Durability Improvements Through Degradation Mechanism Studies

DOE 2011 Annual Merit Review Meeting

May 9 - 13, 2011

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 Plus S.O.W.

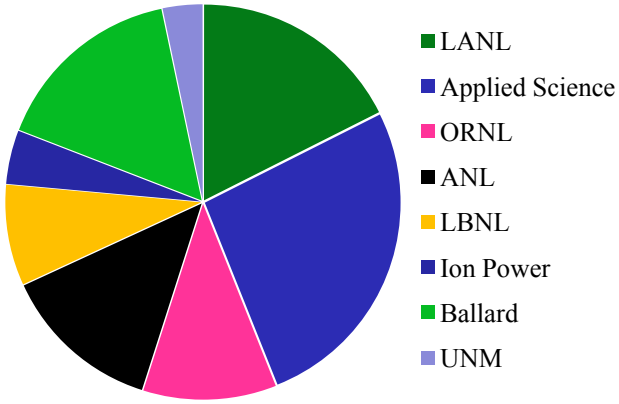
- **Los Alamos National Lab (LANL)**
  - Durability testing and component characterization
  - R. Mukundan, J. Davey, Bo Li, D. Spernjak, J. Fairweather, K. Rau , R. Lujan, D. Langlois
  - Applied Science Task
  - Understanding of electrode structure and degradation mechanisms
  - Christina Johnston, Yu Seung Kim, Baeck Choi, Zhongfen Ding, Piotr Zelenay, Marilyn Hawley, Andrea Labouriau, Rex Hjelm, Nate Mack, Bruce Orler , Cindy Welch
- **Argonne National Laboratory (ANL)**
  - Integrated comprehensive degradation model and model distribution
  - Rajesh Ahluwalia, Xiaohua Wang
- **Lawrence Berkeley National Laboratory (LBNL)**
  - Fundamental modeling
  - Adam Weber, Ahmet Kusoglu
- **Oak Ridge National Laboratory (ORNL)**
  - Characterization (TEM) and metal bipolar plates
  - Karren More, Mike Brady
- **Ballard Power Systems (BPS)**
  - Stack integration components interactions, component interactions
  - Paul Beattie, Sylvia Wessel, G. James, D. Ramrus, S. Loif, W. Williams
- **Ion Power**
  - Specialized MEAs, membranes, Ionomer and MEAs
  - Steve Grot, Walter Grot
- **University of New Mexico (UNM)**
  - Characterization (XPS) and carbon corrosion measurements
  - Kateryna Artyushkova, Plamen Atanassov, Anant Patel

Budget

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

Yr 1	Yr 2	Cumulative
$2000k	$2000k	$8225k

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

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

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

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

Approach

- **Understand Degradation Mechanisms**
  - Individual component testing
  - Measurements of degradation
    - Life testing: Drive cycle, Accelerated Stress Tests (ASTs), Shut-down/start-up
    - Matrix evaluation of different materials (catalysts, ionomers, supports …)
  - Analysis to define individual component contributions to loss in performance

- **Characterization of Component Degradation**
  - Chemical characterization of components
    - Understand/quantitate the changes in surface species of component materials
  - Morphological evaluation of components
  - Physical characterization using porosimetry, surface energy analysis, contact angle, surface area, pore size, pore volume, etc.

- **Understand and Correlate Electrode Structure to Durability (Applied Sci.)**
  - Understand connection between structure and performance/durability
    - Vary the ionomer and catalyst with different solvents to assess impact
  - Simulate the electrode formation process and evaluate dispersions (SANS, NMR)
  - Evaluate structure and local chemical environment of Nafion® dispersed in different solvents and solvent mixtures

Approach

- **Modeling**
  - Fundamental degradation mechanisms (LBNL)
    - Chemical – Mechanical Degradation
      - Model for void-growth due to swelling – deswelling
      - Determine model parameters using the experimental data
    - Model water profiles during degradation
  - Individual degradation models – kinetic/rate based (ANL)
    - Pt Dissolution Model
    - Transport Model
  - Integrated comprehensive model (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
  - Share data, develop more comprehensive models
    - Model develop via ANL jointly with Nuvera project

Approach - FY2011 Milestones

Mon Yr	Milestone	
Nov 2010	Fabricate multiple (3 or more) MEAs using LANL technology and provide to industrial partner for evaluations.	Delayed – MTA and NDA in process Multiple partners
Mar 2011	Characterize electrode structure using short side chain ionomers and different sized Pt catalysts and perform electrode performance durability test.	Ionomer portion – complete Catalyst portion -- ongoing
Mar 2011	Complete surface energy characterization of 2 GDLs for aging times of 0, 200, 400, 600, 1000 hours.	Experiments complete
May 2011	Demonstrate the electrode structures from at least three dispersing solvents by new spectroscopic tools (NMR and SANS).	Experiments complete Analysis of SANS data of electrode structures ongoing
June 2011	Complete segmented cell measurements for spatial performance characterization after performing catalyst cycling AST (0.6 to 0.95 V) and potential hold (1.2 V) AST in H_2/Air.	Experiments completed and continuing
Sept 2011	Complete fluorine emission measurements for mixed Nafion®/Hydrocarbon MEA to identify catalyst layer degradation rate.	Experiments complete plus on-going

Material - MEA Variations for Durability Matrix

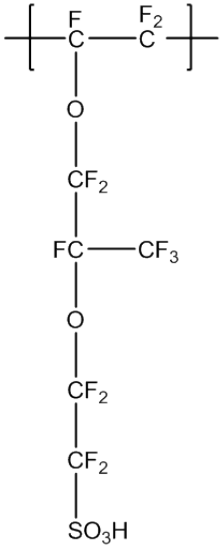
MEA Variables:

- Catalysts
  - Loadings
  - Supports (graphitization/surface area)
- Membranes
  - Nafion® / Reinforced / Stabilized
  - Hydrocarbon (separate ionomer analysis)
- Electrode Layer Ionomers
  - Long side chain (LSC)
  - Short side chain (SSC)
  - Stabilized/ Un-stabilized Nafion®
  - Nafion® – digested after degradation
- Electrode Structure
    - Solvent effect

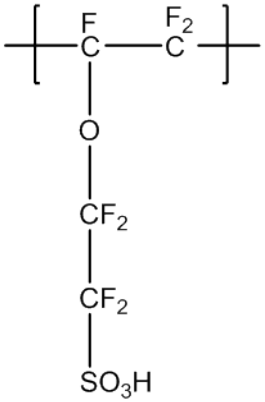
Ion Power – 22 MEA Variants
Catalyst Loadings
Membranes
Supports

Perfluorinated sulfonic acid polymers

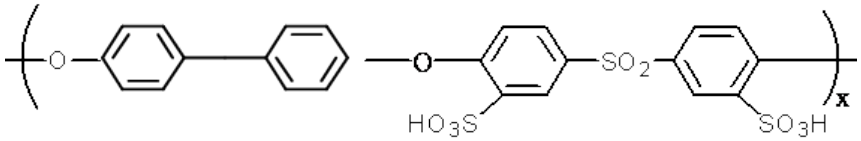
Long side chain (LSC) PFSA (Nafion®)



Short side chain (SSC) PFSA (Aquivion®)

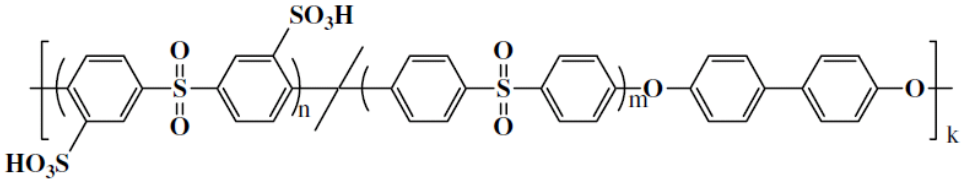


MC sulfonated polysulfone*



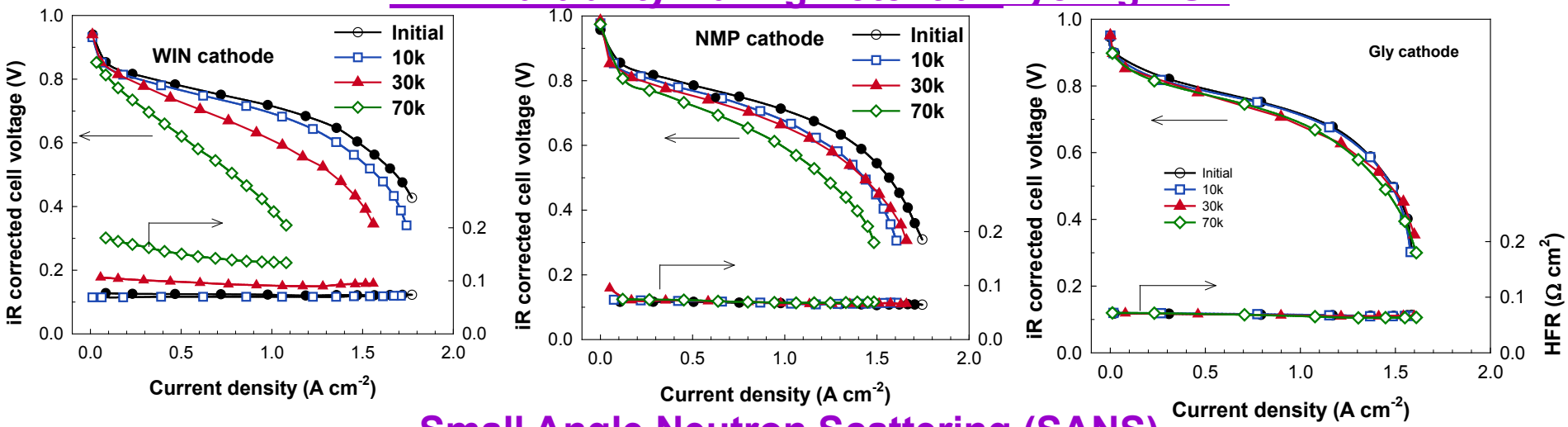
*Ref. Y.S.Kim et al. Polymer 47 (2006) 4026

Sulfonated poly(arylene ether sulfone)s (*BPSH*)

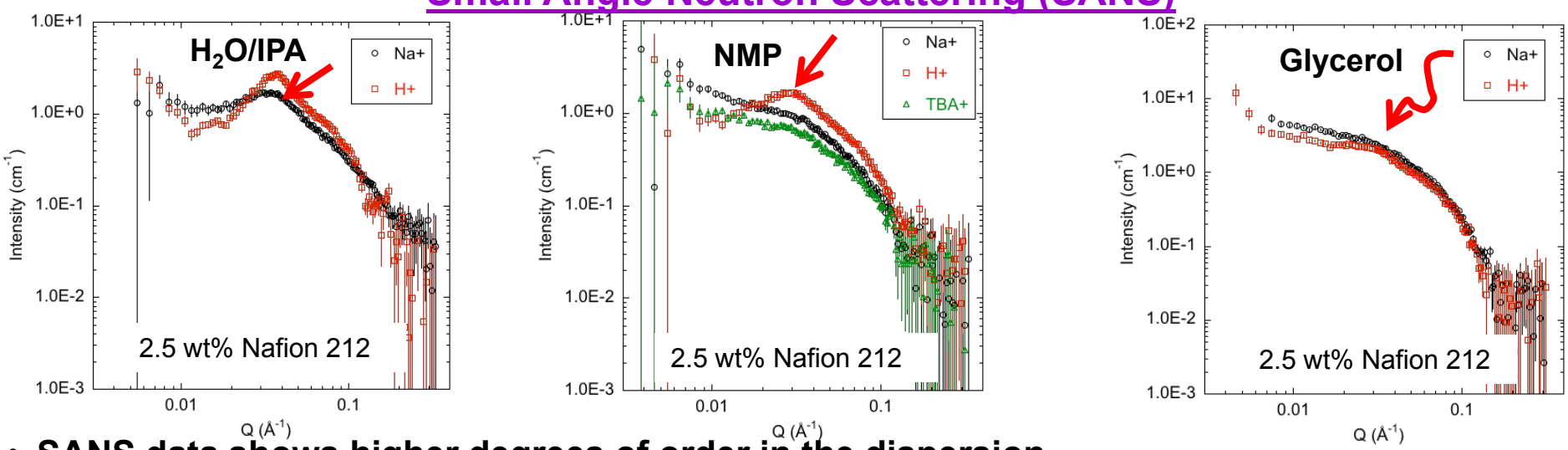


Correlating Nafion®/Electrode Structure to Durability

MEA Durability During Potential Cycling AST



Small Angle Neutron Scattering (SANS)



