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FC-APOLLO

***F**uel*
***C**ell*
***A**pplication*
***P**ackage for*
***O**pen-source*
***L**ong-**L**ife*
***O**peration*

# Open-Source Performance and Durability Model

## Consideration of Membrane Properties on Cathode Degradation

David Harvey

**FC049**

June 8, 2015

# Project Overview

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## 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

# Project Background

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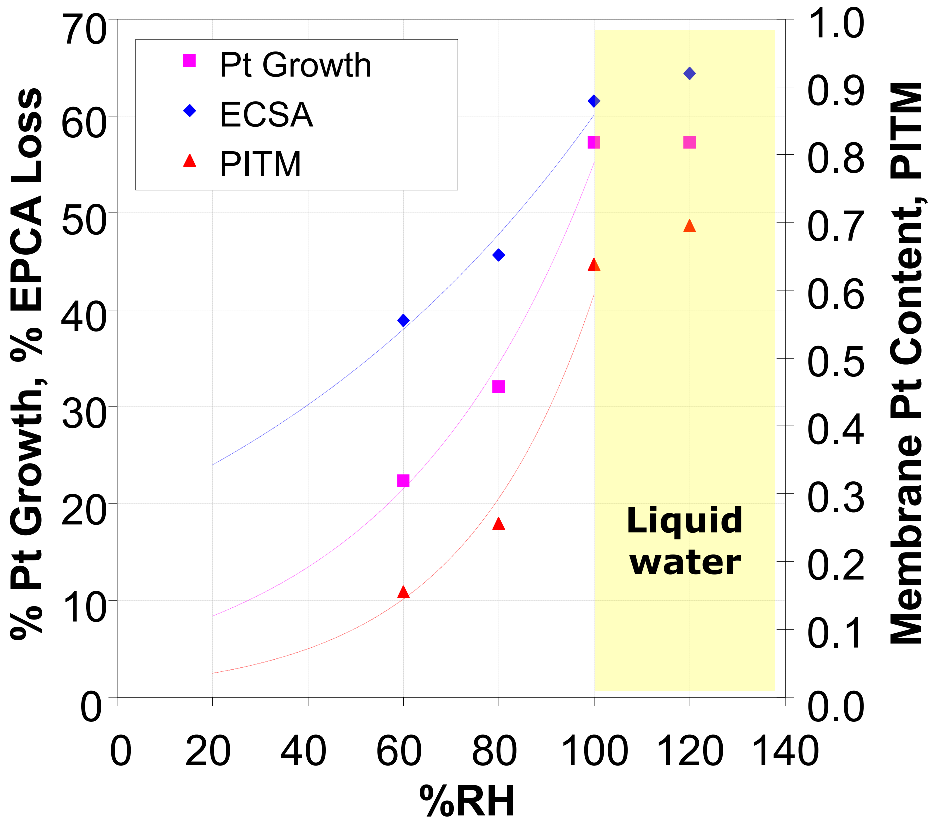
## Under Project DE-EE0000466,

## 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/$H_2$, 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"**

# Project Background
# Impact of Membrane Type

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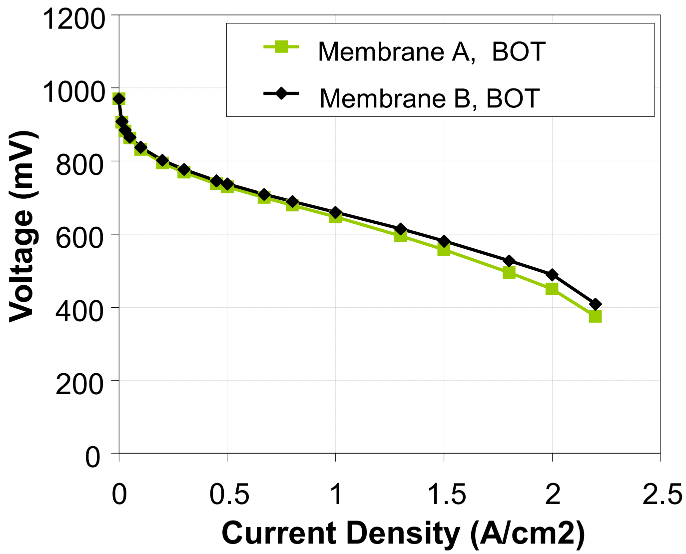
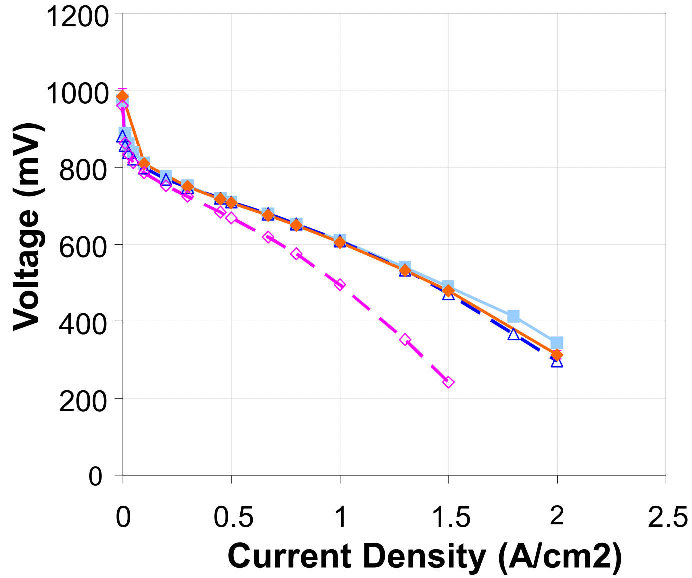
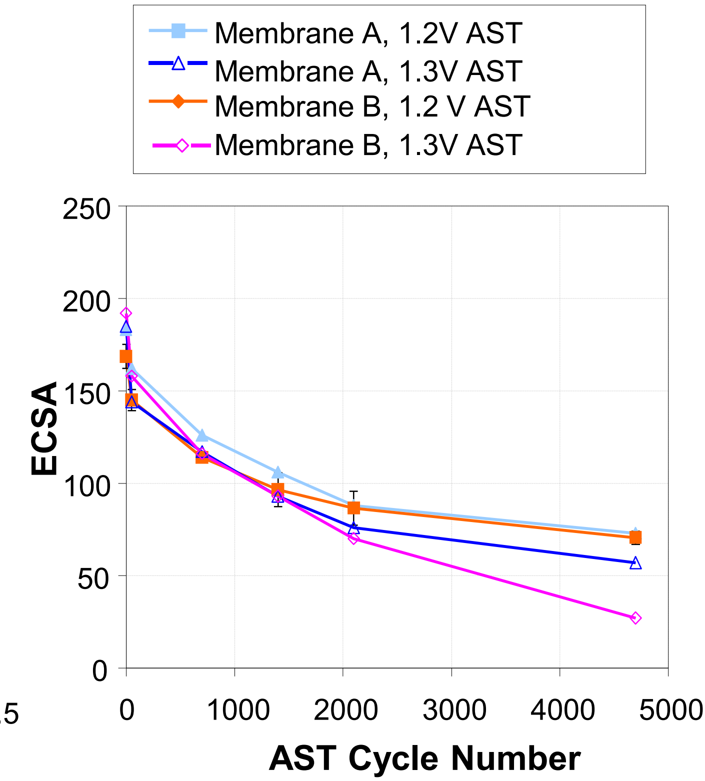
## Membrane A and B are coated with the same catalyst layers (LSAC50, 0.4mg/cm²)

AST: 0.6V (30sec)→1.2V (60 sec) 4700 cycles @ 100% RH, 80°C
Diagnostic Air Polarization (STC) Air/$H_2$,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

**FC049**

## June 8, 2015

# Experimental Approach

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MEA

Conditioning

BOT

MOT 1

MOT x

EOT

AST Testing

## In-situ diagnostics

- $H_2$/Air Polarization
  - Performance
  - Limiting current
- $H_2/O_2$ polarization
  - V-loss break-down: Kinetic, Ohmic, Mass Transport
- Cyclic Voltametry
  - CO stripping/ECSA
  - Double layer charging current
  - $H_2$ cross-over
  - Pt surface understanding
- Electrochemical Impedance Spectroscopy (EIS)
  - Cell resistance
  - Ionomer resistance
  - Double layer charging current
- Mass and specific activity
- Water Cross-over

Selected BOT/EOT Samples for XPS/TEM Analysis at UNM

## 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/$H_2$, 100% RH, 5 psig, 75°C

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

# Experimental Approach
# Accelerated Stress Tests

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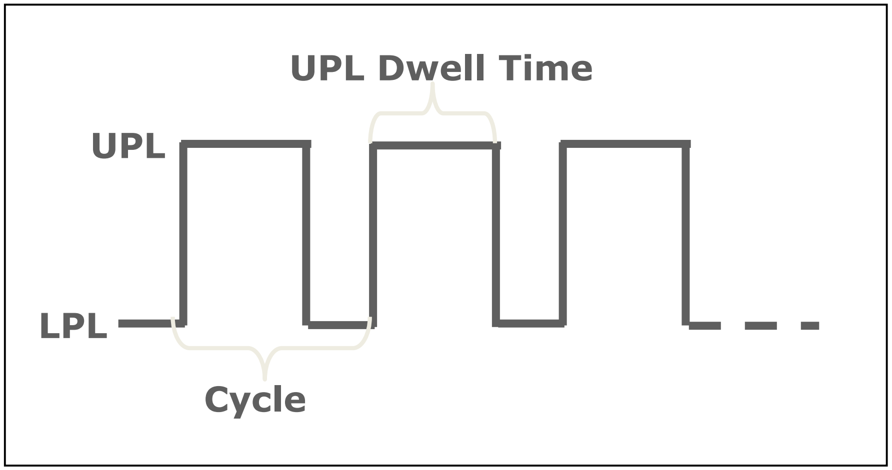
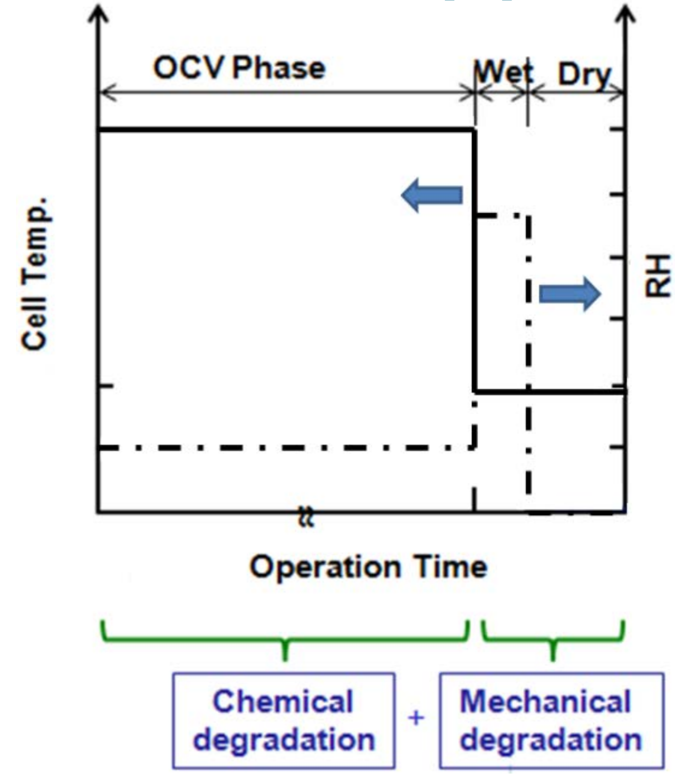
## Cathode AST




