Durability Improvements Through Degradation Mechanism Studies

DOE 2013 Annual Merit Review Meeting

May 13 - 17, 2013

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 Power Systems, Ion Power
University: University of New Mexico

Organizations / Partners /Collaborators

- **Los Alamos National Lab (LANL)**
- R. Mukundan, J. Davey, D. Spernjak, J. Fairweather, K. Rau , R. Lujan, D. Langlois, D. Torraco, J. Chlistinoff; Applied Science Task; D. Langlois, N. Mack, M. Hawley and Y. S. Kim

- **Argonne National Laboratory (ANL)**
  – Rajesh Ahluwalia, Srikanth Arisetty, Dionissios D. Papadias

- **Lawrence Berkeley National Laboratory (LBNL)**
  – Adam Weber, Ahmet Kusoglu, Kyle Clark

- **Oak Ridge National Laboratory (ORNL)**
  – Karren More, Mike Brady

- **Ballard Power Systems (BPS)**
  – Paul Beattie, Silvia 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 (Federal Portion)

As Proposed 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 90% through project: ~ 4 months left

Participant	FY13 (Year 4)
LANL	$1400k
Industrial + Univ. Partners (Ballard, Ion Power, UNM)	
Other National Labs (ANL, LBNL, ORNL)	$1250k

- LANL
- Applied Science
- ORNL
- ANL
- LBNL
- Ion Power
- Ballard
- UNM
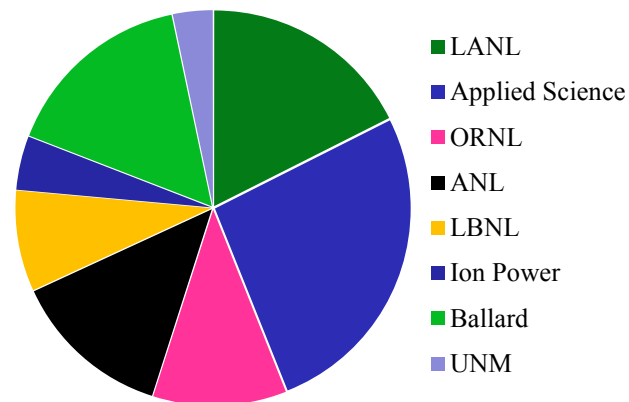
Relevance and Objectives

- **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

[h] Based on U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and Polarization Curve Protocols (http://www.uscar.org/commands/files_download.php?files_id=267), Table 6, <10% drop in rated power after test.

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

Modeling Development Schematic

Two sets of models are under development: component-specific durability models and combined reaction-diffusion model for performance degradation

Membrane Durability (LBNL, LANL)

- OCV, FER, and pinhole formation/growth
- Water uptake of degraded samples
- Mechanical Properties, crystallinity

Catalyst Stability (ANL, LANL, Nuvera)

- Pt dissolution
- Particle growth
- Pt Transport
- ECSA loss
- ORR activity loss
- Mass transfer losses

Material Characterization

- TEM (ORNL)
- XPS (UNM)
- Performance testing, Electrochemical, Materials (LANL)
- Carbon Plates (Ballard)
- Seals (Ballard)
- Membrane properties, GDLs, MEAs (LBNL)

Support Durability (ANL, LANL)

- Kinetics of carbon corrosion
- Performance degradation due to carbon corrosion

**Integrated Model (ANL)
Single Component Models (ANL, LBNL)**

MEA Design (Ion Power, LANL)

Pt loading
Electrode thickness
Pt/C/I ratios
Ionomer and membranes

Others:
   SGL Carbon
   W.L. Gore
   Tanaka
   DuPont
   Solvay
   ETEK

Bipolar Plate Durability (ANL, LANL, NREL, ORNL)

- Kinetics of protective oxide growth and metal dissolution
- Interfacial contact resistance

Membrane/Electrode Durability (ANL, LANL)

- Electrode degradation correlation
- Performance degradation due to ionomer degradation

Modified catalyst durability model to account for changes in Pt size distribution due to carbon corrosion

- Growth in size of Pt particles: coalescence kernel derived from BOT and EOT size distributions (TEM data)

- Loss of electrical contact with Pt particles: decrease of Pt utilization determined from measured ECSA and Pt size distribution

- Densification of cathode catalyst layer (TBD)

- ECSA loss is due to the combined decrease of Pt utilization and coalescence with V-type carbon, and is primarily due to decrease in Pt utilization with E-type carbon
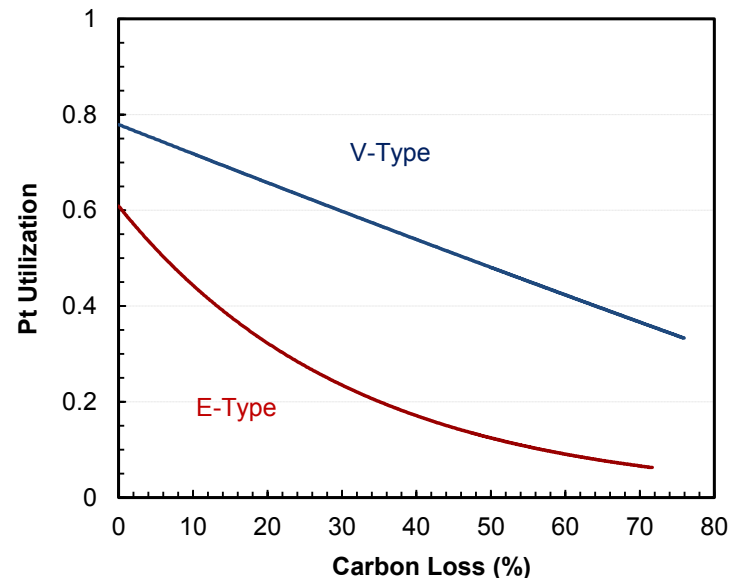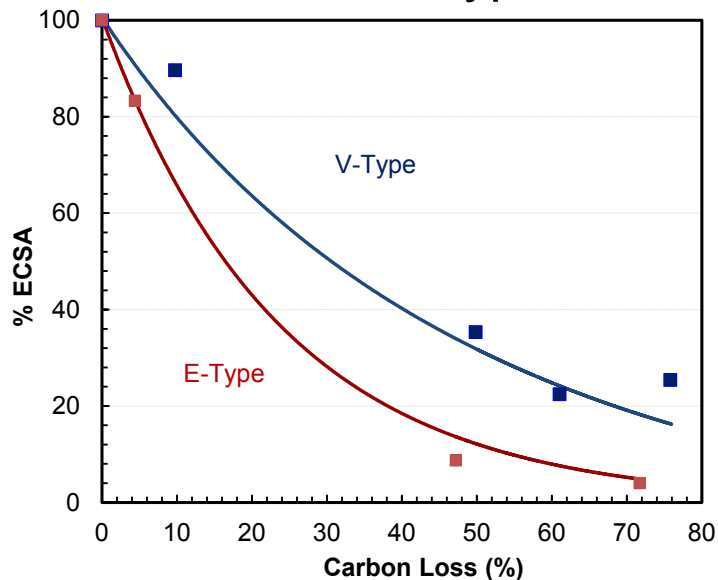
Carbon Corrosion: CO$_2$ via NDIR

High Surface Area (E), Intermediate (V), Low (graphitized - EA)

80°C, 100%RH, H$_2$/N$_2$, 5 mV/s scan

High surface area (Pt on Tanaka E)

Intermediate (Pt on Vulcan XC-72)

Graphitized (Pt on Tanaka EA)
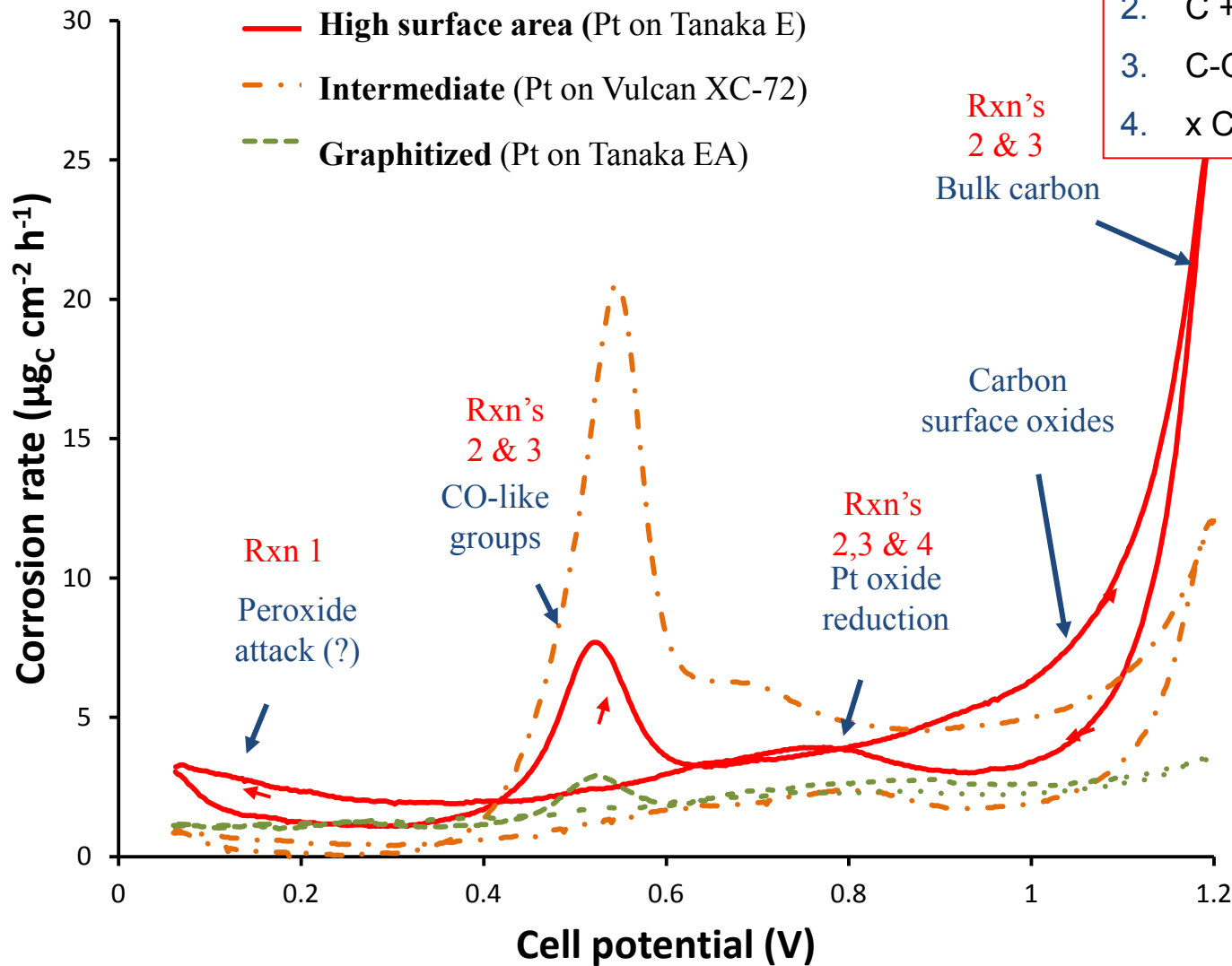
1. $C + H_2O_2 \rightarrow CO_2 + 2\,H^+ + 2e^-$
2. $C + H_2O \leftrightarrow C\text{-}O + 2\,H^+ + 2e^-$
3. $C\text{-}O + H_2O \rightarrow CO_2 + 2\,H^+ + 2e^-$
4. $x\,C + H_2O \leftrightarrow C_x\text{-}O + 2\,H^+ + 2e^-$

Rxn's 2 & 3
Bulk carbon

Carbon surface oxides

Rxn's 2 & 3
CO-like groups

Rxn's 2,3 & 4
Pt oxide reduction

Rxn 1
Peroxide attack (?)

Completed models for Pt catalyzed corrosion of Ketjen black (E-type), Vulcan® XC-72 (V-type) and graphitized carbon (EA-type) supports

- Determined rate constants from CO$_2$ emission data for potentiostatic and cyclic potentials at different T, RH and scan rates
- Related Peak I to corrosion by peroxide, Peak II to surface coverage by active oxides, and Peaks III and IV and hysteresis to Pt and surface coverage by passive oxides

Corrosion rate (µg$_C$ cm^{-2} h^{-1})

Cell potential (V)

Support Aging Effects: Variety in Carbon Surface Oxides

High surface area
(Pt on Tanaka E)

Intermediate
(Pt on Vulcan XC-72)