- **SANS data shows higher degrees of order in the dispersion**
- **H^+ form induces higher order in IPA/H_2O and in NMP; less in glycerol**
- **Aggregation leads to lower mechanical properties (stress/strain analysis)**
  (see slide in supplemental section on mechanical properties)

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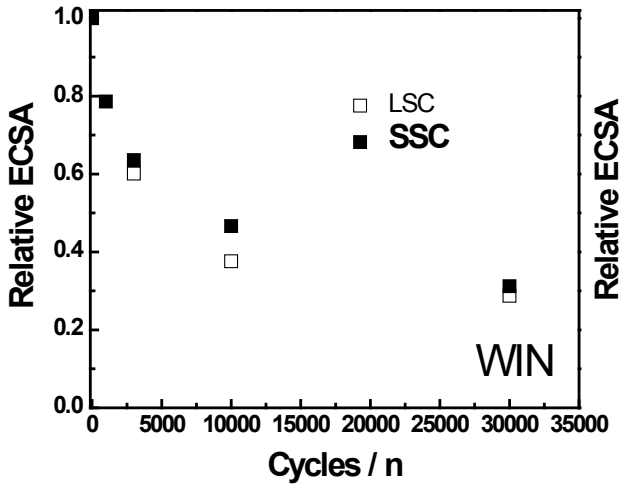
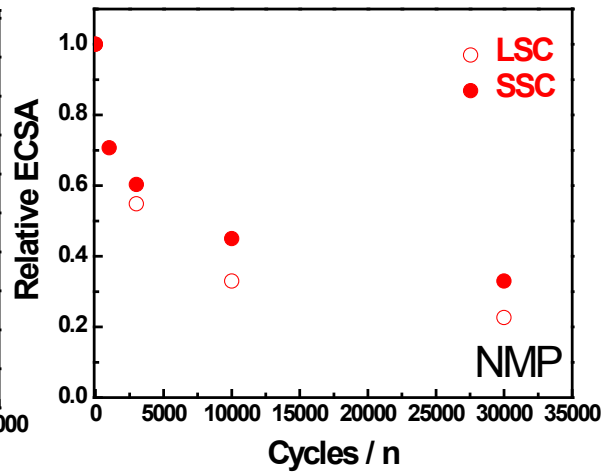
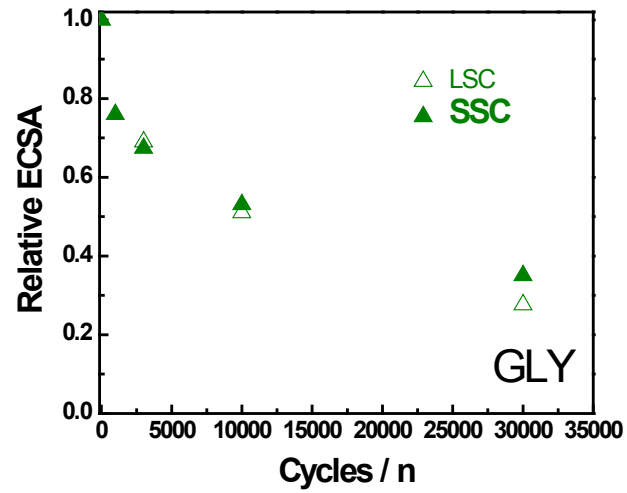
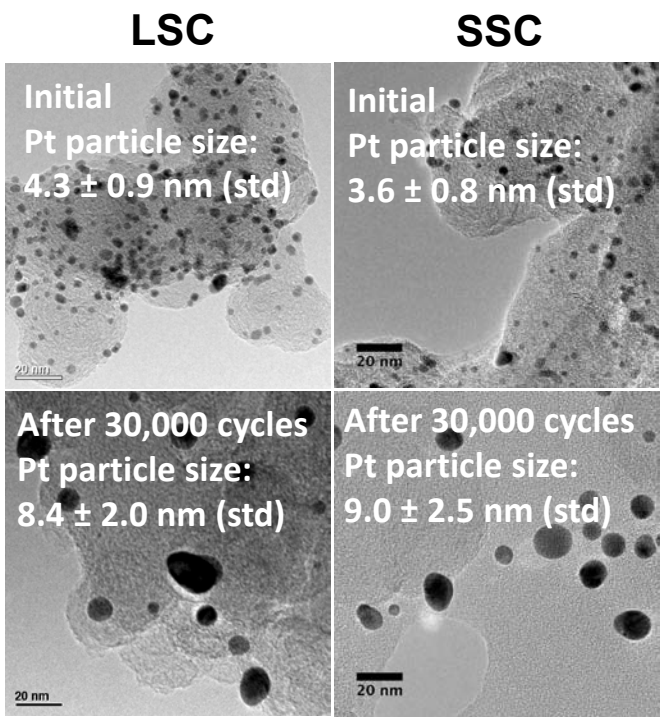
ECSA Changes during Potential Cycling Test: LSC vs. SSC







Example: Water/alcohol cathodes



- Initial ECSA is higher using (1) NMP solvent, or (2) SSC, by ~50%
  - ECSA differences do not correlate to performance
- On an absolute scale, more ECSA is lost with SSC electrodes than LSC
- On a relative scale, the rate of surface area loss is similar between LSC and SSC
- TEM data support that ECSA losses come from Pt particle size increase; show similar pattern between all sample types

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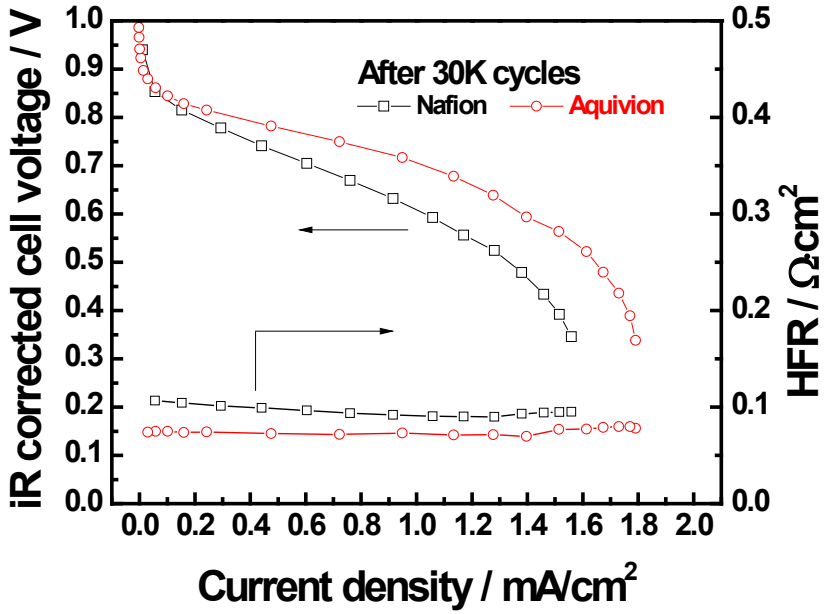
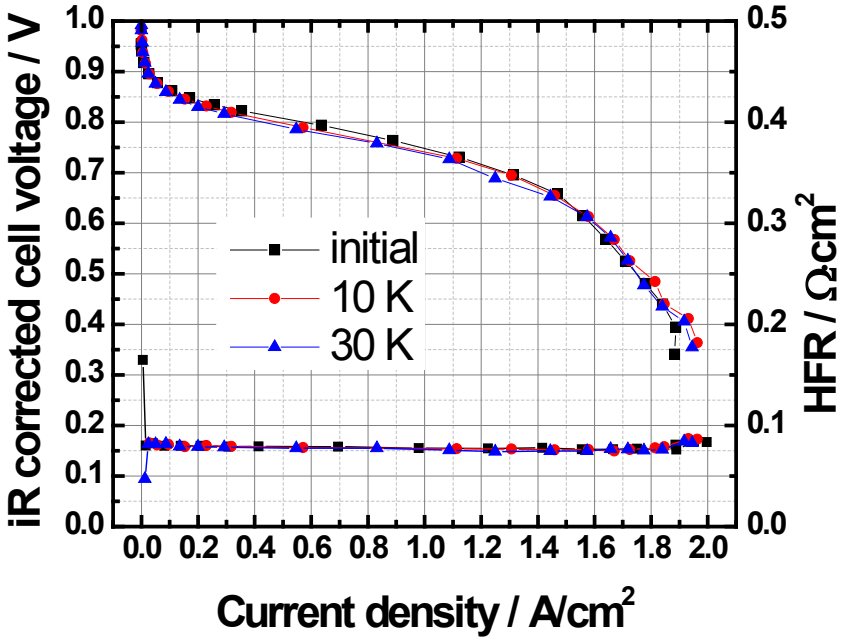
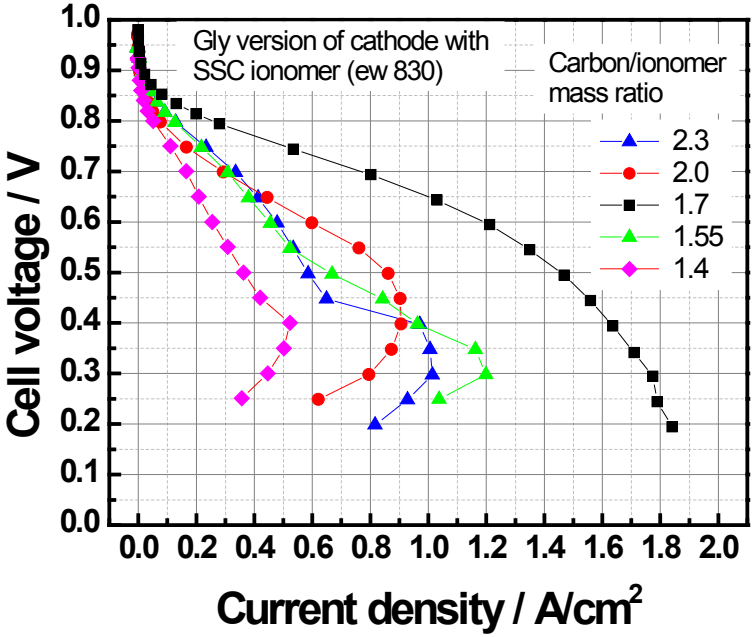
Good Performance and Durability Possible for SSC Cathode through Reduction of Ionomer Content





- **Reduction in ionomer content allowed for best performance in study to date without loss in potential cycling durability**
- **Demonstrates that "ideal" carbon/ionomer ratio depends on the electrode structure and processing**
- **Disconnect between ECSA and performance for Pt/C reinforced**



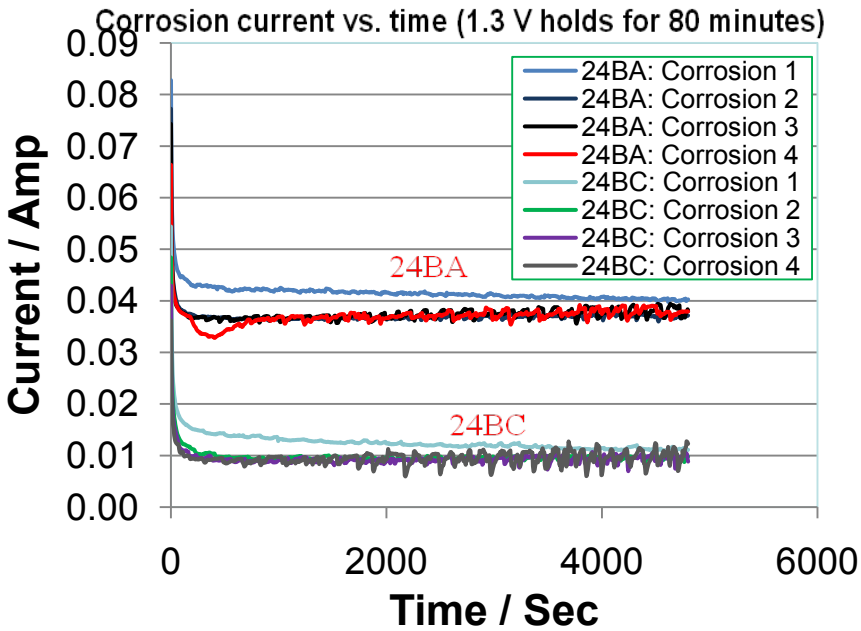
Carbon Corrosion - GDL/Water Effect on Catalyst Support Degradation