## Membrane AST (Cyclic OCV)




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

- **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

# Impact of Membrane Properties Performance

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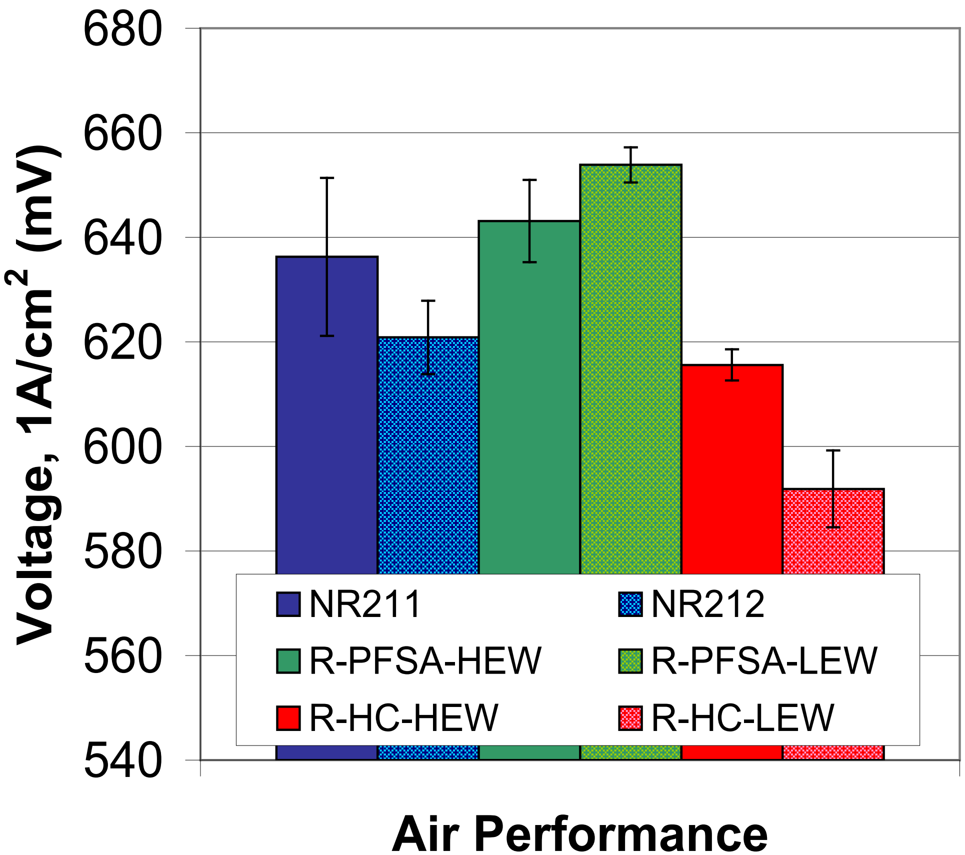
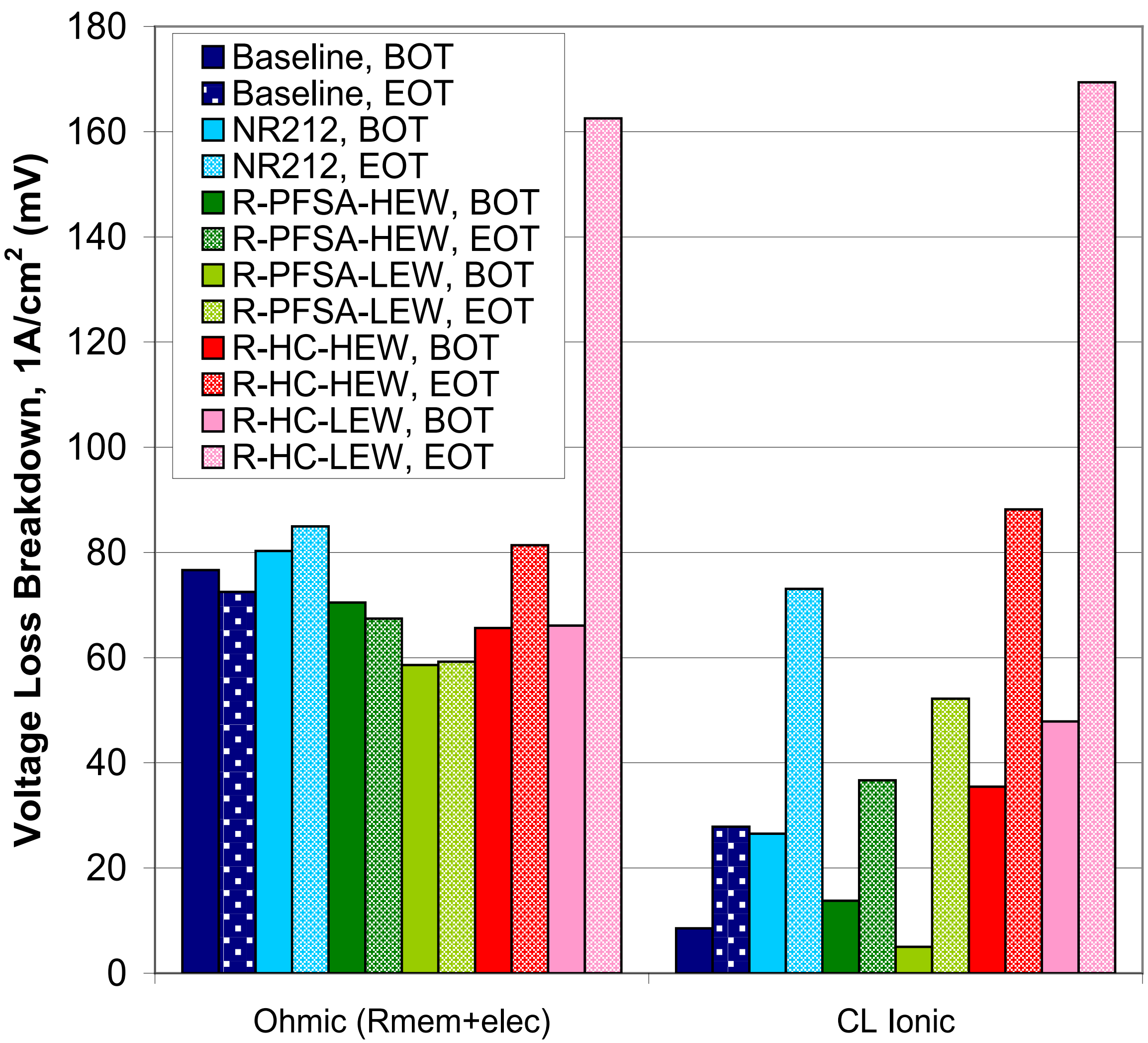



- **PFSA: NR211 > NR212**
  - Performance should decrease due to the additional resistance from the increased thickness
- **R-PFSA: LEW > HEW**
  - Performance should increase with the lower EW material
- **R-HC: LEW < HEW**
  - LEW showed membrane degradation with BOL operation
  - SEM showed irregular thickness and reinforcement band
  - **Results not considered representative***

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

# Impact of Membrane Properties on Performance




- **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

# Impact of Membrane Properties Cathode Pt Dissolution

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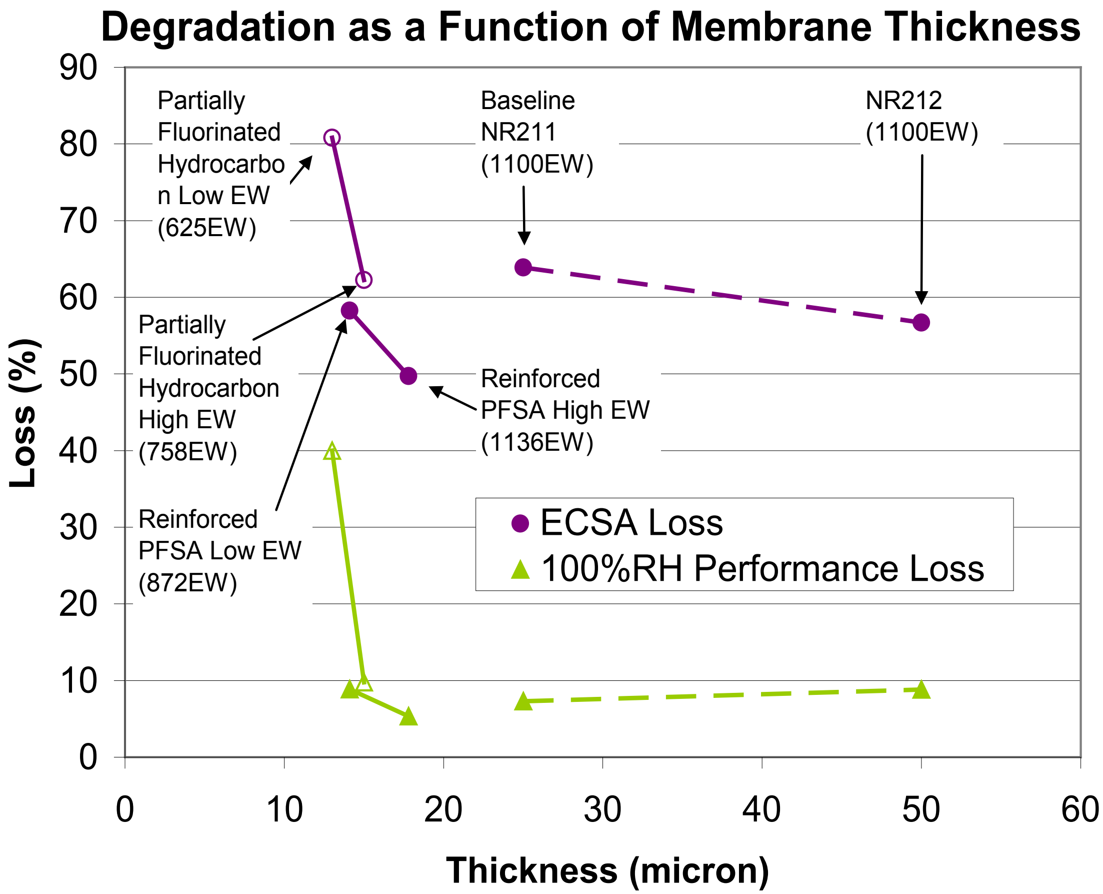


- **EW Effect: Greater ECSA loss for thinner, lower EW membrane in each membrane group.**
  - PFSA thickness effect is small , EW more dominant
  - Lower EW membranes → higher water content → higher water content at the membrane / catalyst interface where the Pt dissolution is the greatest.
- **Membrane 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

# Chemical Degradation of Membranes

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| 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 |

# Impact of Membrane Degradation Performance

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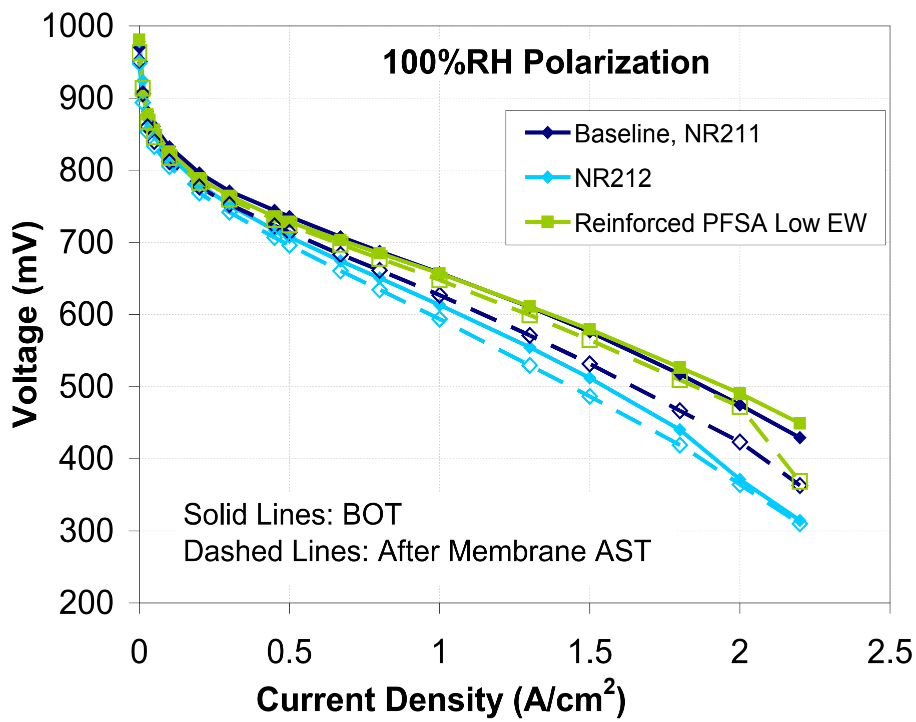


