

BALLARD[®]

FC-APOLLO

*Fuel
Cell*

*Application
Package for
Open-source
Long-Life
Operation*



Open-Source Performance and Durability Model

Consideration of Membrane Properties on Cathode Degradation

David Harvey

FC049

June 8, 2015

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Timeline

- Start Date: January 2014
- End Date: October 2014
- NCE Date: March 2014

Barriers

- A. Durability
 - Pt/carbon-supports/catalyst layer
- B. Performance
- C. Cost (indirect)

Budget

- Total Project: \$552,464
 - \$ 429,264 DOE
 - \$ 123,199 Ballard

Project Partners

- K. Karan – University of Calgary
- P. Atanassov -University of New Mexico

Objective

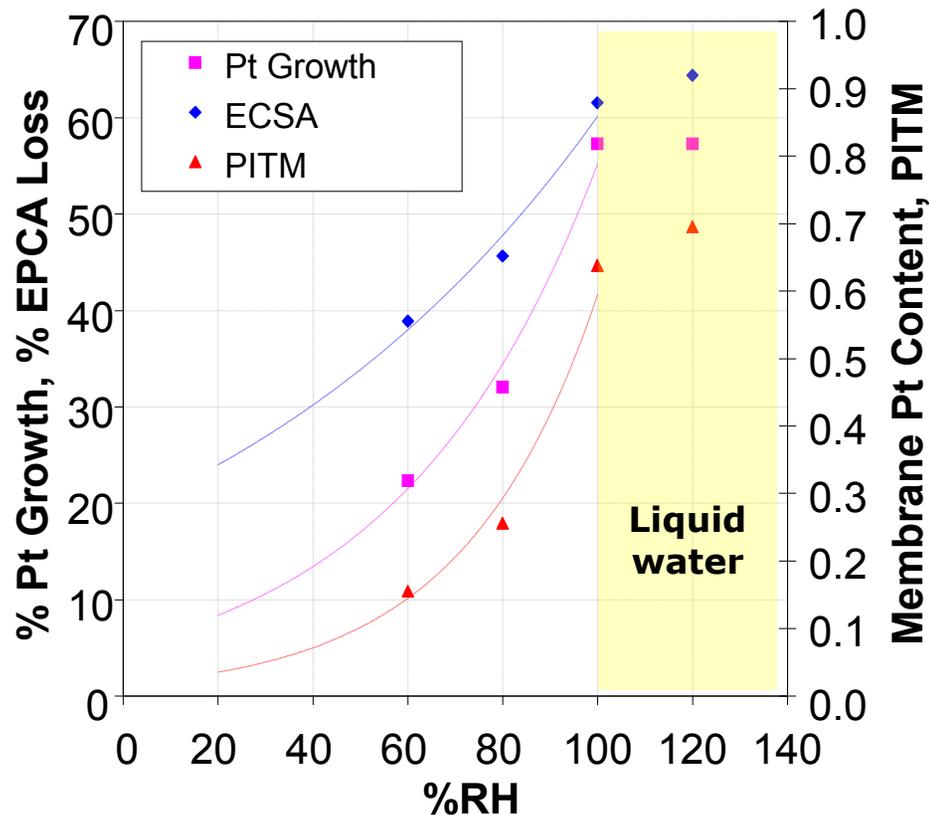
- Enhancement of FC-APOLLO predictive capability
 - Include interaction effects of membrane transport properties (e.g. water transport, proton conductivity changes, water uptake,..) and catalyst layer local conditions to understand driving forces for Pt dissolution

Under Project DE-EE0000466,

The following observations were made:

- 1. Catalyst Layer degradation was observed to be influenced by water content within the MEA**
 - a) Relative humidity was shown to have a substantial effect on the degradation rates
- 2. Membrane/Ionomer is a key part of the water management within an MEA (eg. Water sorption/crossover/phase change)**
- 3. The majority of membrane models are not capable to capture the effect of the liquid/vapor system nor the linkage between characteristic properties and overall behaviour.**
 - a) FC-APOLLO was developed with a simplified membrane model and validated only for the PFSA NR211

Project Background: Effect of RH on Pt Dissolution



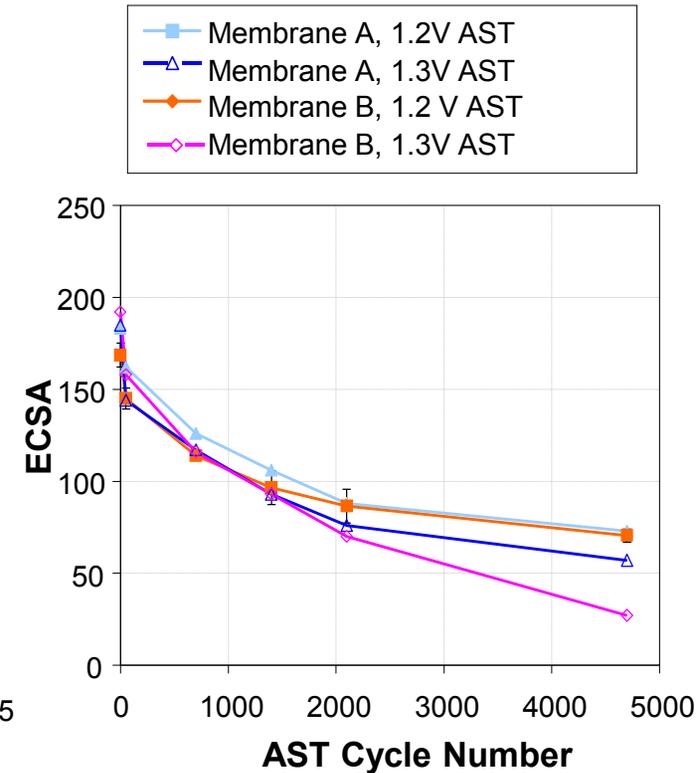
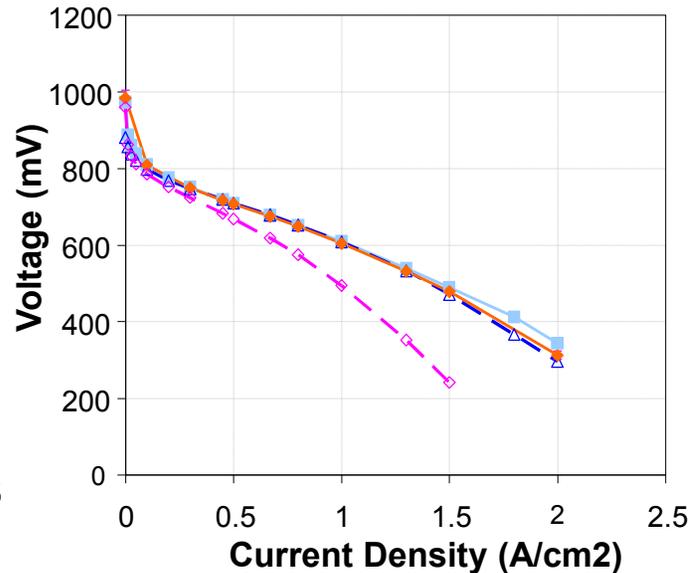
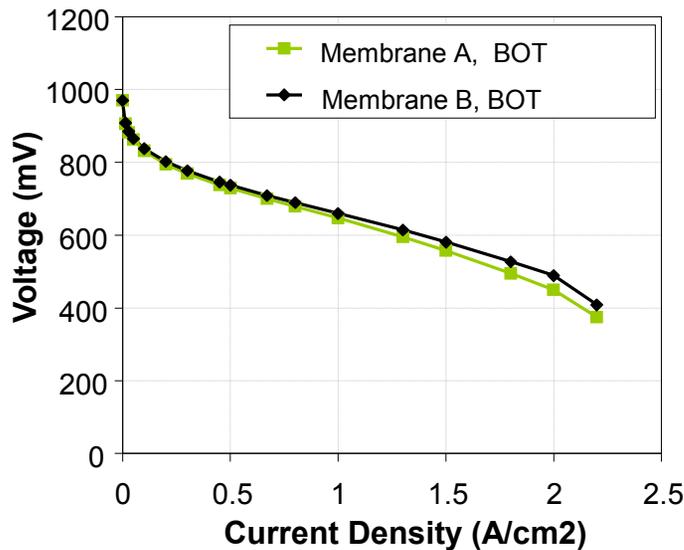
- Pt dissolution rate decreases with lower reactant RH (<100%)
- Decrease in Pt growth, ECSA, PITM
- Relatively small increase in Pt dissolution from 100%RH to saturated (120%RH)

Baseline MEA:50:50 Pt/LSAC, Nafion® ionomer (23%),
0.4/0.1 mg/cm² (Cathode/anode), NR211, BMP GDLs
AST: 0.6 V (30sec)→ 1.2 V (60 sec), 4700 cycles, **X RH**, 80C
Diagnostic Air Polarization (STC): Air/H₂, 100% RH, 5 psig, 75°C

“Understanding the effect of material properties and the structure of MEA components is critical to understanding MEA performance and degradation”

Membrane A and B are coated with the same catalyst layers (LSAC50, 0.4mg/cm²)

AST: 0.6V (30sec)→1.2V (60 sec) 4700 cycles @ 100% RH, 80°C
Diagnostic Air Polarization (STC) Air/H₂, 100% RH, 5 psig, 75°C



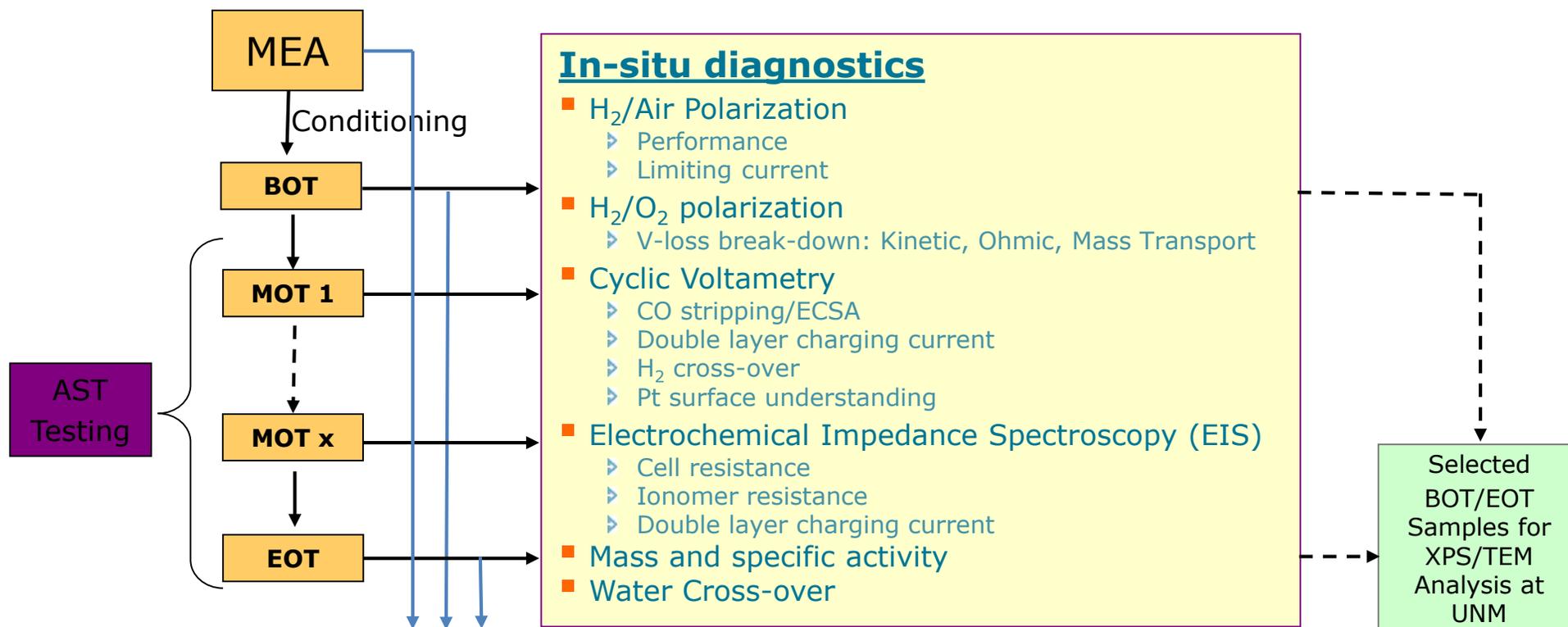
- BOL Performance and degradation at 1.2V UPL are insensitive for the two membranes
- AST cycling at 1.3V UPL shows lower performance loss for Membrane A
- Degradation rates (Pt dissolution and corrosion) were impacted by water content

Accomplishments

**Consideration of Membrane Properties on Cathode
Degradation**

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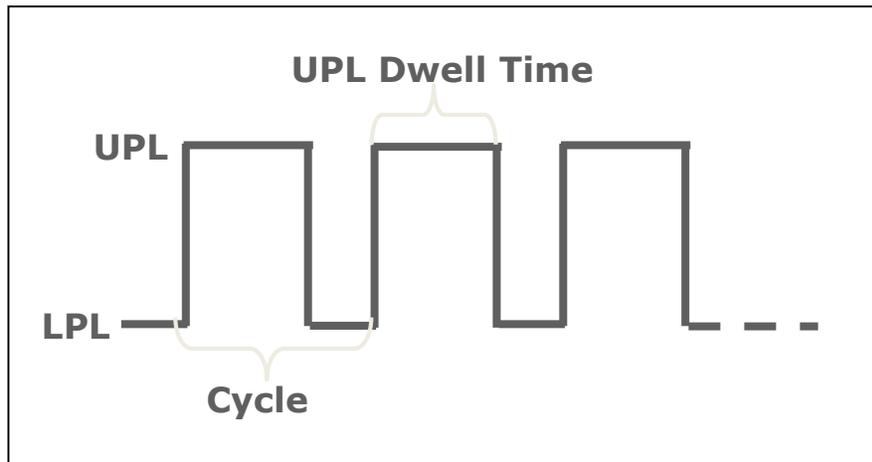
Ex-situ Diagnostics*

- SEM: Catalyst/membrane thickness
- SEM/EDX: Pt content in membrane and catalyst layer
- XRD: Pt crystallite size and orientation
- BPS Diagnostic Tool
 - Limiting Current

Standard AST: 0.6V (30sec)→1.2V (60 sec), 4700 cycles, 100% RH, 80°C
 Standard Diagnostic Air Polarization (STC):
 Air/H₂, 100% RH, 5 psig, 75°C

