Development of Micro-Structural Mitigation Strategies for PEM Fuel Cells:

Morphological Simulations and Experimental Approaches

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Project ID# FC049

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Overview

Timeline

- Start Date: January 2010
- End Date: March 2013
- Percent Complete: 99%

Barriers

A. Durability
   - Pt/carbon-supports/catalyst layer

B. Performance

C. Cost (indirect)

Budget

- Total Project: $6,010,181
  - $ 4,672,851 DOE + FFDRC
  - $ 1,337,330 Ballard
- Funding Received:
  - $ 4,672,851 (Total)
    - FY 2012: $ 1,409,851

Project Partners

- Georgia Institute of Technology
- Los Alamos National Laboratory
- Michigan Technological University
- Queen's University
- University of New Mexico

Relevance and Objective

- **Objective**
  - **Identify/Verify Catalyst Degradation Mechanisms**
    - Pt dissolution, transport/ plating, carbon-support oxidation and corrosion, and ionomeric changes and conductivity loss
    - Mechanism coupling, feedback, and acceleration
  - **Correlate Catalyst Performance & Structural Changes**
    - Catalyst layer morphology and composition; operational conditions
    - Gas diffusion layer properties
  - **Develop Kinetic and Material Models for Aging**
    - Macro-level unit cell degradation model, micro-scale catalyst layer degradation model, molecular dynamics degradation model of the platinum/carbon/ionomer interface
  - **Develop Durability Windows**
    - Operational conditions, component structural morphologies and compositions
- **Impact**
  - **Increasing catalyst durability**
    - Based on understanding of the effect of structure and operating conditions

DOE Technical Targets
Electrocatalyst and Support

Electrocatalyst and Support Degradation	
Metric	**Target**
Polarization curve from 0 to >1.5 A/cm2**	<30 mV loss at 0.8 A/cm2
ECSA/Cyclic Voltammetry***	<40% loss of initial area
Pt Dissolution Protocol: Triangle sweep cycle: 50 mV/s between 0.6 V and 1.0 V for 30,000 cycles. Single cell 25-50 cm^2, 80°C, H_2/N_2, 100/100%RH, ambient pressure	
Carbon Support Corrosion Protocol: Hold at 1.2 V for 24 h; run polarization curve and ECSA; repeat for total time of 400 hours, single cell 25-50 cm^2, 80°C, H_2/N_2, 100/100%RH , 150kPa (abs)	

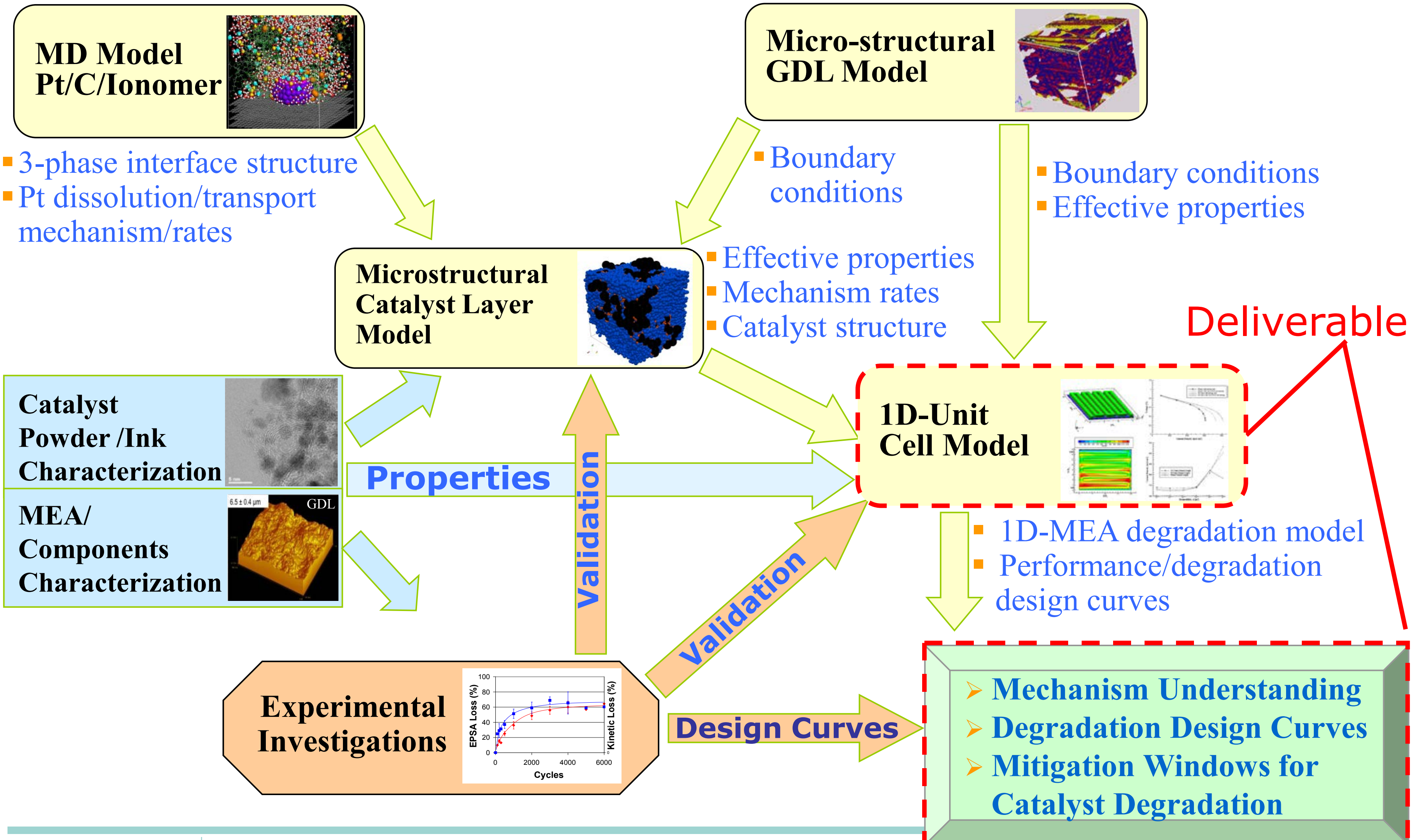
** Polarization curve per Fuel Cell Tech Team Polarization Protocol
*** Sweep from 0.05 to 0.6V at 20mV/s, 80ºC, 100% RH.

