# Accelerated Testing Validation

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**FC016**

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# Project Overview

## Timeline

- Project Start Date
  - **August 2009**
- Project Duration
  - **4 Years (End: Sept '13)**
- ≈ 90% complete

## Budget

- Total project funding
  - 4 Years : $4,159,790
  - DOE Cost : $4,000,000
  - Cost Share : $159,790
- Funding for FY12/FY13

| | |
|---|---|
| LANL | $ 397k, 750k |
| + Partners (Industry) | |
| Other National Labs | $ 300k, 250k |
| FY12/FY13 Total | $ 697k, 1000k |

## 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)

Bus

1016 : 18,000 hours

Accelerated testing protocols need to be developed to enable projection of durability and to allow for timely iterations and improvements in the technology.

## Partners

- Ballard Power (System Integrator)
- Ion Power (Materials Supplier)
- ORNL (Metal Bipolar Plates)
- LBNL (Modeling)

# Objectives/Barriers - Relevance

## The objectives of this project are 3-fold

1. Correlation of the component lifetimes measured in an AST to real-world behavior of that component.
2. Validation of existing ASTs for Catalyst layers and Membranes
3. Development of new ASTs for GDLs, bipolar plates and interfaces

## Technical Targets

Automotive : Durability with cycling: 5,000 hours (2010/2015): 2005 Status (2000 hours for stack and 1000 hours for system)
Stationary : Durability: 40,000 hours (2011): 2005 Status = 20,000 hours
Bus Data : 18,000 hours (2016); 25,000 hours (ultimate); Status = 12,000 hours.

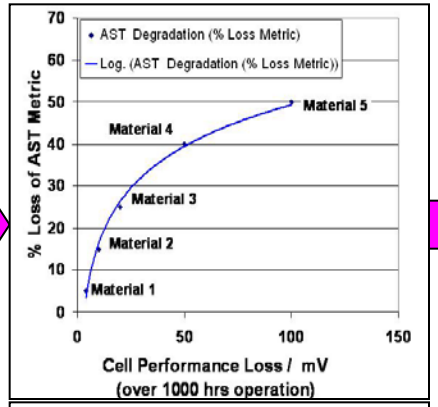
## Importance of Accelerated Stress Test (AST)

- Allows faster evaluation of new materials and provides a standardized test to benchmark existing materials
- Accelerates development to meet cost and durability targets
- Different ASTs are available (DOE-FCTT, USFCC and JARI)
  - Lack of correlation to “Real World” Data
  - No tests available for GDLs and other cell components
  - Value of combined vs individual tests

# Approach

## Materials

- BPS provides materials used in Bus Stack
- W. L. Gore provides commercial MEAs
- Ion Power provides custom MEAs
- SGL carbon provides commercial GDL materials
- ORNL provides metal bipolar plates




LANL performs DOE-FCTT ASTs
Develops GDL, bipolar plate ASTs

## Characterization

Fuel Cell Performance
VIR, Impedance, HelOx, Modeling

Catalyst
- ECSA, Mass activity, particle size, layer thickness, composition, loading

Membrane
Cross-over, shorting resistance, HFR, thickness

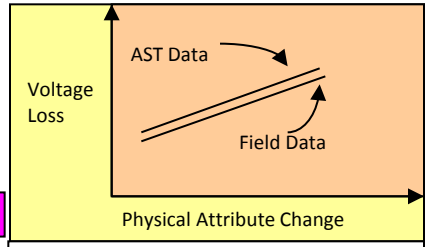
GDL
- Impedance, Hydrophobicity

## BPS Bus Fleet Data

- Voltage degradation distribution data from P5 fleet & HD6 Module
- Cell Data (36 Cells)
- MEA Characterization (108 MEAs)

## LANL Drive Cycle Testing

- Automotive drive cycle testing
- RH, Temp, Pressure effects




## Statistical Correlation

- Relate field and AST data to physical attribute change
- Good correlation if AST slope similar to "Real World Data" slope

## Goals

- Recommend improved catalyst and membrane ASTs that correlate to real world data
- Recommend ASTs for GDL and bipolar plate materials
- Co-ordinate efforts with FCHEA and USDOE-FCTT

# Approach - Milestones

Begin 08/09 | M1 12/11 | M2 03/12 | M3/M4 04/12 | M5/M6 12/12 | M7 04/13 | M8 06/13 | M9/M10 09/13 | End 09/13

Milestones

M1: Complete failure analysis of LANL AST samples (Complete 12/2011)

M2: Developed improved multi-model and multi-variable fitting algorithm. (Complete 03/2013)

M3: Complete failure analysis of Ballard samples (Complete 04/2012)

M4: Complete AST testing on a high SA and a low SA carbon (Complete 04/2012)

M5: Delivery of AST, field, and virgin membranes to LBNL for testing. (Complete 12/2012)

M6: Complete failure analysis of LANL AST samples including 3 different catalyst layers on DuPont XL membranes. (Complete 12/2012)

M7: Deliver a total of 50 MEAs customized for 2 different MEA types (standard, FCT, 50 $cm^2$ and 50 $cm^2$ for GM/RIT hardware) (Complete 04/2013)

M8: Complete drive cycle testing on 3 different membranes and 3 different catalyst layers (33% complete)

M9: Propose validated GDL, membrane and start/stop ASTs (80% complete)

M10 : Final Statistical correlation of AST and Bus data to material property and AST lifetimes to drive cycle of materials with varying lifetimes

# Materials Used



- Gore™ MEAs (AST: 2010 AMR, F/A: 2011 AMR)
  - Gore™ Primea® MESGA MEA A510.1/M720.18/C510.2
  - Gore™ Primea® MESGA MEA A510.2/M720.18/C510.4
  - Gore™ Primea® MESGA MEA A510.1/M710.18/C510.2
- Ballard P5 and HD6 MEAs (AST: 2011 AMR, F/A: 2012 AMR)
- Ion Power MEAs (AST, F/A: 2012 AMR)
  - DuPont XL membranes
  - Tanaka Catalysts
    - TEC10E50E, TEC10E40E, TEC10E20E (High Surface area carbon 50 wt%, 40 wt% and 20 wt% Pt)
    - TEC10V40E, TEC10V20E (Vulcan carbon 40 wt%, 20 wt% Pt)
    - TEC10E40EA Low Surface area carbon 40 wt% Pt
- GDL
  - SGL 24BC (5% PTFE-substrate/23% PTFE MPL)
  - Varying PTFE content and substrate porosity
- Bipolar plates
  - G35 and Ni50Cr: Corrosion testing (coupons) and fuel cell testing (plate)
  - No degradation observed in short term testing in MEA (awaiting input from other LANL durability project)

M710 : Discontinued product. Lower chemical and mechanical durability sample

M720 : technology circa 2005. Higher chemical and mechanical durability sample

F/A = Failure Analysis

# Field Data

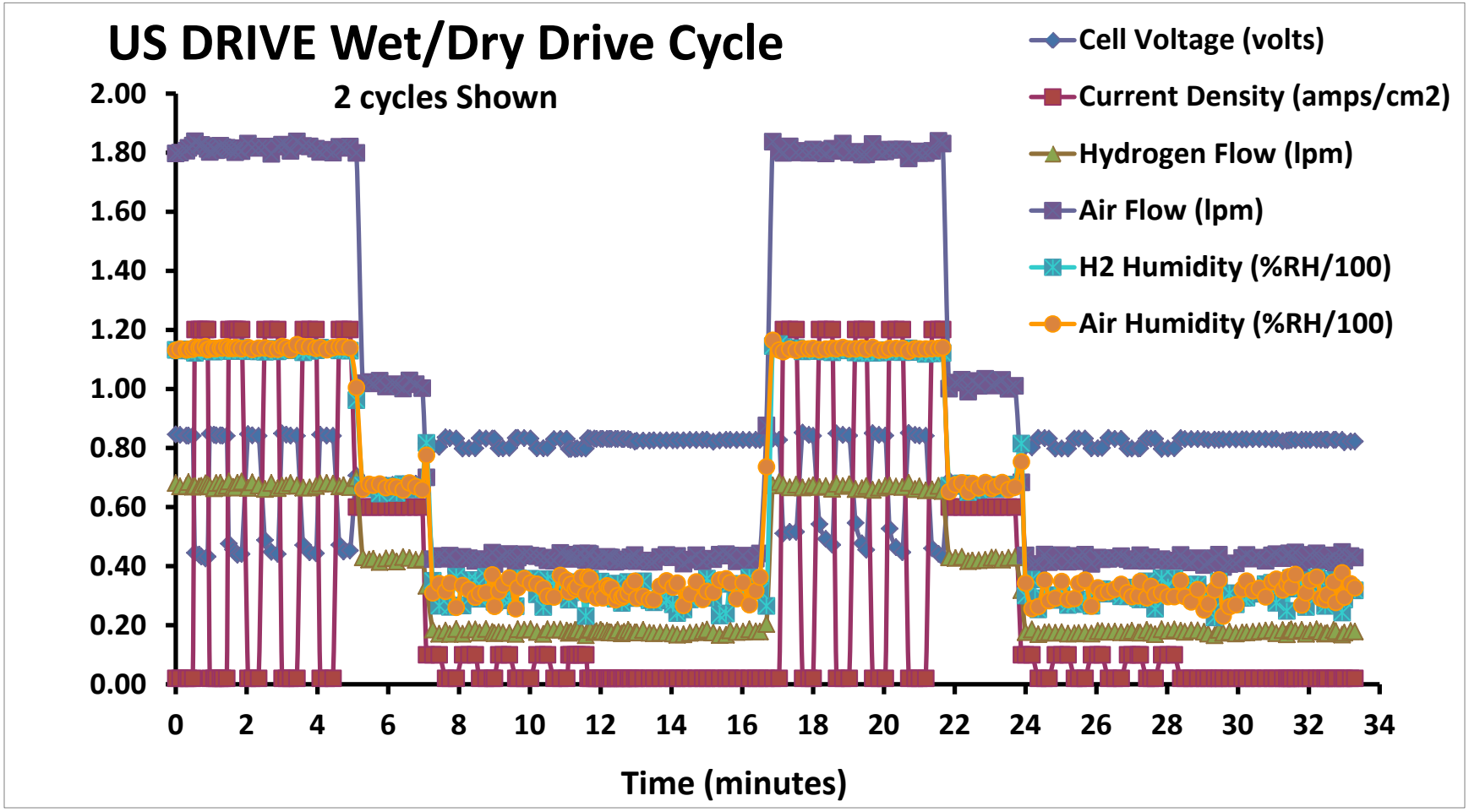


- History of P5 Stacks are as follows:
  - PE4 with 2,769 hours of operation
  - PE22 with 3,360 hours of operation
  - PE24 with 2,597 hours of operation
  - All 3 buses operated in Hamburg for their life
  - Data over a sample stretch of 1-2 hours were analyzed to define performance degradation
  - 8-10 time periods per stack were analyzed to ensure enough points to develop a good average performance degradation rate
- HD6 Stack is designated as follows:
  - SN5096 with 6,842 hours of operation
  - Stack was system tested in lab under Orange County Transit Authority (OCTA) cycle
  - Due to pull outs of MEAs from stack will have failure analysis (FA) data at ~2,400 hours, 4,300 hours and 6,842 hours

