

Durability Improvements Through Degradation Mechanism Studies

DOE 2015 Annual Merit Review

June 10, 2015

Presented by: Rod Borup

National Lab Partners:

Los Alamos National Lab (LANL)

Argonne National Lab (ANL)

Oak Ridge National Lab (ORNL)

Lawrence Berkeley National Lab (LBNL)

Project Overview

Timeline

- Original Project Start Date: **August 2009**
- Original Project Duration: **4 Years**
- In FY14, transitioned to National Lab project
- In FY15, merged with LANL AST project
- Project End Date
 - Project continuation and direction determined annually by DOE

Barriers

Fuel cells: 2011 Technical RD&D Plan

A. Durability

Automotive

5,000 hours (10% degradation)

Stationary

60,000 hours (20% degradation)

Cost/Durability/Performance are directly related

Budget

Funding for:	FY14	FY15*
LANL	\$1000k	\$1350k
Industry	\$0k	\$0k
ANL/LBNL/ORNL	\$550k	\$575k
FY14/FY15 Total	\$1550k	\$1925k

*Combines LANL separate Durability and AST projects

Partners

- Current project includes funding for 4 national labs
 - LANL
 - ANL
 - LBNL
 - ORNL
- Other Partners on no-cost basis

Organizations / Partners / Collaborators

- **Los Alamos National Lab (LANL)**
 - Fuel Cell testing, performance analysis, electrochemical characterization, ASTs, component characterization: (R. Borup, R. Mukundan, D. Spornjak, A. Baker, U. Tylus, K. Rau, D. Langlois, D. Torraco, R. Lujan, M. Stewart, F. Garzon)
- **Argonne National Laboratory (ANL)**
 - Component degradation modeling, integrated models: (R. Ahluwalia, D.D. Papadias)
- **Lawrence Berkeley National Laboratory (LBNL)**
 - Component modeling, component characterization; SAXS, WAXS: (A.Z. Weber, A. Kusoglu, S. Shi, H.-S. Shiao)
- **Oak Ridge National Laboratory (ORNL)**
 - TEM characterization (K. More)
- **University of Delaware (No direct funding, supporting Ph.D. student)**
 - (A. Baker [from LANL], M. Santare [from LBNL]; Advisors: Suresh Advani, Ajay Prasad)

No-Cost Partners

- **CEA - Commissariat à l'énergie atomique et aux énergies alternatives**
 - Characterization, SAXS and water imaging, transport, leverage EU durability project: (L. Gautez, J. Pauchet, S. Escribano, A. Morin, P.-A. Jacques, M. Gerard)
- **University of Nancy, Lorraine France**
 - SD/SU segmented cell measurements: (G. Maranzana, A. Lamibrac, J. Dillet, S. Didierjean, O. Lottin)
- **NIST- National Institute of Standards and Technology**
 - Neutron imaging: (D. Hussey, D. Jacobson)
- **Ion Power, General Motors, IRD Fuel Cells (supplying MEAs)**
 - MEAs and MEA design

Relevance, Objectives and Approach

Relevance

- Improve fuel cell durability → not at the expense of component cost/performance
- Primarily applicable to materials and conditions relevant to transportation
- Enable lower-cost durable fuel cells; especially lower Pt loadings

Objectives

- Identify and quantify degradation mechanisms
 - Components, component interfaces, component interactions and degradation mechanisms
 - Discern impact of electrode structure on durability and performance
- Develop advanced in situ and ex situ characterization techniques, AST protocols
- Develop models related to degradation mechanisms
- Explore non-system related mitigation

Approach: FY15 Approach and Primary Tasks

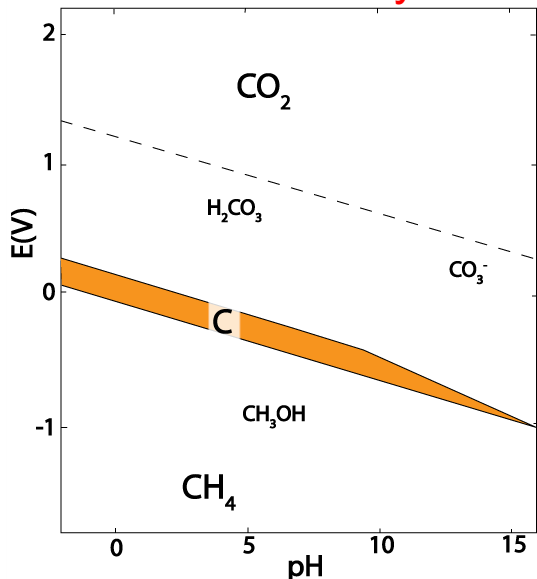
- Catalyst layer morphology affect on durability - (Carbon Corrosion during Drive Cycle)
- Membrane Structural changes and Cerium Migration/Stabilization
 - Changes in properties including: crystallinity, water up-take, transport, mechanical strength, swelling, crack propagation
- AST Validation and New AST Protocol Development
- Metal Bipolar Plates

(Mostly) Not covered in this presentation:

- Reversible Degradation, Transport (GDL effects), Shut-down/Start-up
- Durability evaluation of Pt alloys, affect of Pt and alloy migration on membrane

Carbon Corrosion Measurements Matrix for Mechanistic Definition

Carbon thermodynamics



Adapted from M. Pourbaix, *Atlas of Electrochemical Equilibria* (1966)

- Experimentally measure carbon corrosion during operation
 - Direct CO₂ measurement by NDIR
- Modeling to identify carbon corrosion mechanism and rates related to carbon and Pt surface oxidation

Carbon Supports

E (High Surface Area)
EA (Graphitized or Low Surface Area)
V (Vulcan [®])

Vary Upper Potential Limit

0.95 V – 0.40 V
 0.90 V – 0.40 V
 0.85 V – 0.40 V

 0.55 V – 0.40 V

Vary Lower Potential Limit

0.95 V – 0.40 V
 0.95 V – 0.45 V
 0.95 V – 0.50 V

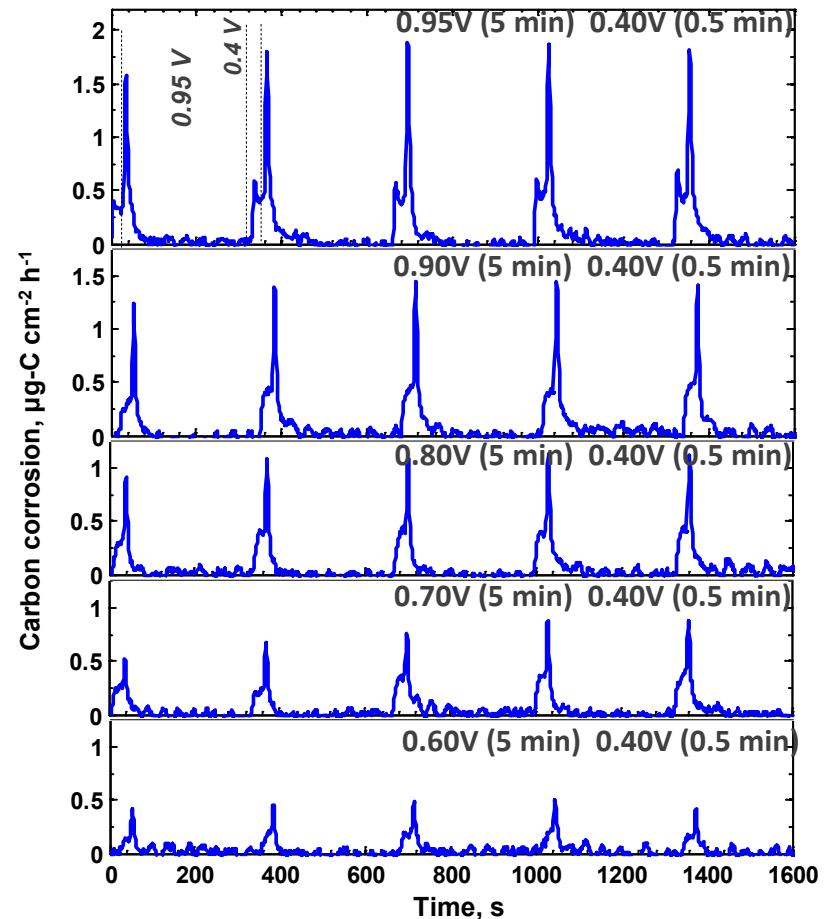
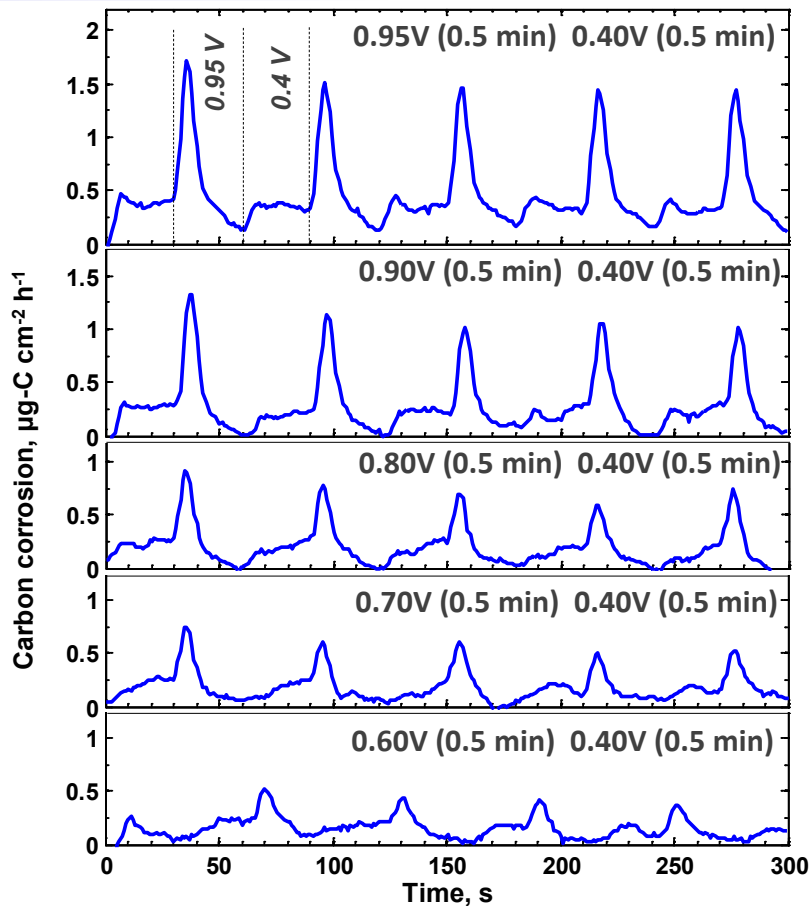
 0.95 V – 0.80 V

Potential Reset Times

0.5 min
 1 min
 2 min
 5 min

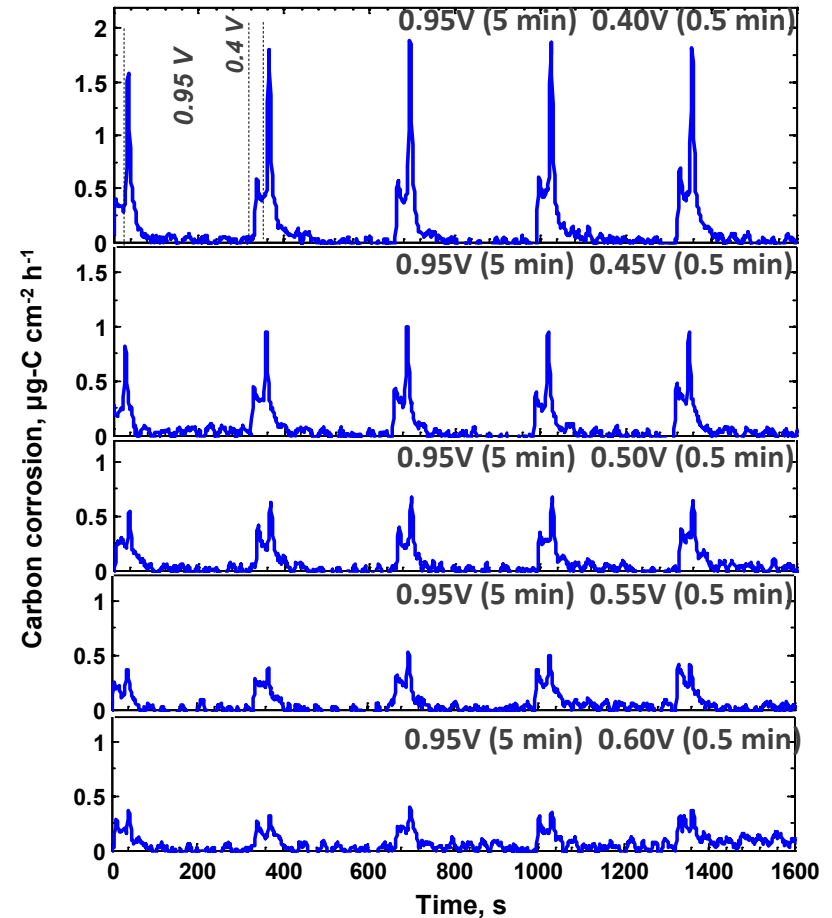
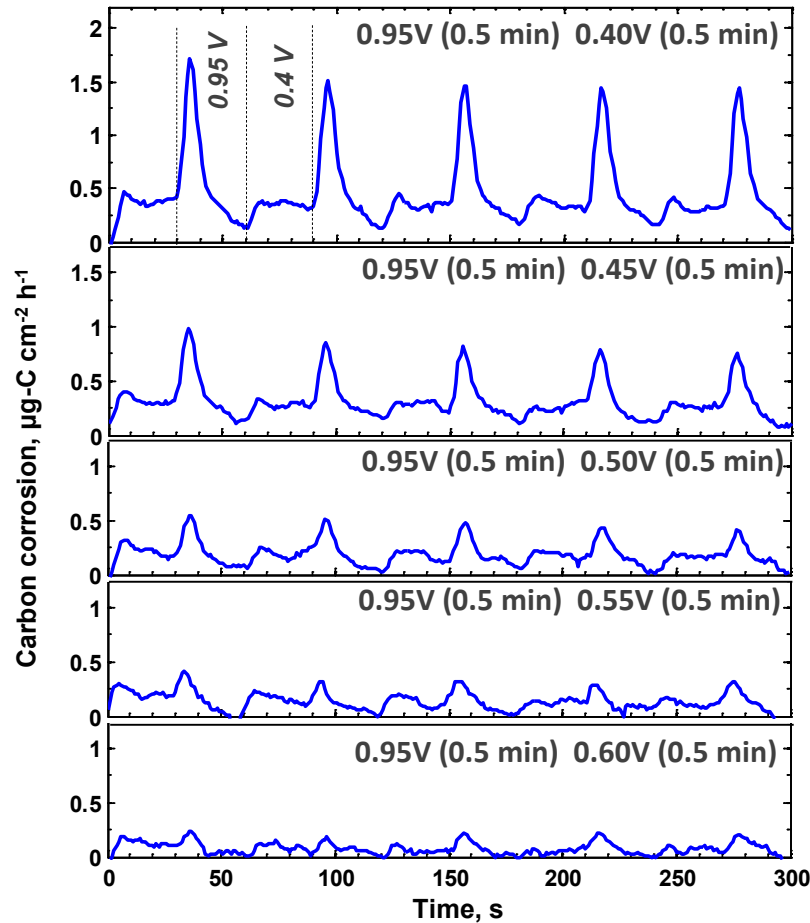
Fuel Cell operation largely as per DOE/FCTT Drive Cycle Protocol