- 2020 Durability Targets
  - Automotive Drive Cycle: 5000 hours
  - CHP and Distributed Generation
    - 1 – 10kW$_e$: 60,000 hours
    - 100kW – 3MW: 80,000 hours

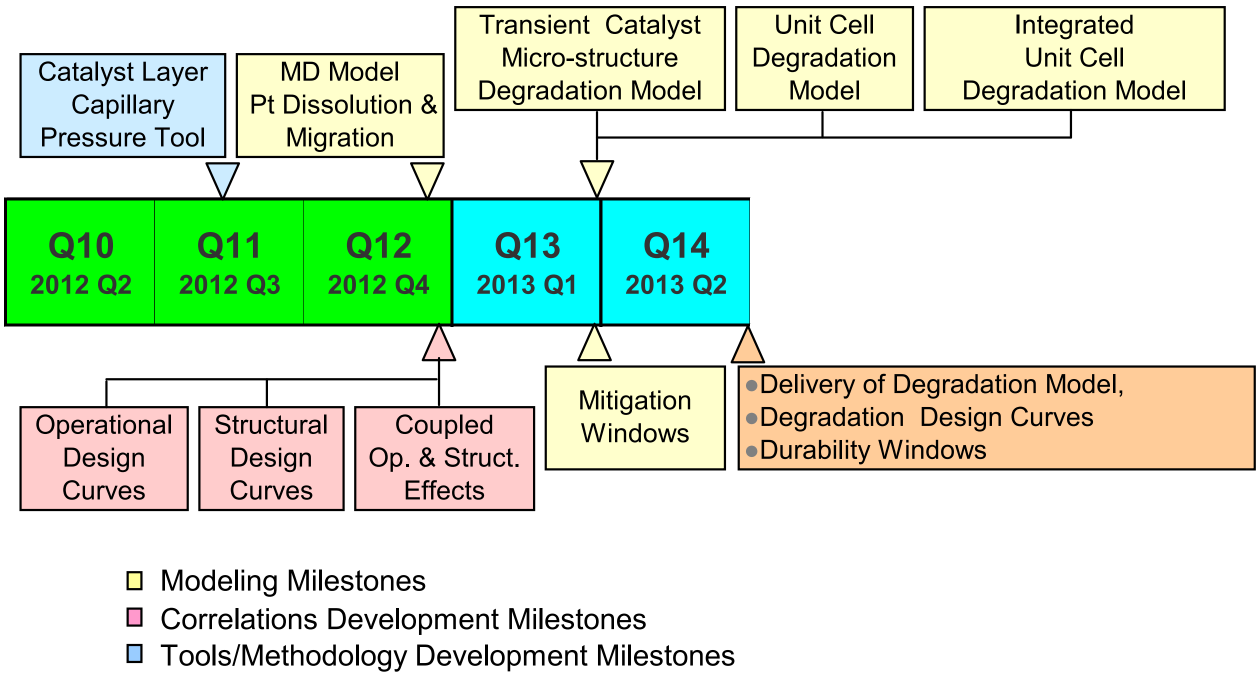
Approach

- **Model Development**
  - 3 scale modeling approach
    - Molecular dynamics model of the Pt/ carbon/ionomer interface, Pt dissolution and transport process
    - Microstructural catalyst layer model to simulate the effect of local operational conditions and effective properties on performance and degradation
    - Unit cell model predicting BOL performance and voltage degradation
- **Experimental Investigations/Characterization**
  - Systematic evaluation of performance loss, catalyst layer structural and compositional changes of different catalyst layer structures/compositions under a variety of operational conditions
    - Carbon support type, Pt/C ratio, ionomer content, ionomer EW, catalyst loading
    - Potential, RH, O_2 partial pressure, temperature
    - Accelerated stress tests (ASTs) combined with in-situ/ex-situ techniques
    - Performance loss breakdown to determine component contribution
    - In-situ/ex-situ characterization to quantify effect of electrode structure and composition on performance and durability
- **Develop Durability Windows**
  - Operational conditions, component structural morphologies and compositions
- **DOE Working Groups (Durability and Modeling)**
  - Interaction and data exchange with other projects

Approach Schematic



Milestones & Timeline
FY 2012 to 2013



- **Deliverables (June 2013)**
  - Validated 1D-MEA Durability Model (OpenFoam) and documentation
  - Correlations linking operational conditions, catalyst component properties, layer structure and composition with performance and degradation
  - Durability Windows

2012/2013 Milestones

Model Development

- 1-D MEA Model ✓
  - Pt dissolution
    - Linking platinum dissolution to multi-step ORR (underway)
    - Pt-dissolution, agglomeration, formation of PITM (underway)
  - Carbon support oxidation/ corrosion
    - 2-stage pathway
  - Validation with AST cycling
  - Correlations and development of design windows
- Micro-structural Catalyst Model
  - Mass transport limitations and low loaded catalysts ✓
  - Platinum dissolution, Carbon corrosion ✓
- Molecular Dynamics Model ✓
  - Platinum dissolution within 3-phase interface
  - Transport of Pt^{n+} within membrane phase

Experimental Investigations ✓

- Complete operational studies for carbon corrosion and platinum dissolution
  - Selected experimental studies for model development support
- Correlations and development of design windows

Collaborators Activities

- Complete chemical structural analysis of degraded catalyst layers/MEAs ✓
- Capillary pressure measurements on catalyst layer ✓
- Quantify interface changes in degraded MEAs X

