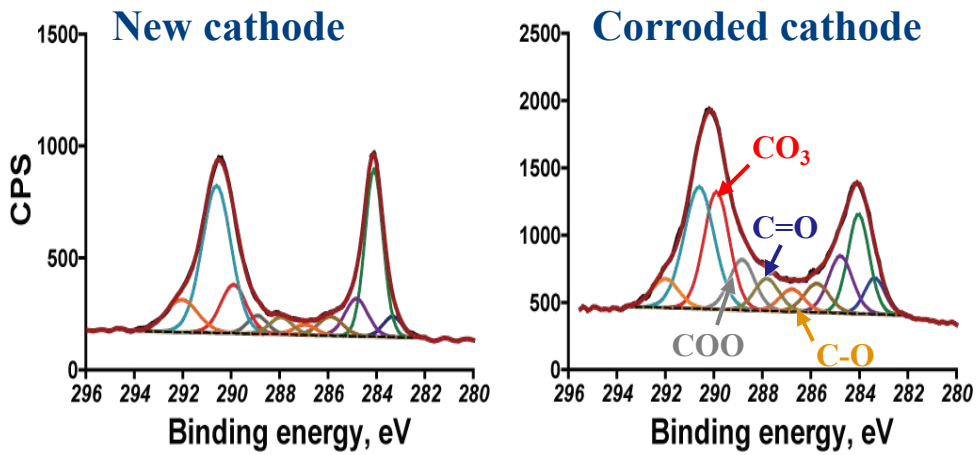
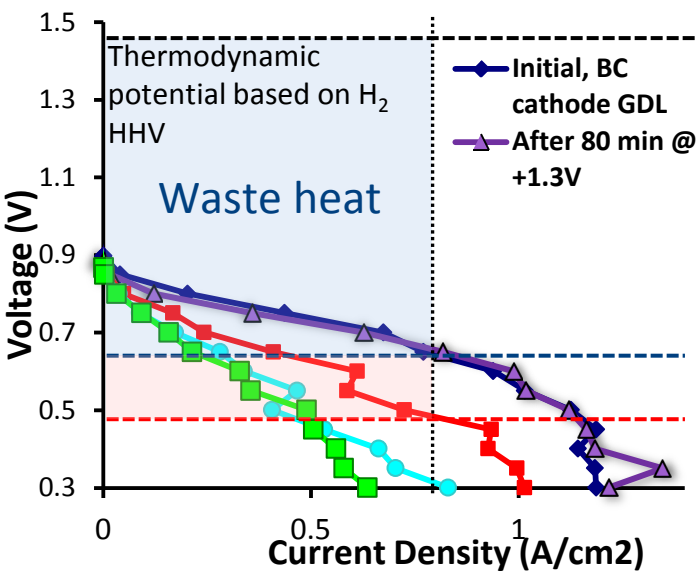
Post-mortem Characterization: XPS + SEM

Cathode Materials Become More Hydrophillic→ Heat Genation dominates

Surface oxides increase→ more hydrophillic



Species:	C-OH/C-OC %	C=O %	COOH %	$C(O)_3$ %
New cathode	1.9	3.7	5.2	9.6
Corroded cathode	3.6	5.4	8.6	18.4



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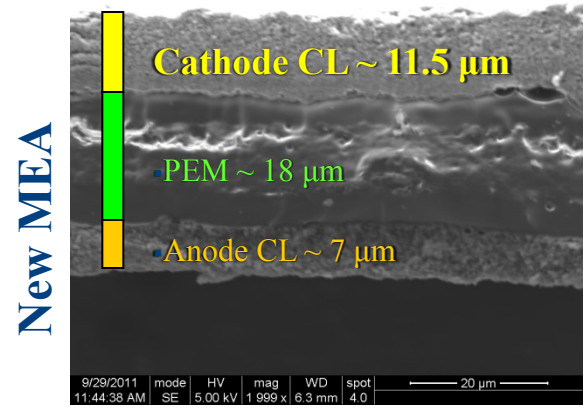
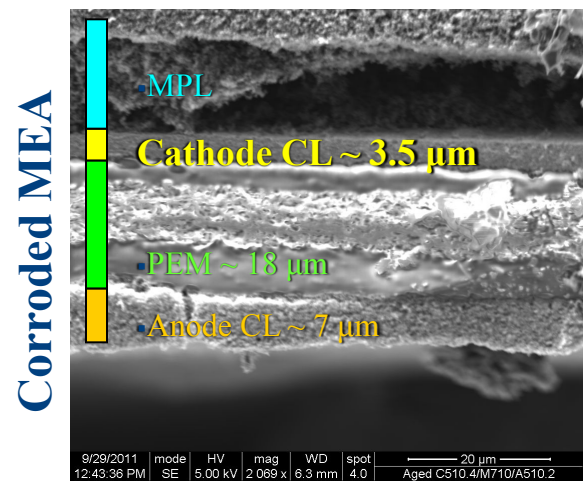
…but bigger change is collapse of cathode layer





