Durability Improvements Through Degradation Mechanism Studies

DOE 2014 Annual Merit Review Meeting

June 16 - 19, 2014

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

Los Alamos

Project Overview

Timeline

- Project Start Date
  - **August 2009**
- Project Duration
  - **5 Years (1 year extension)**
- Project End Date
  - **Project continuation and direction determined annually by DOE**

Barriers

Fuel cells: 2011 Technical Plan

A. Durability

Automotive

5,000 hours (10% degradation)

Stationary

2017 : 40,000 hours (20% degradation)

2020 : 60,000 hours (20% degradation)

Cost/Durability/Performance are directly related

Budget

- Total project funding
  - 5 Years   : $9,726,000
  - DOE Cost   : $9,225,000
  - Cost Share : $501,000

Funding for:	FY13,	FY14
LANL	$1550k	$800k
Industry	$ 427k	$0k
Other Nat. Labs	$ 822k	$550k
FY13/FY14 Total	$2799k	$1350k

Partners

- Combination of Industrial, University, National labs, and additional no-cost partners
- See list following page

Organizations / Partners /Collaborators

- **Los Alamos National Lab (LANL)**
  - Fuel Cell testing, performance analysis, electrochemical characterization, ASTs, component characterization: (R. Mukundan, J. Davey, D. Spernjak, K. Rau, R. Lujan, D. Langlois, D. Torraco, M. Stewart, F. Garzon

- **Argonne National Laboratory (ANL)**
  - Component degradation modeling, integrated models: (R. Ahluwalia, S. Arisetty, D. D. Papadias)

- **Lawrence Berkeley National Laboratory (LBNL)**
  - Component modeling, component characterization; SAXS, WAXS: (A.Z. Weber, A. Kusoglu, K. Clark)

- **Oak Ridge National Laboratory (ORNL)**
  - TEM characterization and metal bipolar plates (K. More, M. Brady)

- **Ballard Power Systems (BPS)** **(No funding in FY14)**
  - Carbon composite bipolar plates, seal durability (P. Beattie, W. Williams, D. Ramrus, S. Loif, S. Wessel)

- **Ion Power** **(Funding in FY14 from carry-over)**
  - MEAs and MEA design: (S. Grot)

- **University of New Mexico (UNM)** **(No funding in FY14)**
  - Surface characterization – XPS: (K. Artyushkova, P. Atanassov)

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)

- **NIST- National Institute of Standards and Technology**
  - Neutron imaging: (D. Hussey, D. Jacobson)

- **University of Nancy, Lorraine France**
  - SD/SU segmented cell measurements: (G. Maranzana, A. Lamibrac, J. Dillet, S. Didierjean, O. Lottin)

Relevance and Objectives

Relevance

- Improve fuel cell durability
  - → not at the expense of component cost or 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 and component interactions and degradation mechanisms
  - Elucidation of component interactions and operating conditions leading to degradation
  - Develop advanced in situ and ex situ characterization techniques
  - Discern impact of electrode structure on durability and performance
    - Lead to better designed, and more stable electrode structures

- Methods to mitigate degradation of components
  - Use degradation mechanisms to design new materials/structures to improve durability
  - Develop operating strategies to improve durability
  - Provide predictive comparisons for material durability related operational aspects

- Develop models relating components and operation to fuel cell durability
  - Individual degradation models of individual fuel cell components
  - Development and public dissemination of fuel cell degradation models

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.

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Approach

- **Define and Interpret Degradation Mechanisms**
  - Measurements of degradation ex situ and in situ
    - Fuel cell testing and diagnostics (e.g. segmented cell, impedance, HelOx ...)
  - Characterization of Component Degradation
    - Apply characterization capabilities at the National Labs to determine structural and material property changes
    - Advanced characterization (e.g. neutron imaging, SAXS, TEM …)

- **Modeling**
  - Analysis to define individual component contributions to loss in performance
    - Define performance losses due to individual component degradation
    - Component degradation models – kinetic/rate based (ANL)
    - Fundamental degradation mechanisms (LBNL)

- **Mitigation**
  - Explored Pt/carbon loading, carbon mixtures, catalyst layer thickness on relative degradation
  - Membrane degradation vs. SD/SU carbon corrosion
  - Radical scavenger effect and washout
  - Modeling comparisons of degradation rate by component and operating condition
    - For example: Develop tool able to predict the cost of durability of a start/stop of a fuel cell and function of mitigation strategies to minimize the degradation of catalyst support

- **Coordinate activities with other durability projects**
  - DOE Durability Working Group, joint material testing with LANL-AST project

2014 Milestones

No.	Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Go/No-Go Decision Criteria	
1	Q1	12/31/2013	Regular	Quantify degree of cerium migration during fuel cell operation in membranes comparing relative drive cycle operation and steady-state operation to determine potential effect on ceria migration	NA	Complete
2	Q2	3/31/2014	Regular	Quantify and compare the loss of pore volume after drive cycle tests of 0, 50, 100, 200, 400, 1000 hours	NA	Fuel Cell tests complete; MIP, TEM measurements complete
3	Q3	6/30/2014	Regular	Complete testing comparison of single type carbons and mixed carbon (HSAC and graphitized) comparing the structure effect on mass transport losses	NA	Complete, but continuing
4	Q4	9/30/2014	Go/No-Go	Evaluate the effect of catalyst layer cracks on membrane durability during RH cycling such as in wet/dry drive cycle tests. Compare two different crack densities/geometries on gas crossover during durability test.	Determine applicability and effectiveness of electrode crack/durability test. Measure time to failure in AST: if different by > 10% in the preparation/absence of cracks, expand tests to membranes with/without mechanical reinforcement and develop and propose Electrode Structure/Membrane AST in FY15.	MEAs made 3D Tomography doesn't show intended cracks, by multi-layer catalyst application, so different method will be utilized

Responses to Previous Year Reviewers' Comments

Mitigation

(1) Mitigation recommendations are very minimal. More substantial recommendations are expected from LANL. Mixing of stable cathode supports into single electrode is good, though not very novel and already utilized in the industry.

(2) ….. work should focus on mitigating, and continued work on predicting: i.e. if you shut down like this; this is how long your catalyst will last.

We agree that more needs to be done in terms of mitigation and comparing mitigation, and we have done more this FY and is included in this presentation; however, at the same time, this project works to stay pre-competitive and not infringe upon Fuel Cell developers IP. The work of Kim et al. as part of this project with the electrode structure/solvent work was directly related to mitigation, as was the mentioned supports. Work in FY14 related to membrane durability vs. carbon corrosion related to SD/SU, and work on radical scavengers we feel will lead to mitigation strategies.

Bipolar Plates

(1) A large effort to obtain bipolar plates from as many manufacturers and OEMs would make this part helpful.

(2) It is recommended to delete most of the membrane and bipolar plate work if there is no way to extrapolate from materials under study to materials that will be used in a future commercialized fuel cell system.

Bipolar plate work de-emphasized for FY14. Work won't continue unless we observe component interactions which are important to the overall performance; We have not observed component interactions to date, and have not been able to measure cation migration into the catalyst/membrane from base metal plate corrosion provided for this project.

Membranes

(1) Because contemporary material sets may differ, it may be good to reduce work on membranes and bipolar plates.

(2) ….would membranes with radical-scavenging or peroxyl-scavenging additives defeat the utility of membrane model?

(3) Membrane degradation work is very superficial; no insight into mechanism or changes with time given.

We use membranes with mechanical stabilization and radical scavenging; we do not feel that these results are not valid – model development includes both membranes with and without stabilization.

In terms of mechanism and changes with time, we have conducted crystallization measurements (including SAXS, WAXS, TEM) previously, and information related to the structural and water uptake changes with ageing. There is more information in this presentation on this subject. The radical attack mechanism has been addressed by other groups. FY14 includes work on radical scavenger migration, structural (crystallinity) changes, and changes in water uptake.

Cerium Migrates During Operation from Membranes

- Cerium used as radical scavenger to lengthen membrane life
  - Issues with Cerium migration, reduced performance and long-term durability
    - F.H. Garzon, The Science And Engineering of Durable Ultralow PGM Catalysts
    - M.V. Lauritzen et al., (Ballard), Grove Fuel Cell Event, 3-4 April 2014, Netherlands

Change in cerium concentration for DuPont™ XL membrane

Concentration (micrograms/cm²) vs:
- Starting XL Membrane: ~7
- Pressed: ~5.4
- Conditioned: ~4.9
- 400 Hours: ~3.2
- 750 Hours: ~1.5
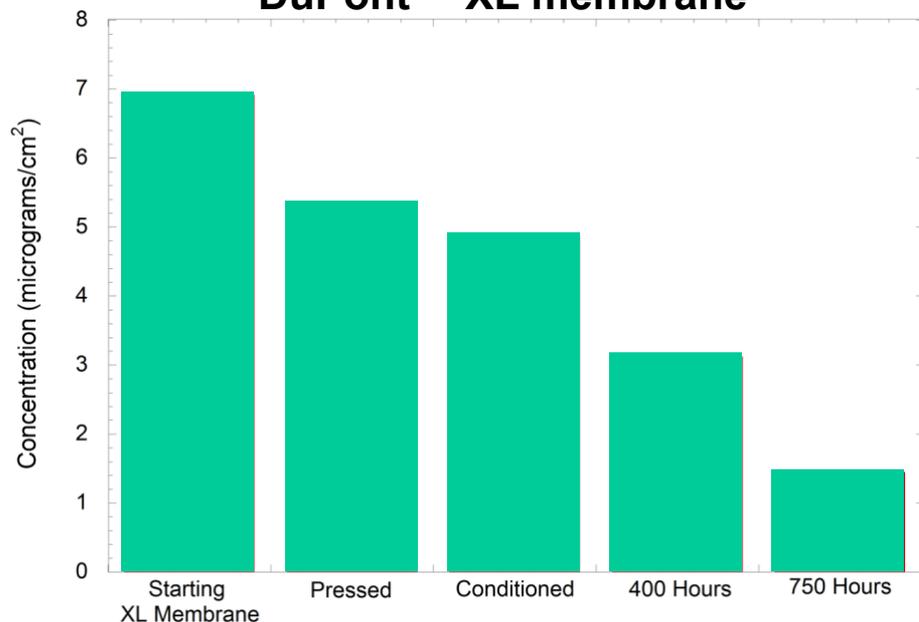
Cerium Concentration Before/After 10 min Hot Press at 90š7

Cerium Concentration / $\mu g/cm^2$ — Initial (green), Final (blue):
- N211: Final ~2.1
- XL: Initial ~6.9, Final ~2.1
- N211: Final ~2.7
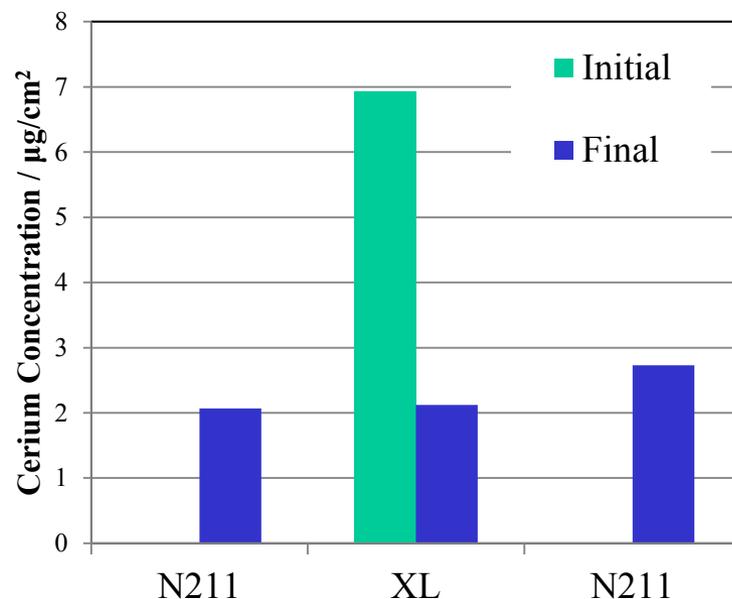
- **Cerium is very mobile in fuel cells**
- Cerium migrates from the membrane into both anode and cathode catalyst layers
- Ceria in cathode catalyst layer will migrate from the cathode catalyst layer through the membrane, to the anode catalyst layer, little cerium remaining in the membrane.

- Garzon, F., S. M. Stewart, R. Borup, M. Wilson, and A. Datye, Accepted to J. Electrochem. Soc..
- Stewart, S. M., R. Borup, M. Wilson, A. Datye, F. Garzon, ECS Electrochemistry Letters (2014), 3(4), F19-F22.