Graphitized
(Pt on Tanaka EA)
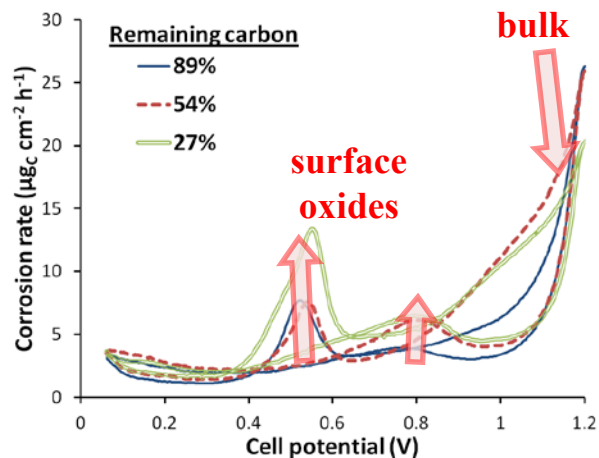
Surface oxides increase as bulk carbon and Pt decrease
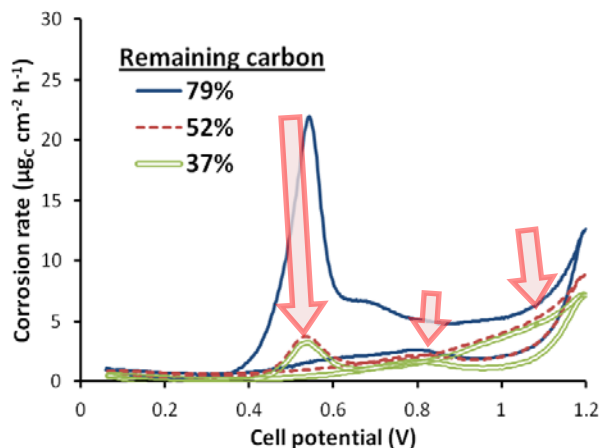
All surface and bulk signals drop with aging
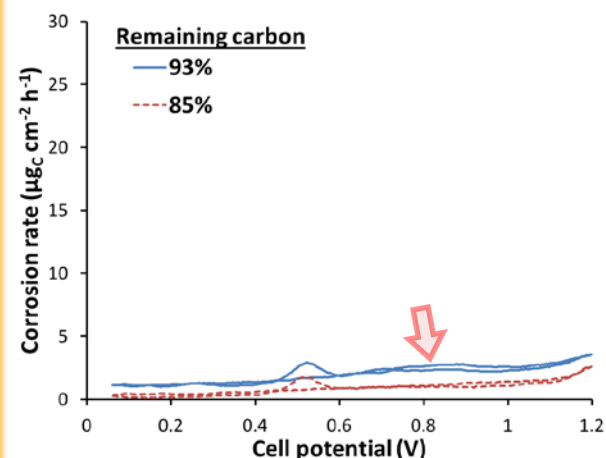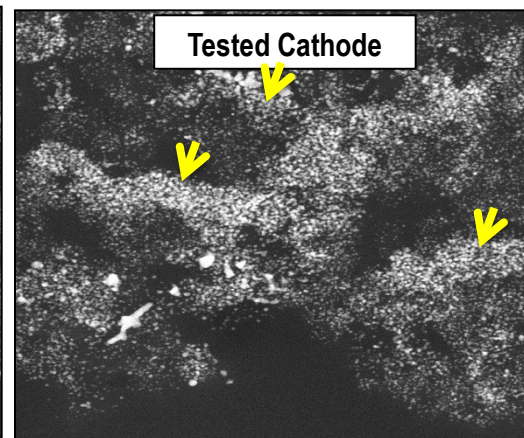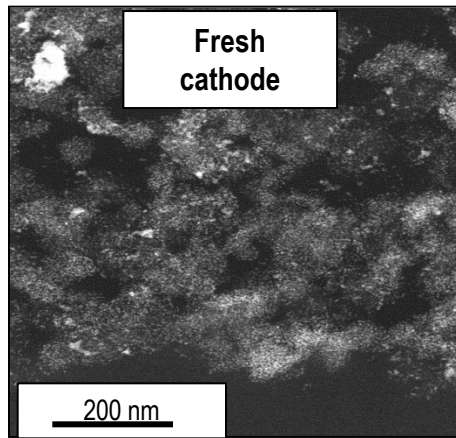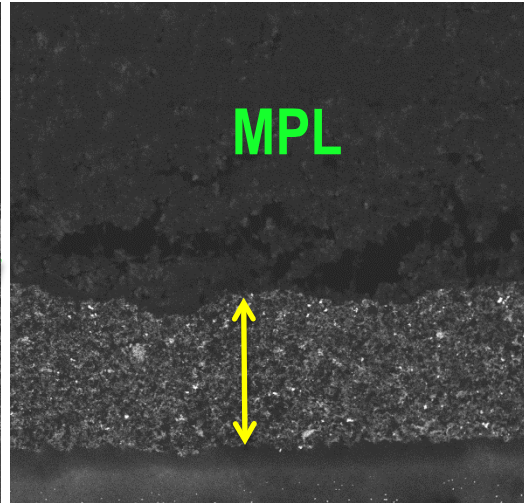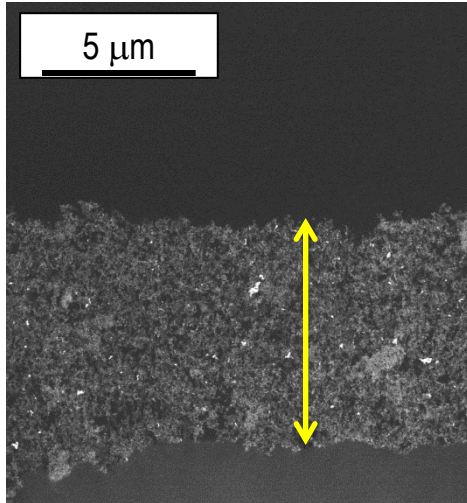
Low initial corrosion rate → small changes only
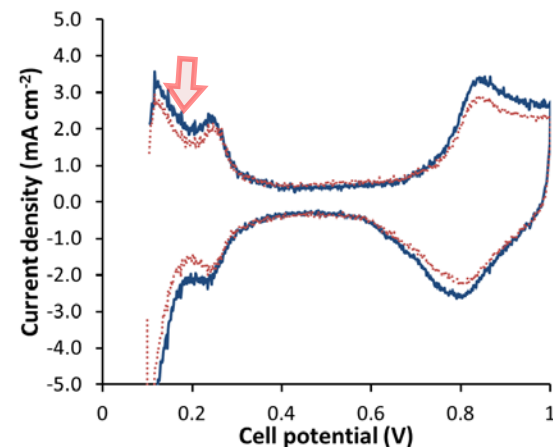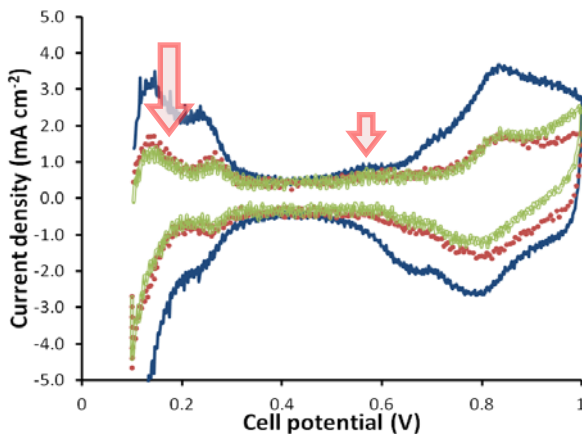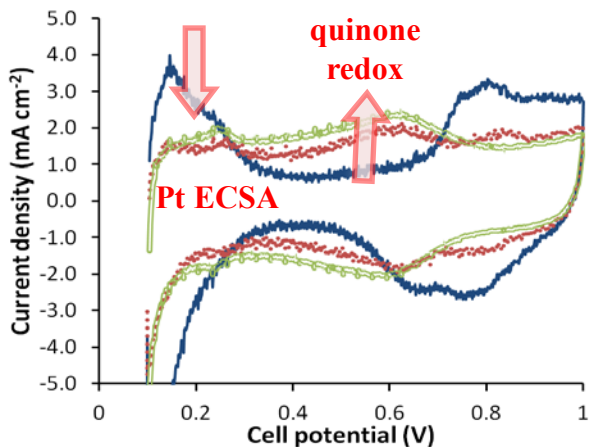
- **Activation process occurs at OCV, and may be somewhat independent of potential**
  → chemical reduction of passive oxides, or chemical attack leading to active oxides

Microscopic Characterization of Degradation During DOE/FC Tech Team Drive Cycle

Fresh cathode

5 μm

Tested cathode

MPL

Fresh cathode

Tested Cathode

200 nm

Elemental Analysis by XPS

Graphitic Carbon

Oxygen O1s

Carbon Corrosion AST (1.2V) Time / Hr

Ion Power MEAs with different carbon support

- MEA 0.2mg/cm2 of TEC10E20E - Cgr
- MEA 0.4mg/cm2 of TEC10E40E - Cgr
- MEA 0.15mg/cm2 of TEC10V40E - Cgr
- MEA 0.2mg/cm2 of TEC10E20E - O1s %
- MEA 0.4mg/cm2 of TEC10E40E - O1s %
- MEA 0.15mg/cm2 of TEC10V40E - O1s %
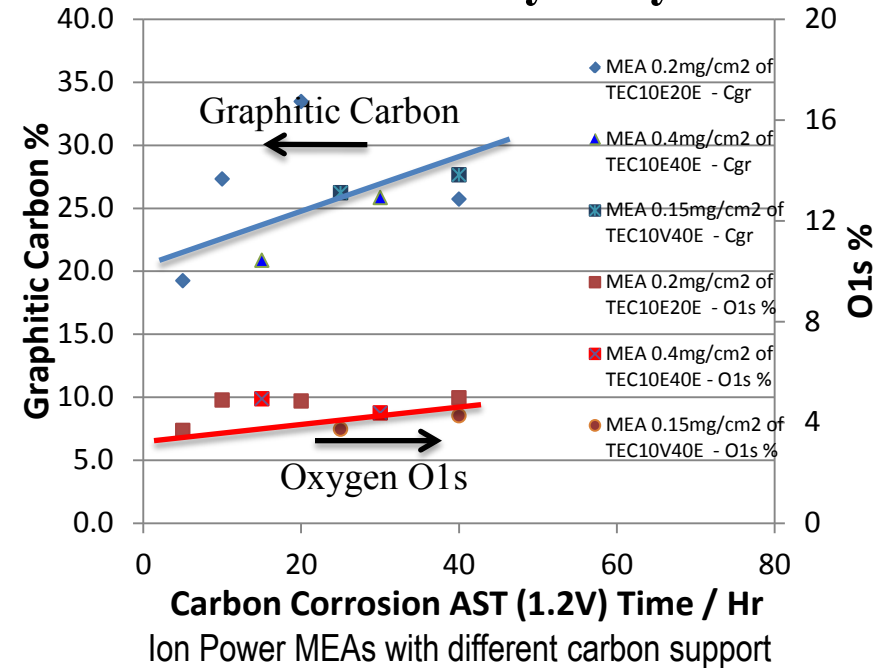
- Graphitic content increases (as %)
  - Likely → decrease of amorphous carbon
- Oxygen content increases
  - Likely → increasing oxygen content on carbon surface
- Changing hydrophobicity effects transport

~30% compression/thinning of cathode layer due to "localized" HSAC corrosion

Gore® "fresh" vs. Drive Cycle Tested (389 hr wet/dry drive cycle)

HAADF-STEM images

Microscopic Characterization of Carbon Corrosion
(After DOE Drive Cycle Test)
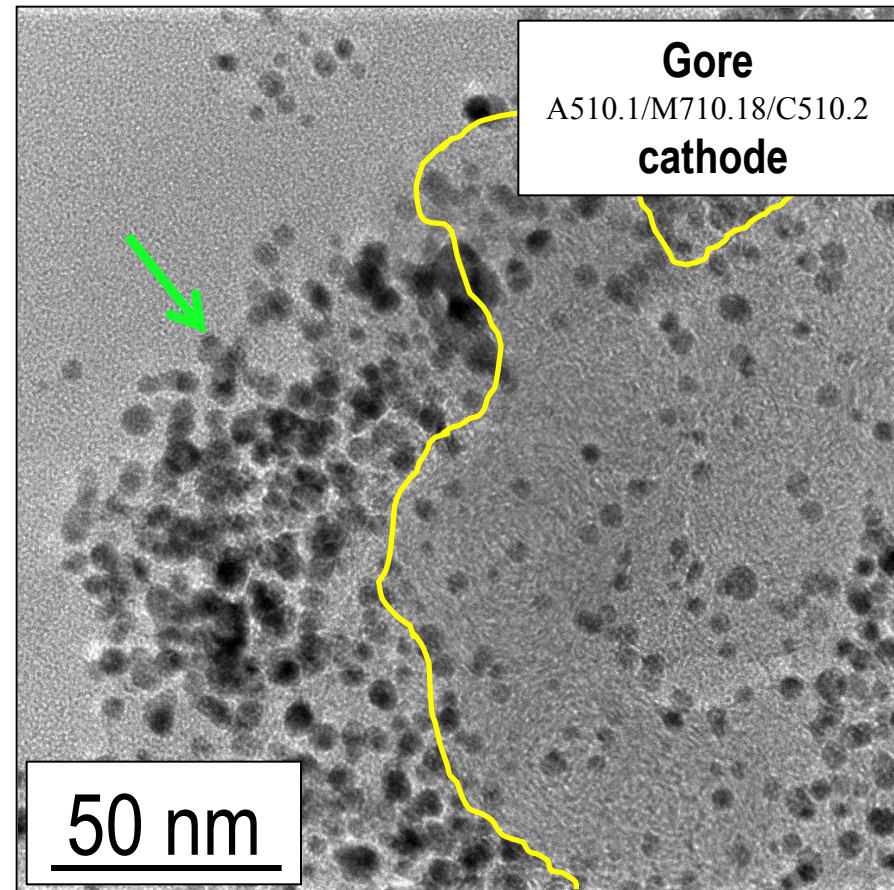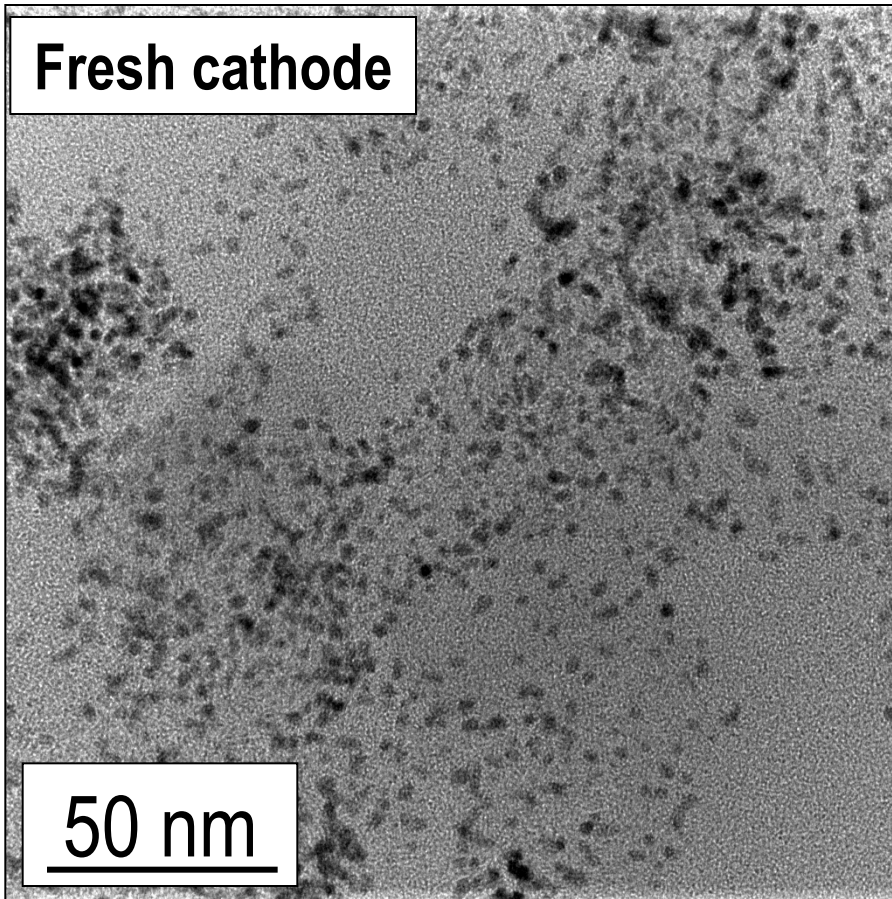
- **"localized bands" of HSAC corrosion (green arrow), which are correlated to increased Pt particle sizes and closer Pt-Pt interparticle spacings. Typically, these oxidized regions of carbon surround non-oxidized regions (inside yellow outline).**
- **Regions of non-oxidized HSAC retain graphitic structure and are correlated with smaller Pt particle sizes**

TEM images

Modeling Carbon Corrosion : Effect of Aging

Determined the effect of aging on the specific surface area of carbon (S_C, m^2-C/g-C) for the three supports

- S_C increases with aging of E-type carbon, consistent with the observed increase in double-layer capacitance
- Smaller increase in S_C of V-type carbon
- Data for EA-type carbon in progress