Measure GDL Effect on Cathode Carbon Corrosion

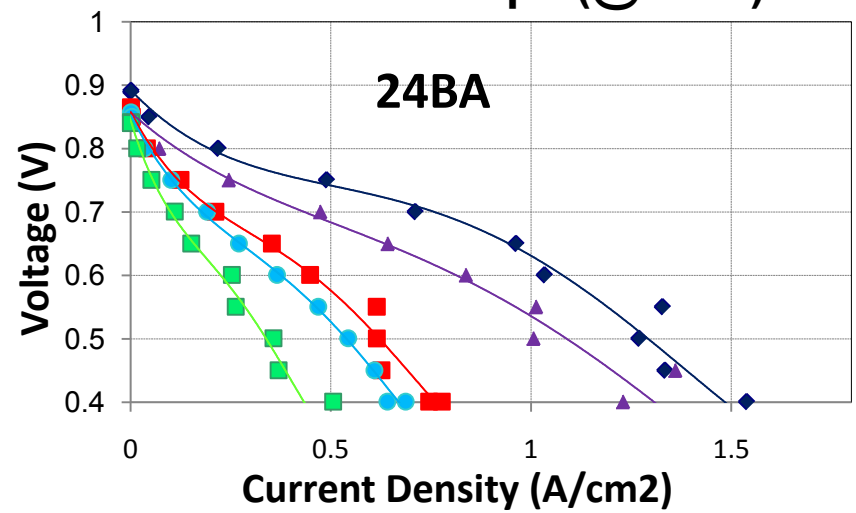
SGL 24BA (GDL with no MPL)
SGL 24BC (GDL with MPL – 5%/23% PTFE)

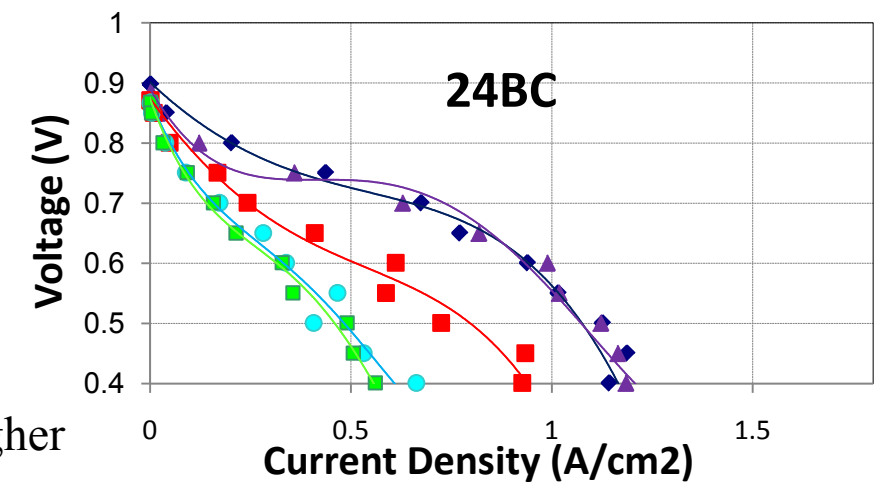
Corrosion Current

Cathode GDL 24BA vs. 24BC



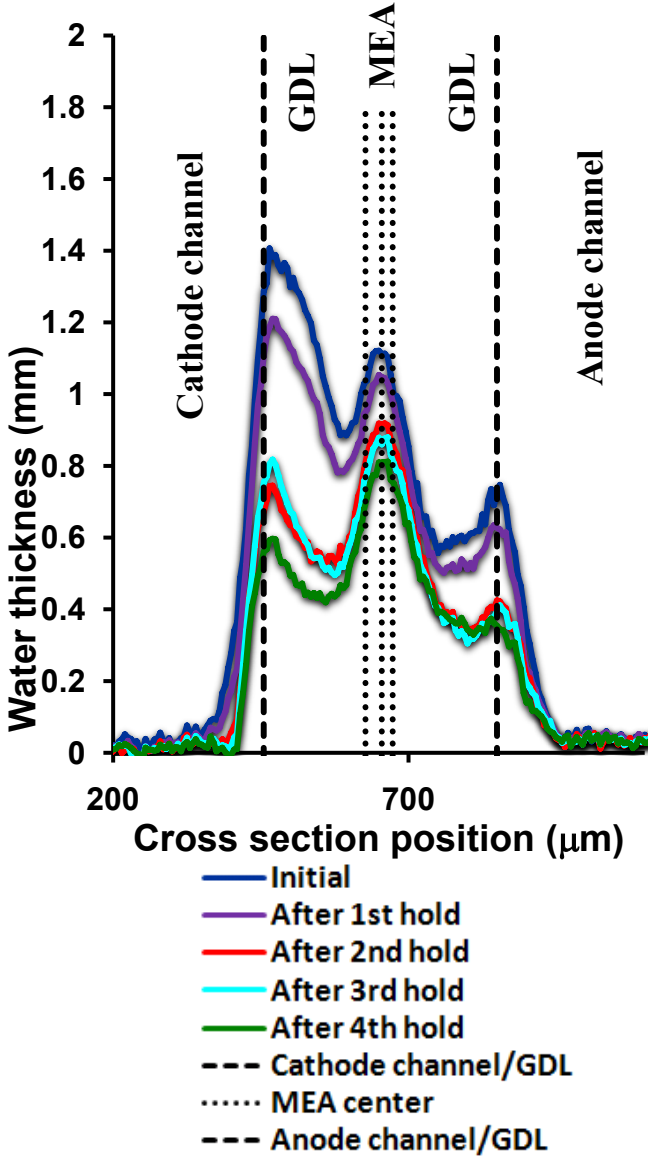
VIRs between 80-minute corrosion steps (@ 1.3V)





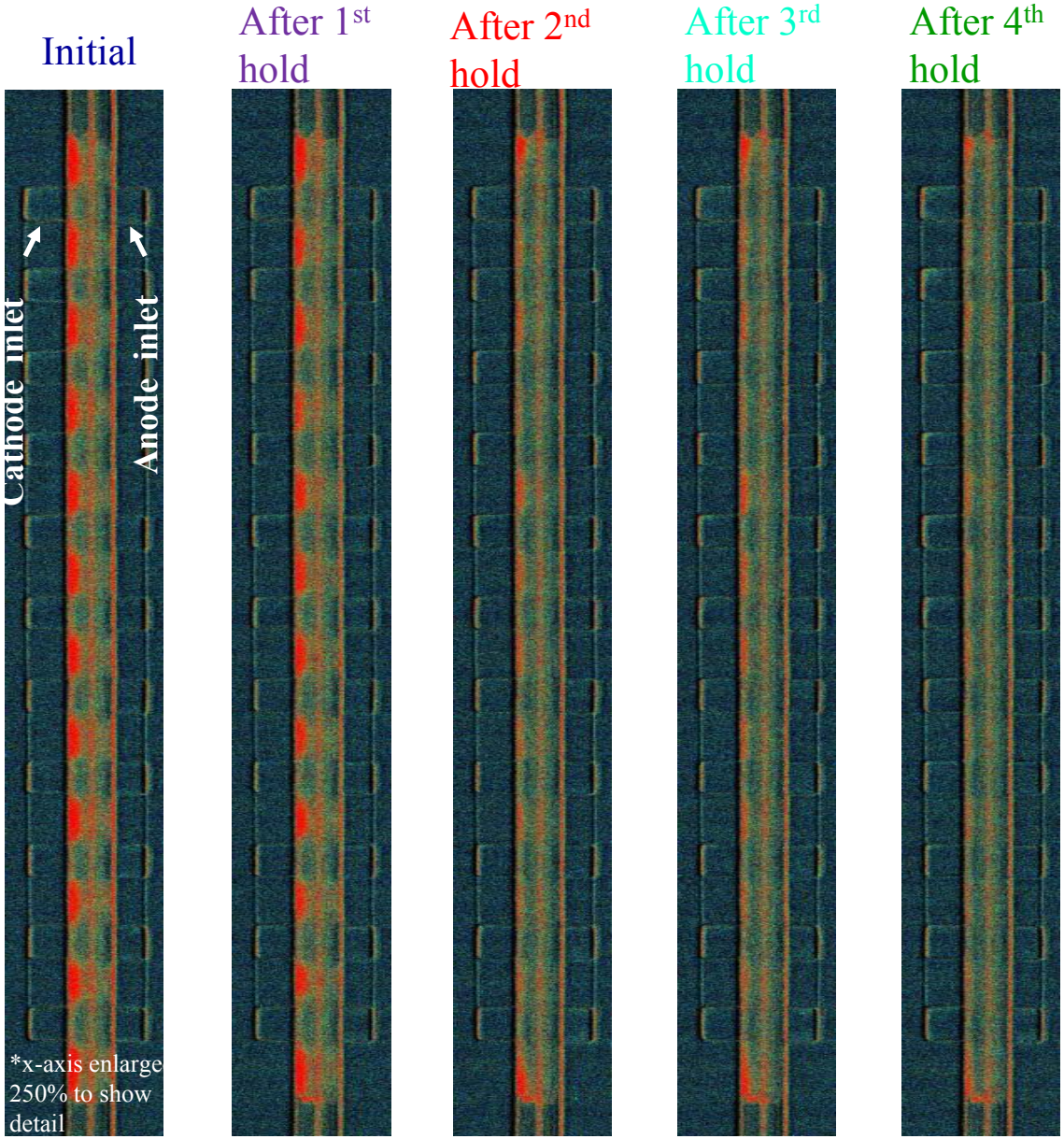
- Carbon Corrosion with Cathode GDL 24BA higher
- Both GDL cases:
- First corrosion step current slightly higher, then similar for steps 2,3,4

Water Profiles During Carbon Corrosion



0.8 A/cm^2, 80°C, 100%RH

24BC/24BC corrosion series images

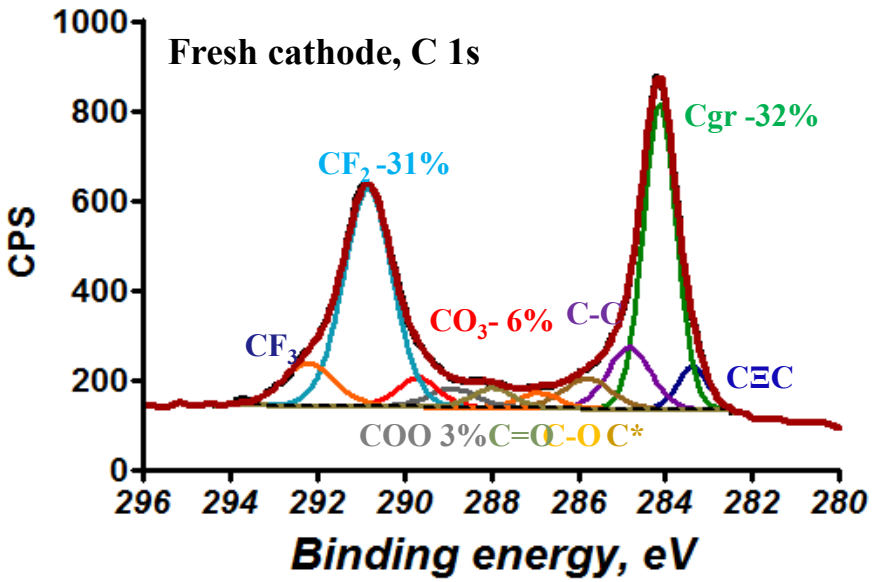


- Dominating effect on water content appears to be cathode overpotential for both GDL series
- Modeling to confirm water profiles

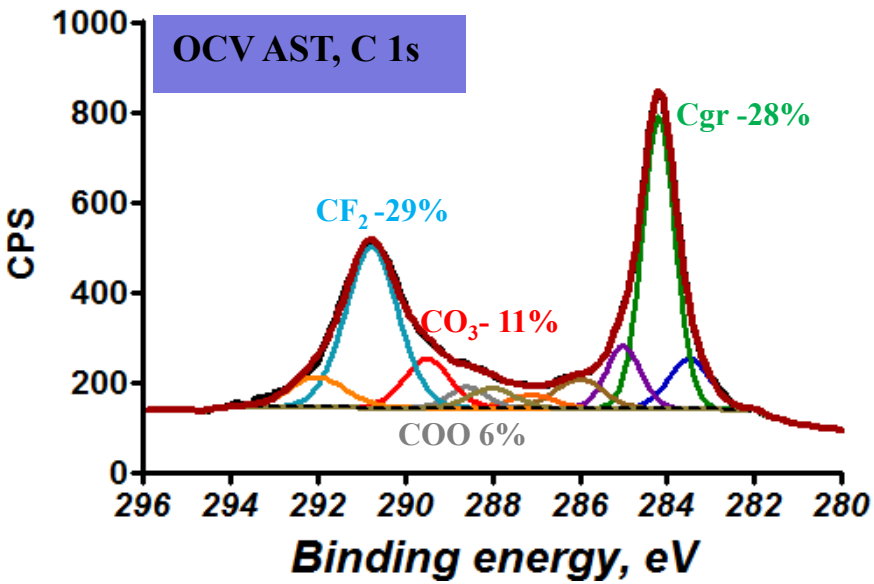
Measuring Component Surface Species Change (XPS)