Cerium Migration to Catalyst Layers

Cerium/Platinum Elemental Line Scans from APS-Argonne
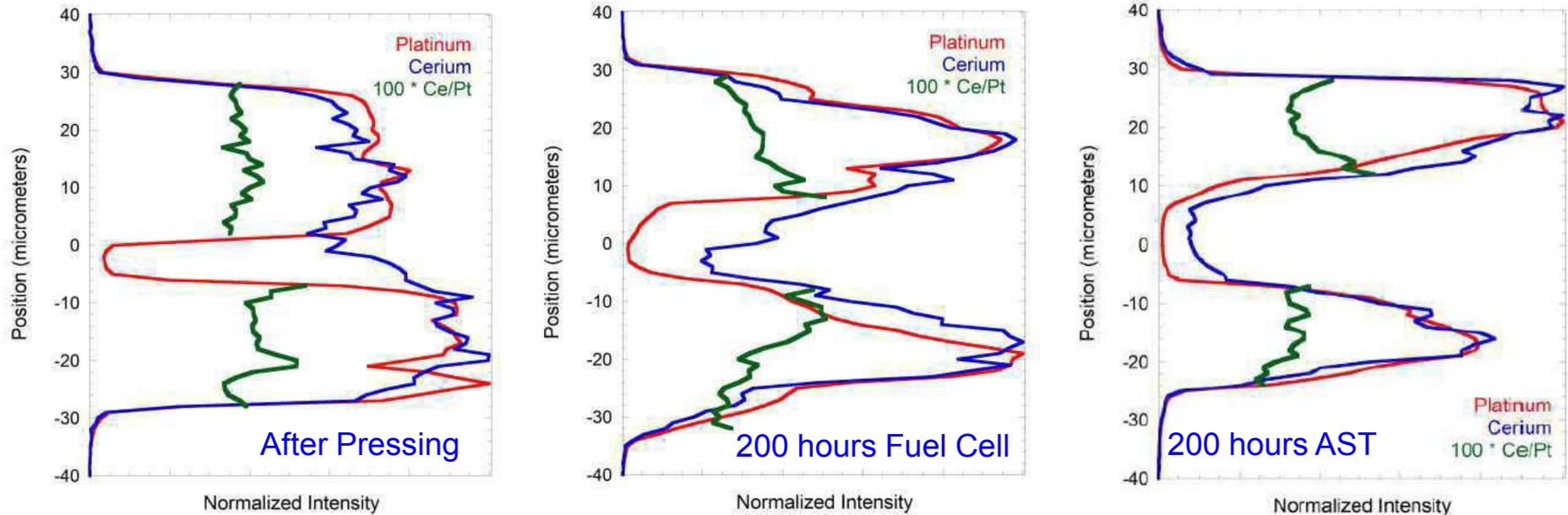
- Cerium starts in the membrane (none in catalyst) and migrates
- Cerium is depleted from the membrane - migrates into both catalyst layers
  - No preference for cerium in either the anode or cathode catalyst layers
- Migration cause:
  - Solely Diffusion: the cerium profile should even across the membrane
  - Electrostatic forces: no concentration profile observed expected from charge
  - Profile of cerium more closely resembles that of the platinum
    - Strong affinity for cerium for the catalyst layer
      - Possibly due to interactions of cerium with platinum or carbon
      - Functional groups on carbon may be sequestering cerium cations
  - Low (no) affinity for cerium in the membrane

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SD/SU Mitigation - Membrane Degradation at Low Temperatures

- Measure membrane degradation under polarized conditions at room temperature to compare Membrane vs. SD/SU degradation – cool stack vs. anode purge
  - Evaluated limits: Wet (100% RH) and Dry (0% RH)
  - N212 – non-chemically stabilized to see degradation limits

- No Membrane degradation observed with wet conditions
  - No increase in H_2 cross-over, FER below detection limits
- Initial membrane degradation with dry conditions
  - However degradation levels off
- Pt ECSA decreases with wet conditions
- Pt ECSA increases with dry conditions (see additional Pt facet), followed by decrease
  - Unclear of causes of Pt ECSA change
  - Carbon corrosion, Pt particle growth to be determined by post-characterization

Nafion® 212:
0.05mg/cm² TEC10V20E
0.2mg/cm² TEC10V40E

MEA Post- OCV Testing- Cathode Surface Analysis
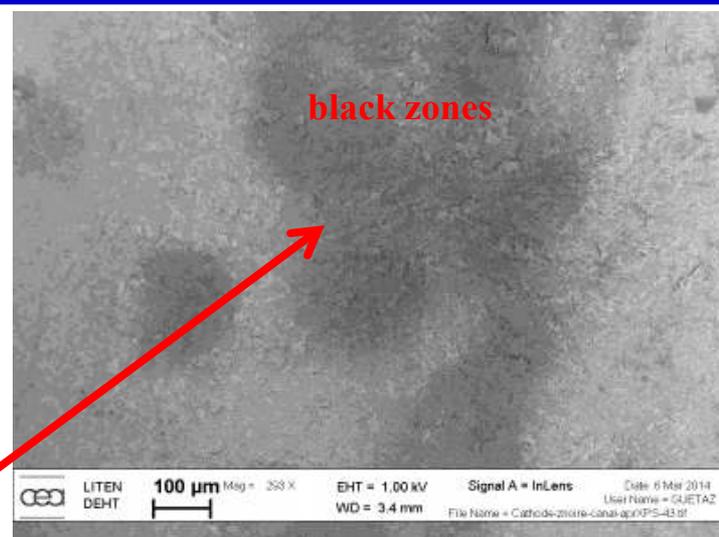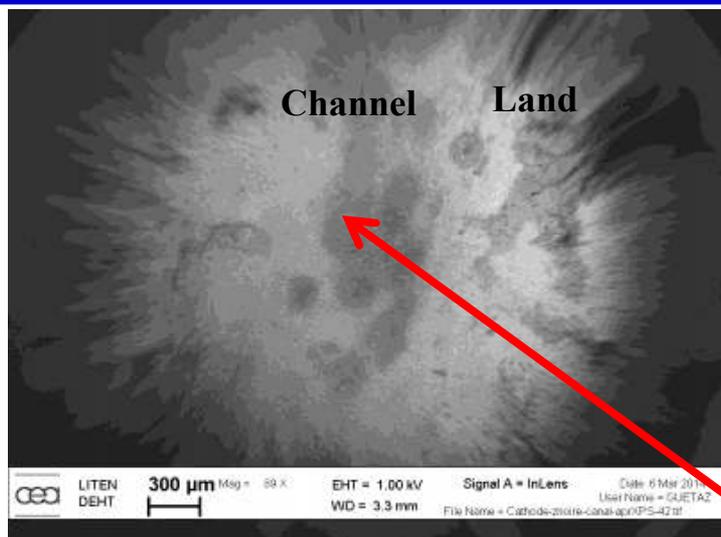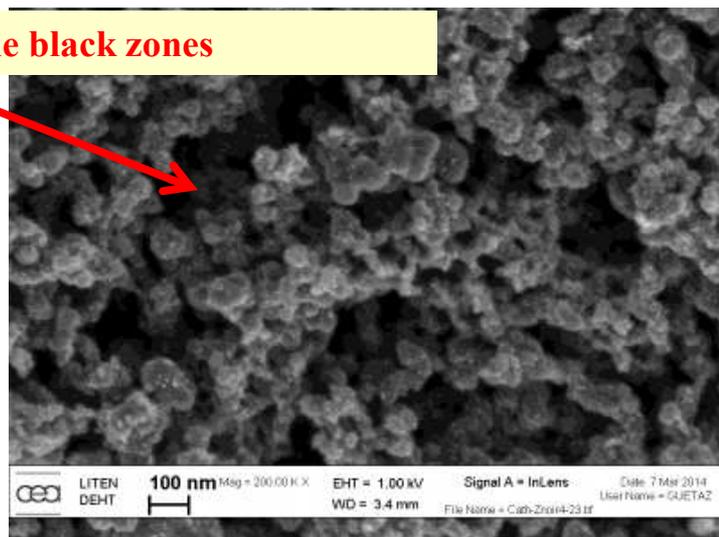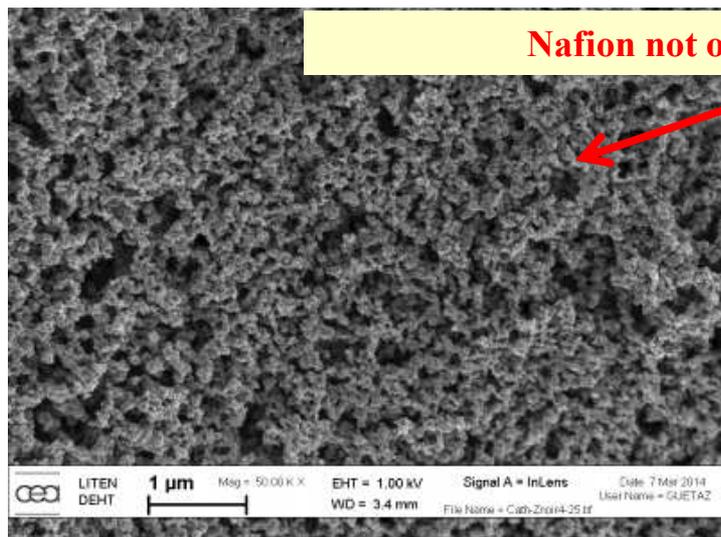
- Black zones are observed in the channel surface (where no MPL remained).
- In surface zones under the land (where MPL remained), the images are similar to the fresh MEA, a lot of Nafion® is observed
- Black zones not observed with MEAs from 1000-hr drive cycle testing

MEA Post-OCV Testing – Cross-section Analysis

Reinforcement
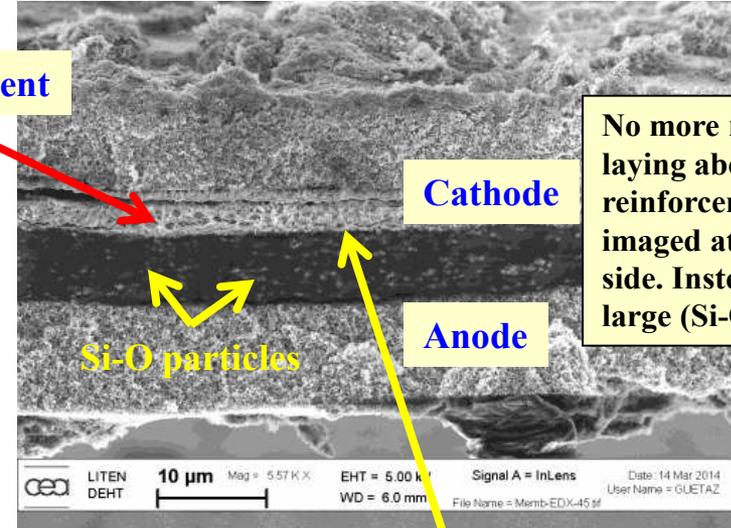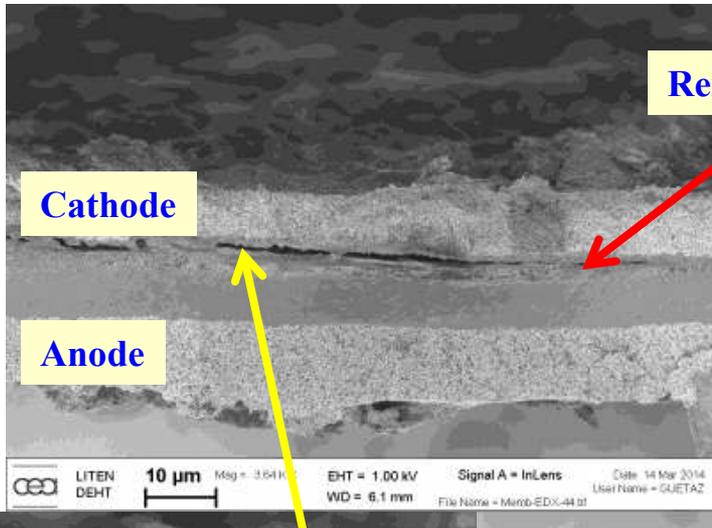
Cathode

Anode

No more membrane laying above the PTFE reinforcement is imaged at the cathode side. Instead there are large (Si-O) particles !

Cathode

Si-O particles
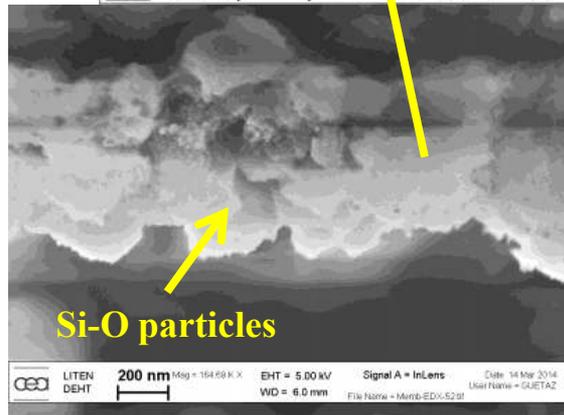
Anode

(Si-O) crystals observed at the cathode/PTFE reinforcement interface

Si-O particles

(Si-O) crystals observed at the anode/PTFE reinforcement interface

Reinforcement

Si-O particles
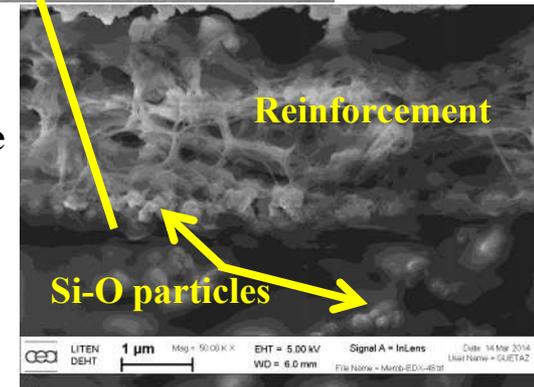
- Sample images show that there is a "de-cohesion" inside the membrane at the PTFE reinforcement interface
- No more cathode active layer is observed, neither the "cathode membrane" above the PTFE reinforcement
- At the membrane anode side, the (Si-O) particles laying at the PTFE reinforcement interface look like the (Si-O) particles present in the fresh membrane
- At the membrane cathode side, the (Si-O) particles look different

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Localized Pt Particle Agglomeration and Carbon Corrosion

TEM

Fresh – 2.3nm
Cond. – 3.3nm
50 hr – 5.0nm
100 hr – 5.3nm
400 hr – 6.3nm
1000 hr – 7.3nm

Number of Pt Particles

Pt Diameter / nm

XRD

Crystallite Size (nm)

Pt Crystallite Size (X-Ray)

Before Conditioning (Fresh)