Presented in 2011/2012 AMR

# Drive Cycle Testing





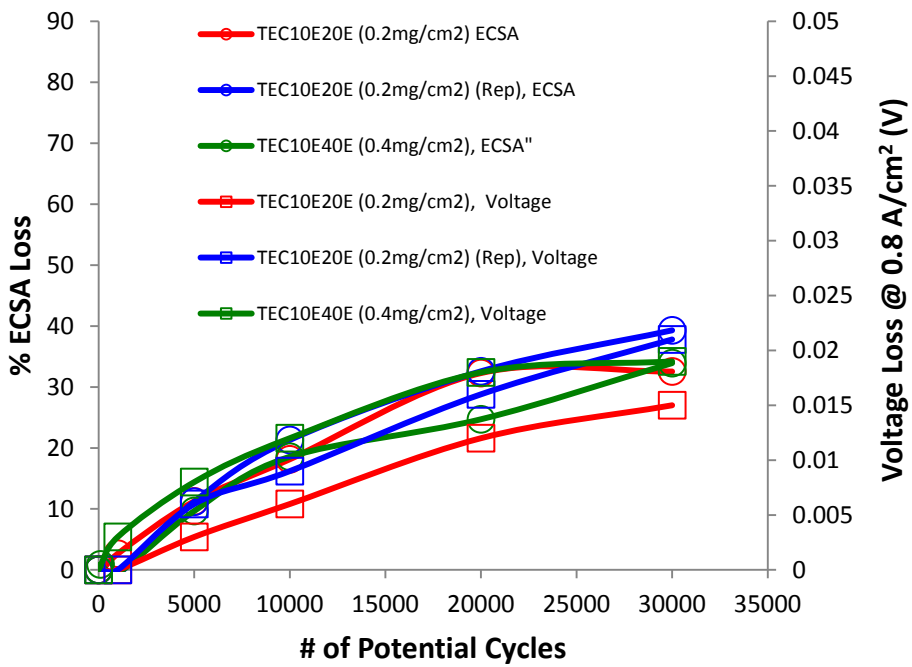

Use 100% $H_2$ instead of 80% $H_2$

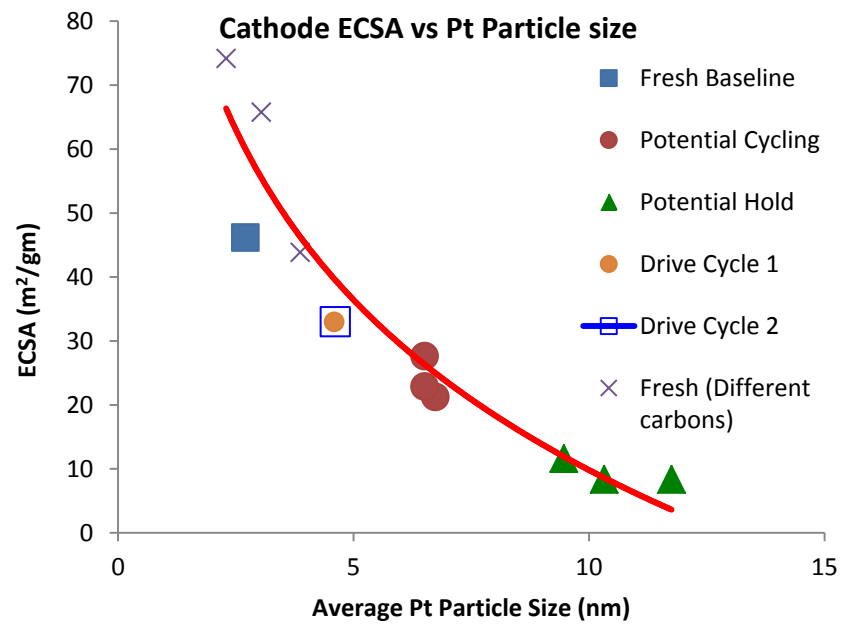
Only one station capable of RH control (bottle = 90°C, adjust dry and wet flows)

Also performing cycles at the high RH conditions (Wet Cycling)

# Potential Cycling AST

Accomplishments /Progress




- Pt particle size growth observed in both TEM and XRD
- Correlates with decreasing ECSA
  - Observed in both electro-catalyst (potential cycling) and carbon corrosion (high potential hold) AST
- Mass activity, voltage loss, and increased impedance in kinetic region observed
- 40% ECSA loss corresponds to approx. 20 mV voltage loss



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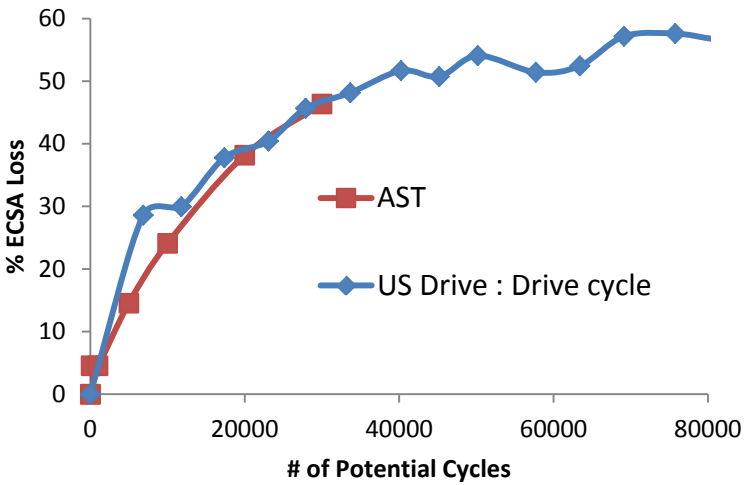
# Correlation of AST and Drive Cycle



- 30,000 cycles ≈ 2000 hours of bus operation (Both P5 and HD6)
- 30,000 cycles ≈ 850 hours of US DRIVE Drive-Cycle
- 30,000 cycles ≈ 500 hours of wet drive cycle
- 5000 hours ≈ 175,000 cycles
- Need > 30,000 cycles for 5000 hour automotive durability



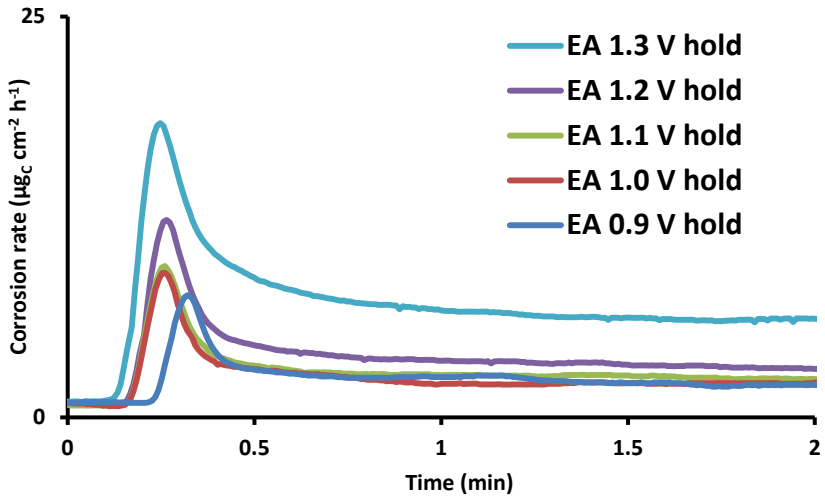

| Catalyst | AST 30000 Cycles | Drive Cycle 30000 cycles |
|---|---|---|
| C510.2 | 53.80% | 53.7%, 54.3% |
| C510.4 | 46.3%, 46.8% | 46.60% |

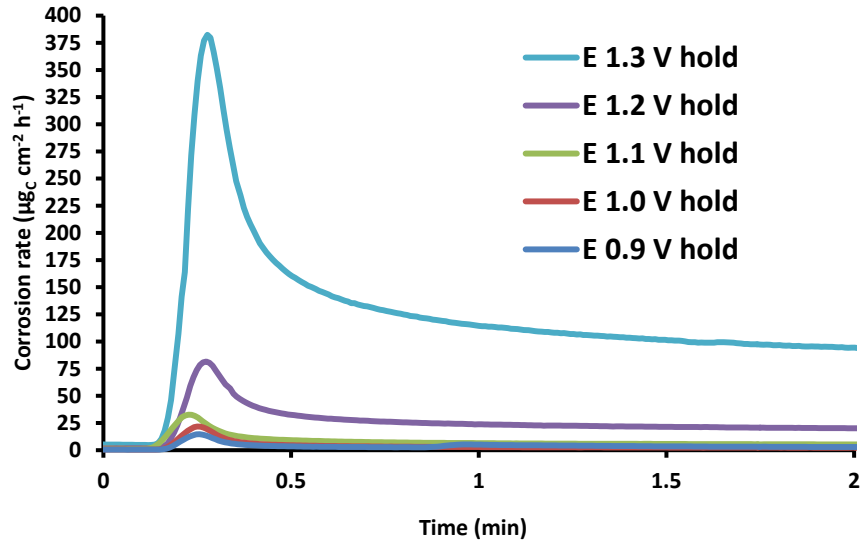
- Pt particle size increase.
  - Consistent with potential cycling AST
  - Larger Pt growth in drive cycle samples than AST samples

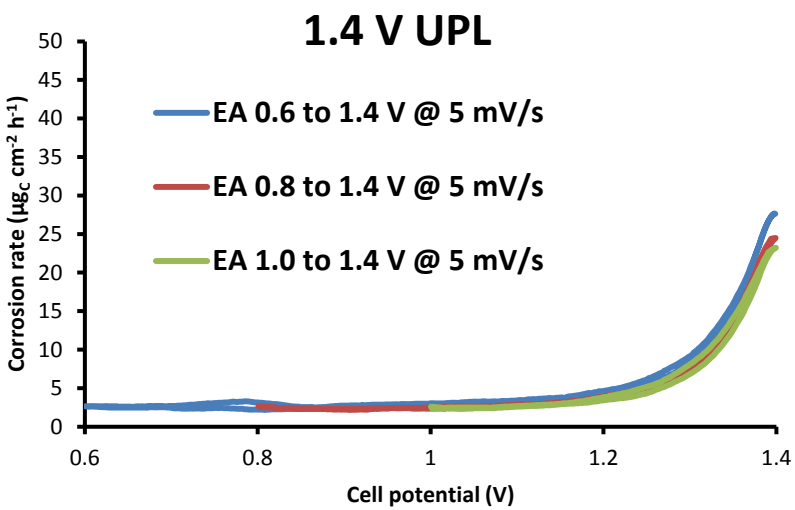
6.5 nm after 30,000 cycles
9.5 nm to 11.5nm after 1.2 V AST
9.4 nm after 2000+ hours wet/dry cycle
7.5 nm after 1200 hours wet cycle
5.6 nm after 300 hours wet cycle

# Carbon corrosion at low potentials

Accomplishments /Progress




Significant carbon corrosion observed @ 0.9 V for high surface area carbon

Corrosion can be significantly accelerated using higher upper potentials and cycling instead of holds

FCTT adopting 1 – 1.5 V cycling



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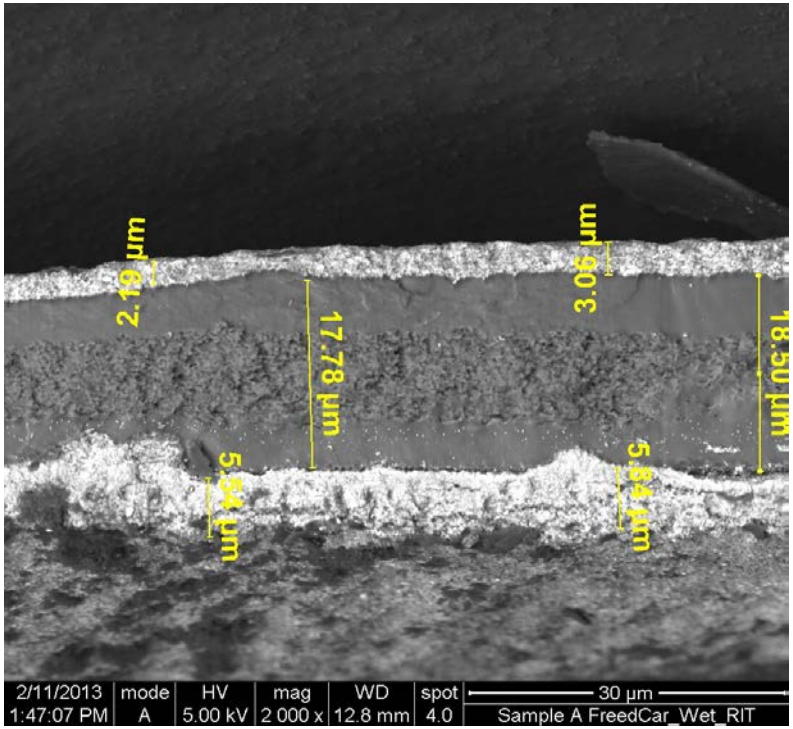
# Drive Cycle: Catalyst degradation (HSAC)