Specific Surface Area of Carbon (m^2/g)				
Carbon Loss	0%	25%	50%	75%
E-Type	735	1250	1840	2135
V-Type	250	390	410	625
EA-Type	236 (TBD)			
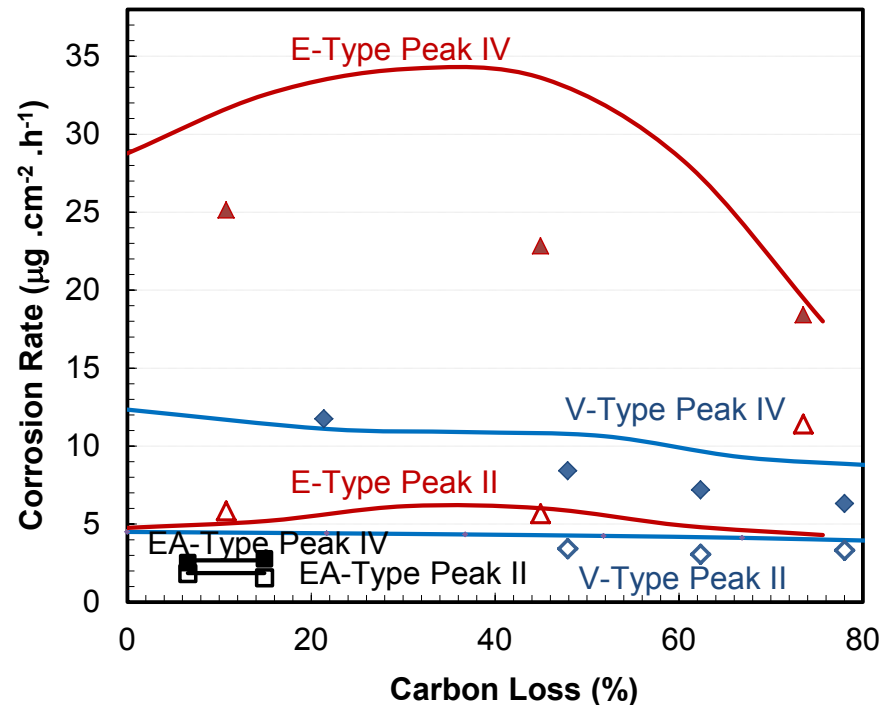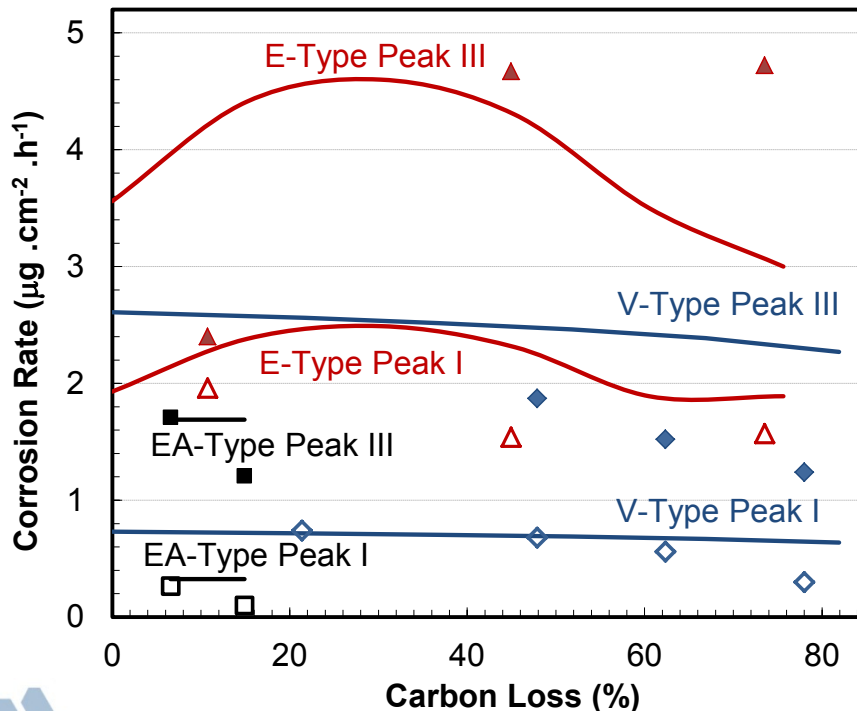
Catalyst Degradation: E vs. EA (Bilayer)
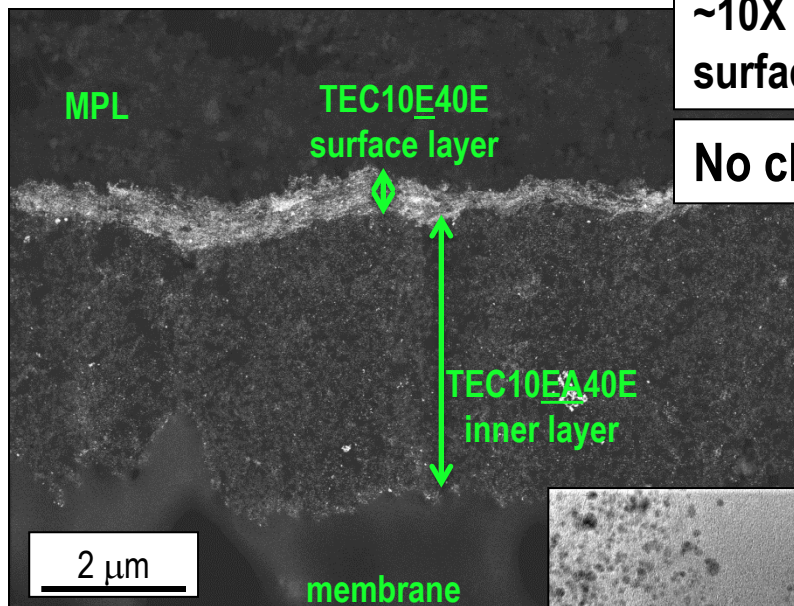
~10X compression/thinning of E-carbon surface layer due to carbon corrosion
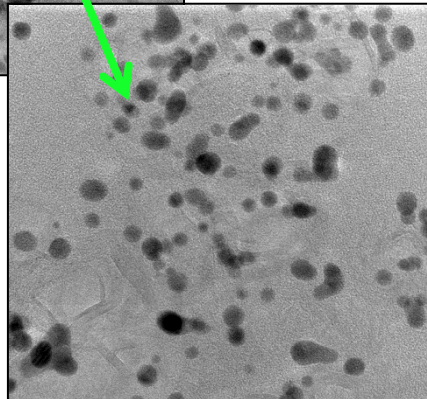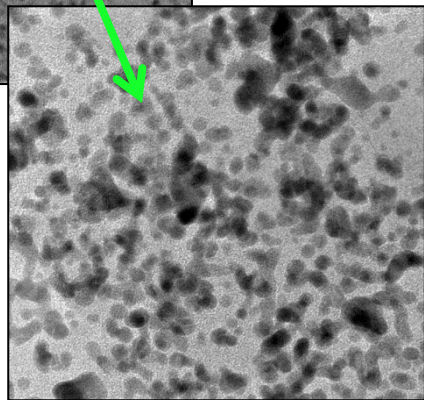
No change to EA-carbon layer

% change in Pt particle size much greater for Pt supported on E-carbon in surface layer than Pt particles supported on EA-carbon in inner layer
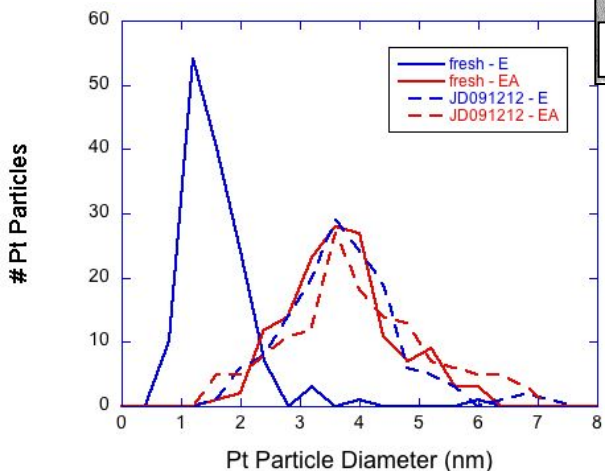
MPL
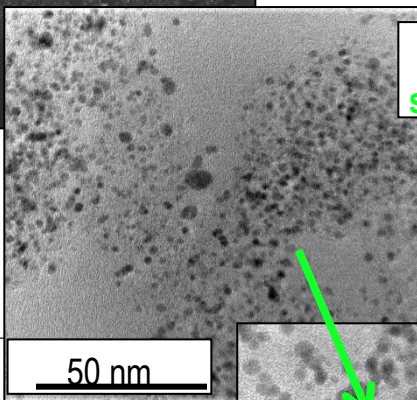
TEC10E40E surface layer

TEC10EA40E inner layer

2 μm

membrane

TEC10E40E surface layer

50 nm
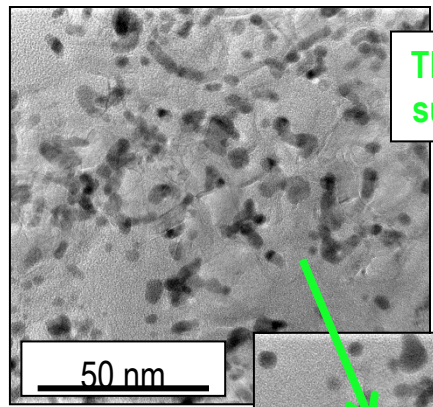
TEC10EA40E surface layer

50 nm

HAADF-STEM image

Pt Particles

Pt Particle Diameter (nm)

fresh - E
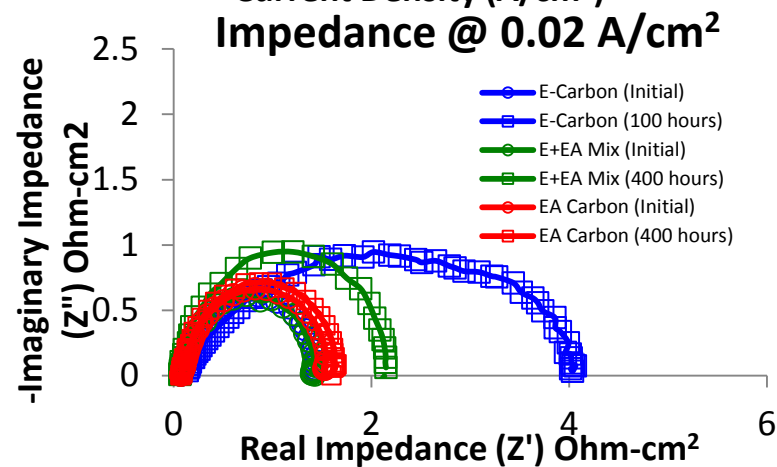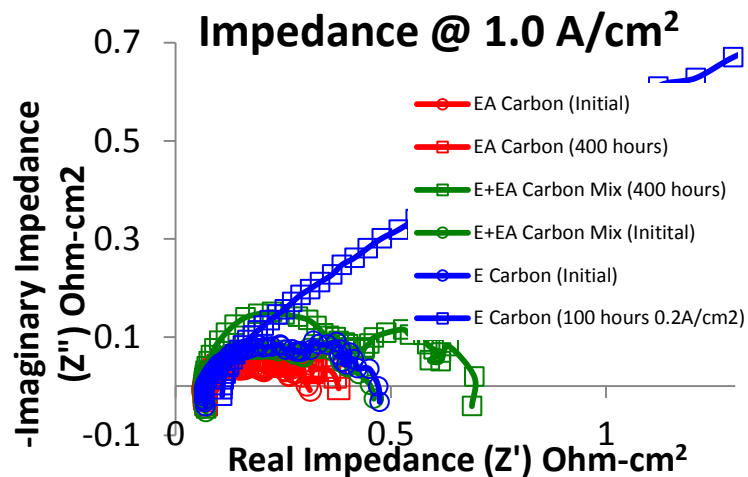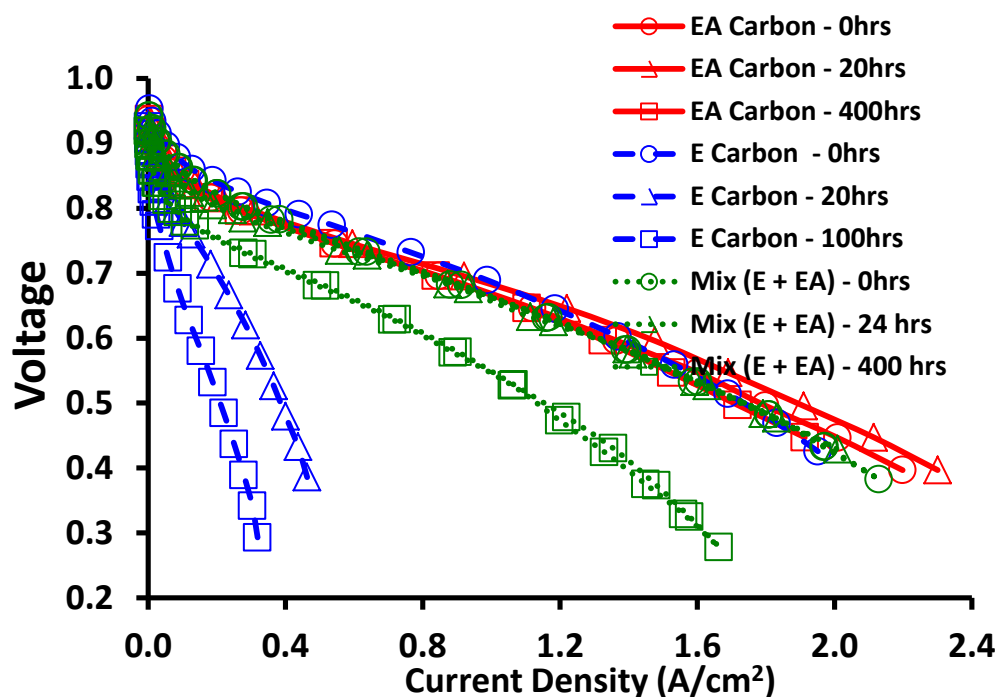fresh - EA
JD091212 - E
JD091212 - EA

Comparison of Carbon Corrosion – Potential Mitigation of Transport Losses → Mixing Stable Materials to Keep CL Structure

Waterfall Plot of Mass Activity and ECSA
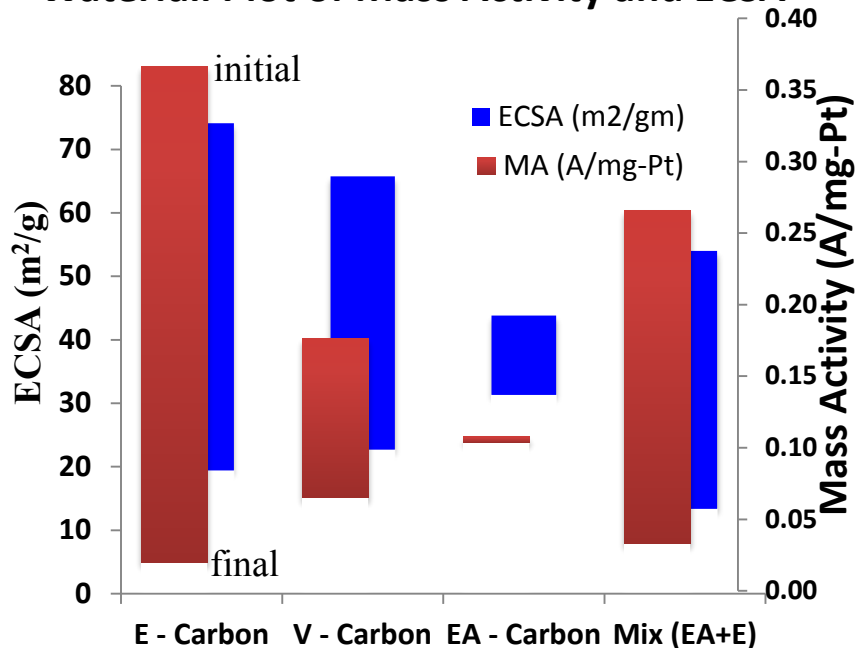
Polarization Curves after Time at 1.2 V Hold

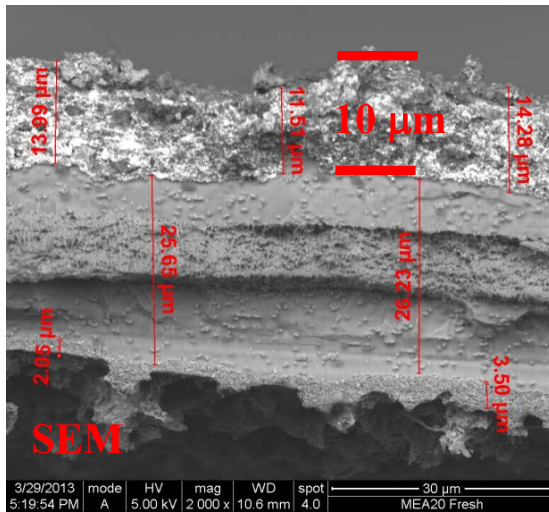**Impedance @ 1.0 A/cm²**

Impedance @ 0.02 A/cm²

Note: MEA Pt loadings were: 0.15 mg/cm² (E) / 0.15 mg/cm² (Ea+E) / 0.25 mg/cm² (EA)
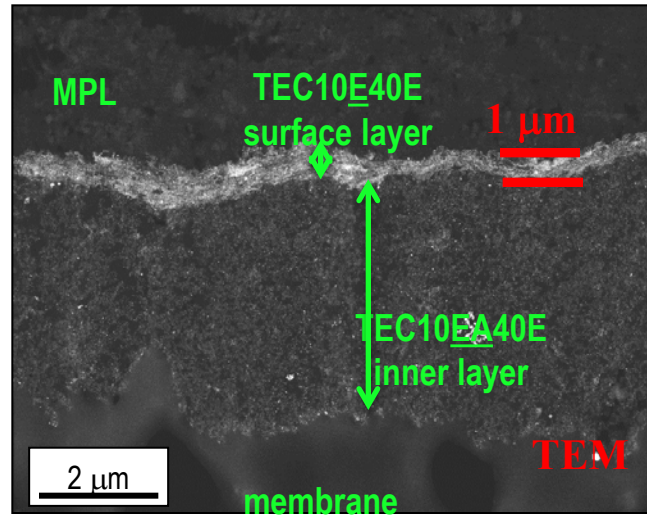
Comparison of Carbon Corrosion – Potential Mitigation of Transport Losses

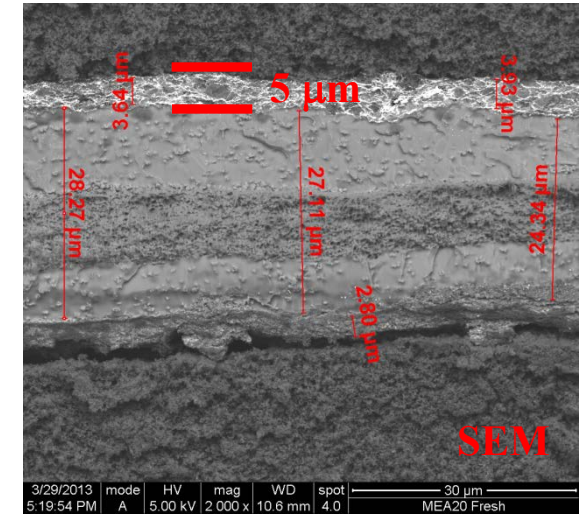## Mixing Carbon Support Materials to Keep CL Structure and Activity