Ageing Time (Hrs)
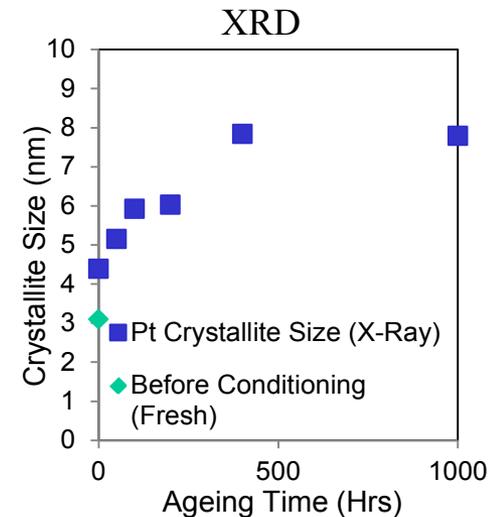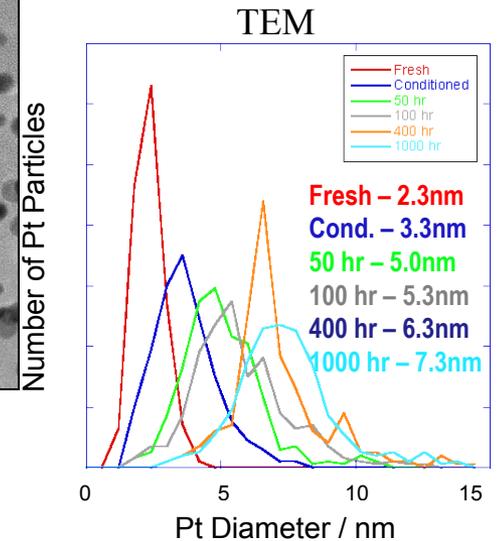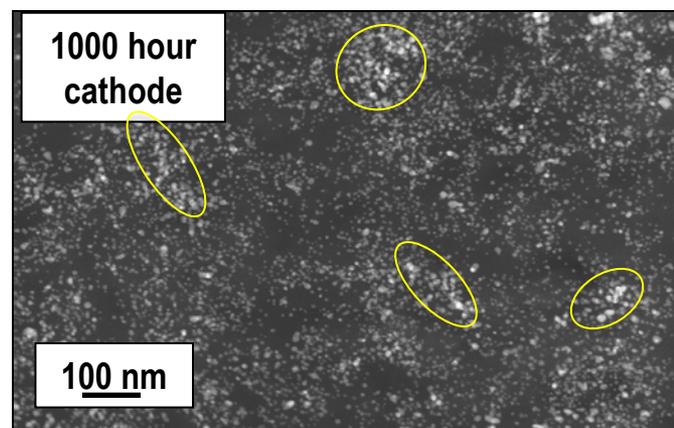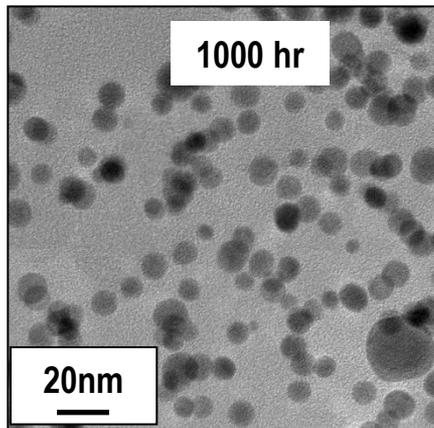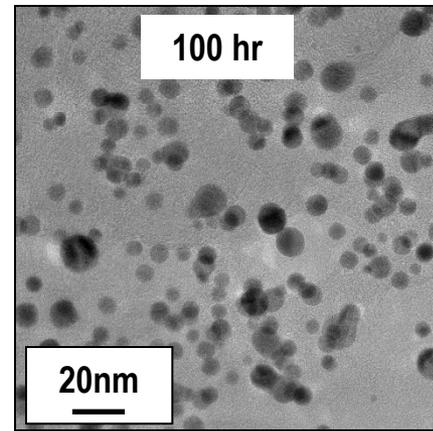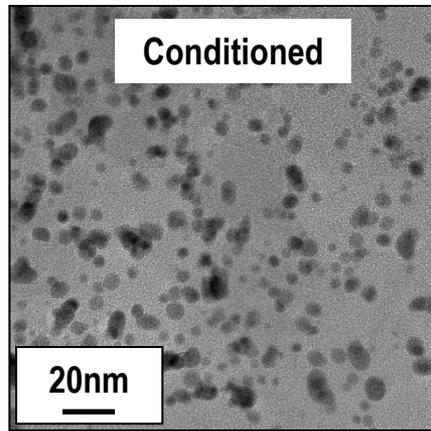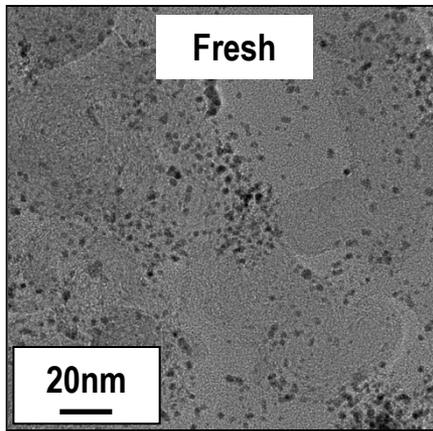
- ~2X change in Pt particle size observed within first 50 hr
- Followed by slower size increase, reaching limit of ~ 8 nm
  - XRD and TEM Pt PSD agree closely
- Localized carbon corrosion associated with regions exhibiting larger Pt particles only observed after 1000 hrs.
- Note that these regions are typically only 100-500 nm in size and highly dispersed.

Ion Power MEA: DuPont™ XL, Anode: 0.05 mg Pt/cm^2 TEC10V20E, Cathode 0.15 mg Pt/cm^2 TEC10V40E

Catalyst Layer Thins/Compacts During Drive Cycle Operating (Vulcan Carbon over 1000 hrs – Wet DC)

Cathode

Pt-ITM

3 μm
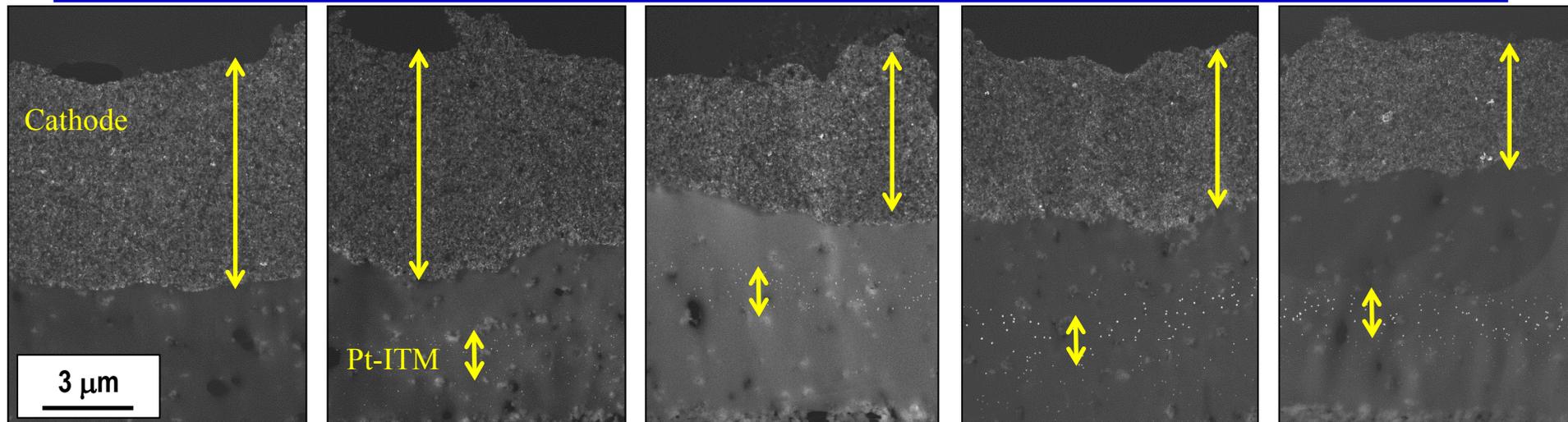
Conditioned | 50 hr | 100 hr | 400 hr | 1000 hr

- After 1000 hr, the cathode loses ~50% of its thickness, with ~30% loss after 100 hr
- While the cathode has thinning/compression, there is little evidence for carbon corrosion
  - Majority of the Vulcan retains its meso-graphitic structure.
  - Structure of the carbon support is unchanged (see lots of typical Vulcan graphitic structure)
  - Don't see much densification (banding) until 1000 h, and even at this point it is minimal
  - Structure very different than during carbon corrosion holds
- Increased Pt migration into membrane with drive cycle time

15
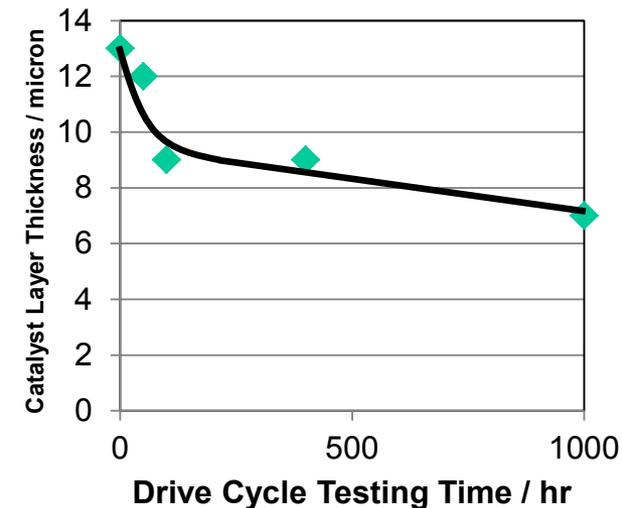
Catalyst Layer Porosity During Drive Cycle Series
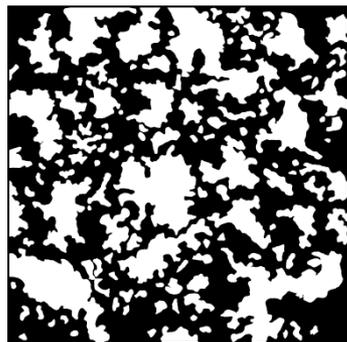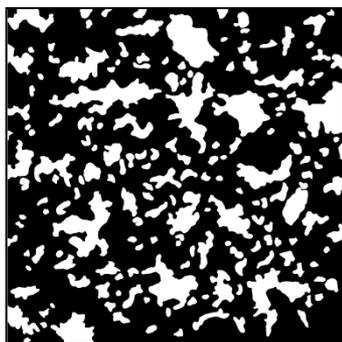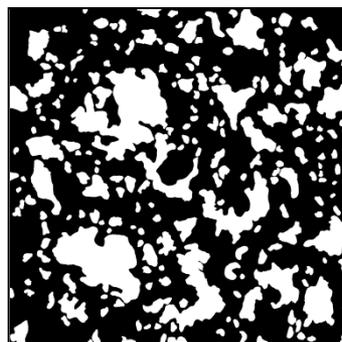
| Fresh - 44% | 50 hr – 30% | 100 hr – 32% | 400 hr – 24% | 1000 hr – 22% |

Estimated Porosity % vs. Drive Cycle Time / Hr
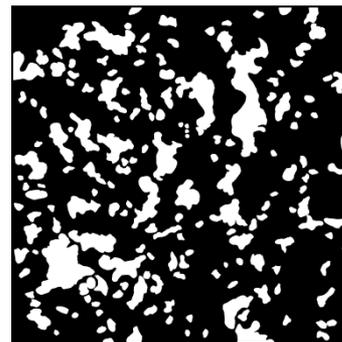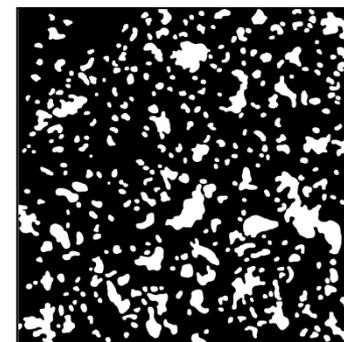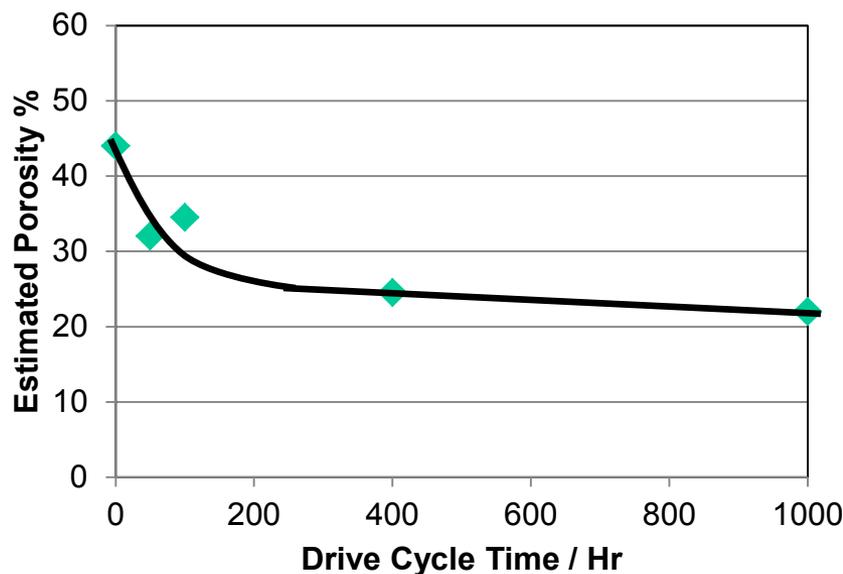
- Measurements in reduction of catalyst layer thickness over time correlate well to measurements of porosity decrease
- Estimation of pore shape and (area) volume % from 2D image "slices"
- Overall pore size and % decrease with increasing drive cycle time
- Large initial decrease in porosity followed by gradual decline which appears to reach a limit