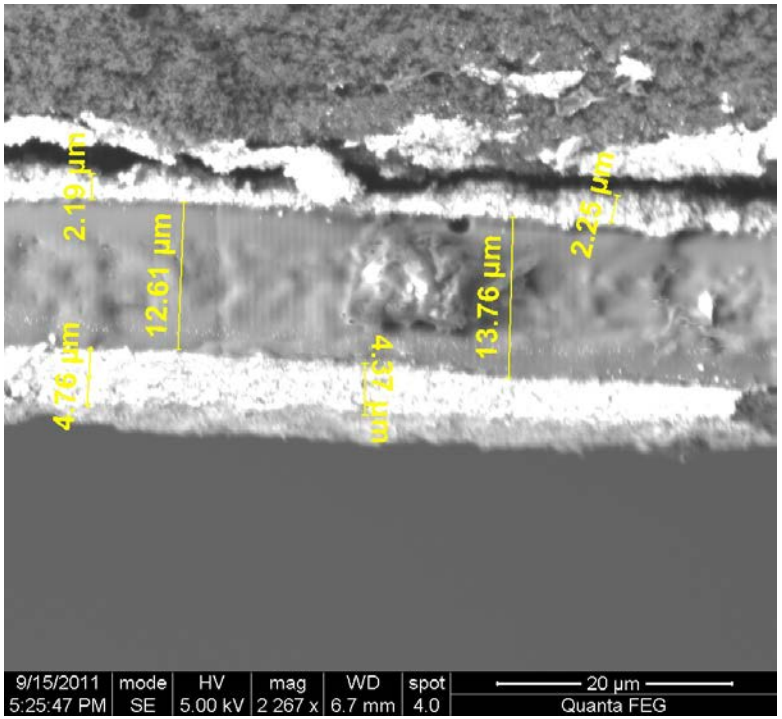
Accomplishments /Progress

HSAC : High surface area carbon

860 hrs wet drive cycle




1224 hrs wet drive cycle




Pt band observed on cathode side of MEA. Band clearly visible after 2000 hours with high (0.4 mg.Pt/cm$^2$) loaded catalyst

860 hours results in 10% thinning of catalyst layer, 1200 hours results in 25 % thinning and 2000+ hours in 50% thinning



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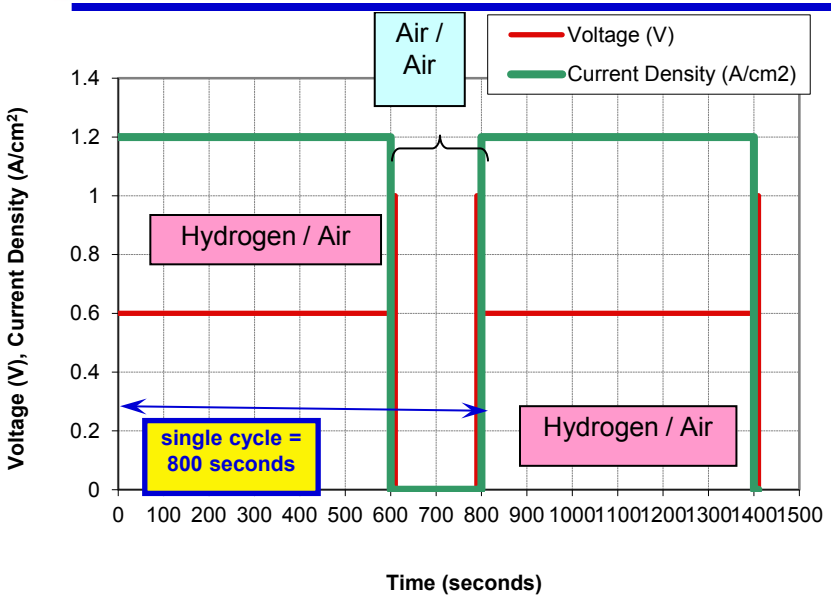
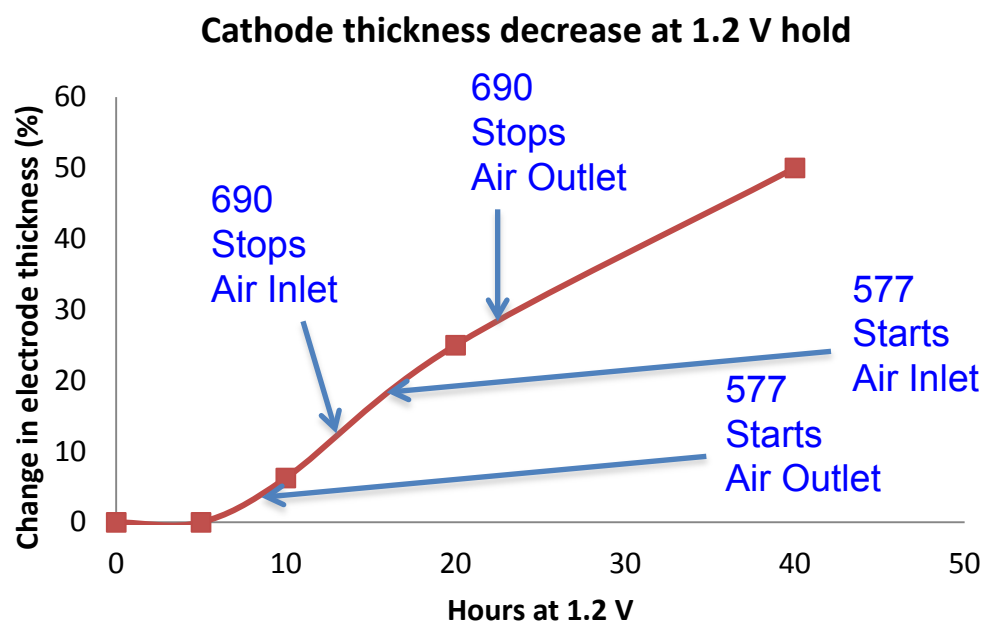
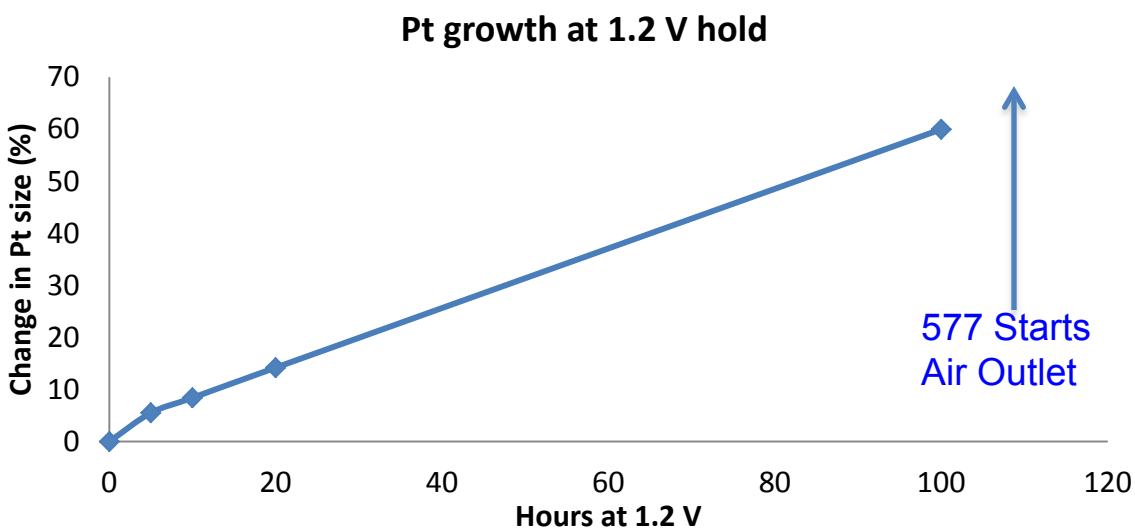
# Carbon Corrosion : Correlations



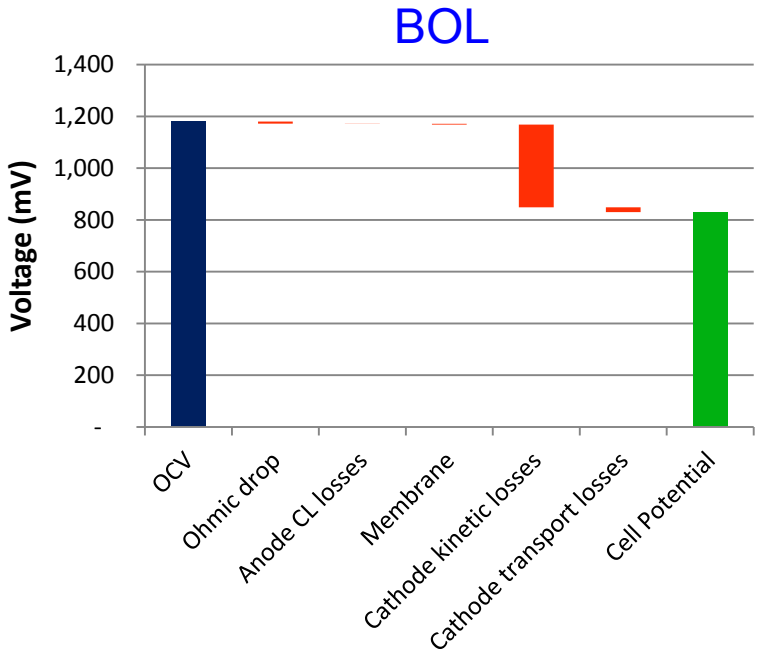



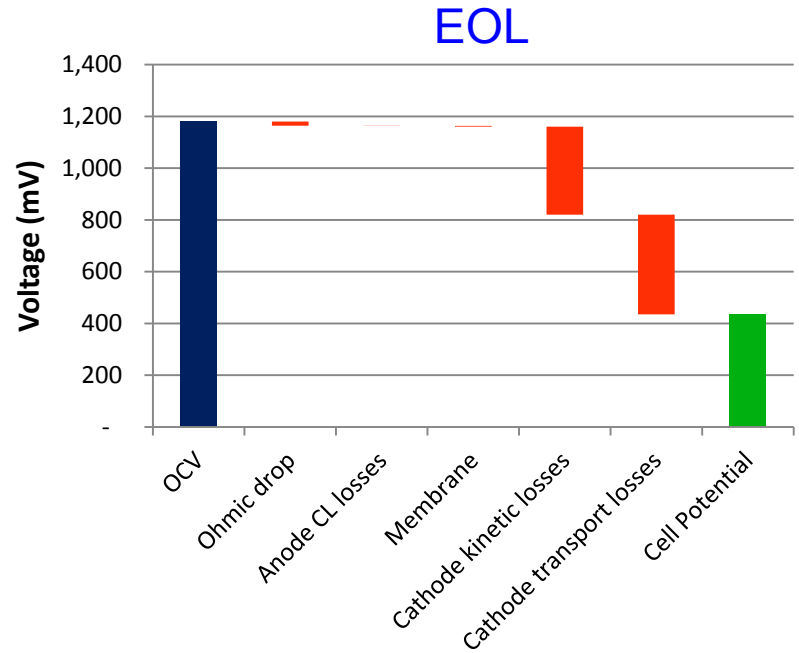



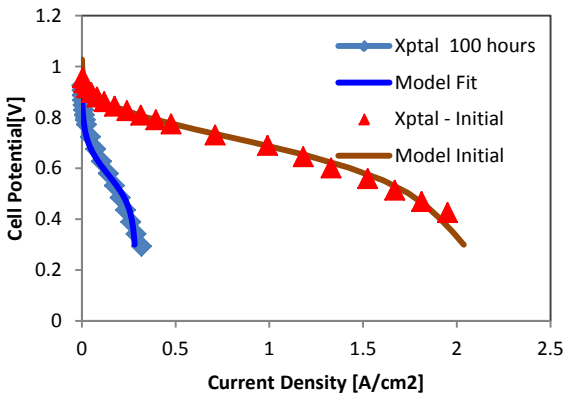

- Large spatial variations in corrosion due to start/stop
- Longer times at air/air potential results in greater corrosion
- Pt particle size growth much larger during start/stop tests.