Ketjen Black[®] Carbon (E-type): Low Potential = 0.4 V, High Potential = 0.95 – 0.6 V



- Spikes in carbon corrosion rate are observed during a step increase or step decrease in cell potential
- Magnitude of spikes decreases as the high cell potential is reduced from 0.95 V to 0.6 V
- Corrosion rate at high cell potential decreases in time, indicating formation of passivating carbon surface oxides
- A non-zero corrosion rate is observed at low cell potentials (0.4 V)

Ketjen-Black Carbon (E-type): High Potential = 0.95 V, Low Potential = 0.4 – 0.6 V

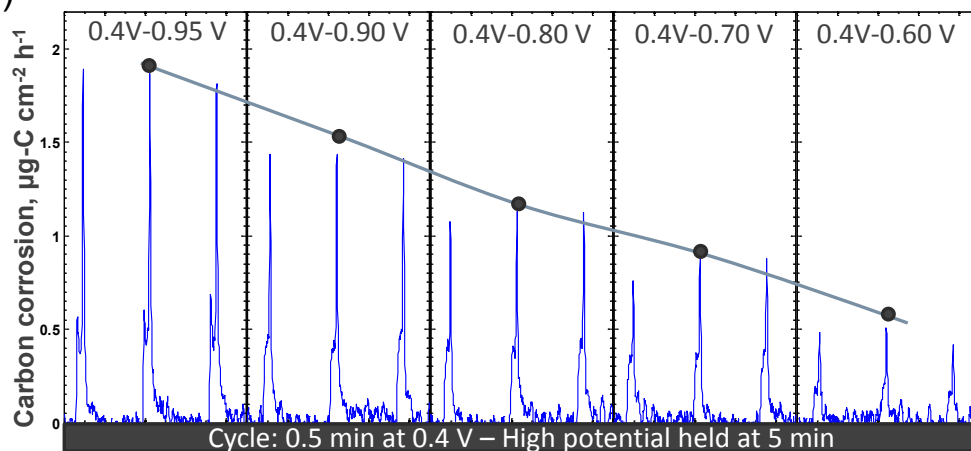
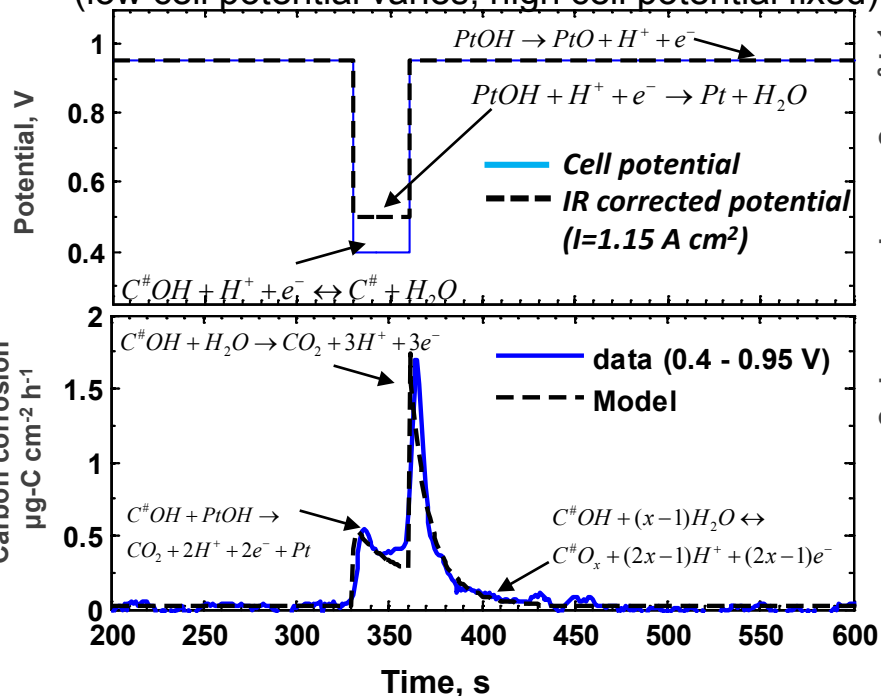


- For fixed high cell potential (0.95 V), the magnitude of spikes decreases as the low cell potential is raised from 0.4 V to 0.6 V
- Corrosion rate strongly depends on the amplitude of the square potential cycle



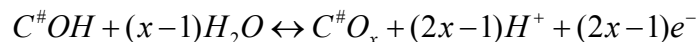
Preliminary model is able to predict the corrosion behavior during potential cycling conditions

- Preliminary model in good agreement with transient data (E-type carbon): 0.6-0.95 V high cell potential
- Model currently being expanded to analyze all carbons (E-, V- and EA-type) and low cell potential variations (low cell potential varies, high cell potential fixed)



- Magnitude of spikes reduced as the high potential is lowered
- Magnitude is reduced as low potential is increased

1) Formation of active ($\text{C}^\# \text{OH}$) and passive ($\text{C}^\# \text{O}_x$) carbon surface oxide species



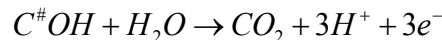
2) Formation of OH and oxide surface species on Pt



3) Oxidation of active carbon surface species ($\text{C}^\# \text{OH}$) with OH spill-over from Pt at intermediate potentials

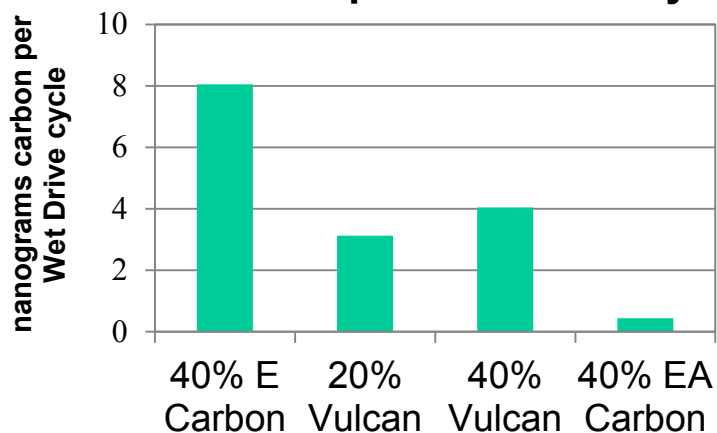


4) Oxidation of active carbon surface species ($\text{C}^\# \text{OH}$) with H_2O at high potentials

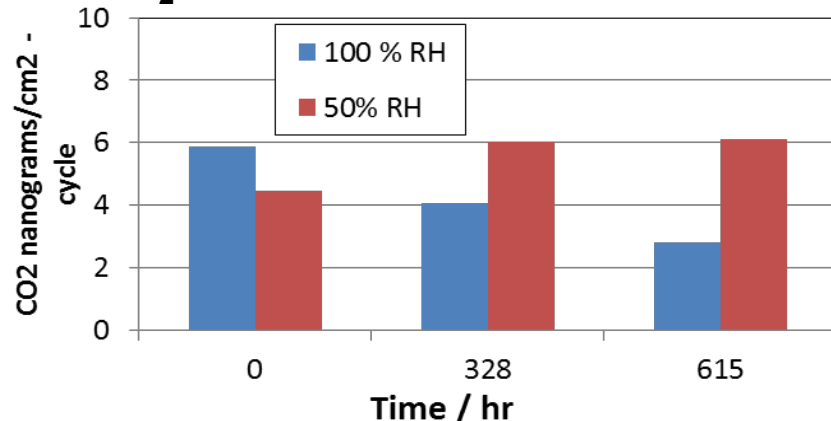


Carbon corrosion during drive cycle

Corrosion Rate per Wet Drive Cycle



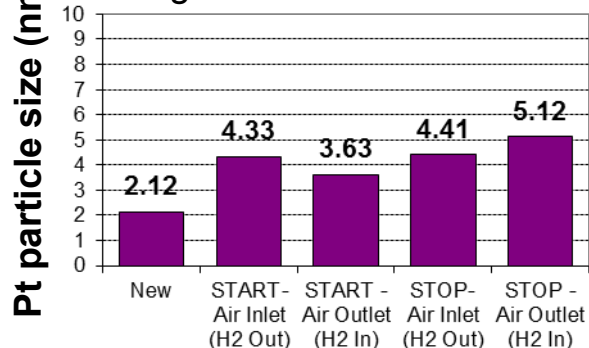
CO₂ Production Measured over Time



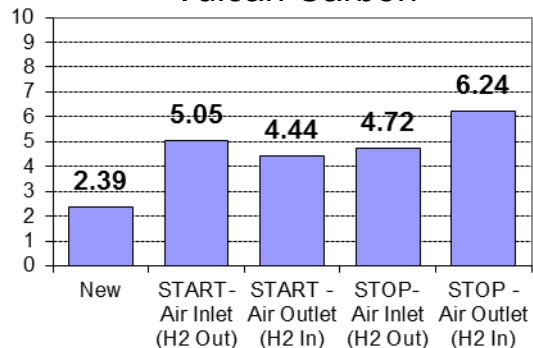
- Carbon Corrosion E>V>EA, Carbon corrosion rate continues with time

Pt Particle growth during SD/SU doesn't correlate with carbon corrosion

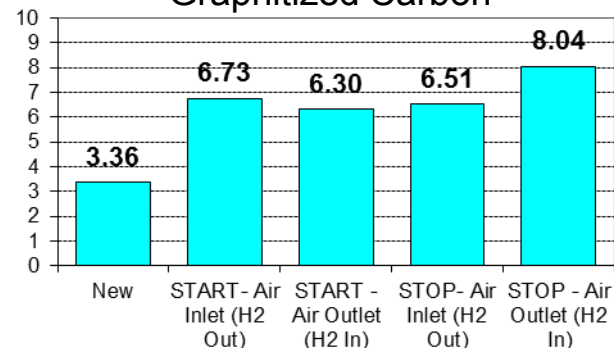
High Surface Area Carbon



Vulcan Carbon



Graphitized Carbon



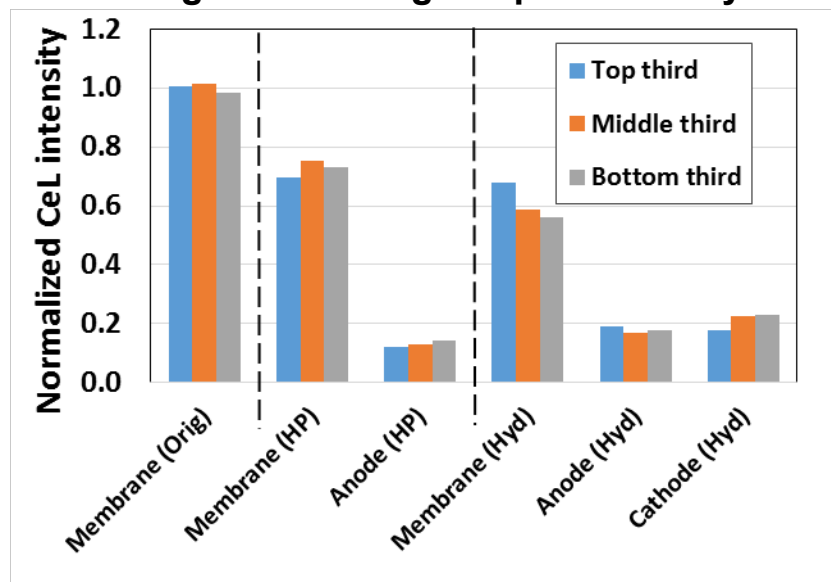
- Graphitized carbon has lower carbon corrosion rate, but greater Pt particle growth during SD/SU

- Pt particles need stabilization on graphitized carbon supports for a durable catalyst

Cerium dissolution and migration during fuel cell operation

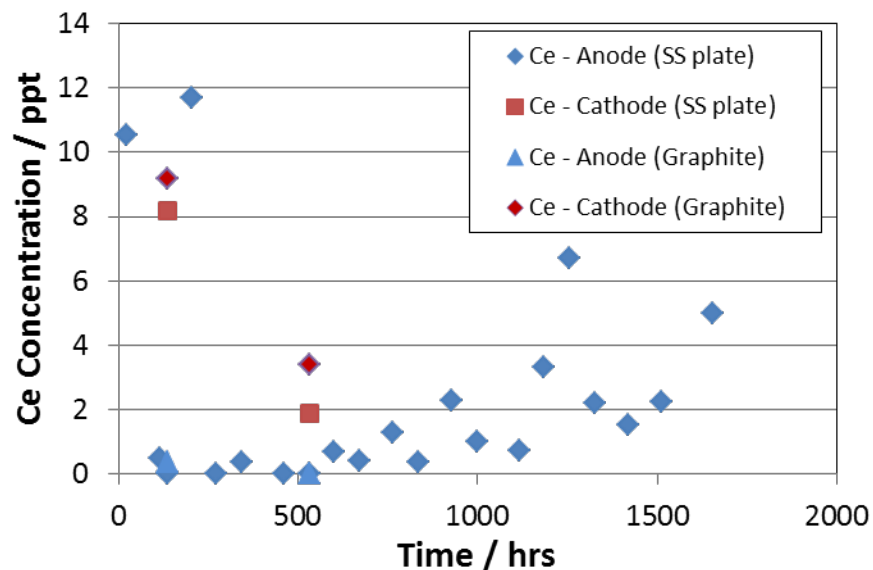
- Cerium (and others including Pr, Mn, Gd, Zr) used for membrane chemical stabilization/radical scavenging
 - Issues with cerium migration and “wash-out,” reduced performance, long-term durability
 - F.H. Garzon: DOE FCTO 2013, 2014 AMR
 - M.V. Lauritzen et al. (Ballard), Grove Fuel Cell Event April 2014
 - Investigate cerium migration: driving force, in situ concentration profiles, leaching rates
 - Stabilize cerium, localize for long-term increase in durability