Heat generation dominates changes in hydrophilicity during carbon corrosion AST conditions

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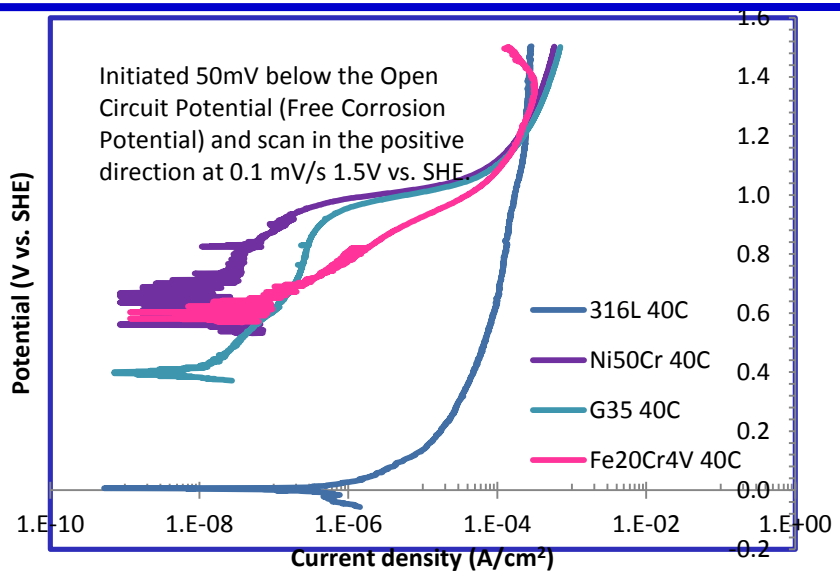
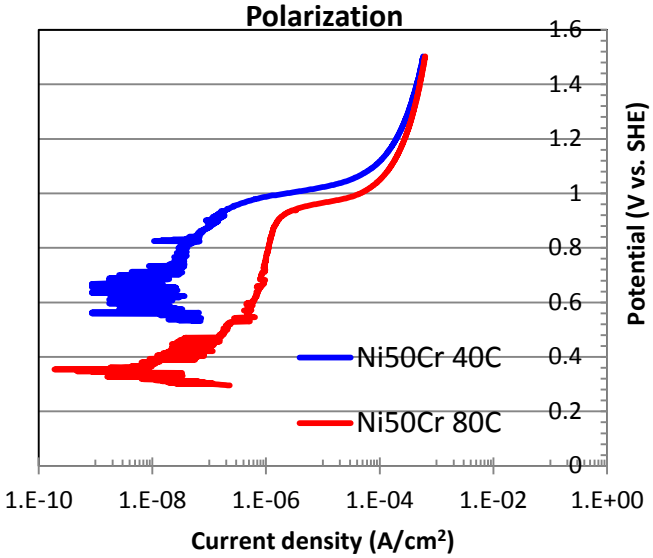
Metal Bipolar Plate Anodic Polarization Corrosion Results

- 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

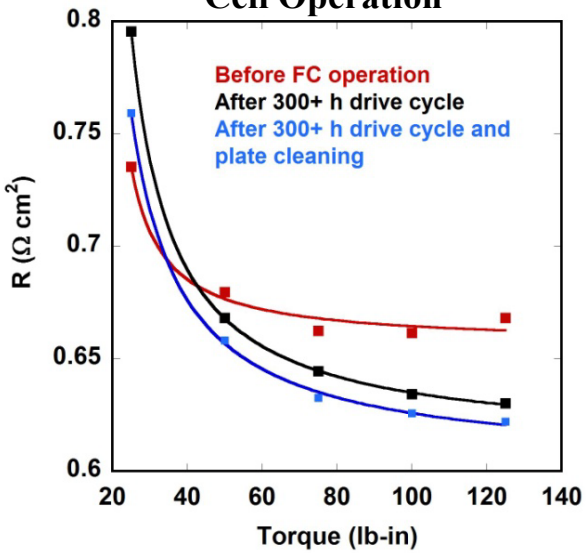
- **Temperature increases corrosion rate**
  - **Decreases Free Corrosion Potential (OCV)**
- Other testing in progress



Temperature Effect on Ni50Cr Polarization



Contact Resistance after Fuel Cell Operation



Increase in plate contact resistance observed at low contact force

Post-MEA Analysis

Component	Total metal content µg cm^{-2}
Endplate	∞
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