Fresh MEA (EA)   **Tested MEA (E)**   **Tested MEA (EA+E)**

- **High Surface Area Carbon shows 10x decrease in CL thickness ~ 1 µm after test**
- **Mixed with graphitized carbon shows ~ 50% decrease in CL thickness**
  - **Keeps porosity available for transport**
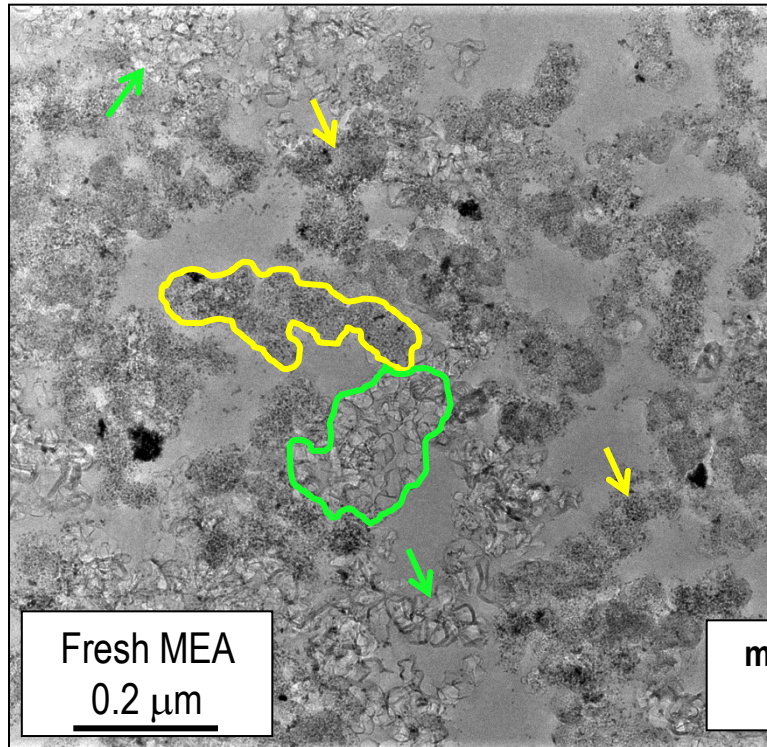- **Pt particle size growth observed for both types of carbon**

Carbon Corrosion AST – 1.2 V potential hold

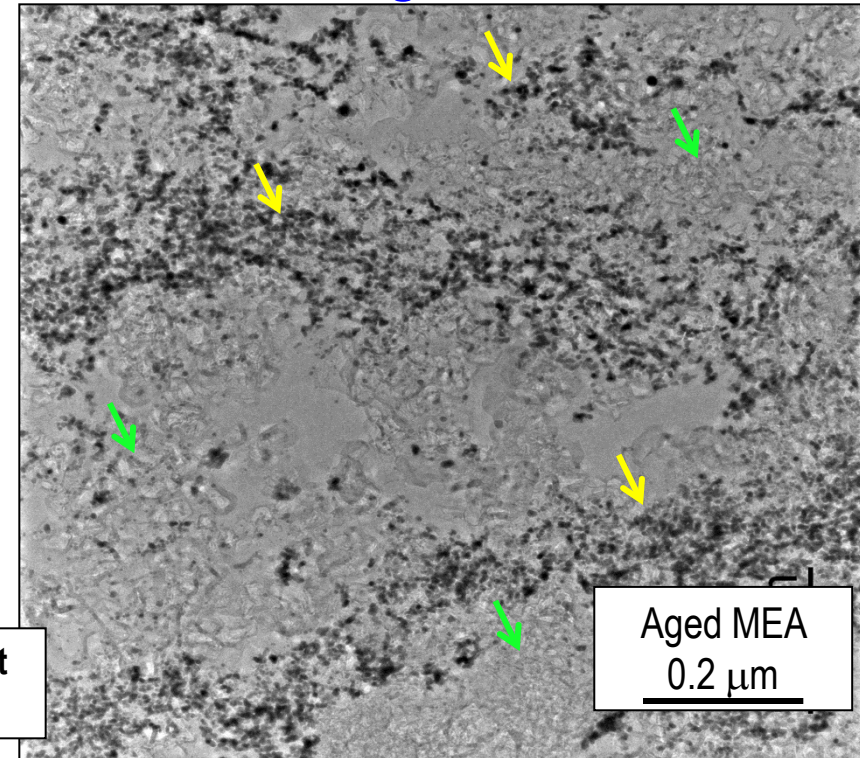Note: MEA Pt loadings were: 0.15 mg/cm² (E) / 0.15 mg/cm² (EA+E) / 0.25 mg/cm² (EA)
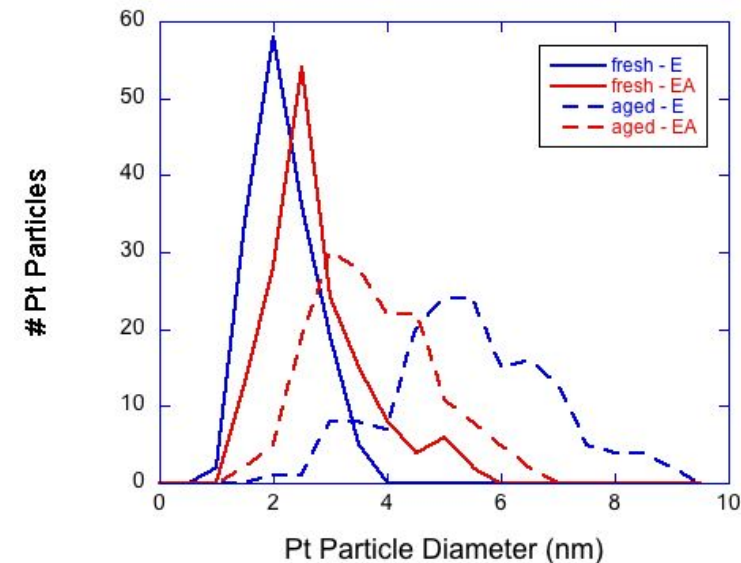
# Mixed Catalysts (E + EA) – Fresh vs. Carbon AST

Fresh

Aged

Fresh MEA
0.2 μm

membrane is at bottom

Aged MEA
0.2 μm

- E-carbon regions (yellow) are distinct and separate from EA-carbon regions (green)

- Regions remain distinct and separate
- Note "directional" banding of oxidized E-carbon vs. non-oxidized EA-carbon parallel to membrane

- **EA mixed with E maintains pore structure of CL – maintains transport**
- Show preferential oxidation of E-carbon forming bands of dense "graphite-oxide" encapsulating large Pt nanoparticles
- The bands are oriented parallel to membrane surface in compression direction.
- EA-carbon shows essentially *NO* oxidation, retaining its graphitic structure -   Pt particle size changes are significant for E-carbon and little for EA-carbon.

Mixed Catalysts (E + EA) – Fresh vs. Carbon AST
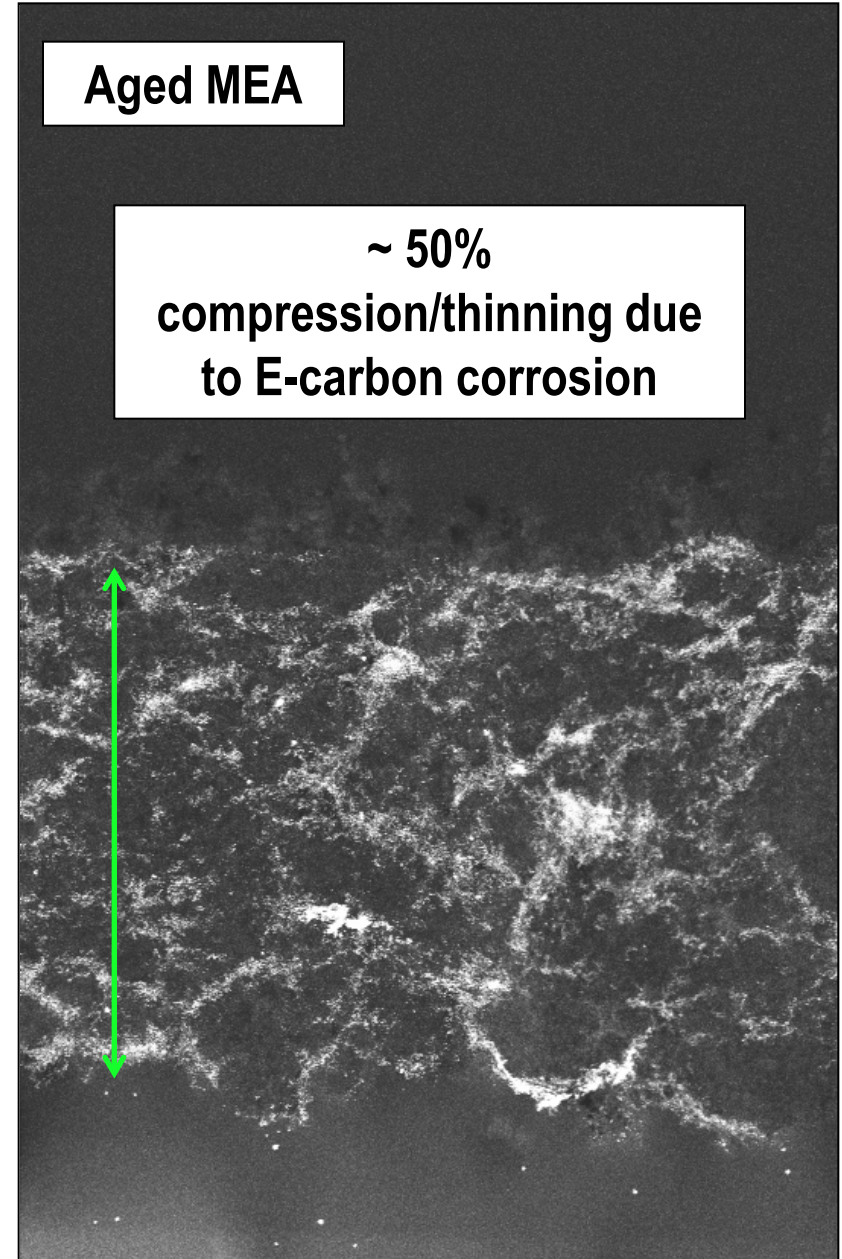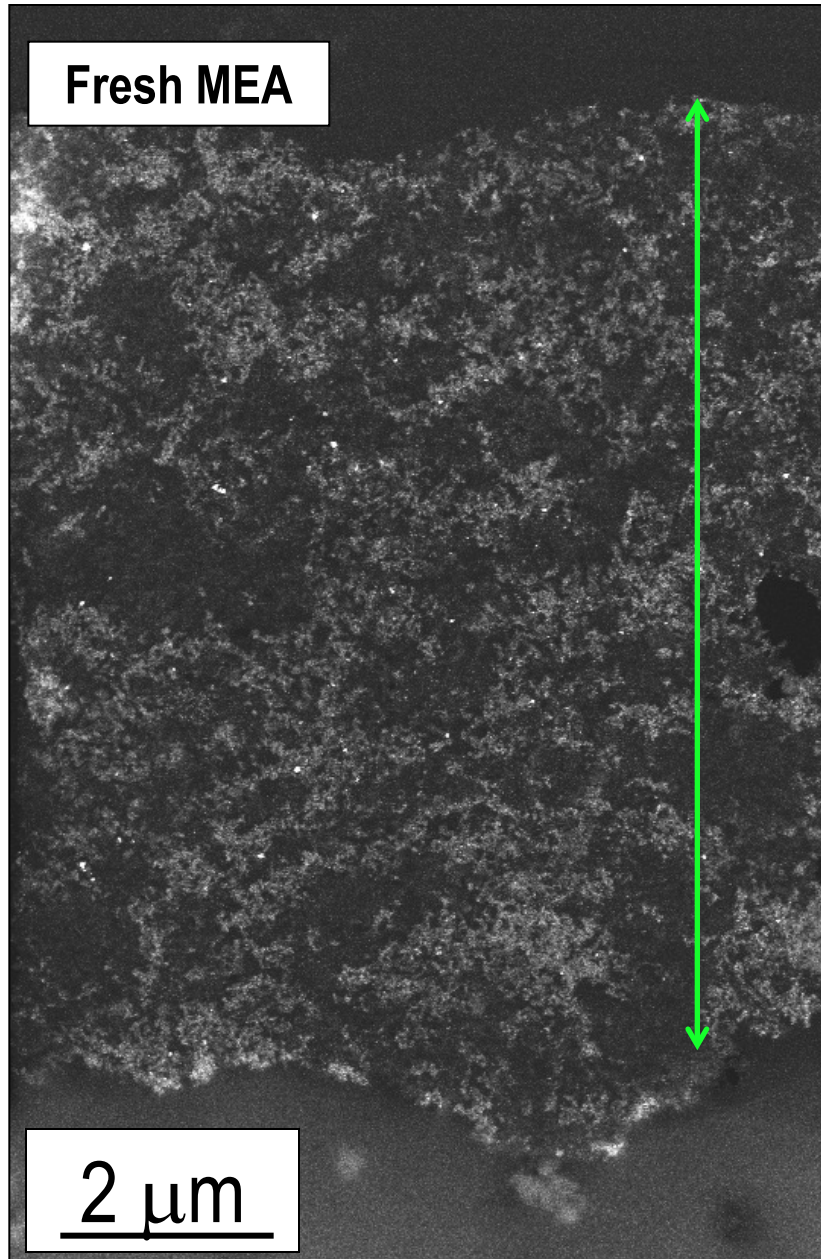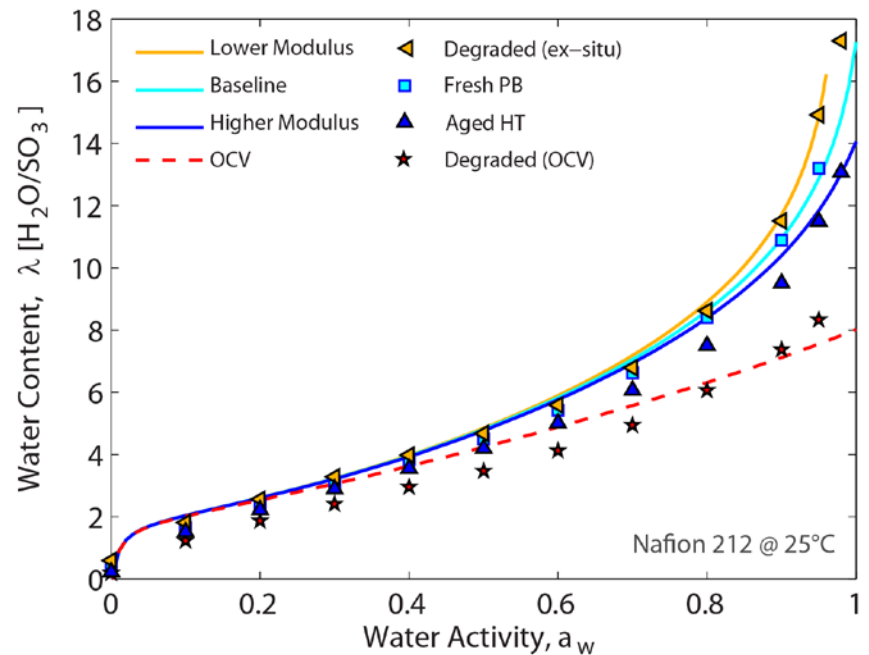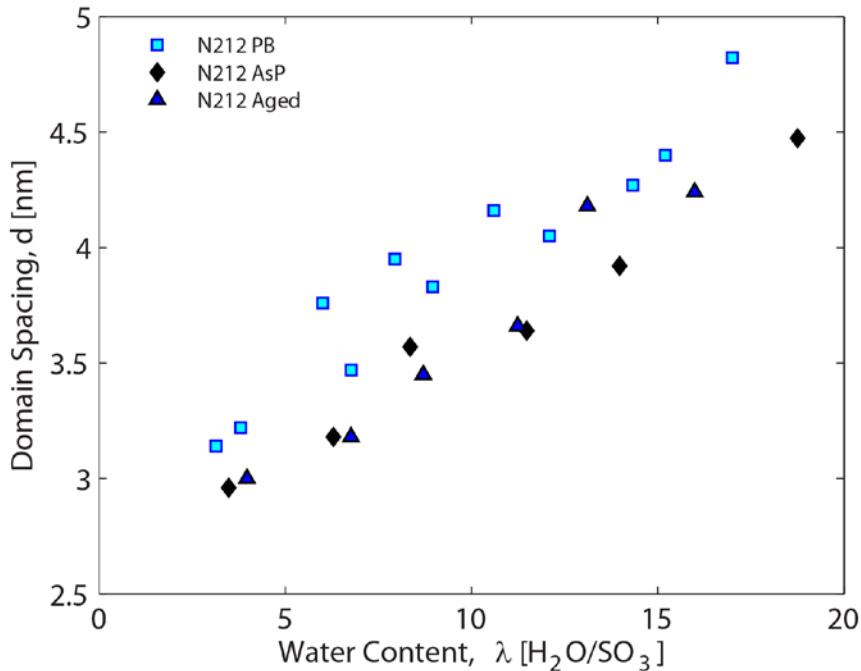
- **Model Parameters**