# Voltage loss Breakdown Analysis





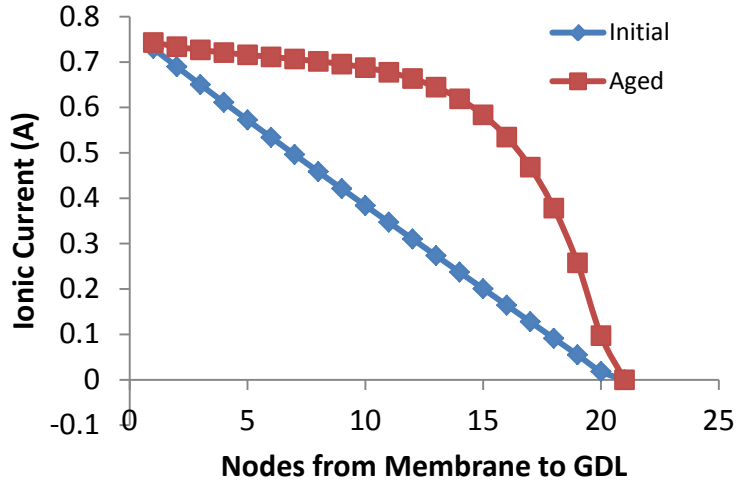




- LBNL modeling used for VLB
- Catalyst coarsening causes slight increase in cathode kinetic loses
- Little Ohmic changes
- Major loss is cathode transport losses consistent with collapse of cathode structure
- Will be compared with drive cycle testing using multiple catalyst layers to get statistical correlations

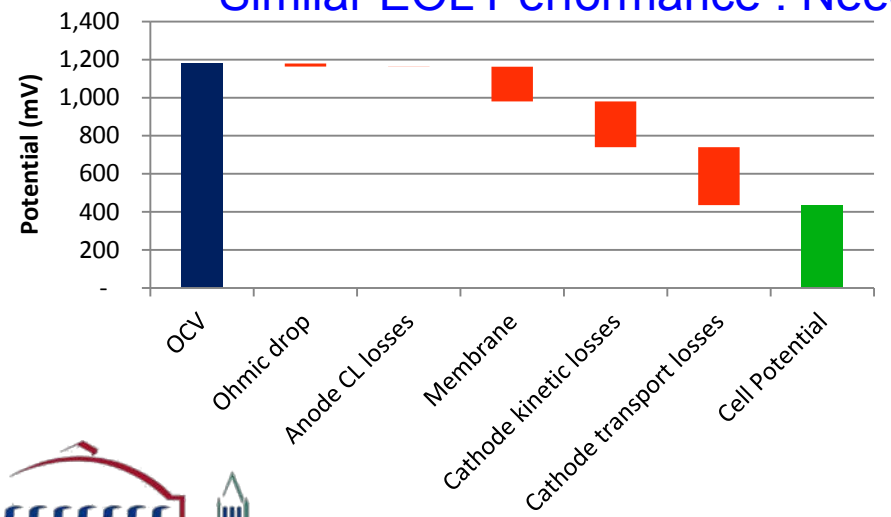
# Voltage loss Breakdown Analysis

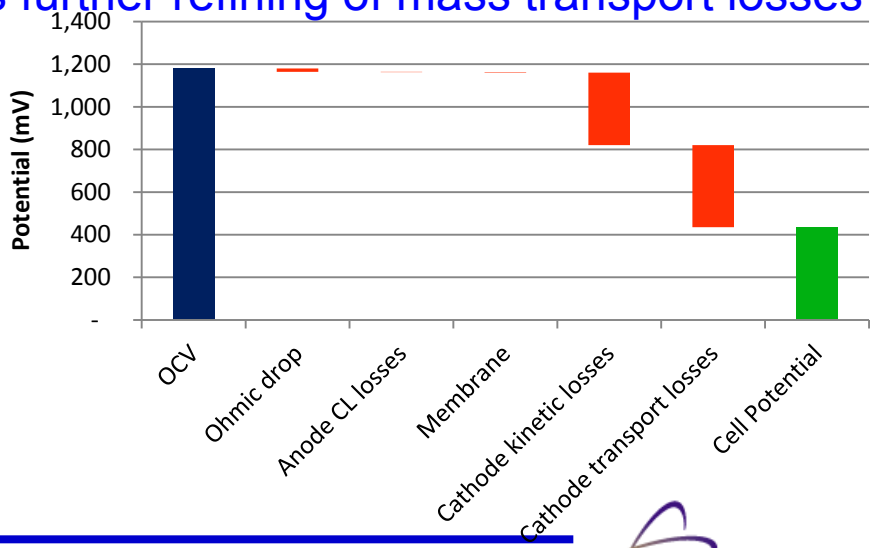
Accomplishments /Progress



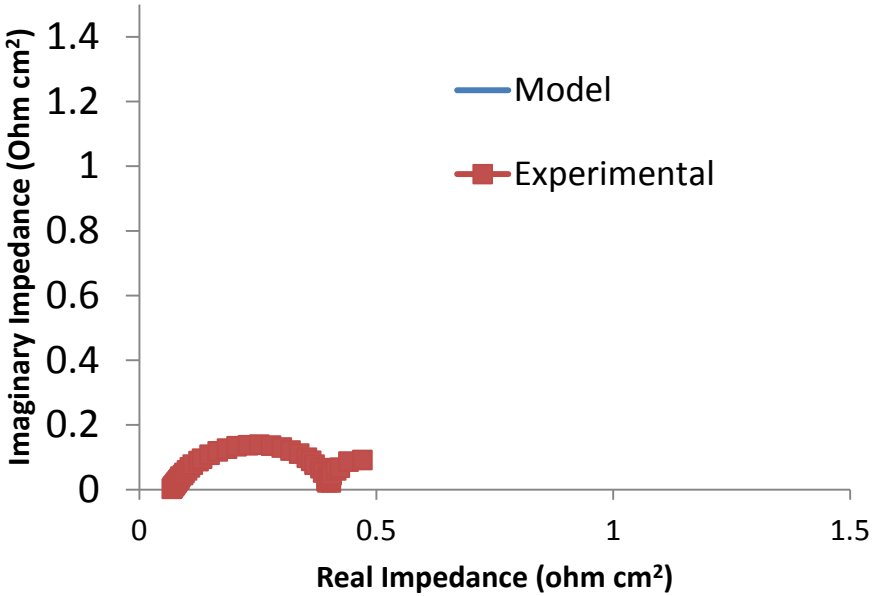

- Similar performance could be achieved for different distribution of resistance
- Manual supervision is required to allot appropriate weight to the various resistances
- Reaction distributions in the catalyst layers need adjustment
- Mass transport losses in ionomer, catalyst layer pores, GDL

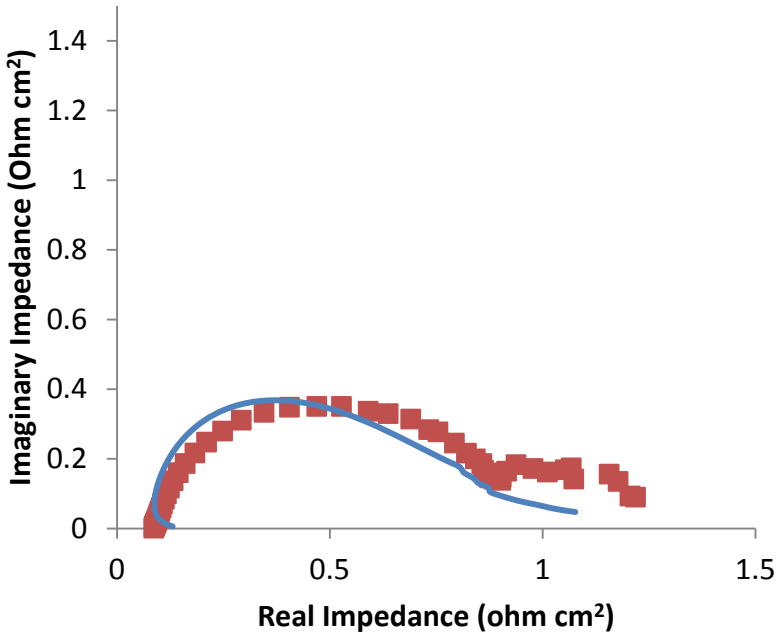
Similar EOL Performance : Needs further refining of mass transport losses



# Voltage loss Breakdown Analysis

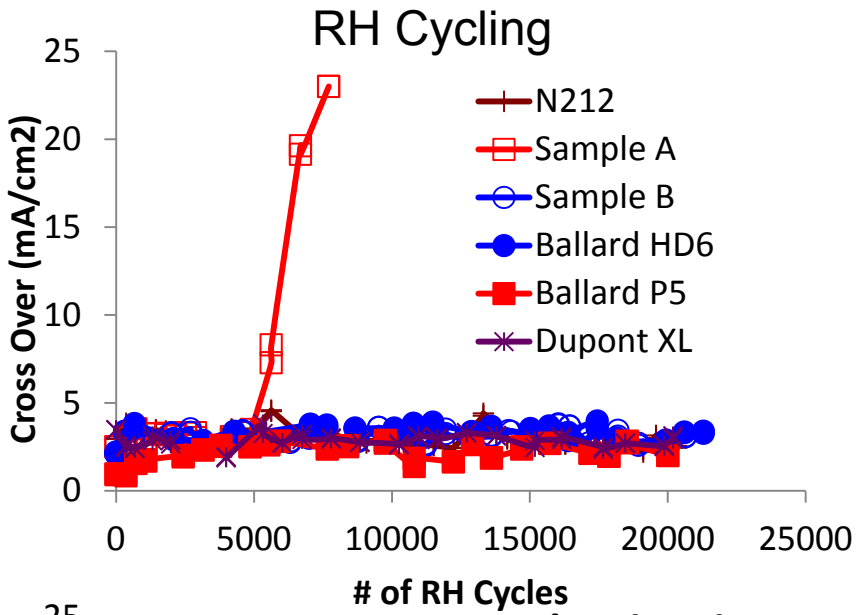


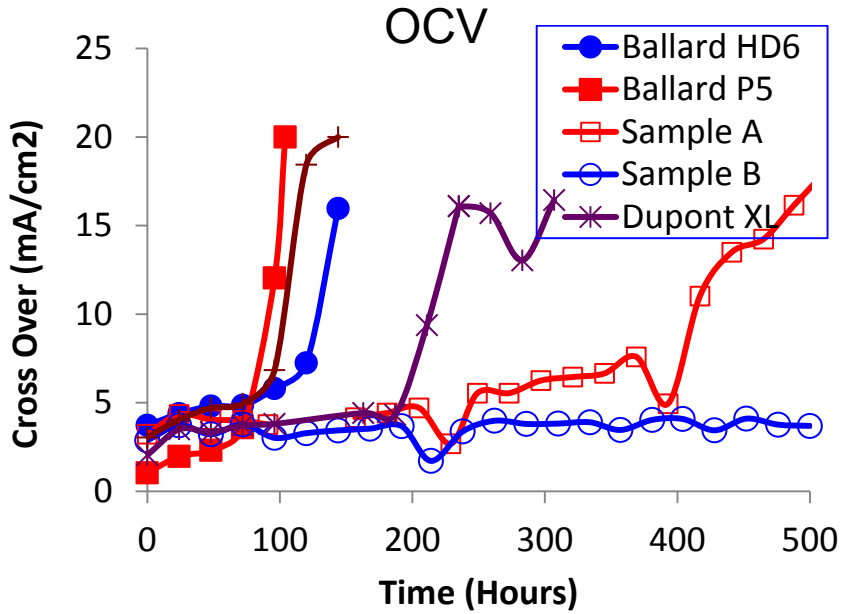



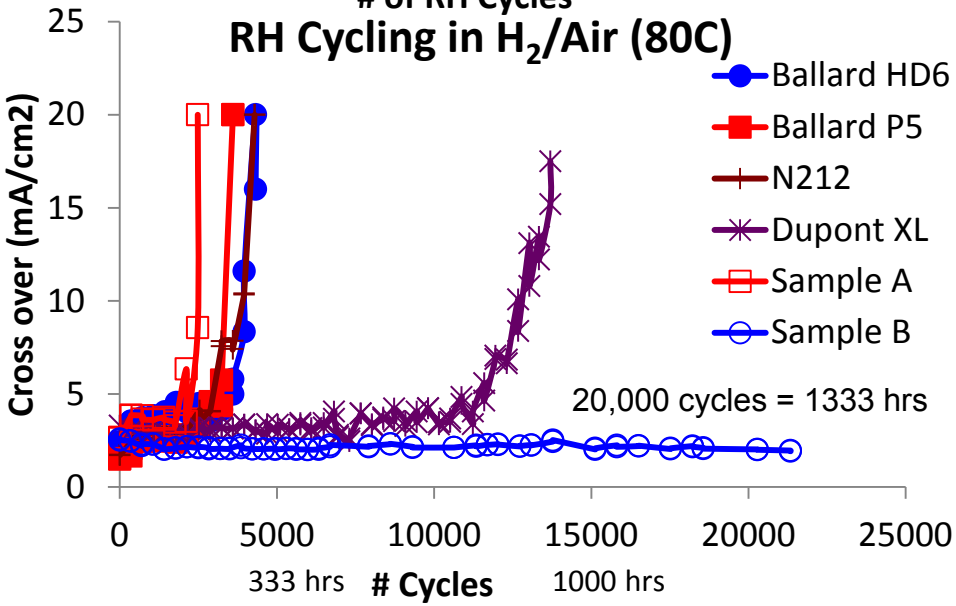

- Good agreement in the kinetic region
- The second capacitance loop is associated with channel effects
- Modeling impedance gives an accurate determination of individual resistance
- Simultaneous fitting of Air and HelOx data at different current densities