Measuring compositional and chemical environment (C, O, F, Pt)

Carbon Spectra for Fresh Cathode



Carbon Spectra for Cathode after OCV AST



- Increase in C-O species is detected after AST (CO_3 and COOH).
- Both main components of catalyst (C graphitic) and ionomer (CF_2 and CF_3) decrease

Binding Energies for Carbon Species

	CΞC/ Pt-C	Cgr	C-C	C*	C-OH/ C-OC	C=O/ C-F	COOH	CO_3	CF_2	CF_3
	283.3	*284.1*	*284.8*	*285.8*	*286.9*	*287.9*	*288.8*	*289.7*	*290.7*	*292.1*
Fresh cathode	**5.5**	**31.9**	**7.9**	**4.7**	**2.0**	**2.8**	**2.7**	**5.6**	**30.8**	**6.2**
OCV AST cathode	**2.4**	**28.0**	**8.9**	**5.9**	**3.1**	**2.0**	**5.8**	**10.7**	**29.5**	**3.6**

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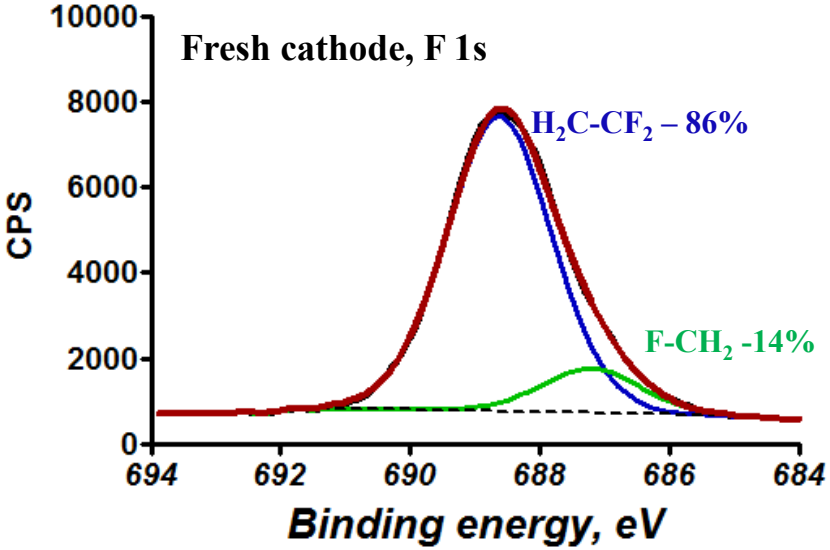

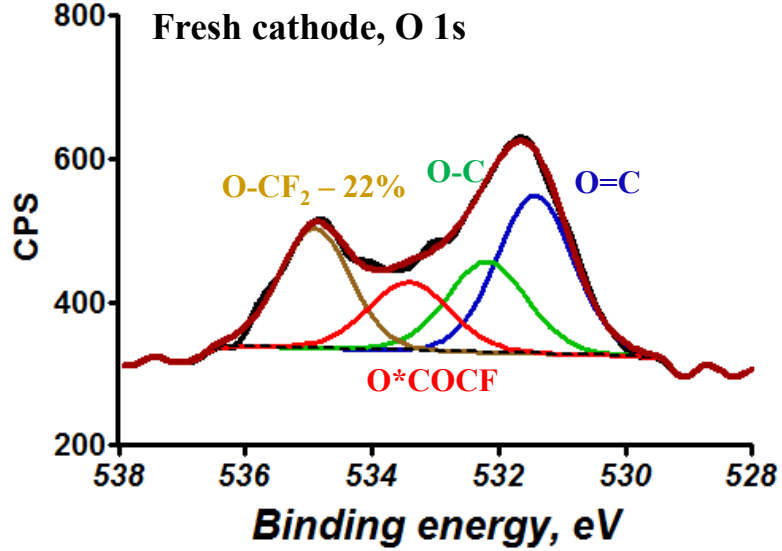

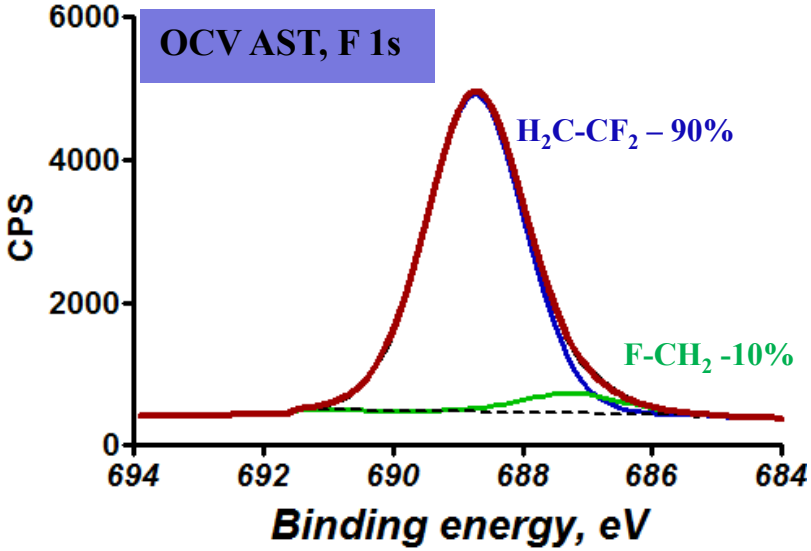

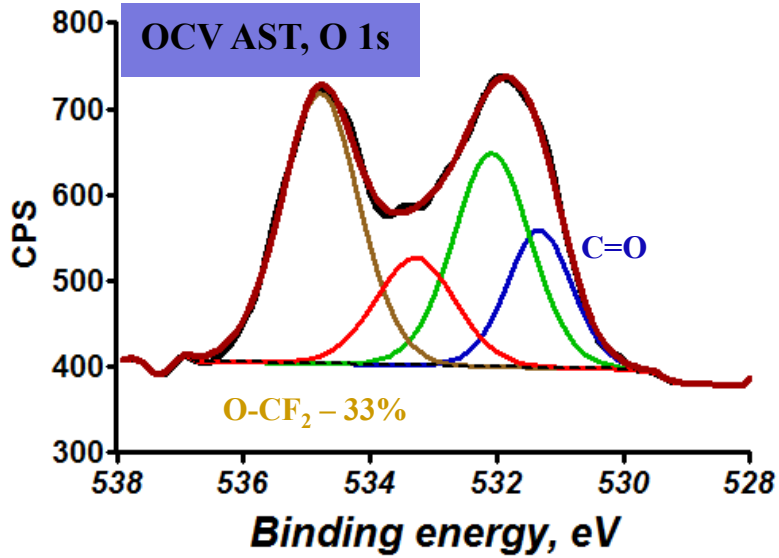

- Increased saturation with F species is detected after AST (CF_2 vs CF)
- Increase in oxygen-fluorine types of species is detected in O 1s spectrum, while C_xO_y species decrease

	O=Car	O-C al / OCO*CF_x	O-C ar/ O*$COCF_x$	O-CF_2
	531.3	*532.2*	*533.4*	*534.7*
Fresh cathode	35.0	23.8	19.1	22.1
OCV AST cathode	23.4	25.4	17.8	33.4

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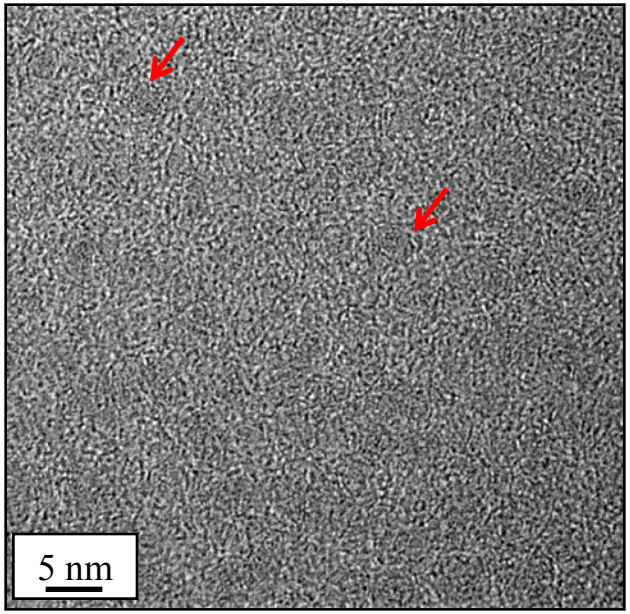
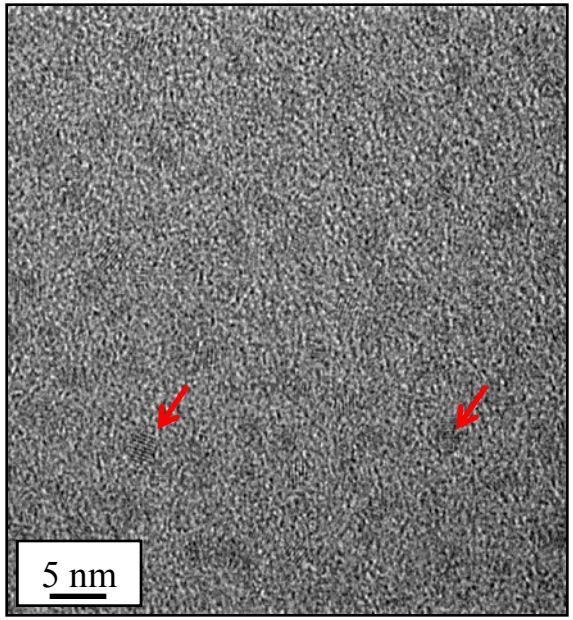
TEM of Membrane Crystallinity

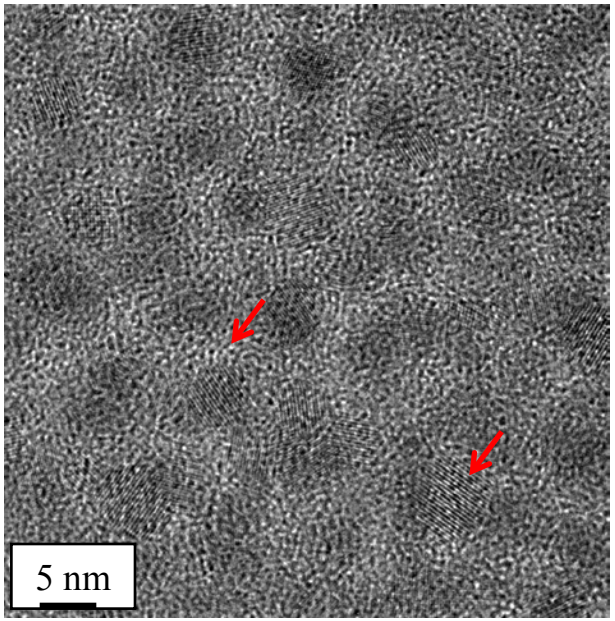
Fresh MEA membrane next to cathode



OCV-aged MEA membrane next to cathode



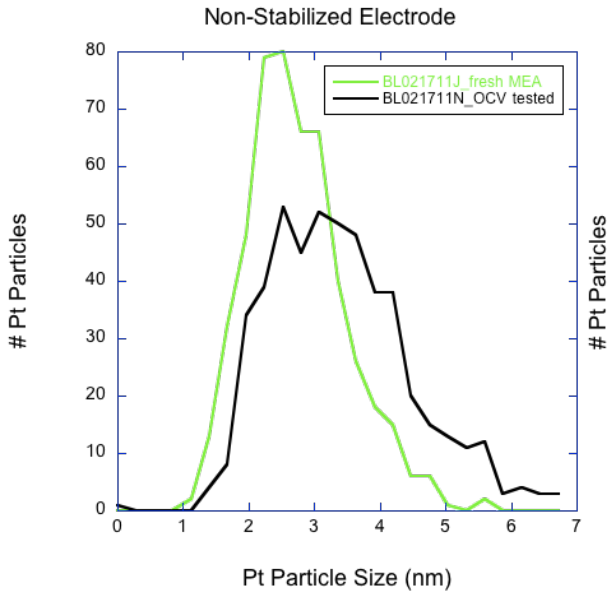
OCV-aged MEA membrane next to anode

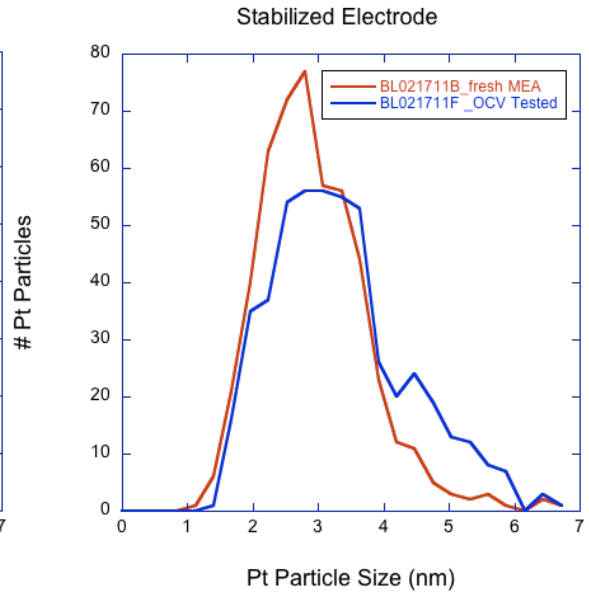


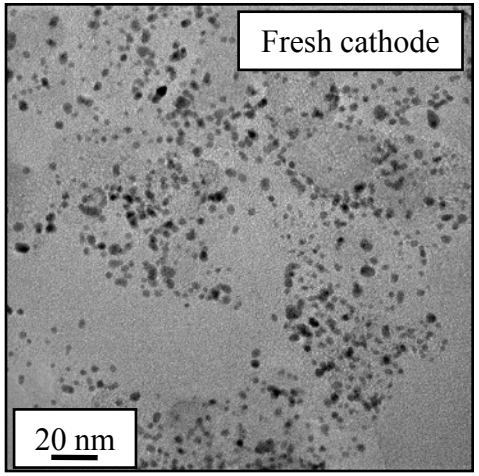
- In the fresh MEA, small F-rich clusters are observed throughout the thickness of the membrane (from cathode to anode)
  - Features exhibit some crystalline nature but are not highly crystallized nor have well-defined surfaces.
- After OCV-aging, these small F-rich clusters exhibited increased crystallinity on the cathode side without increasing in size.
- Effects more severe on the anode side of the membrane