  We continue measuring properties for model

- **Structural** (see below)

- **Chemical** (EW)

- **Mechanical** (modulus)

- **Sorption Model (in-progress)**

Structural	•Domains •Phase-Separation
Chemical	•Interactions •EW (IEC)
Mechanical	•Backbone Modulus •Crystallinity

$a_p(\lambda)$

E_{pm}

Water

Humidifed Air
$a_w(RH)$

Legend (left plot):
- N212 PB
- N212 AsP
- N212 Aged

Domain Spacing, d [nm] vs Water Content, λ [H_2O/SO_3]

Legend (right plot):
- Lower Modulus
- Baseline
- Higher Modulus
- OCV
- Degraded (ex–situ)
- Fresh PB
- Aged HT
- Degraded (OCV)

Water Content, λ [H_2O/SO_3] vs Water Activity, a_w

Nafion 212 @ 25°C

A. Kusoglu, S. Savagatrup, K.T. Clark, A.Z. Weber, *Macromolecules*, 45 (**2012**) 7467

SAXS (Small Angle X-Ray Scattering)
Results for membranes degraded by different protocols

Nafion® 212 Membrane
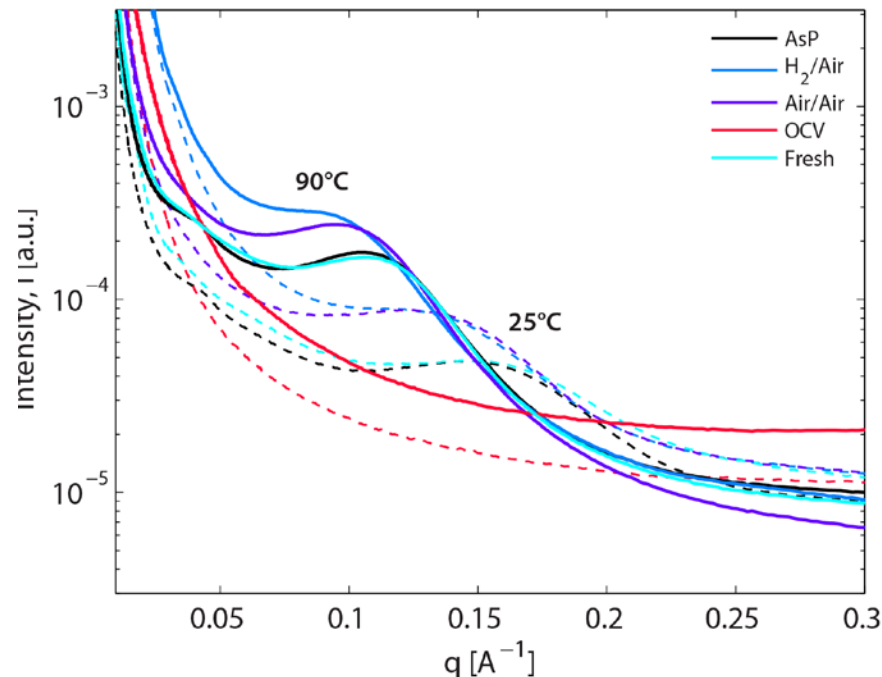

Nafion ® XL100

XL100 | Liquid @ 25 vs 90 °C
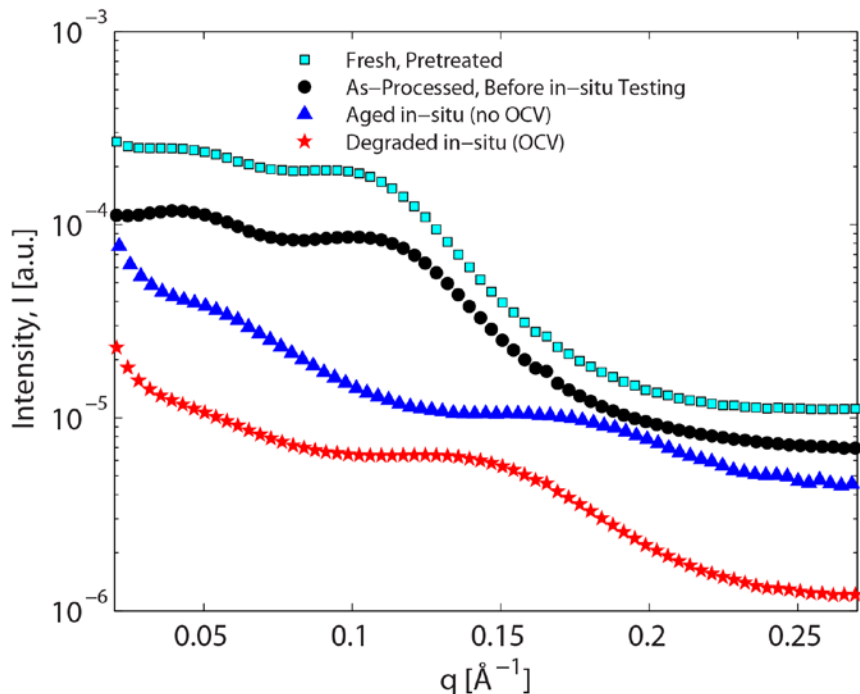
Nafion ® 212 Membrane

- **Upon boiling of aged membrane, d-spacing increases**
- **Still lower than fresh membrane**

Nafion ® XL100

- **Upon boiling of aged membrane, d-spacing increases**
- **Becomes higher than fresh membrane**
- **Break-up of reinforcement allows more water uptake**

- **Wide-Angle X-Ray Scattering**
- **Crystallinity of Degraded samples**

- **XL100 (LANL AST Tests)**
  - As-processed
  - H_2/Air
  - Air/Air
  - OCV

- **Increased crystallinity upon degradation (OCV is highest)**
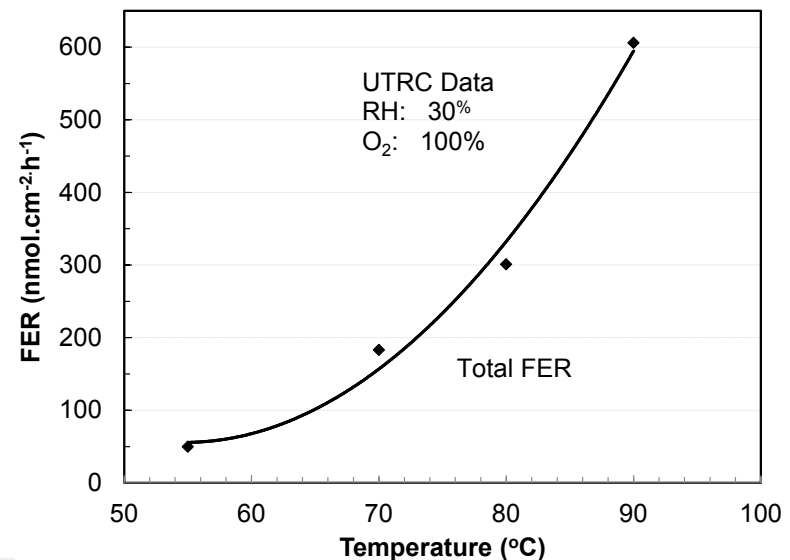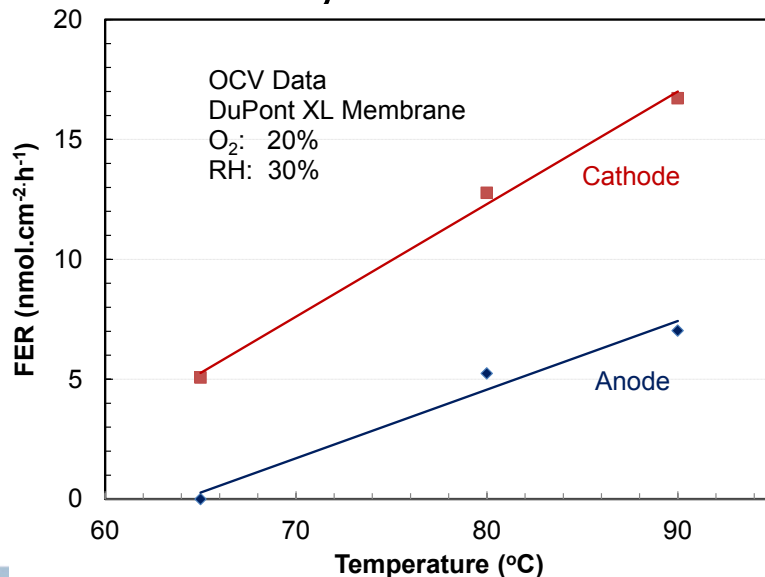- **Consistent with TEM**
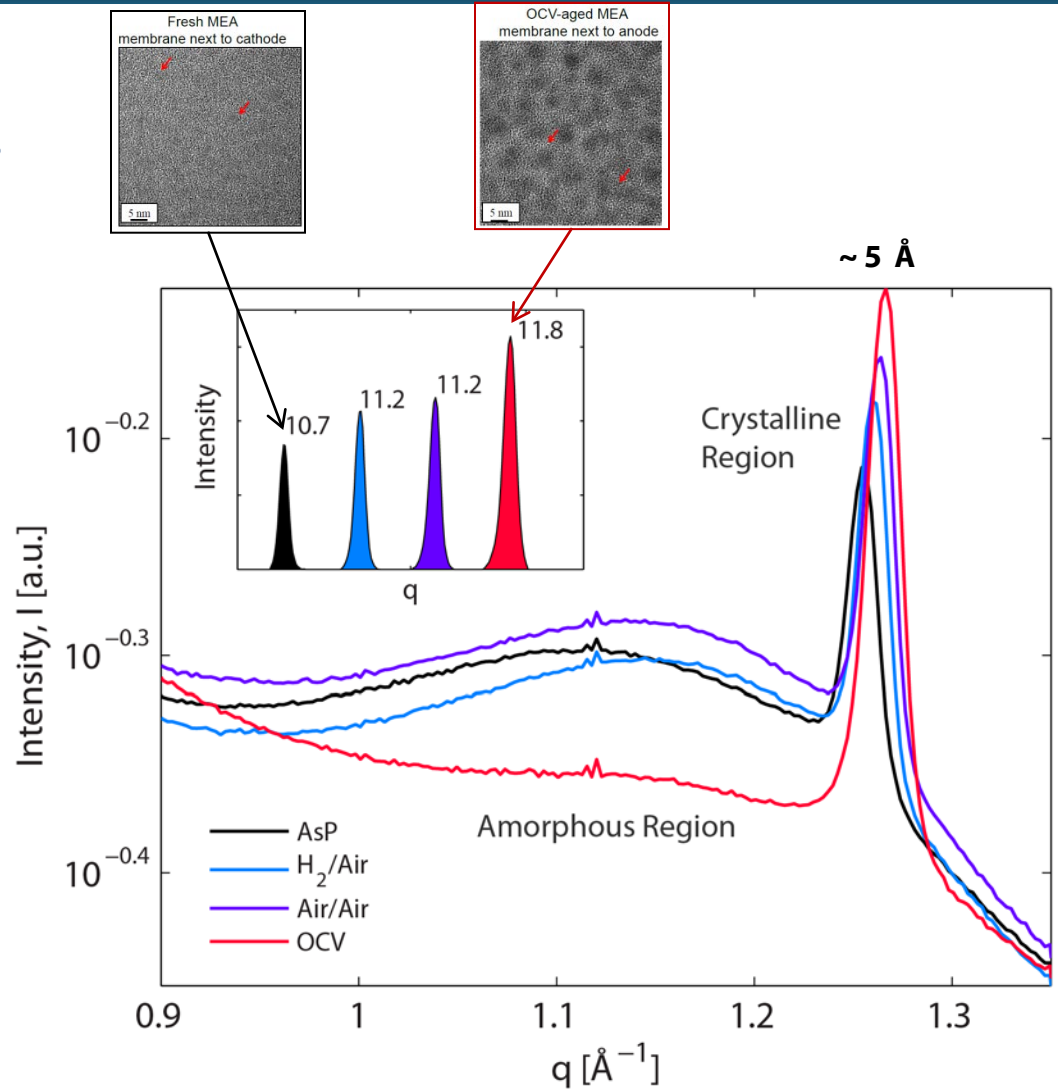
TEM Images: Oak Ridge National Laboratory.
Rod Borup (LANL), DoE 2011 AMR Meeting

Membrane/Electrode Degradation Kinetics Model

Initial test completed on chemical stability of Ion Power MEA with chemically stabilized and mechanically reinforced DuPont XL membrane, and 0.23 mg/cm^2(c) and 0.034 mg/cm^2(a) Pt loading

- At 90°C and 30% RH, FER from XL membrane is generally 1/50th the FER from non-stabilized PFSA membranes
- FER from cathode is generally higher than from anode
- XL membrane shows weaker RH, P(O$_2$) and cell V dependence than literature data for non-stabilized membranes
- FER from XL membrane correlated with RH, T, V, and P(O$_2$) but more accurate analytics needed to reduce the error band

OCV Data
DuPont XL Membrane
O$_2$:   20%
RH: 30%

Cathode

Anode

FER (nmol.cm^{-2}.h^{-1})

Temperature (^{o}C)

UTRC Data
RH: 30%
O$_2$:   100%

Total FER

FER (nmol.cm^{-2}.h^{-1})

Temperature (^{o}C)