OAK RIDGE
National Laboratory

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No Thinning during Drive Cycle with Graphitized Carbon - 3600 Hr Pt/LSAC Drive Cycle (wet/dry)

fresh

3593 hr

3 μm

3 μm

Pt band
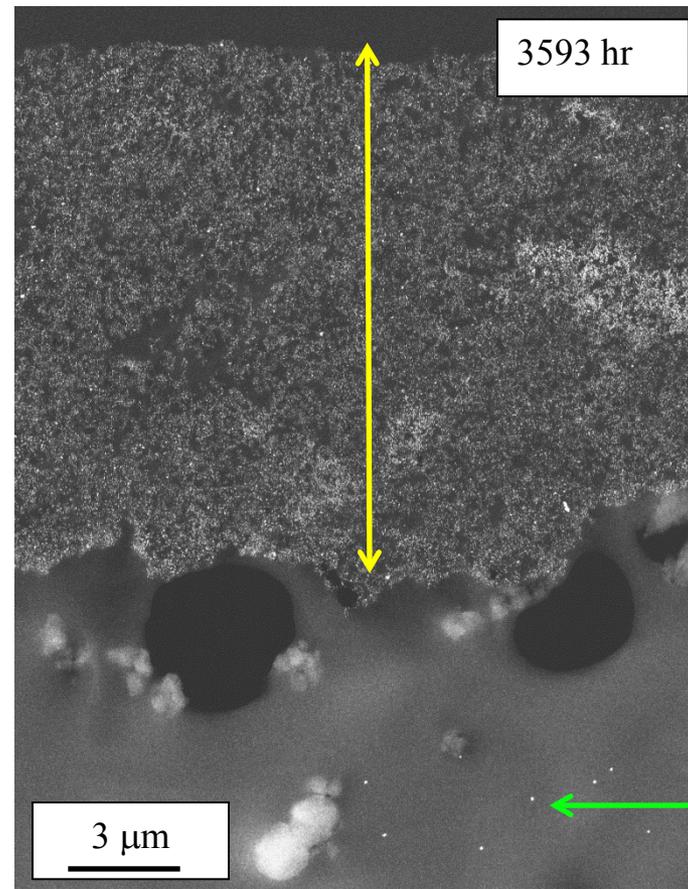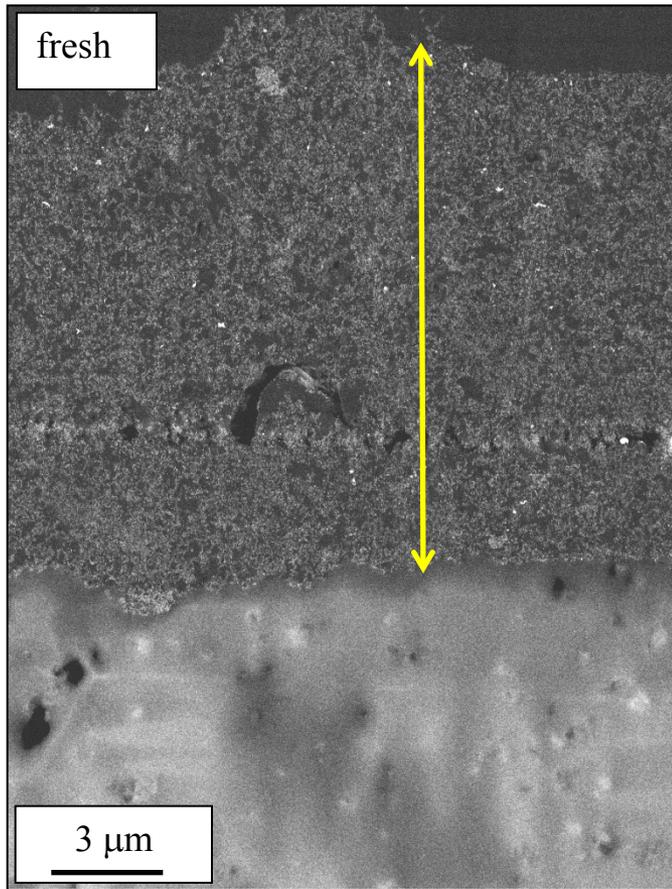
- No change in MEA thickness after 3593 hour wet/dry drive cycle
- Low concentration of Pt particles observed in membrane after 3593 hour wet/dry drive cycle

Ion Power: Dupont™ XL, Anode: 0.05 mg/cm^2 of TEC10V20E, Cathode: 0.2 mg/cm^2 of 40%Pt/LS Carbon

Particle Size Growth during 3600 Drive Cycle with Graphitized Carbon

fresh

20 nm

3593 hr

20 nm

Fresh – 3.2nm
3593 hr – 6.8nm

Pt/LSAC-fresh
3593 hour wet-dry drive cycle

Number of Pt Particles

Pt Particle Diameter (nm)
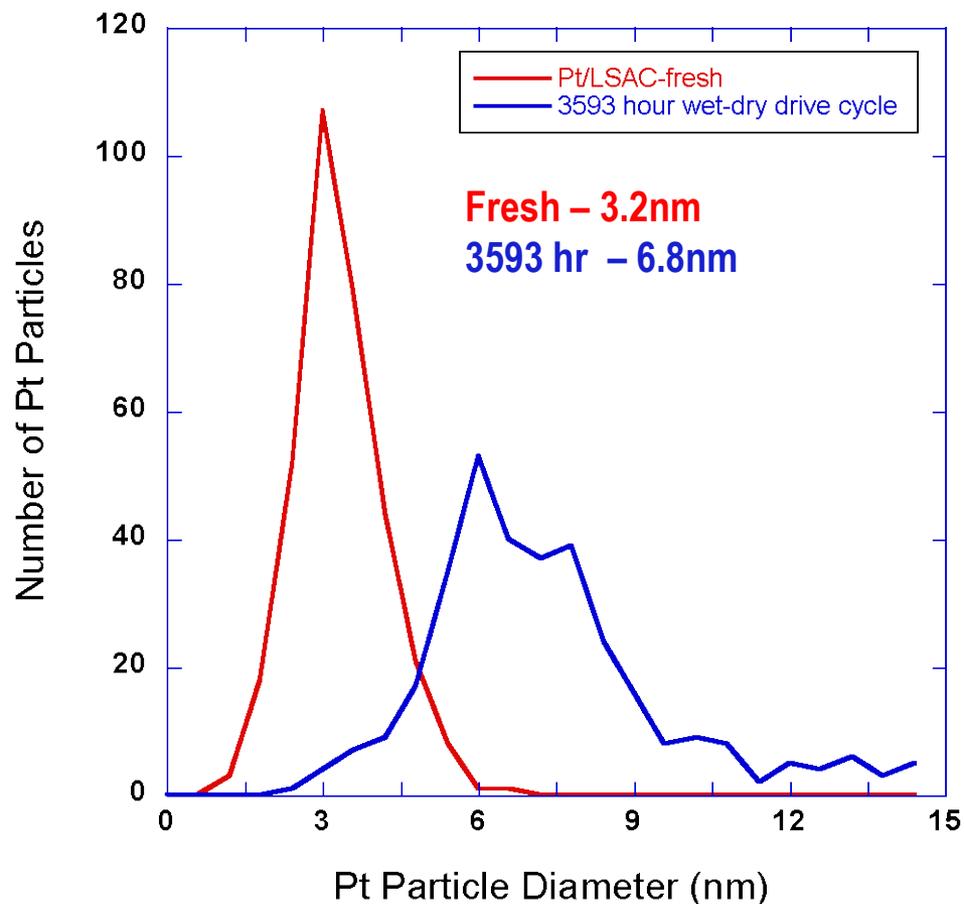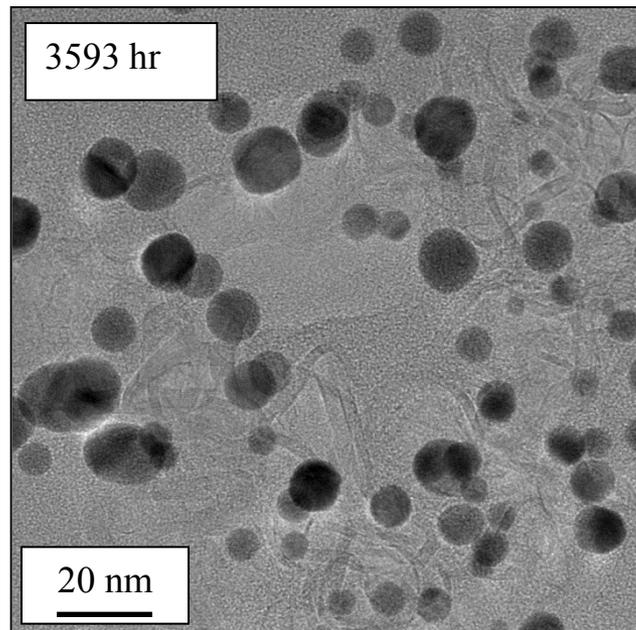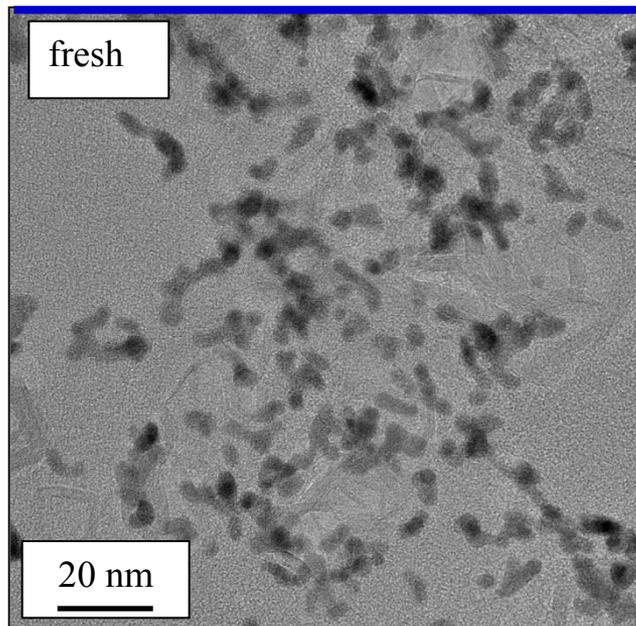
- ~2X increase in Pt particle size
- Slower growth than with Vulcan carbon
- Smaller overall particle size than after 1000 hrs with Vulcan during Drive Cycle (wet)

Changing Pore-Size-Distributions During Carbon Corrosion

Porosity Measured by MIP Based on 0.01 to 0.2 Micron Pores
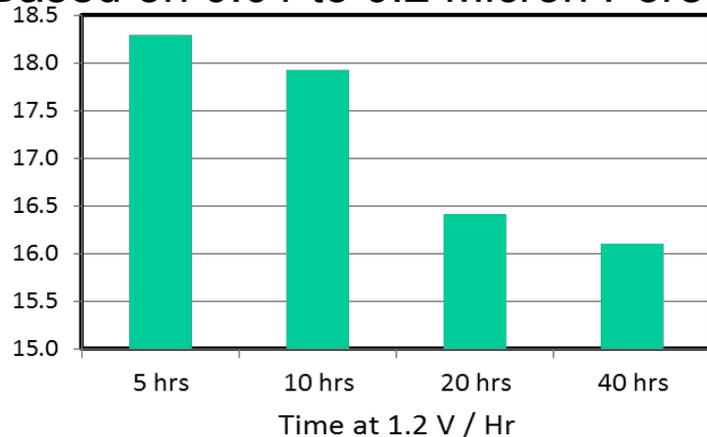
Porosity From TEM
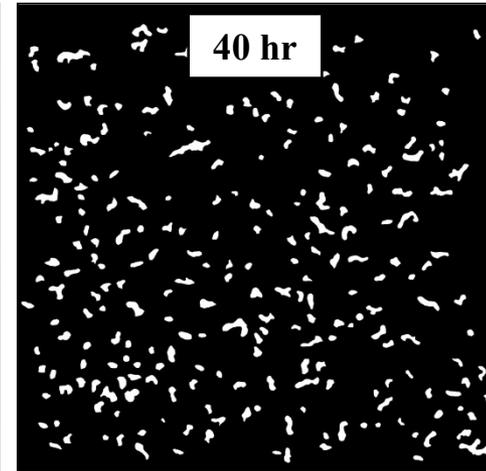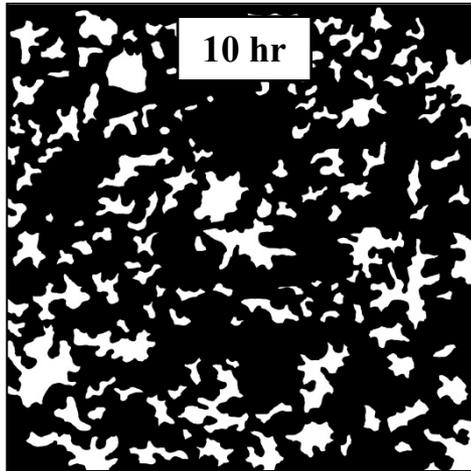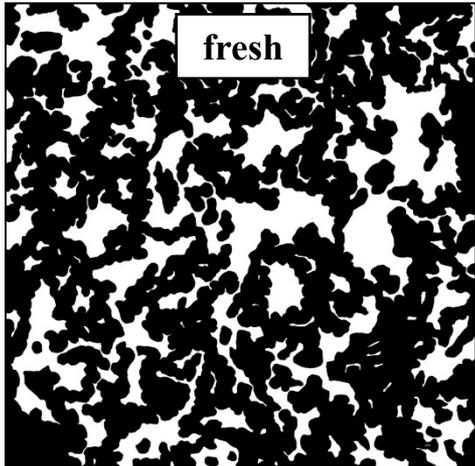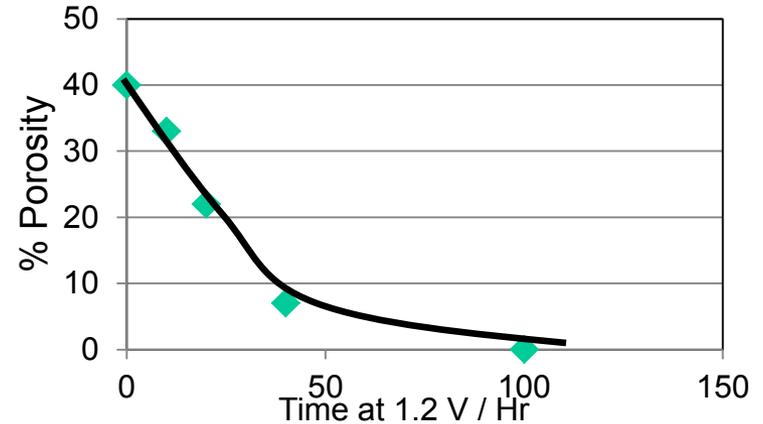
- Vulcan carbon continues corrosion with corresponding catalyst layer thinning, and Pt growth
  – TEM analysis and Mercury Intrusion show commensurate porosity loss of catalyst layer
- Graphitized carbon has cathode layer thickness loss of ~10-12% after 100 hrs - thickness remains constant for subsequent 300 hours.