✓= Completed, ✓= expected completion by end of project, X = Dropped

Summary of Technical Accomplishments

Completed Studies
Operational Parameters

Summary of Operational Effect				
Stressor Evaluated	**Testing Modifications**	**BOT Performance**	**Mechanism Investigated**	**Degradation Rate**
Upper Potential (UPL)	0.9-1.6V (LSAC)*	Not Applicable	Pt Dissolution C-Corrosion	Increases with UPL
	0.9 - 1.4V (MSAC)**			
Lower potential Limit	0.1, 0.4, 0.6, 0.8 to 1.0V	Not Applicable	Pt Dissolution	Lower degradation @ LPL >0.6V
Cycle Number	1.2 V, 0 to 4700 Cycles	Not Applicable	Mixed: Pt Dissolution, C-Corrosion	Increases with Cycling
	1.4 V, 0 to 2100 Cycles		C-Corrosion	Increases with time at UPL
Dwell Time	1.0V, 5 – 600 seconds	Not Applicable	Pt Dissolution	Increases with dwell time
	1.4 V, 5-600 seconds		C-Corrosion	Increases with time at UPL
Relative Humidity	50%RH to Oversaturated	Increases with RH	Pt Dissolution C-Corrosion	Increases with RH
Temperature	60-85°C	Insignificant impact for loadings >0.2 mg/cm² Pt Decreases with T for loading ≤0.2mg/cm² Pt	Pt Dissolution	Slight increase with T
	60-85°C, 1.4V		C-Corrosion	Increases with T
O_2 Concentration	Air vs. N_2	Not Applicable	Pt Dissolution	N_2 (No PITM) < Air (PITM)
	5% to 100%	Increases with O_2	Pt Dissolution	No impact
H_2 Concentration	20, 60, 100% H_2	Not Applicable	Pt Dissolution	No Impact on rate Impact on PITM*** band location

Standard AST: Air/H_2, 100% RH, 5 psig, 80°C, 0.6 V (30 sec) to 1.2V (60 sec), 4700 cycles
Pt Dissolution AST: Air/H_2, 100% RH, 5 psig, 80°C, 0.6 V (30 sec) to 1.0 V (60 sec), 4700 cycles
C-Corrosion AST: Air/H_2, 100% RH, 5 psig, 80°C, 0.6 V (30 sec)--> 1.4V (Time TBD), Cycles
Reference MEA: 50:50 Pt/C, Nafion® ionomer, 0.4/0.1 mg/cm² (Cathode/anode), Ballard CCM, Nafion® NR211, BMP GDLs
Ballard Test Cell: 1D, 45cm² active area

* LSAC = Low surface area carbon support
** MSAC = Medium surface area carbon support
*** PITM = Pt in the membrane

Completed Studies
Structure/Composition Parameters

Summary of Structure/Composition Effect

Structure Evaluated	Testing Modifications	BOT Performance	Mechanism Investigated	Degradation Rate
Catalyst Loading	0.05 - 0.5 mg/cm^2 Pt	Decreases with loading < 0.2mg/cm^2 Affected by RH, T and [O2] operation	Pt Dissolution C-Corrosion	Increases for loadings < 0.2 mg/cm^2 Pt
Carbon Ratio	30, 40, 50, 60, 80 Pt/C	No Impact (30-60 Pt/C) Decreases for Pt/C = 80	Pt Dissolution C-Corrosion	Decreases with Pt/C ratio (30 to 60)
Carbon Support	LSAC50, MSAC50, Vulcan® 50, HSAC50 (1), HSAC50(2)	Kinetic Loss: HSAC < MSAC < LSAC Performance: No trend	Pt Dissolution C-Corrosion	HSAC > MSAC >LSAC
	1.0V UPL		Pt Dissolution	No significant Impact
Carbon Support (Heat Treated Catalyst)	HSAC50-HT(1), HSAC50-HT(2)	Decreases with HT	Pt Dissolution C-Corrosion	Improves with HT
Ionomer Loading	Nafion® Content: 12, 23, 30, 38, 50%	Optimal @ 30%	Pt Dissolution C-Corrosion	Optimal @ 30%
Ionomer EW	850-1100 EW	No Significant Impact	Pt Dissolution C-Corrosion	No significant Impact
Impact of Membrane	Reinforced Membrane (1.2V&1.3V AST)	Similar to baseline	Pt Dissolution C-Corrosion	Similar wrt baseline Lower wrt baseline (1.3VAST)
Catalyst Layer Process	1 and 8% crack area	similar	Pt Dissolution C-Corrosion	Similar 8% cracked CCL substantially higher (1.3V AST)
Impact of GDL-MPL	No MPL	Lower wrt baseline	Pt Dissolution C-Corrosion	No Impact

Standard AST: Air/H_2, 100% RH, 5 psig, 80 ^{o}C, 0.6 V (30 sec)--> 1.2V (60 sec), 4700 cycles

Pt Dissolution AST : Air/H_2, 100% RH, 5 psig, 80 ^{o}C, 0.6 V (30 sec)--> 1.0 V (60 sec), 4700 cycles

C-Corrosion AST: Air/H_2, 100% RH, 5 psig, 80 ^{o}C, 0.6 V (30 sec)--> 1.4V (Time TBD), Cycles (TBD)

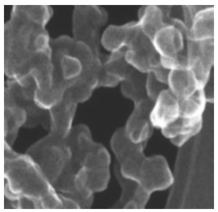
LSAC = Low surface area carbon support
MSAC = Medium surface area carbon support
HSAC = High surface area carbon support

Reference MEA: 50:50 Pt/C, Nafion® ionomer, 0.4/0.1 mg/cm^2 (Cathode/anode), Ballard CCM, Nafion® NR211, BMP GDLs

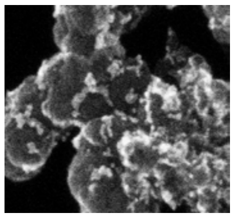
Ballard Test Cell: 1D, 45cm^2 active area

Correlations
Structure → Properties → Performance

Carbon Support Structure → **Catalyst Powder Structure** → **Processing** → **Catalyst Layer Structure** → **Catalyst Layer Properties** → **Performance**



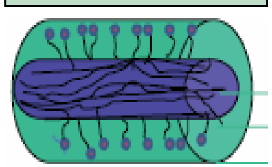
- Aggregate Size & Surface Area
- Morphology
- Surface Species (XPS, SEM)
- Aggregate Pore Size Distribution & Porosity



- Bulk Density
- Pt Agglomerate Size
- Morphology
- Surface Species (XPS, SEM)
- Pt/C Pore Size Distribution & Porosity