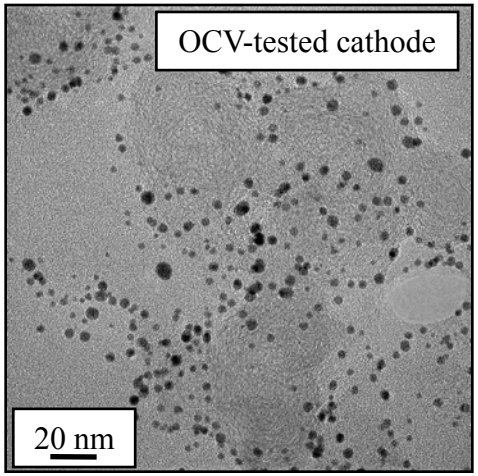
OCV-Tested MEAs

Non-Stabilized and – Stabilized Ionomers in MEA









Fresh Cathode	2.5 nm
OCV-Tested Cathode	3.2 nm

Fresh Cathode	2.5 nm
OCV-Tested Cathode	2.5 nm

(with second distribution centered ~4.5 nm)

- MEAs with NON-STABILIZED and STABILIZED show similar results
  - No cathode thinning/compression
  - Mo microstructural evidence for carbon corrosion
  - Cathode thickness (and porosity) remains the same as in the FRESH MEA.
  - No Pt migration into membrane
  - Nafion® 212 membrane experienced microstructural changes; changes identical for both ionomers

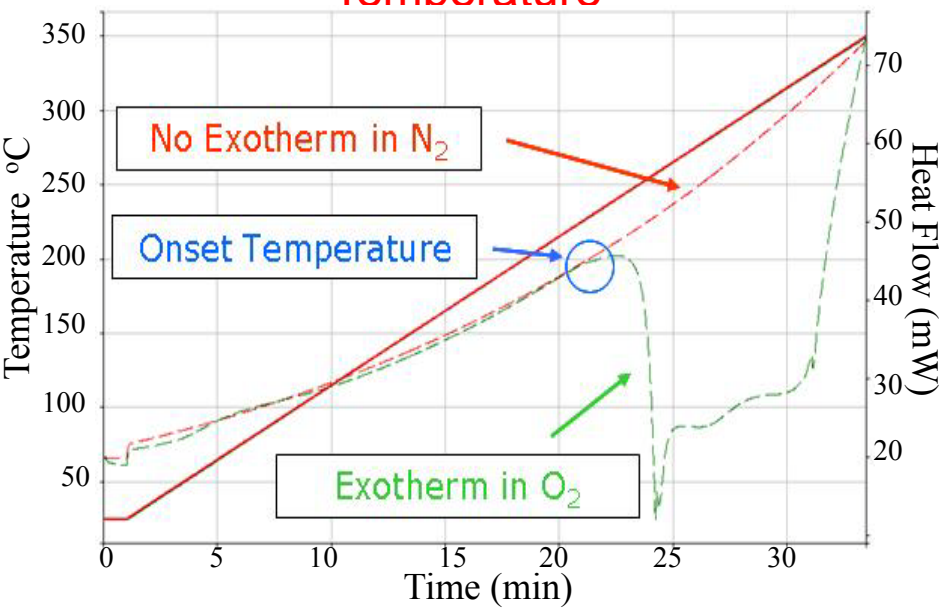
Ion Power, Inc Los Alamos Oak Ridge National Laboratory

Gasket Durability Evaluation

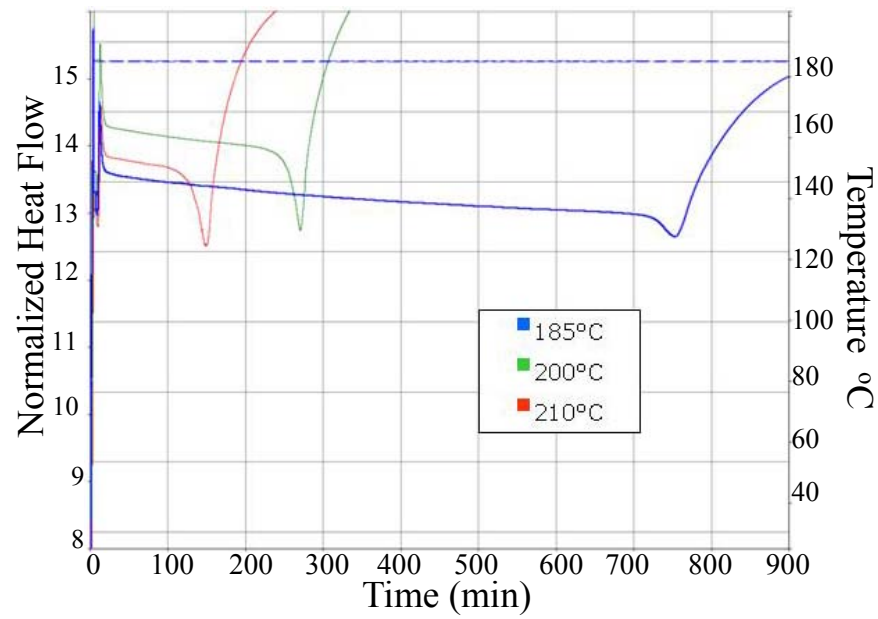
- Investigating durability and property changes to gasket materials
  - EPDM (Ethylene Propylene Diene Monomer)
- Effects on other materials performance

Differential Scanning Calorimetry (DSC) of EPDM

Oxidative Induction Time (OIT) onset Temperature



OIT varies with test temperature



- Developed analytical techniques to compare gasket material properties
- Accumulated data supporting seal life prediction; historical reports and archived samples.
  - Data to build future predictive models
  - Historical samples will be subjected to new characterization methods
  - Data will be compared to existing information.

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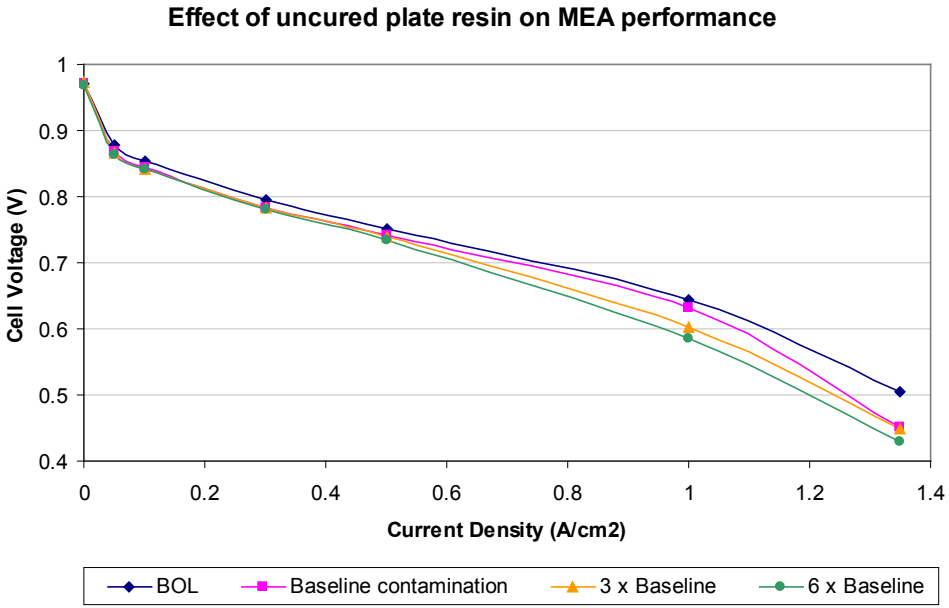
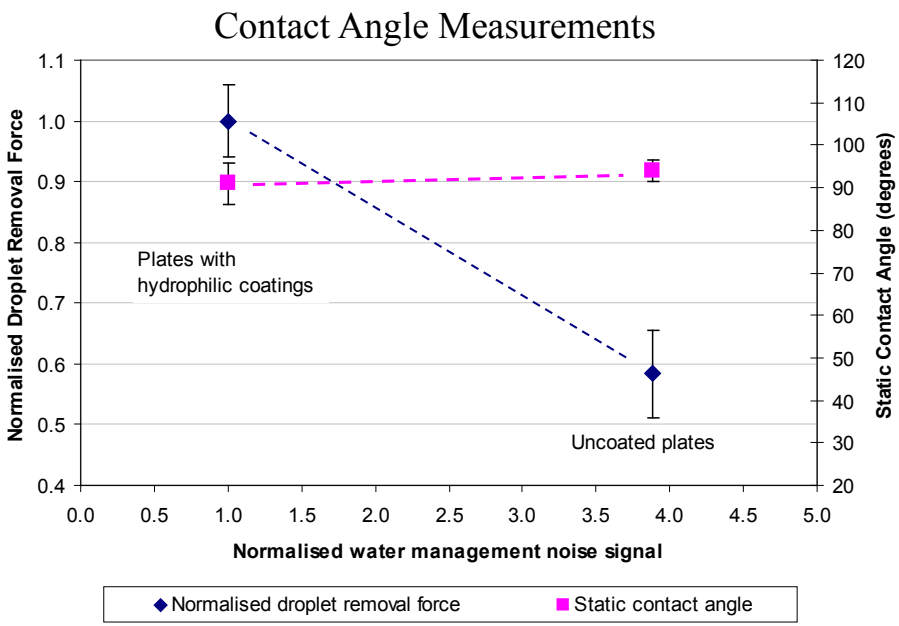
Bipolar Plate Durability





- Plate Leachates:
  - Quantifying plate leachates using solvent and DI water based extractions
  - Assembled a database of plate leachate chemistries for different classes of plate materials
  - List of potential plate contaminants from the methacrylate resin plates
  - In process of studying the vinyl ester resin plates
- Series of environmental exposure tests on graphitic plate materials from different resin classes
  - Temperatures between 80°C to 160°C
  - Variety of "fuel cell relevant" fluids (de-ionized (DI) water, mild acid (pH 4), water-ethylene-glycol coolant)
- Bipolar Plate Surface Property Investigation
  - Static contact angle measurements not effective at distinguishing plate properties (probably due to surface roughness)
  - Force measurement required to initiate the water droplet movement shown effective