Pt Particle Size During Carbon Corrosion Comparing Vulcan carbon and Graphitized

Pt / Vulcan

Pt / LSAC (graphitized)
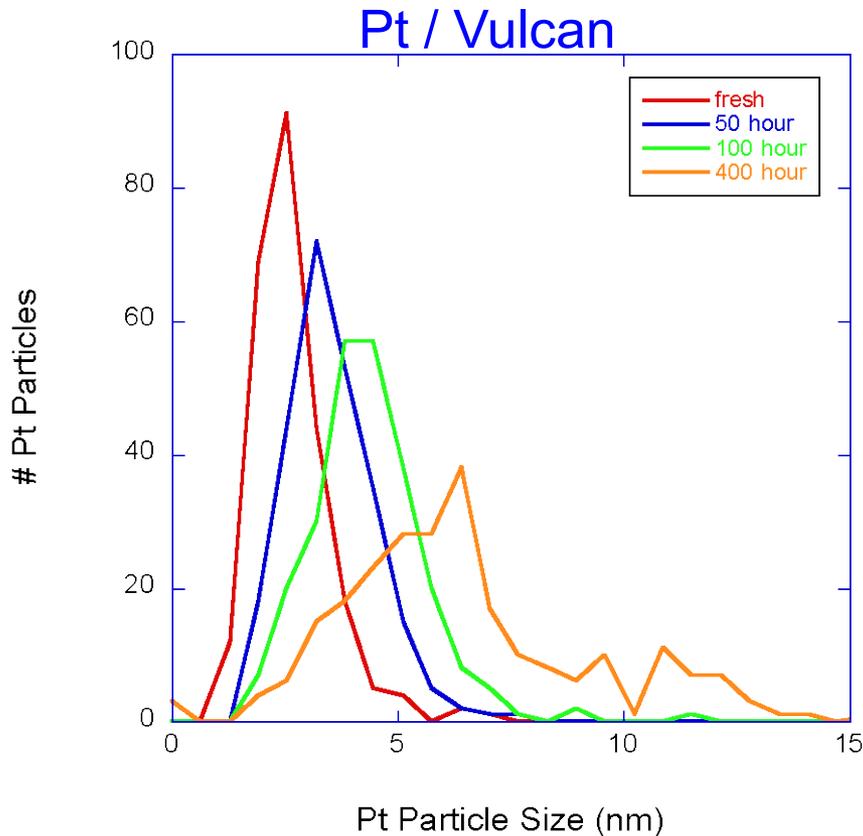
- Progressive increase in Pt particle size observed as a function of time at 1.2V
- Increasing Pt particle size correlates with loss of ECSA
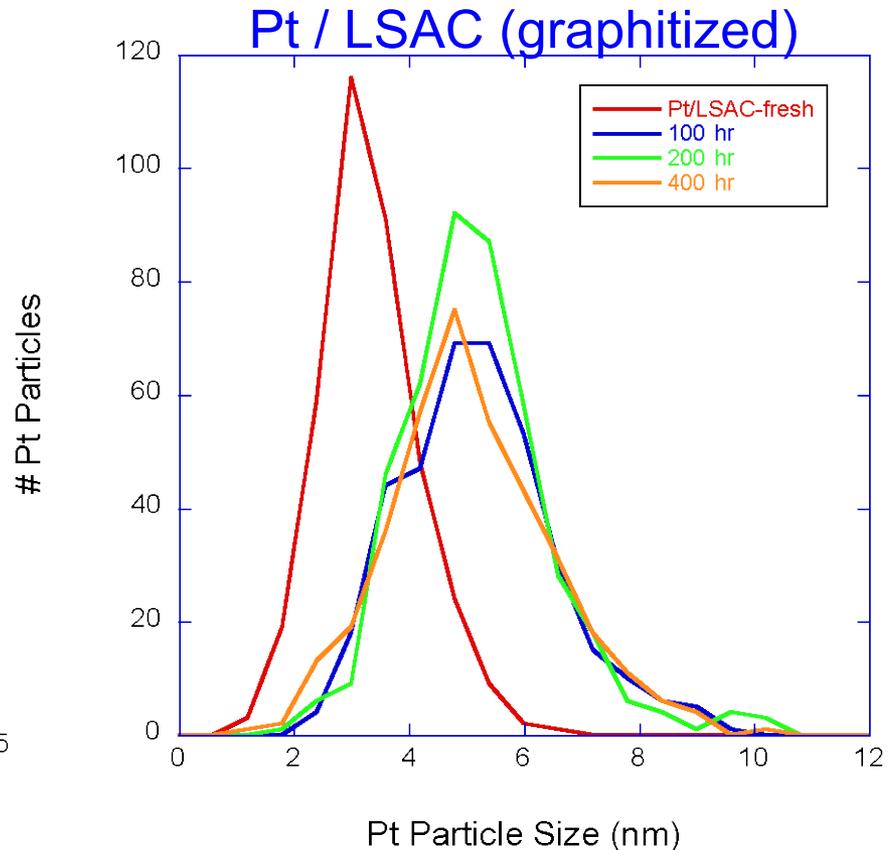
- Change in Pt particle size (3nm-to-5.2nm) occurs within 100 hrs hold @ 1.2V
- Particle size remains unchanged for remaining 300 hr
- Initial Pt dispersion shows extensive Pt agglomeration on LSAC

Diluent Carbon Reduces Performance for Same Catalyst Layer Thickness

VIR over Carbon Corrosion Cycles

Legend:
- 20% Pt/C (0 Cycles)
- 20% Pt/C (1000 Cycles)
- 20% Pt/C (2000 Cycles)
- 40% Pt/C + C (0 Cycles)
- 40% Pt/C + C (1000 Cycles)
- 40% Pt/C + C (2000 Cycles)

Voltage / V vs Current Density (A/cm²)

Impedance @ 0.04 A/cm²

- 20% Pt/C (0 Cycles)
- 20% Pt/C (2000 Cycles)
- 40% Pt/C + C (0 Cycles)
- 40% Pt/C + C (2000 Cycles)

Imaginary Imped. (Z') ohm-cm² vs Real Imped

Impedance @ 0.40 A/cm²

- 20% Pt/C (0 Cycles)
- 20% Pt/C (2000 Cycles)
- 40% Pt/C + C (0 Cycles)
- 40% Pt/C + C (2000 Cycles)

Imaginary Imped. (Z') ohm-cm² vs Real Imped. (Z) ohm-cm²

NDIR (Cathode Outlet)

cycles

- 20% Pt/C (100 - 200 Cycles)
- 20% Pt/C (200 - 500 Cycles)
- 20% Pt/C (500 - 1000 Cycles)
- 40% Pt/C + C (100 - 200 Cycles)
- 40% Pt/C + C (200 - 500 Cycles)
- 40% Pt/C + C (500 - 1000 Cycles)

Corrosion Rate (mg$_C$/cm²/h) vs Time (s)

1.0 – 1.5 V Carbon Corrosion AST

- Adding diluent carbon into catalyst layer doesn't seem effective strategy for carbon corrosion mitigation
  - Increased Pt – Pt distance decreases Pt particle growth
    20% Pt/C grows from 2.4nm to 4.1nm
    40% Pt/C grows from 2.9nm to 4.9nm
  - Lower Pt/C also decreases Pt catalysis of carbon corrosion (20% Pt/C vs. 40% Pt/C)

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Decreasing Pt Wt Loading
Proves more effective than Diluent Carbon

VIR over Carbon Corrosion Cycles

Legend:
- 20% Pt/C (0 Cycles)
- 20% Pt/C (500 Cycles)
- 20% PT/C (1000 Cycles)
- 20% Pt/C (2000 Cycles)
- 40% Pt/C (0 Cycles)
- 40% Pt/C (500 Cycles)
- 40% Pt/C (1000 Cycles)
- 40% Pt/C (2000 Cycles)

Y-axis: Voltage
X-axis: Current Density (A/cm2)

Impedance @ 0.04 A/cm²

Legend:
- 20% Pt/C (0 Cycles)
- 20% Pt/C (2000 Cycles)
- 40% Pt/C (0 Cycles)
- 40% Pt/C (2000 Cycles)

Y-axis: Imaginary Imped. (Z') ohm-cm²
X-axis: Real Imped. (Z) ohm-c

Impedance @ 0.40 A/cm²

Legend:
- 20% Pt/C (0 Cycles)
- 20% Pt/C (2000 Cycles)
- 40% Pt/C (0 Cycles)
- 40% Pt/C (2000 Cycles)

Y-axis: Imaginary Imped. (Z') ohm-cm²
X-axis: Real Imped. (Z) ohm-cm²

NDIR (Cathode Outlet)
Normalized for Carbon Content

Legend:
- 20% Pt/C (500 - 1000 Cycles)
- 20% Pt/C (1000 - 2000 Cycles)
- 40% Pt/C (500 - 1000 Cycles) X 2
- 40% Pt/C (1000 - 2000 Cycles) X 2

cycles

Y-axis: Corrosion Rate (mgC/cm2/h)
X-axis: Time (s)

- Lowering the Pt/C Wt ratio is more effective mitigation strategy than mixing in blank carbon into the catalyst layer
- Similar behavior of 20% Pt/C and 40% Pt/C based MEAs if Pt loading is retained
  - Performances in the kinetic and mass transport regions are identical
  - NDIR (normalized) shows slightly less corrosion from the 40% Pt/C
    - Decreased thickness of 40% Pt/C catalyst layer probably makes water removal easier and decreases corrosion rate

1.0 – 1.5 V Carbon Corrosion AST

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Start-up and Shut-down (SUSD) Model
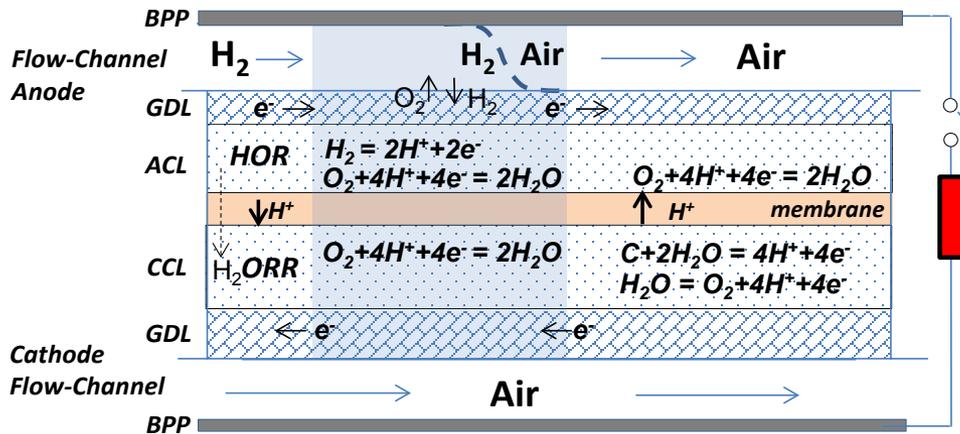
Start-up and Shut-down Model

- Generalized electrochemical reaction model with distributed HOR and ORR on anode, and ORR, OER and COR on cathode