BOT/MOT/EOT = Beginning/Mid/End of Test

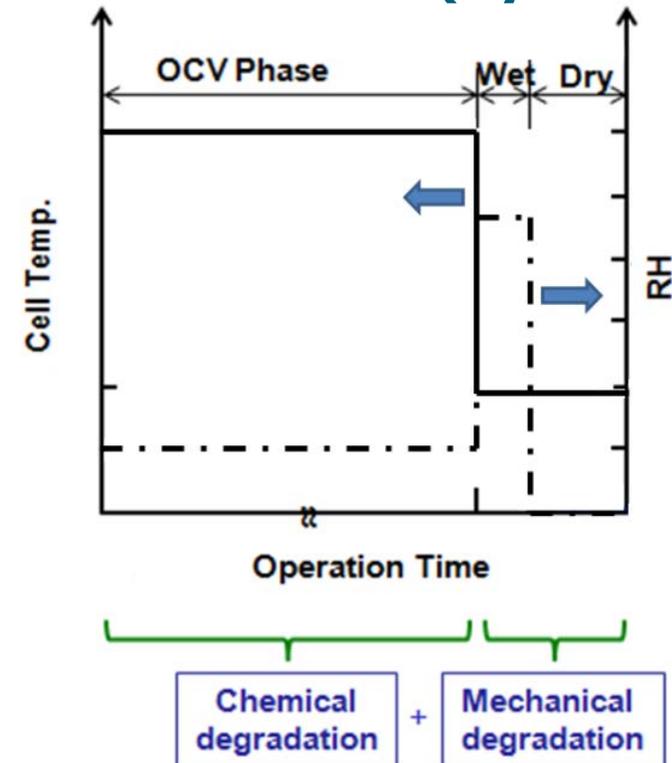
Cathode AST



- **Cathode AST**

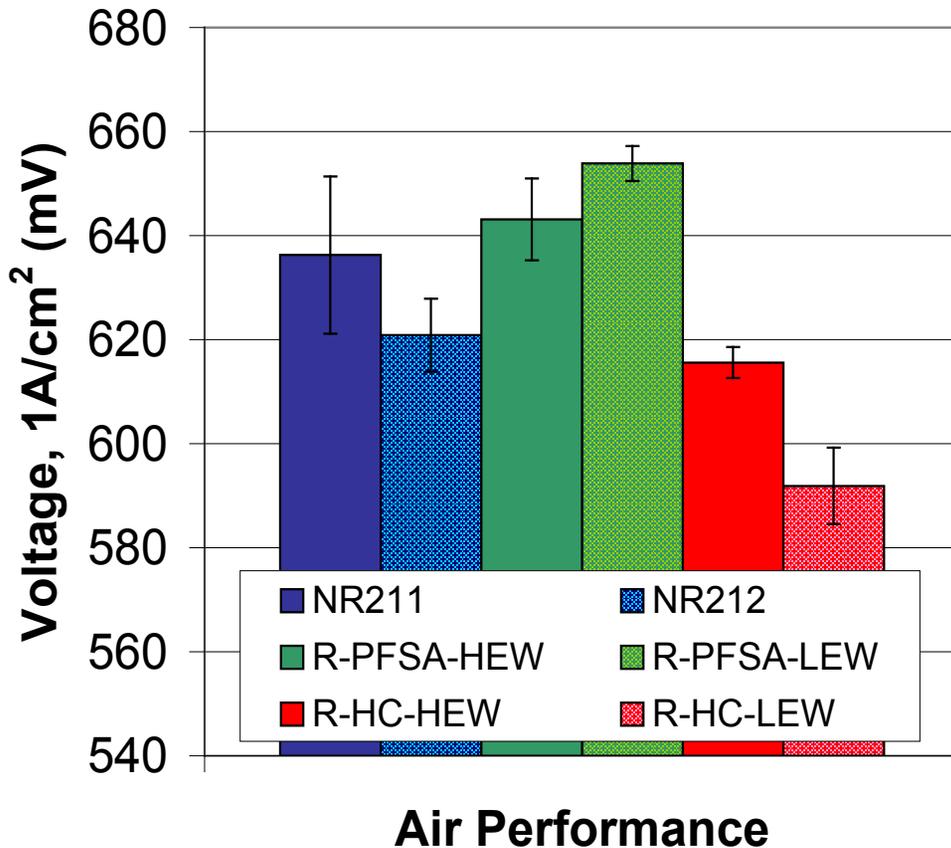
- Air/H₂, 80°C, 100% RH, 0.6 V (30s) to 1.2 V (150s) cycles

Membrane AST (Cyclic OCV)



- **Cyclic OCV AST combines chemical and mechanical degradation**

- Chemical Phase: OCV operation at increased T, low RH, increased oxygen concentration
- Mechanical Phase: N₂ operation, wet/dry cycling



- **PFSA: NR211 > NR212**

- Performance should decrease due to the additional resistance from the increased thickness

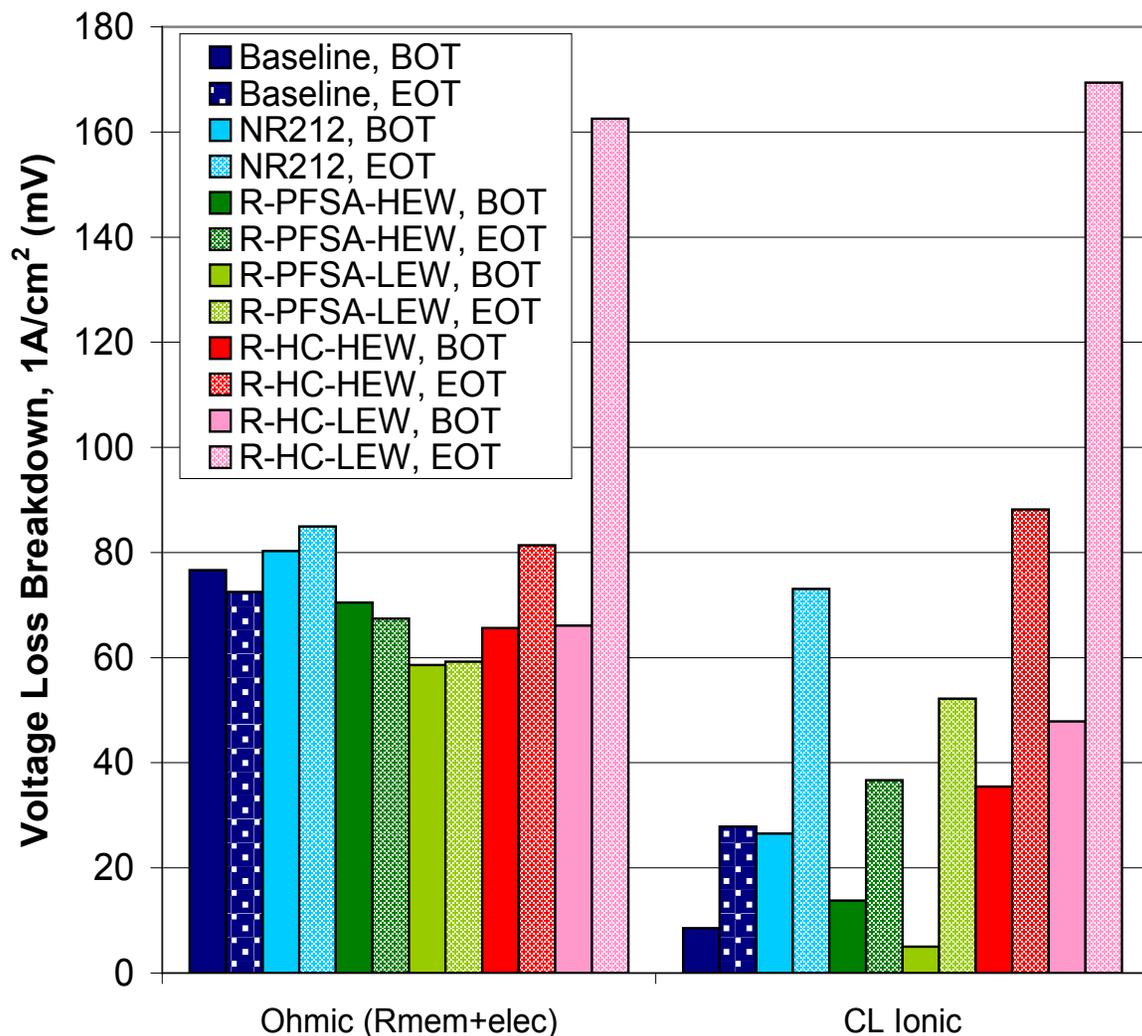
- **R-PFSA: LEW > HEW**

- Performance should increase with the lower EW material

- **R-HC: LEW < HEW**

- LEW showed membrane degradation with BOL operation
- SEM showed irregular thickness and reinforcement band
- **Results not considered representative***

*R-HC membrane materials are considered to be experimental versions



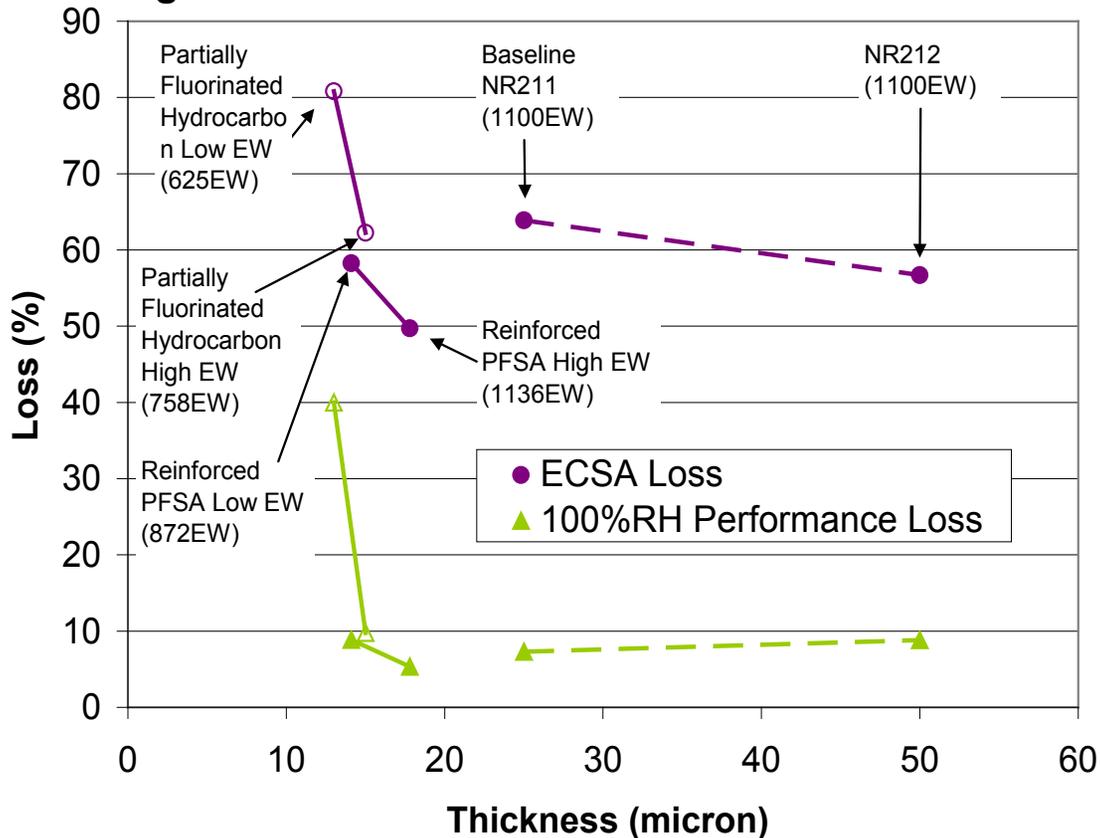
• Performance degradation

- Strongly related to changes in the CL Ionic loss category
- Platinum depletion causes shifts in local current away from the membrane/CCL interface

• R-HC: LEW

- large increase in the ohmic loss
- consistent with observed early degradation

Degradation as a Function of Membrane Thickness

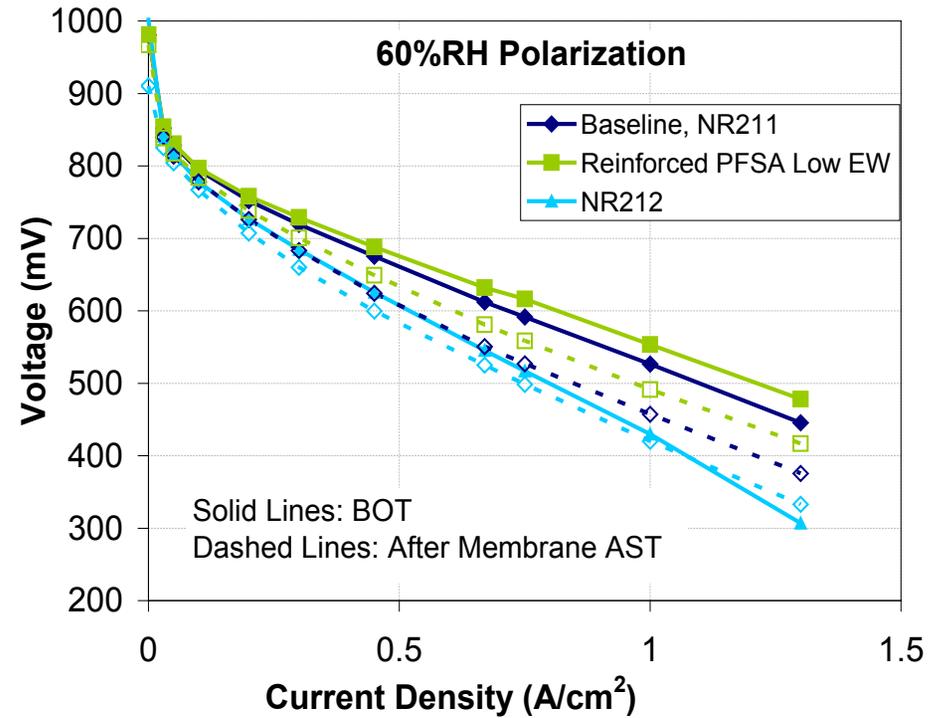
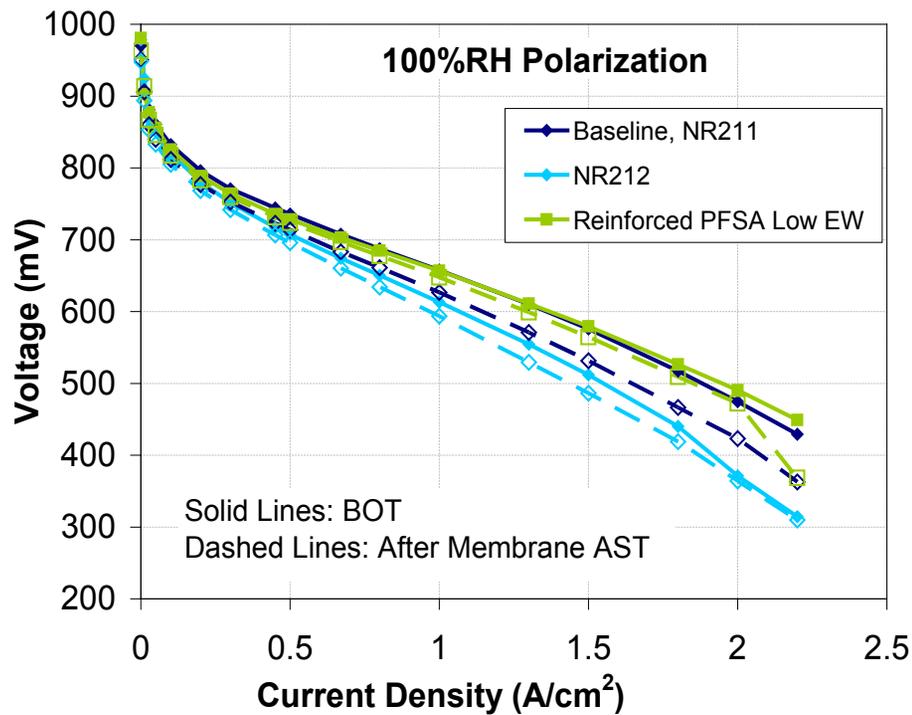


- **EW Effect: Greater ECSA loss for thinner, lower EW membrane in each membrane group.**
 - PFSA thickness effect is small, EW more dominant
 - Lower EW membranes → higher water content → higher water content at the membrane / catalyst interface where the Pt dissolution is the greatest.
- **Membrane water content appears to be more important than the water cross-over for degradation**
 - Membranes with more water cross-over to the cathode had less degradation.