Cerium migration during hot-press and hydration



- Cerium is very mobile in ionomer phase

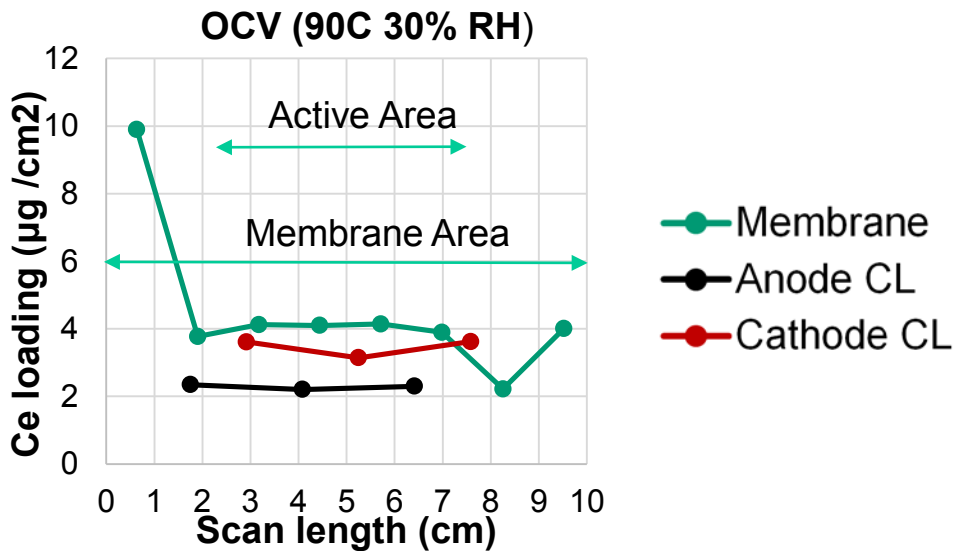
Concentrations of Cerium in water effluent



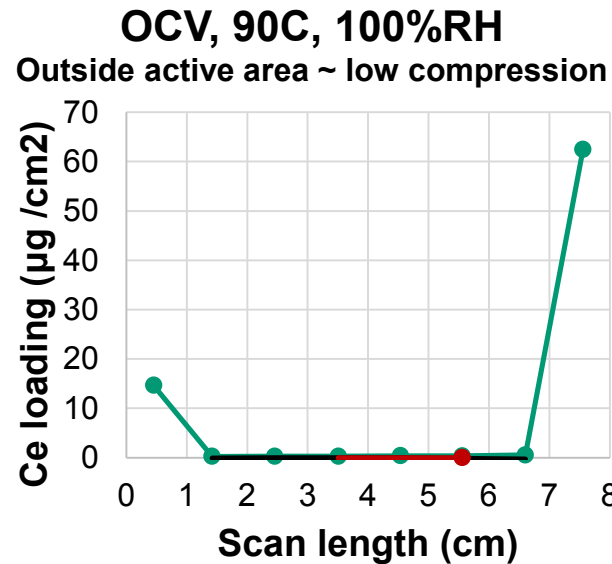
- Cerium in effluent increases

HP = Hot pressing at 130C / 2 minutes
 Hyd = Conditioning at 80C and 100% RH for 24 hours

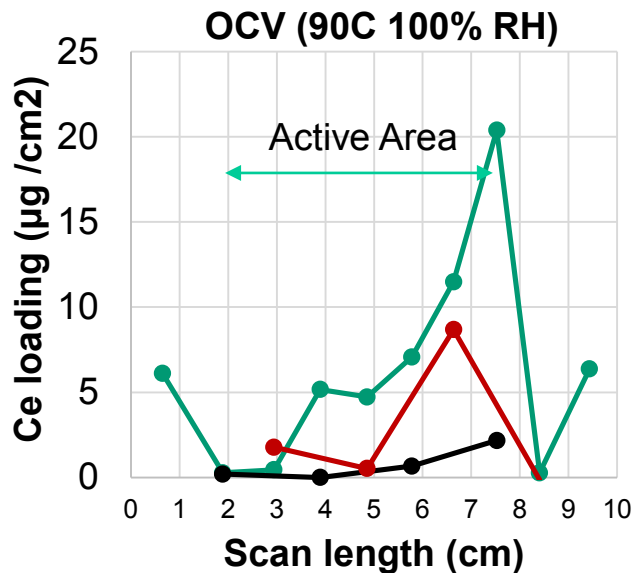
Cerium migration dependent upon conditions



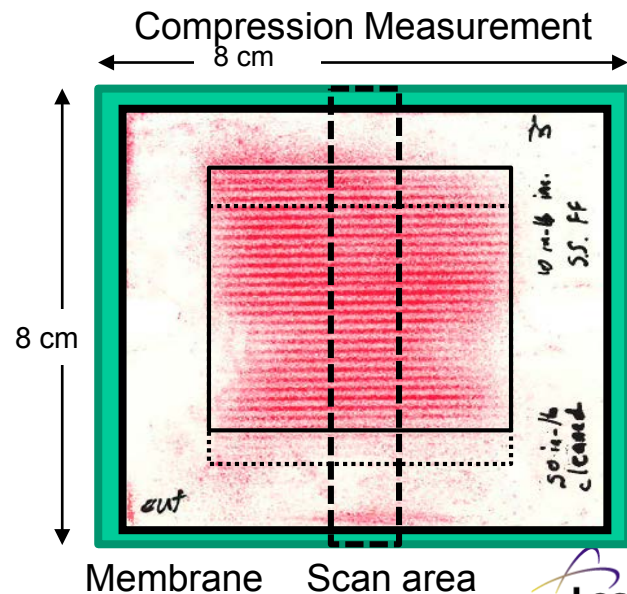
- Cerium concentration ~ flat at 30% RH



- No Cerium left in active area
- Cerium migration to low-compression area



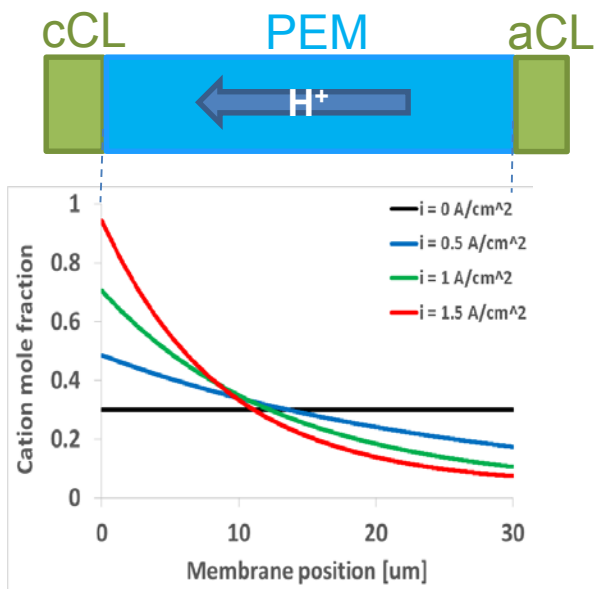
- Cerium migrating to outlet at 100% RH



Cerium cation concentration during operation modeling and experimental

Preliminary Model Description:

- Concentrated solution theory
- Cerium assumed not leaving membrane
- Ion flux has 3 components: diffusion, migration and streaming current (induced by water content gradient in the PEM).

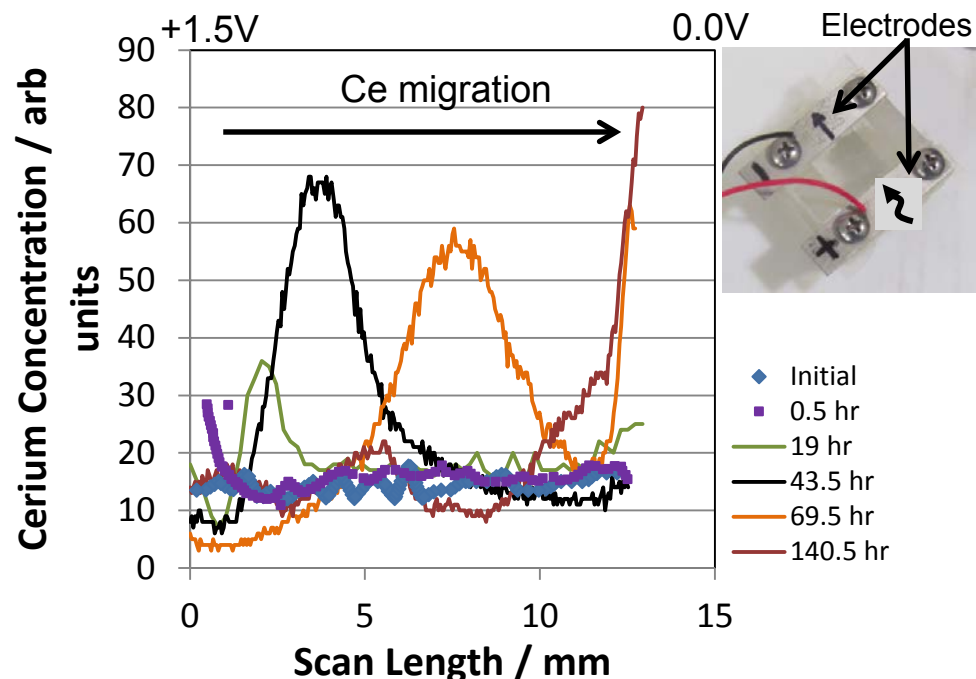


Cerium cation distribution in the membrane

- **With current flow, cerium cations accumulate near the cathode**

In situ Experimental Observations:

- Scanning elemental analysis with applied potential
- Measured Ce in xy plane (over 12.5 mm) with 1.5V
- Future: measure with current
- Future: measure cross-sectional concentration by APS

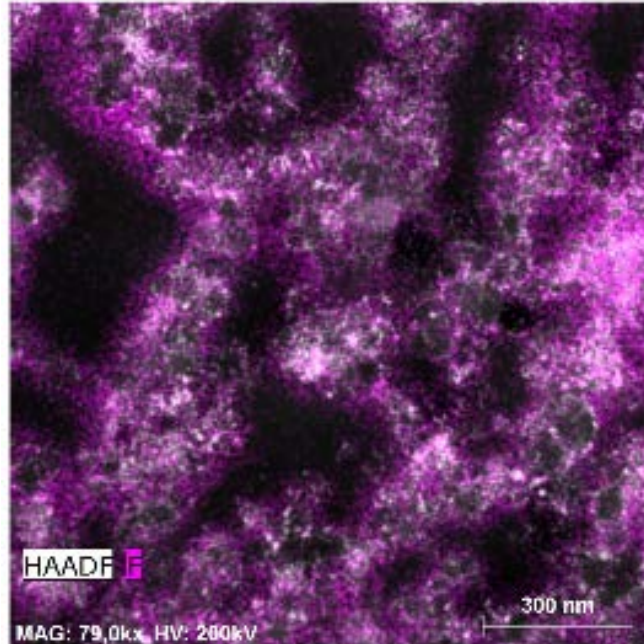


- **Cerium migrated towards lower potential**
 - Potential only, no current flow
- **Cerium migrating from under electrode**
- **Upon potential removal, Ce did not re-equilibrate**

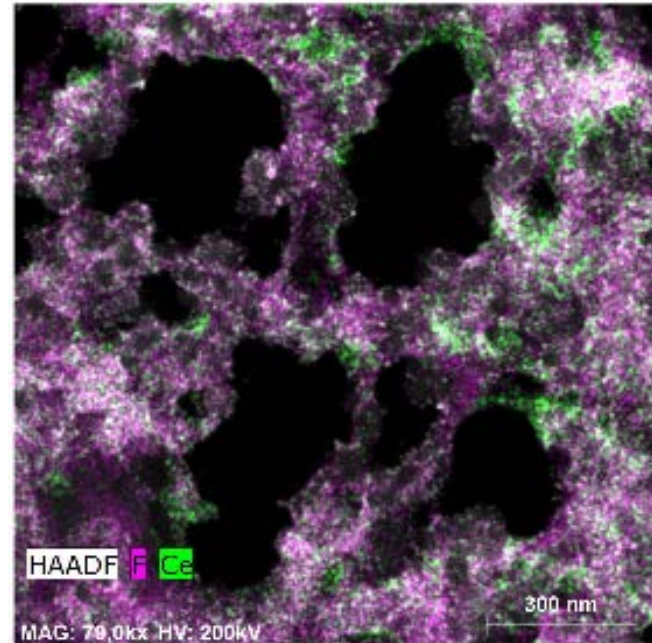
Cerium localized in regions of catalyst layer

Ionomer Mapping of Catalyst Layer Post testing

Nafion[®] layer (pink) around Pt/C



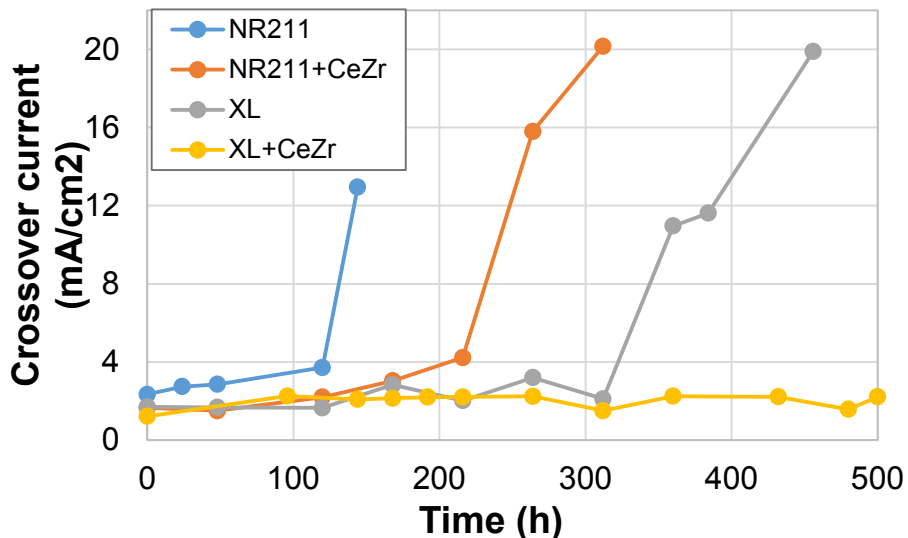
In some ZONES, Ce (green) is observed inside the Nafion[®] layer



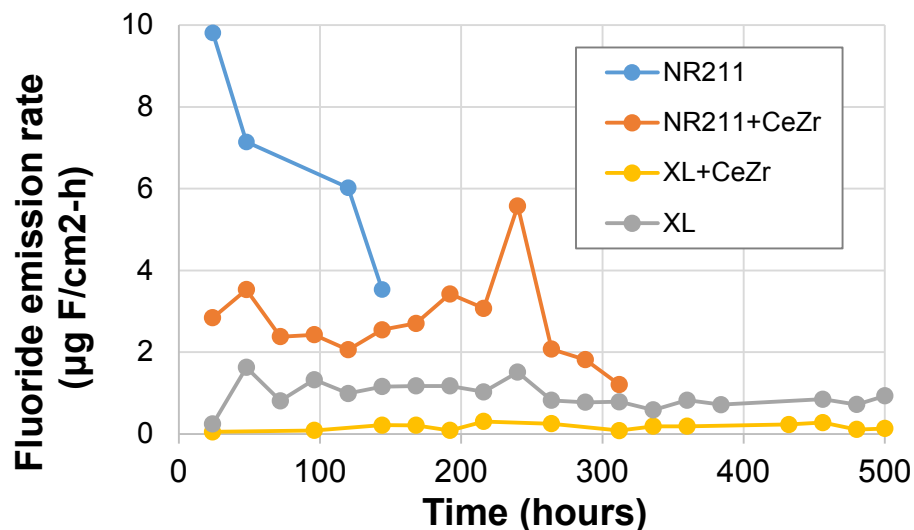
- Localized interactions of Cerium and catalyst/ionomer
 - Cerium localized where sample didn't 'wet' with epoxy
 - Where epoxy wets the CL, are likely the more hydrophobic regions
 - Thus where cerium is localized are the more hydrophilic regions