- Diffusive transport of H_2, O_2, N_2, and $H_2O(v)$ through anode GDL

- Capacitive charging and discharging

Calibrated and validated the SUSD model using Nancy University* data for Ion Power MEAs supplied by LANL, 30-cm^2 segmented cell
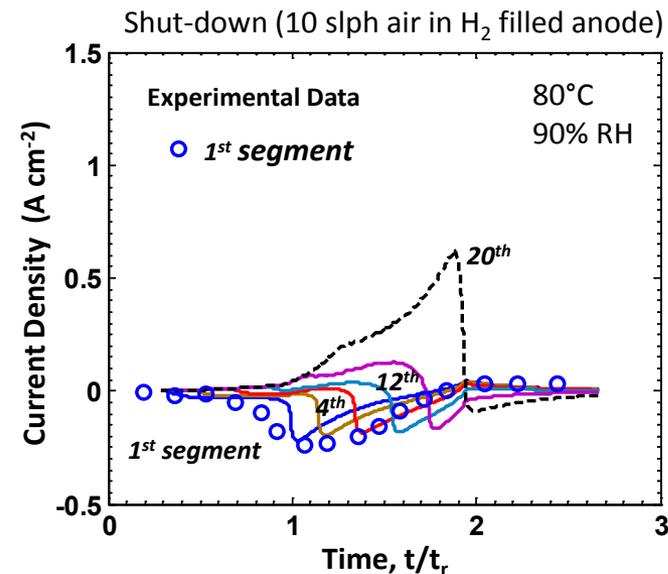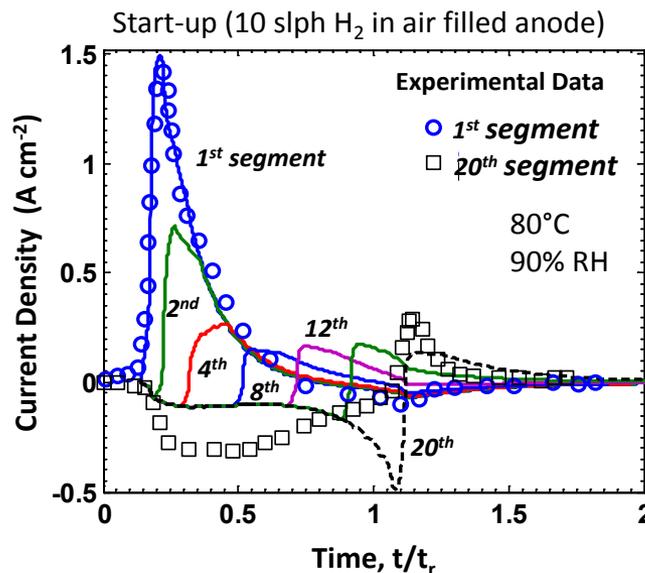
*A. Lamibrac, Maranzana, G.; Lottin, O.; Dillet, J.; Mainka, J.; Didierjean, S.; Thomas, A.; Moyne, C., et al., J Power Sources 190(2011) 9451-9458;
*J. Dillet, Spernjak, D.; Lamibrac, A.; Maranzana, G.; Mukundan, R.; Fairweather, J.; Didierjean, S.; Borup, R. L.; Lottin, O. , J Power Sources 250(2014) 68-79

Modeling of Carbon Loss during SUSD

Smaller carbon loss during shut-down than during start-up due to lower electrode potentials (V_e - V_{ic})

- Difference between SU and SD corrosion levels due to asymmetric capacitive effects during charging and discharging.

- The cell potential profiles (V_e) are nearly independent of the purge rates.

- Significant reduction in carbon corrosion with faster anode purge rates because reduced time at high electrode potentials.

Interfacial Potential Difference
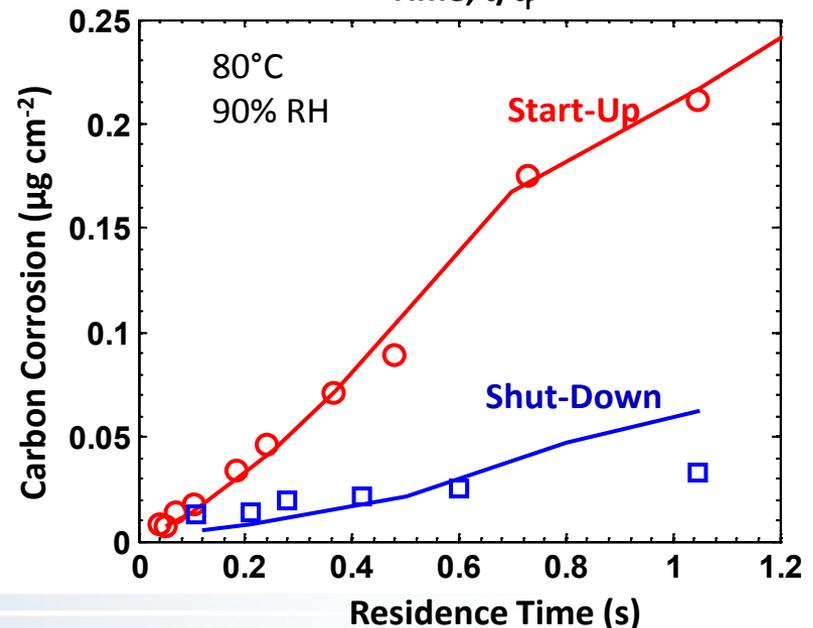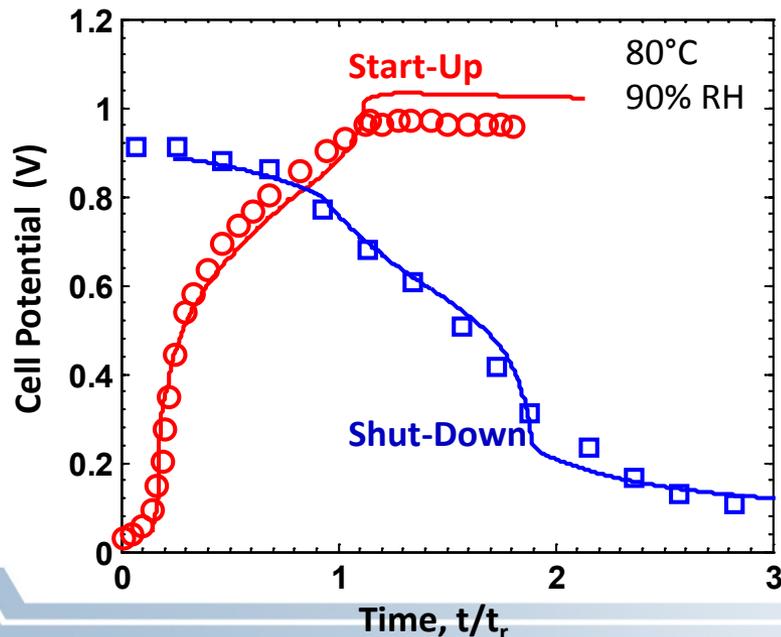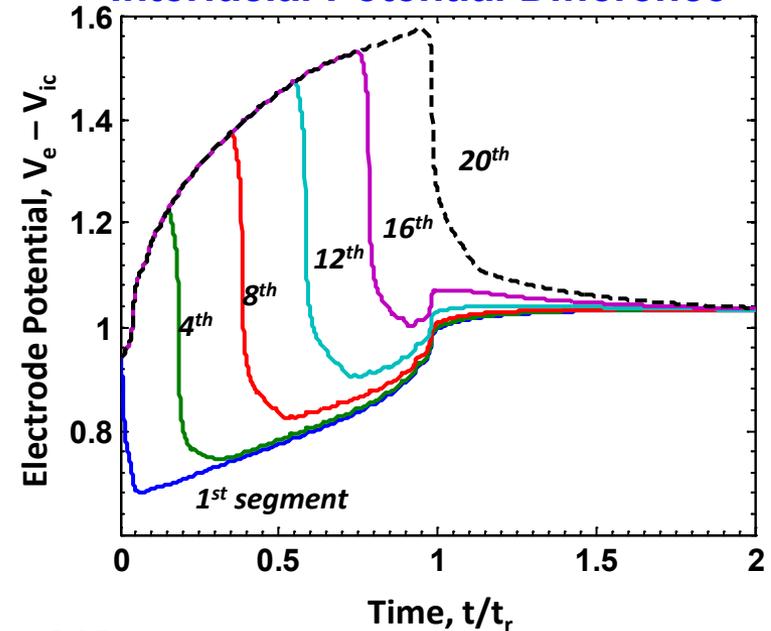
Modeling of SD/SU Mitigation Strategies

Model comparison of carbon corrosion during SD/SU for:

- Faster purge
- Increase Pt loading in cathode
- Reduce Pt loading in anode
- Promote OER on cathode catalyst
- Suppress ORR on anode
- Future: more stable carbon supports, stack shorting/resistive load

For a more complete list of proposed mitigation strategies, see, for example:
Y. Yu, H. Li, H. Wang, Y. Xiao-Zi, G. Wang, M. Pan, J. Power Sources, **205**, 10-23 (2012).

Start-Up (H_2 in air-filled anode)

Start-Down (Air in H_2-filled anode)
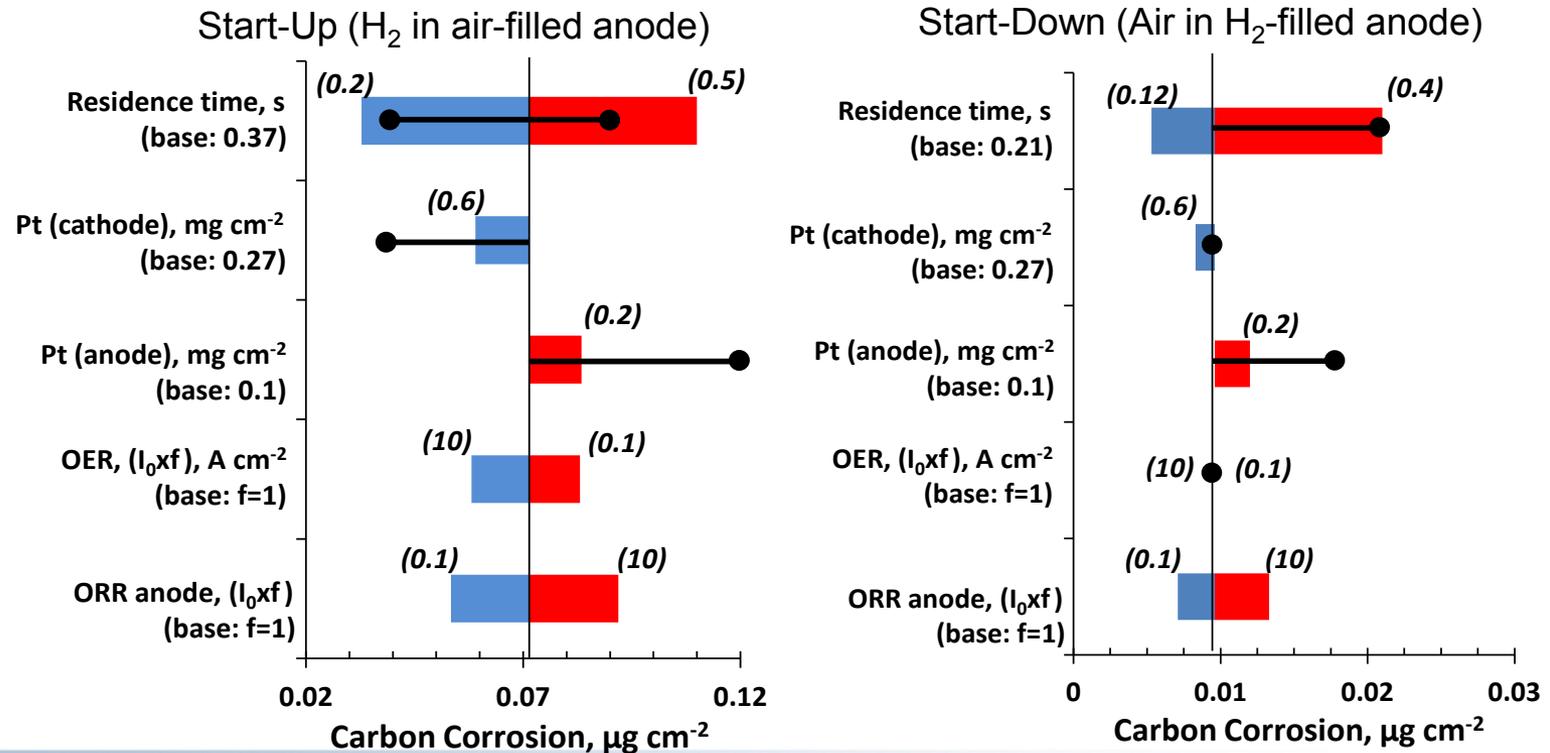
Selected Technical Conclusions/Summary - 1

- **Mitigation**
  - Radical scavengers (Ce) measured to migrate quickly to catalyst layers
    - To prevent wash-out from cell need stabilization
  - Membranes while polarized with wet low temperature conditions, show high stability
    - Leaving polarized eliminates reverse current degradation mechanism
  - Electrode structure can be maintain by mixing stable support materials
  - Measured lowering Pt/C wt ratio appears more effective mitigation strategy than mixing in blank carbon (sacrificial) into the catalyst layer
    - Lower Pt/C also decreases Pt catalysis of carbon corrosion
  - Higher Pt wt loadings show nominally lower carbon corrosion
  - Model comparison of carbon corrosion and SD/SU strategies

- **Model Development**
  - Modeling of carbon corrosion and loss during SD/SU
    - Identified capacitive effects during charging and discharging as differences in SD/SU carbon corrosion
    - Evaluated comparison of carbon corrosion during SD/SU with various mitigation methods
  - Expanded component model for membrane durability (LBNL in supplemental slides)
    - Examine crack energy and stress contours to determine if plastic deformation occurs and the crack propagates
    - Validation and initiation in conjunction with experimental work CL cracks and humidity cycling

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Selected Technical Conclusions/Summary - 2

- **Membrane Degradation**
  - Radical scavengers (Ce) migrate out of membrane (quickly)
    - Higher affinity to catalyst layers
  - Si-O particles precipitating at reinforcement interface with membrane
    - Large Si-O particles left upon cathode side membrane degradation
  - Low (~ zero) membrane degradation at OCV, wet and lower temperatures
    - Leaving polarized eliminates reverse current degradation mechanism