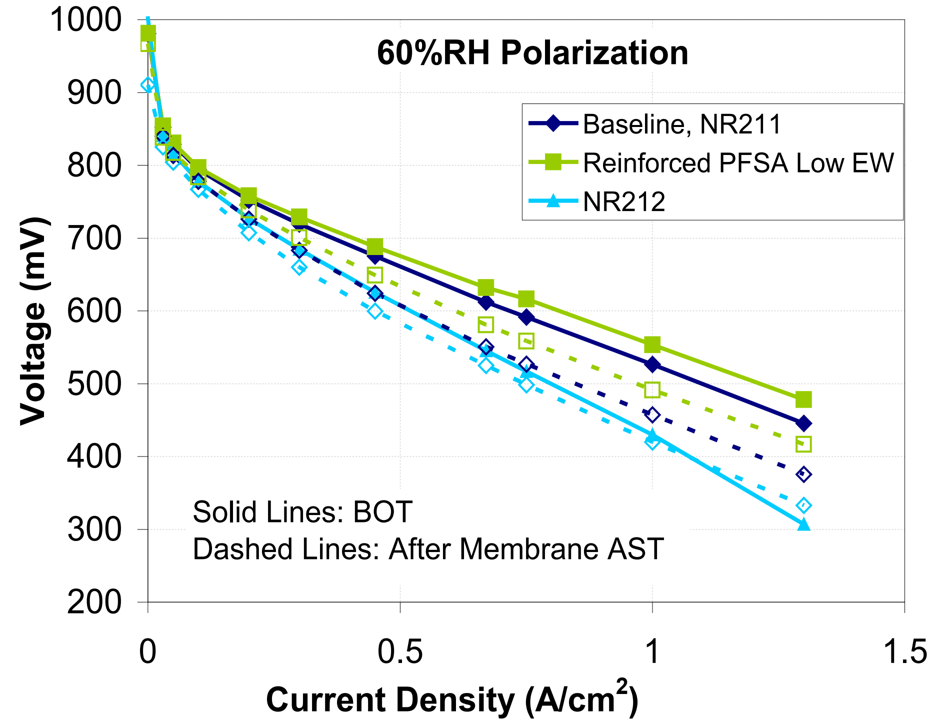


## Effect of Membrane AST on Performance:

- 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

# Impact of Membrane Degradation
# Pt Dissolution

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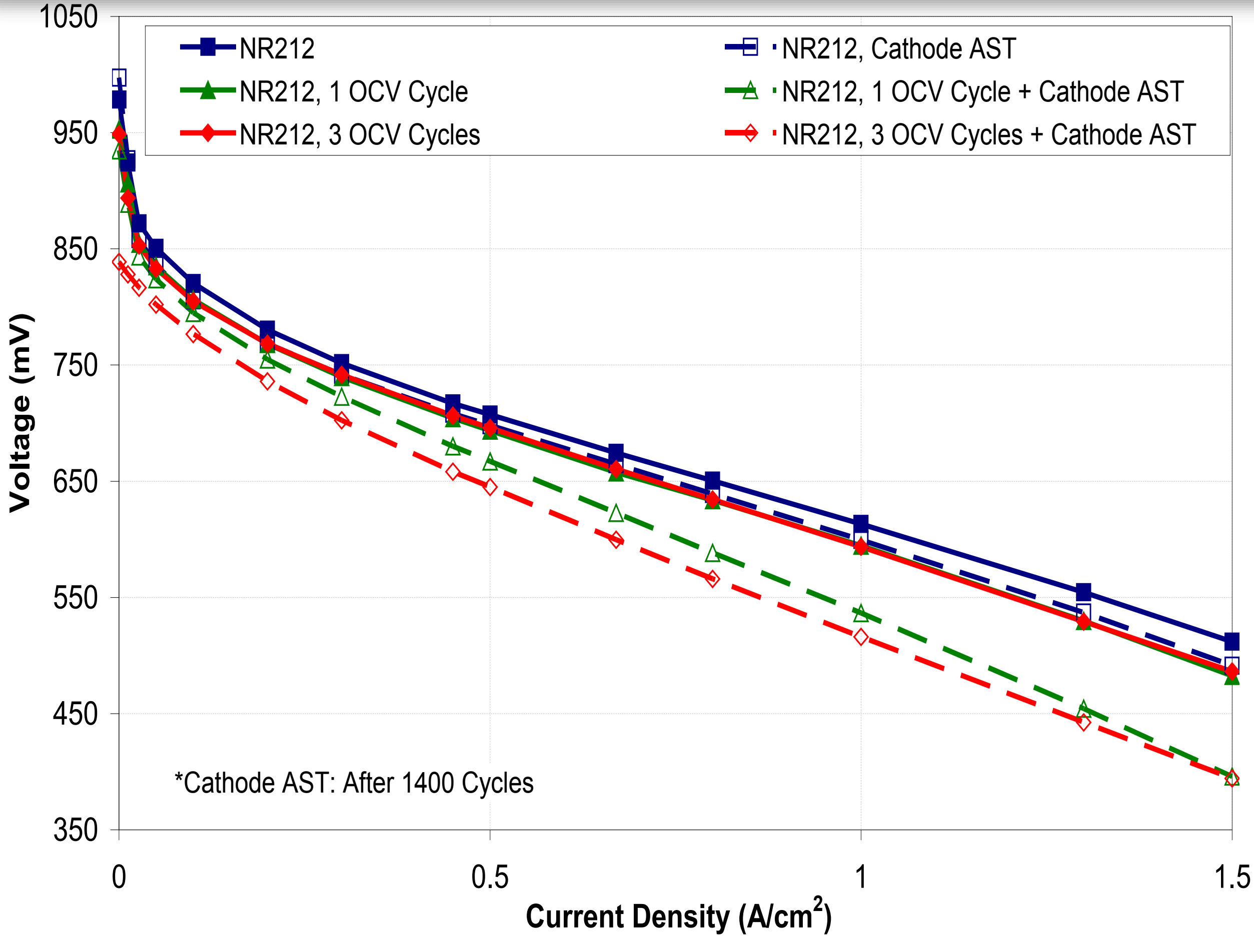


## NR212 Membrane Degradation– Repeated

- 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

# Impact of Membrane Degradation
# Pt Dissolution

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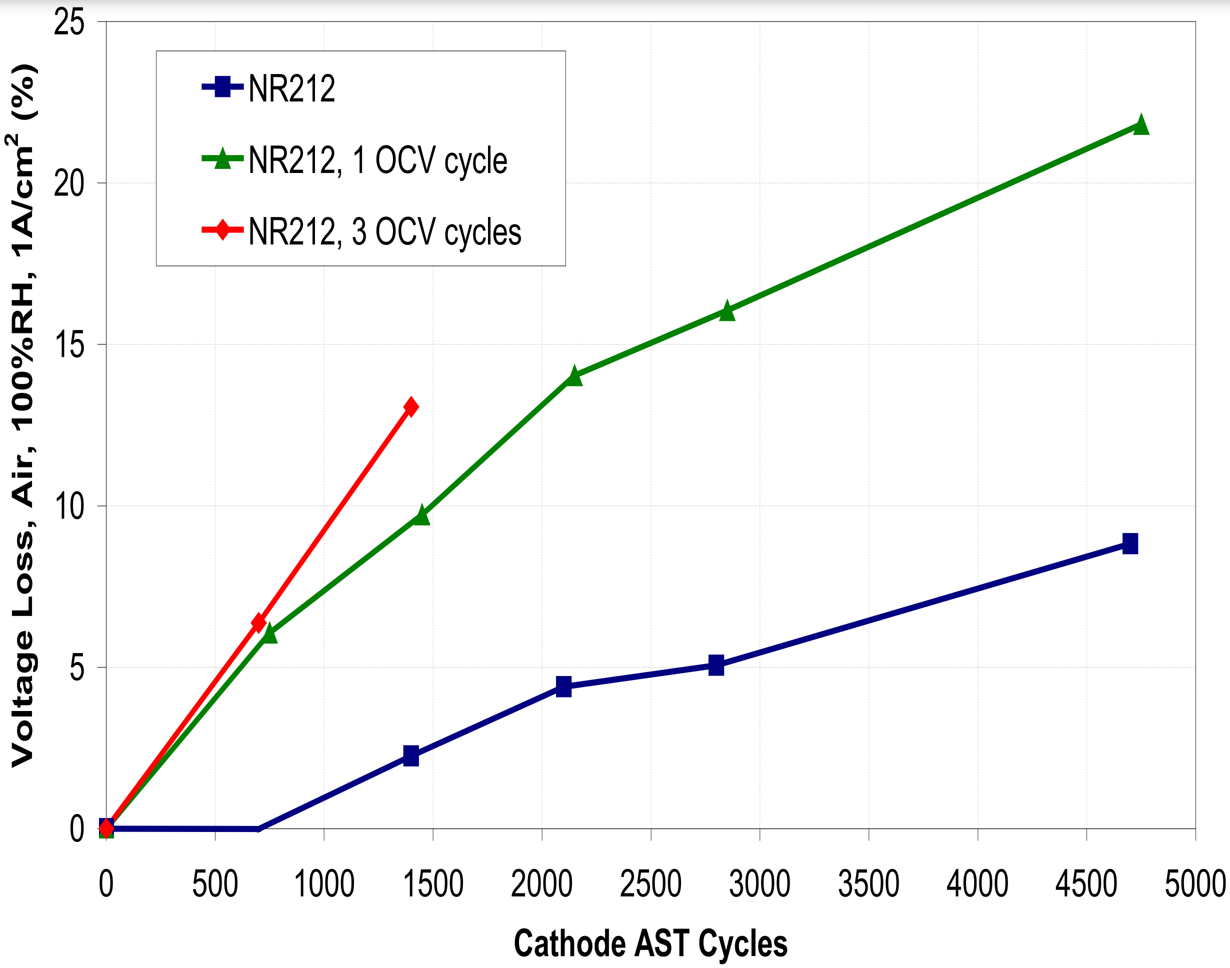


## NR212 – Membrane Degradation Repeated

- 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

# Impact of Membrane Degradation
# Pt Dissolution

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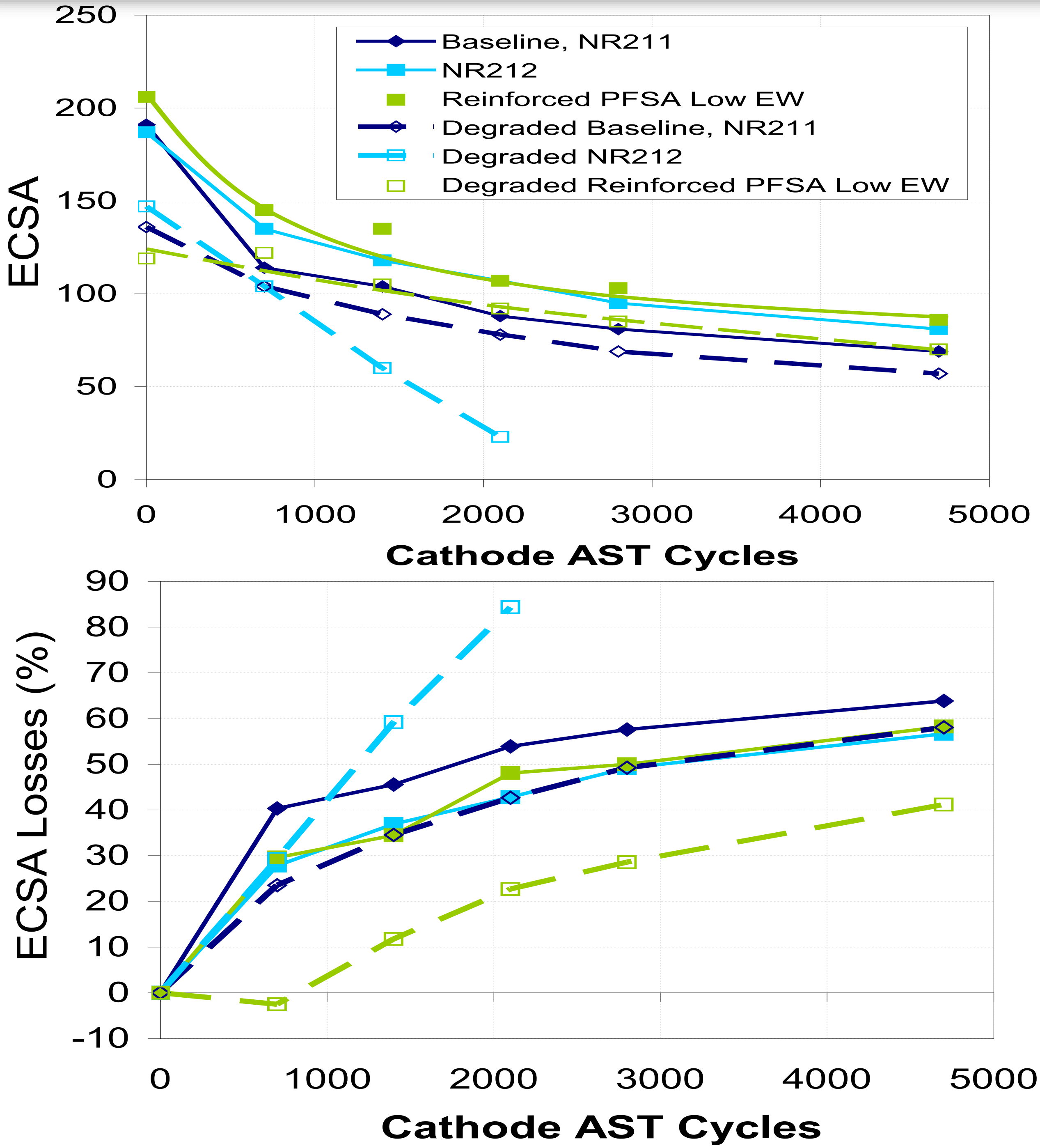
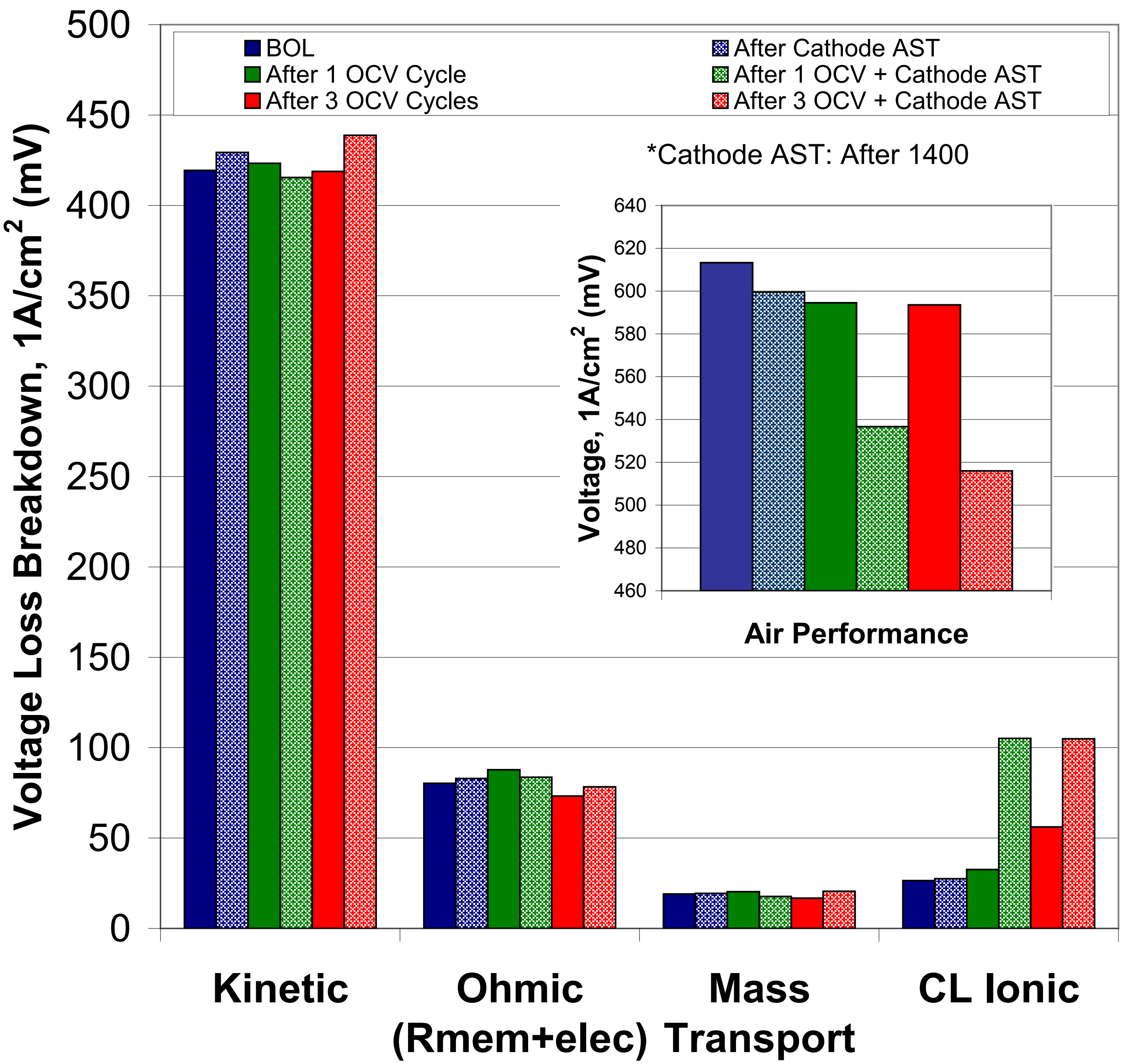