- **The R-PFSA membranes had lower ECSA loss than PFSA, suggesting that change in structure (e.g. reinforcement) also had a beneficial effect.**
- **Similar performance losses at 1A/cm² for all membranes**
 - ECSA values had not reached the critical value near (75% ECSA loss)
 - Exception: R-HC LEW showed signs of membrane degradation, high ECSA and performance losses

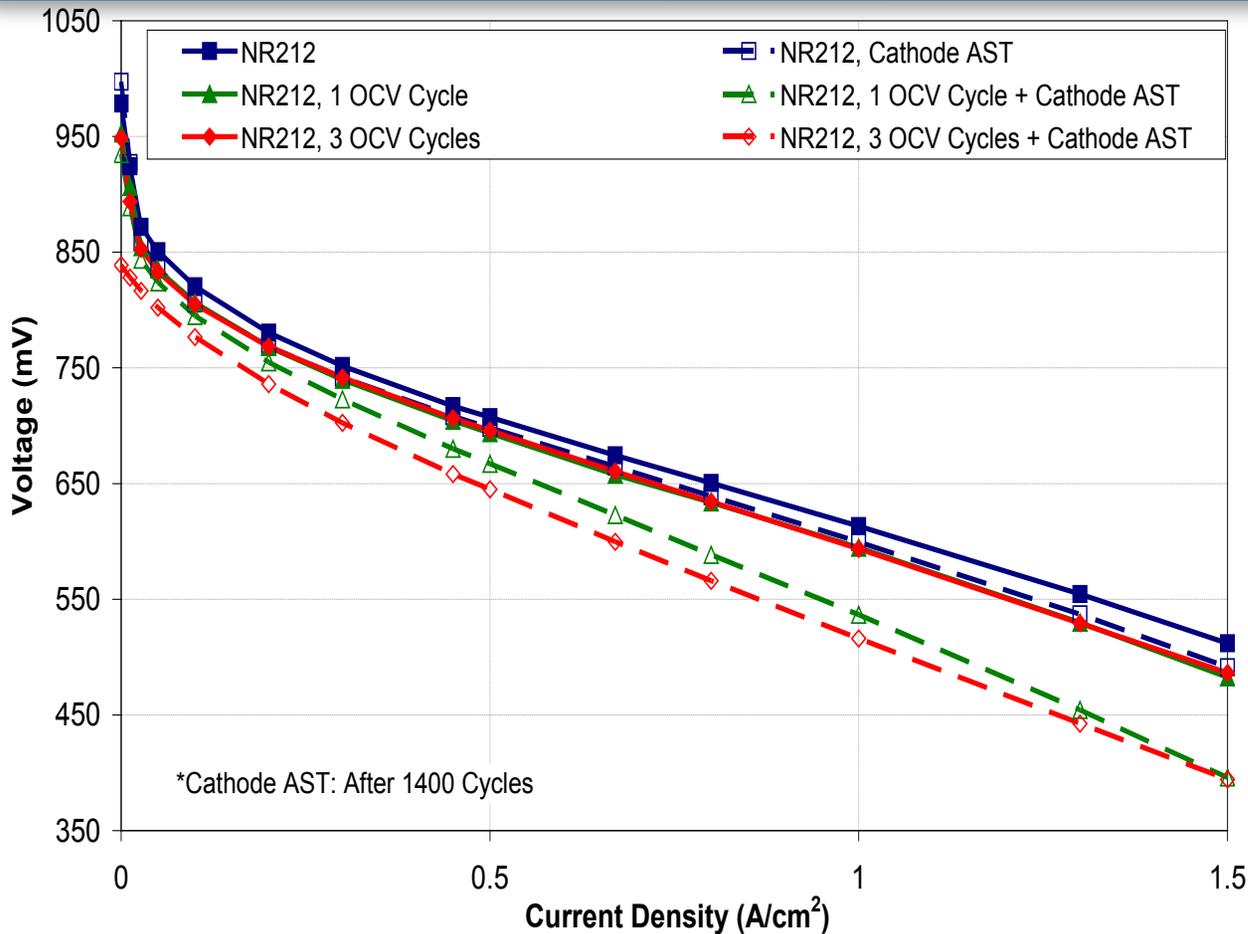
Membrane Type	Membrane Thickness (micron)		Water Crossover, Anode to Cathode at 95%RH cathode,60% RH anode, 1.3A/cm ² (g/min)		H ₂ Permeance 75°C, 100% RH (mol / (m ² s Pa))	
	Conditioned	After Membrane AST	Conditioned	After Membrane AST	Conditioned	After Membrane AST
Baseline: NR211	28	25	-0.15	-0.16	1.6E-07	1.8E-07
NR212	57	35	-0.05	Repeat pending	7.3E-08	6.4E-07
Reinforced PFSA Low EW (R-PFSA-LEW)	19	N/A	-0.25	Data pending	2.4E-07	2.4E-07

Membrane Type	R Cell (mΩ.cm ²)		ECSA		Pt Size (nm)	
	Conditioned	After Membrane AST	Conditioned	After Membrane AST	Conditioned	After Membrane AST
Baseline: NR211	69	66	183	147	5.3	5.1
NR212	101	49	182	143	4.8	5.2
Reinforced PFSA Low EW (R-PFSA-LEW)	60	56	200	147	5.1	N/A



Effect of Membrane AST on Performance:

- All membranes showed performance degradation after the membrane AST
- NR212 thinned the most, the performance was less impacted as compared to NR211 and R-PFSA Low EW



NR212 Membrane Degradation— Repeated

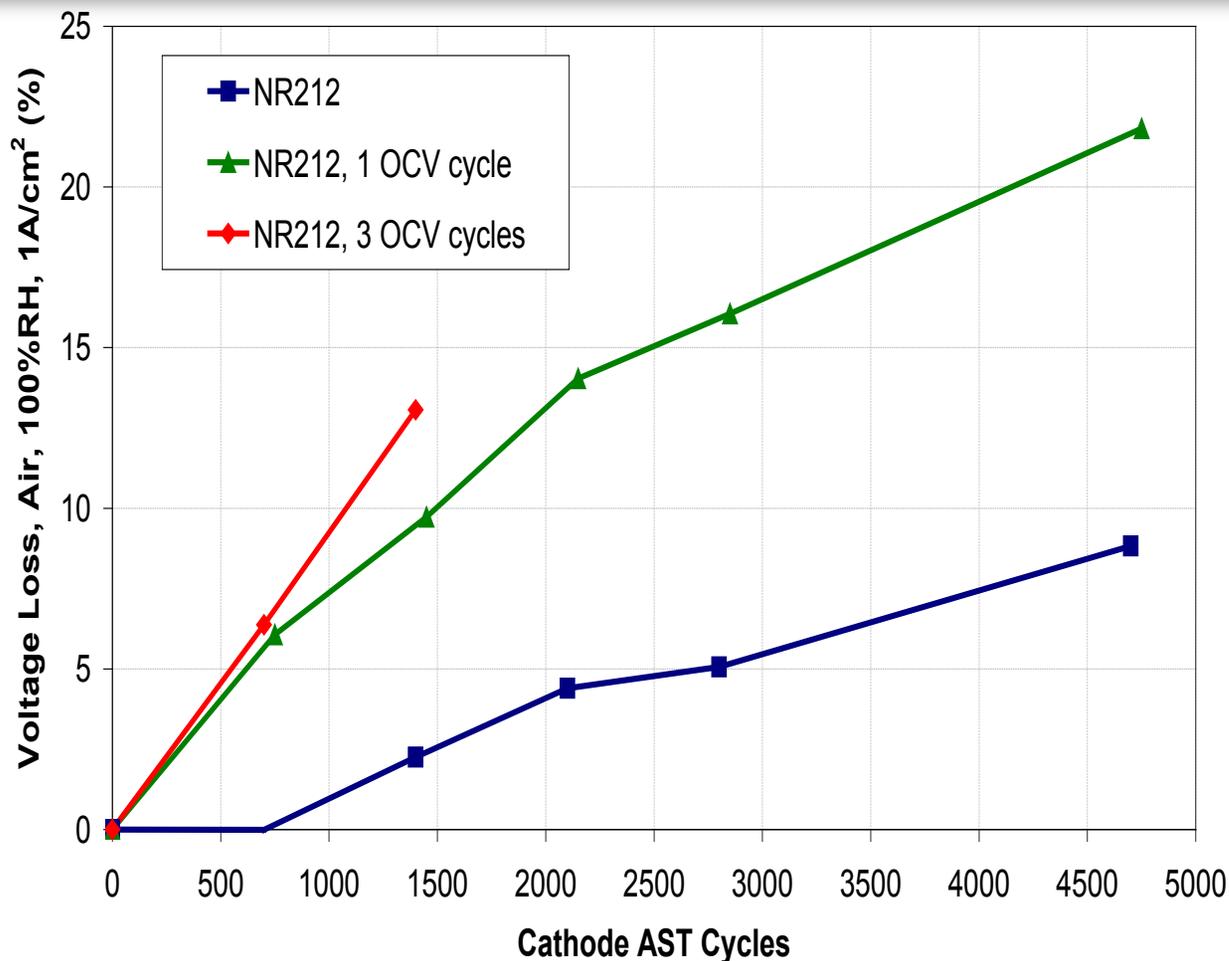
- Significant degradation during first attempt
- Diagnostics decreased
 - Low RH removed
- OCV cycles decreased
 - Less degradation

Cathode AST

- Cycles limited to 1400 due to transfer leak

Membrane Degradation

- 1 to 3 OCV cycles → Similar performance loss
- OCV Cycle + Cathode AST
 - Voltage loss significantly increased vs. individual ASTs
 - Voltage loss increased with increasing OCV cycles

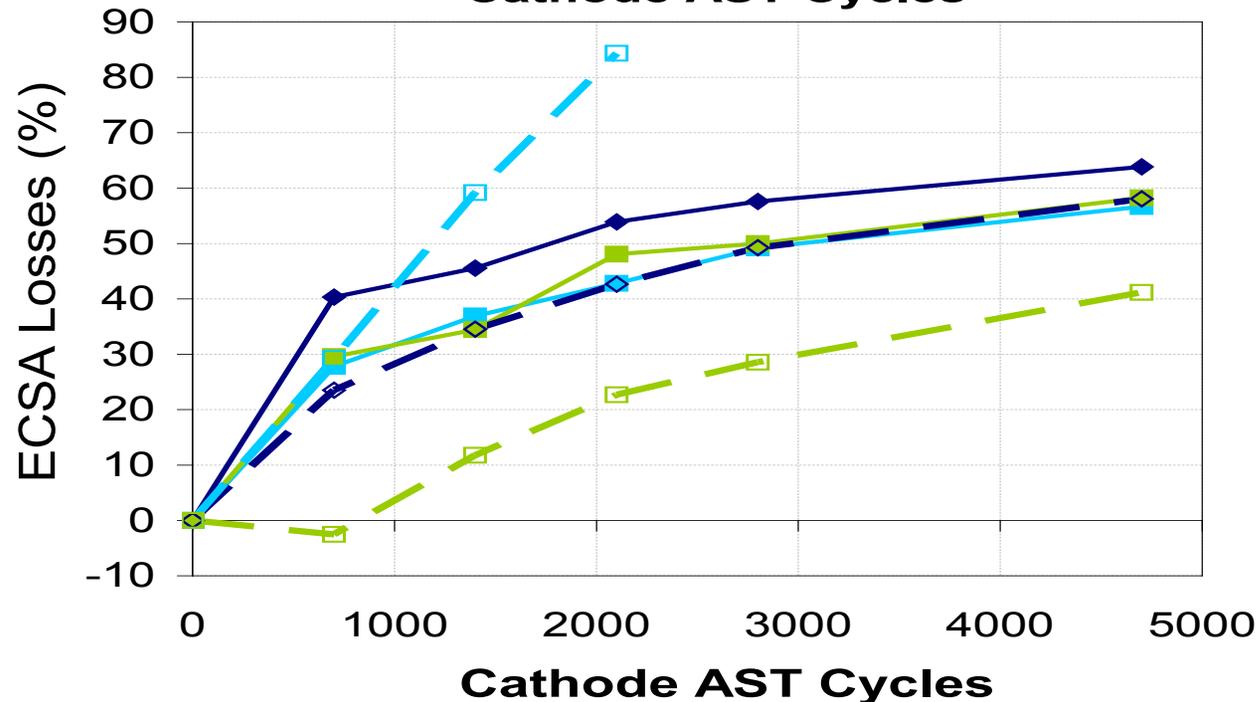
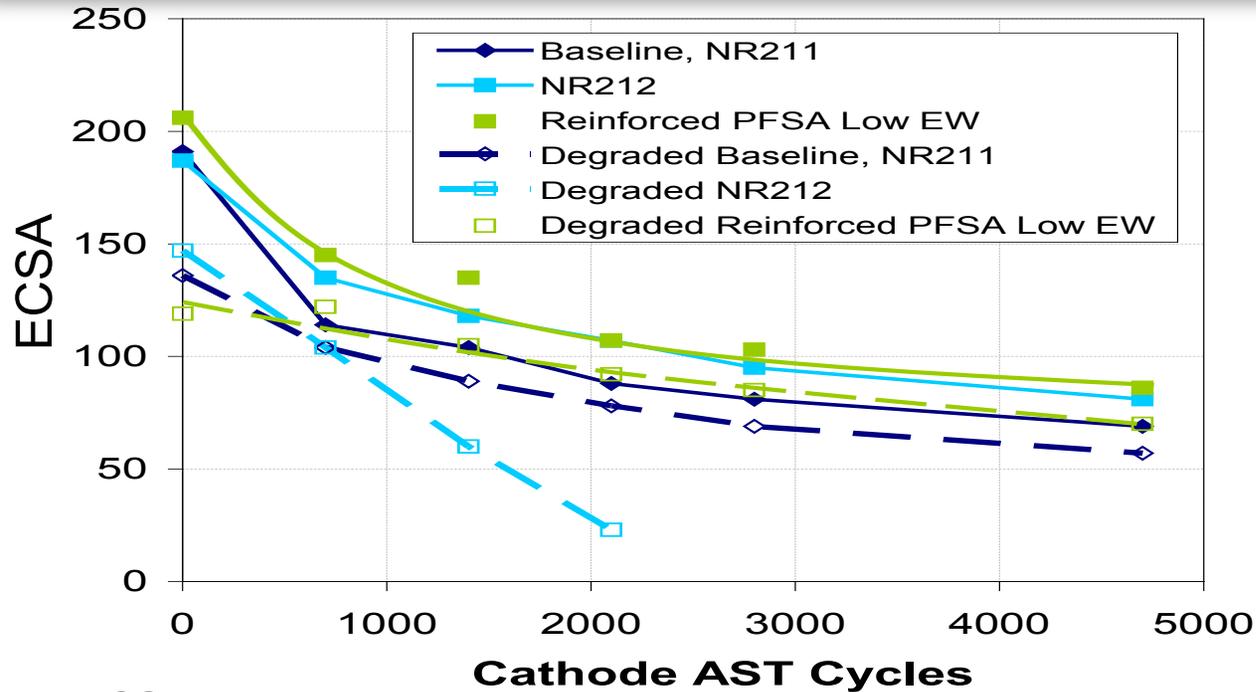