- **MEAs and Catalyst Layer**
  - Quick growth of catalyst particles during drive cycle operation
  - Catalyst layer ionomer degradation evident by areas of ionomer depleted from the cathode catalyst layer during OCV tests
  - Catalyst layers show loss of porosity
    - Compaction during drive cycle operation with limited carbon corrosion
    - Carbon corrosion
    - Localized Pt Particle Agglomeration and Carbon Corrosion only observable at longer times (1000 hrs)
  - Mass transport losses can develop with low-loaded MEAs due to water transport changes
    - Transport losses observed to *develop* in a few hundred hours
    - Does not occur with high loaded MEAs, and is MEA/GDL dependent

Future Work - 1

- **Catalyst layer morphology effect on durability**
    - Quantify relationship between carbon corrosion and resulting changes in CCL structure
        - Quantification of Pt/pore distributions, Pt utilization, ECSA
        - High vs. Low surface area carbon structures and mixed formulations
    - Effect of CL cracks and gaps; formation of cracks
        - Evaluate the effect of catalyst layer cracks on membrane durability
    - Identify uniform methodology for measuring real durability impact of start-up/shut-down, air cycling
        - Identify spatial/areal performance variations over ageing

- **Durability evaluation of Platinum alloys**
    - Define effect of Platinum and alloy migration on membrane durability
        - Experimentally define and model dissolution of Pt at elevated temperatures and in oxygen
    - Expand our previously developed models on Pt dissolution

- **Membrane structural changes and radical scavengers**
    - Effect of Ce (and other radical scavengers) movement on durability
        - Define best form of Ce for radical scavenging
        - Methods to stabilize Ce in membrane and in cell to prevent wash-out
    - Evaluate changes in membrane crystallinity to determine the durability effect, and if these crystallinity changes affect more than water uptake.
    - Examine membrane durability trade-offs with carbon corrosion
        - Compare membrane degradation at shut-down versus start-stop H_2 purging and carbon corrosion

Future Work - 2

- **Discern Carbon/Nafion®/Catalyst interactions and structure on durability**
  - Define catalyst layer porosity loss due to causes other than carbon corrosion
  - Map ionomer in catalyst layer, and define the ionomer chemical/structural changes in the catalyst layer
  - 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)
    - Define dependence upon catalyst loading, MEAs, etc. on increases in mass transport resistance with fuel cell drive cycle testing

- **Mitigation of Degradation**
  - Expand work on mitigation
    - Increasing CL transport and increase stability
      - CL stability through use of structure and stable materials
    - Stabilize cerium and/or other radical scavengers
    - Predict durability cost versus function of mitigation strategies

- **Fuel cell catalyst widening materials models (leverage EU project)**
  - Evaluate the degradation of kinetics of Oxygen Reduction Reaction (ORR) of bi-metallic catalysts and coupling on different supports (carbon black, graphene, nano-tube of carbon)
  - Discern and predict catalyst support corrosion by coupling experiments and simulations
  - Provide support carbon corrosion mechanisms to couple simulations to continuum models of fuel cell
  - Develop tool able to predict the cost of durability of a start/stop of a fuel cell and function of mitigation strategies to minimize the degradation of catalyst supports

Thanks to

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

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- Other materials provided by:
  - SGL Carbon
  - W.L. Gore
  - Tanaka
  - DuPont
  - Solvay
  - ETEK

Technical Backup Slides

ECSA Loss Results From Multiple Degradation Mechanisms Occurring Simultaneously - 1.2 V Hold
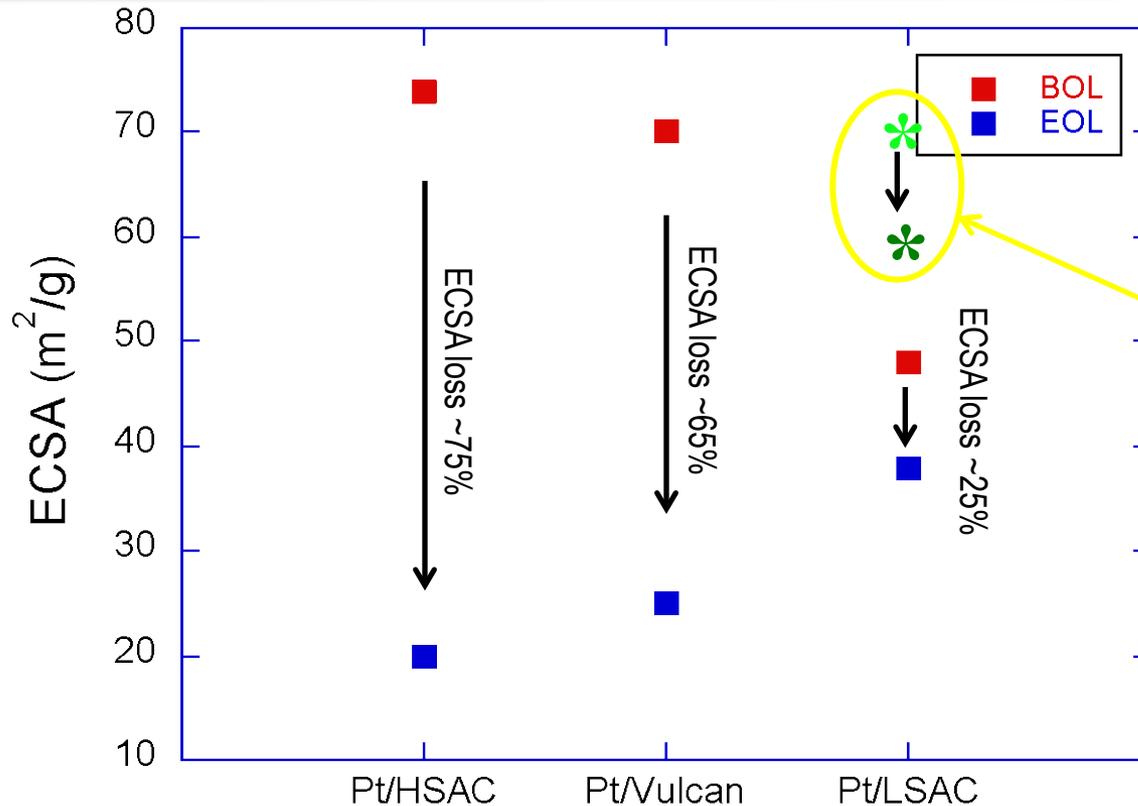
Degradation of Pt/LSAC (lower initial ECSA) can be attributed primarily to Pt catalyst growth/coalescence due to POOR Pt DISPERSION

Much lower durability of Pt/HSAC is due primarily to CARBON CORROSION inducing Pt loss through multiple mechanisms

Dynamics of Start-up

The interfacial potential difference (electrode potential, V_e - V_i) increases with time and drops off after the H_2 front passes a segment.

- Region I: Steep changes in potentials as the H_2 front reaches different segments
- Region II: Slow O_2 diffusion within the anode GDL (ORR at limiting current)
- Region III: Capacitive charging of the anode catalyst layer (ACL)

At start-up, only a fraction of O_2 in anode GDL participates in ORR of H^+ produced by OER and COR in cathode.

- This fraction is smaller if air is purged in shorter residence time.
- The remainder O_2 undergoes ORR with H^+ produced in ACL.
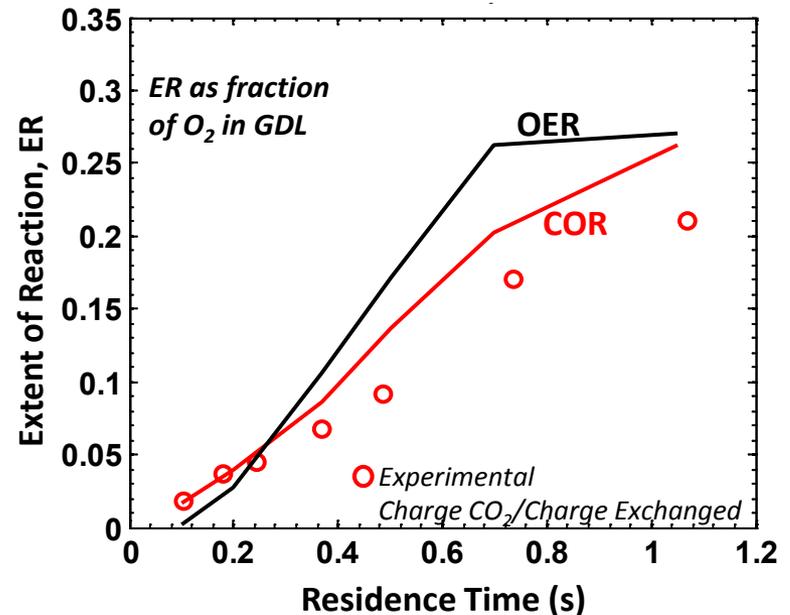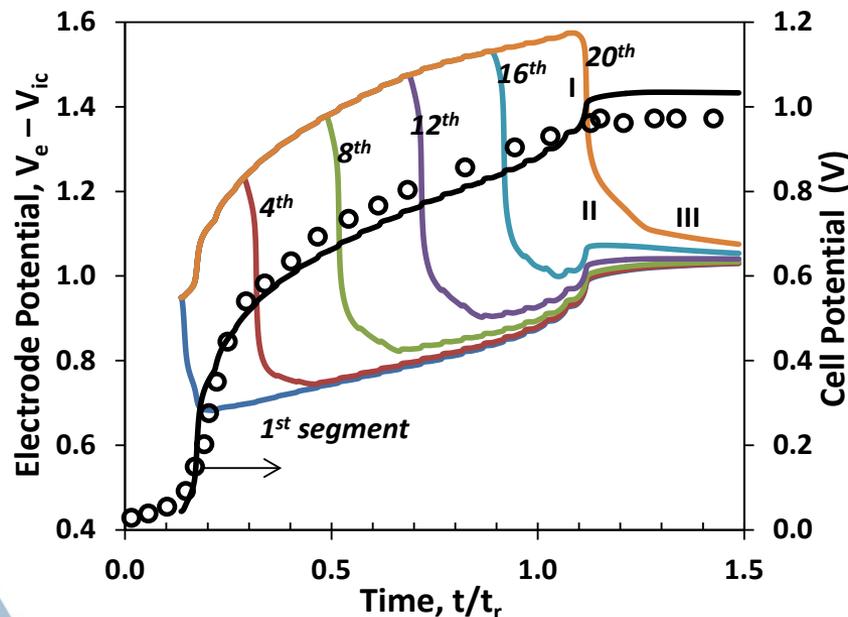
Dynamics of Shut-down

The electrode potential (V_e - V_{ic}) increases with time and drops off after the O_2 front passes a segment.

- Region I: Shape of the air front (time delay)
- Region II: H_2 depletion in the anode GDL
- Region III: ORR slowing because of electrode potential relaxing toward -0.9 V
- Region IV: Slow capacitive discharge of the anode catalyst layer

At shut-down, the extent of OER and COR in cathode corresponds to a small fraction of H_2 in anode GDL.

- This fraction is smaller if H_2 is purged in shorter residence time.
- The remainder H_2 reacts with O_2 through ORR in ACL.
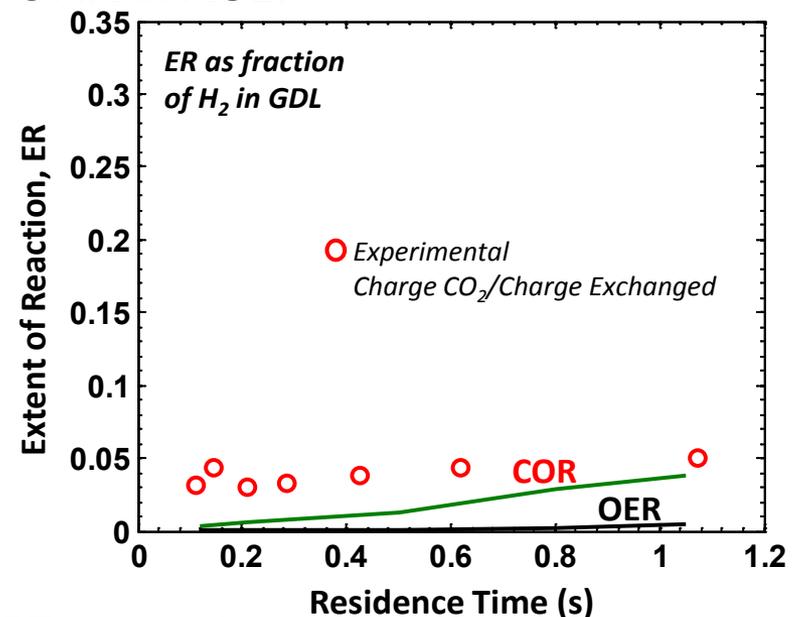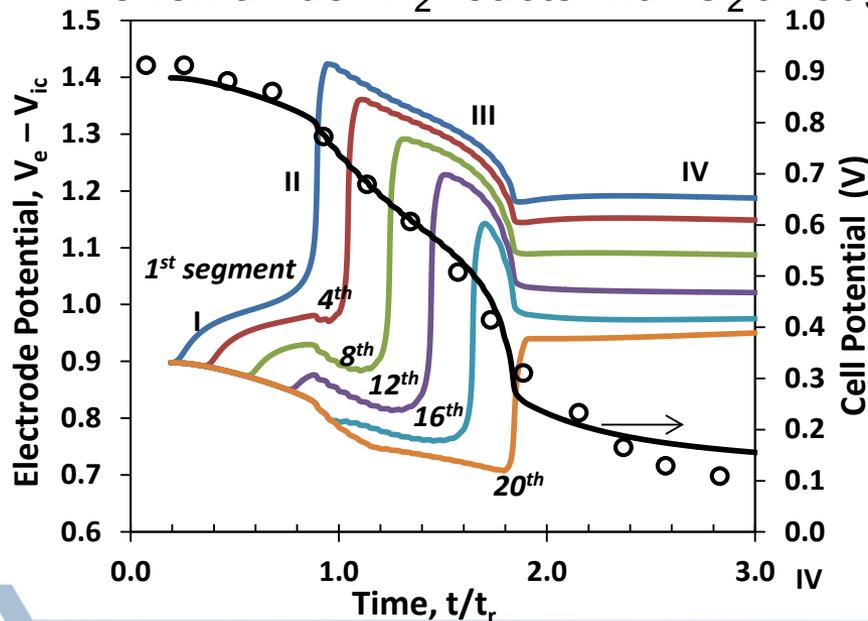
Carbon Corrosion Causes Catalyst Layer Compaction