Ce as CeZr in Cathode CL shows better long-term durability

Crossover during chemical ASTs (90C, 30% RH)

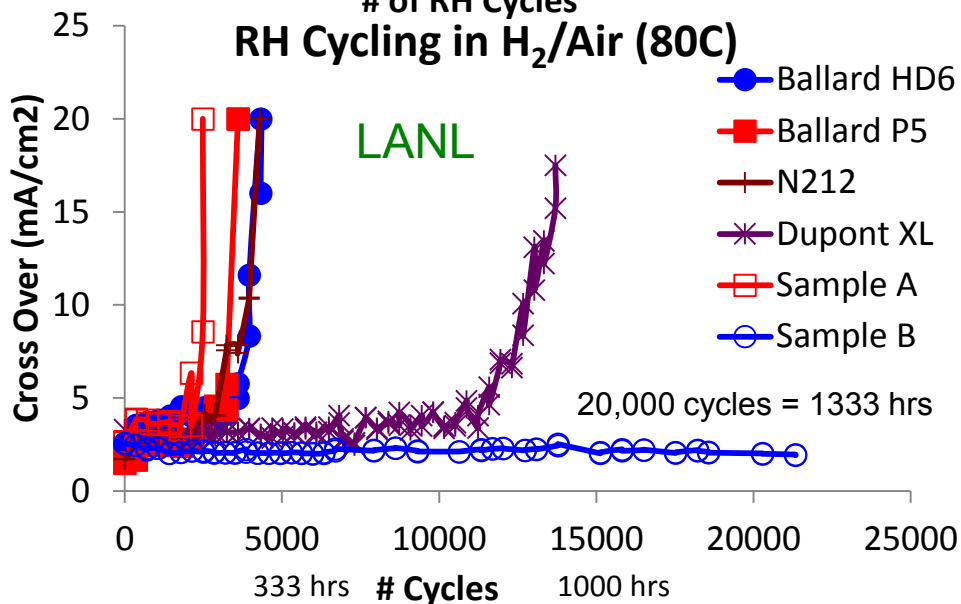
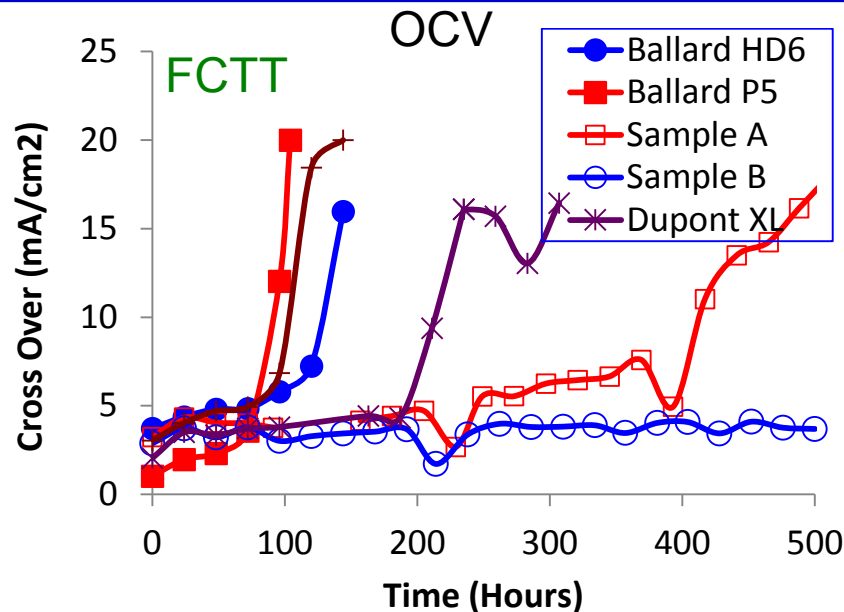
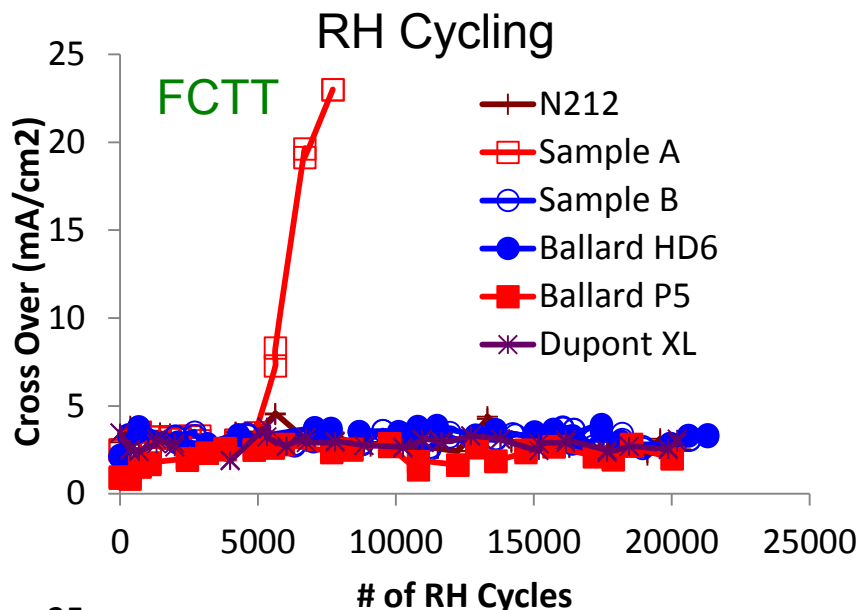


Total fluoride emission rate



- **Addition of CeZr to Cathode Catalyst layer improves membrane durability of both:**
 - N211 (no radical scavenger)
 - XL (with radical scavengers)
- **Substantially reduces FER**

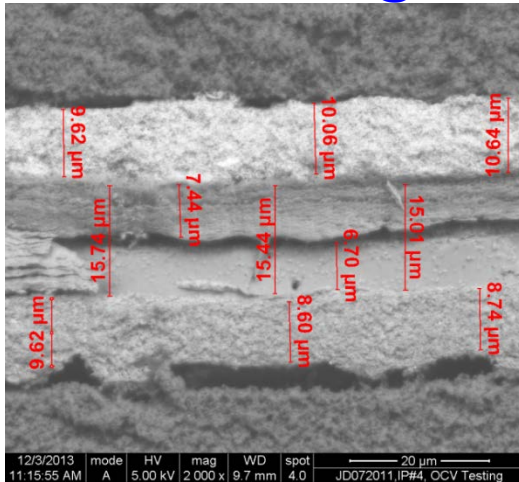
Current membrane ASTs



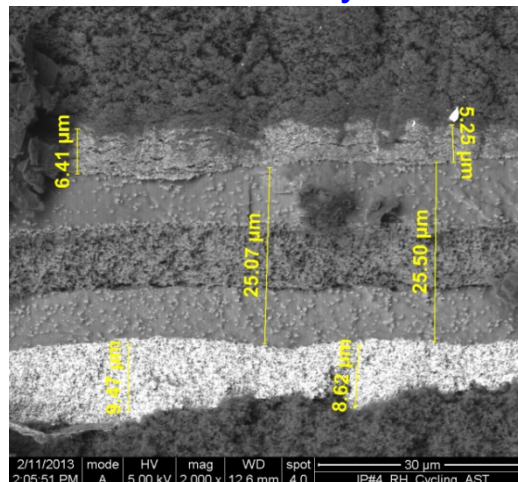
- RH cycling test does not have ability to distinguish between most PFSA membranes
- OCV testing not representative (too severe) compared to drive cycle – no predictive life ability
- Combined mechanical/chemical AST has ability to distinguish between MEAs, needs further acceleration.

Advantages of combined mechanical/chemical AST

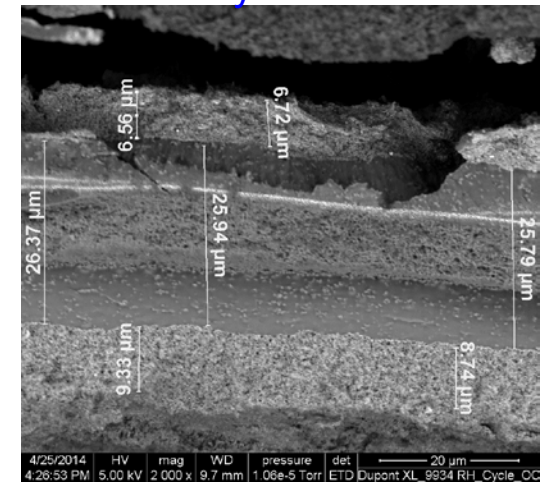
Severe degradation of DuPont XL[®] after 307 hours @ OCV



No degradation of DuPont XL[®] 20098 RH Cycles



Degradation of DuPont XL[®] 9934 RH Cycles in OCV

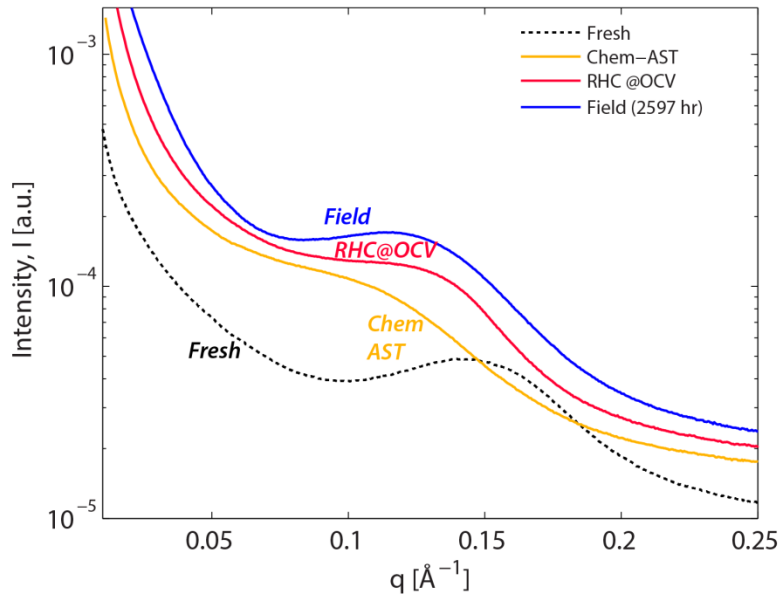


- Chemical Degradation (OCV @ 90 °C, 30% RH)
 - Cathode side of membrane is completely missing after 307 hours of OCV
 - More severe compared to drive cycle and field data
- Mechanical Degradation (RH cycling @ 80 °C in Air)
 - No visible degradation after 20,000 RH cycles
 - Most supported membranes are untouched by this AST

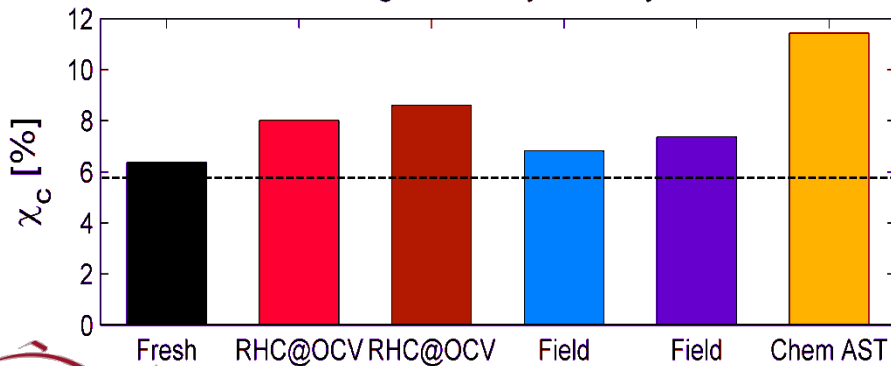
- Combined Mechanical/Chemical Degradation
 - Pt in the membrane
 - Failure by local thinning and tearing with little global thinning
 - More representative of observed field failure

Nanostructure: mechanical/chemical AST

- Water domains and Crystallinity (SAXS/WAXS)



Degree of Crystallinity

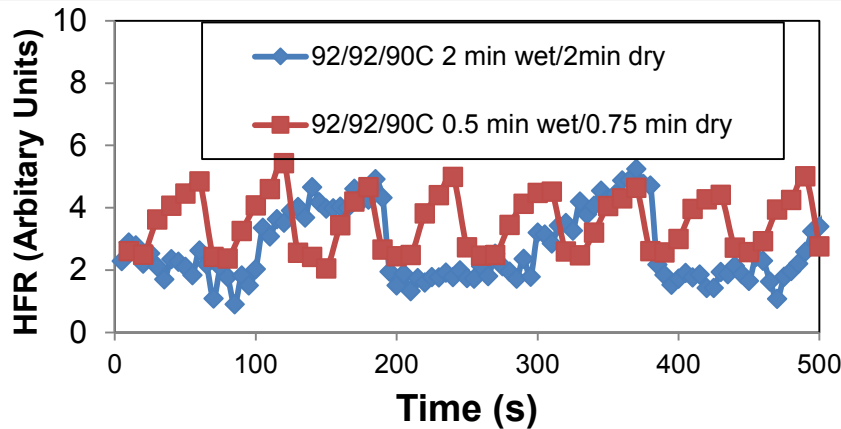


- Degradation alters the balance
 - more crystallinity → less structure
- Comparisons of ASTs
 - RH Cycling @ OCV correlates better than Chemical AST

ASTs:	vs. Field	
	Dry	Liquid
Mechanical RH Cycling	Different ✗	Similar ✓
Chemical AST	Similar ✓	More Severe ✗
Mechanical + Chemical RHC @ OCV	Similar ✓	Similar ✓

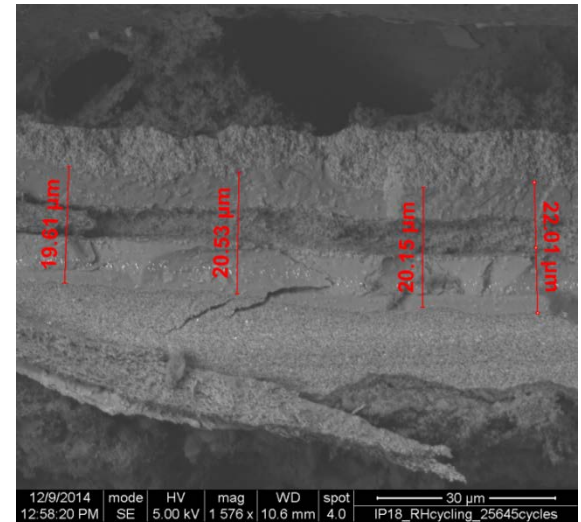
Proposed membrane AST

- 30sec wet and 45sec dry cycles at OCV:
 - $\approx 3X$ faster cycling over 2min/2min
 - Similar RH stresses as determined by HFR

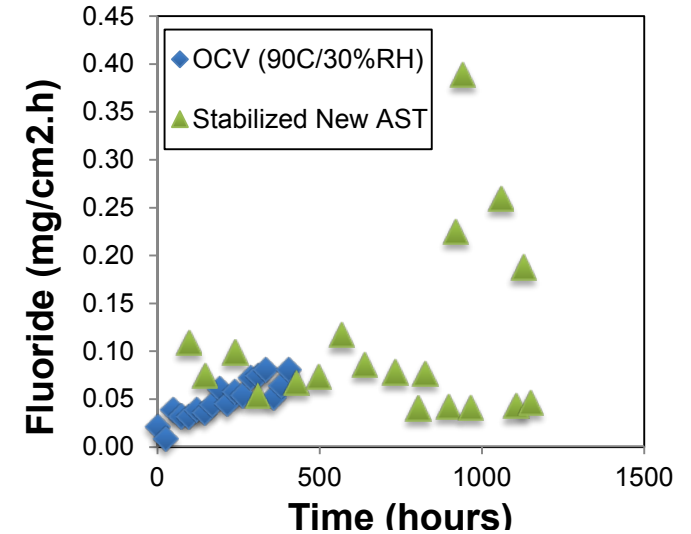


- Un-stabilized sample fails at ≈ 1500 to 2000 cycles. Failure due to mechanical degradation
- Stabilized DuPont™ XL fails in $\approx 25,000$ to $30,000$ cycles (625 hours).