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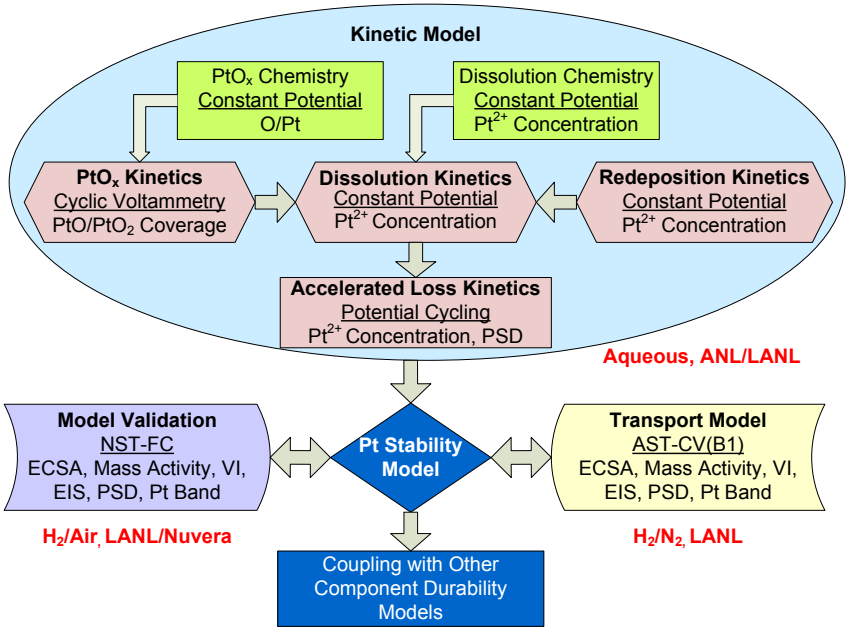
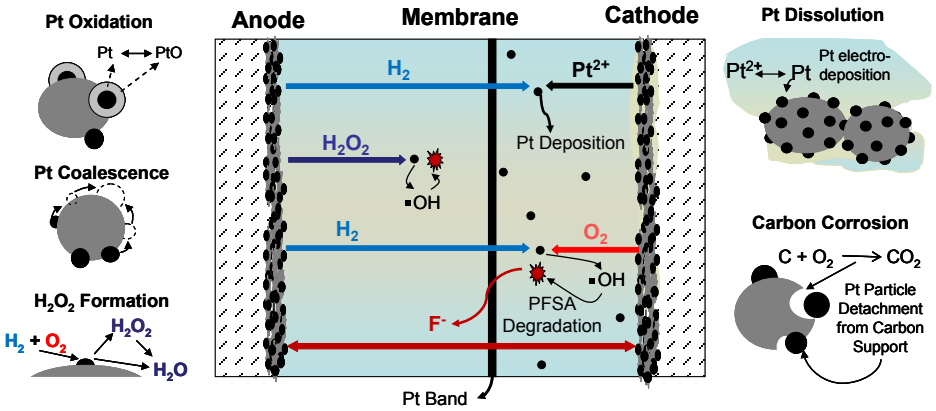
MEA Degradation Model





Pt Dissolution Model

- Represented as competitive balance between dissolution and protective oxide formation at high cyclic potentials
- Equilibrium and kinetic constants from aqueous measurements
- Transport constants from cell tests

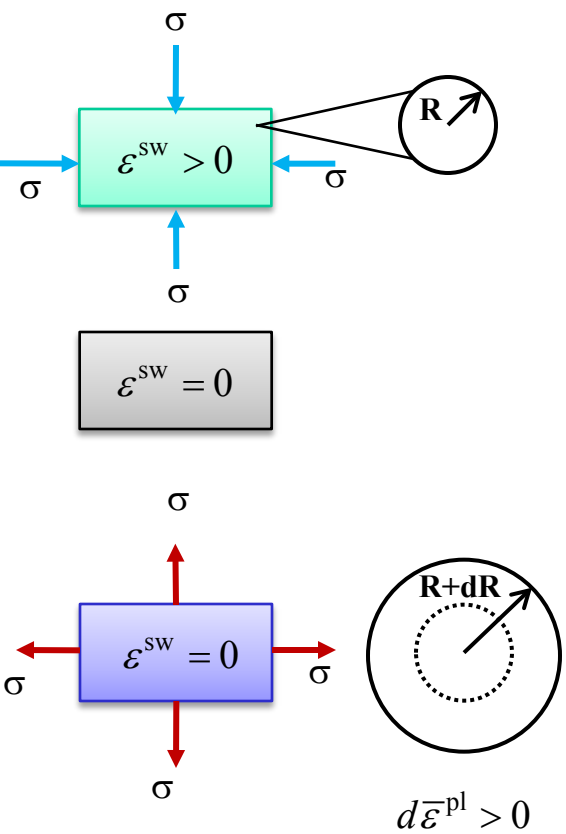
Transport Model

- Pt^{2+} diffusion in ionomer and membrane across potential gradient
- Pt band formation in membrane due to Pt^{2+} reduction by H_2
- H_2O_2 formation on anode catalyst due to O_2 crossover, on cathode catalyst as an ORR intermediate
- ·OH radical formation from H_2O_2 and H_2-O_2 reactions on Pt in membrane, attack on PFSA chain

Investigation of Model Parameters

- Change in void radius

$$\frac{dR}{R} = f\left(\underbrace{\sigma_m}_{\substack{Mean\\Stress}}, \underbrace{d\bar{\varepsilon}^{pl}}_{\substack{Plastic\\Strain}} \right)$$

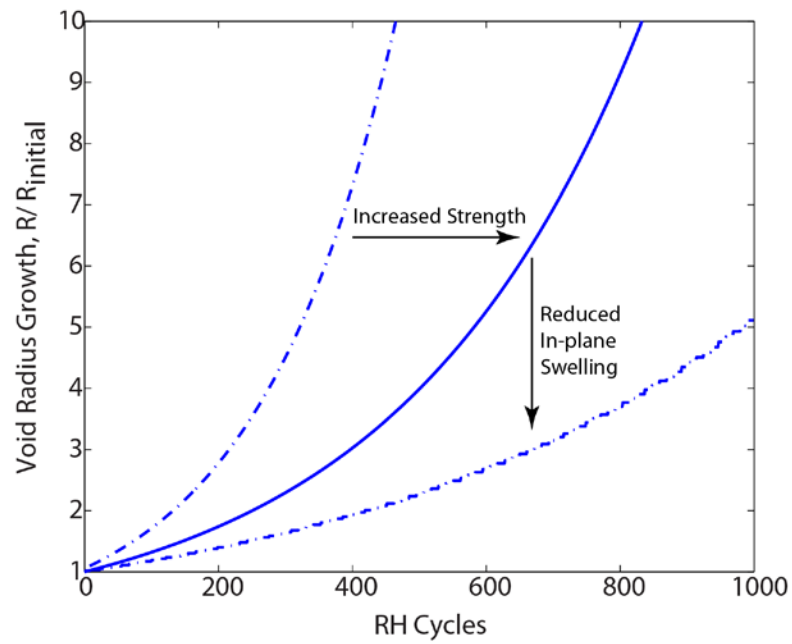


High RH (wet)
Increasing Swelling
Compressive Stress

Low RH (dry)
Decreasing swelling
No residual Stress
If deforms ***elastically***
(i.e., good resistance)

Low RH (dry)
Decreasing swelling
Residual Tensile Stress
If deformed ***plastically***
Leads to Void-growth

- Parameters improving resistance to void growth (e.g., failure):
  - Higher strength
  - Low in-plane swelling
  - Smaller RH amplitudes



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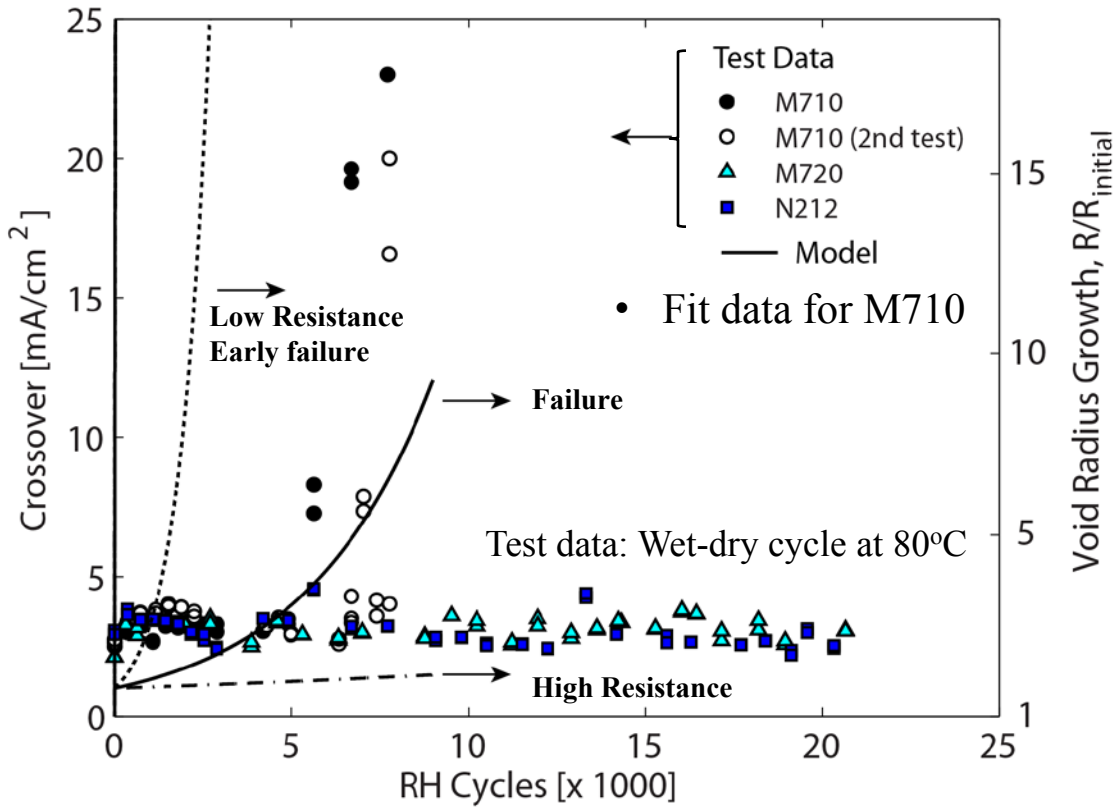
Membrane Life prediction Model
Failure during RH-cycling: Model Validation

- Durability in Fuel Cell Membranes
  - Chemical Degradation ➔ Material loss, void formation/cavitation
  - Stress-induced Damage ➔ Void-growth and cracks
- Stress – Assisted Void Growth during RH-cycling
  - Mathematical model for void-growth due to swelling - deswelling
  - Determine model parameters using experimental data



- Void-growth is driven by stresses induced due to swelling amplitude (RH-cycling)
- Good correlation found between growth of void (pinhole) and crossover

Organizations / Partners Collaborations

Partners:
Los Alamos National Lab (LANL)
Argonne National Laboratory (ANL)
Lawrence Berkeley National Laboratory (LBNL)
Oak Ridge National Laboratory (ORNL)
Ballard Power Systems (BPS)
Ion Power
University of New Mexico (UNM)

Partner organization's logo on individual slides to identify various areas of contribution

Additional Interactions (Not Formal Partners):

- NIST – Neutron Imaging
- NIST - USANS
- W.L. Gore
- SGL Group
- Solvay Solexis
- Nancy University (France)
- DOE Durability Working Group
- GM (in process)

Future Work

Identify and Quantify Degradation Mechanisms

- Vary MEA materials to better define degradation mechanisms
  - Expand mixed hydrocarbon and PFSA materials for unambiguous chemical analysis
- Evaluate degradation rates with MEA materials; guide integrated model development
  - Material variants include: ionomer, membrane, catalyst, support, electrodes
  - > 30 MEA variants, > 6 AST tests, > 3 fuel cell durability tests
  - Incorporate DOE Durability working group protocols into testing (ex. Shutdown/startup)
  - DSC of aged ionomer (stabilized, non-stabilized) to identify changes in water bonding with age and type of ionomer
  - Expand PCA analysis (by XPS) to extract key mathematical principle

Electrode Structure

- Identify causes behind ionomer and solvent impact on MEA durability
  - Combine microscopic data, porosimetry data, helox, O_2, and AC impedance information
  - Develop model for the SANS data already obtained from electrodes
- Establish correlation of electrode structure durability to mechanical strength
  - Assess mechanical properties and interface strength of electrode measurements
  - Correlate VIR durability measurements by scratch testing of electrodes by nanoindentation
  - Develop test to be used to screen quality of dispersions intended for electrodes
- Assess SSC ionomers using dispersion approach for potential cycling/OCV durability
  - Expand electrode structure durability testing to include fuel cell life testing
  - Extend study of electrode durability by characterization at various life points of the MEA

Future Work

Component Interactions

- 5-cell short stack with previously untested seal materials (EPDM grade)
  - Short durability test of ~2000 hours at steady state operation.
  - Analyze product water for contamination over the test time
  - Link contaminant type from stack operation to that determined by leach investigation
  - DSC (OIT) of aged material samples to see if their respective time to oxidation changes
- Metal bipolar plate evaluation and evaluation of interactions with MEA/GDL
  - FE-20Cr-4V, 904L
- Composite (graphite) bipolar plate evaluation
  - Standardize surface evaluation improving data consistency to evaluate surface properties
- Correlate GDL properties and cell water profile measurements to surface property changes
  - (carbon corrosion, hydrophobicity and surface oxidation)