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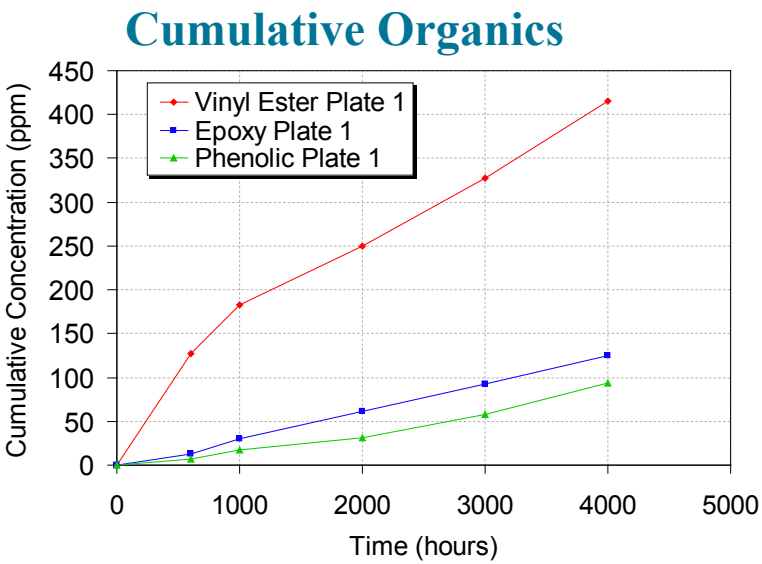
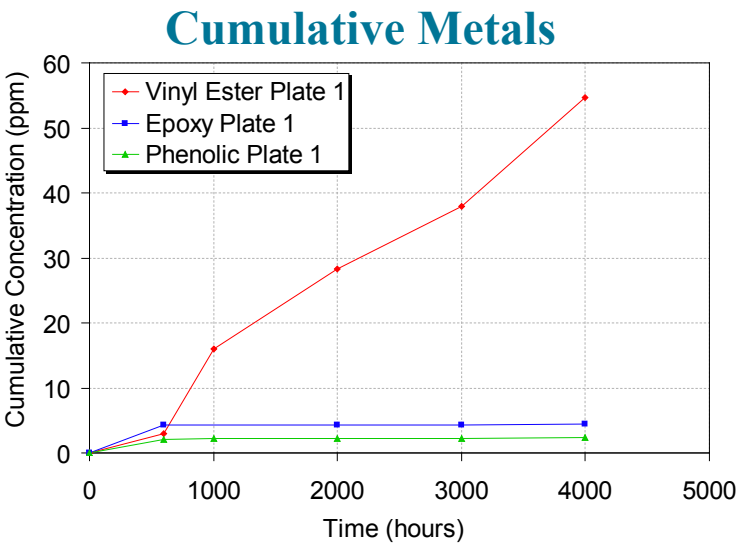
Carbon Bipolar Plates

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





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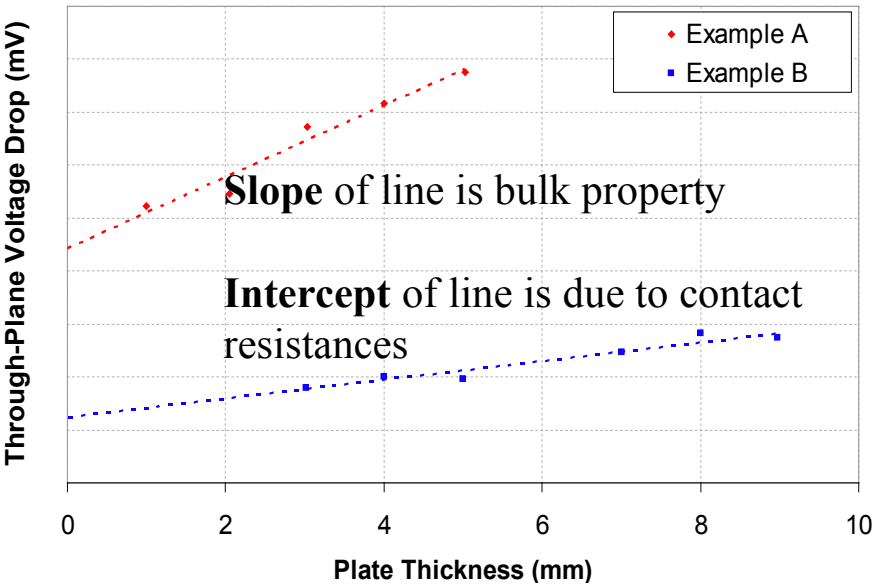
- Levels of contaminants established for different material classes