Membrane/Electrode Performance Degradation Model

Modeling of experimental data indicates that ionomer loss from electrodes rather than membrane degradation is the primary cause of F^- release in the initial test – to be further verified
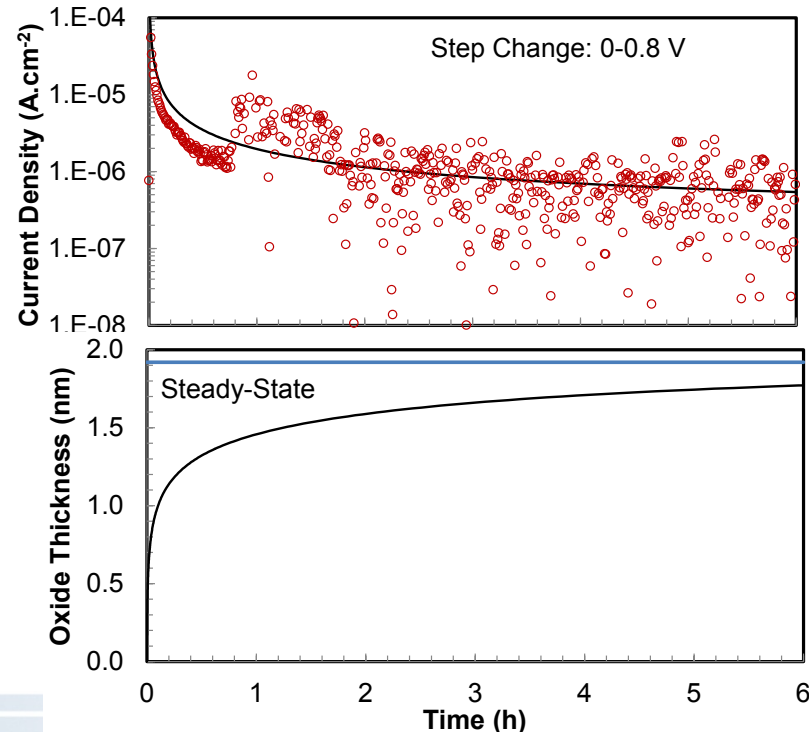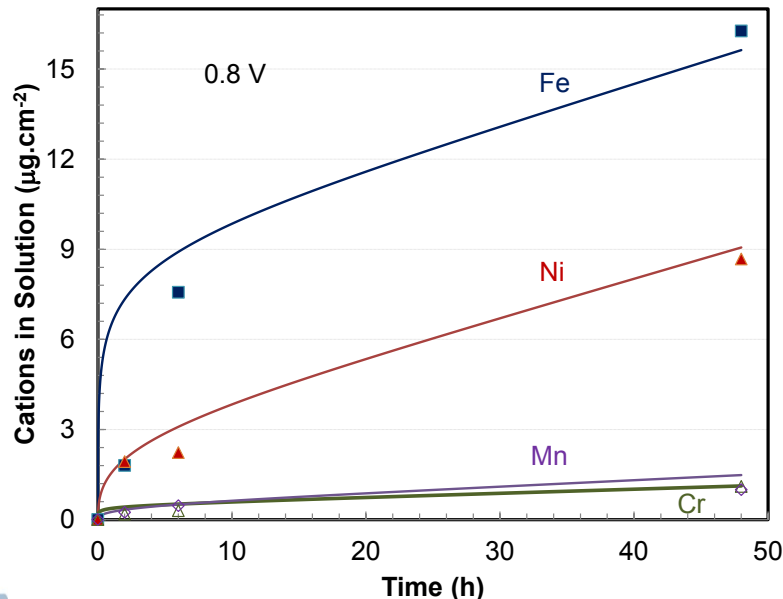
- Small change in H_2 crossover over the test duration
    - ECSA loss attributed to the decrease in Pt utilization caused by ionomer degradation at the three-phase boundary
- Pt particle size in TEM is not affected by ionomer loss
- Higher ECSA loss in the anode than in the cathode
- ECSA loss correlated with cumulative F^- release per unit volume of the catalyst layer
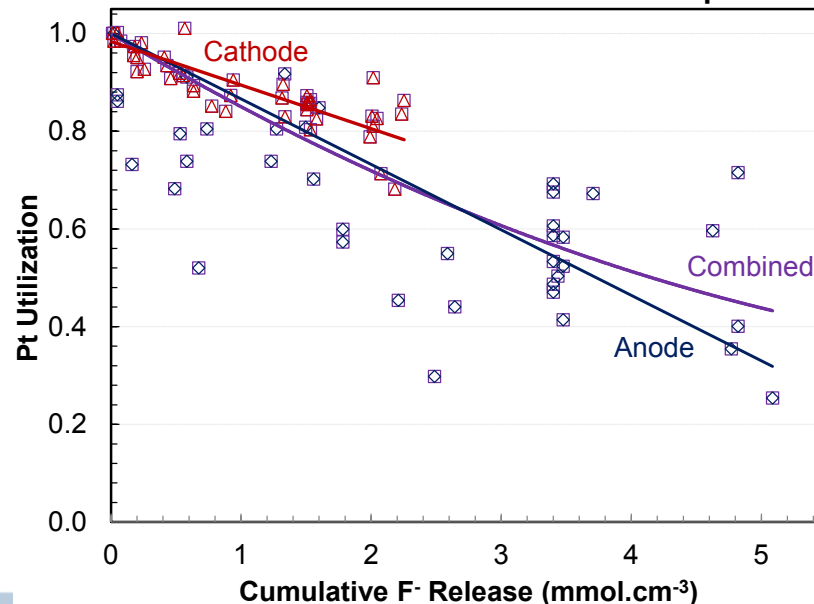
Bipolar Plate Corrosion Model – SS 316L

Point defect model (PDM) developed for passive films in SS 316L

- ORNL electrochemical cell and LANL ICP data: the steady-state current density and metal dissolution rates independent of cell V.
- Rate controlling step assumed to be at the metal/film interface
- Consistent with ORNL XPS measurements 316L is assumed to form protective Cr-rich oxide layer up to 1 V (Fe-rich oxide at higher V)
- PDM calculates the change in oxide thickness due to cyclic potentials and metal (Cr, Fe, Mn and Ni) dissolution rates as a function of oxide thickness

Developed a 2-step lumped surface reaction model for corrosion of nitrided G35 at 0 to 1.5 V

- Rate controlling step assumed to be at the surface/electrolyte interface

- ICP and polarization data used to determine the contributions of individual species (Cr, Ni, Fe, Mn, Mo) to the dissolution current

- In the passive region (0 - 0.5 V), Fe and Ni dissolve preferentially at rates that are function of surface coverage and are weakly dependent on applied potential.

- In the trans-passive region (0.8 - 1.5 V), Ni and Cr dissolve preferentially at rates that depend on surface coverage and potential.
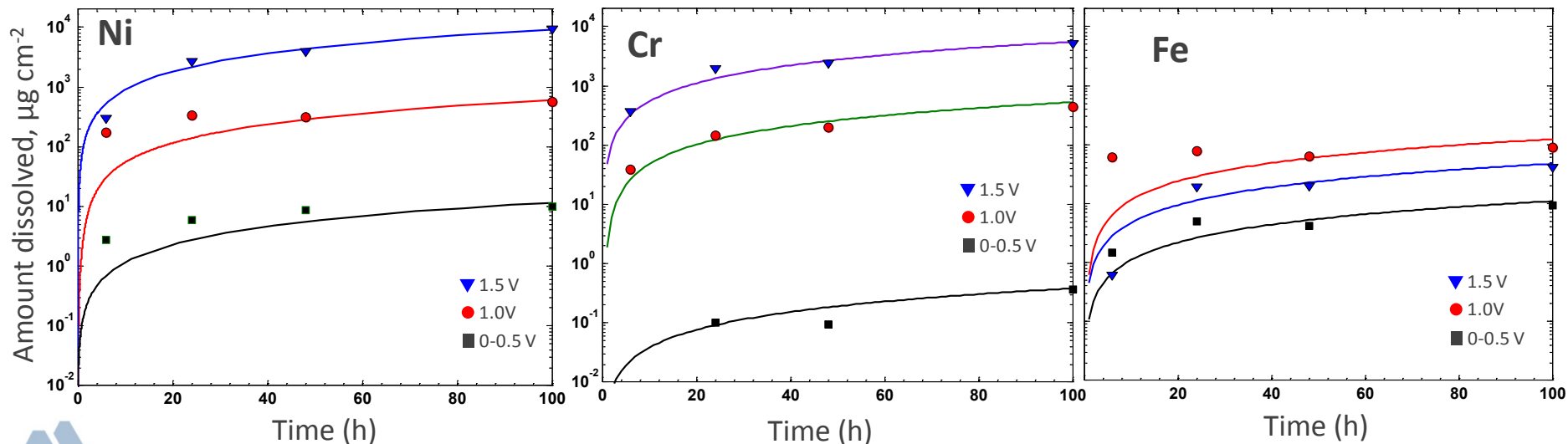
Bipolar Plate Interfacial Contact Resistance

Derived ICR from NREL 2XICR data for ORNL specimens exposed at different potentials, and correlated with compaction force and potential

- ICR inferred as a function of potential (0.2 – 1 V) for 316L correlates well with the modeled thickness of the protective oxide film (passive film).

- Inferred ICR for nitrided G35 shows more complex behavior that may depend on surface properties (roughness, phases). Reduction in ICR between 0.5 - 1 V may be correlated with surface coverage (preliminary analysis). More work needed to correlate ICR above 1 V.
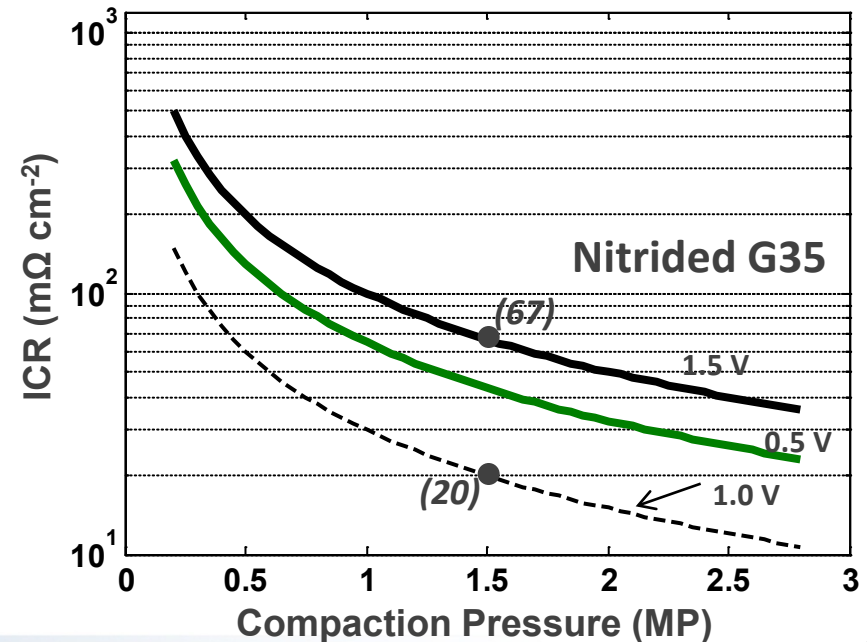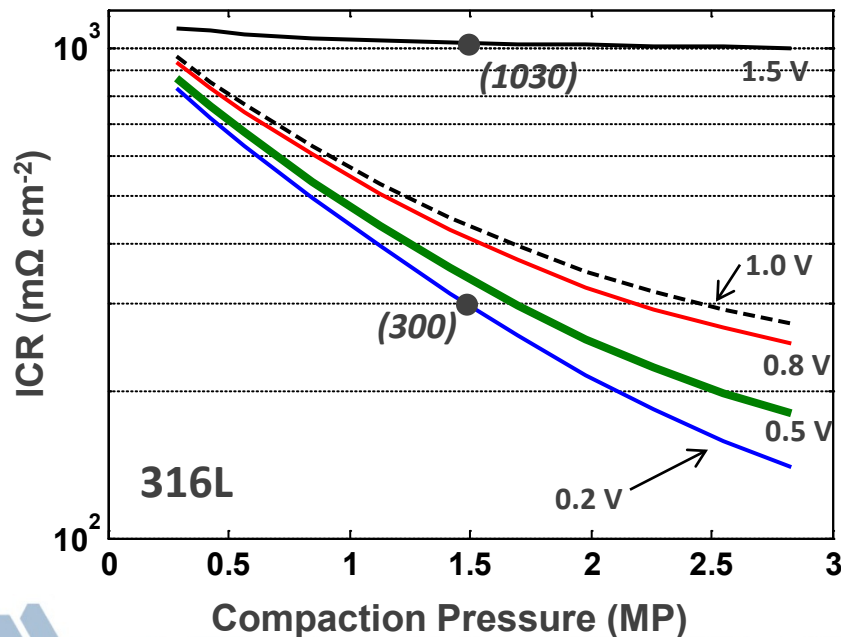
Carbon Bipolar Plates

- ## Plate Electrical Conductivity

  - **Measure bulk and contact resistances for different plate chemistries and surface treatments, and integrate into electrical modeling work**
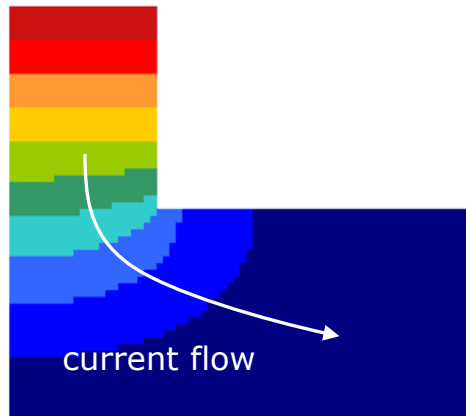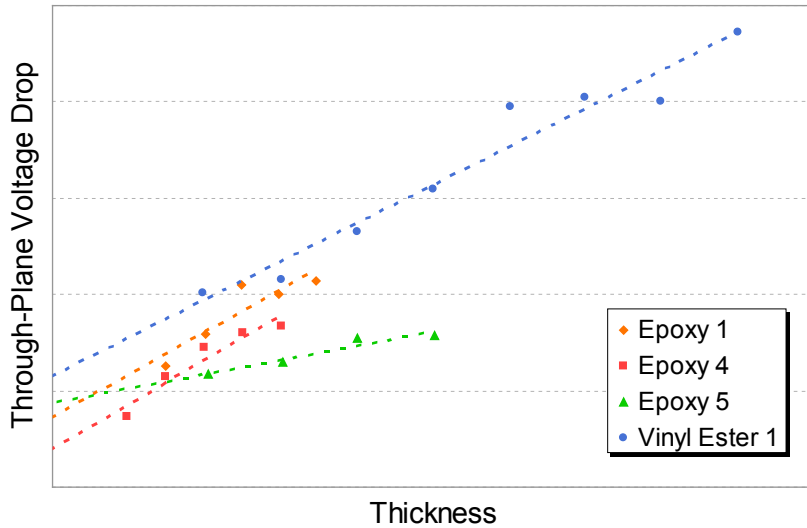
- ## Water Management

  - **Measurement of dynamic surface properties to try to link ex-situ characterization (including models) to in-situ performance**

current flow
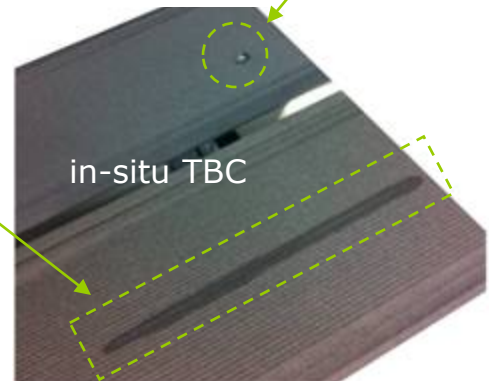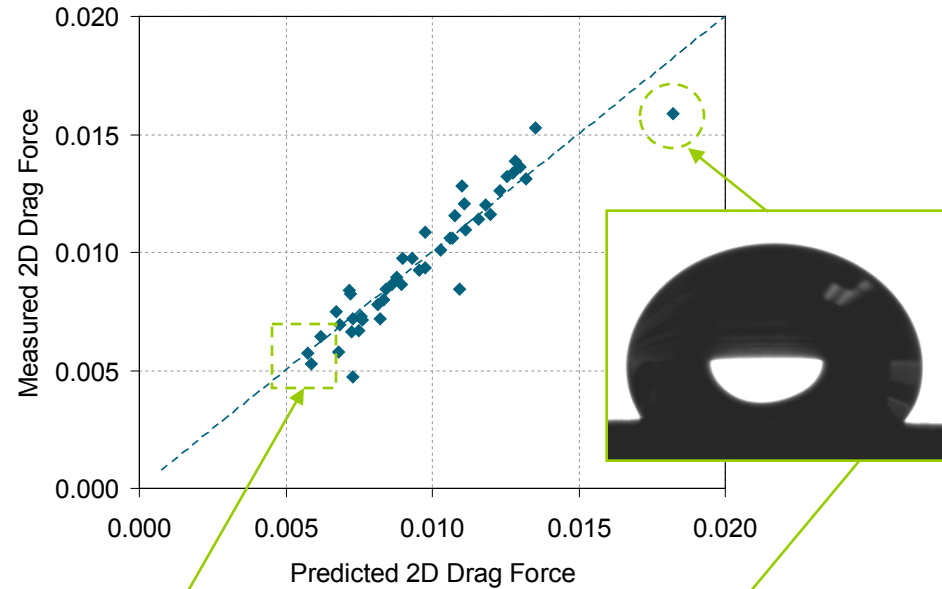
in-situ TBC

- **In-situ testing in development to validate ex-situ characterization work to date**

All Materials – Contamination

BALLARD®

Examples of potential contaminants by component
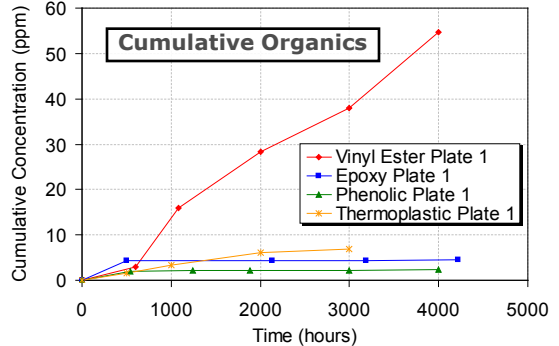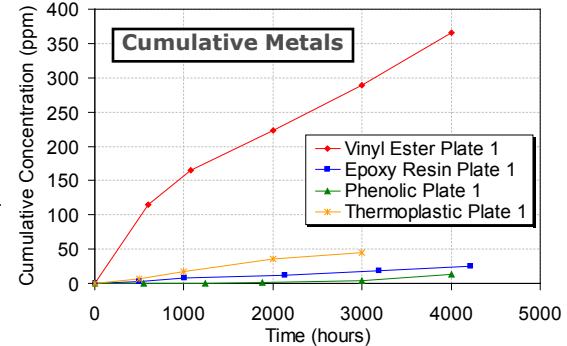
- Acid leach of non-aged materials
  - Plate adhesive data highlights potential extractable Fenton's reagents
  - Film laminates data comparing total metals and total organics
- De-ionized water leachate analysis over time at 100°C
  - Sampling at 500, 1000, 2000, 3000 and 4000 hours
  - Cumulative concentrations presented