# Membrane ASTs

Accomplishments /Progress



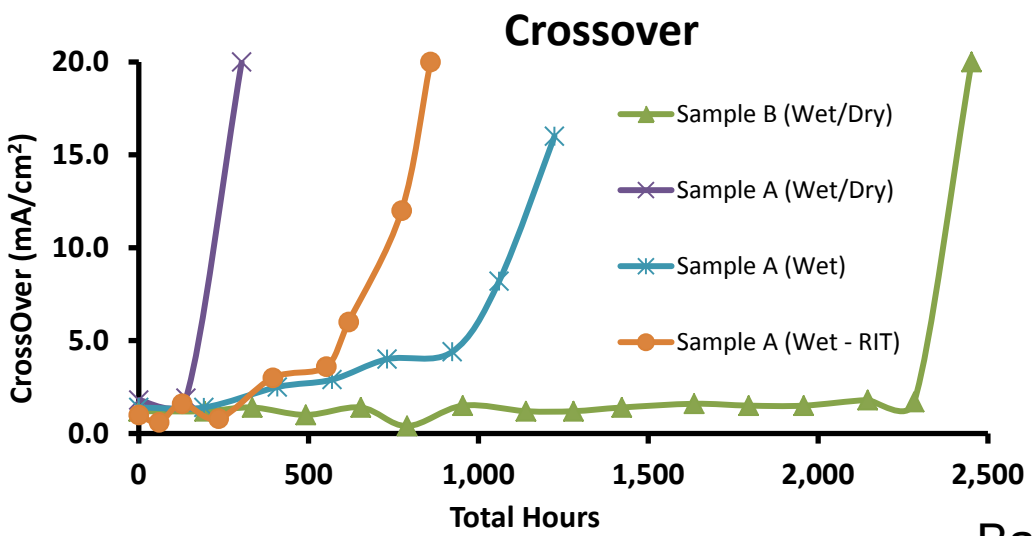




- RH cycling test does not have ability to distinguish between most PFSA membranes
- OCV testing too severe for bus applications
- Combined mechanical/chemical AST has ability to distinguish between MEAs, needs further acceleration.

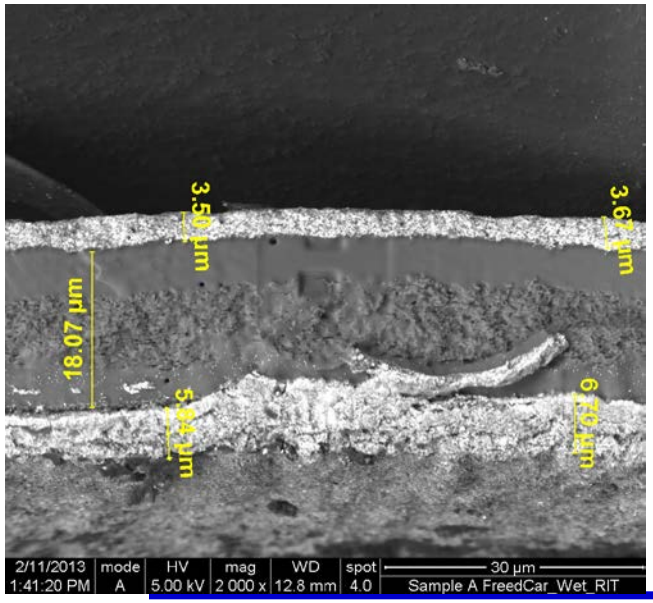
# Drive Cycle: Membrane failure modes

Accomplishments /Progress

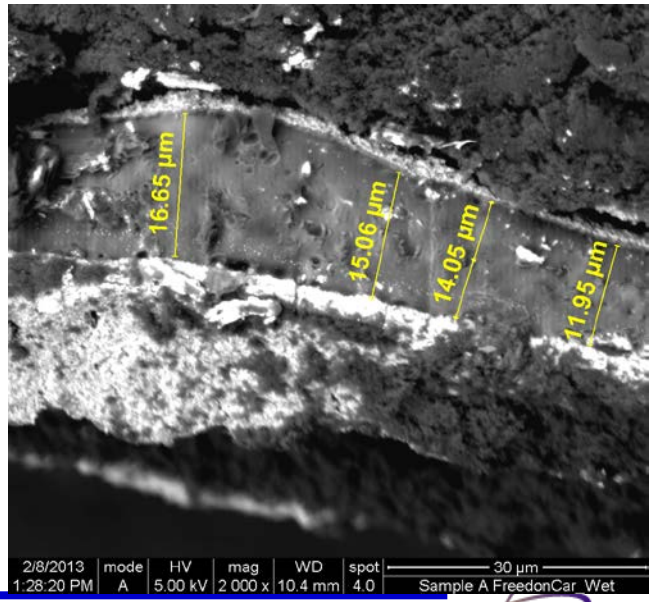



- Both Wet/Dry and Wet cycles result in crossover increases and membrane failure
  - Little thinning observed in membrane (< 10% to none)
  - Consistent with field data from buses
  - Not compatible with OCV AST.

Baseline: 850+ hours wet cycling




Baseline: 1200+ hours wet cycling



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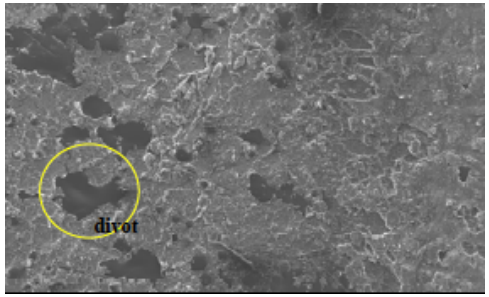
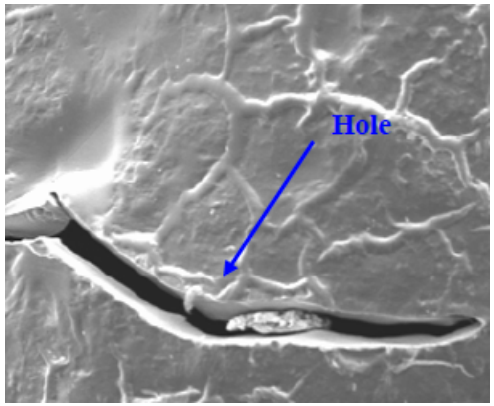
# AST/Field correlation - Membrane



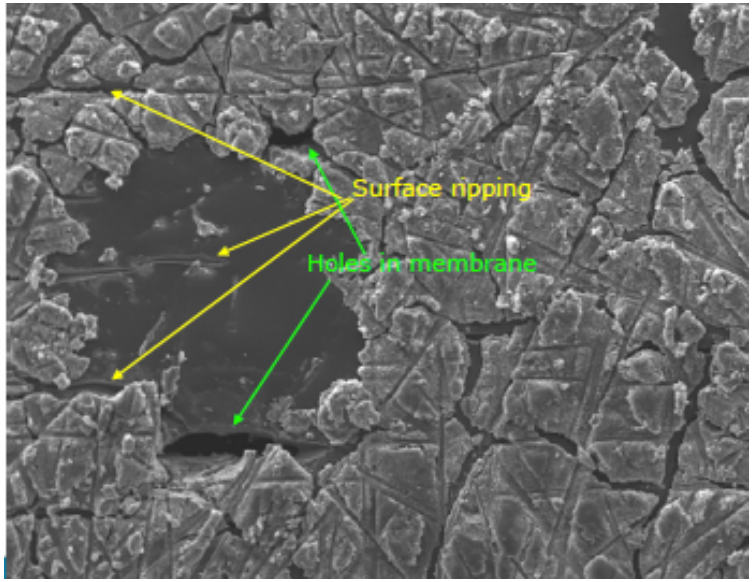
HD6 Field Sample

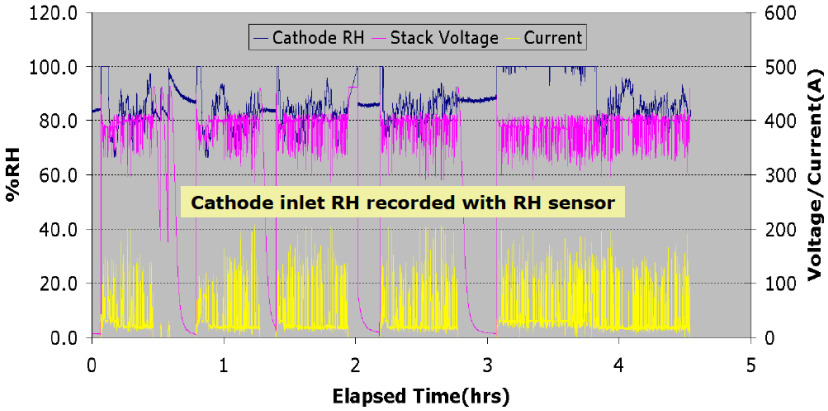



P5 Field Sample




P5 sample after $H_2$/Air RH cycling AST

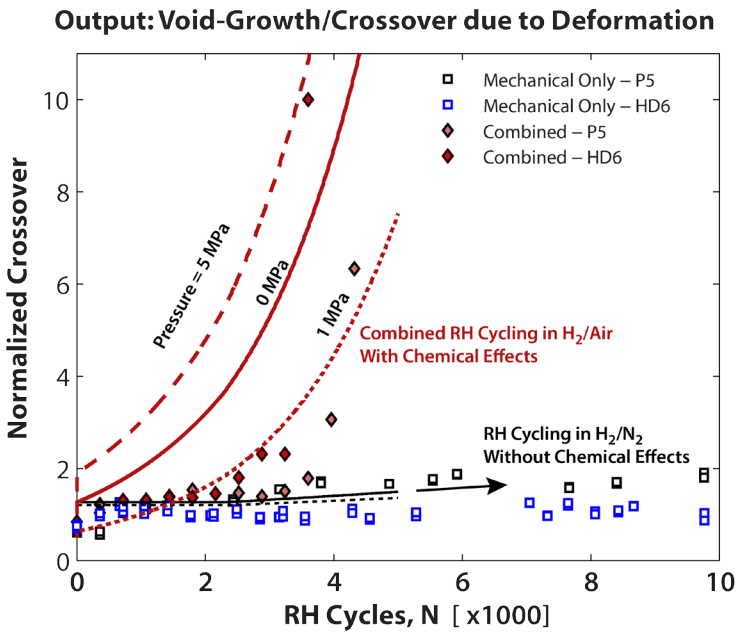


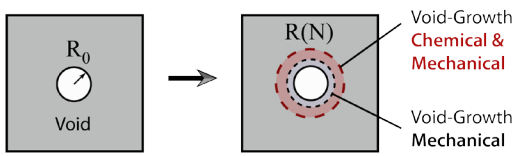




- RH cycling data being analyzed
- Membrane failure time decreases with increased time > 0.8 V
- Membrane failure time increases with increasing inlet RH