Carbon Bipolar Plates

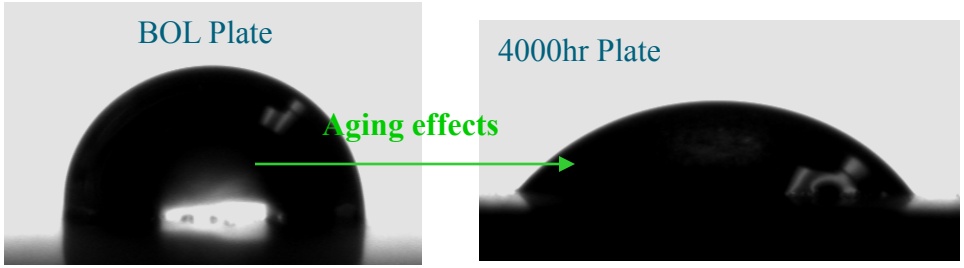
Electrical Property Change

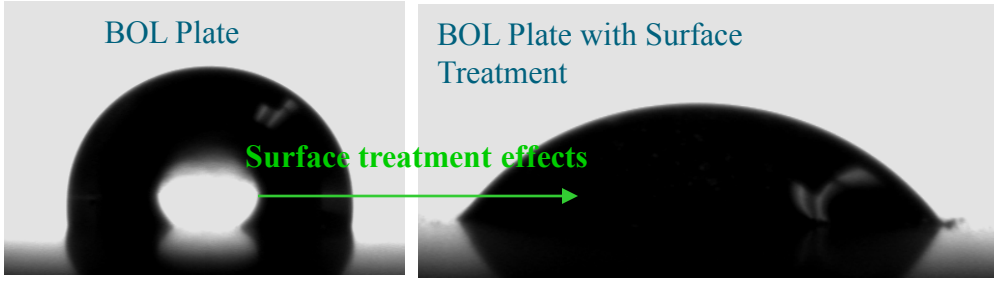
- Investigating separation of bulk properties and contact resistances
- Method distinguishes different material types



Surface Change

- 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





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Summary

- **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

- **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_2 originates from the MPL, not the catalyst layer

Selected Technical Conclusions - 2

- **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_2 crossing over from the anode (i_{xa}) and O_2 crossing over from the cathode (i_{xc})
  - Pt particle degradation and migration effects the membrane H_2 crossover
- **GDL effects Catalyst layer Performance Degradation**
  - Surface oxides of carbon of catalyst layer and GDL increase
  - Hydrophillicity 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

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_2 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_2/air

V	T	RH	% O_2	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

- PO_2, RH and Temp dependence of membrane degradation
- Data for Pt dissolution from ANL study (D. Myers)

Catalyst Support Cycle

150 kPa Fuel/Oxidant H_2/N_2

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

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

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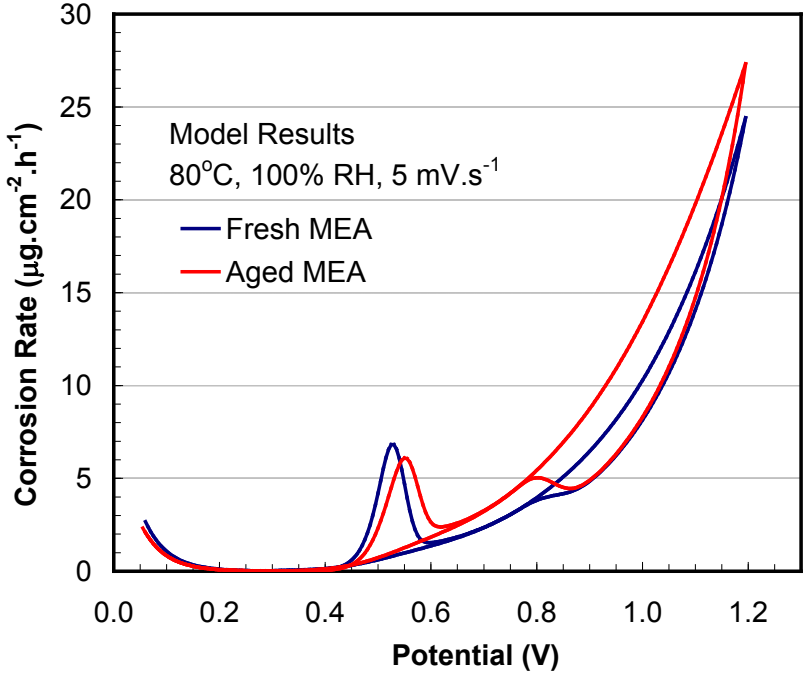
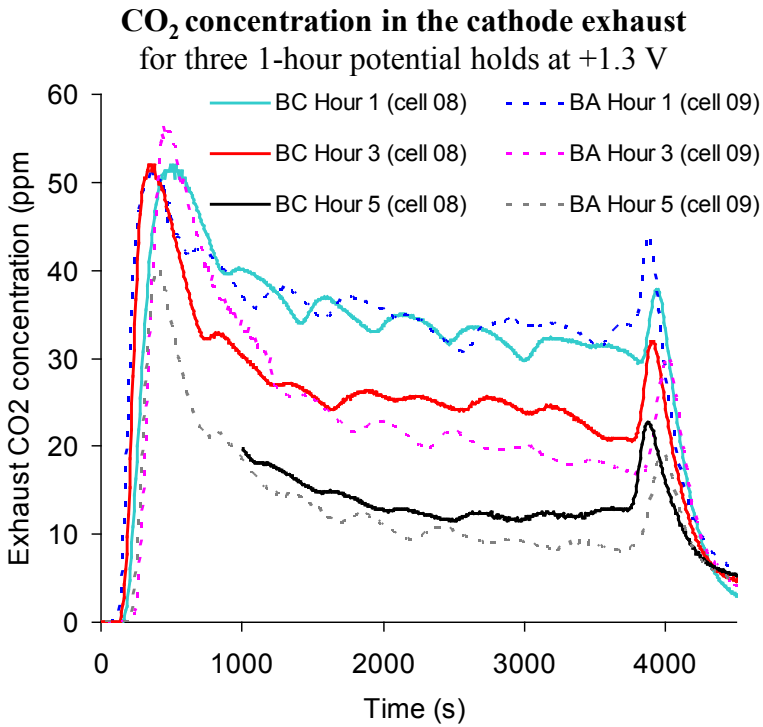
Future Work: Carbon Corrosion