Modeling

- Water profile modeling during carbon corrosion comparing overpotential and hydrophobicity changes to water transport
- Correlate experimental data with detailed membrane modeling to allow prediction of synergistic effects on membrane degradation
- Completion of Pt Dissolution Model and Pt Transport Model
  - Addition of impurity degradation
  - Inclusion of other component durability models into integrated model

Summary

- **Identify and Quantify Degradation Mechanisms**
  - Define, quantitate, elucidate durability of components and component interactions
  - Utilized Advanced Characterization Techniques
    - Data shown for: SANS, TEM, Neutron Imaging, XPS, DSC
  - Material variants include: ionomer, membrane, catalyst, support, electrodes
    - > 30 MEA variants, > 6 AST tests, > 3 fuel cell durability tests
- **Understand Electrode Structure Impact**
  - Correlate different electrode structures to fuel cell tests and durability
    - Potential correlation of electrode durability to mechanical strength
      - Likely due to ionomer structure and polymer interactions
  - Define different fabrication effects (esp. solvents) on electrode structure
    - NMP and glycerol-derived electrodes show good durability to potential cycling
- **Component and Component interactions**
  - Including GDLs, Bipolar Plates (graphite composite and metal), seals
- **Develop Models Relating Components and Operation to Durability**
  - Individual degradation models of individual fuel cell components
  - Development of integrated model of cell degradation
- **Strong Collaboration with Many other Durability Projects**
  - Shared materials, techniques, data

Thanks to

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

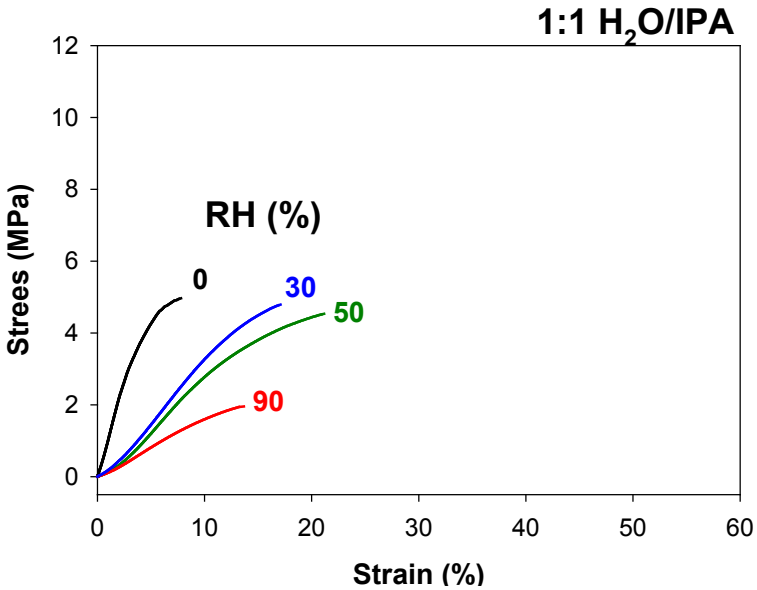
Other Acknowledgments:

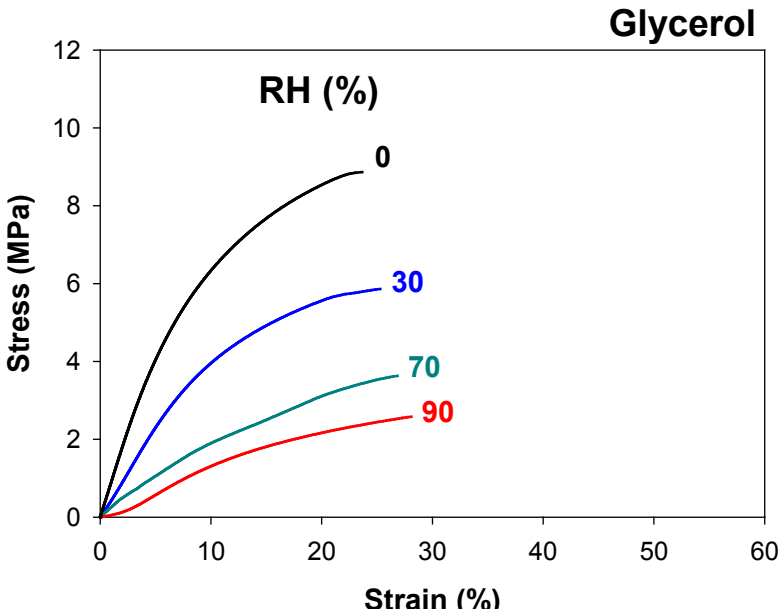
- SANS beam time provided by
  - Los Alamos Neutron Science Center: LQD beam line
  - NIST: NG3, NG7 beam lines
- Neutron imaging beam time provided by
  - National Institute of Standards and Technology: BT-2
- Other materials provided by:
  - W.L. Gore
  - Solvay
  - SGL Carbon Gmbh

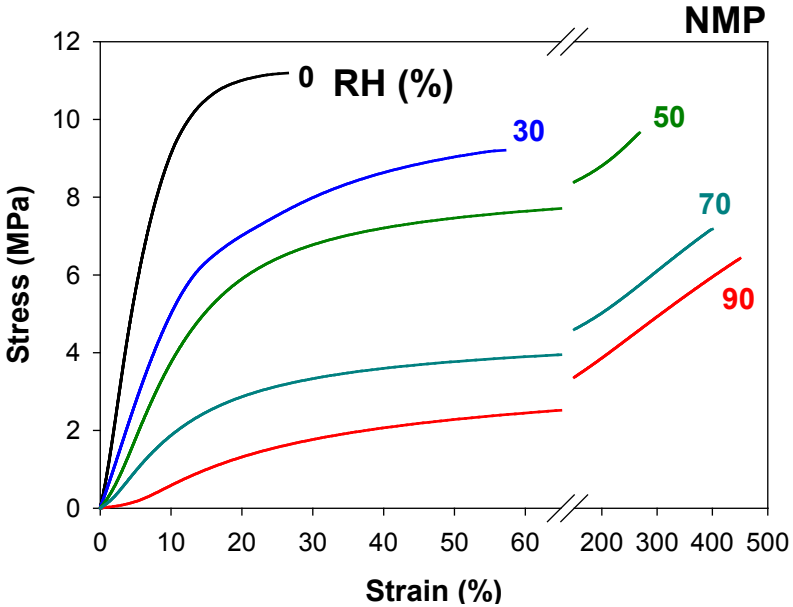
Back-up Slides

Mechanical Properties of Dispersion-Cast Nafion® Films

Solvent Effect



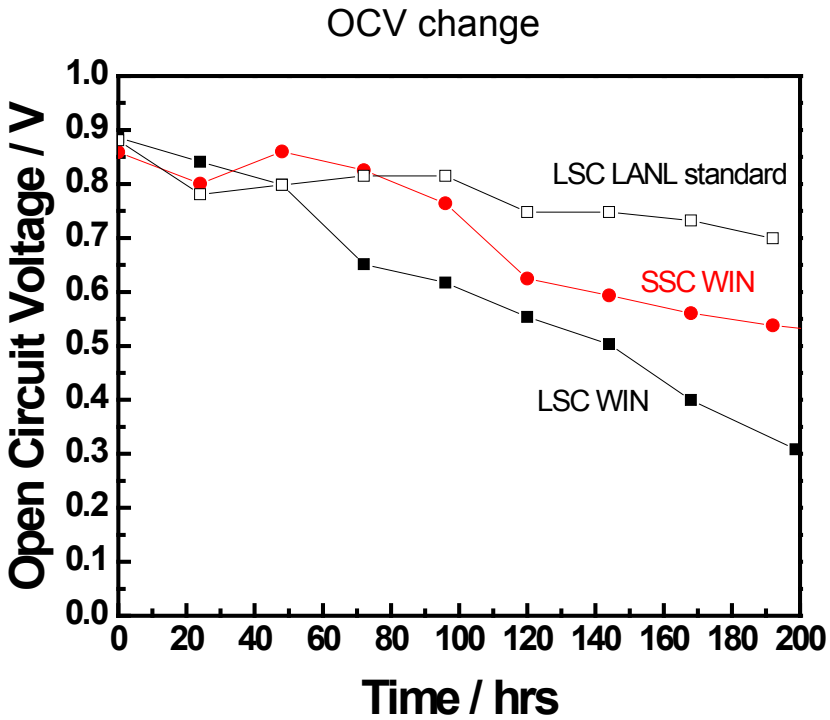


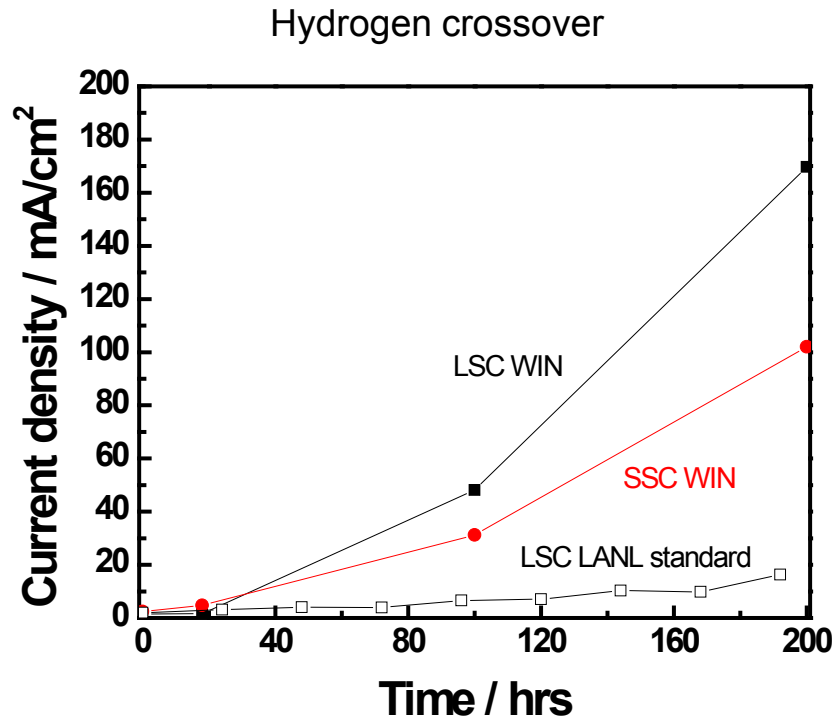


- Mechanical properties of the NMP film were best
- The glycerol-cast film showed better mechanical properties than the water/IPA-cast film
- Both NMP- and glycerol-derived electrodes show good durability to potential cycling; if correlation can be further established, this mechanical test could be used to screen quality of dispersions intended for electrodes

Los Alamos

Effect of Ionomer Type on MEA Chemical Stability





OCV test conditions: Cell temperature: 90C, RH: Anode/Cathode 30/30%, anode/cathode pressure 150 kPa
Crossover current was measured by USFCC "single cell test protocol, Nafion® 212 used for PEM

- ✓ PEM degradation is affected by ionomer type and electrode structure
- ✓ The MEA using SSC ionomer at the cathode electrode showed better durability than the MEA using LSC ionomer
- ✓ LSC electrode prepared from glycerol /water/alcohol dispersing solvent (LANL standard) showed better durability than electrode prepared from water/alcohol dispersing solvent; even better durability expected when 100% glycerol solvent is used (future work)