## Original Dataset

## 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

# Impact of Membrane Degradation
# Pt Dissolution



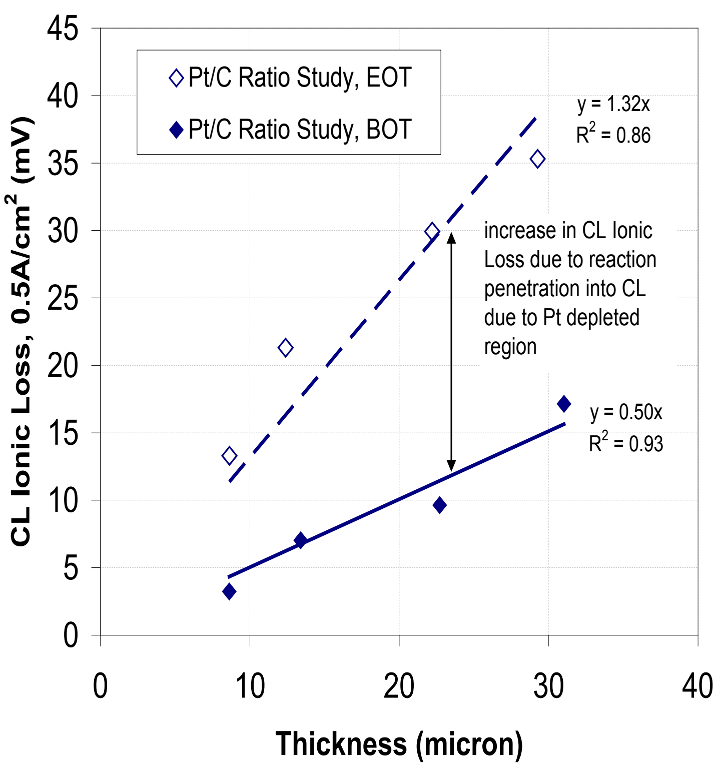

## Original Dataset

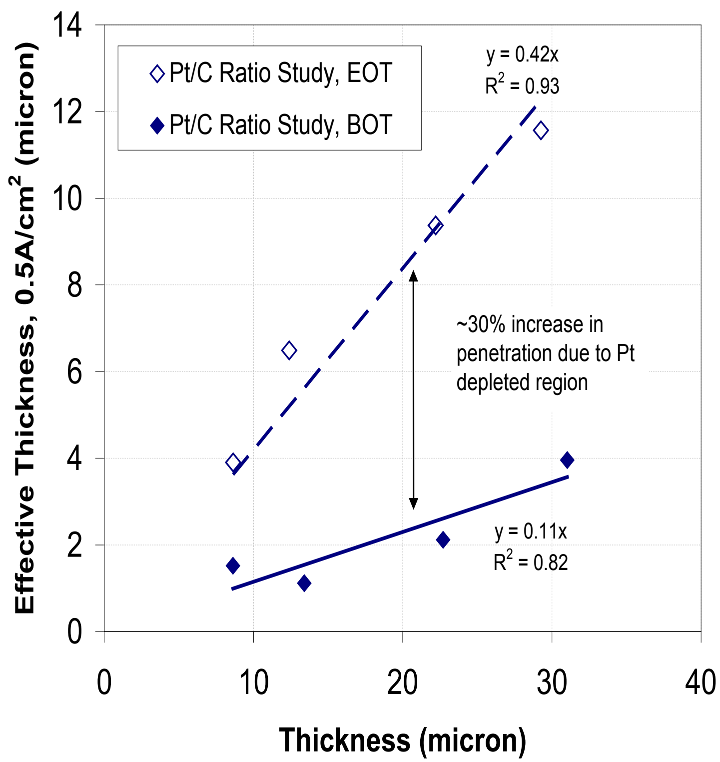
## Membrane Degradation

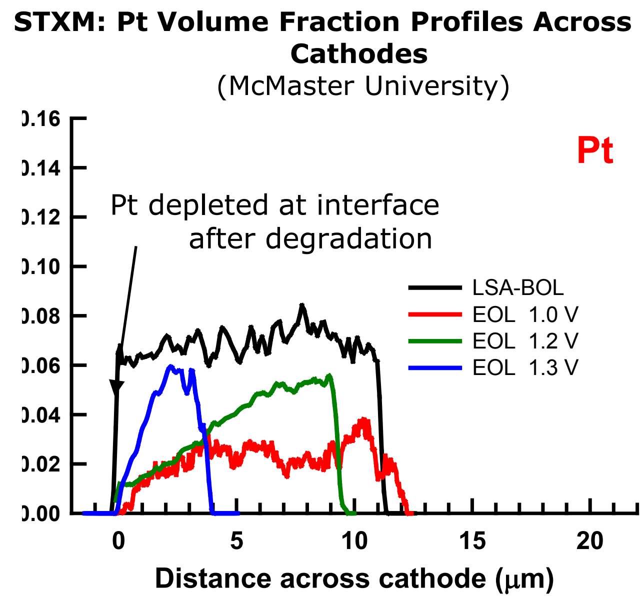
- **1 vs 3 OCV cycles**
  - **Increased CL Ionic Losses with increased OCV cycles**
- **OCV Cycle vs Cathode AST baseline**
  - Increased CL Ionic losses for OCV/Cathode AST vs. OCV cycled only
  - **Significantly greater CL ionic losses vs. cathode AST only**
  - Results are consistent with original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

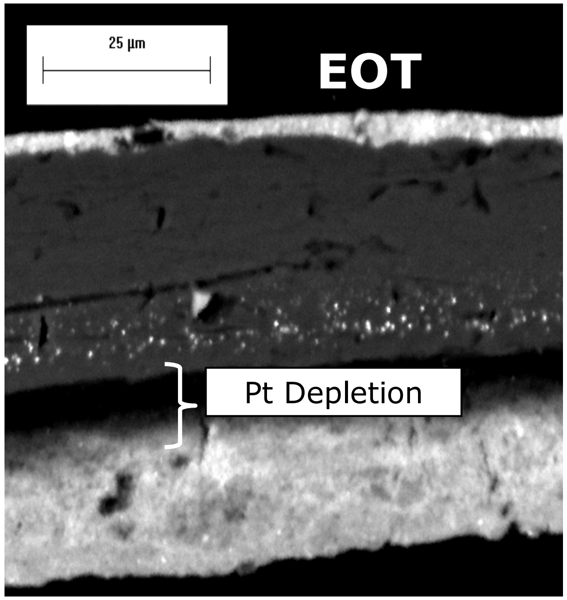
# CL Ionic Losses
# Effect of Pt depletion

- **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**



# Driving Force of Water Permeation and its Types

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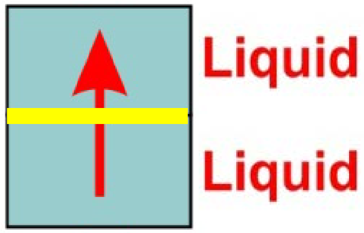
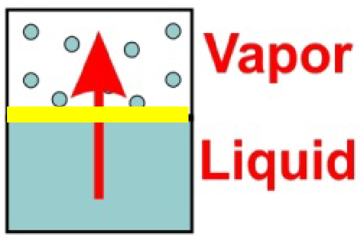



Membrane is immersed in liquid water. Pressure is applied on one side to create hydraulic pressure driven permeation.