Ionomer

- Type
- EW
- Surface Energy

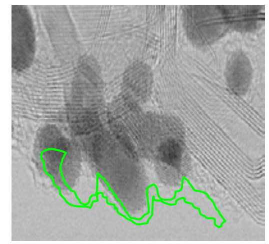


Composition:
- Ionomer Content
- Pt loading

Component Properties:
- Ionomer
- Catalyst

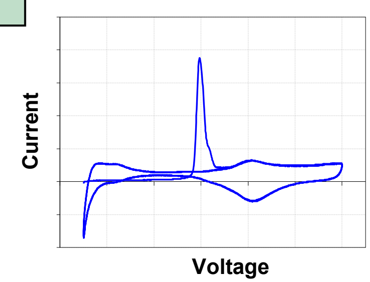
Processing Parameters

Catalyst and Ionomer Dispersion

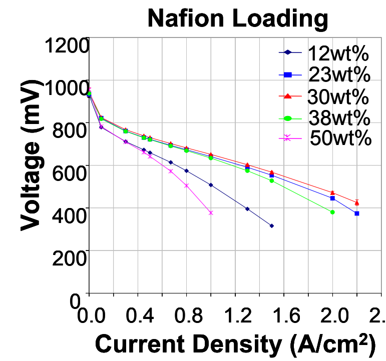


- CL Thickness
- Ionomer Volume Fraction
- Porosity
- Pore Size Distribution
- Tortuosity (ionomer & pore)
- ECSA