NR212 – Membrane Degradation Repeated

- Diagnostics decreased
 - Low RH removed
- OCV cycles decreased
 - Less degradation

Membrane Degradation

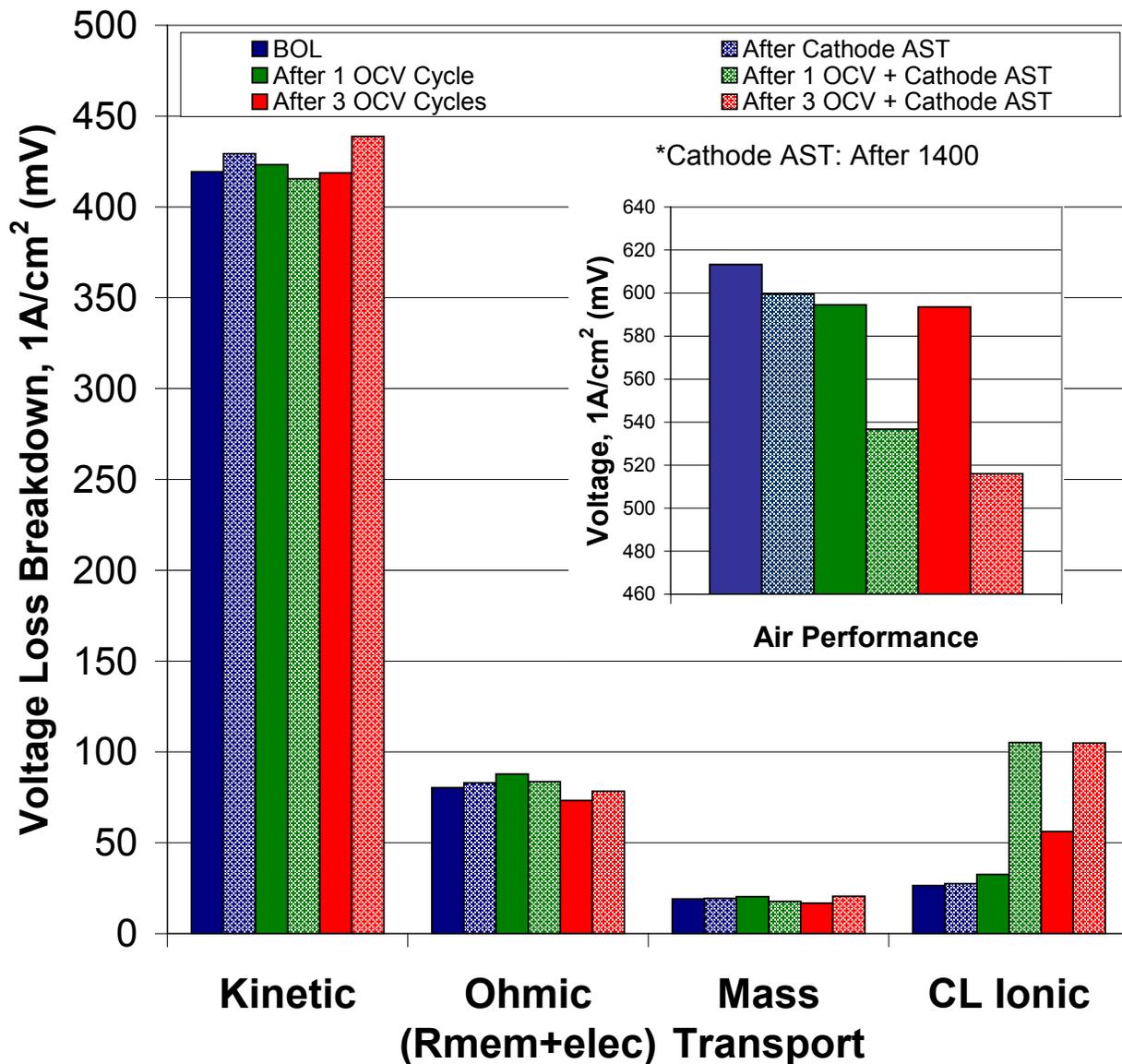
- 1 vs 3 OCV cycles → Transfer Leak for 3 OCV cycle MEA at ~1400 Cycles
- OCV Cycle vs Cathode AST baseline
 - Rate of voltage loss appears to be faster over the course of the AST test as a function of the number of OCV cycles



Original Dataset

Membrane Degradation

- **1 vs 3 OCV cycles**
 - NR211 and NR212 don't show differences until ~700 Cycles (both datasets)
- **OCV Cycle vs Cathode AST baseline**
 - For NR211 and R-PFSA
 - ECSA losses decreased with membrane degradation
 - Both NR212 samples showed increased H₂ crossover with AST cycling
 - Membrane degradation due to Cathode AST for NR212



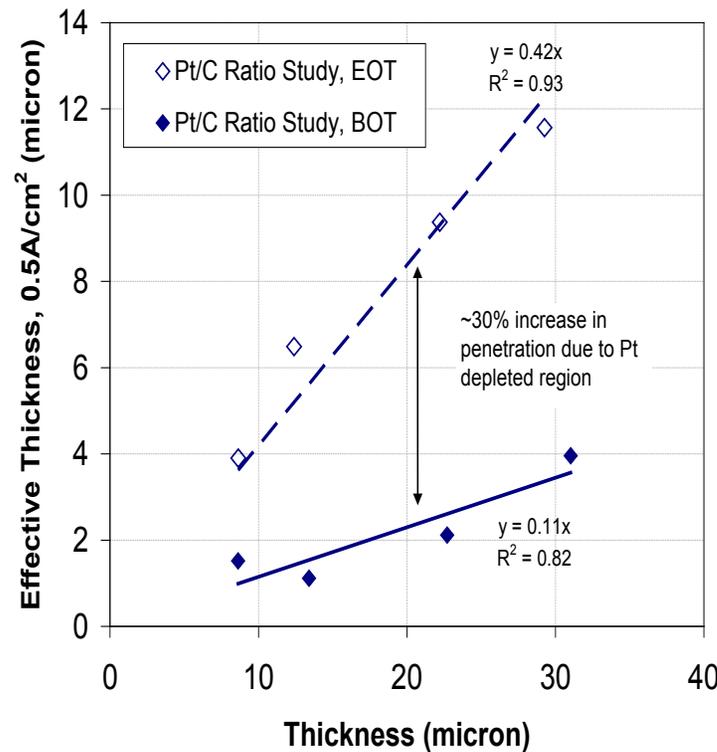
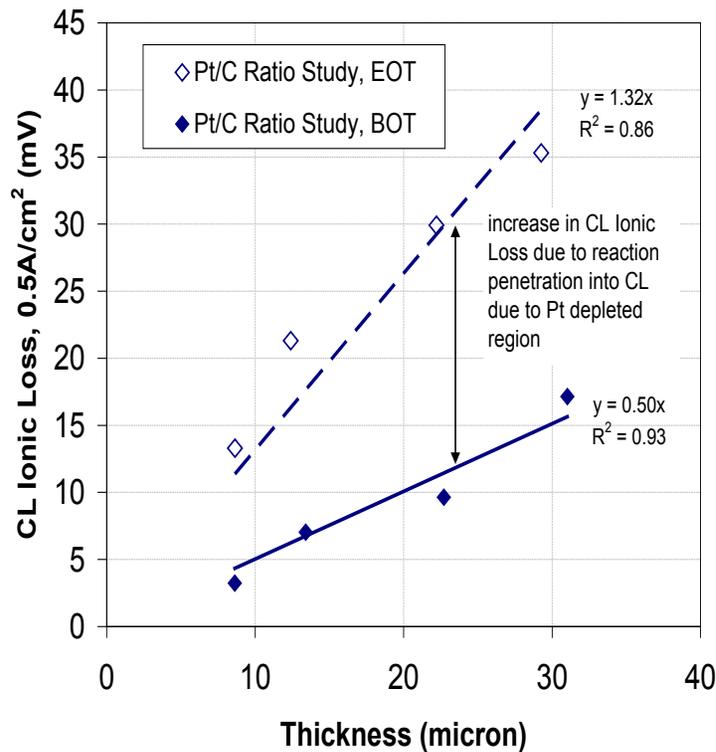
Original Dataset

Membrane Degradation

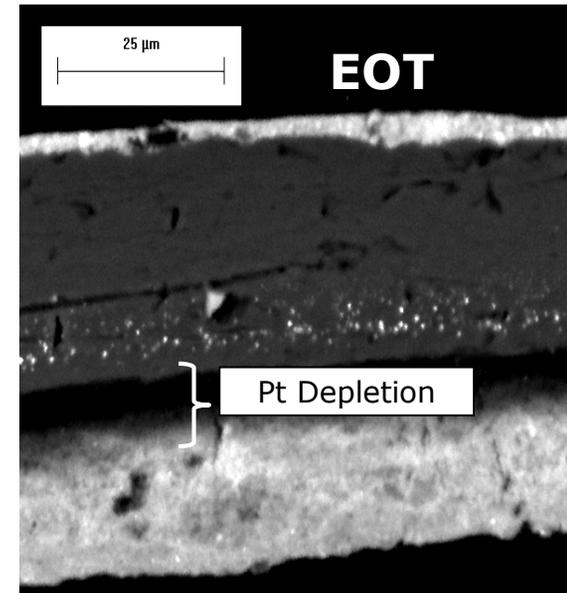
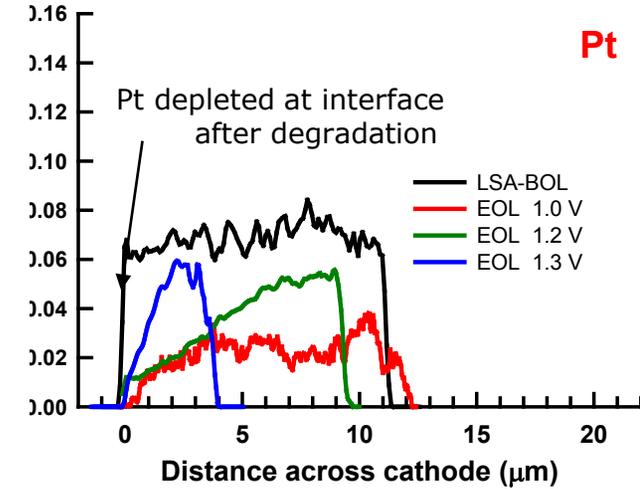
- **1 vs 3 OCV cycles**
 - Increased CL Ionic Losses with increased OCV cycles
- **OCV Cycle vs Cathode AST baseline**
 - Increased CL Ionic losses for OCV/Cathode AST vs. OCV cycled only
 - **Significantly greater CL ionic losses vs. cathode AST only**
 - Results are consistent with original dataset for NR211 and R-PFSA
 - **Platinum depletion near the membrane/CCL interface may be a possible cause**

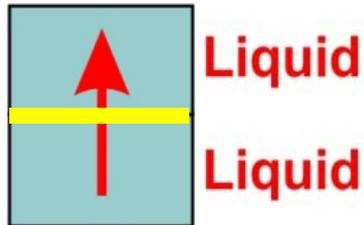
CL Ionic Losses Effect of Pt depletion

- CL Ionic Loss increase from BOT to EOT due to Pt depletion which shifts the reaction penetration further into the layer
- Increase in Effective Thickness (penetration) equal to ~30% of full thickness agrees with the thickness of the Pt depleted region by SEM



STXM: Pt Volume Fraction Profiles Across Cathodes (McMaster University)

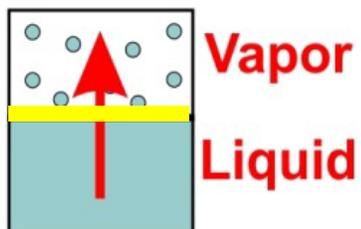




Membrane is immersed in liquid water. Pressure is applied on one side to create hydraulic pressure driven permeation.