➡ **Liquid-Liquid permeation (LLP)**

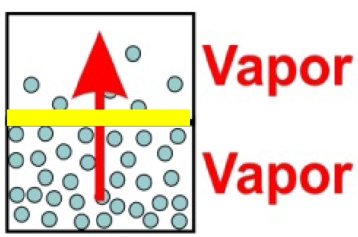
*Okada et al. (2002)*
*Villaluenga et al. (2003)*
*Evans et al. (2006)*




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)*
*Majsztrik 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)*
*Majsztrik et al. (2007)*
*Romero et al. (2008)*

# Relating Theory to Experiment

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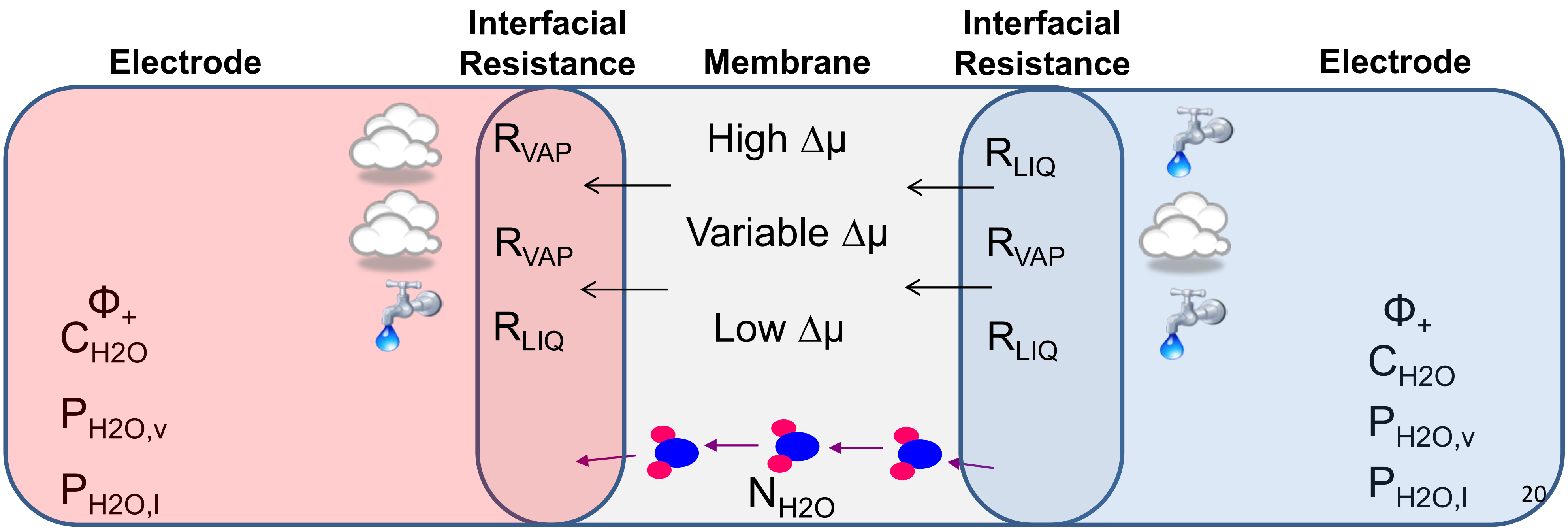
- **Experimentally**
  - Liquid-Vapour boundaries show the highest crossover and Liquid-Liquid show the lowest.
- **This is explained by a combination of**
  - Bulk membrane transport equations (e.g., Weber)
  - Interfacial resistances from sorption and phase change (e.g., Monroe)

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



# Steady State FC-STC (New MEA)

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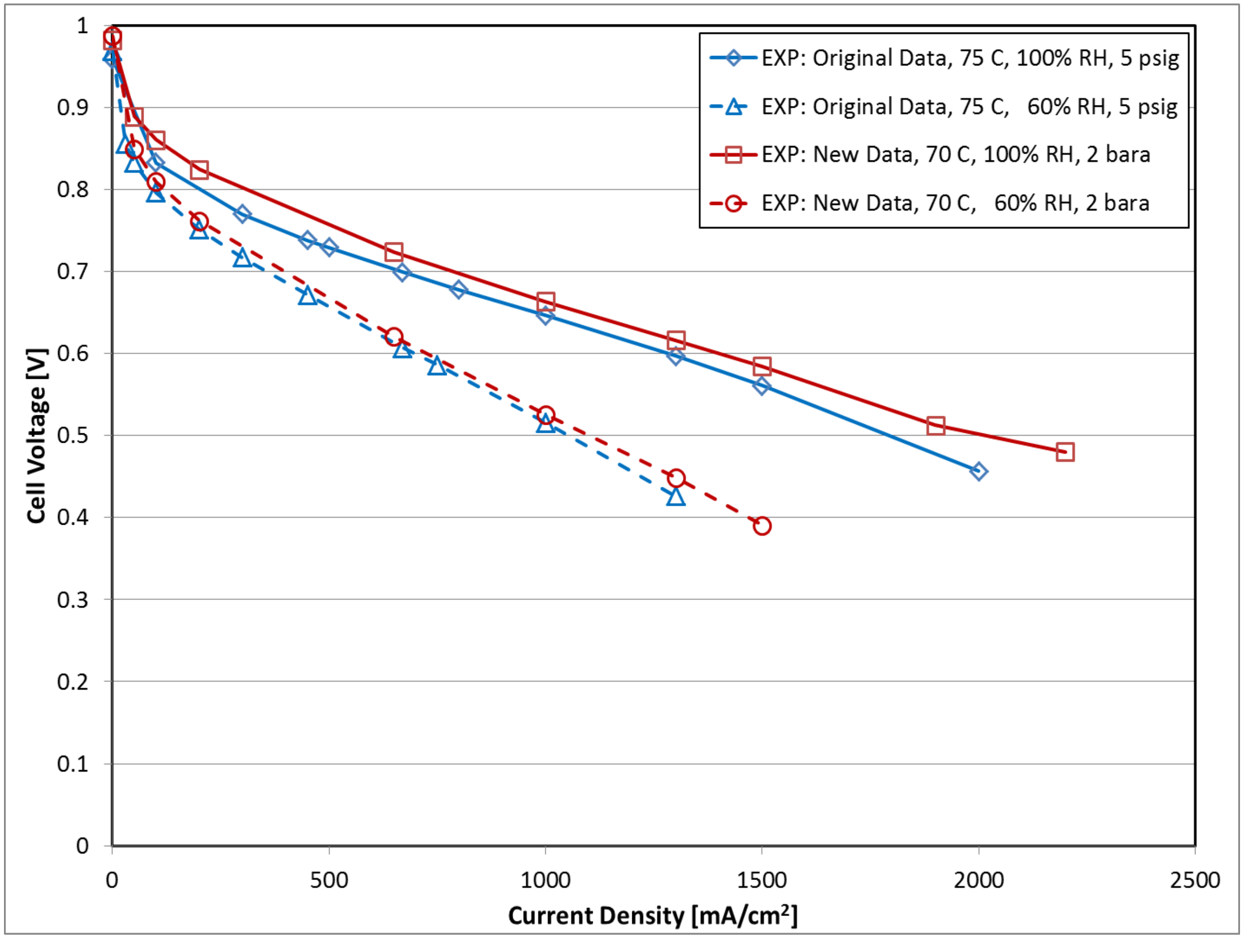


## Experimental Datasets

## 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

# Steady State FC-STC (New MEA)

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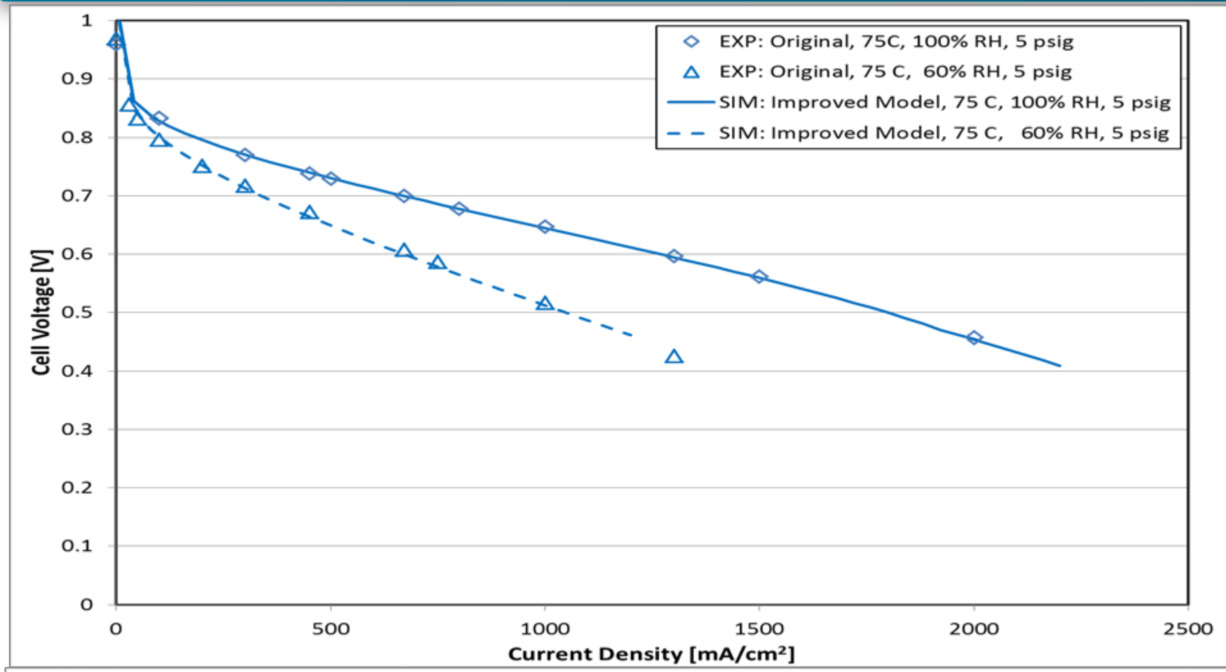


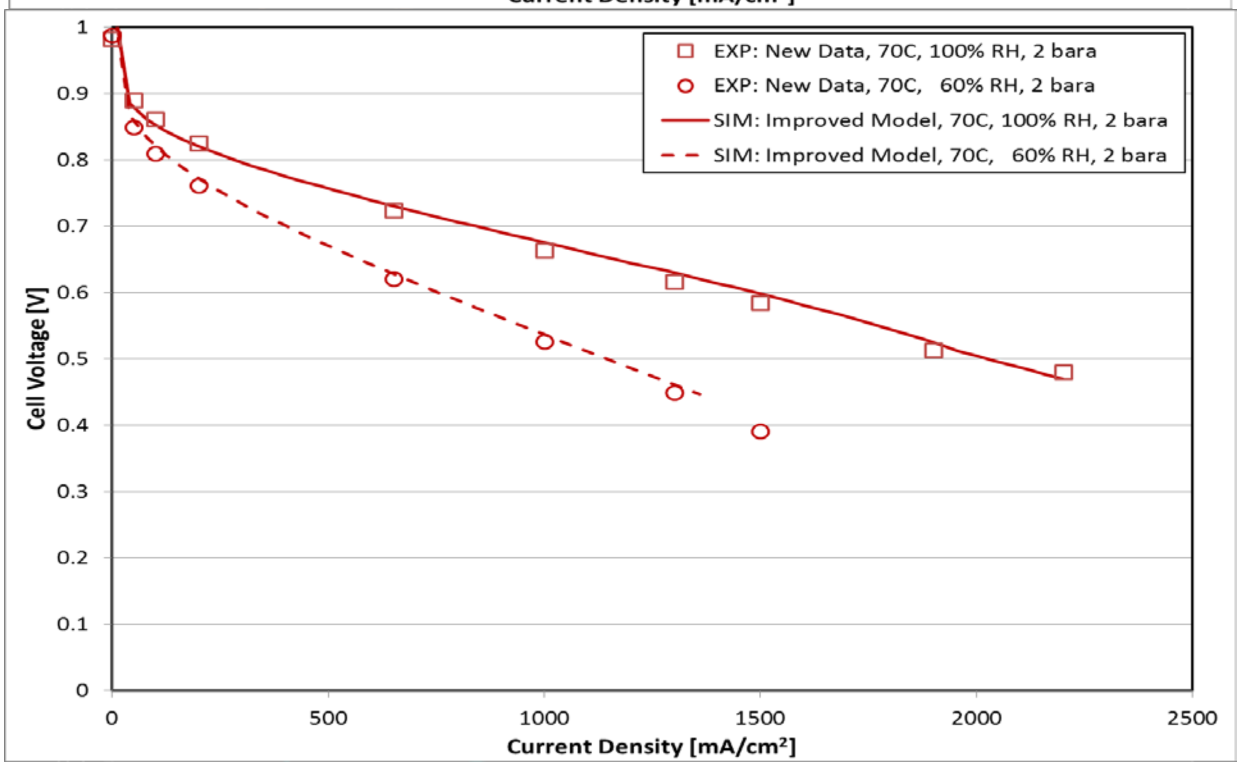


## Experimental Datasets

## 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

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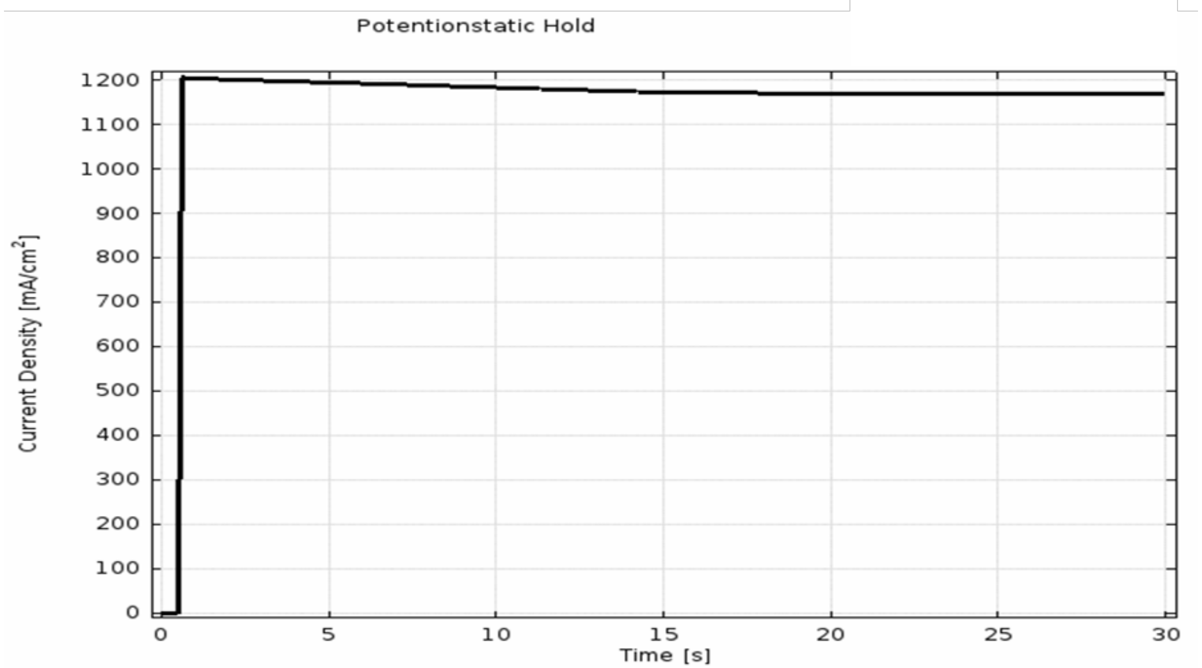