- Protonic Conductivity
- O2 Diffusivity
- ECSA
- Thickness

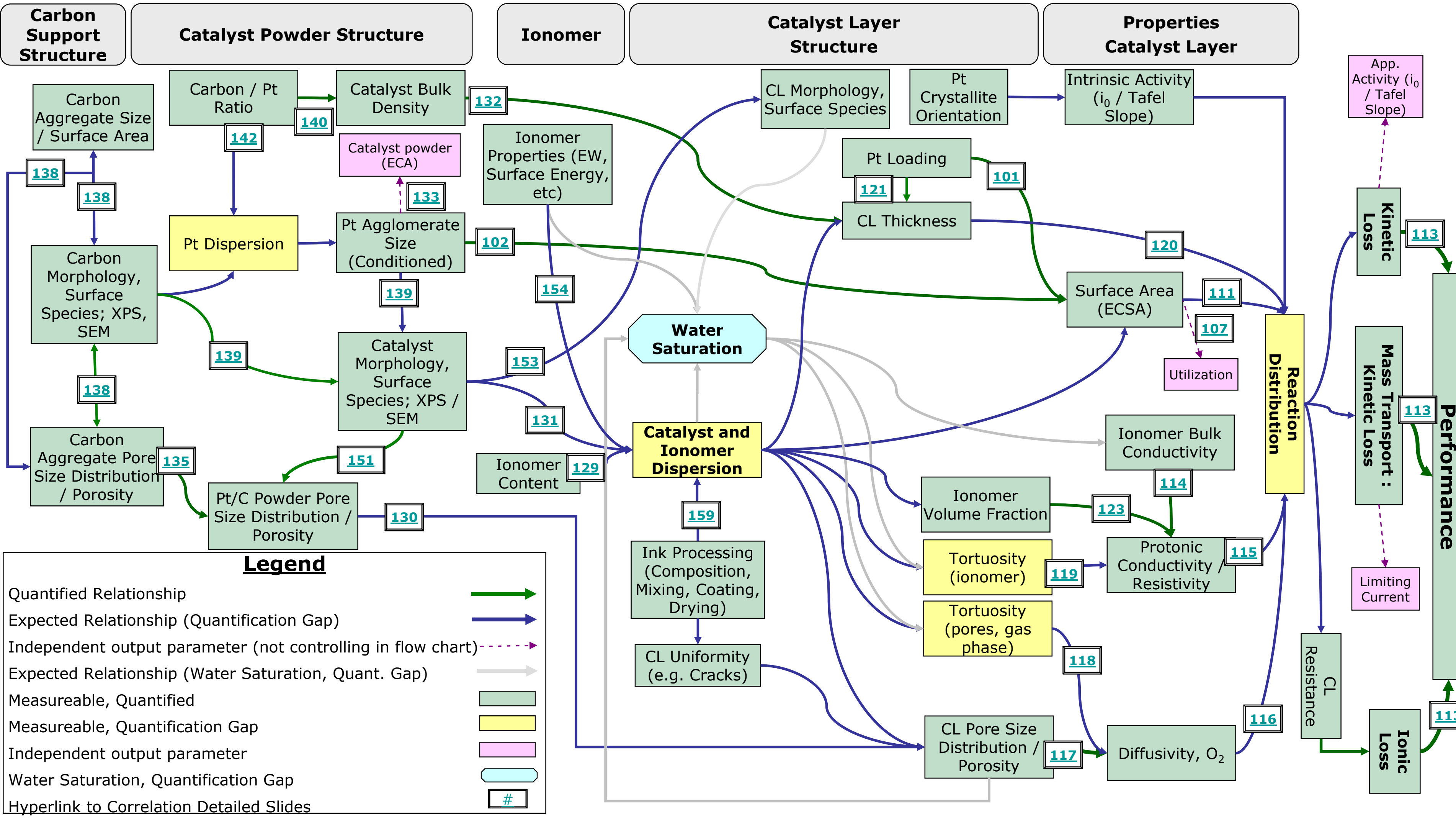


Reaction Distribution

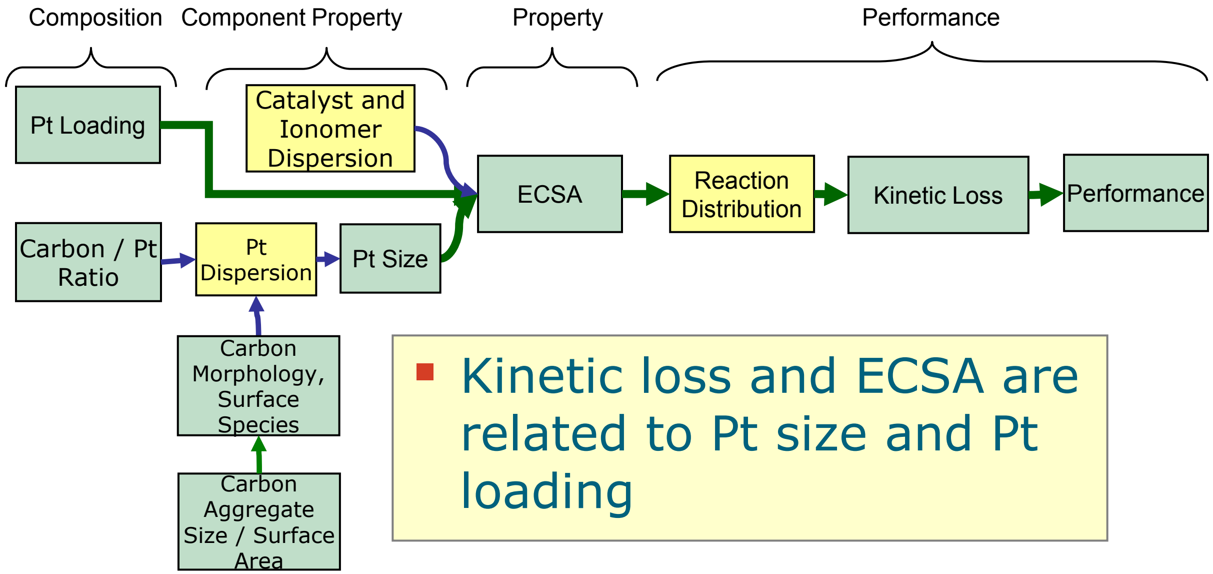


Polarization Losses:
- Kinetic
- Ohmic
- Mass Transport

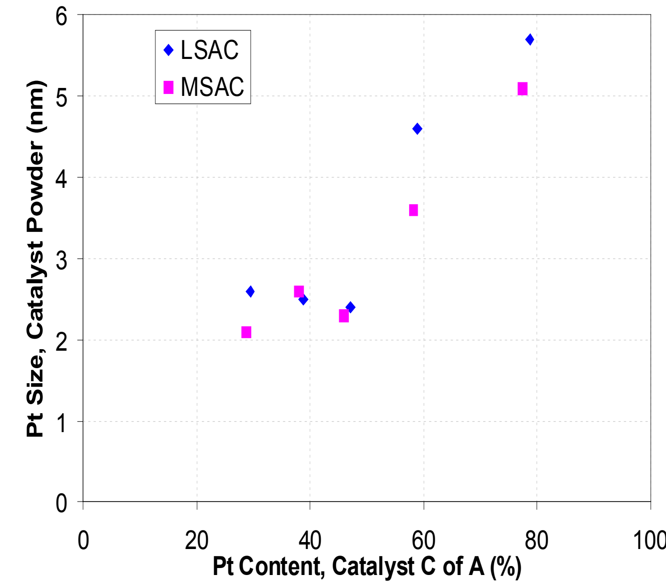
Interactions Flowchart