# Membrane Degradation





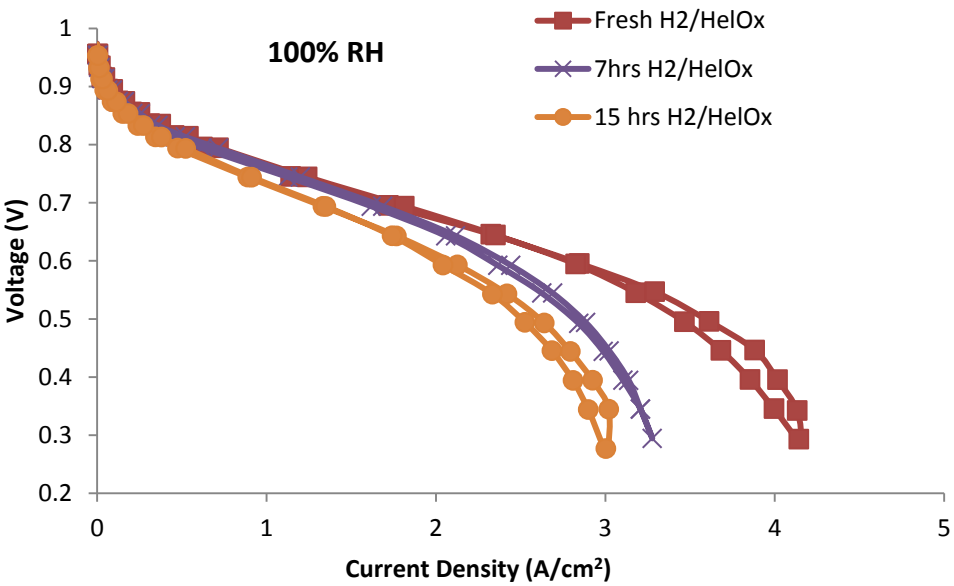



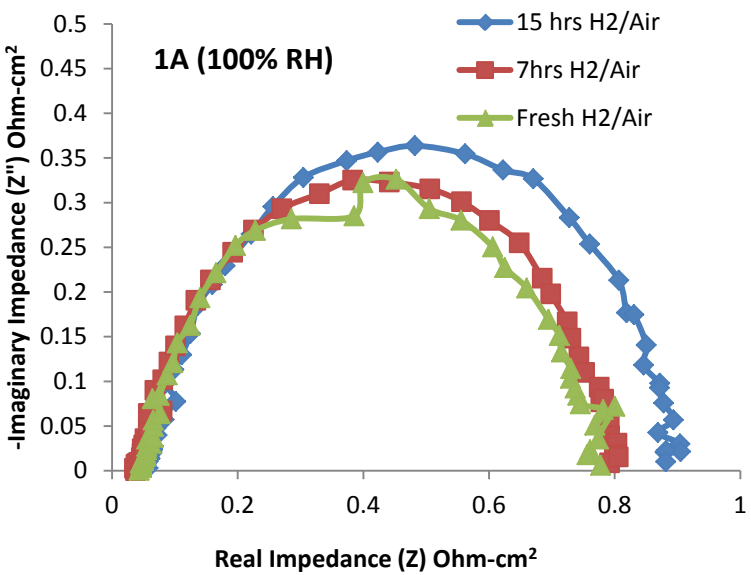

| | vs. Field | |
|---|---|---|
| | Dry | Liquid |
| RH Cycling **Mechanical** | Different | **Similar** |
| **Chemical** AST | **Similar** | More Severe |
| RHC @ OCV **Mechanical / Chemical** | **Similar** | **Similar** |

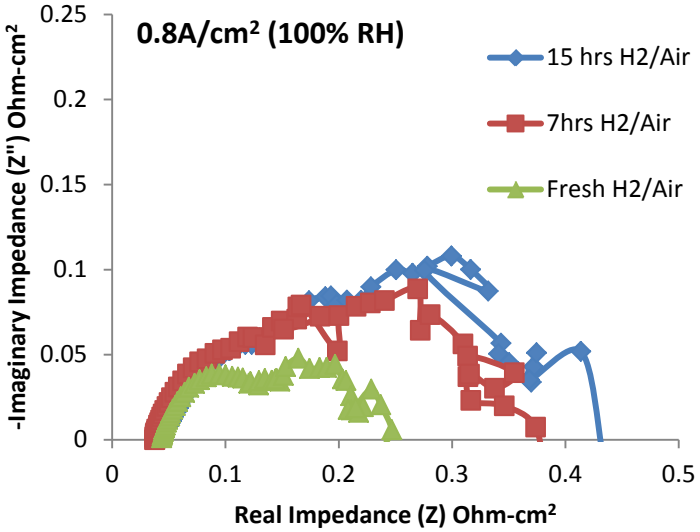
SAXS reveals similar membrane degradation in field samples as those aged under the combined mechanical/chemical cycle.

The OCV aging is too severe and the RH cycling is too benign.

# Develop GDL AST




Collaborative development with UTC to examine observed field GDL degradation

GDLs aged at 95°C in 30% $H_2O_2$

(Original procedure from Decode project, Peter Wilde: SGL Carbon)

Simulates loss of hydrophobicity

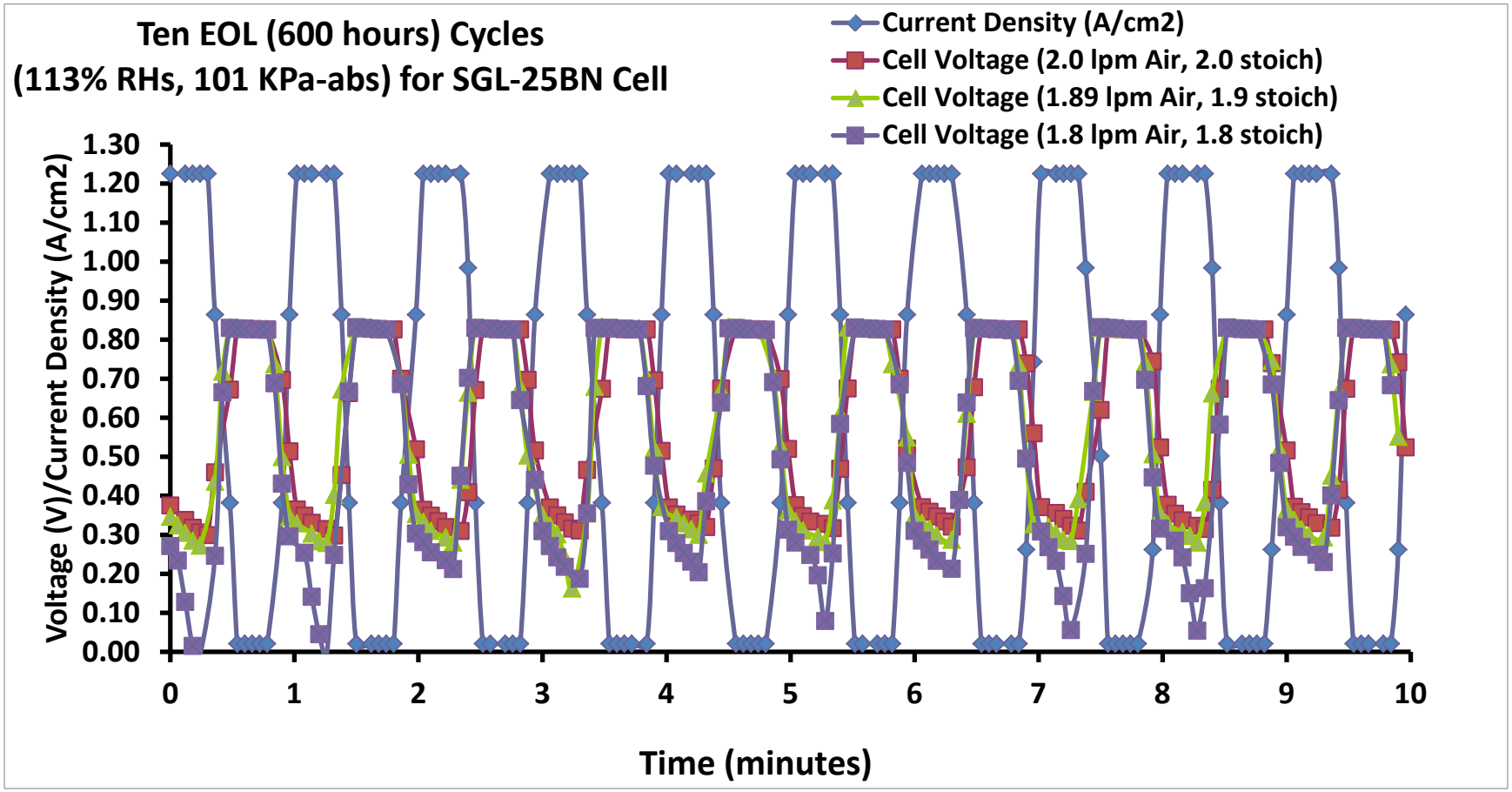
Substrate pore volume increases

Low current/ low RH performance similar

Degradation in high current/high RH performance

# Drive Cycle: GDL Failure mode





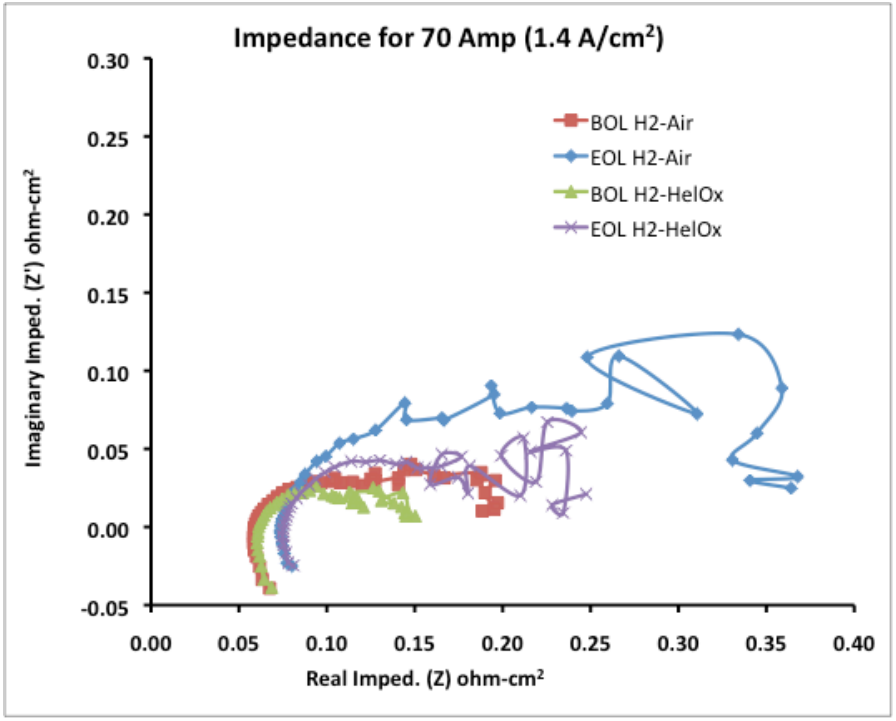

- Mass transport issues. Catalyst layer/GDL flooding
- Slightly higher flow rates can easily restore performance to almost BOL levels