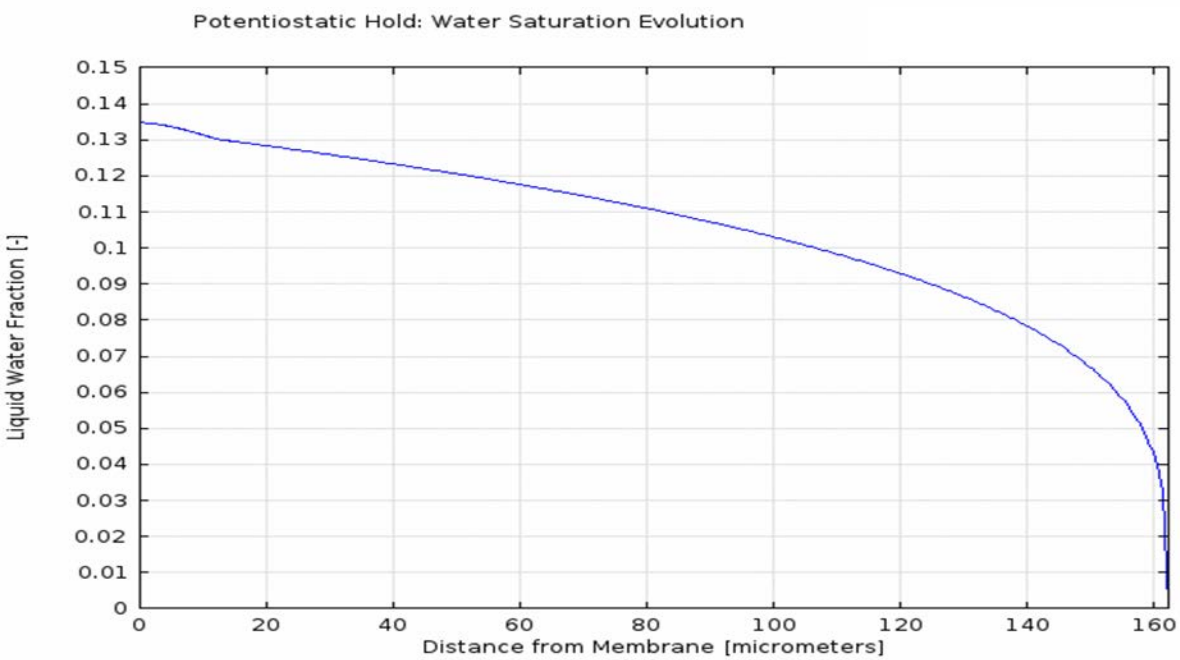


**Transient Effects & Water Content**

- 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 break-through at channel face and then broadens, forming the steady state profile

# Transient effects
# Improved Membrane Model

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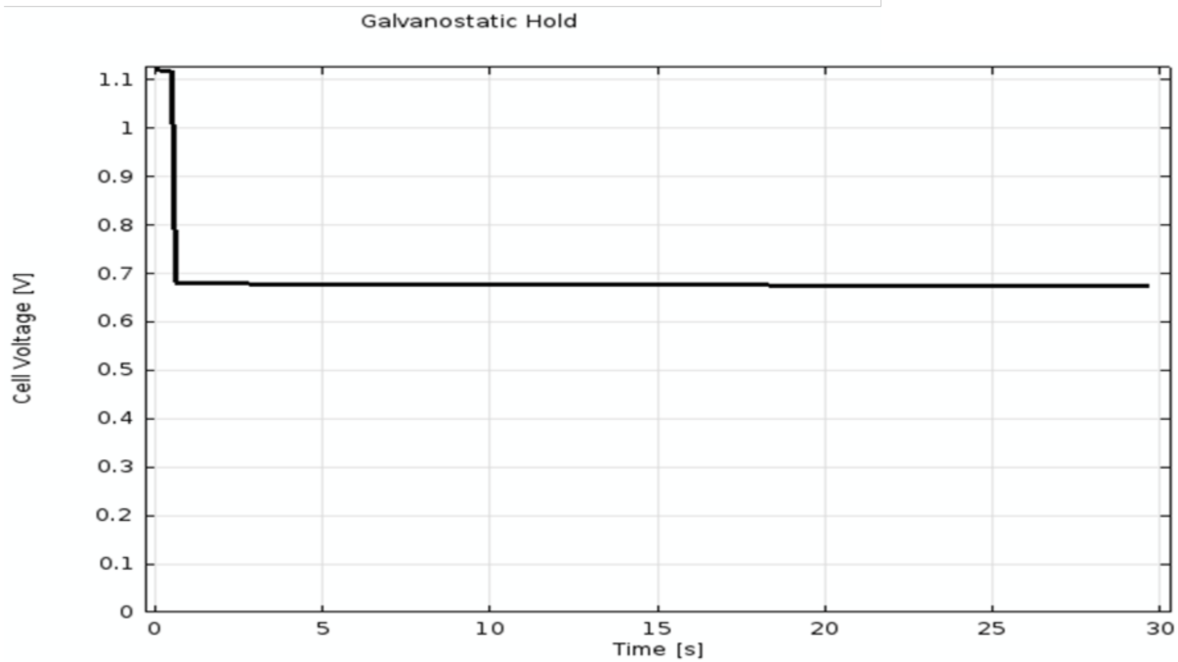


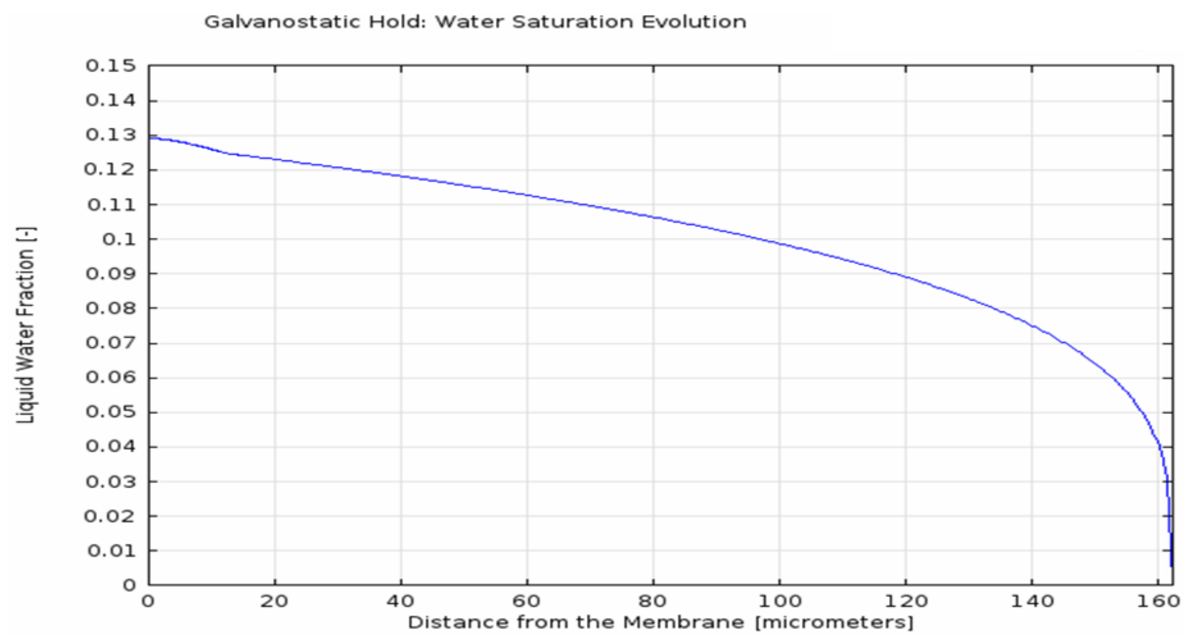


## Transient Effects & Water Content

- **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

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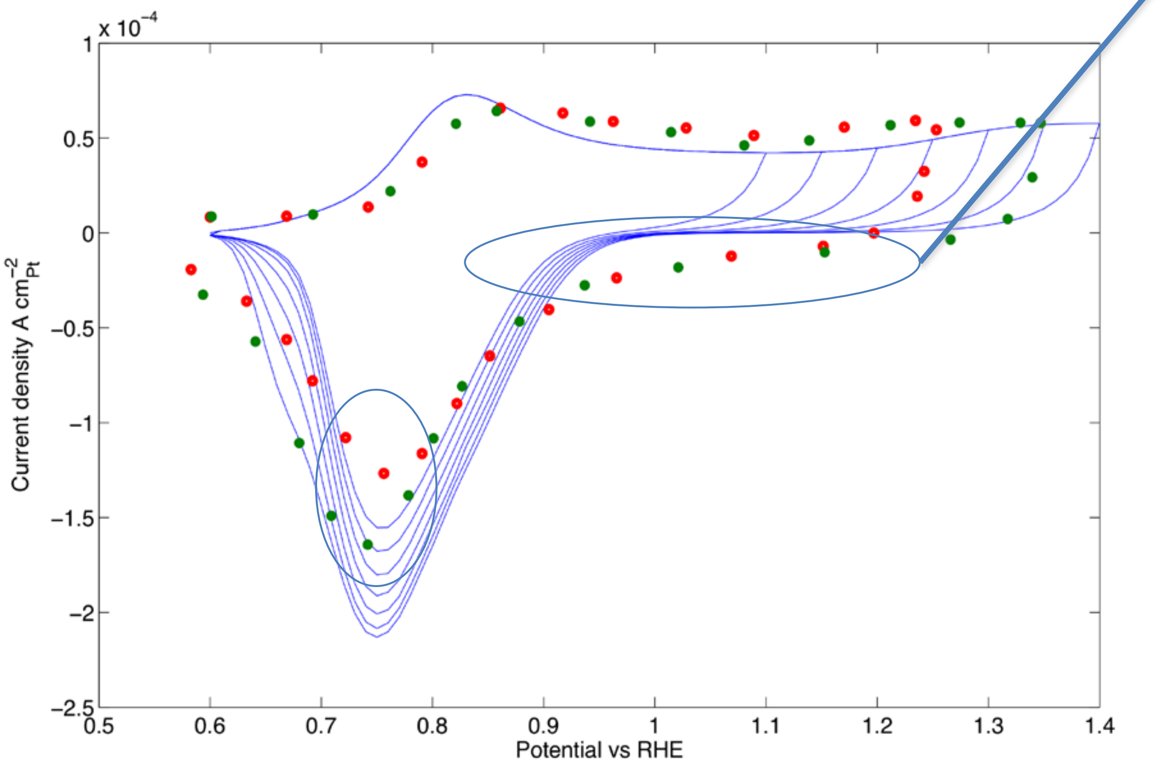
- **O-Pt-OH dissolution, it can potentially cause the incoming degradation rate to have the same slope**
- **O-Pt(2) lingers and causes the outgoing rate to reduce over a wide potential window**
- **Cause of the cathodic peak potential shift:**
  - RH/Sub surface O/Proton concentration




Mismatch because certain species are not considered in the mechanism?