Glues (9 grades)

Laminates (2 grades)

Plates (4 grades)

Potential Extractable Fenton's Reagents from Plate Adhesives
Metals & Trace Elements by ICP-AES, Method 6010C

Legend: Chromium, Copper, Iron, Titanium, Vanadium, Zinc

X-axis: Epoxy 7, Epoxy 2, Epoxy 6, Vinyl Ester, Epoxy 1, Epoxy 3, Epoxy 4, Epoxy 8, Epoxy 5
Y-axis: Concentration [ppm]

Legend: Total Metals, Total Semivolatiles
X-axis: Polyester Film 1, High Temp Thermoplastic Film 1
Y-axis: Concentration (ppm)

Cumulative Metals
Legend: Vinyl Ester Plate 1, Epoxy Resin Plate 1, Phenolic Plate 1, Thermoplastic Plate 1
Y-axis: Cumulative Concentration (ppm)
X-axis: Time (hours)

Cumulative Organics
Legend: Vinyl Ester Plate 1, Epoxy Plate 1, Phenolic Plate 1, Thermoplastic Plate 1
Y-axis: Cumulative Concentration (ppm)
X-axis: Time (hours)

Impact of Electrode Structure on Cathode Durability

Electrode from Water/IPA

Electrode from NMP

Electrode from Glycerol
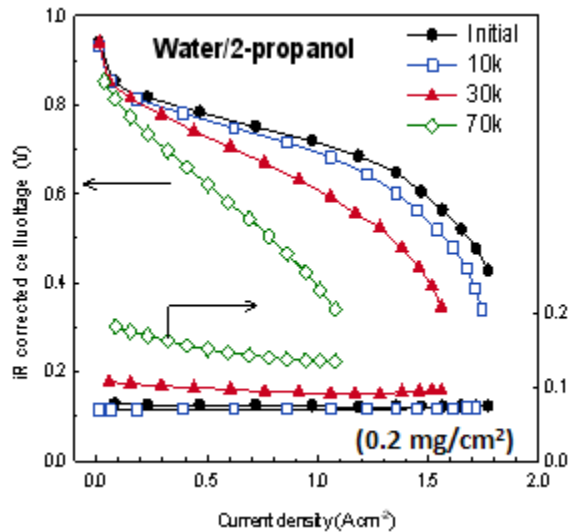
Nafion®: **dispersion**
Pt/C: poorly dispersed
Mechanical property: poor
Polymer relaxation: fast

TYPE I degradation:

Fast degradation :
  Major contributions –
  Decreasing ECSA
  Decreasing transport

Other solvents with similar effects: water/methanol, water ethanol, water/n-propanol

Nafion®: **solution**
Pt/C: well dispersed
Mechanical property: good
Polymer relaxation:
intermediate

TYPE II degradation:

Moderate degradation:
  Major contributions –
  Effects of decreasing ECSA

Other solvents with similar effects: DMAc, DMF, DMSO, water/glycerol

Nafion®: **dispersion**
Pt/C: well dispersed
Mechanical property: moderate
Polymer relaxation: slow

TYPE III degradation:

Slow/little degradation:
  Effects of increasing transport counter decreasing ECSA

Other solvents with similar effects: propylene glycol, butanediol

Ionomer Relaxation by Contacting 100°C Water Vapor Measured by AFM

	After casting	After 100°C H₂O vapor/1h	After 100°C H₂O vapor/3h	Relaxation rate

Water/low alcohol (water/IPA 1:1) — *Fast*
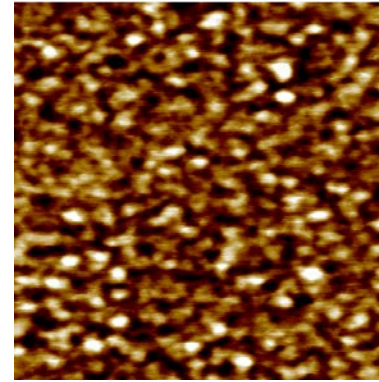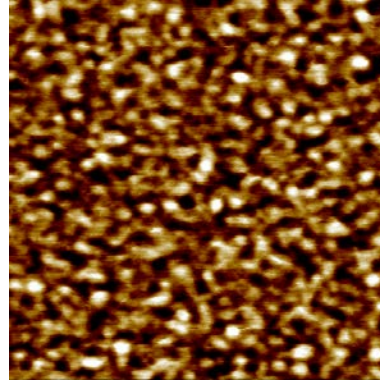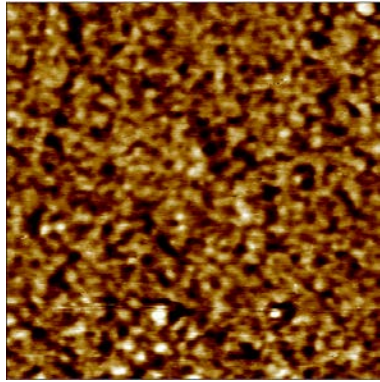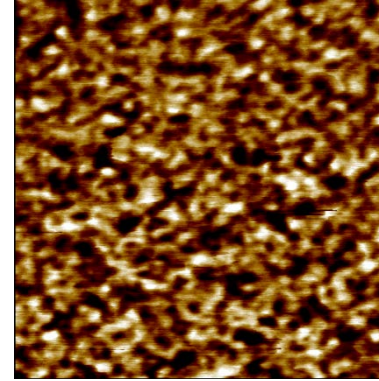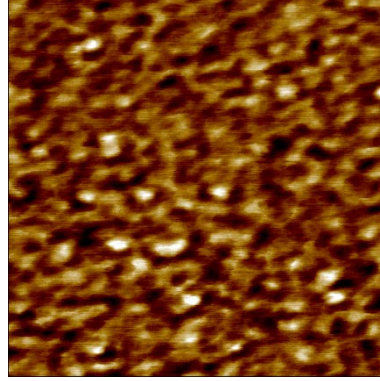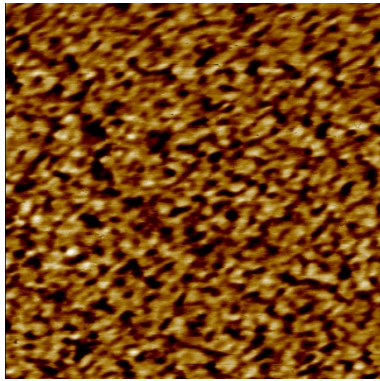
Aprotic polar (NMP) — *Intermediate*

High alcohol (propylene glycol) — *Slow*
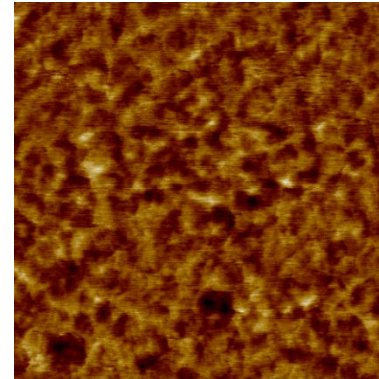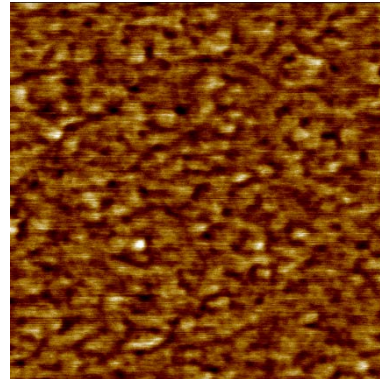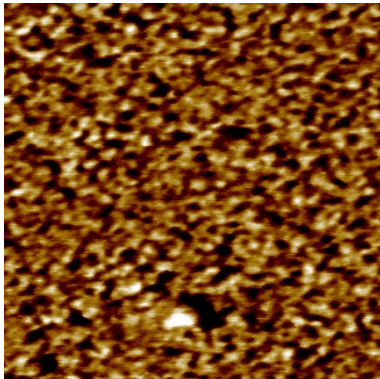
TM-AFM (500 × 500 nm scale) measured under ambient conditions

Impact of Cathode Pt Loading on Durability and Degradation Modes

0.25 mg/cm² TYPE II Degradation

0.11 mg/cm² TYPE III Degradation

0.05 mg/cm² TYPE III Degradation
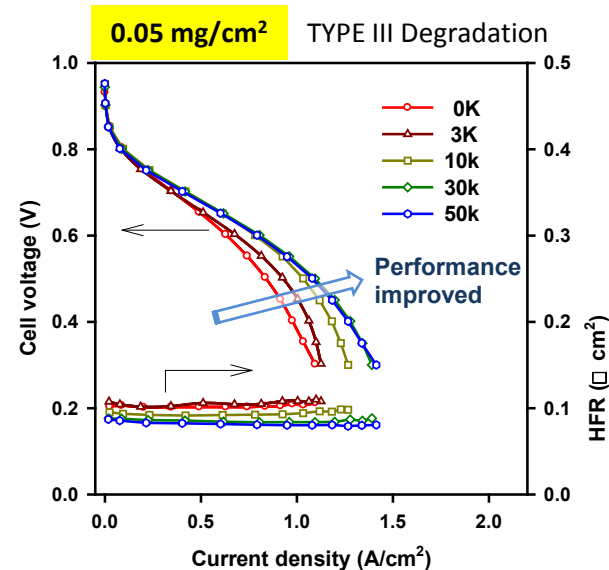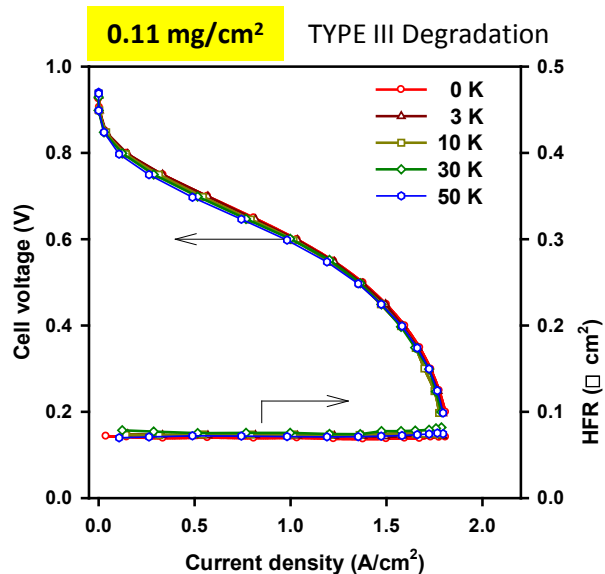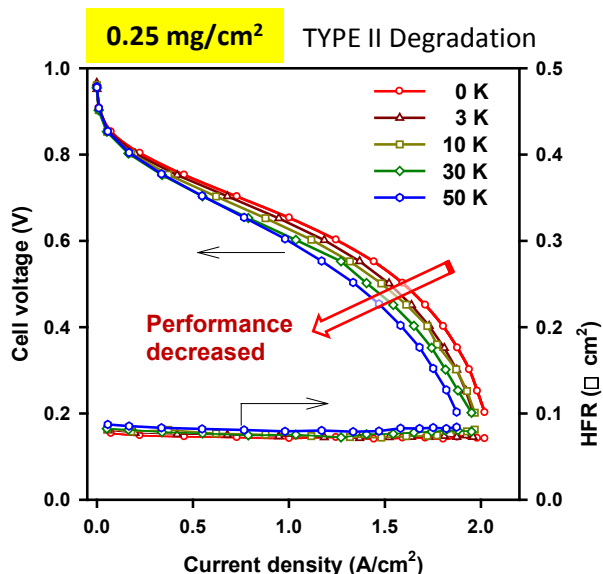
Electrochemical surface area

Cathode Pt Loading (mg/cm²)	ECSA (m²/g_Pt)			
	0 K	10 K	30 K	50 K
0.25	50	35	28	22
0.11	49	28	24	22
0.05	52	29	21	14

- **0.25 mg/cm² cathode: TYPE II Degradation**
- **0.11 mg/cm² cathode: TYPE III Degradation**
- **0.05 mg/cm² cathode:**
  - **Significant mass transport issue initially but improved overtime**
  - **Slightly faster Pt particle growth & ECSA change**
  - **Need to improve the poor initial performance**

Dispersing Solvent: commercial Nafion+glycerol/propanol/H_2O; ionomer: Nafion; ionomer to Pt/C composition: 30wt.%; Anode: 0.2 mg_{Pt} cm^{-2} (20 wt.% Pt/C, BASF), Cathode: 0.05-0.25 $mg_{Pt}cm^{-2}$ (20 wt.% Pt/C, BASF); Membrane: Nafion® 212; Operating conditions: cell temperature: 80°C, backpressure: 30 psi, Potential cycling conditions: 0.6 – 1.0 V under H_2/N_2 at 80°C

Approaches to Improve Durability of Low Pt Loaded Cathodes

Approach 1
Reduce ionomer to Pt/C ratio

Dispersing Solvent: Water/glycerol; *ionomer:* Nafion; *ionomer content: 22wt.%;* *Cathode:* 0.05 $mg_{Pt}cm^{-2}$ (20 wt.% Pt/C, BASF);

ECSA (m^2/g_{Pt})		
0 K	10 K	30 K
53	35	31

- **Poor initial performance with flooding**
- **Improved performance after 30K**
- **TYPE III degradation**

Approach 2
Use water/IPA dispersion

Dispersing Solvent: Water/IPA; ionomer: Nafion; *ionomer content: 30wt.%;* *Cathode:* 0.05 $mg_{Pt}cm^{-2}$ (20 wt.% Pt/C, BASF);

ECSA (m^2/g_{Pt})		
0 K	10 K	30 K
53	28	23
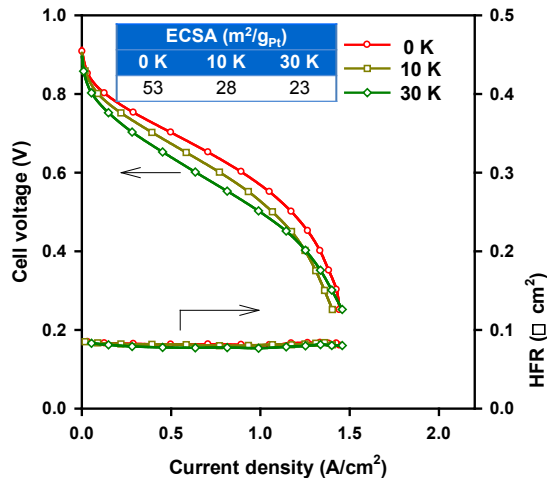
- **Improved initial performance**
- **No flooding issue**
- **TYPE III degradation**

Approach 3
Lowered Pt to carbon ratio

Dispersing Solvent: Water/glycerol; *ionomer:* Nafion; *ionomer content: 30wt.%;* *Cathode:* 0.05 $mg_{Pt}cm^{-2}$ *(10 wt.% Pt/C, BASF);*

ECSA (m^2/g_{Pt})		
0 K	10 K	30 K
52	29	20
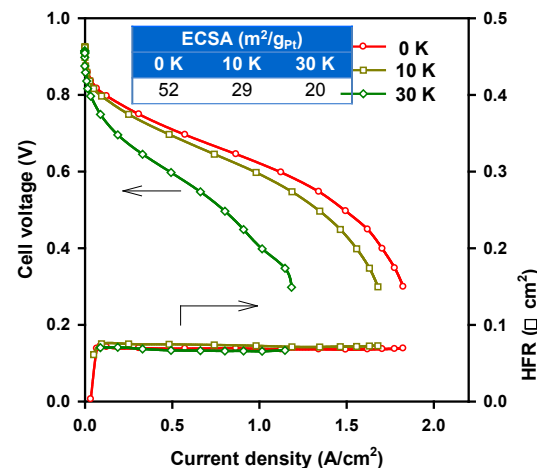
- **Excellent initial performance**
- **Performance decrease after 30K**
- **TYPE I degradation**