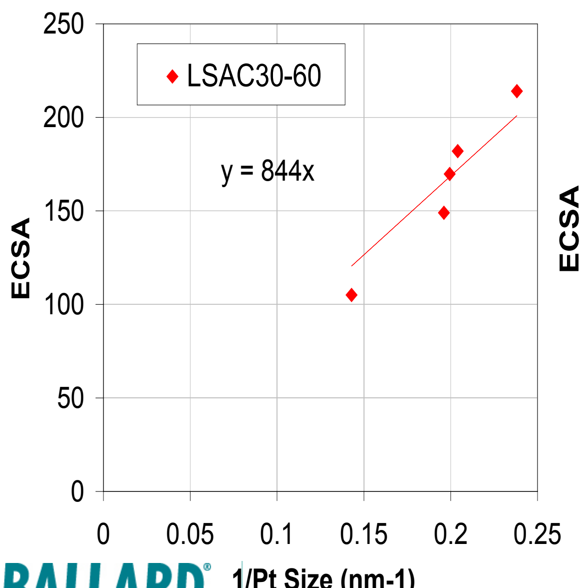


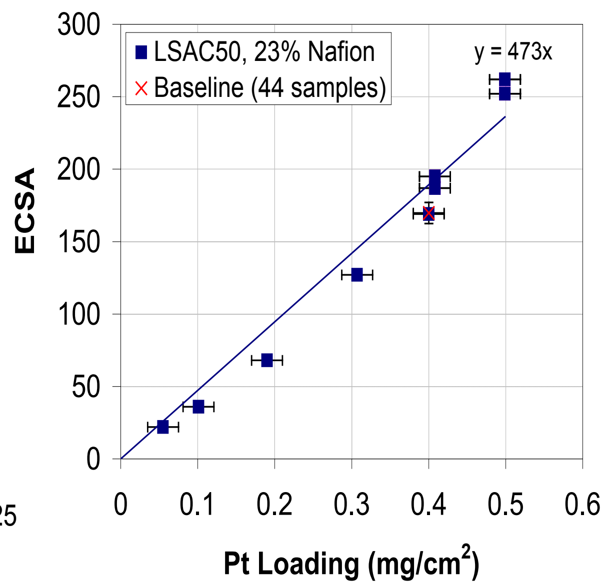
Design Lever Example
ECSA

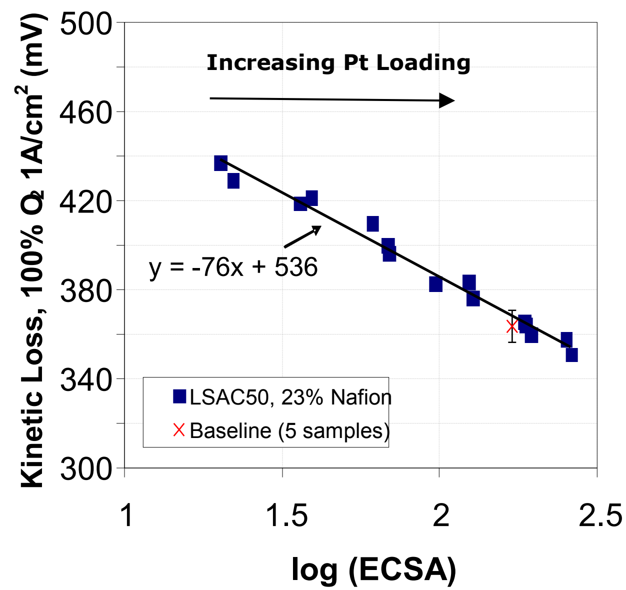


- Kinetic loss and ECSA are related to Pt size and Pt loading

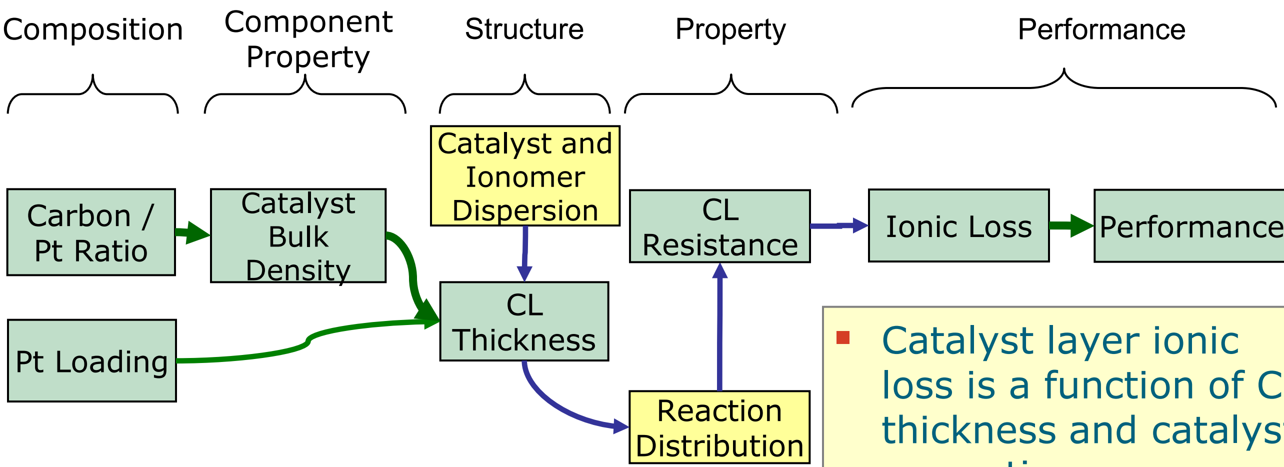


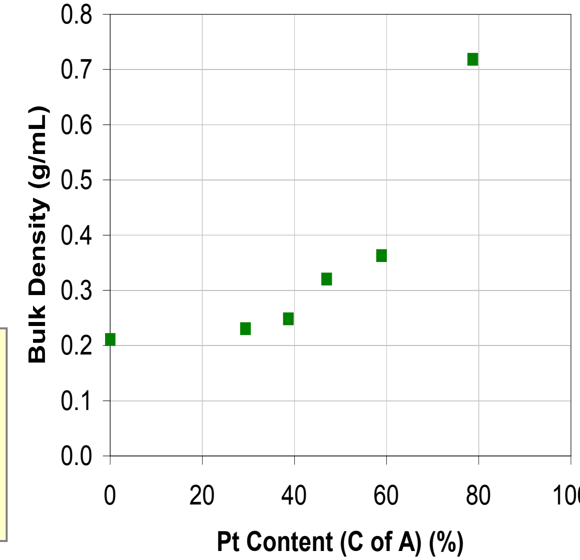