- **This AST better reproduces drive cycle failure**
- **Significant acceleration over drive cycle and other membrane ASTs**

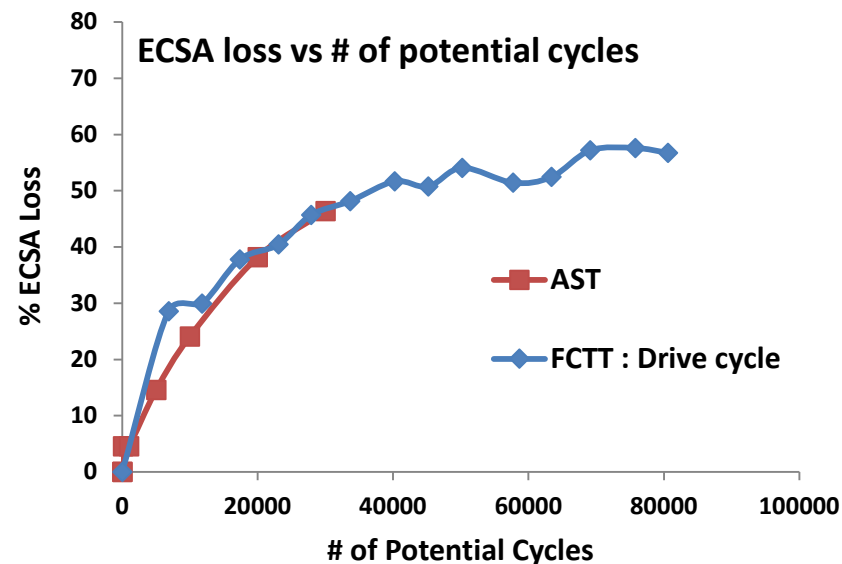
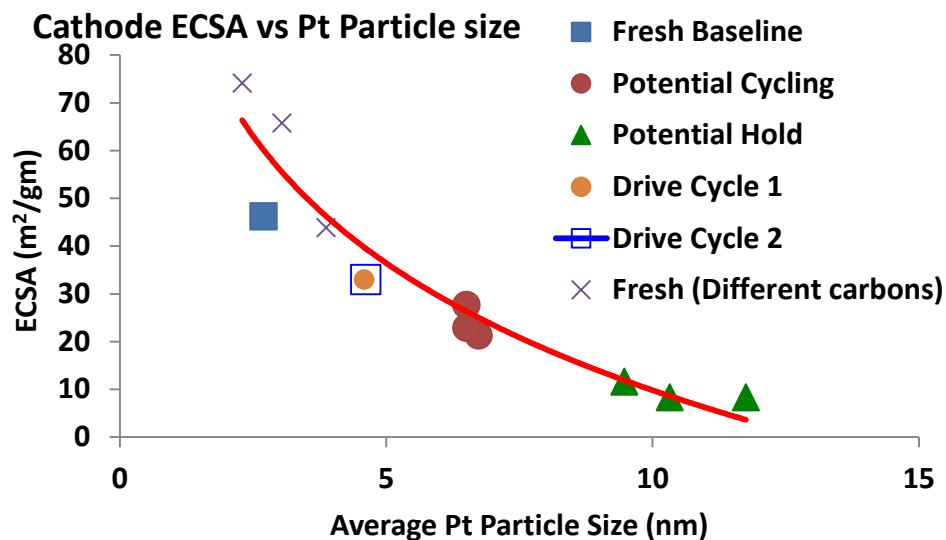


FER Comparison OCV hold and New AST



FER similar to OCV test

Current electrocatalyst AST



- Current AST of 0.6 to 1.0V results in Pt agglomeration with good correlation between loss in ECSA, increased Pt particle size, and mass activity/voltage loss
- The upper potential of 1V causes significant carbon corrosion (especially with high surface area carbons)
- 30,000 cycles \approx 2000 hours of bus operation \approx 500 hours of FCTT recommended durability protocol
- Need \gg 30,000 cycles for 5000 hour automotive durability (5000 hours \approx 175,000 cycles)
- 30,000 cycles \approx 133 hours; 100,000 cycles will be 443 hours

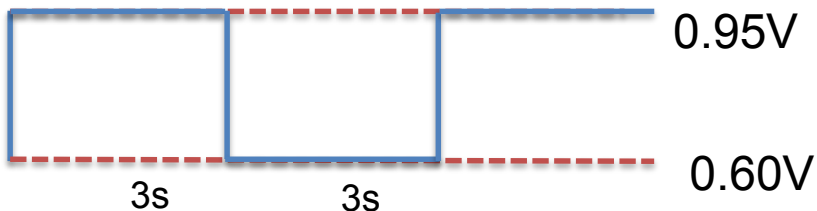
• **Need to significantly accelerate this AST**

Proposed electrocatalyst AST

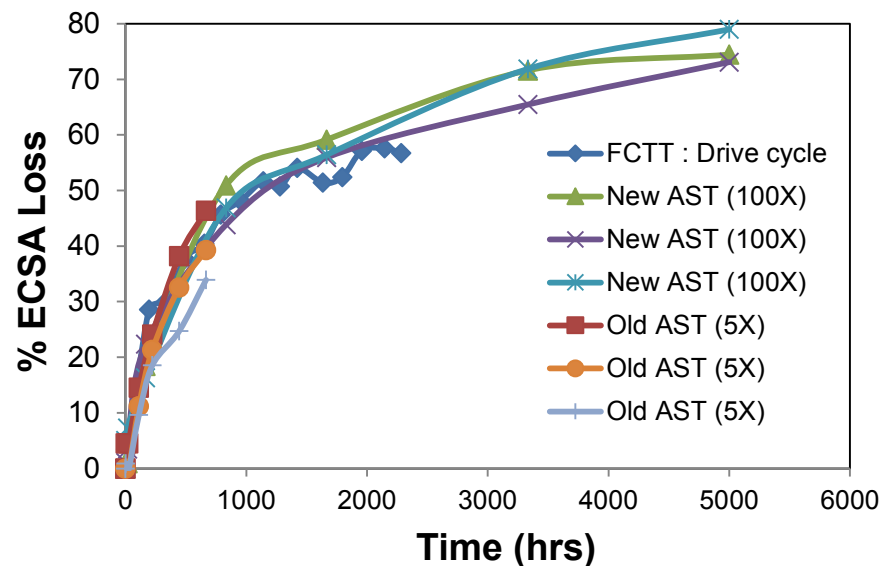
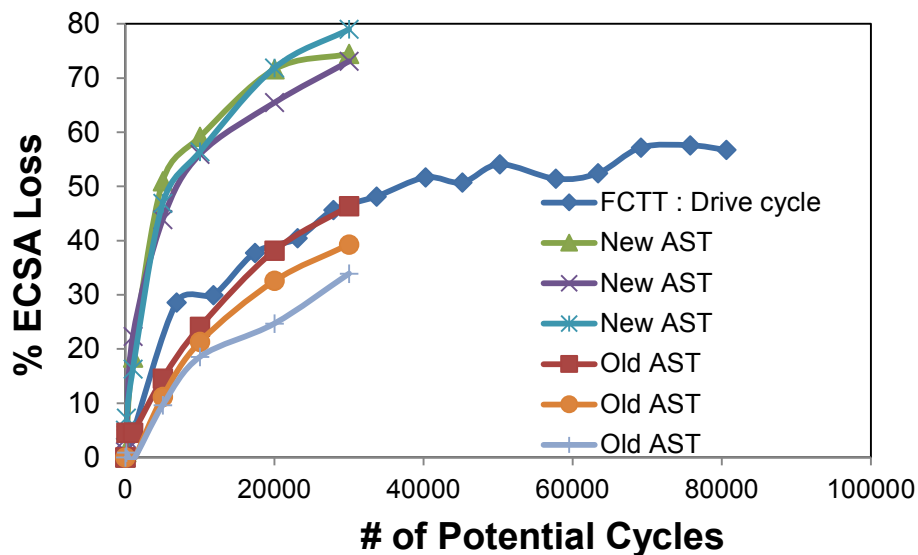
- Faster degradation can be achieved with
 - Square waves, Shorter cycle time, Slower cathodic scans
- Modify Nissan AST of 3s @ 0.6V and 3s @ 1.0V

M. Uchimura et al. ECS Transactions, 11(1), 1215-1226 (2007)

Ohma et al. ECS Transactions, 41 (1) 775-784 (2011)

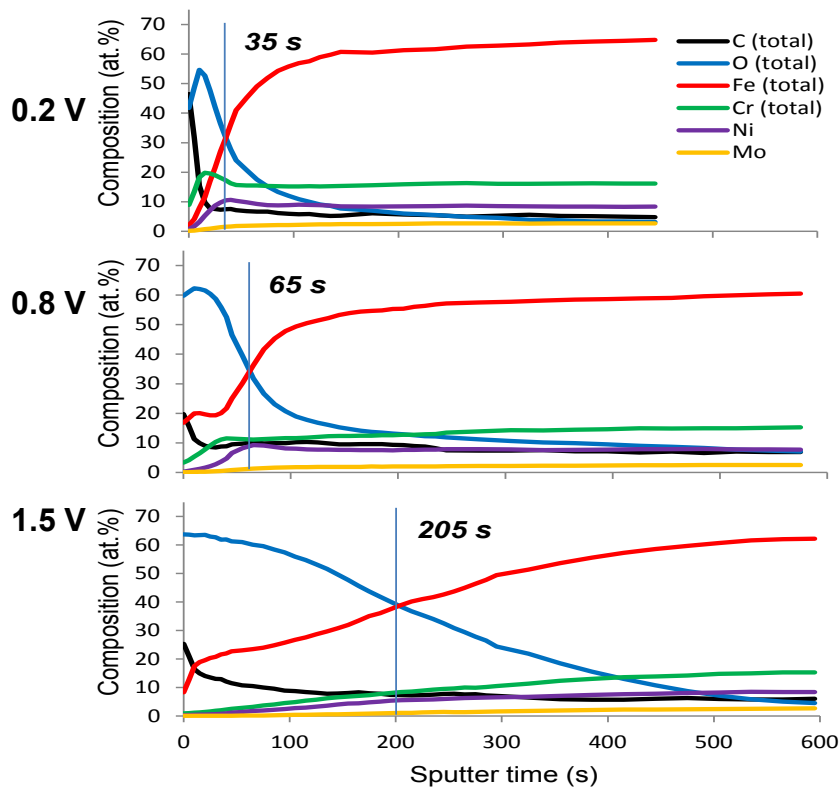


- **New AST 20X faster than old AST and 100X faster than FCTT durability protocol**

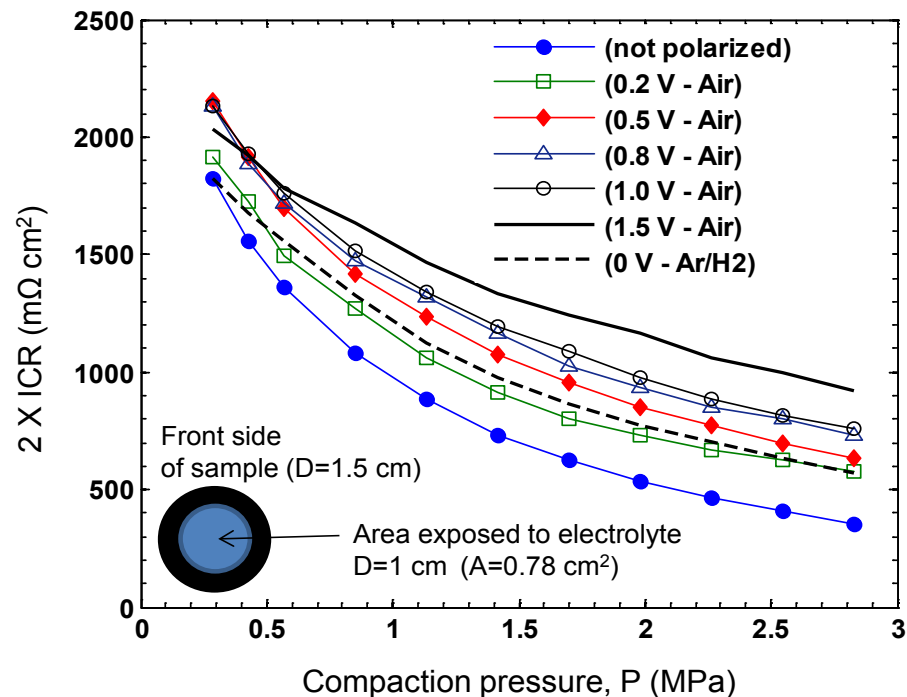


Metal bipolar plate corrosion – 316L

Elemental Compositional Profile (XPS)