- 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 ~90%, carbon mass decreased by ~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)

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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
- All project partners and personnel

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- SANS beam time provided by
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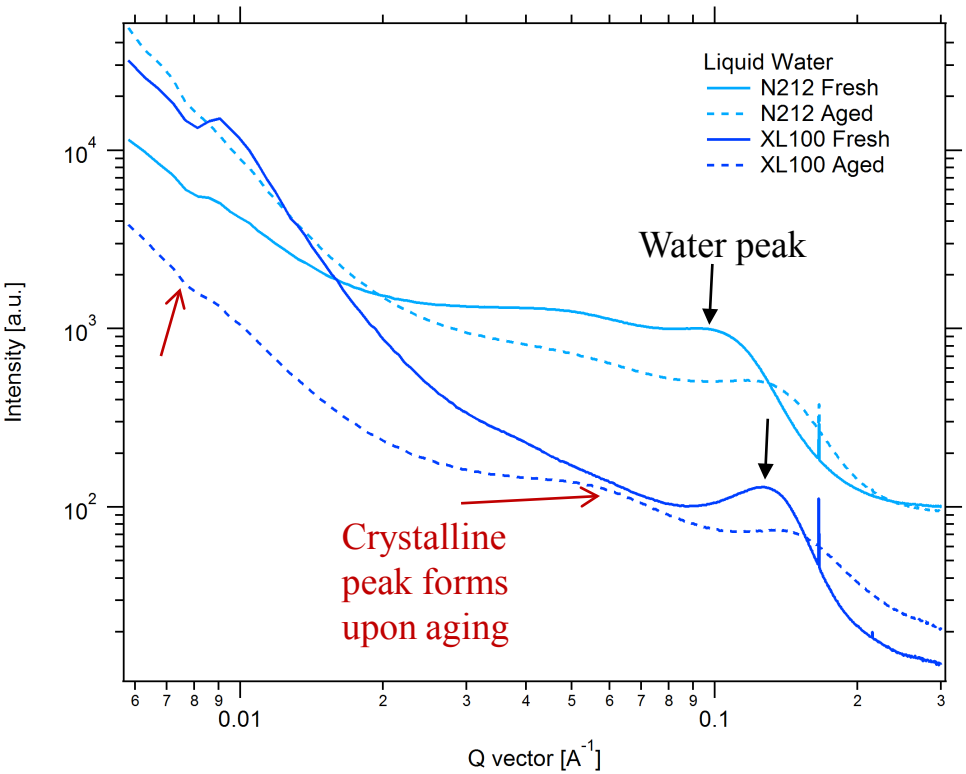
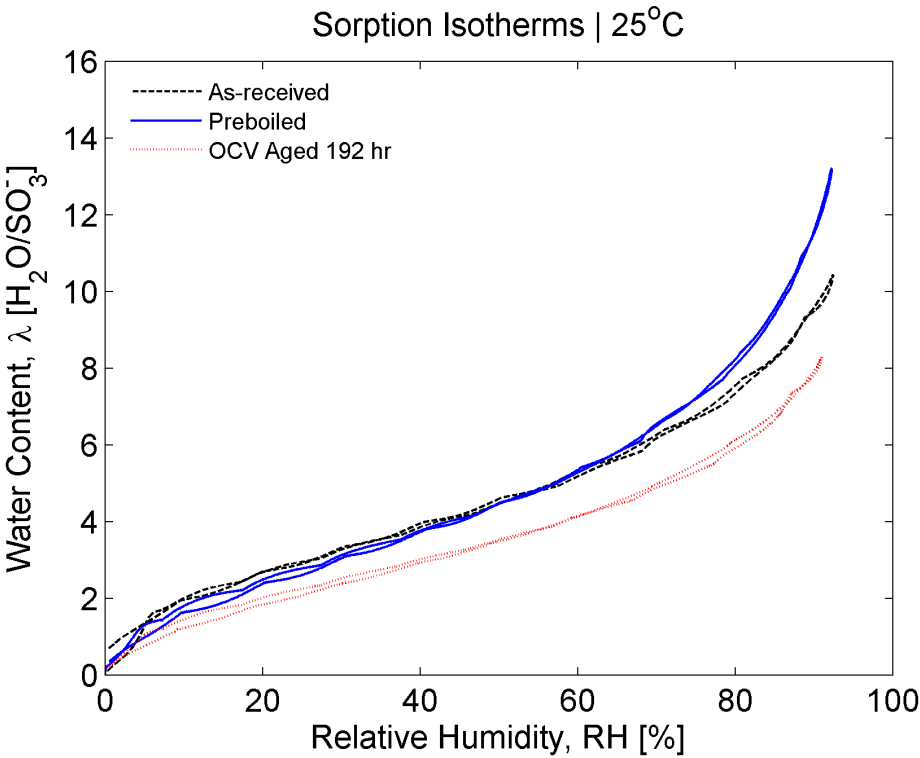
  - NIST: NG3, NG7 beam lines
- Neutron imaging beam time provided by
  - National Institute of Standards and Technology: BT-2
- Other materials provided by:
  - W.L. Gore
  - Solvay
  - SGL Carbon Gmbh