Pt/V after holds at 1.2V
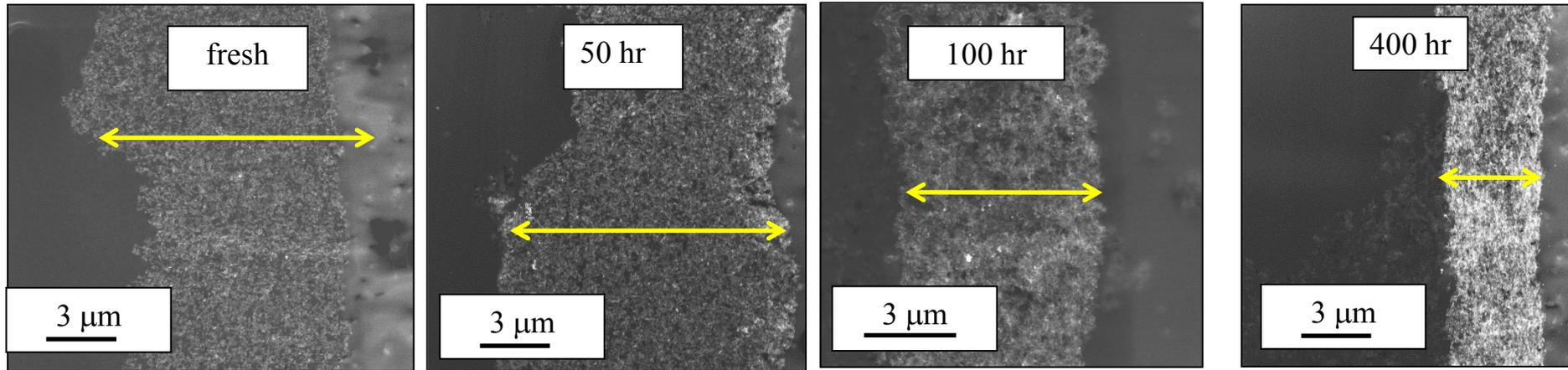
Pt/LSAC after hold at 1.2V
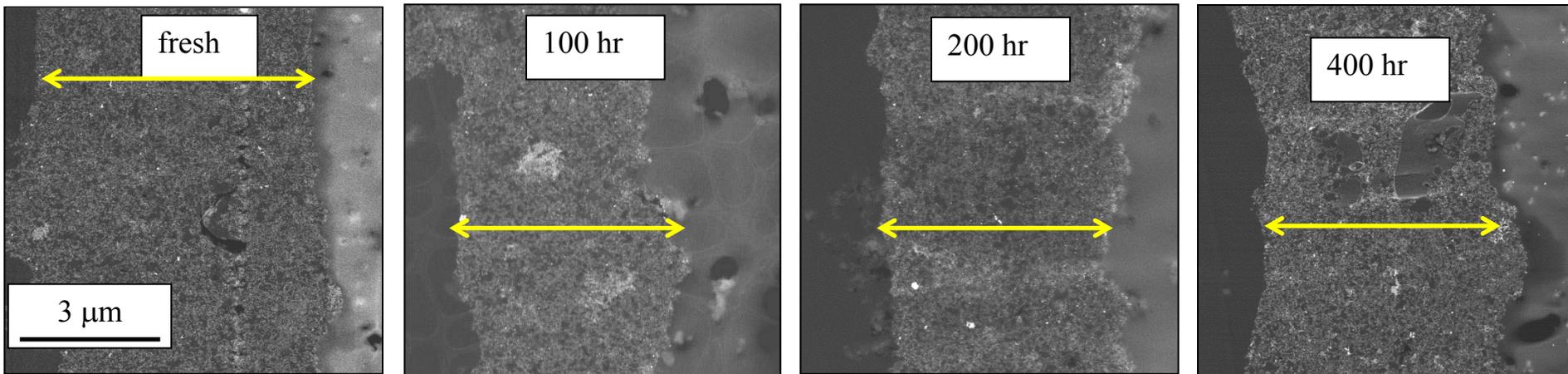
After initial hold for 100 hours @ 1.2V, cathode layer thickness loss is ~10-12% - thickness remains constant for subsequent 300 hours for LSAC. Vulcan carbon continues to corrode with corresponding catalyst layer thinning, and continuing Pt particle growth

Characterization of Ionomer in PEMFC by CEA

Coverage of the carbon-black particles by the ionomer in PEMFC

2 different quantities of Nafion® (1= 33%Nafion ; 2 = 15% Nafion

100 nm
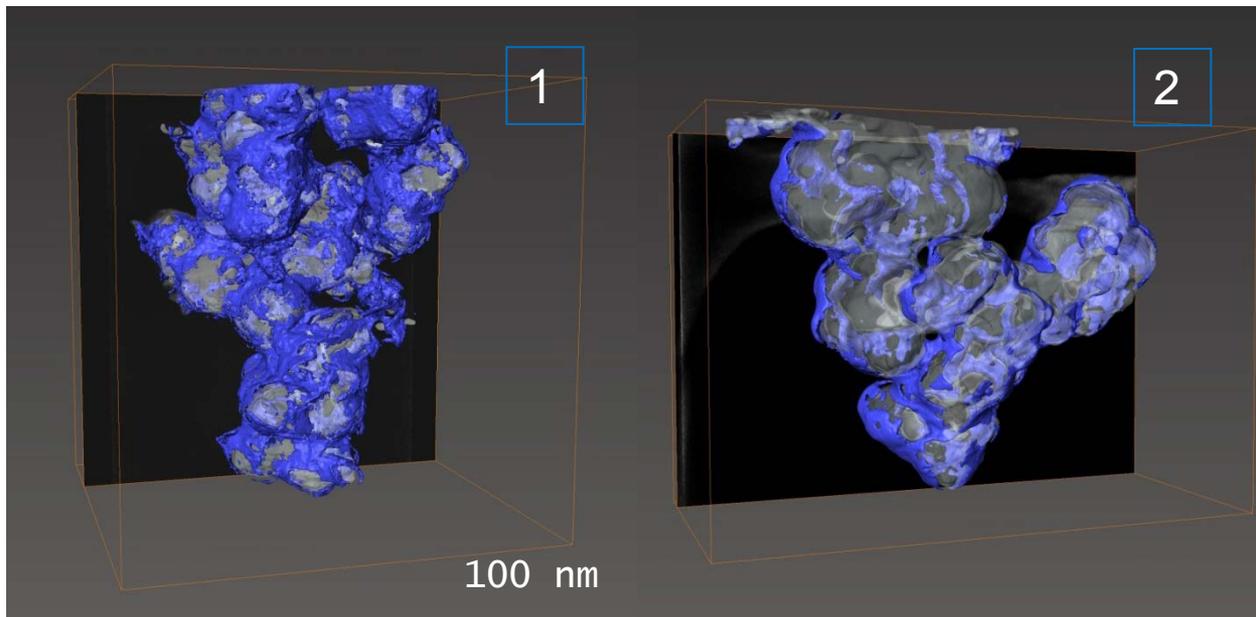
Ionomer is staining by Cs$^+$
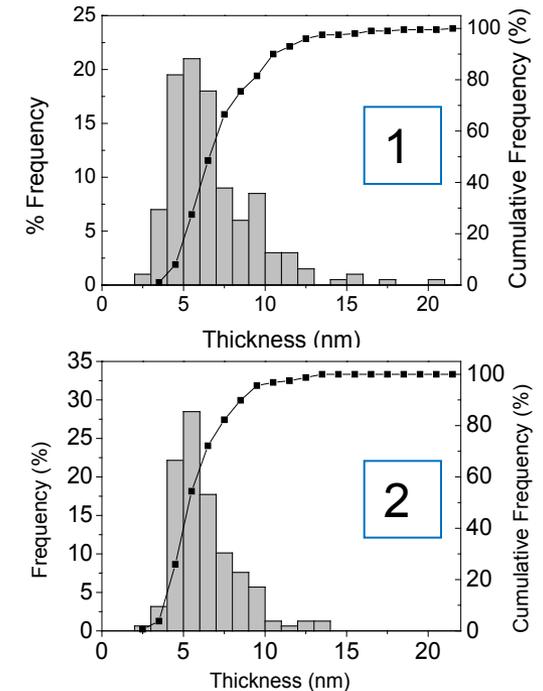
- ❑ The average thickness of the ionomer is 6 nm for the two samples
- ❑ The degree of coverage depends on the ionomer content (1 = 74% of CB coverage; 2= 39%)

Characterization of Ionomer in PEMFC by CEA
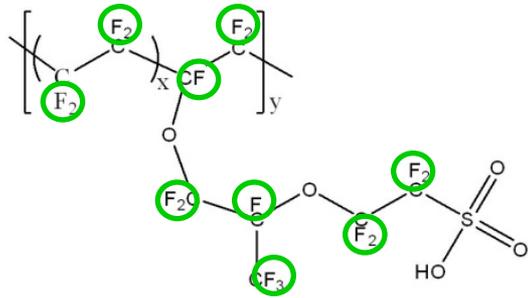
X-EDS cartography of fluorine and carbon

Fluorine

Fluorine and Carbon
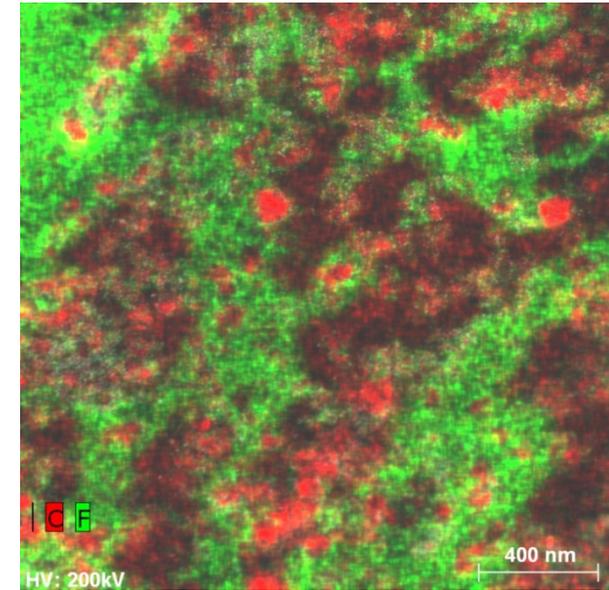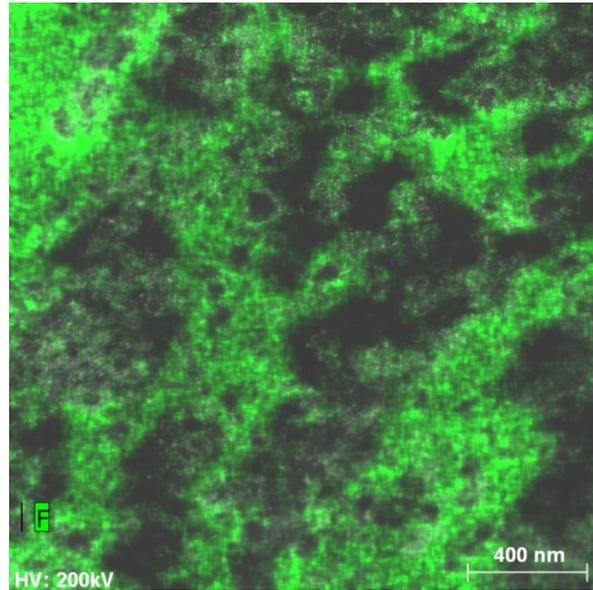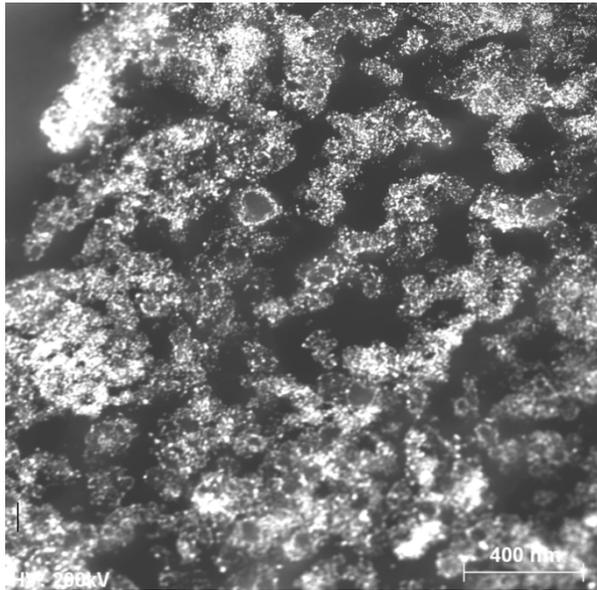
Proposed study with CEA:
1) Study durability effect, redistribution, degradation
2) Study redistribution by different manufacturing methods (i.e. different solvent casting)