➡ **Liquid-Liquid permeation (LLP)**

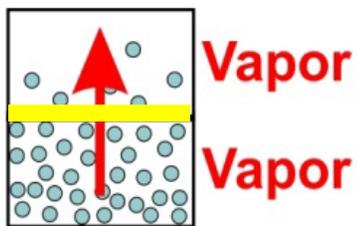
Okada et al. (2002)
Villaluenga et al. (2003)
Evans et al. (2006)



Membrane is floated on liquid water. Humidified air is flowed on one side to create concentration gradient driven permeation.

➡ **Liquid-Vapour permeation (LVP)**

Motupally et al. (2000)
Ge et al. (2005)
Majsztzik et al. (2007)
Romero et al. (2008)



One side of the membrane is exposed to saturated water vapour. Humidified air is flowed on one side to create concentration gradient driven permeation.

➡ **Vapour-Vapour permeation (VVP)**

Motupally et al. (2000)
Ge et al. (2005)
Majsztzik et al. (2007)
Romero et al. (2008)

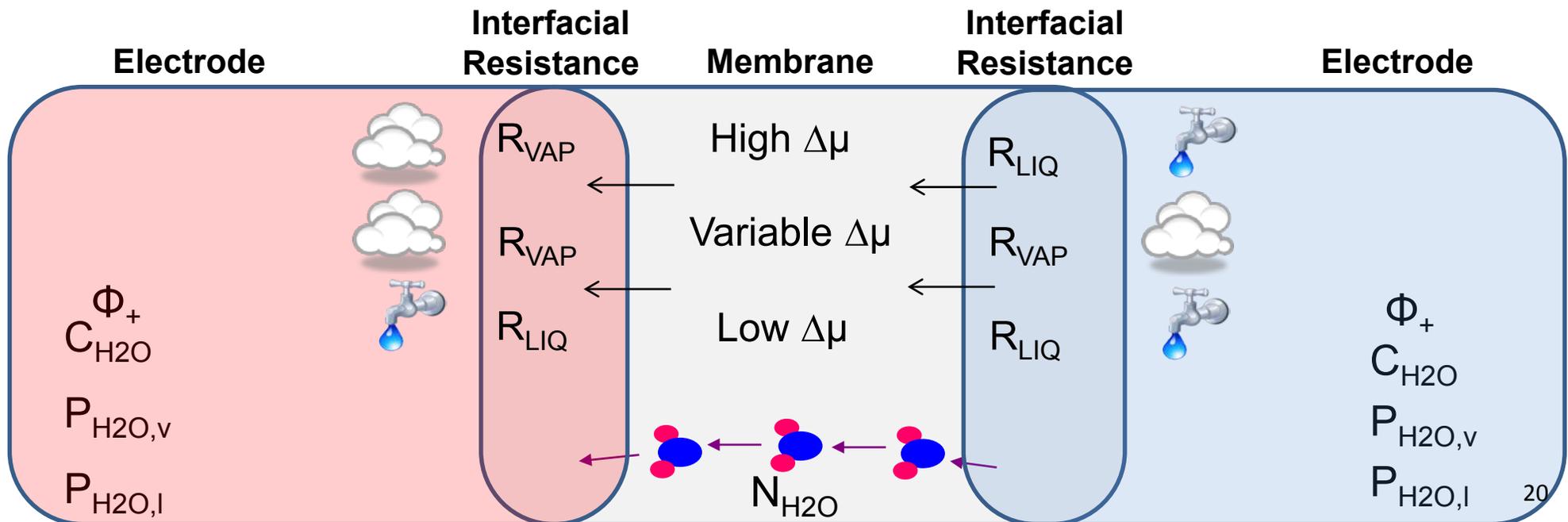
- **Experimentally**

- Liquid-Vapour boundaries show the highest crossover and Liquid-Liquid show the lowest.

- **This is explained by a combination of**

- Bulk membrane transport equations (e.g., Weber)
- Interfacial resistances from sorption and phase change (e.g., Monroe)

$$\frac{1 - \theta_V^\infty}{\theta_V^\infty} = \left(\frac{1}{k_V} + \frac{Lp_{SAT}}{RTDC_{max}^{liq}} \right)$$



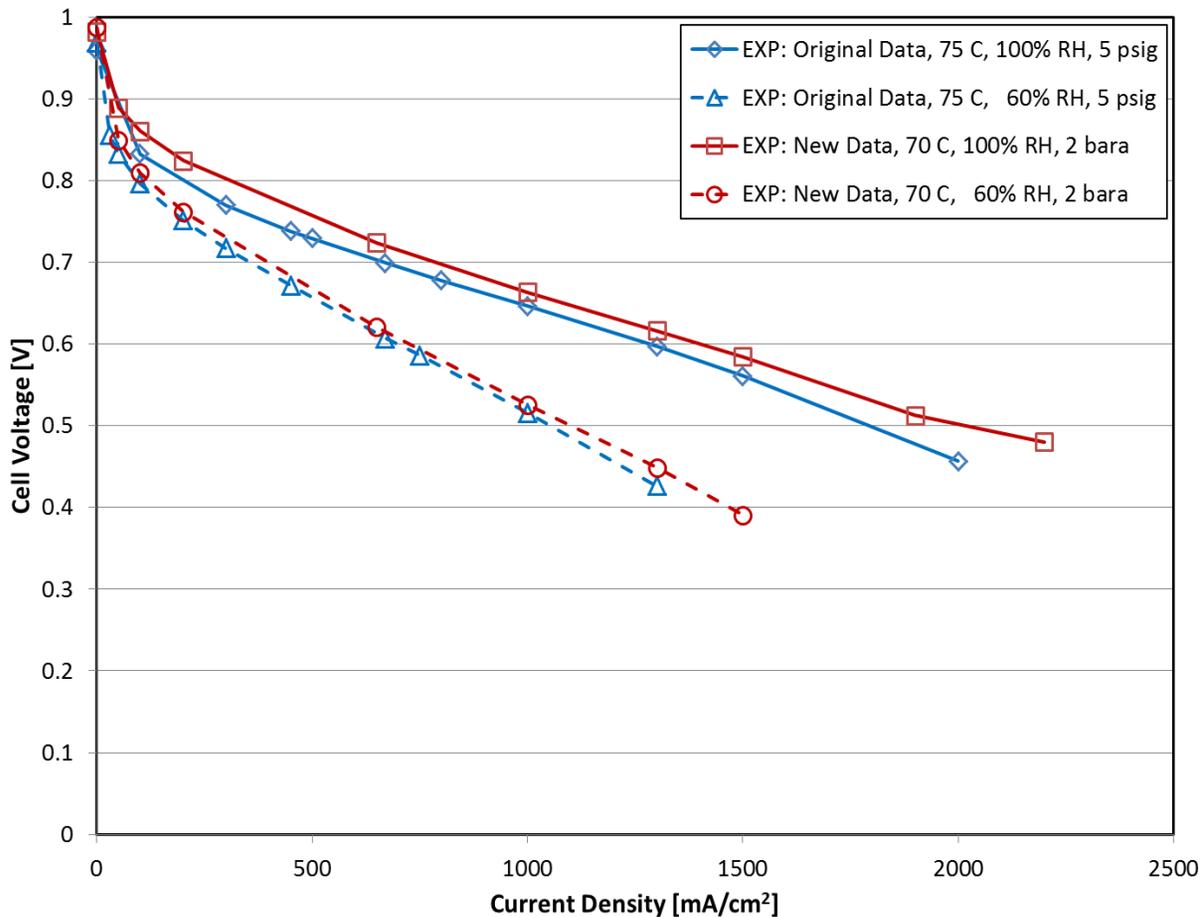
Experimental Datasets

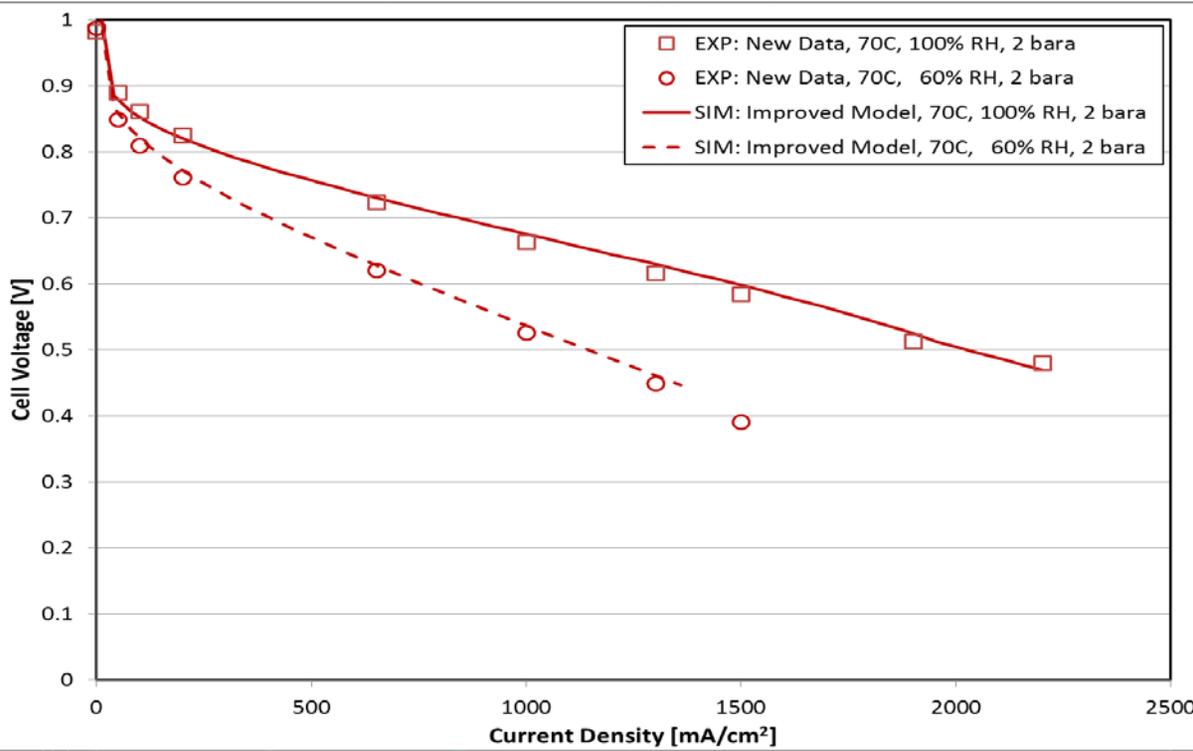
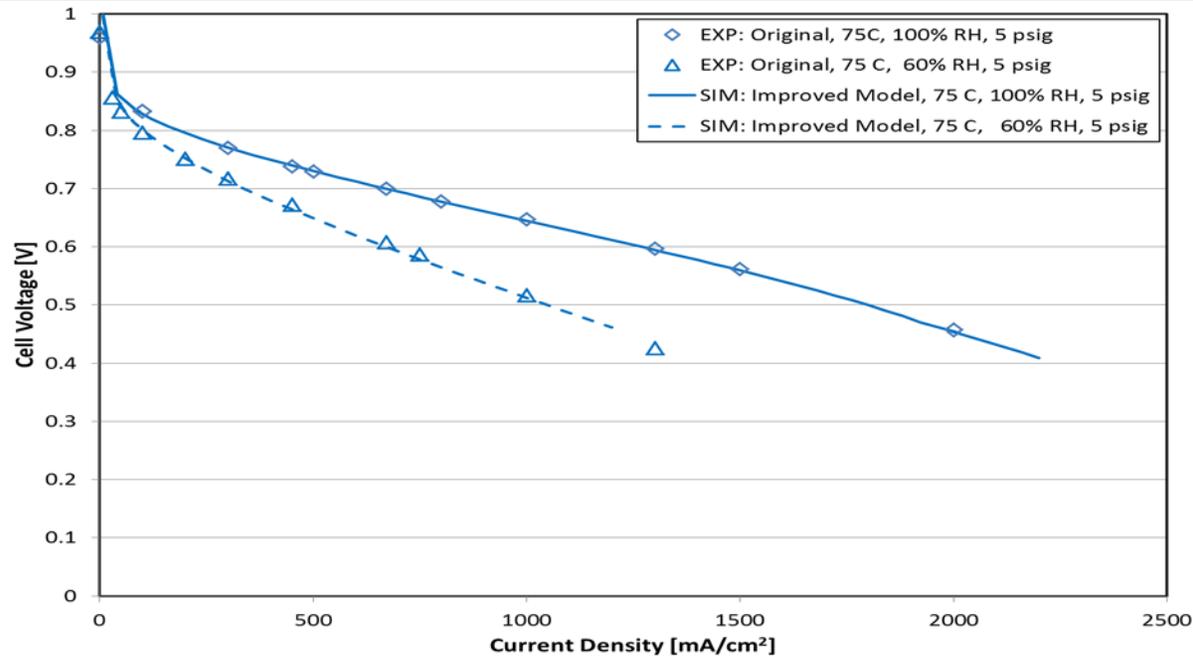
Original vs New Data

- Increase in performance due to higher operating pressure
- Performance gains are not retained under low RH
 - Proton transport limiting reaction rates

Testing New Membrane Model

- Improved model captures ..
 - Pressure based increase in performance
 - Low RH limitation on the reaction rates