Approach 4
MEA Pre-treatment

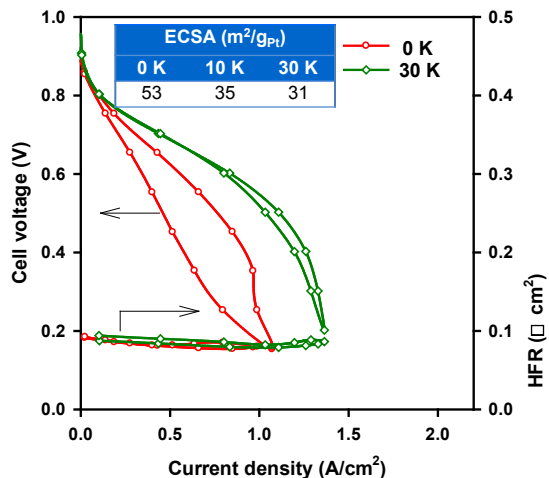*Dispersing Solvent: Water/glycerol; ionomer: Nafion; ionomer content: 30wt.%;* *Cathode:* 0.05 $mg_{Pt}cm^{-2}$ *(20 wt.% Pt/C, BASF);*
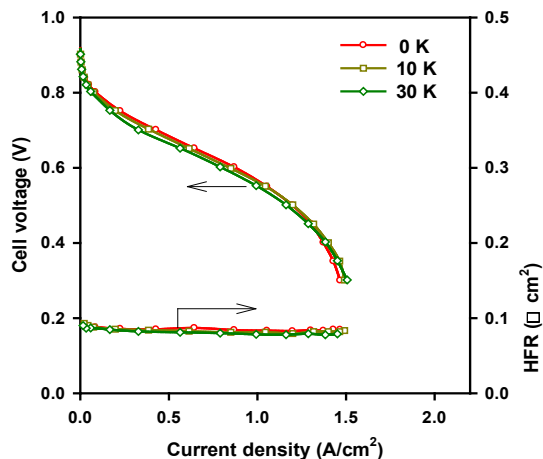
- **Improved initial performance**
- **Catalyst sintering (and ECSA reduction only affects at very high potential (~ 0.9 V)**
- **TYPE III degradation**

ECSA and current density Pre-treated MEA

No. potential cycles	0 K	10 K	30 K
ECSA (m^2/g_{Pt})	48	27	23
$i_{0.90V}$ (mA/cm²)	1.47	1.03	0.78
$i_{0.86V}$ (mA/cm²)	12.2	10.3	7.3
$i_{0.80V}$ (mA/cm²)	84	75	58
$i_{0.4V}$ (A/cm²)	1.3	1.3	1.3

Selected Technical Conclusions/Summary - 1

- **Model Development**
  - Completed initial development of Pt dissolution model in 2012
    - 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)
  - Completed initial development of carbon corrosion model
    - Modified catalyst durability model to account for changes due to carbon corrosion
    - Completed models for Pt catalyzed corrosion of Ketjen black (E-type), Vulcan XC-72 (V-type) and graphitized carbon (EA-type) supports
    - Determined the effect of aging on the specific surface area of carbon (S_C, m^2-C/g-C)
  - Modeled gas crossover
    - 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 affects the membrane H_2 crossover
  - Developed component model for combined chemical/mechanical membrane durability
    - Component model for combined chemical/mechanical membrane durability – combined sorption model can predict change in H_2O uptake based on nanostructure degradation
    - Aging effects on crystallinity effecting water uptake
    - Catalyst layer ionomer degradation modeled as contributing cause to ECSA loss
  - Bipolar Plates
    - Model developed for SS 316L and G35 metal bipolar plates

- **Catalyst**
  - % change in Pt particle size much greater for Pt supported on E-carbon in surface layer than Pt particles supported on EA-carbon in inner layer
  - Significant Pt growth/coarsening observed ONLY in E-carbon surface layer due to pronounced carbon corrosion throughout entire thickness of this layer.
- **Carbon corrosion ubiquitous over cathode potentials**
  - Loss of meso-graphitic structure in catalyst layer
  - Structure shows localized structure changes
  - Structure change mass transport
  - Mixing more stable materials retains structures with transport properties
  - Elemental changes
    - Catalyst Layer shows increasing graphitic content
    - Increasing oxygen concentration

Selected Technical Conclusions/Summary - 3

- **Ionomer Degradation**
  - Modeling of experimental data indicates that ionomer loss from electrodes rather than membrane degradation is the primary cause of F$^-$ release in the initial test – to be further verified
  - 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})

- **Membrane Degradation**
  - Cycling in the absence of chemical effects does not cause failure (SOA reinforced membranes)
    - Combined chemical/mechanical degradation leads to early failure
  - Increased crystallinity upon degradation (OCV is highest)
    - Aging reduces uptake & domain size
  - Nanostructure to characterize degradation
    - Reinforced membrane could lose its integrity

- **MEAs**
  - Low loaded cathodes (0.05 mg/cm^2) durability response different than > (0.10 mg/cm^2)
  - Nafion$^®$ relaxation in catalyst layer

- **Mitigation**
  - Electrode structure can be maintain by mixing stable support materials
  - Different solvent approaches can strengthen the Nafion$^®$/catalyst layer

Future Work (this project)

Modeling:

- Incorporate component membrane model into integrated model
- Modeling of transport losses due to carbon corrosion
- Incorporate transport of dissolved cations through catalyst ionomer and membrane from carbon plates, seals and metal bipolar plates

Component Interactions:

- Measure transport of dissolved cations through catalyst ionomer and membrane
- Further quantitate relationship between carbon corrosion and resulting changes in CCL structure (Pt/pore distributions, Pt utilization, ECSA)
  - Quantification of E vs. EA carbon structures and mixed formulations
- Refined analytics and test protocols for reproducible FER measurements for chemically-stabilized membranes

Future Work

- **Understand Carbon/Nafion®/Catalyst structure and durability effects**
  - Understand structure of catalyst layer effect on durability; different methods of forming catalyst layers
  - Improve durability/performance of low loaded MEAs (0.05 mg/cm^2)
  - Identify ionomer degradation source for FER (CL vs membrane)

- **Define effect of carbon corrosion on CL structure and transport losses**
  - Quantitate relationship between carbon corrosion and changes in CL structure
  - Identify uniform methodology for measuring real durability impact of start-up/shut-down, air cycling
  - Spatial/areal performance variations over aging remain largely undetermined

- **Catalyst durability**
  - Reduce solubility of Pt via increasing support interactions, alloying
  - Understand/model dissolution of Pt at elevated temperatures and in oxygen
  - Understand effect of Pt transport and band formation

- **Component surface properties**
  - Understand effects of changing surface chemistry on: bipolar plates, catalyst support, GDL

- **Mitigation of Degradation**
  - Increasing CL transport, stability through use of structure and stable materials

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

Technical Backup Slides

Approach - FY2013 Milestones

| Mon Yr	Milestone	
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)	Completed
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)	Completed
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	Completed - at lower loadings; from 0.05 to 0.4
July 2013	Quantify carbon surface oxidation of GDL carbon by newly proposed GDL AST by titrimetric technique. Complete correlation between AST and in situ fuel cell operation. Determine if method is applicable to carbon catalyst supports by finishing evaluation of 3 different catalyst support carbons by identical techniques (Vulcan, Ketjen and EA (highly graphitized carbon).	Completed on GDLs
Sept 2013	Demonstrate H_2/air fuel cell performance of 0.05 mg/cm^2 cathode > 0.6 A/cm^2 at 0.7 V	Completed
March 2013	Develop models for platinum transport in the membrane, and the resulting reactions between crossover H_2 and O_2 and fluoride emission rates	Completed
June 2013	Develop model for effect of carbon corrosion on cell performance for different carbon structures	Partially completed
Sept 2013	Integrate the models for degradation of MEA components and evaluate the potential of reaching 5000-h durability target for automotive fuel cells	Pending
March 2013	Determination of the change in lambda vs. d-spacing for membranes aged 4 different ways.	Completed
March 2013	Deliver a total of 20 catalyst layers on PTFE membrane with different ionomer:carbon ratio, carbon type, Pt/C ratio, and ionomer equivalent weight.	Completed (at least to satisfaction)
Sept 2013	Characterize aged bipolar plates in terms of changes in water balance and water-management related performance as a function of different surface modifications.	Nominally completed

Mixed Catalyst Layer E + EA – Fresh
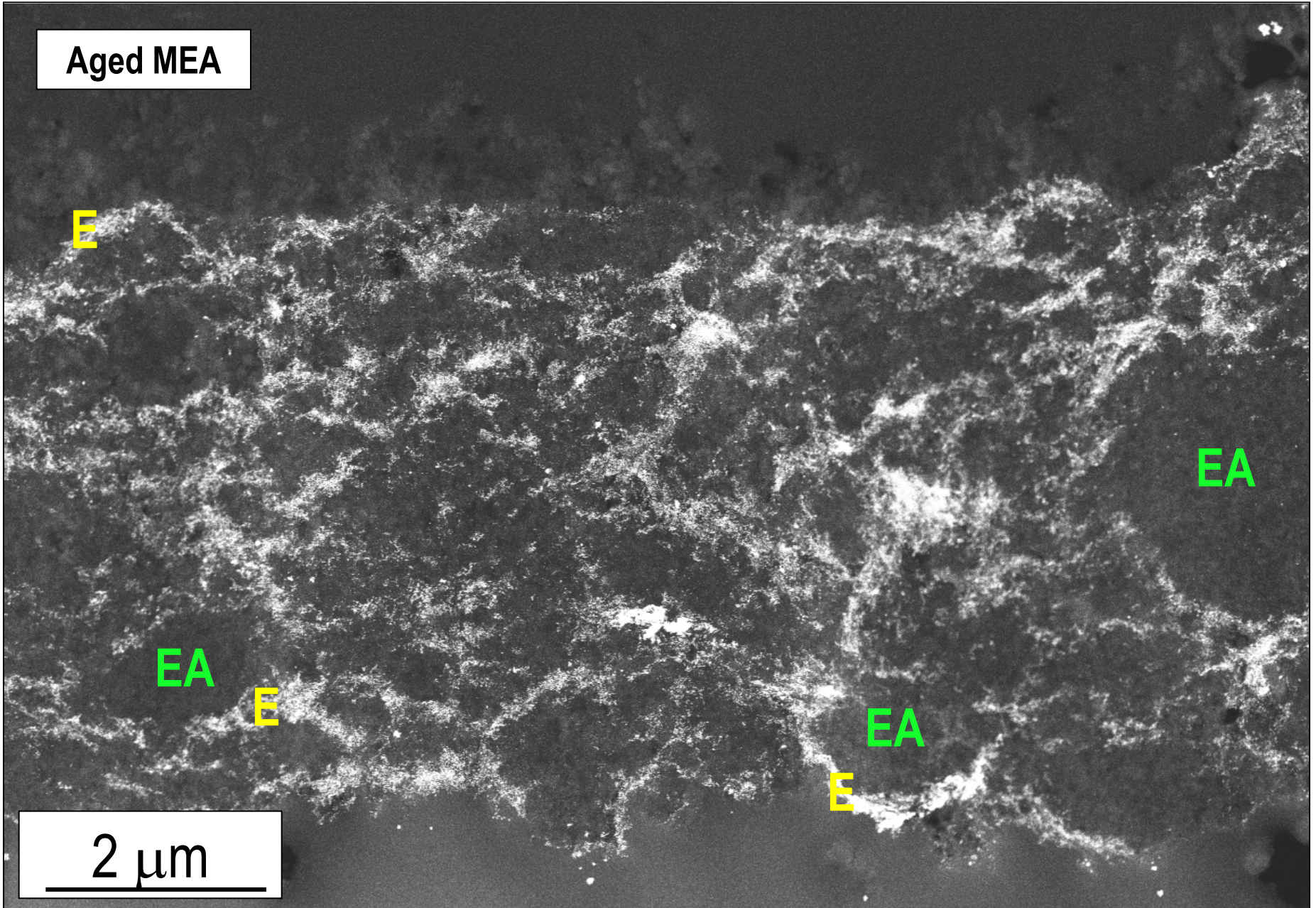
Fresh vs. Aged (1224 hr wet drive cycle)

Fresh cathode

JD091212 cathode

200 nm

"localized bands" of HSAC corrosion observed, which are correlated with regions of increased Pt particle sizes and closer Pt-Pt interparticle spacings (yellow arrows)

Degradation Mechanisms of Pt/C Cathode during Potential Cycling

| Degradation	**Type I**	**Type II**	**Type III**
Typical processing solvent	Water/low alcohol	Aprotic polar or water/high alcohol	Single high alcohol
Porosity [a]	High	Low	Low
Degradation mechanism	Pt particle growth[b] **Electrode disintegration** due to poor mechanical properties	Pt particle growth[b]	Pt particle growth[b] **Ionomer relaxation** due to continuous contact with saturated water
Features	Good initial mass transfer Sudden drop of fuel cell performance	Good initial and long-term mass transfer Reasonable reflection of Pt particle growth	Poor initial but good long-term mass transfer Performance could be improved overtime

[a] BET measurement; [b] The degree of Pt particle aggregation during potential cycling is comparable

Commercial MEAs exhibited Type II degradation behavior during potential cycling test.

LANL developed novel electrode processing which showed Type III degradation behavior.

Under severe fuel cell operation (e.g. start-stop cycling, high potential holding), all electrodes can show Type I degradation.

Impact of Polymer Relaxation on Low RH Nafion Conductivity
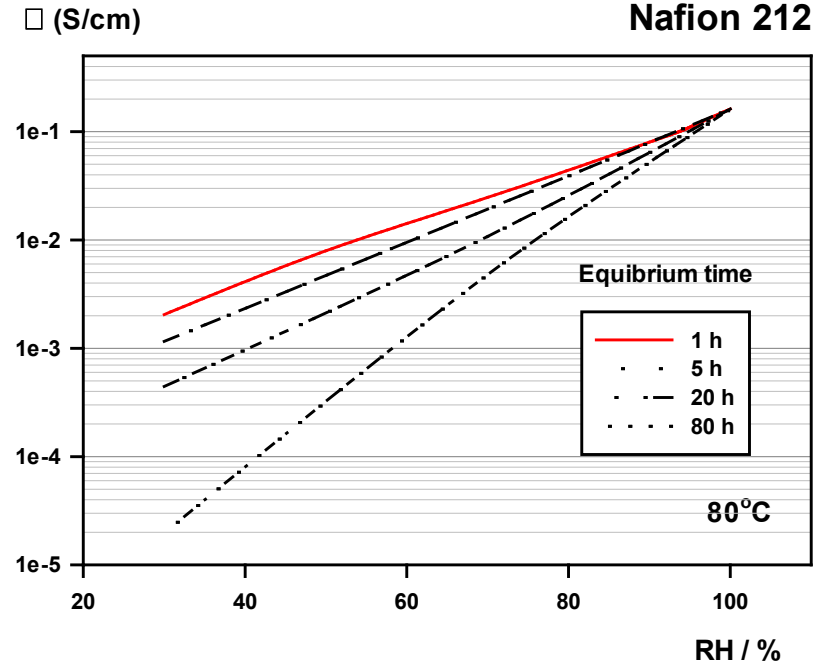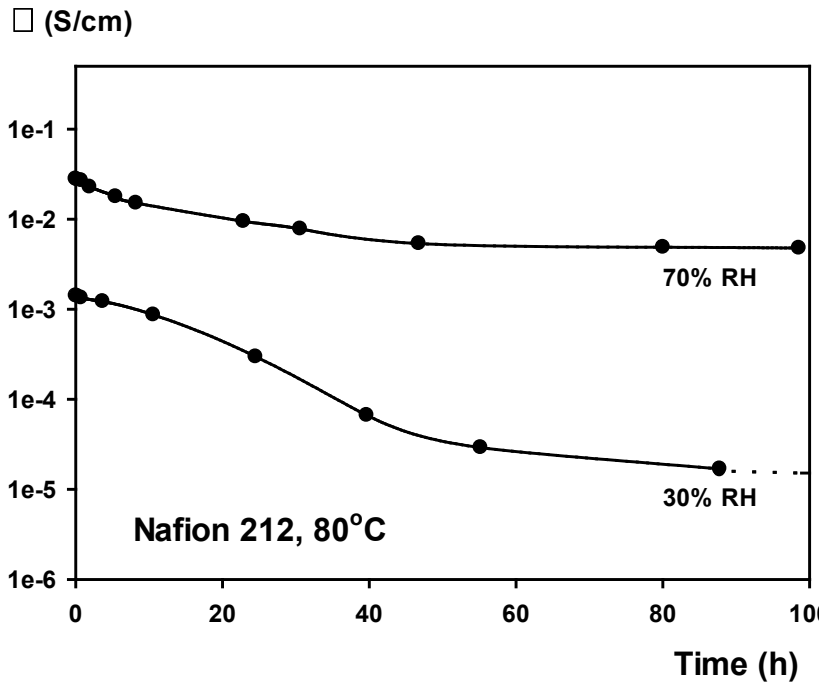
The conductivity of Nafion® was high at low RH with short equilibrium time.

The low RH conductivity of Nafion® gradually decreased → impossible to run fuel cell at extended dry conditions.

Slowing down the relaxation rate of Nafion® and water management are two key parameters for low RH fuel cell operations.