# Mass transport losses : HSAC

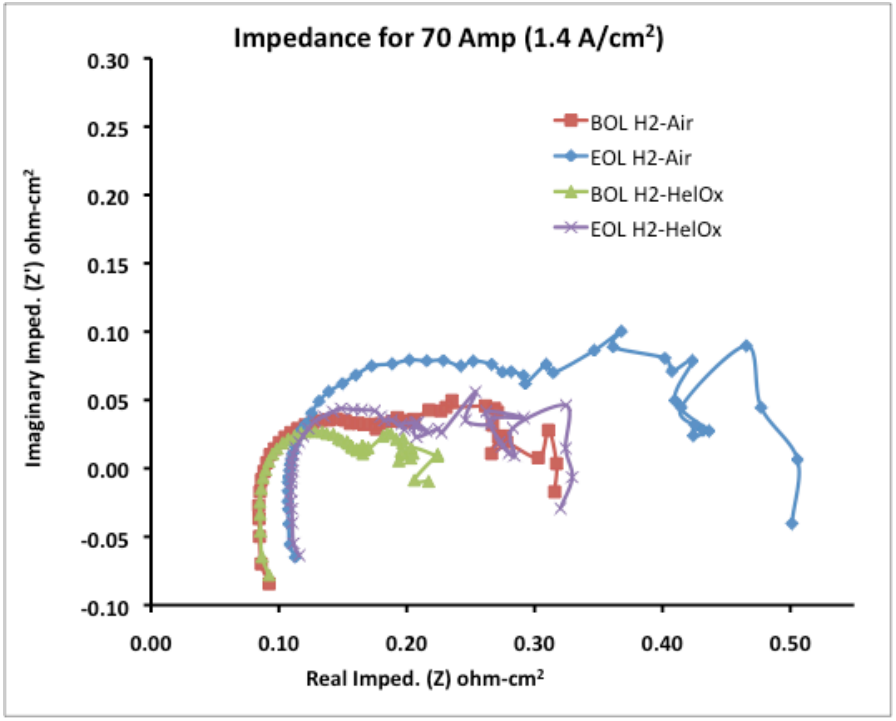


## HSAC : High surface area carbon

3040 hours of drive cycle




1224 hours of wet drive cycle



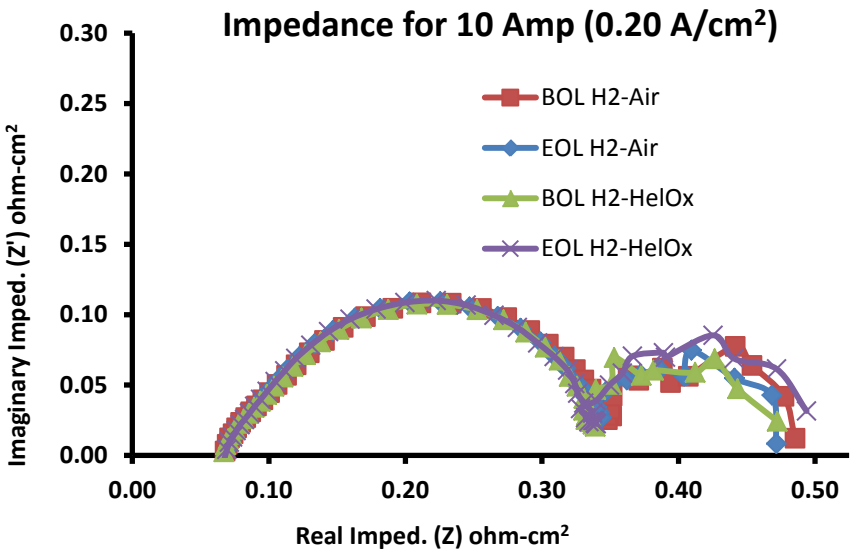

Significant increase in mass transport losses

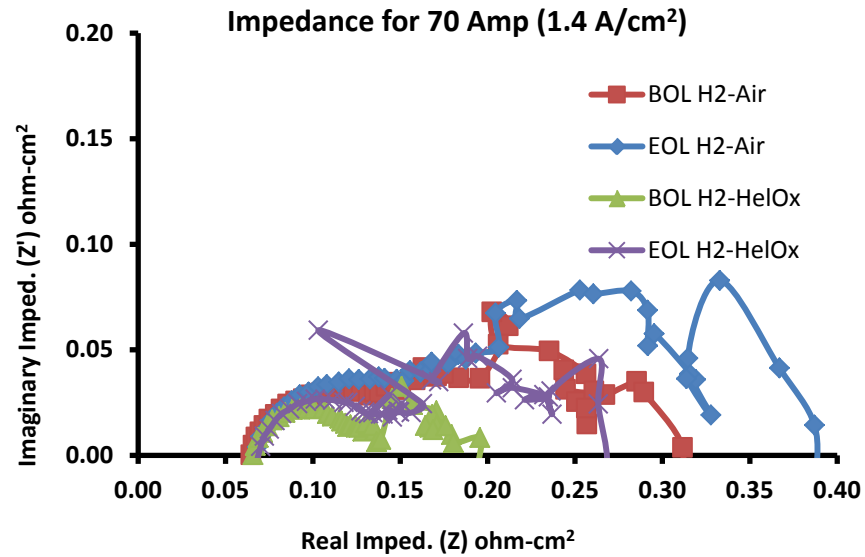
GDL degradation?
Difficult to de-couple catalyst layer effects

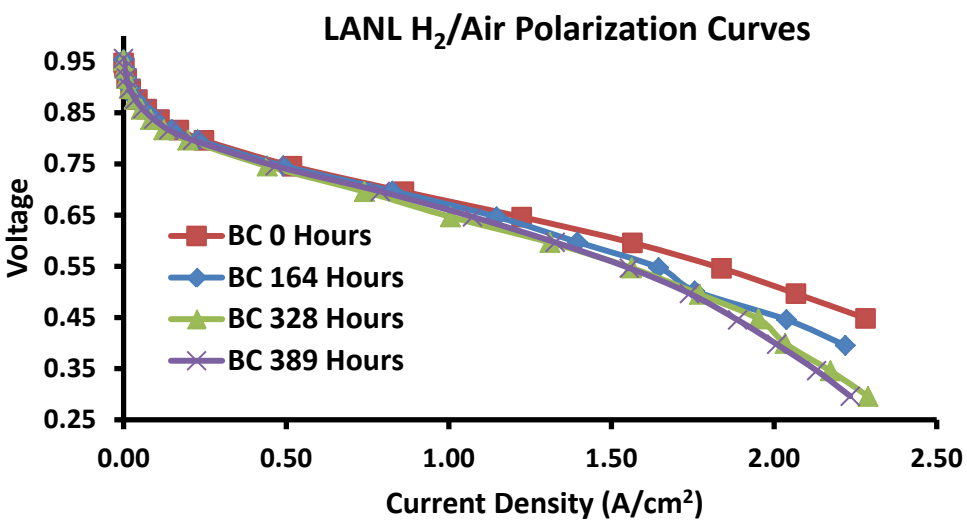
# Mass transport losses : LSAC

Accomplishments /Progress

## LSAC : Low surface area carbon (Graphitized)




- Mass transport losses : Stopped Wet Drive cycle testing @ 382 hours. (Cannot sustain high currents, Cell Reversal)
- Little thinning observed.
- 30-35% ECSA loss with 80% increase in Pt particle size



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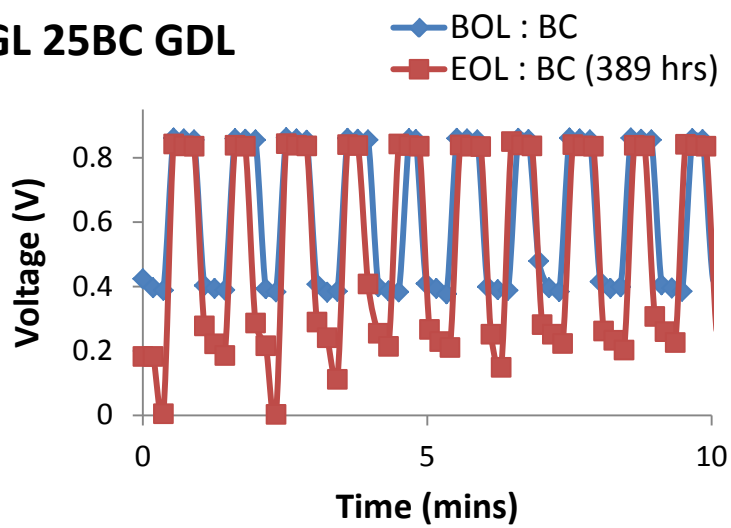
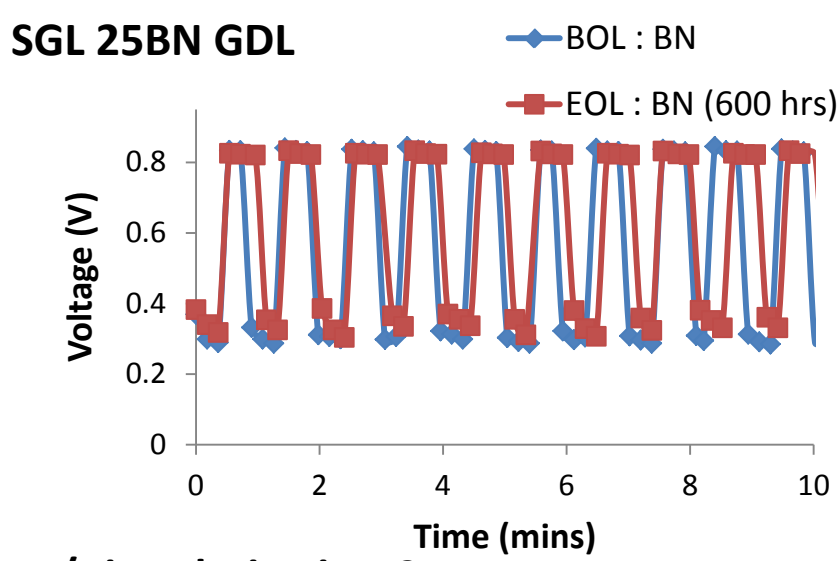
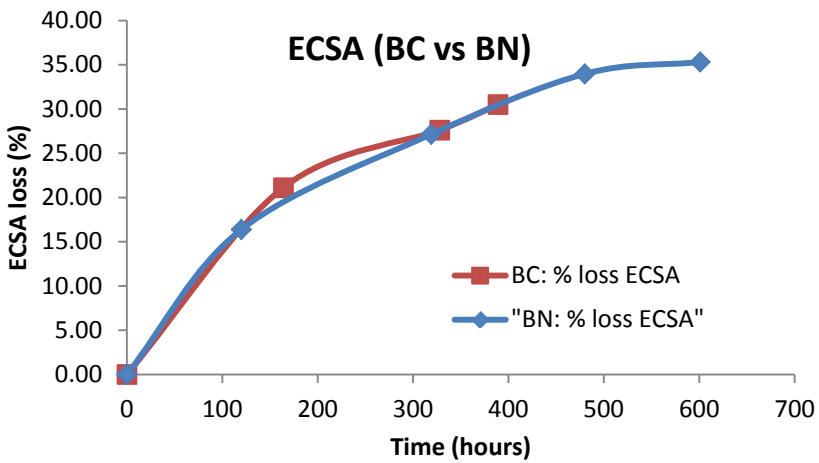
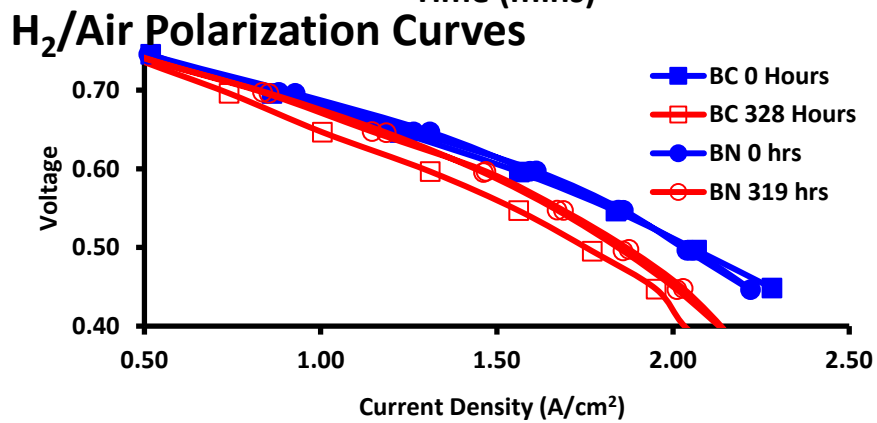
# Drive Cycle Testing: Varying GDLs

Accomplishments /Progress




Same MEA: Similar Catalyst Degradation and ECSA loss

XPS confirms increase in $C_xO_y$ peaks in aged GDLs (AST, Drive cycle, ex situ aged)



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# Collaborations

LANL (**Rangachary Mukundan, Rodney Borup, John Davey, David Langlois, Dennis Torraco, Roger Lujan, Dusan Spernjak, Joe Fairweather and Fernando Garzon)**

• Co-ordinate project; Perform all ASTs and Drive cycle testing; Materials Analysis of BOL and EOL materials

Ballard Power Systems (Paul Beattie, Greg James, Dana Ayota)

• Analyze Bus Data; Deliver BOL MEAs used in Buses; Analysis of MEAs

LBNL (Adam Weber, Siva Balasubramanian, Wonseok Yoon)

• Detailed Voltage loss break-down; Statistical correlation of materials properties to lifetimes and AST metric loss of materials with differing durabilities

Ion Power (Steve Grot)

Deliver MEAs with varying durability

ORNL (Mike Brady, Karren More)

Deliver metal bipolar plates/TEM

W. L. Gore and Associates Inc., and SGL Carbon (materials suppliers)

Durability working group (Start/Stop protocol)

Nancy University (Start/Stop segmented cell testing)
Olivier Lottin (PI)

# Summary/Future Work - I

- Initial AST (electrocatalyst, catalyst support, membrane chemical and mechanical) performed
  - Baseline materials from W.L. Gore, P5 and HD6 and Ion Power MEAs with three different catalyst supports
  - Failure analysis from all ASTs
- Bus Data analysis completed on P5 and HD6 bus stacks
  - Data on number of RH cycles and potential cycles from the buses are being analyzed
- Automotive drive cycle (FCTT) testing in progress on GM-RIT and quad-serpentine hardware
  - Baseline materials completed
  - Ion Power materials initiated.
  - GDL degradation issues have been addressed (need to be quantified)
  - Start/Stop will not be incorporated in drive cycle. The Durability Working Group protocol for start/stop is being studied separately.