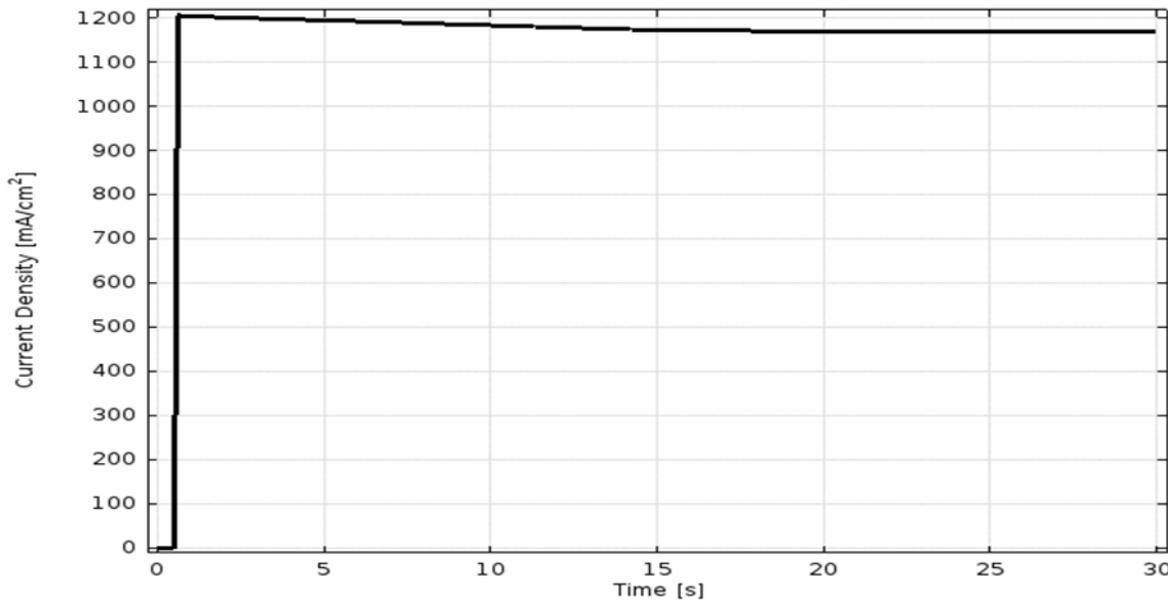
Experimental Datasets

Testing New Membrane Model

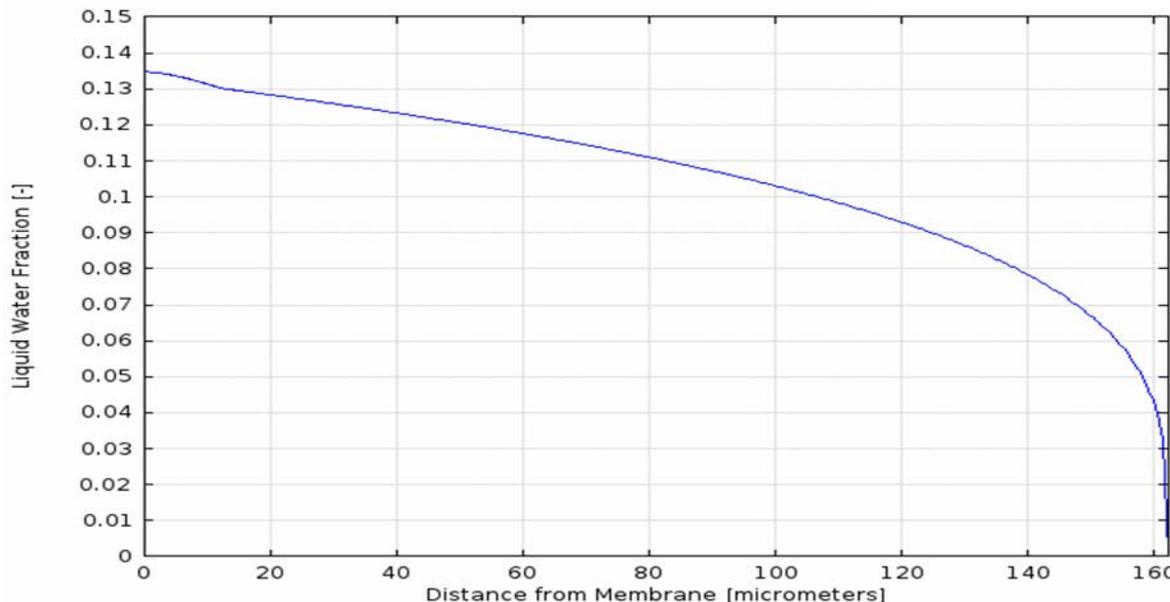
- The improved model captures:
 - Pressure based increase in performance
 - Low RH limitation on the reaction rates
- The model is able to capture the shift in the datasets
 - The parameter sets are constant and not changed
 - The physical aspects of the different MEAs ARE accounted for:
 - Loading changes, Nafion® content, GDL porosity etc.

Transient effects Improved Membrane Model

Potentiostatic Hold



Potentiostatic Hold: Water Saturation Evolution

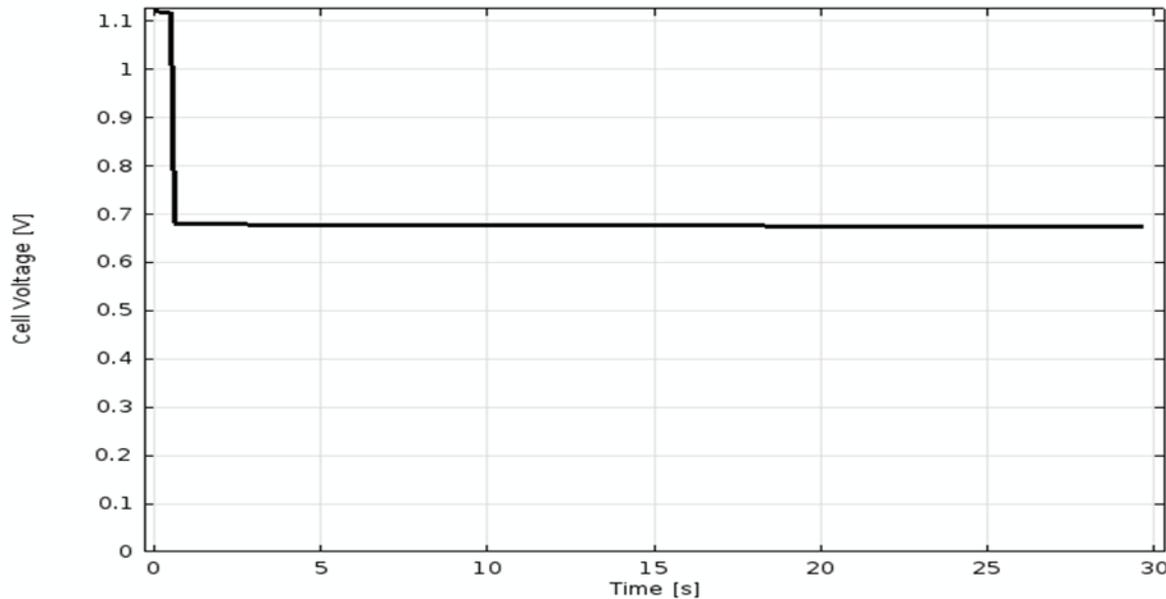


Transient Effects & Water Content

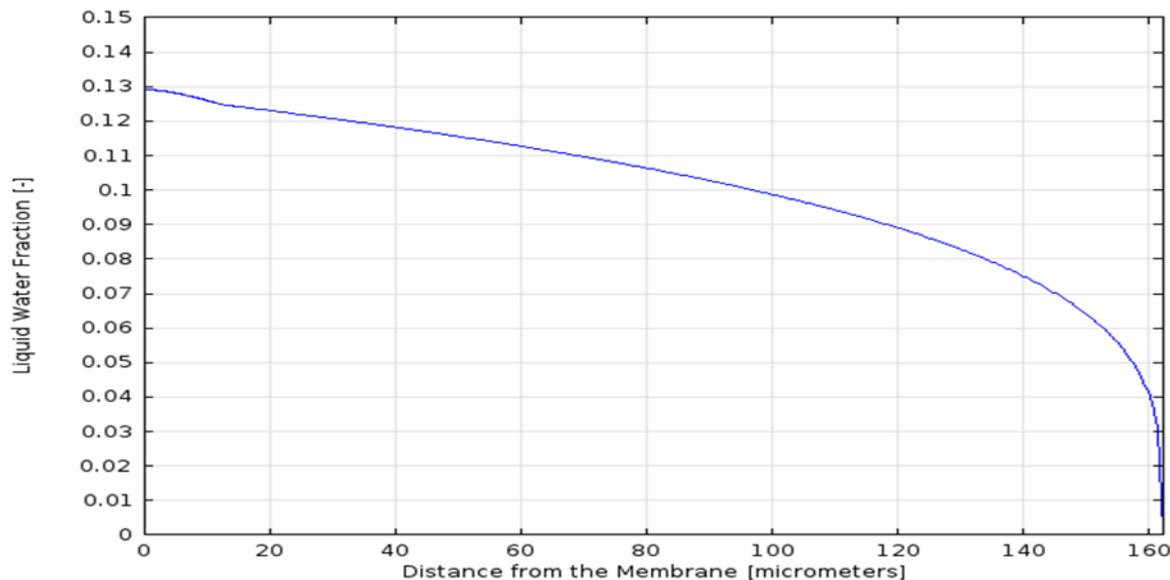
- Initial conditions
 - “no load” start
 - Uniform RH, concentration, Temp, Pressure
 - Small load applied mimicking load bank at 0 A (OCV)
 - Load is drawn/Voltage applied at 0.5[s]
 - Small ramp over 0.1s simulates “load on”
- Reaching Steady-state
 - Polarization curve levels out as the system balances the forming water and changes local reactant concentrations
 - Water Content Reaches breakthrough at channel face and then broadens, forming the steady state profile

Transient effects Improved Membrane Model

Galvanostatic Hold



Galvanostatic Hold: Water Saturation Evolution



Transient Effects & Water Content

• Initial conditions

- “no load” start
- Uniform RH, concentration, Temp, Pressure
- Small load applied mimicking load bank at 0 A (OCV)
- Load is drawn/Voltage applied at 0.5[s]
- Small ramp over 0.1s simulates “load on”

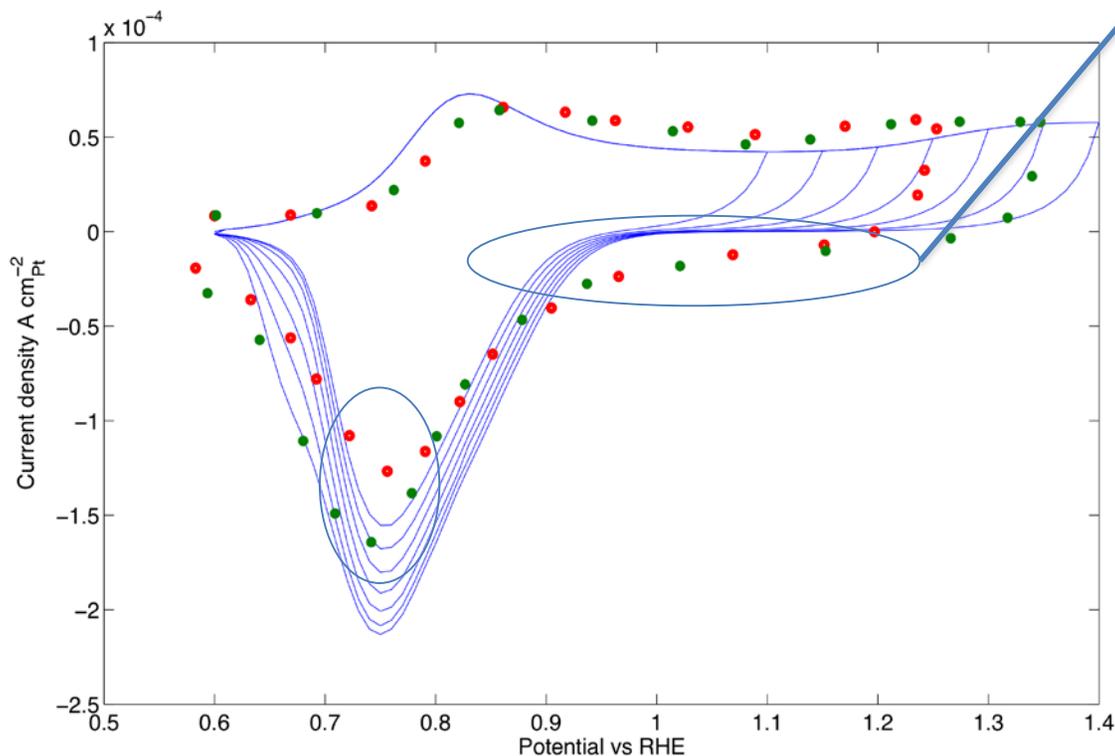
• Reaching Steady-state

- Differences in the early decay are related to the “rate” or speed at which the MEA reaches the steady water content.
- Constant current holds tend to have a faster development than voltage holds do to the constant rate of reaction (hence water production)