Interfacial contact resistances of 316L

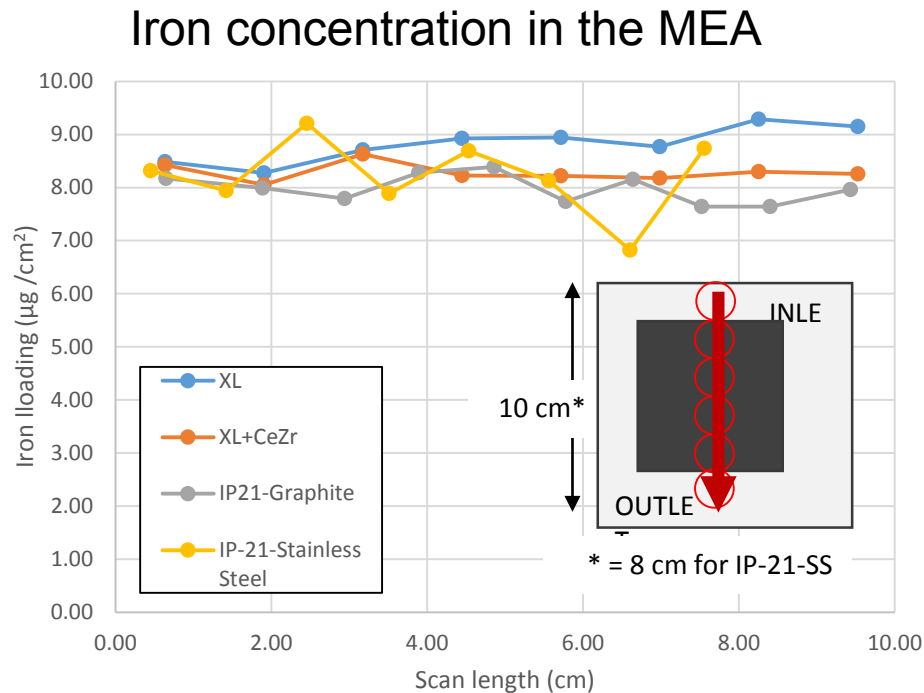
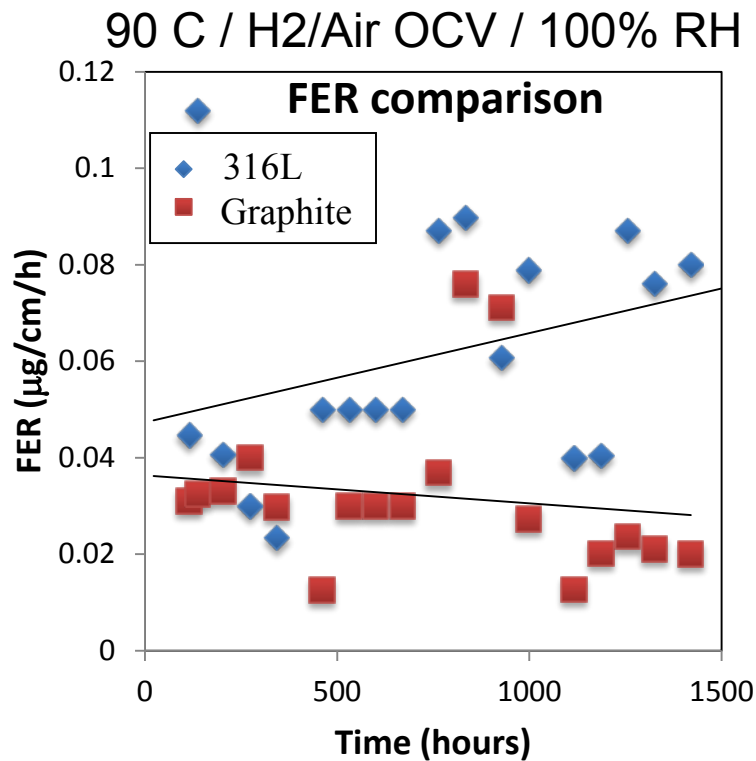


- Mixed Cr/Fe oxides on surface at lower potentials
- High voltages induce different surface structure
 - Fe oxide dominates surface at 1.5V

- Increasing oxide thickness increases contact resistance
- High contact resistance at 1.5 V not simply an increase in film thickness
 - Change in film composition

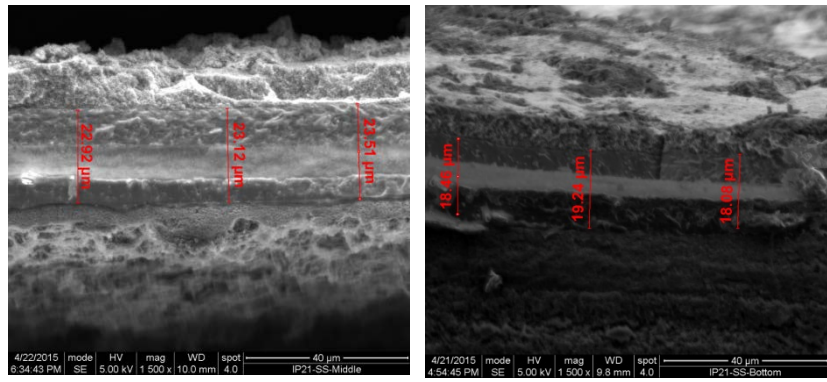
Degradation of SS316L bipolar plates in simulated fuel cell environment: Corrosion rate, barrier film formation kinetics and contact resistance, Papadias, D. D.; Ahluwalia, R. K.; Thomson, J. K.; Meyer, I Brady, M.I P.; Wang, H.; Turner, J. A.; Mukundan, R.; Borup, R., J Power Sources (2015), 273, 1237-124!

MEA testing comparison graphite vs. 316L S.S. plates



• No increase in Fe in MEA during testing

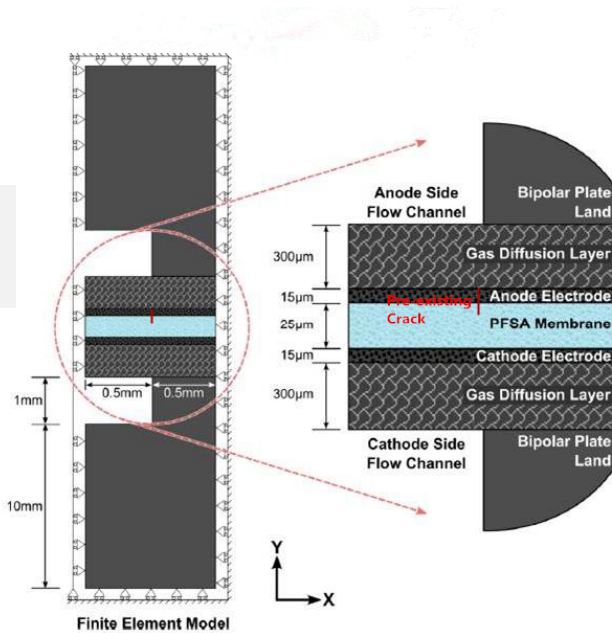
- More membrane thinning with S.S. Plates
 - (~18 micron vs. 23)
- Higher FER with S.S. plates
- However: S.S. OCV 30-40 mV higher than graphite plates



2D computational mechanics model for simulating crack propagation in a fuel-cell membrane

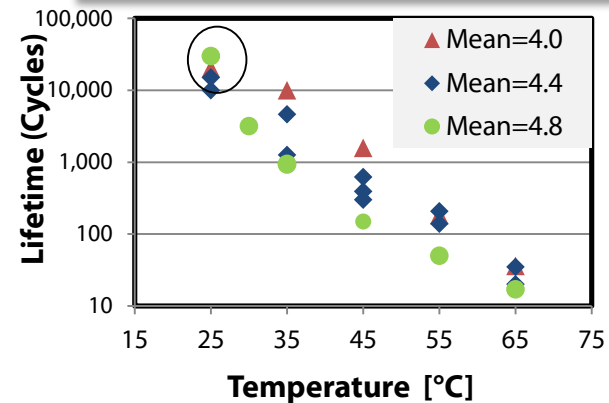
- Membrane properties are incorporated as a function of time, T, RH
- Plastic energy during deformation is used to determine crack-growth criteria
- Growth of an initial crack during RH/T cycling is monitored for various conditions

2D cell model



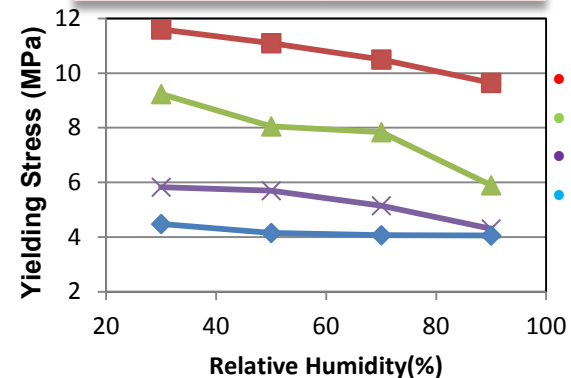
- Temperature and Humidity dependent Nafion® Membrane properties
- (Elastic with linear Hardening)

Fatigue limit v. temperature



RH (50%)

Yield Strength vs. RH

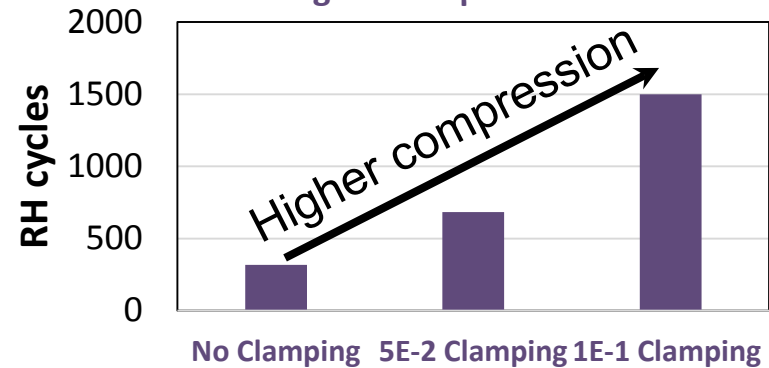


- Red T = 25 ° C
- Green T = 45 ° C
- Purple T = 65 ° C
- Blue T = T = 80 ° C

Simulation Results: Crack Propagation

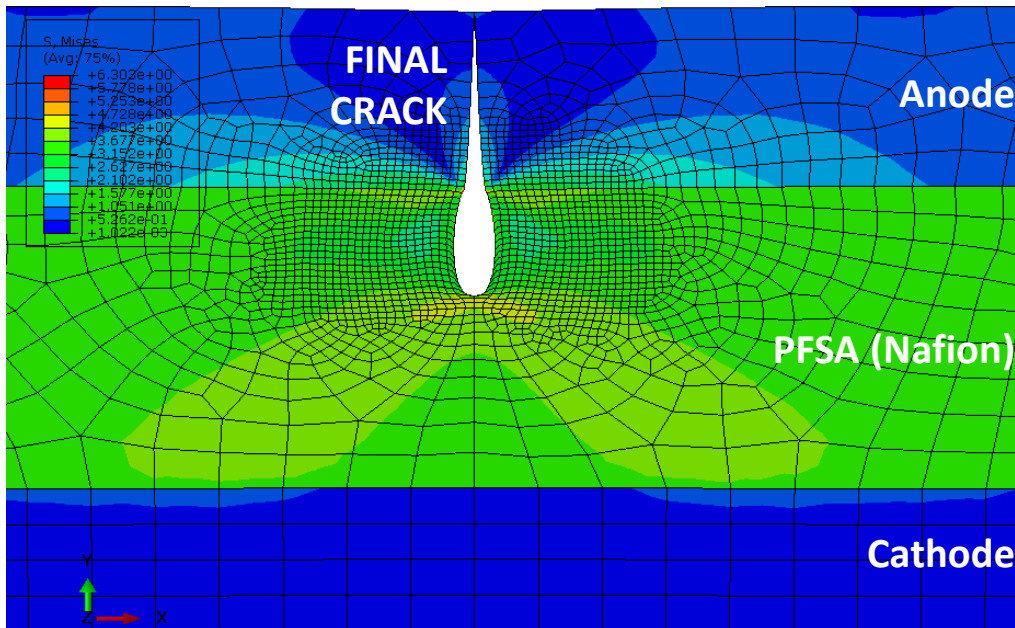
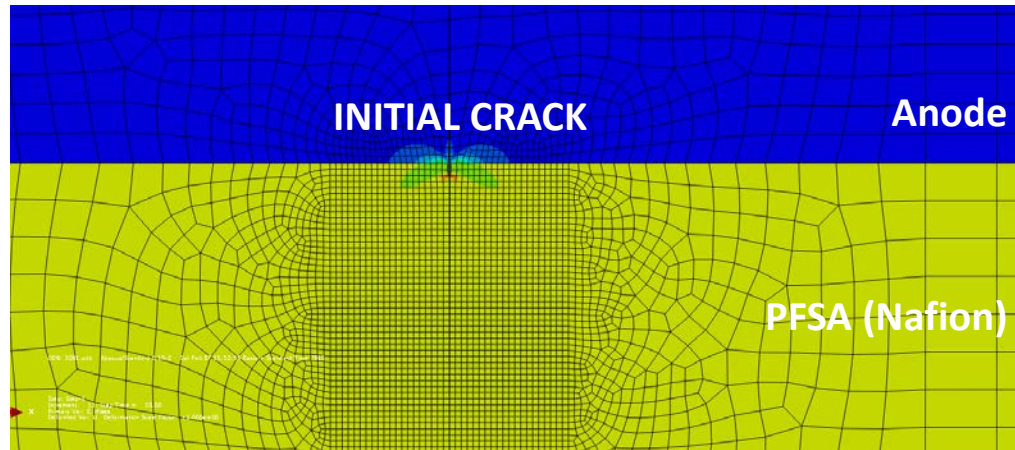
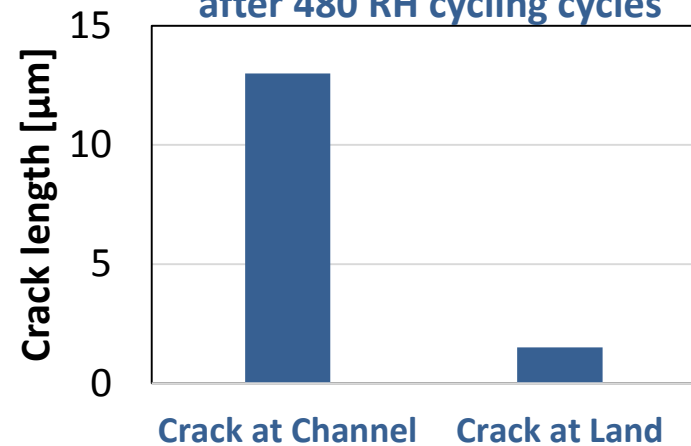
- Effect of Clamping Pressure

Number of RH cycles required to reach crack length of 7.5μm into membrane



- Effect of Crack Location

Crack length into membrane after 480 RH cycling cycles



Responses to FY14 Reviewers' Comments (Weaknesses)

No Consensus from the FY14 Reviewers

Carbon Corrosion

(1) *The OEMs* have suggested a decreased emphasis here as they have mitigation strategies that they are happy with.

(2) ... catalyst layer porosity loss during drive cycle particularly interesting

(3) Very good work done on carbon corrosion modelling and tornado plot ...