# ORR Multistep/Platinum Dissolution
# Time Resolution of Platinum Dissolution

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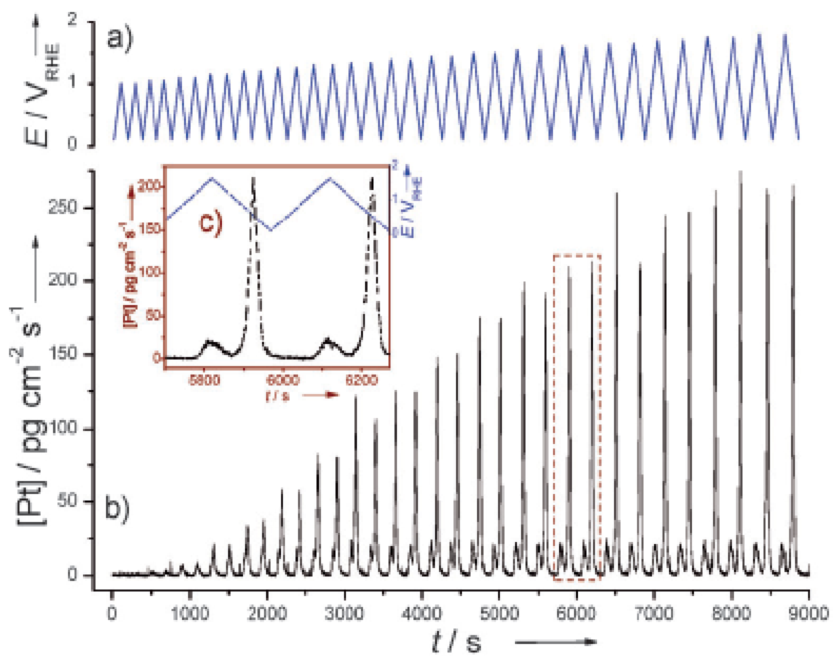


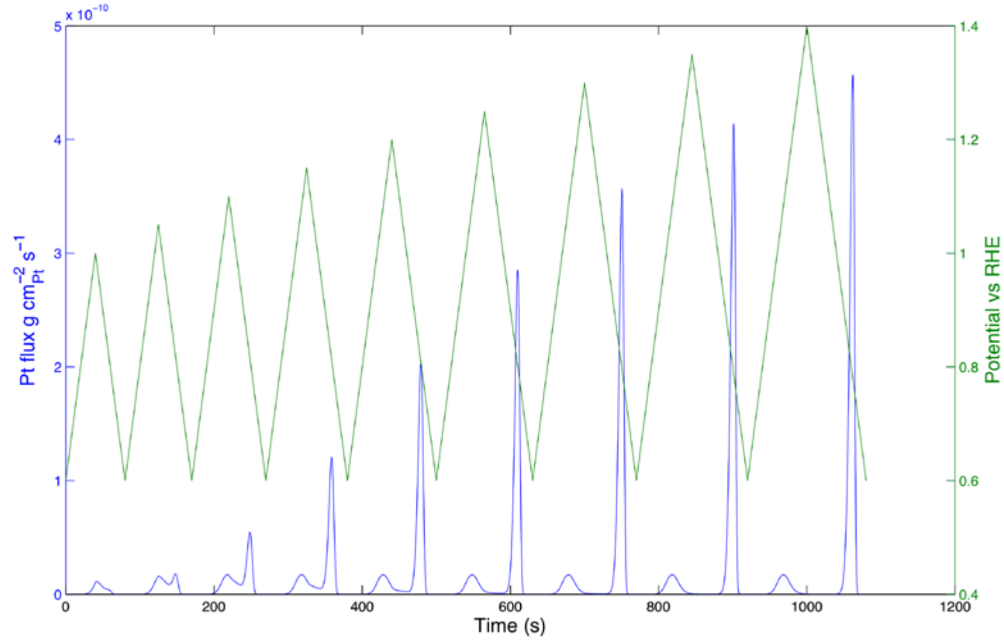


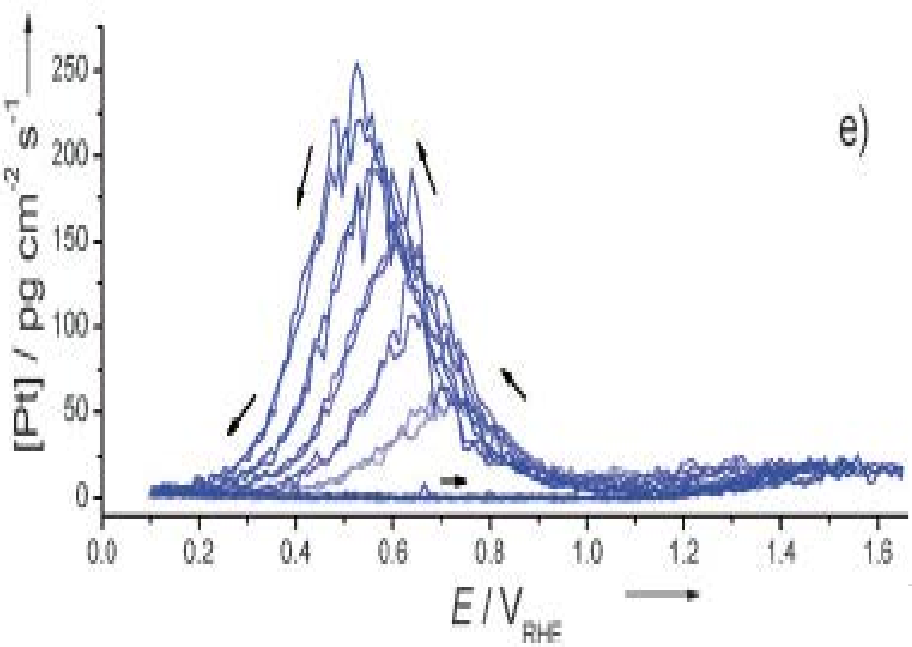


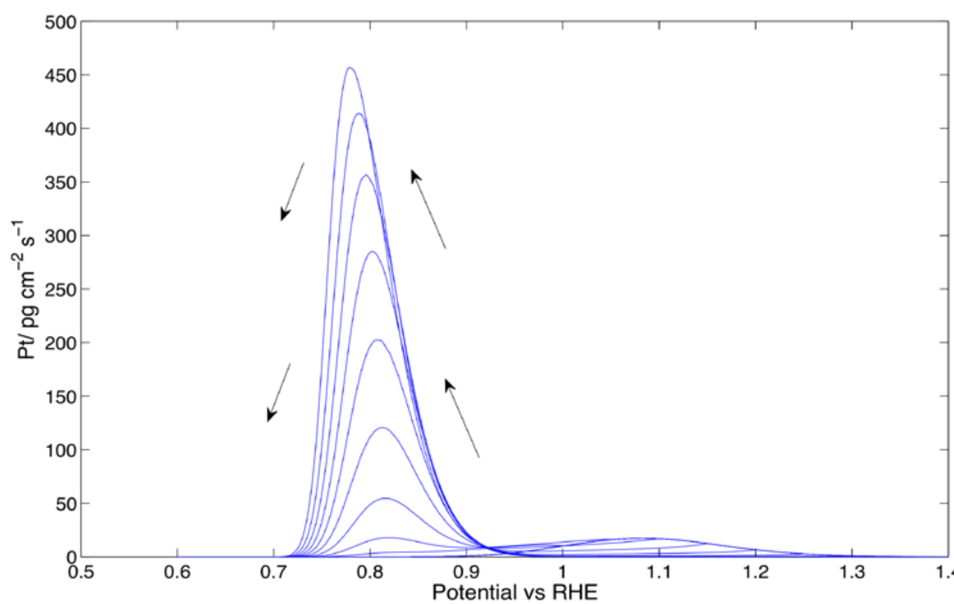

# Summary & Path Forward

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## 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

# FC-APOLLO – BETA Status

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## 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

# Access to FC-APOLLO

- **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

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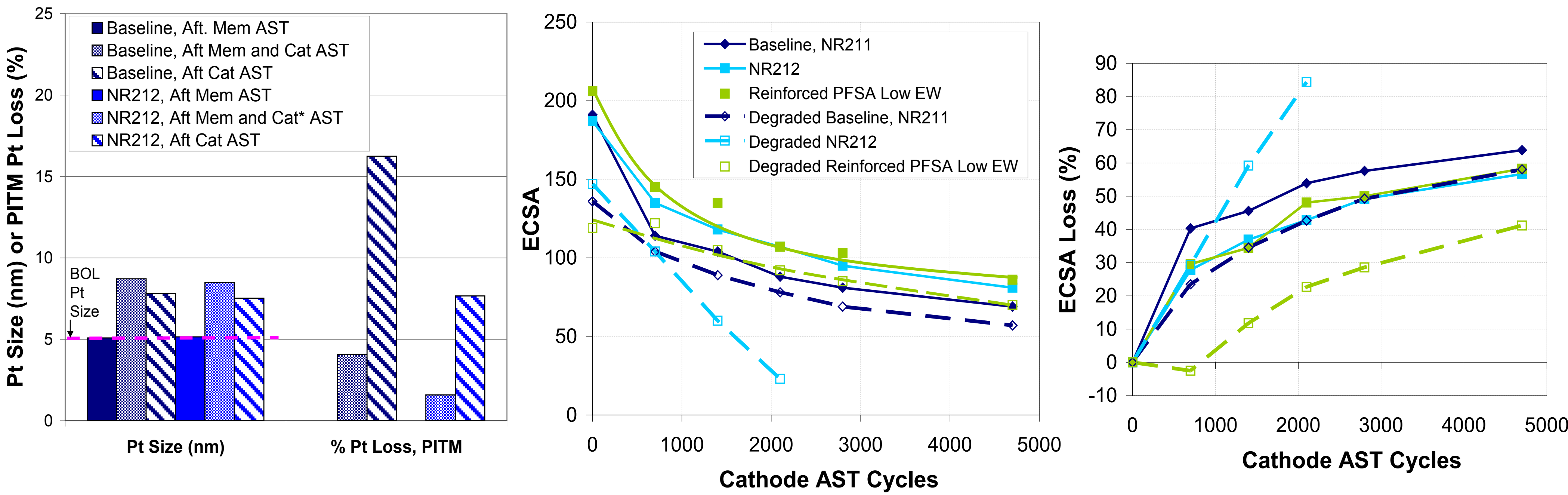


- **Membrane AST does not cause Pt growth or PITM**
  - Lower ECSA is observed – some Pt loss from cathode, not found in membrane may occur
- **Membrane Degradation causes slightly higher Pt growth, but substantially less PITM after cathode AST**
  - Lower ECSA loss occurs with degraded membranes (except NR212 which had transfer – to be repeated)

# Impact of Membrane Degradation
# Pt Dissolution

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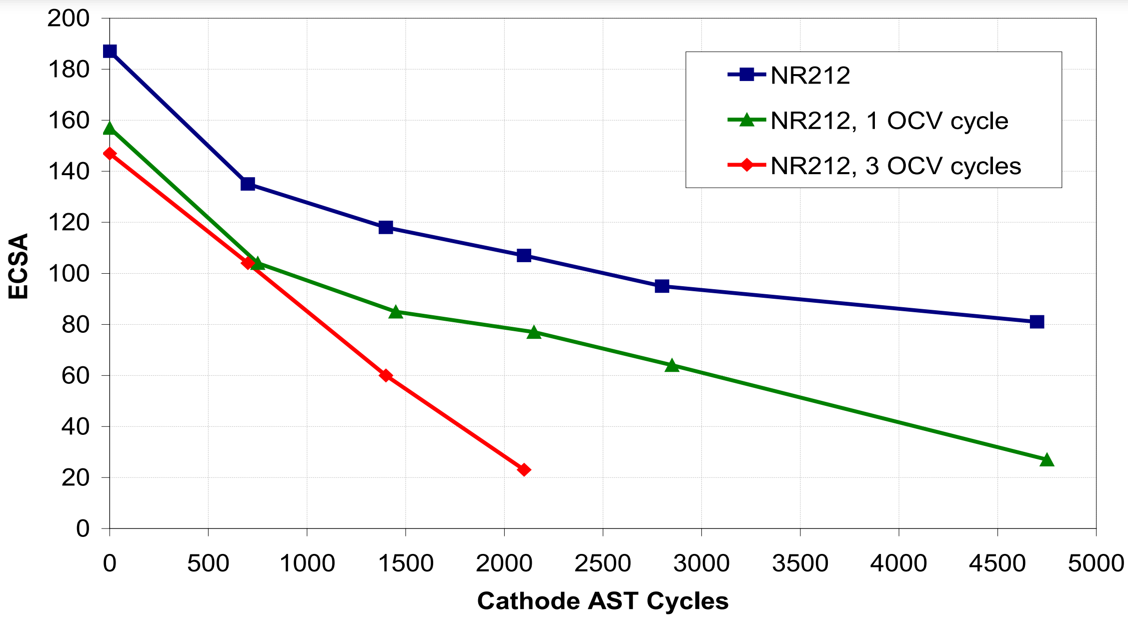