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 ~ 0.06 A^{-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

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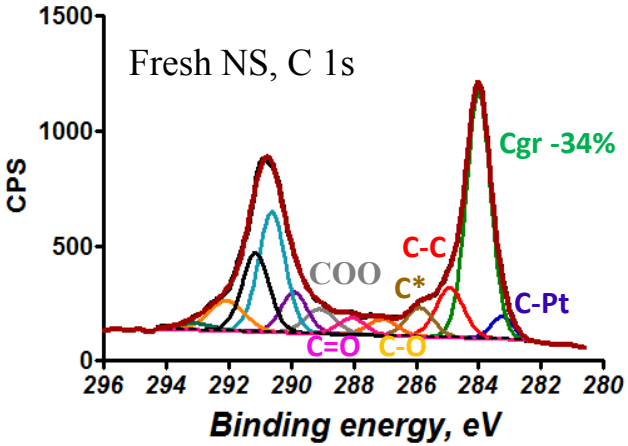
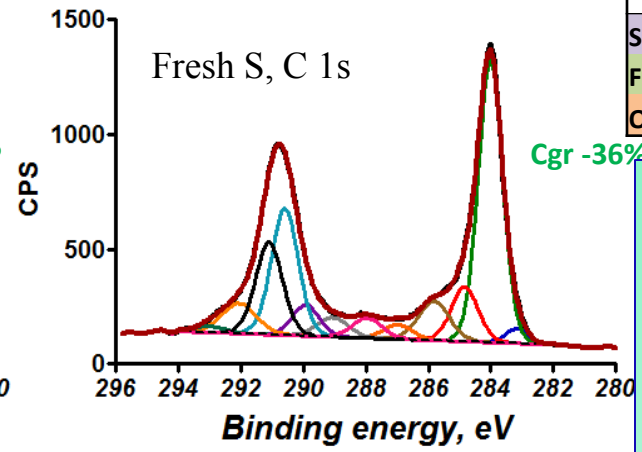
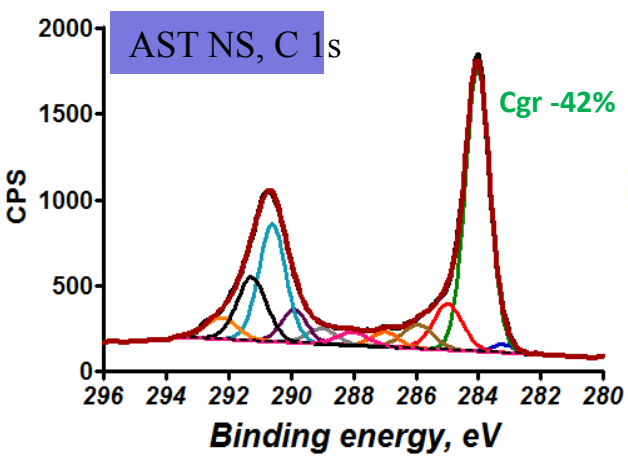
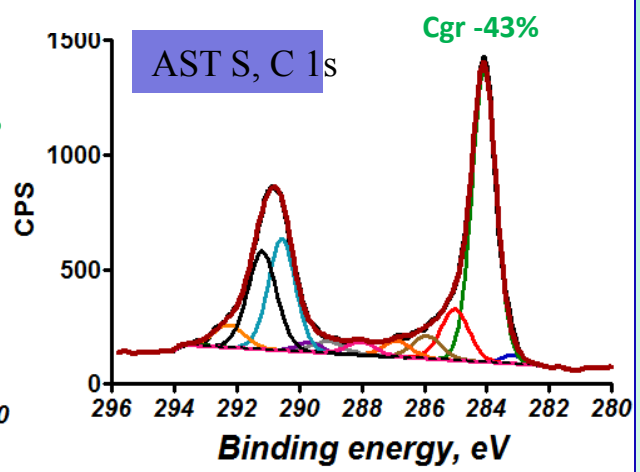
Chemical Analysis of Ionomer Degradation: Carbon 1s