(4) Most analysis on carbon corrosion is accurate

•The majority of feedback on this topic is that the work is valuable; for FY15, we have concentrated on carbon corrosion during drive-cycle measurements to stay away from the mitigation strategies being used during SD/SU

Electrode Layer Cracks

(1) LANL should not include the impact of catalyst layer cracks on membrane durability. OEMs already know they need to eliminate electrode cracks and they know how to do it.

(2) The following should be kept: study of catalyst layer cracks and their effect on membranes ...

•Focus for FY15 on modeling related to membrane crack propagation, which helps define membrane structural requirements

Cerium

(1) phenomena observed ... are known ... or conflict with at least some OEM's observations (i.e. Ce wash out).

(2) More work on cerium

(3) The results of cerium migration from membrane ... is interesting .. Which warrants a quantitative study...

•Ce washout has been publicly presented by an OEM and other projects; our results indicate this is a relevant and beneficial area of study. Concentration has been on understanding cerium migration; there are also likely some operating condition effects (e.g. RH and water saturation) that are worthy of understanding

Metal Bipolar Plates

2013 Comment: A **large effort to obtain bipolar plates** from as many manufacturers and OEMs

2014 Comments: Recommend bringing back plate work ... Fe from plate initiating PEM degradation

Fruitful work to be done on bipolar plate durability studies... lower grad metals such as ferritics

•For FY15, looking at metal bipolar plates, and will continue to examine metal plates and interactions

Technology Transfer

- Transitioned to a National Lab program in 2013
 - Maintained collaborations with several organizations on no-cost basis

- **Since last AMR:**

- ECS and other presentations
 - ~ 9 publications / ~16 presentations
- AST Protocols proposed to DOE/FCTT
 - Protocol for un-mitigated Shut-down/Start-up
 - Combined chemical/mechanical membrane AST
 - Freeze Tolerance (no consensus reached to date)
- MEAs from 5 industrial vendors/developers
 - (Ion Power, IRD FC, WL Gore, 3M, GM)
- Three site visits to discuss durability results
 - (Ford, GM, Ion Power)
 - Evaluation of 3 different Ion Power manufacturing processes

Summary: Membrane Degradation & Mitigation Strategies

- **Catalyst layer morphology effect on durability – (Carbon Corrosion during Drive Cycle)**
 - All types of carbon show carbon corrosion during drive-cycle testing
 - Potential steps induce carbon corrosion, greatly reduced with small potential deviations
 - Size of potential step has greater effect than absolute potential (in normal operating range)
 - Must stabilize Pt particles on graphitized carbon supports for a durable catalyst
 - Model developed to fit E-carbon corrosion data. Model will be refined to include effect of RH, temp and will be extended to other carbons.
- **Membrane Structural changes and Cerium Migration/Stabilization**
 - Ce shown to diffuse in x-y plane and z direction, very quickly
 - Operational conditions (RH, potential and compression) affect cerium concentration
 - Preliminary model developed to explain Ce-migration
 - Initial experiments show Ce migration with applied potential
- **AST Validation and New AST Protocol Development**
 - New catalyst AST is 20X accelerated over FCTT AST while reducing carbon corrosion
 - Combined mechanical/chemical AST better able to represent field failures and much accelerated over current RH cycling test
 - Current OCV test not representative of field failures
- **Metal Bipolar Plates**
 - Oxide layer and contact resistance dependent upon potential
 - Preliminary results show slightly increased Fluoride emission and membrane thinning with SS plates. Effect of Fe being further examined.

Future Work

- **Ionomer/Electrode stability and structural changes**
 - Characterize and model performance losses (kinetic and mass transfer) in low-loaded MEAs
 - Effect of ionomer durability in ultra low-loaded catalyst layers
 - Chemical degradation of ionomer (increased radicals)
- **Durability of Catalysts**
 - **Alloy catalyst materials**
 - Stability of PtCo/C or de-alloyed PtNi/C catalysts in CV, RDE and aqueous dissolution apparatus
 - Effect of transitional metals (from alloys)
 - **Support stability**
 - Quantitative relationship between carbon corrosion and resulting changes in CCL structure (Pt/pore distributions, Pt utilization, ECSA)
 - Correlate catalyst and support durability
- **Accelerated Stress Testing and Protocol Development**
 - Finalize combined chemical/mechanical AST protocol
 - Compare fast RH cycling with Water concentration cycling by induced current profiles
 - Metal Bipolar Plate in situ AST Durability Protocol
 - Freeze Tolerance MEA Protocol
- **Benchmark durability status**
 - SOA catalyst/MEAs in DOE/FCTT durability protocol
 - Un-mitigated SD/SU
 - Metal Bipolar plates
 - Durability comparison of ultra-low loadings
- **Bipolar Plate Durability**
 - Corrosion of advanced bipolar plate materials
 - Transport of dissolved cations through catalyst ionomer and membrane
 - In situ protocol for AST testing of metal bipolar plates

Future Work

Membrane Structural/Chemical Degradation and Radical Scavenger Effect

- Structural/chemical changes to membranes
 - Including the effect of RH and temperature, and flow rate
 - Crystallinity changes and crystallinity effect on proton and water transport and gas crossover
- Mechanistic modeling of chemical degradation including effect of ceria
 - Fatigue crack-growth model for interfacial cracks and multiple defects
 - Effect of loading conditions, cell design, membrane
 - Validation with experimental AST data and failed membrane SEMs
 - Combined Crossover/pinhole model with chemical-degradation effects
- Cerium/radical scavenger migration
 - Model ceria/cation migration in the membrane with reaction terms
 - Measurement of cerium dissolution and migration
 - Concentration profile (in situ mapping) during fuel cell operation in both x-y and z directions
 - Define driving forces behind cerium migration (RH, current, potential)
- Mitigation
 - Cerium stabilization and localization
 - Cerium encapsulation and time-release
 - Model mitigation strategies

Thanks to

- U.S. DOE - EERE Fuel Cell Technologies Office for financial support of this work
 - Technology Development Manager: Nancy Garland
 - Additional funding being leveraged from NNSA
- All project partners and personnel

Technical Backup Slides

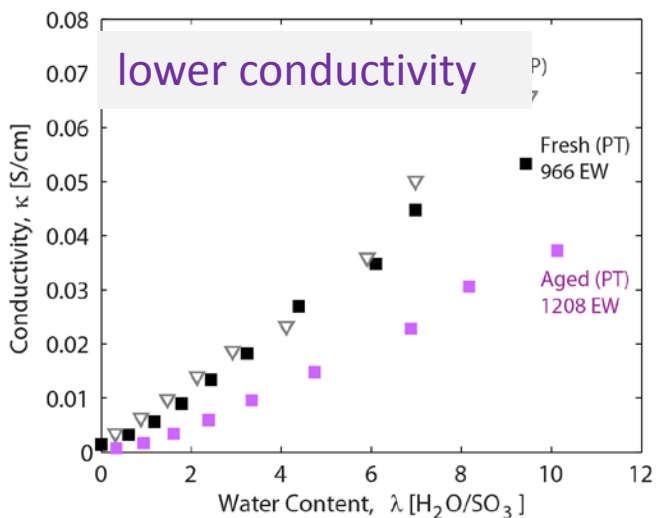
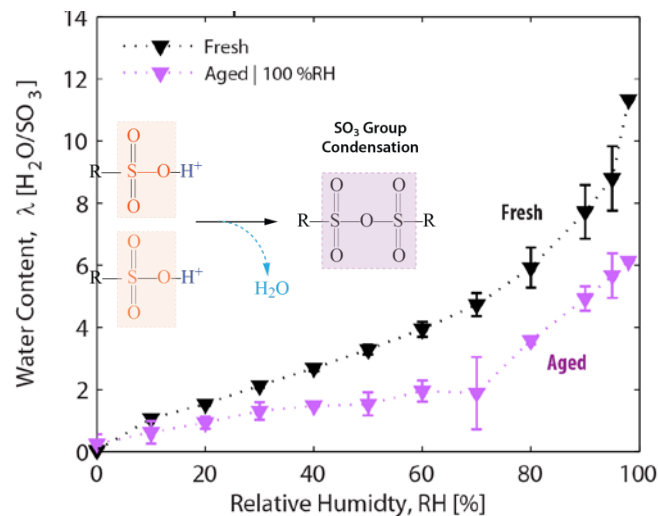
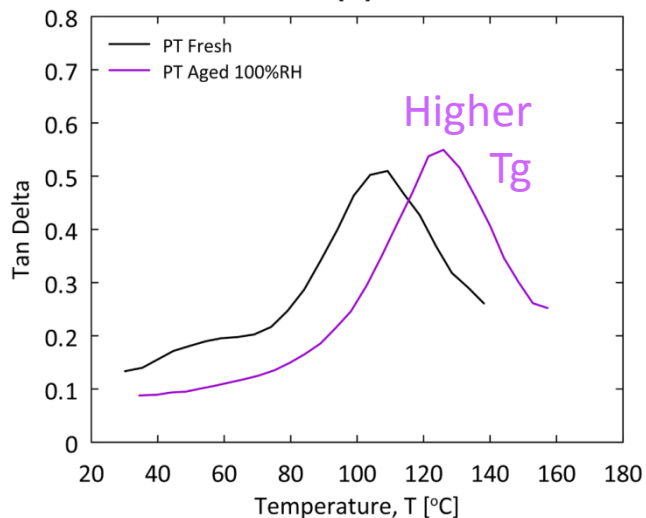
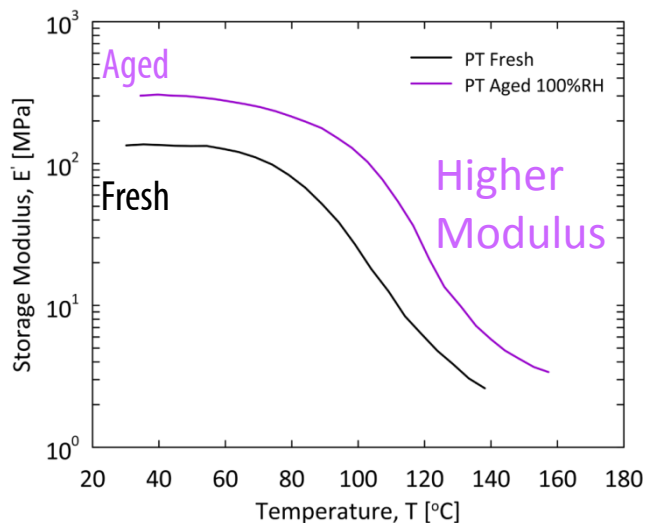
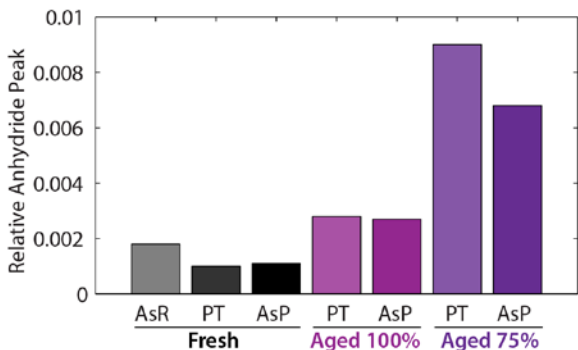
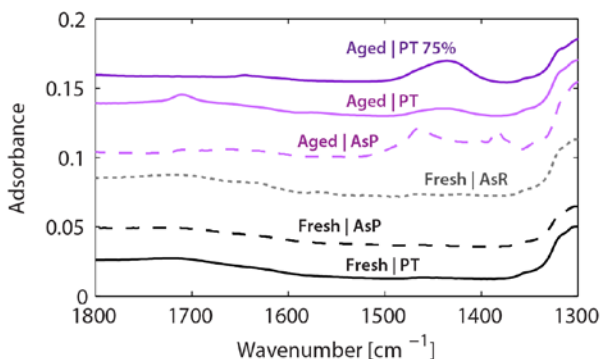
Impact of Anhydrides on Membrane

Hygrothermal ageing of pretreated and hot-pressed membranes.

In the presence of anhydrides, significant reduction in uptake and transport properties of aged membranes.

Ionic group condensation
 → Crosslinks → higher modulus

Less ionic groups + high modulus →
 less water uptake



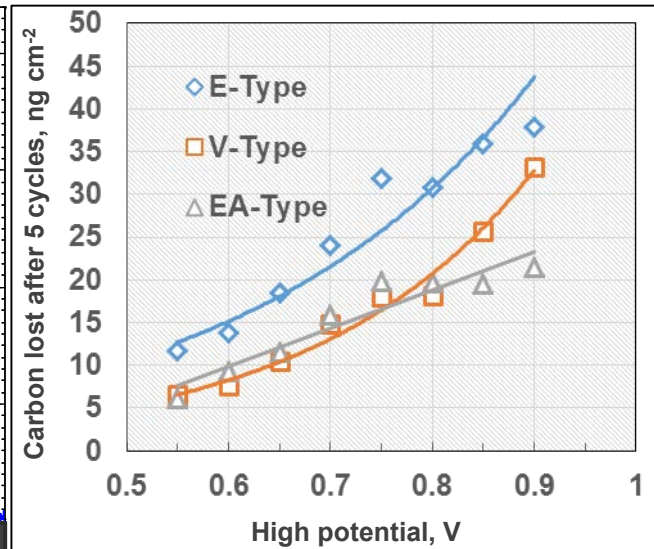
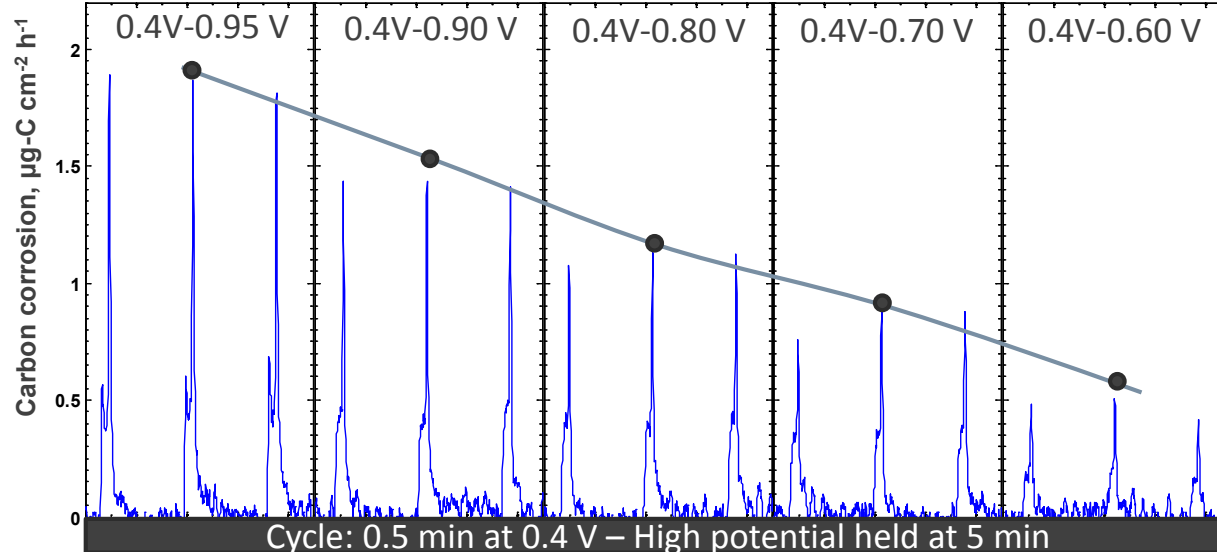
Carbon corrosion during potential cycling

Effect of varying the high potential

Carbon corrosion determined using the asymptotic CO_2 concentration at the highest potential as the baseline.