ORR Multistep/Platinum Dissolution

Sources of Error and discrepancies

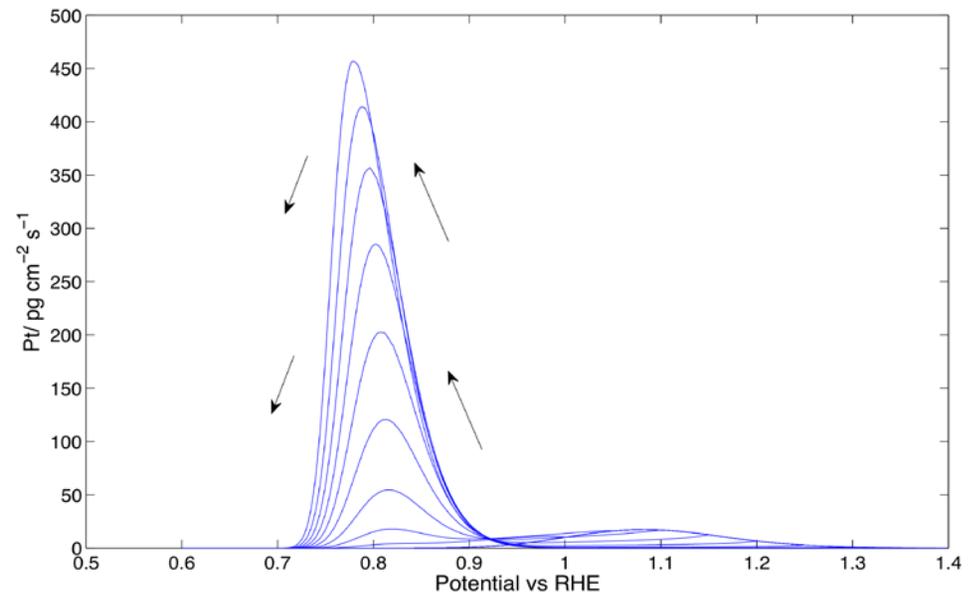
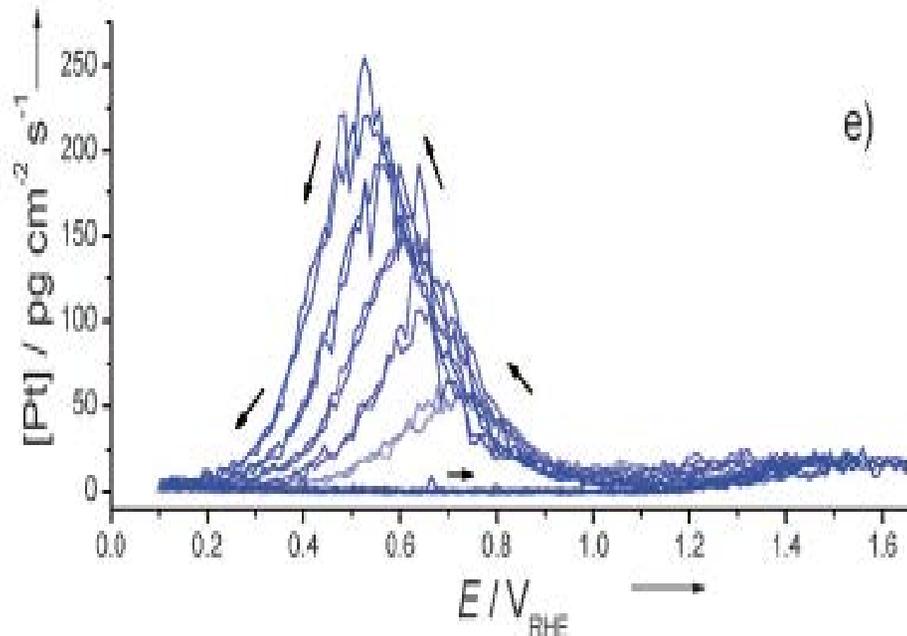
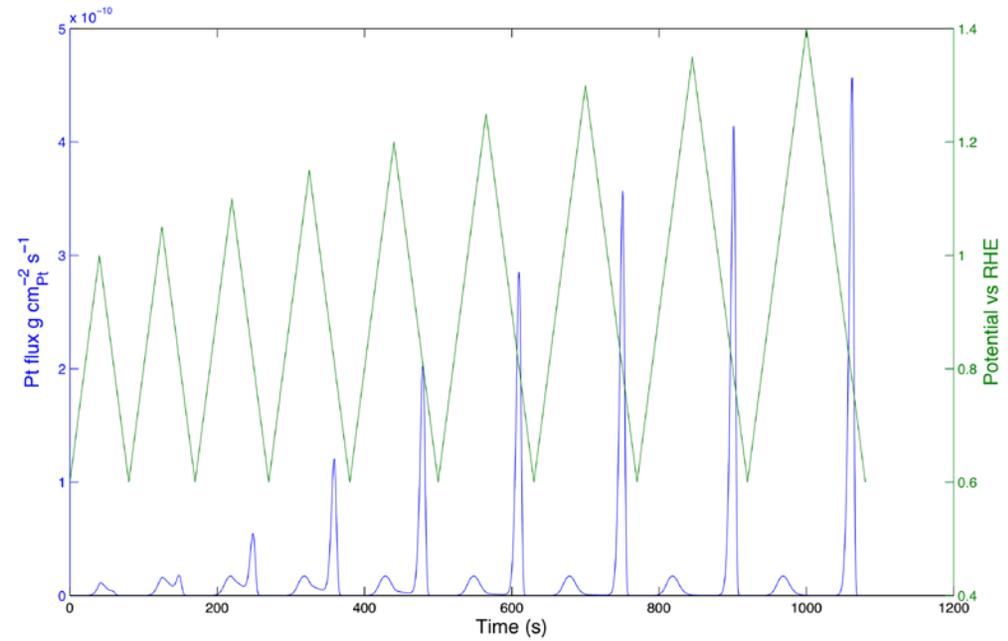
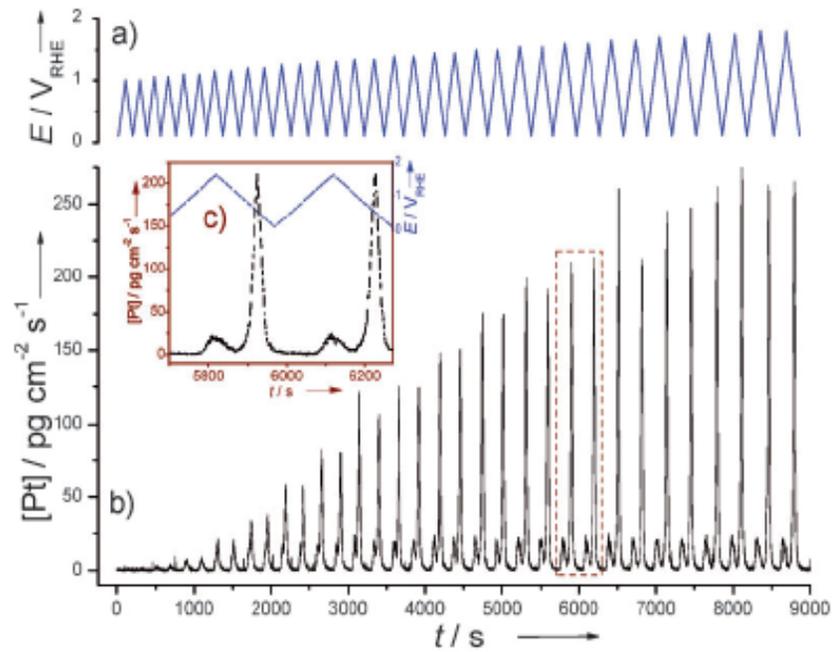
- O-Pt-OH dissolution, it can potentially cause the incoming degradation rate to have the same slope
- O-Pt(2) lingers and causes the outgoing rate to reduce over a wide potential window
- Cause of the cathodic peak potential shift:
 - RH/Sub surface O/Proton concentration



Mismatch because certain species are not considered in the mechanism?

ORR Multistep/Platinum Dissolution

Time Resolution of Platinum Dissolution



Summary:

- Repeated NR212 has been completed
- NR212 showed significantly increased sensitivity to the combination OCV/Cathode AST as compared to the other membranes
- NR212 may have experienced membrane degradation during the Cathode AST whereas the other materials did not
- Rate of ECSA loss appears to accelerate with increased OCV cycling for NR212

Project Wrap-up and Reporting:

- Complete Analysis of Low-loaded catalyst tests
- Complete correlations and model validation package

FC-APOLLO Development and Release:

- **Complete community-driven integration of improved sub-modules:**
 - **Transient Weber/Newman membrane sub-model in branch**
 - **Transient Channel Flow Solver**
 - **Improved ORR/OER and Platinum Dissolution Sub-model**
- **On-going Ex-situ validation with L/L, L/V, V/V ex-situ test**
- **Continue Beta testing with users (exit stage mid-summer)**
- **Complete Documentation package for FC-APOLLO (D. Harvey Thesis)**
- **Release code following a BETA test schedule**
 - **Simple CCM – April 2015**
 - **Simple MEA – May 2015**
 - **Steady-state, full MEA – June 2015**
 - **Transient, Full MEA – July 2015**
 - **Transient, Full MEA with Degradation – August 2015**
 - **Transient, Full MEA with Degradation/Membrane Model – September 2015**

BETA Testing:

- **Work with BETA users began in November 2014.**
- **Current BETA user list:**
 - 1) Johnson-Matthey/U.British Columbia, (Lead: Peter Gray/David Wilkinson)
 - 2) Pajarito Powder/U.Michigan (Lead: Barr Halevi/Scott Barton)
 - 3) AFCC (Lead: Andreas Putz)
 - 4) Queen's University (Lead: J. Pharoah)
 - 5) Simon Fraser University (Lead: Erik Kjeang)
- **Working with each user to setup hardware/OS, OpenFOAM[®]/Foam-Extend, and a series of gradual demo codes for training in FC-APOLLO**
 - Download via GIT
 - Nightly software builds/updates
 - Functionality and consistency between locations is being confirmed
 - Parallelization is functional, working with OpenCFD to apply a series of improvements for efficiency (speed up in degradation runs) and code standard conformity
 - Current Improvements have yielded a 2 – 20x speedup, depending on the case

■ Linux

- Model runs in a Linux based environment
- Hosting internally is done via cluster and remote login
- Local installs are done using a Git repository

■ OpenFoam®

- Simulation suite was built using foam-extend-3.1
- FC-APOLLO builds will remain current against the

■ Paraview

- www.paraview.org
- FC-APOLLO is built against the latest Paraview™ release

■ SourceForge

- Public repository
- www.sourceforge.net/projects/fcapollo

■ GitHub

- “PRIVATE” repository for BETA users

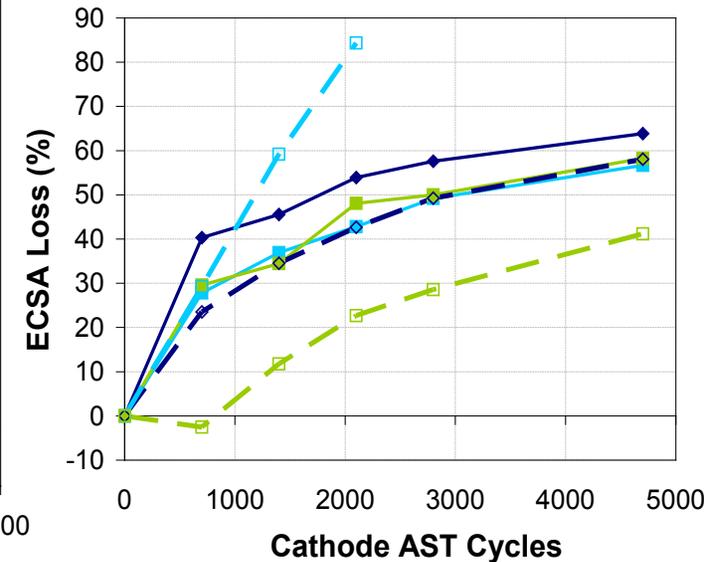
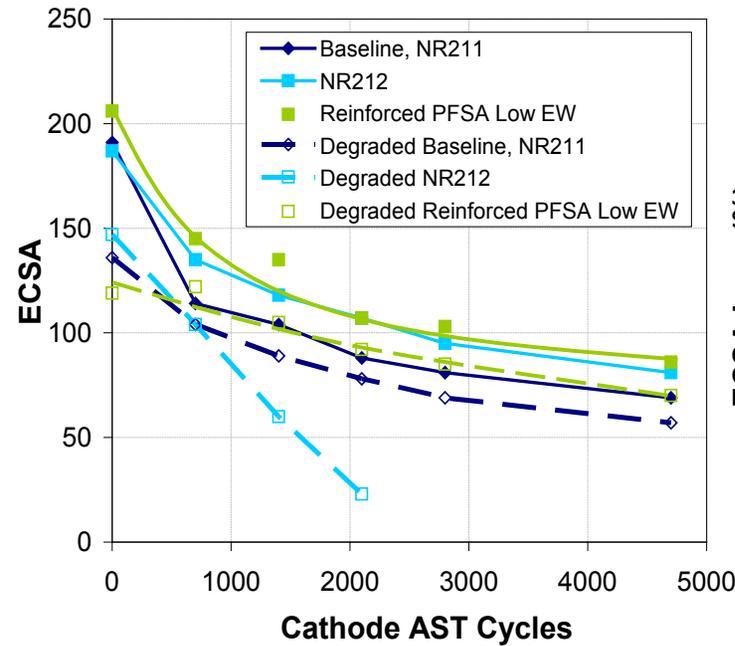
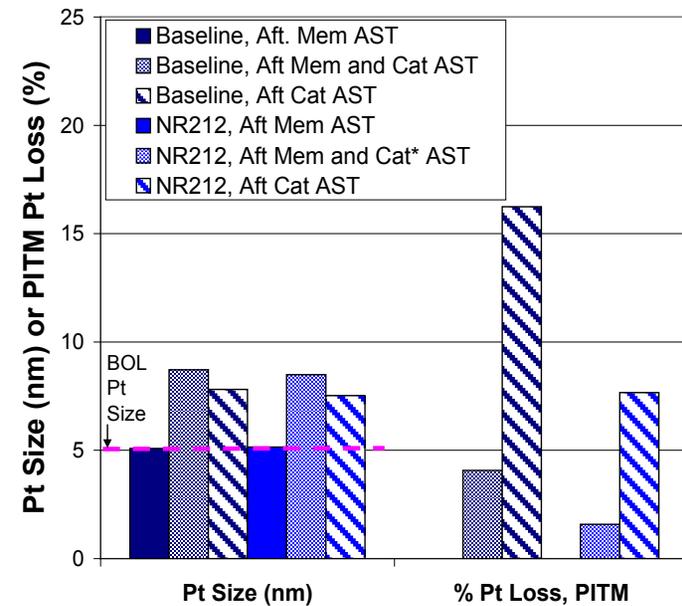
Technical Backup Slides