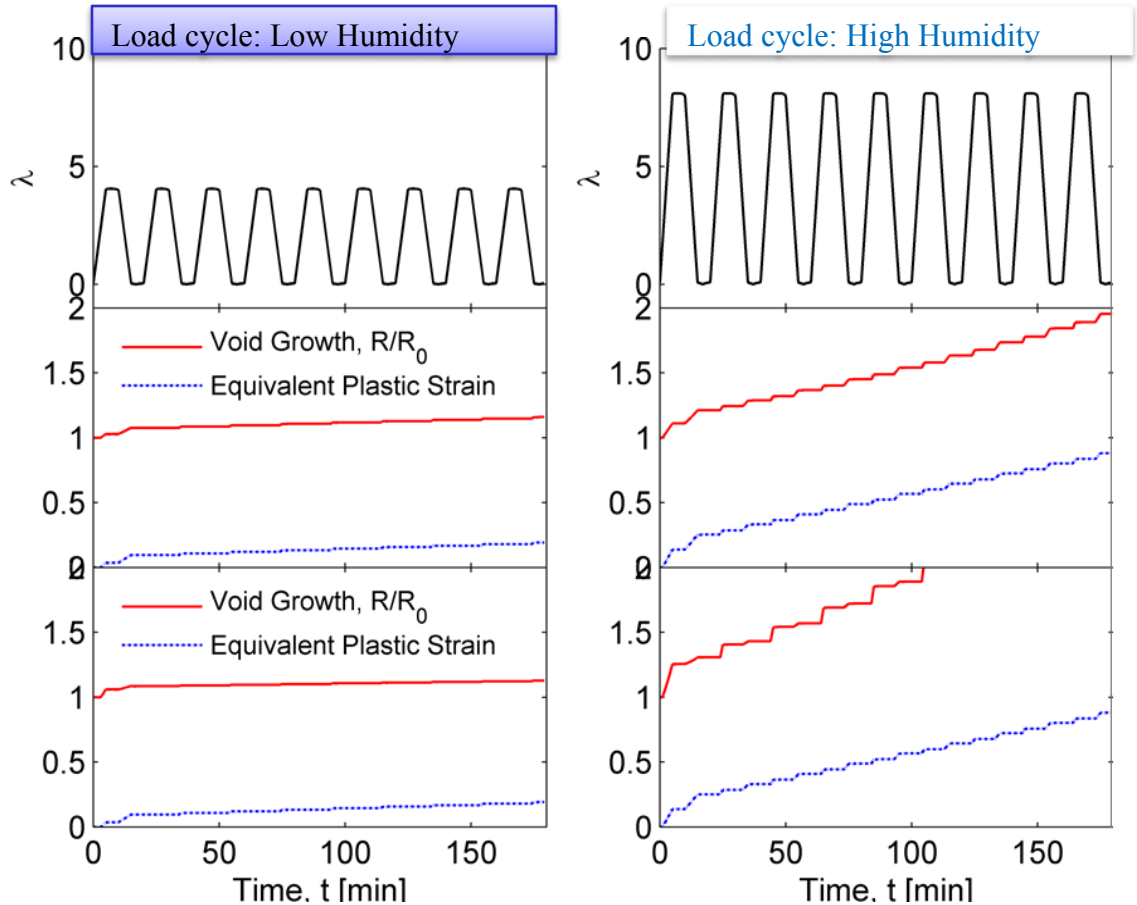
Los Alamos

Membrane's in-situ Response: Void-growth

- Mechanical RH cycling

Low Compression Pressure is 0 MPa

High Compression Pressure is 5 MPa



Can account for shape change by examining what type of in-plane stresses

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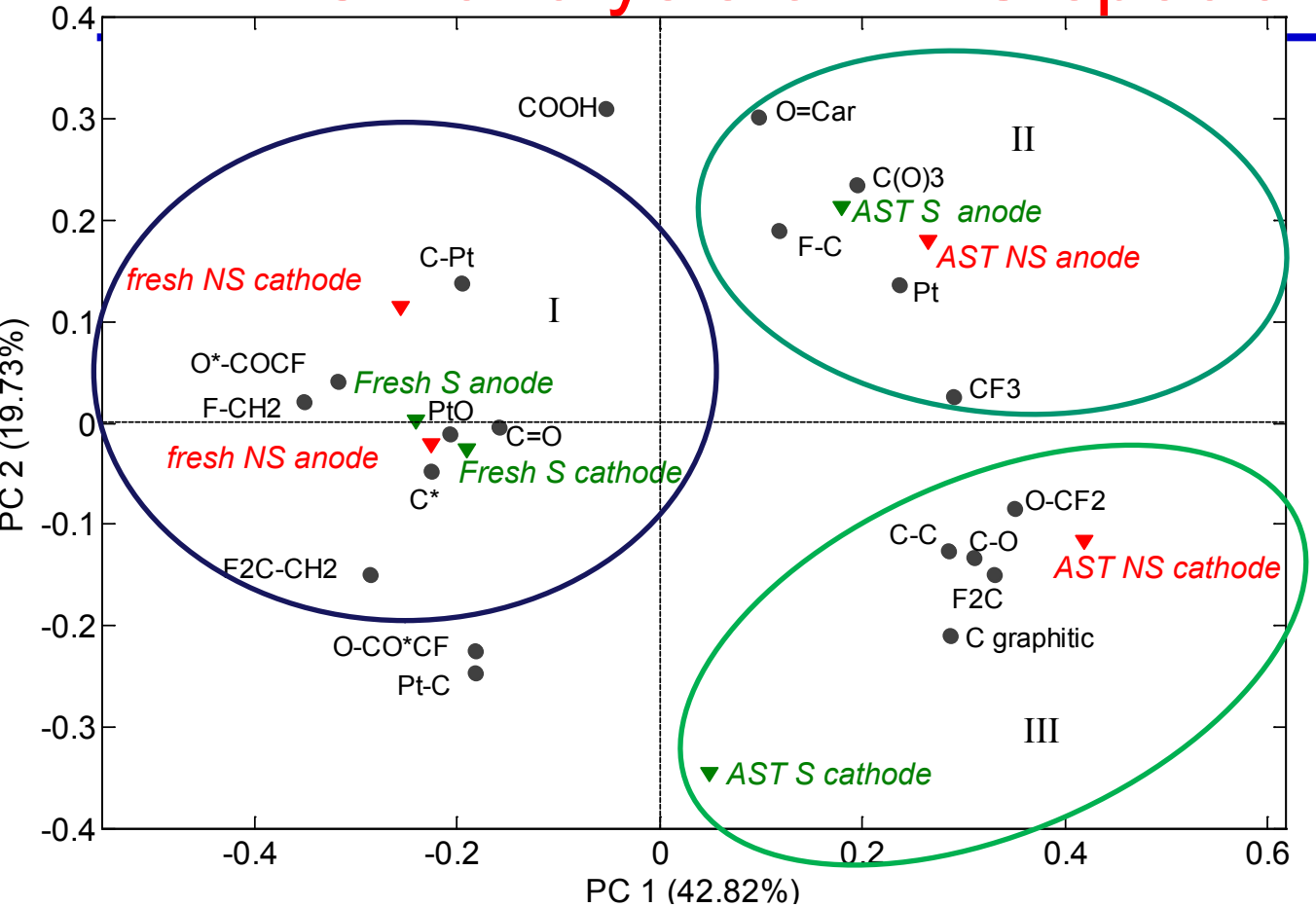
PCA analysis of XPS speciation



- Tested samples are separated from fresh samples by PC1.
- Tested anode samples separated from tested cathode samples by PC2

- Following clustering of samples and associated significant variables is observed:

I. I. All FRESH samples – have higher than tested amounts of PtO, Pt-C, F-CH_2, COOH species

II. II. Anode NS and S samples – have highest amount of metallic Pt, CF_3 and CO_3

III. III. Cathode NS and S samples – have highest graphitic and aliphatic C and telf

The further from y-axis to the right the samples and associated variables – the larger separation of them from group of fresh samples on the left from y-axis.
Degree of difference introduced by AST is the following (from least to largest):
S cathode< S anode<NS anode<NS cathode

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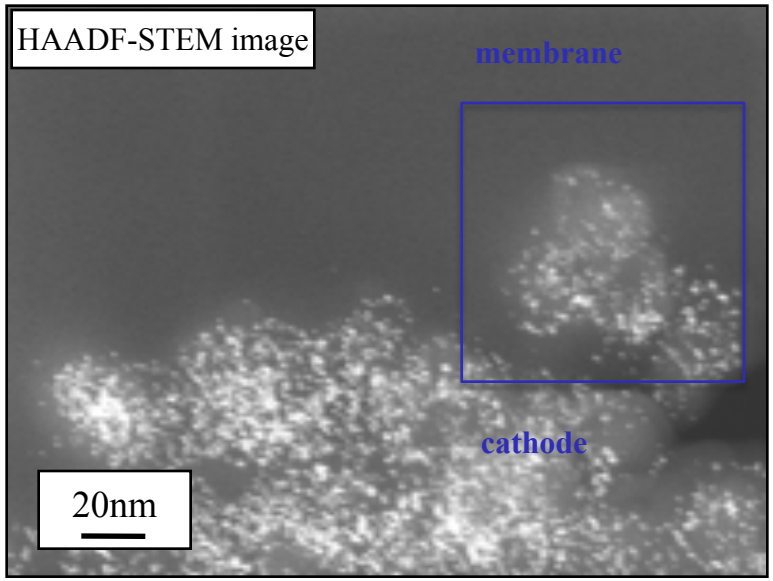
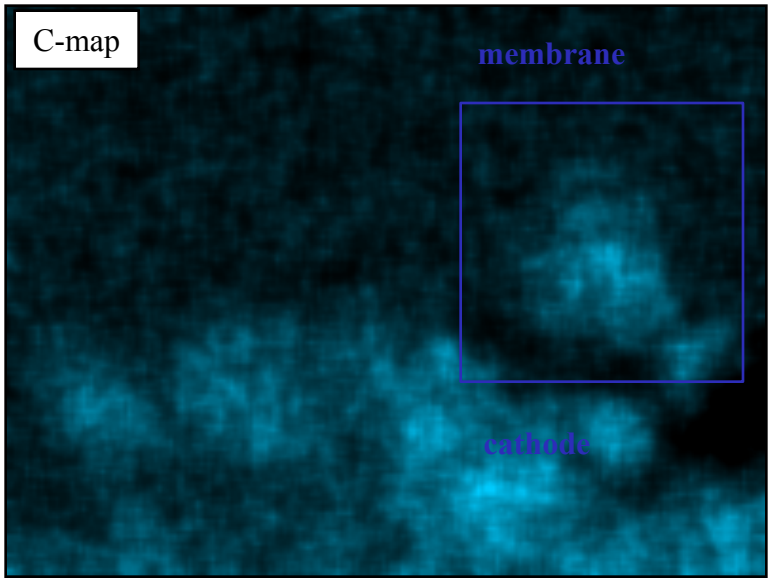
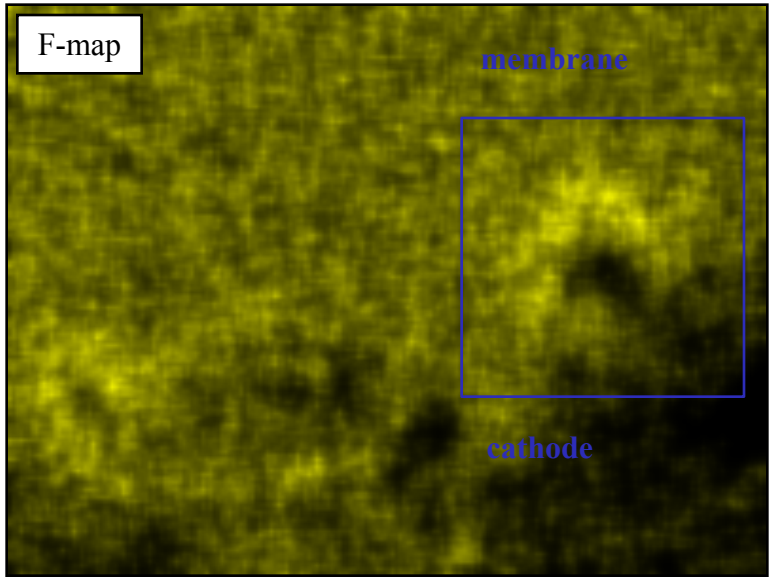
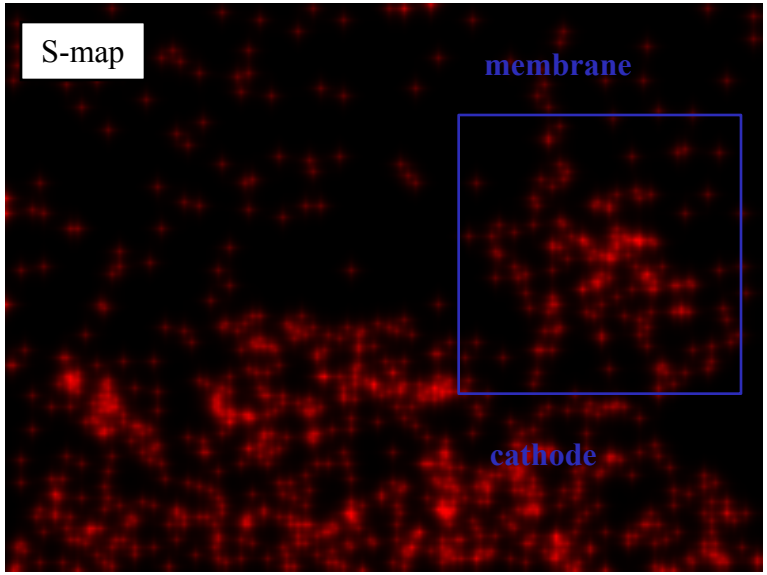
Fresh MEA (non-stabilized ionomer)









Fluorine appears highest in localized regions adjacent to cathode. Sulfur is highest within the electrode (associated with Pt/Carbon regions?)

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