	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_2 ends/no CO
- Increase in graphitic C is detected for both nonstabilized and stabilized
  - Larger graphitic C increase for NS system
- Amount of CxOy species decreased after testing
- CFx species is unchanged
- Overall trend during testing
  - Decrease in high BE C
  - Increase in low BE C
  - More pronounced for nonstabilized system

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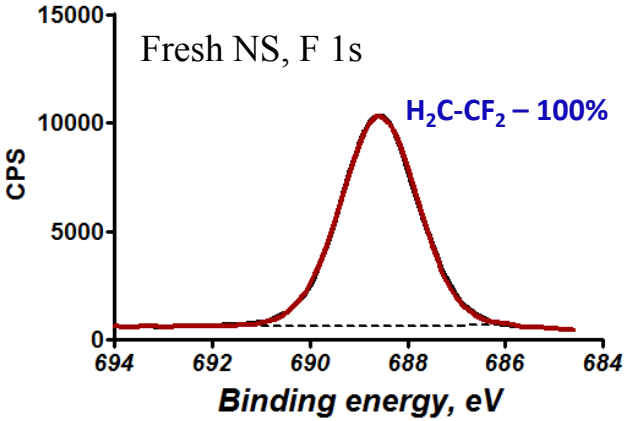
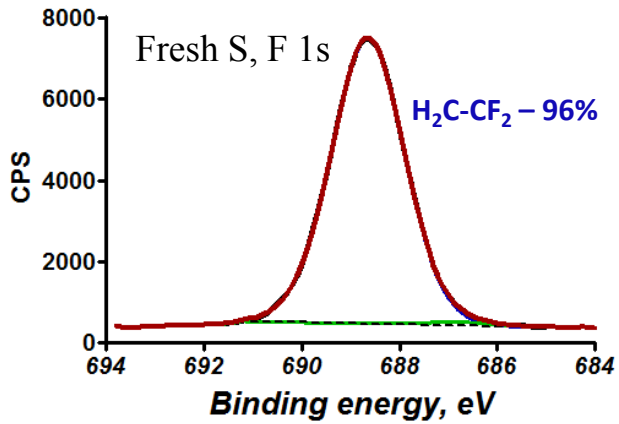
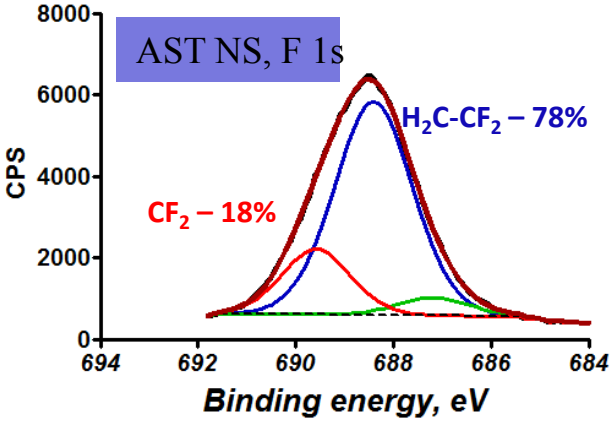
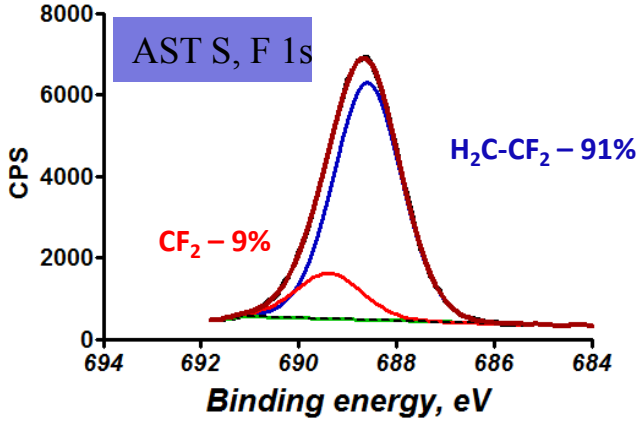
Chemical Analysis of Ionomer Degradation: Fluorine 1s