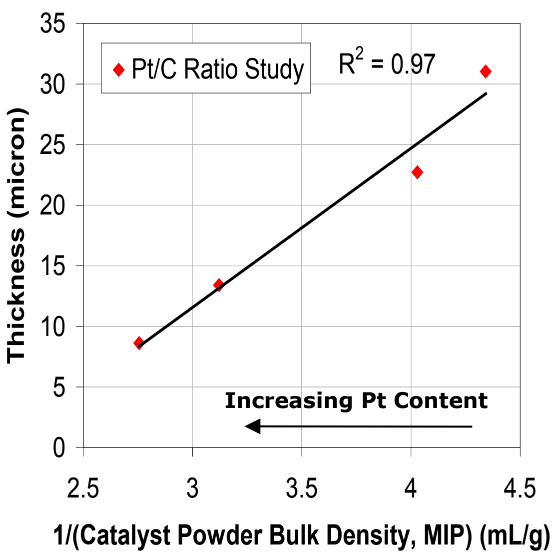


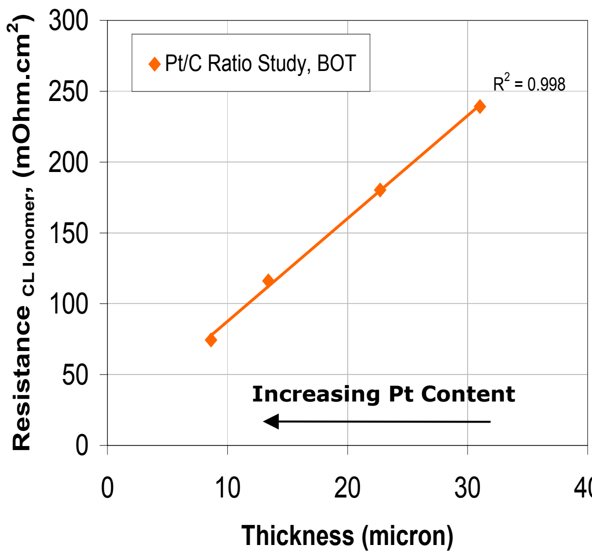
Design Lever Example
Thickness

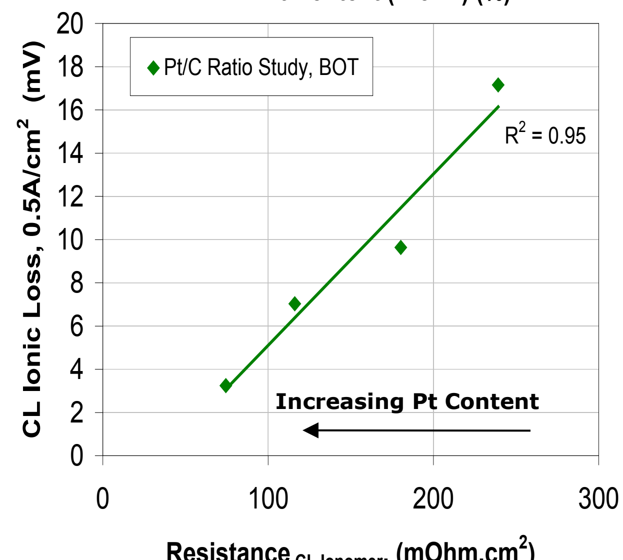




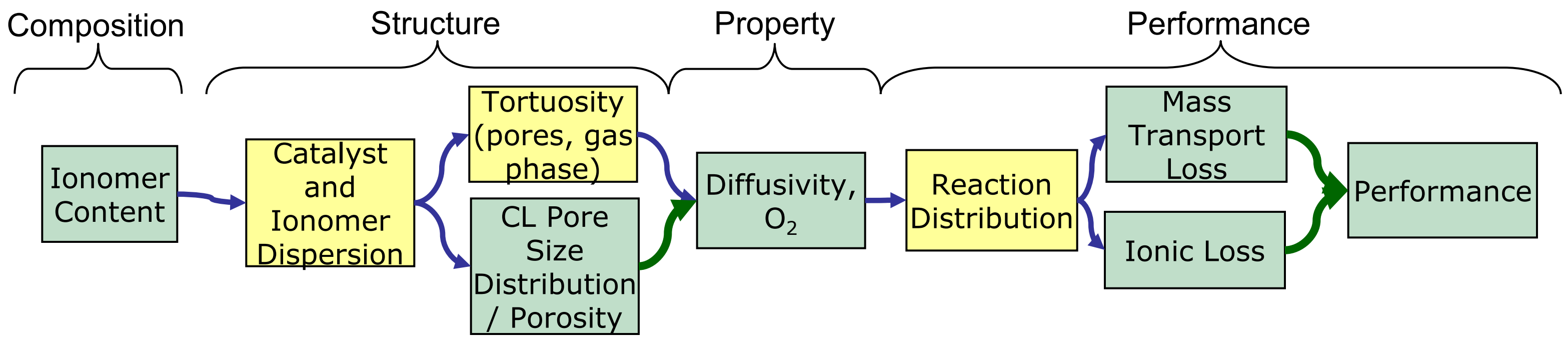
- Catalyst layer ionic loss is a function of CL thickness and catalyst properties