- Low cell potential constant at 0.4 V (0.5 min hold-up time), high cell potential varies
- Determine total carbon loss over 5 cycles, corrosion decreases as the high cell potential is lowered from 0.95 V to 0.55 V
- Carbon corrosion during potential cycles from 0.4 V to 0.8 V and higher
E-Type > V-Type > EA-Type

Carbon corrosion (E-Type) during cycling between 0.4 V to high potential (0.95-0.6V)

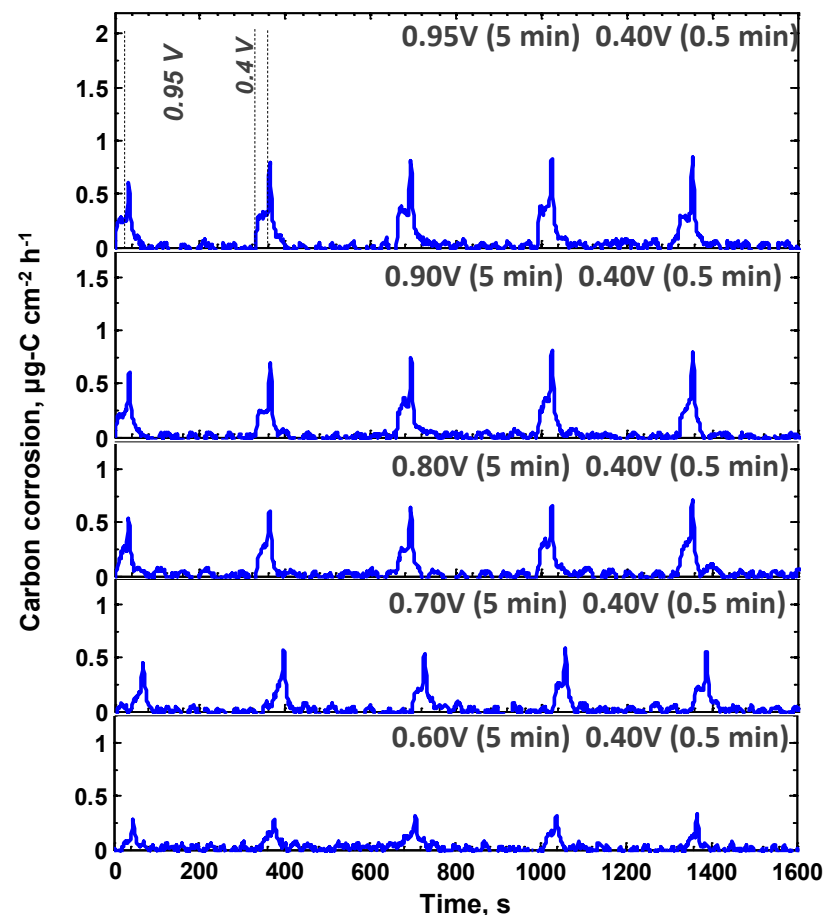
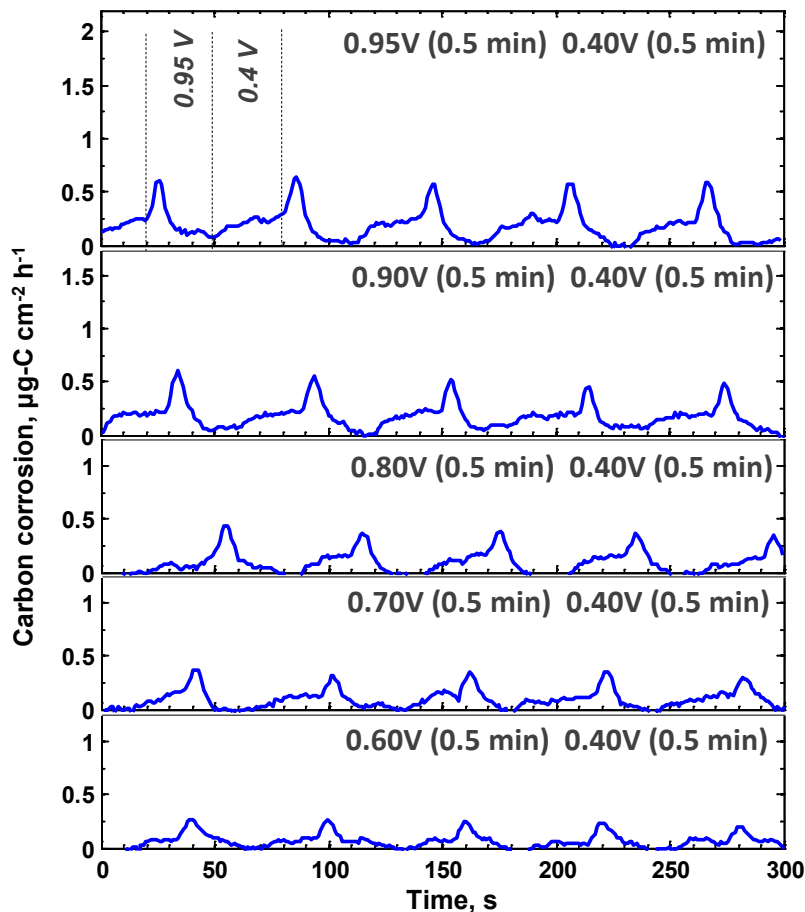


- Magnitude of spikes reduced as the high potential is lowered

Carbon corrosion during 5 cycles as function of upper potential and carbon type.
Low potential: 0.4 V (0.5 min)
High potential: 0.55-0.95 V (5 min)

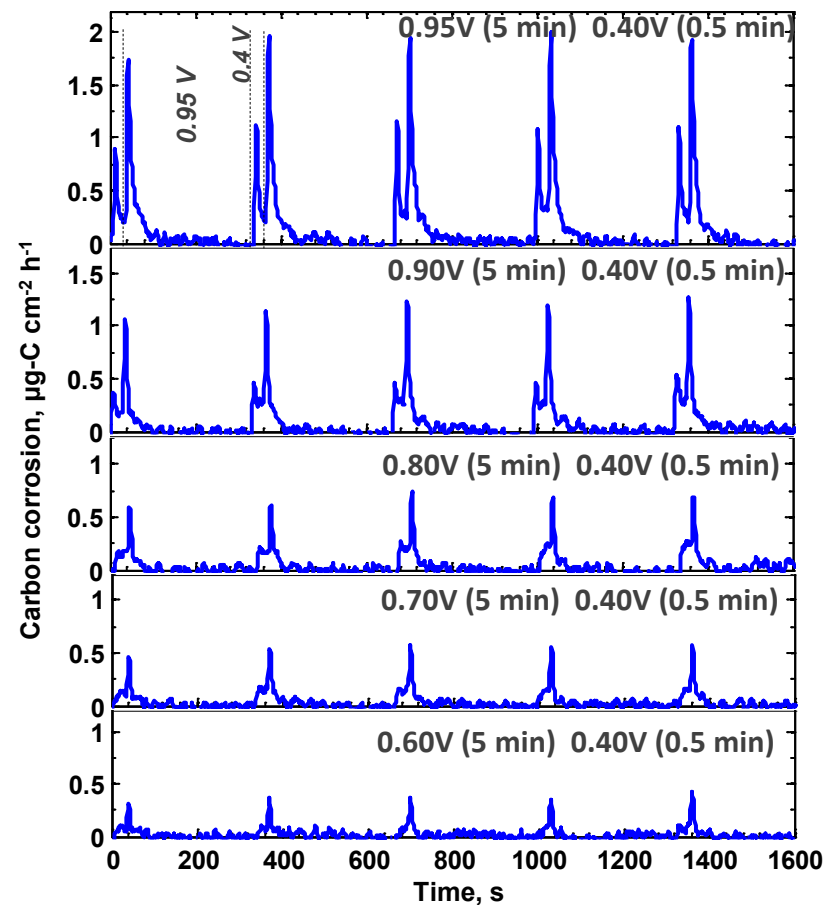
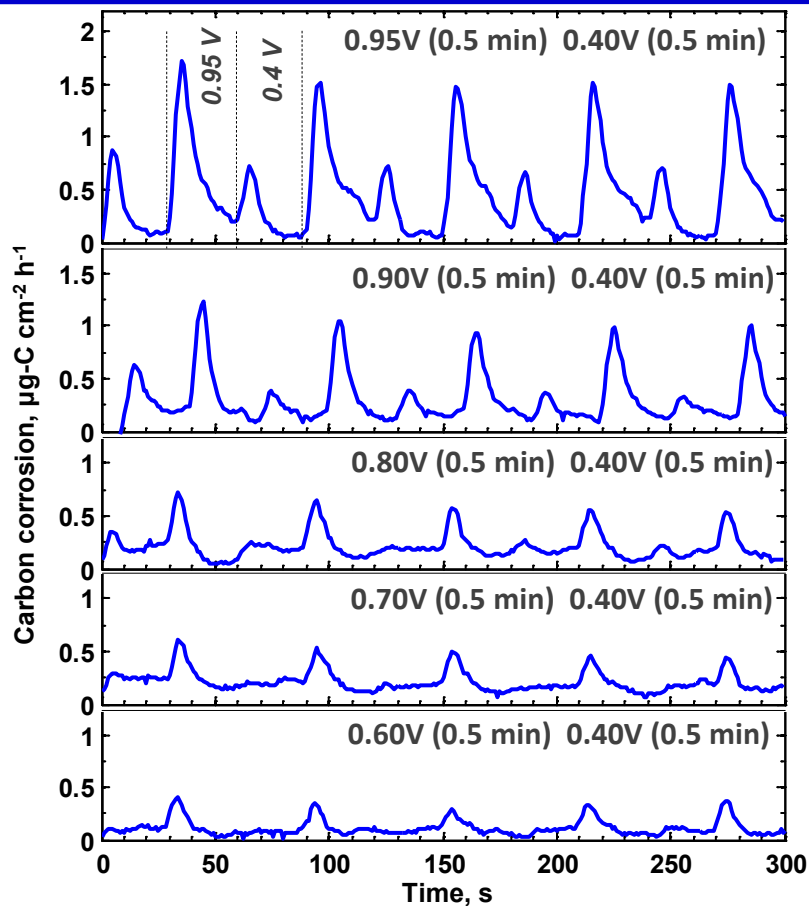


Graphitized Carbon (EA-type): Low Potential = 0.4 V, High Potential = 0.95-0.6 V



- For potential cycles to 0.8 V and higher (fixed 0.4 V low potential), corrosion rates are lower for graphitized carbon (EA-type) than for other carbons analyzed (E-type, V-type)
- For potential cycles below 0.8 V, the magnitude of spikes upon a step change in potential similar as for V-type carbon

Vulcan Carbon (V-type): 0.4 V Low Potential, 0.95 - 0.6 V High Potential

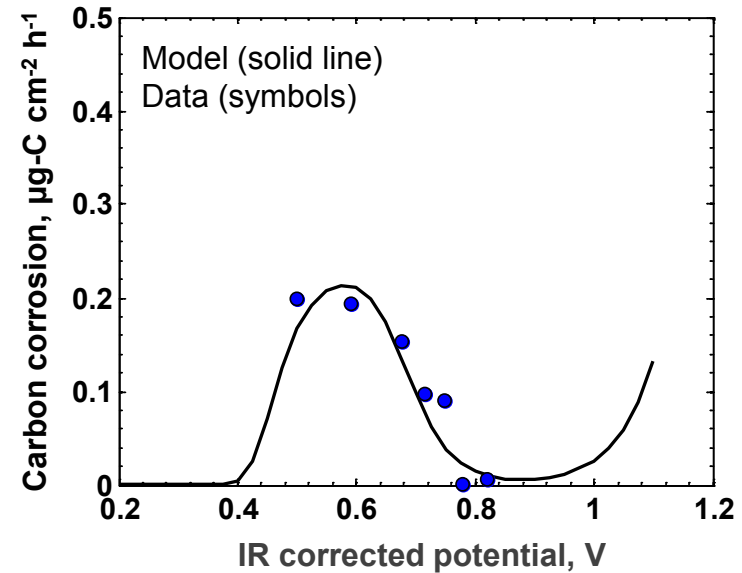
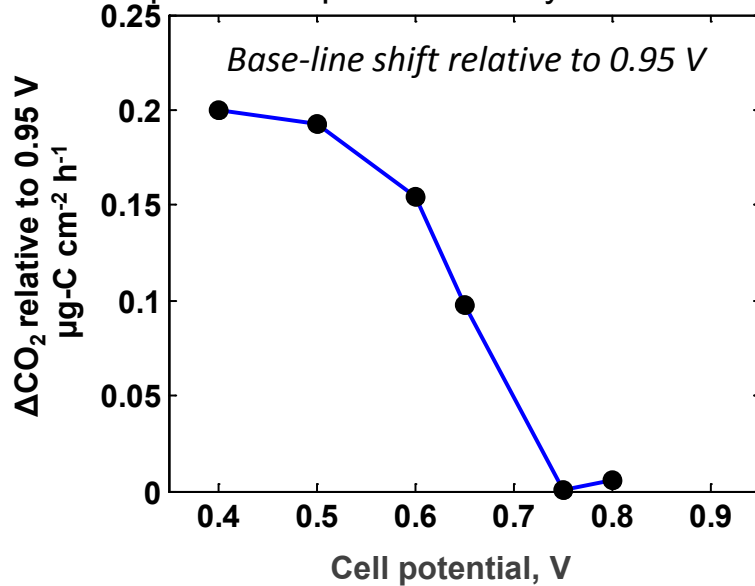


- Vulcan[®] carbon (V-type) shows qualitatively similar trends as Ketjenblack[®] carbon (E-type)
- For potentials 0.9 V and lower, the magnitude of spikes upon a step change in potential is lower for V-type carbon than for with E-type carbon



Model predicts the corrosion behavior at steady state conditions

- Steady-state corrosion rates at low potentials determined from the difference in base-line concentration relative to 0.95 V
- Preliminary model matches steady-state corrosion rates at potentials between 0.5-0.8 for E-type carbon
- Model predicts a peak in steady-state corrosion at 0.6 V (IR corrected potential)



Corrosion Model

- Formation of active ($C^{\#}OH$) and passive ($C^{\#}O_x$) carbon surface oxide species



- Formation of OH and oxide surface species on Pt



- Corrosion of active carbon surface species ($C^{\#}OH$) with OH spill-over from Pt at intermediate potentials



- Corrosion of active carbon surface species ($C^{\#}OH$) with H_2O at high potentials