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

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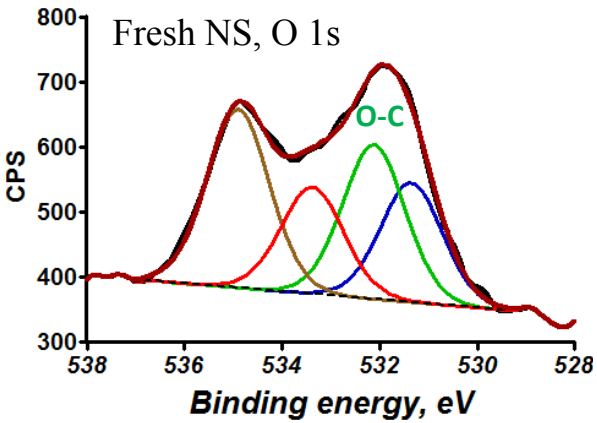
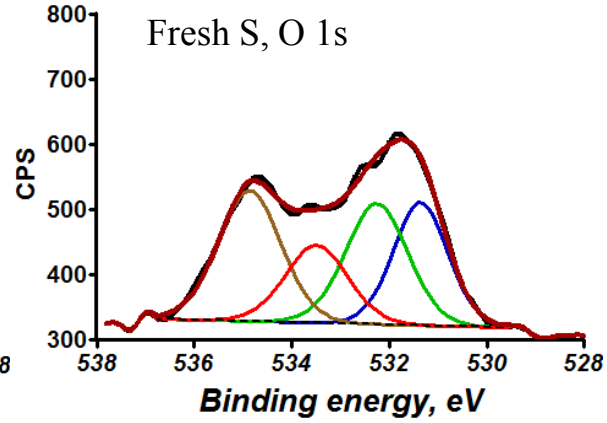
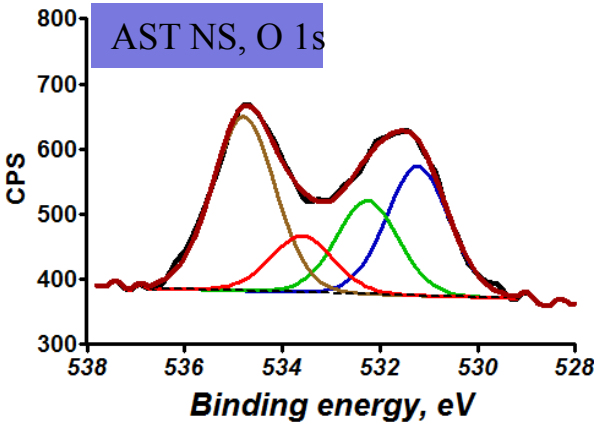
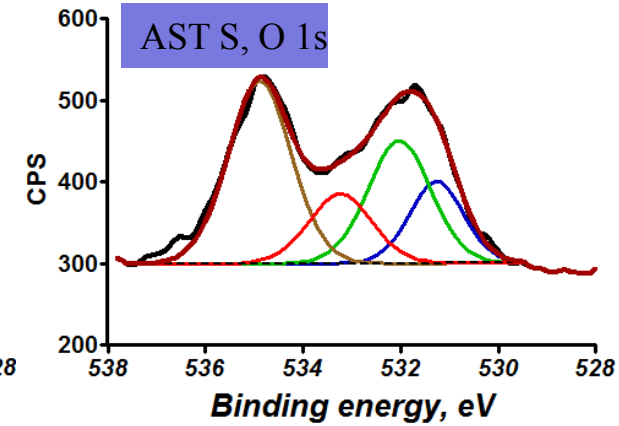
Chemical Analysis of Ionomer Degradation: Oxygen 1s

	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
S IONOMER		27.4	12.4	60.2
Fresh S cathode	25.6	23.2	22.9	28.2
AST S cathode	21.4	25.3	17.1	36.3









- **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®-like species detected for both**
  - **Slightly bigger increase for NS**

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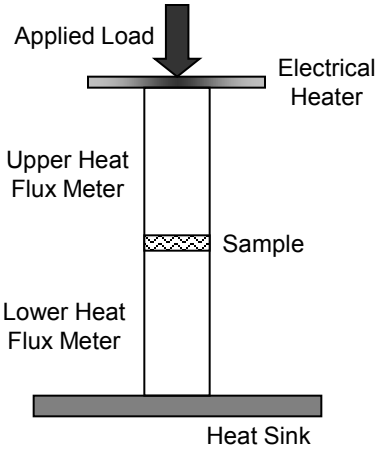
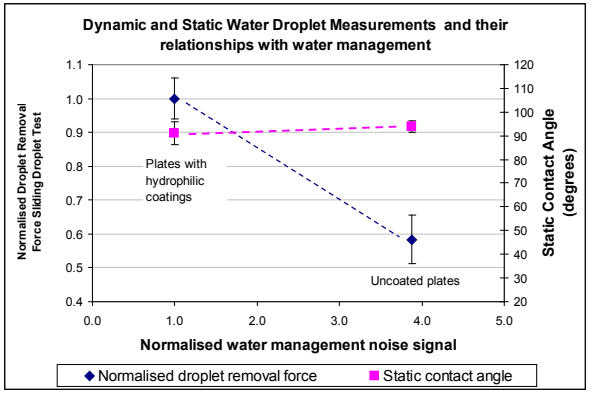
FC Tech Team Action items

- 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





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