# Summary/Future Work - II

- Start/Stops performed at Nancy University
  - Large spatial variations make average correlations difficult
  - Extremes will be studied
- Voltage loss break down modeling being refined
  - Down the channel effects being added to simultaneously fit impedance data
  - Models to be refined for better fit at > 1 A/cm$^2$ (GDL transport)
- NEW ASTs
  - GDL AST proposed. Surface oxidation of carbon observed in all samples. Degradation mechanism similar in drive cycle, AST and ex situ samples
  - Membrane mechanical/chemical AST found to reliably simulate field and drive cycle failure modes
  - 1 to 1.5 V carbon corrosion AST to be evaluated
- Compile all data in a Web site in addition to publications

# Acknowledgements

Nancy Garland
(DOE – EERE – Fuel Cell Technologies – Technology Development Manager)
Dimitrios Papageorgopoulos

Fuel Cell Tech Team (Craig Gittleman, Jim Waldecker and Balsu Lakshmanan) for guidance on ASTs

W. L. Gore and Associates (MEAs)

SGL Carbon (GDLs)



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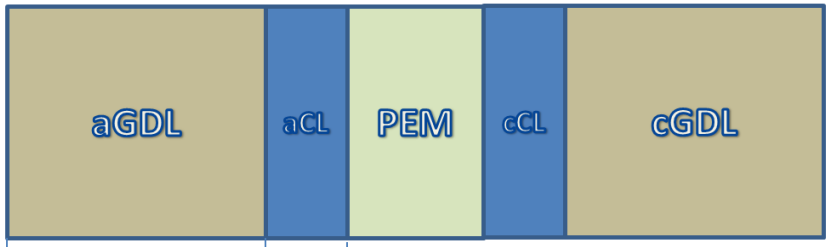
# Technical Backup Slides

# 1-D simplified model




- The model is 1-D, steady state
- Add in transient terms to do impedance

$$x_i = \bar{x}_i + \mathrm{Re}\{\tilde{x}_i \exp(j\omega t)\}$$

Steady-state solution  Complex function

$$Z = \frac{\tilde{V}}{\tilde{i}}$$

- Model is updated and leveraged from work in other LBNL projects
- Fitting parameters depend on AST, but are typically effective transport coefficients, surface area (if not measured), *etc.*

- Catalyst layer
  - Agglomerate model using Pt-oxide coverage terms and ionomer film

    Yoon and Weber JES **158**, B1007
  - Gas transport mainly by Knudsen diffusion
- Diffusion media
  - Stefan-Maxwell diffusion
  - Liquid water with Darcy's law
  - Use capillary pressure and contact-angle distribution model

    Weber JPS 195, 5292
    - This is being reevaluated
- Membrane
  - LBNL chemical-potential approach

Weber and Newman, in *Device and Materials Modeling in PEM Fuel Cells*, Paddison and Promislow, Eds, Springer, 157-198 (2009).

# 1-D simplified model

## Inputs

- Operating/test conditions
- Cyclic voltammetry (active area)
- Electrochemical impedance
- Polarization curve

## Model

- 1-D simple model
- Modify to calculate/fit EIS profiles and polarization curves using physical equations
- Fit parameters to data

## Outputs

- VLB
- Sensitivity to model fit parameters
- Look for controlling dimensionless groups

$$\begin{vmatrix} 1 & 0 & 0 & 0 \\ \frac{\partial f_2}{\partial i_f} & -1 & \frac{\partial f_2}{\partial c_i} & \frac{\partial f_2}{\partial \gamma_k} \\ \frac{\partial f_3}{\partial i_f} & \frac{\partial f_3}{\partial V} & -1 & \frac{\partial f_3}{\partial \gamma_k} \\ \frac{\partial f_4}{\partial i_f} & \frac{\partial f_4}{\partial V} & \frac{\partial f_4}{\partial c_i} & -1 \end{vmatrix} \bullet \begin{vmatrix} \tilde{i}_f \\ \tilde{V} \\ \tilde{c}_i \\ \tilde{\gamma}_k \end{vmatrix} = \begin{vmatrix} \tilde{i}_f \\ 0 \\ 0 \\ 0 \end{vmatrix}$$

$$\tilde{x}_i = \tilde{x}_i^{\mathrm{Re}} + j.\tilde{x}_i^{\mathrm{Im}}$$

$$\begin{vmatrix} J^{\mathrm{Re}} & -J^{\mathrm{Im}} \\ J^{\mathrm{Im}} & J^{\mathrm{Re}} \end{vmatrix} \bullet \begin{vmatrix} \tilde{x}_i^{\mathrm{Re}} \\ \tilde{x}_i^{\mathrm{Im}} \end{vmatrix} = \begin{vmatrix} G^{\mathrm{Re}} \\ G^{\mathrm{Im}} \end{vmatrix}$$

- Jacobian matrix from the steady state model is used to estimate the impedance in the frequency domain

# Tech Team Protocol (Pt Catalyst)

**Table 1**
**Electrocatalyst Cycle and Metrics**
**Table revised March 2, 2010**

| | | |
|---|---|---|
| **Cycle** | Triangle sweep cycle: 50 mV/s between 0.6 V and 1.0 V. Single cell 25-50 $cm^2$ | |
| **Number** | 30,000 cycles | |
| **Cycle time** | 16 s | |
| **Temperature** | 80°C | |
| **Relative Humidity** | Anode/Cathode 100/100% | |
| **Fuel/Oxidant** | Hydrogen/$N_2$ ($H_2$ at 200 sccm and $N_2$ at 75 sccm for a 50 $cm^2$ cell | |
| **Pressure** | Atmospheric pressure | |
| | | |
| **Metric** | **Frequency** | **Target** |
| **Catalytic Mass Activity*** | At Beginning and End of Test minimum | ≤40% loss of initial catalytic activity |
| **Polarization curve from 0 to ≥1.5 A/$cm^2$**** | After 0, 1k, 5k, 10k, and 30k cycles | ≤30 mV loss at 0.8 A/$cm^2$ |
| **ECSA/Cyclic Voltammetry***** | After 10, 100, 1k, 3k, 10k, 20k and 30k cycles | ≤40% loss of initial area |

* Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% $H_2$ (bal $N_2$)/$O_2$ {or equivalent thermodynamic potential}, 100%RH, 80°C normalized to initial mass of catalyst and measured before and after test.
** Polarization curve per Fuel Cell Tech Team Polarization Protocol in Table 5.
*** Sweep from 0.05 to 0.6V at 20mV/s, 80°C, 100% RH.

# Tech Team Protocol (Catalyst Support)

**Table 2**
**Catalyst Support Cycle and Metrics**
**Table revised March 2, 2010**

| | | |
|---|---|---|
| **Cycle** | Hold at 1.2 V for 24 h; run polarization curve and ECSA; repeat for total 400 h. Single cell 25-50 $cm^2$ | |
| **Total time** | Continuous operation for 400 h | |
| **Diagnostic frequency** | 24 h | |
| **Temperature** | 80°C | |
| **Relative Humidity** | Anode/Cathode 100/100% | |
| **Fuel/Oxidant** | Hydrogen/Nitrogen | |
| **Pressure** | 150 kPa absolute | |
| | | |
| **Metric** | **Frequency** | **Target** |
| **Catalytic Activity*** | Every 24 h | ≤40% loss of initial catalytic activity |
| **Polarization curve from 0 to ≥1.5 $A/cm^{2**}$** | Every 24 h | ≤30 mV loss at 1.5 $A/cm^2$ or rated power |
| **ECSA/Cyclic Voltammetry***** | Every 24 h | ≤40% loss of initial area |

* Mass activity in A/mg @ 150 kPa abs backpressure at 857 mV iR-corrected on 6% $H_2$ (bal $N_2$)/$O_2$ {or equivalent thermodynamic potential}, 100%RH, 80°C normalized to initial mass of catalyst and measured before and after test.
** Polarization curve per Fuel Cell Tech Team Polarization Protocol in Table 5
*** Sweep from 0.05 to 0.6V at 20mV/s, 80°C, 100% RH.

# Tech Team Protocol (Membrane/Chemical)

**Table 3**
**MEA Chemical Stability and Metrics**
**Table revised December 10, 2009**

| | | |
|---|---|---|
| **Test Condition** | **Steady state OCV, single cell 25-50 $cm^2$** | |
| **Total time** | 500 h | |
| **Temperature** | 90°C | |
| **Relative Humidity** | Anode/Cathode 30/30% | |
| **Fuel/Oxidant** | Hydrogen/Air at stoics of 10/10 at 0.2 $A/cm^2$ equivalent flow | |
| **Pressure, inlet kPa abs (bara)** | Anode 150 (1.5), Cathode 150 (1.5) | |
| | | |
| **Metric** | **Frequency** | **Target** |
| **$F^-$ release or equivalent for non-fluorine membranes** | At least every 24 h | No target – for monitoring |
| **Hydrogen Crossover ($mA/cm^2$)*** | Every 24 h | $\leq$2 $mA/cm^2$ |
| **OCV** | Continuous | $\leq$20% loss in OCV |
| **High-frequency resistance** | Every 24 h at 0.2 $A/cm^2$ | No target – for monitoring |
| **Shorting resistance**** | Every 24 h | >1,000 ohm $cm^2$ |

* Crossover current per USFCC "Single Cell Test Protocol" Section A3-2, electrochemical hydrogen crossover method.

** Measured at 0.5V applied potential, 80°C and 100% RH $N_2/N_2$. Compression to 20% strain on the GDL.

# Tech Team Protocol (Membrane/Mechanical)

| Table 4<br>Membrane Mechanical Cycle and Metrics<br>(Test using a MEA)<br>Table revised December 10, 2009 | | |
|---|---|---|
| **Cycle** | **0% RH (2 min) to 90°C dewpoint (2 min), single cell 25-50 $cm^2$** | |
| **Total time** | Until crossover >2 $mA/cm^2$ or 20,000 cycles | |
| **Temperature** | 80°C | |
| **Relative Humidity** | Cycle from 0% RH (2 min) to 90°C dewpoint (2 min) | |
| **Fuel/Oxidant** | Air/Air at 2 SLPM on both sides | |
| **Pressure** | Ambient or no back-pressure | |
| | | |
| **Metric** | **Frequency** | **Target** |
| **Crossover*** | Every 24 h | $\leq$2 $mA/cm^2$ |
| **Shorting resistance**** | Every 24 h | >1,000 ohm $cm^2$ |

* Crossover current per USFCC "Single Cell Test Protocol" Section A3-2, electrochemical hydrogen crossover method.

** Measured at 0.5 V applied potential, 80°C and 100% RH $N_2/N_2$. Compression to 20% strain on the GDL.