Consideration of Membrane Properties on Cathode Degradation

FC049

June 2015

Impact of Membrane Degradation Pt Dissolution

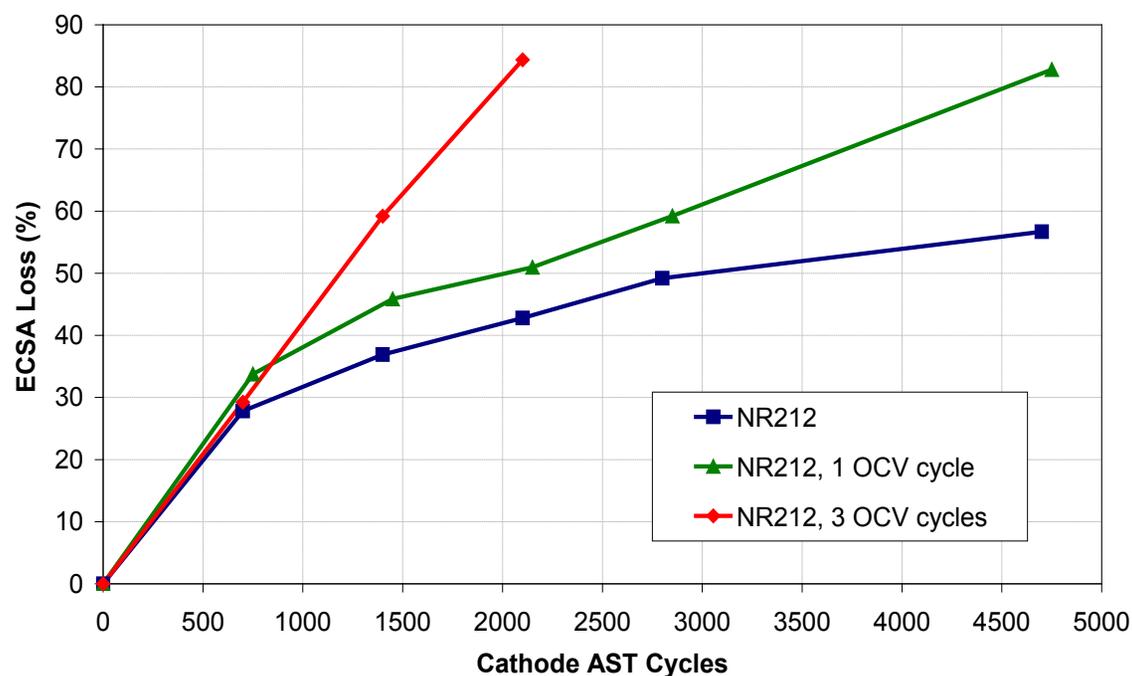
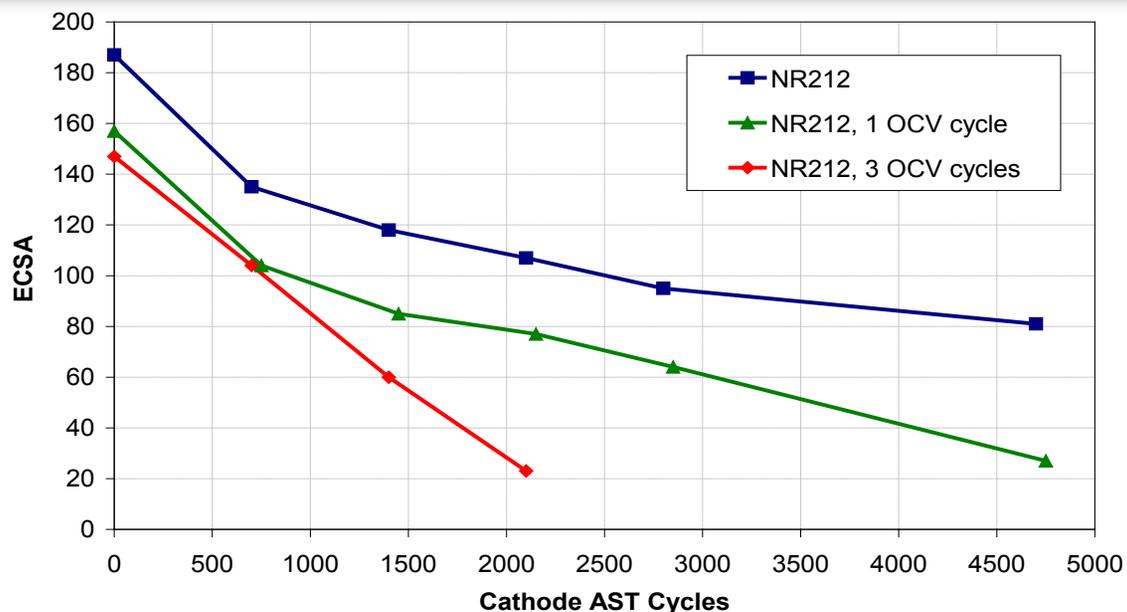


- **Membrane AST does not cause Pt growth or PITM**

- Lower ECSA is observed – some Pt loss from cathode, not found in membrane may occur

- **Membrane Degradation causes slightly higher Pt growth, but substantially less PITM after cathode AST**

- Lower ECSA loss occurs with degraded membranes (except NR212 which had transfer – to be repeated)



NR212 – Repeated

Membrane Degradation

- **1 vs 3 OCV cycles**

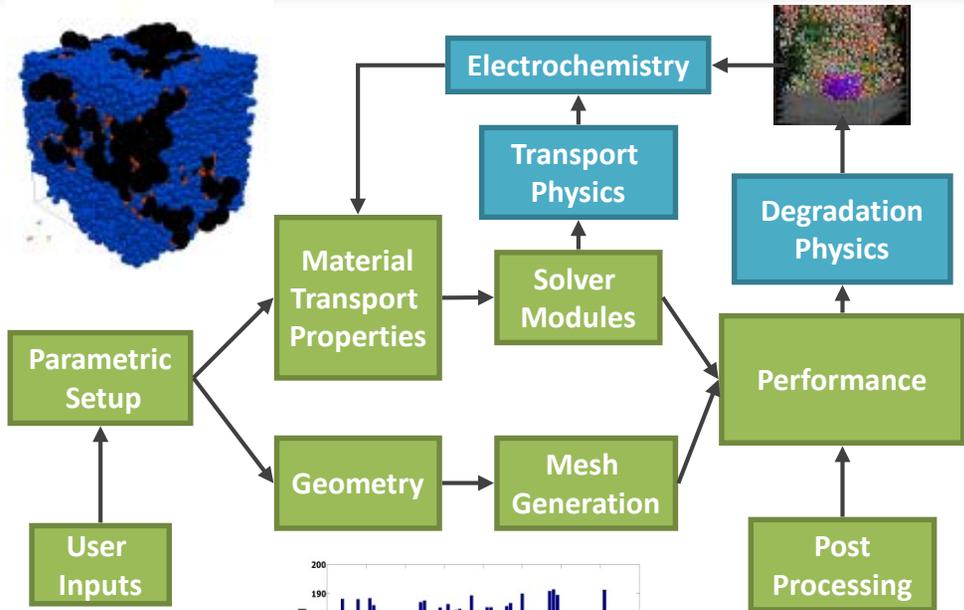
- Transfer Leak for 3 OCV cycle MEA at ~1400 Cycles

- **OCV Cycle vs Cathode AST baseline**

- ECSA changes for the baseline and 1 OCV cycle share a similar trend after accounting for the initial offset
 - 3 OCV cycle starts out in the same pattern and then continues with a steep decrease in ECSA

FC-APOLLO Simulation Suite

Fuel Cell Application Package for Long Life Operation

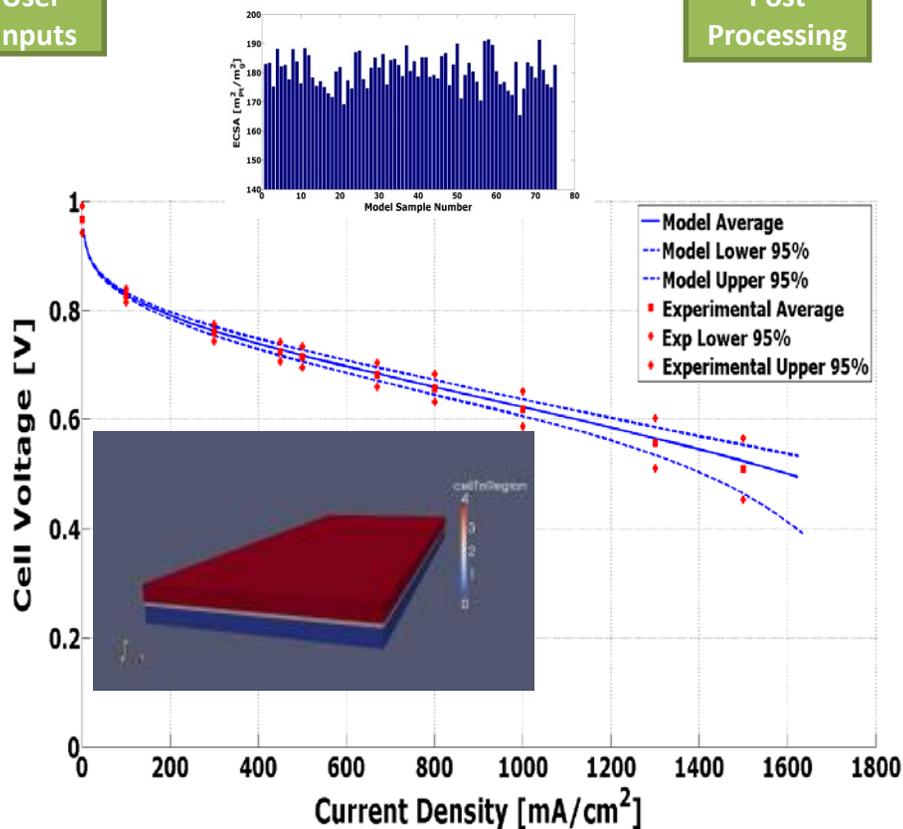


■ Features:

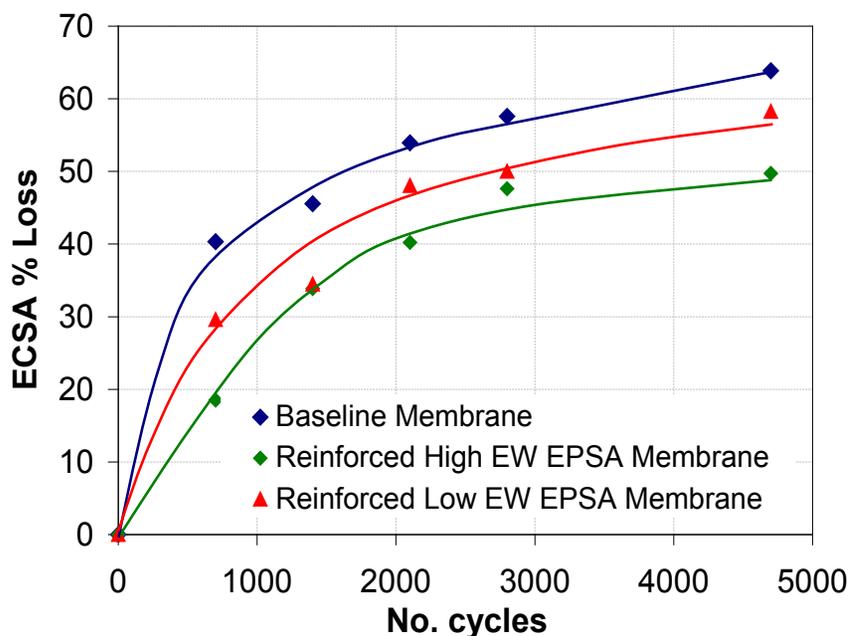
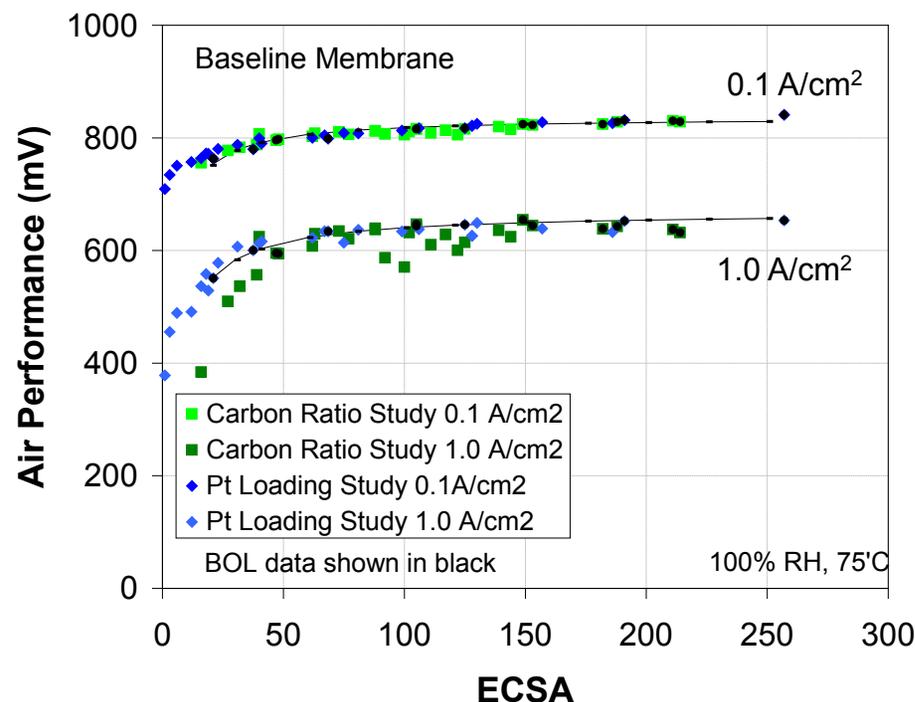
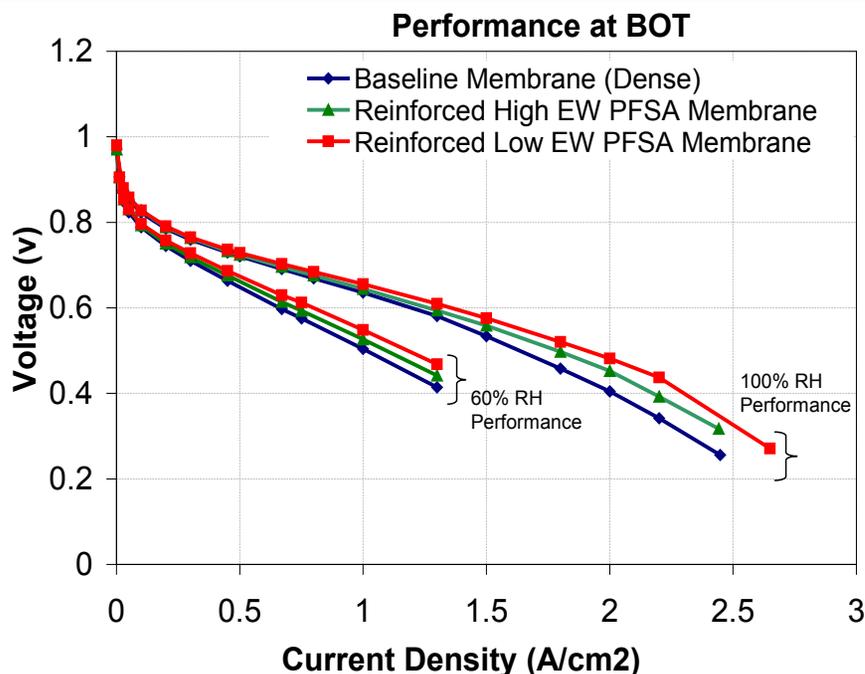
- Performance and durability simulation
- Catalyst layer optimization
- Accelerated Stress Test (AST) behaviour
- Scalable simulations (1D → 3D)
- Fully open source package

■ Simulation Validation

- Performance - Material Composition
 - Pt Loading (0.05 – 0.4 mg/cm²)
 - Pt:Carbon Ratio (0.3 – 0.8)
 - Pt:Ionomer Ratio (0.13 – 0.43)
- Performance - Operational Conditions
 - Relative Humidity (60% and 100%)
 - Oxidant Fraction (5 – 100%)
 - Temperature (60, 70, 80 C)
- Durability – Pt-Dissolution (square wave/triangle wave)
 - AST cycle (0.6 – 1.2V) up to 2000 Cycles
- Durability – Carbon Corrosion (square wave/triangle wave)
 - AST cycle (0.6 – 1.4V) (pending)



Experimental Status Update Low Loaded Catalyst Layers



- Beginning of Test
 - Low current performance (<1 A/cm²) appears to be insensitive to EW
 - High current performance (>1 A/cm²) may reflect difference in water content of the MEA
- ECSA loss <70% may not be significant (performance impact)