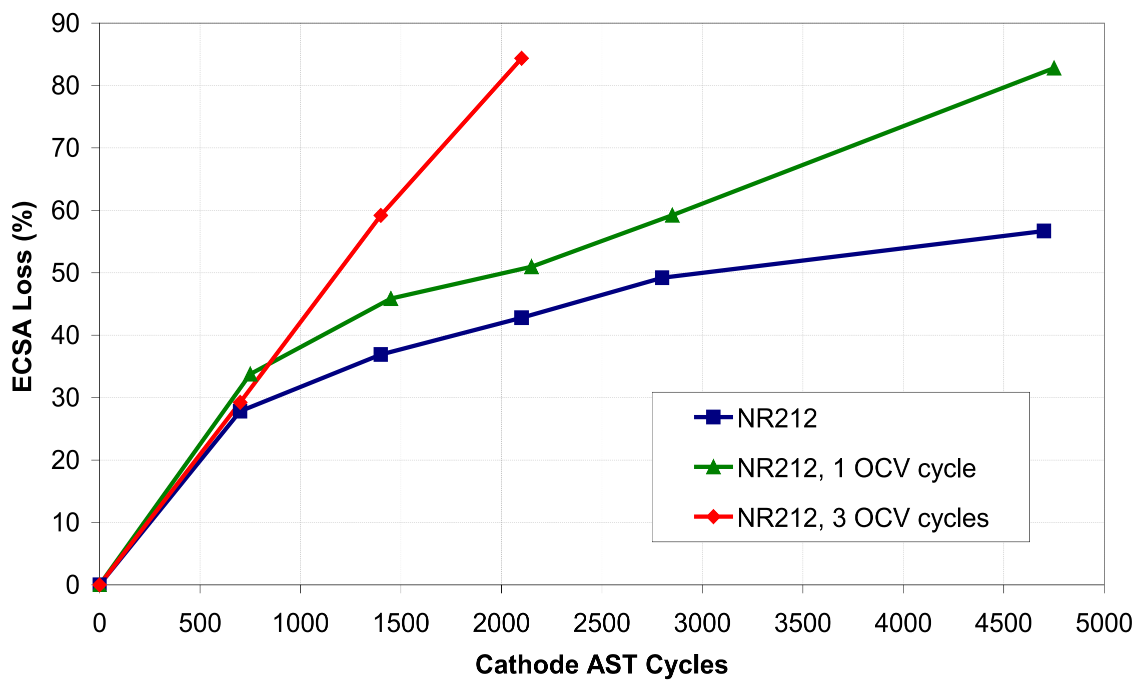


## NR212 – Repeated

## 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

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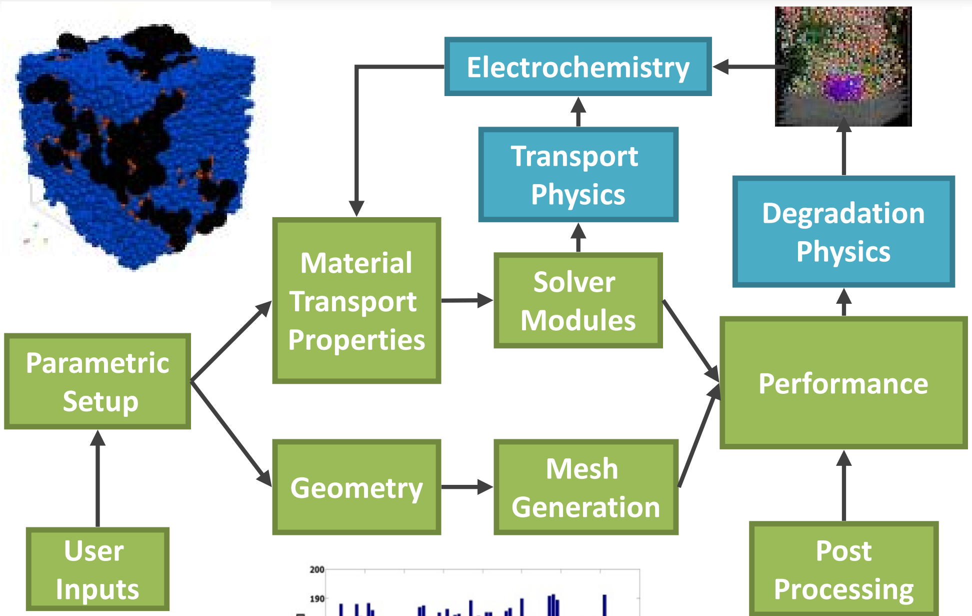


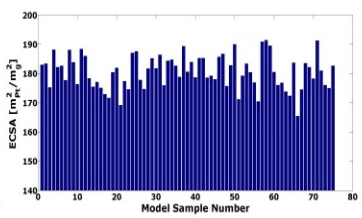


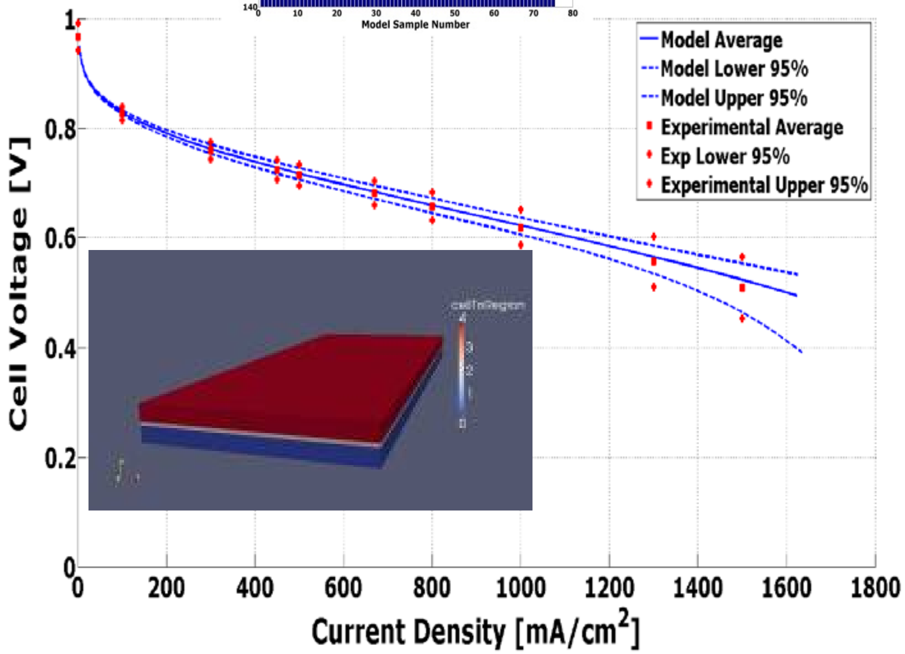


- **Features:**
  - Performance and durability simulation
  - Catalyst layer optimization
  - Accelerated Stress Test (AST) behaviour
  - Scalable simulations (1D → 3D)
  - Fully open source package
- **Simulation Validation**
  - Performance - Material Composition
    - Pt Loading (0.05 – 0.4 mg/cm2)
    - 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

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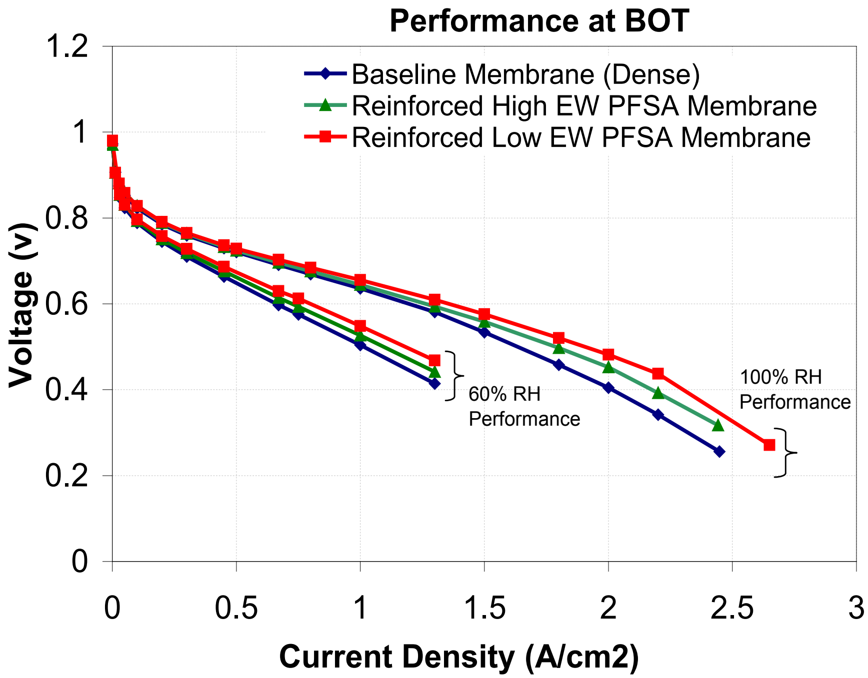


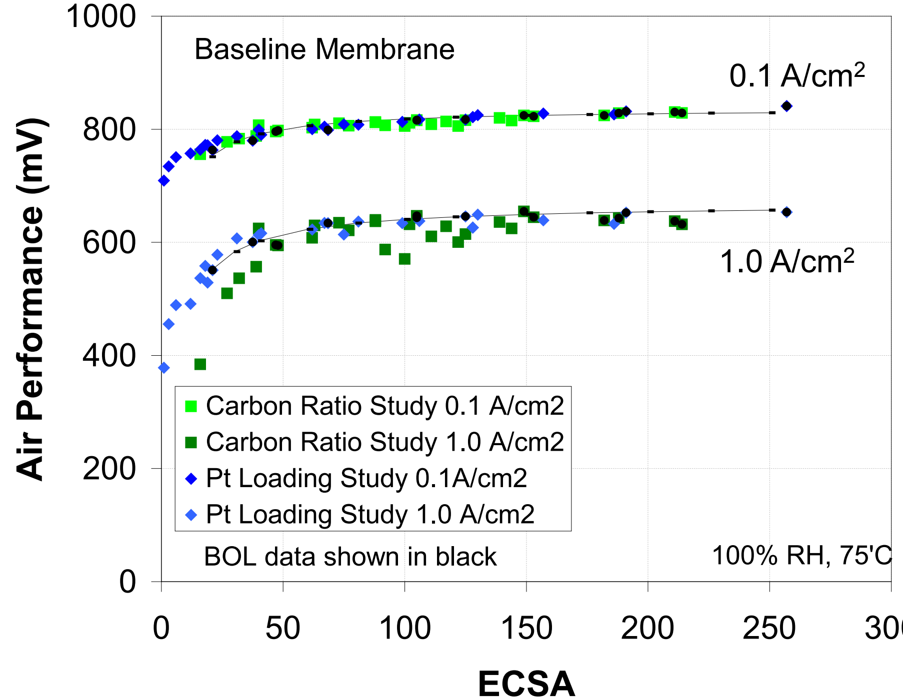


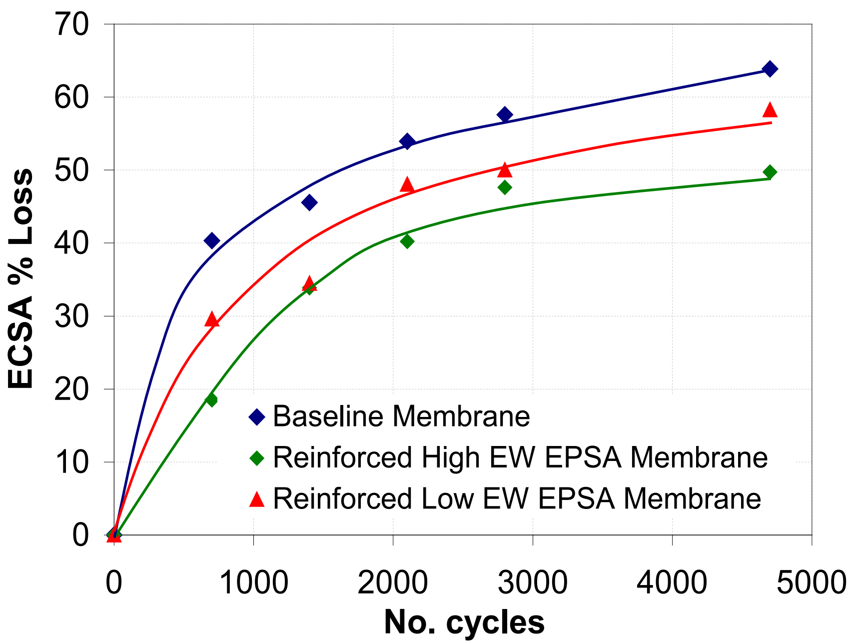


- Beginning of Test
  - Low current performance (<1 A/cm2) appears to be insensitive to EW
  - High current performance (>1 A/cm2) may reflect difference in water content of the MEA
- ECSA loss <70% may not be significant (performance impact)