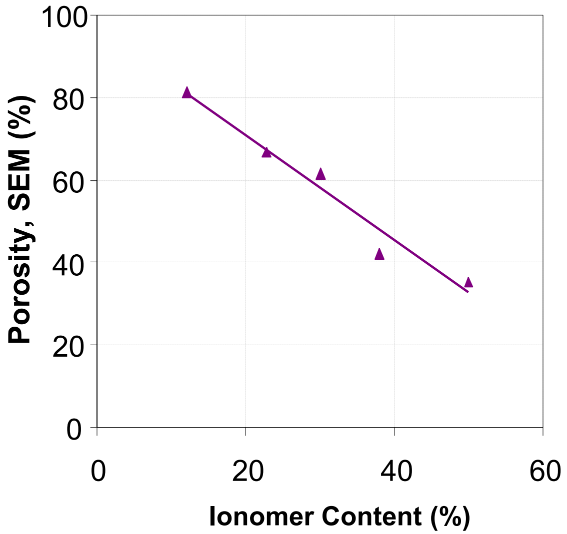


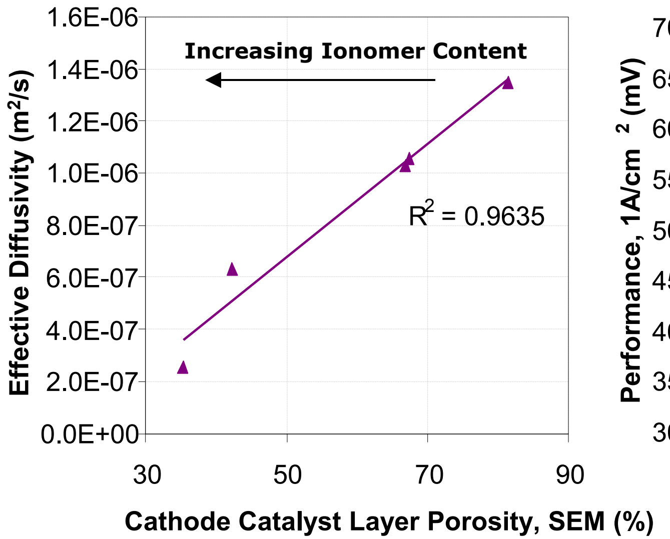


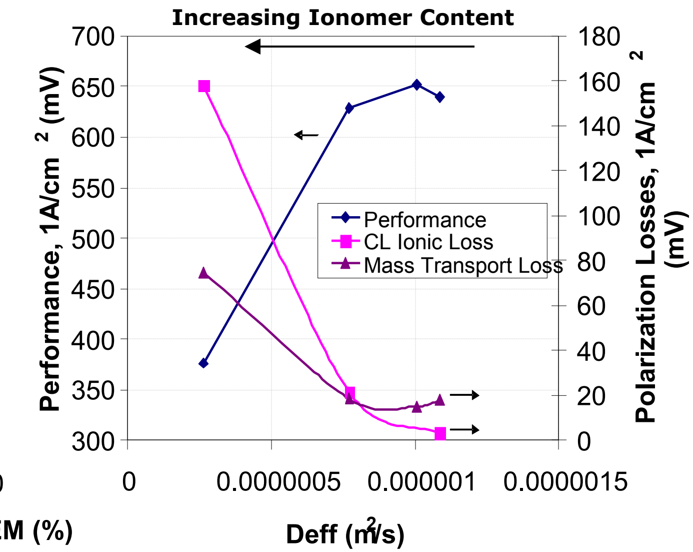


Design Lever Example
Effective Diffusivity



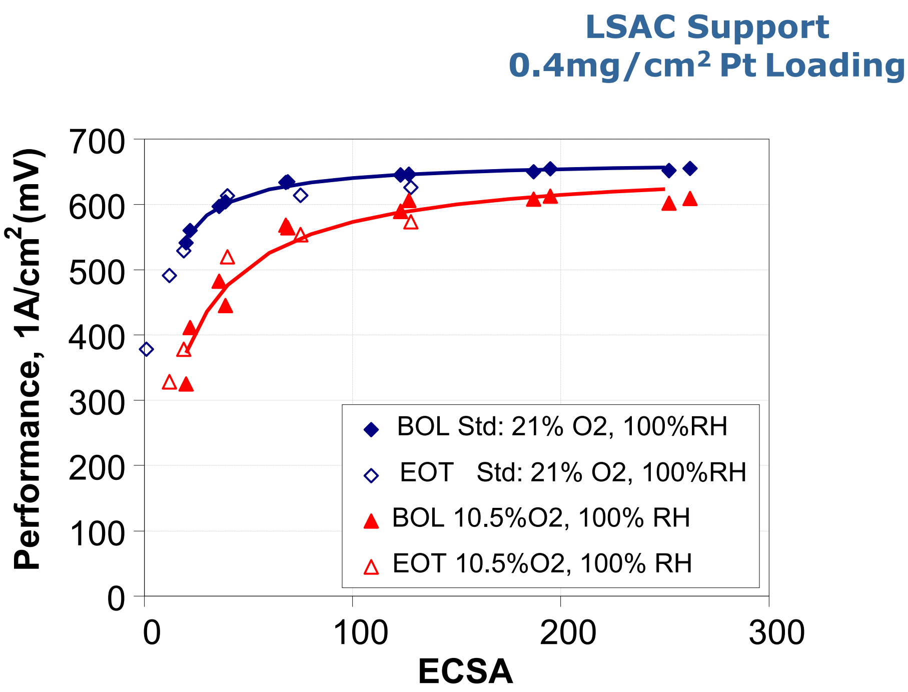


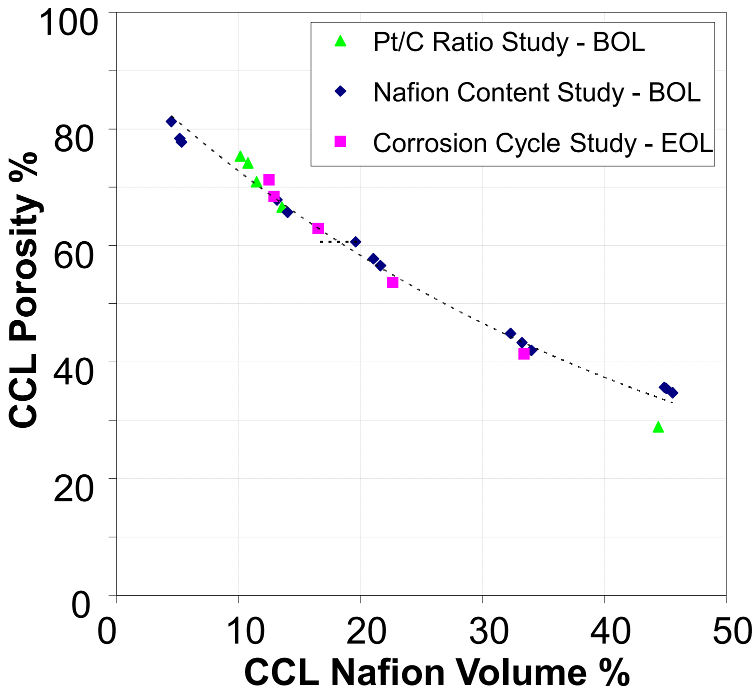




- Increase in ionomer content decreases porosity and diffusivity
  - Increase in mass transport losses (oxygen concentration effects)
  - CL Ionic losses increase due to reaction distribution shifting further into the catalyst layer

BOT and EOT Trends - Examples





- Performance correlates with ECSA of BOL and degraded catalyst layers
- The relationship between catalyst layer porosity and Nafion® volume% follows same trend for BOT and EOT catalyst layers

Catalyst Layer Component Properties
Impact Matrix - Catalyst Layer Composition

Effect of Composition and Component Properties on Catalyst Layer Degradation

	Design Lever	Range Studied	Pt Dissolution Change in Parameter of Range Studied				Carbon Corrosion
			ECSA Loss	Total Pt Loss	PITM	Pt growth	Catalyst Layer Thinning
Ionomer	**Ionomer Content** (1.2V UPL)	12 % to 50 %	48 to 70 %		0.02 to 0.16 mg/cm^2		
Ionomer	**Ionomer Property: EW** (1.2V UPL)	850 EW to 1050 EW					
Carbon Support*	**Graphitic Content, Carbon Powder** (Carbon Type Effect, 1.0V UPL)	49 % to 57 %		↓ 0.23 to 0.07 mg/cm^2	↓ 0.08 to 0.05 mg/cm^2		↓ 38 to 15 %
Carbon Support*	**Graphitic Content, Carbon Powder** (Carbon Type Effect, 1.2V UPL)	49 % to 57 %	↓ 94 to 62 %	↓ 0.28 to 0.10 mg/cm^2	↓ 0.11 to 0.06 mg/cm^2	↓ 6.1 to 2.7 nm	↓ 69 to 18 %
Platinum	**Thickness** Pt/C Ratio, 1.2V UPL)	9µm to 29µm	↓ 62 to 52 %	↓ 0.09 to 0.05 mg/cm^2	↓ 0.09 to 0.05 mg/cm^2		
Platinum	**Pt Loading** (Absolute Values) (1.2V UPL)	0.05 to 0.50 mg/cm^2	12 to 124 ECSA Units	↓ 0.09 to 0.07 mg/cm^2	0.03 to 0.07 mg/cm^2	↓ 4.2 to 2.8 nm	
Platinum	**Pt Loading** (% Change Values) (1.2V UPL)	0.05 to 0.50 mg/cm^2	↓ 81 to 43 %	↓ 78 to 7 %	↓ 58 to 7 %	↓ 78 to 59 %	
Other	**MPL Effect** (1.3V UPL)	Baseline vs. No Cathode MPL layer					
Other	**Membrane Effect** (1.3V UPL)	N211 vs. Supplier A	↓ 88 to 69 %		↓ 0.09 to 0.07 mg/cm^2		↓ 71 to 59 %

* other parameters may also have an impact

Legend
Negligible Effect (within error)
Small Effect <30% ECSA Loss or Thinning Variation
Large Effect >30% ECSA Loss or Thinning Variation

Degradation Effect
Impact Matrix - Catalyst Layer Structure

<table>
<tr><th colspan="6">Effect of Degradation on Catalyst Layer Structure / Properties and Polarization Losses</th></tr>
<tr><th colspan="2">Degradation Mechanism</th><th>Composition / Component Property Affected</th><th>CL Structure Change</th><th>CL Property Change</th><th>Polarization Loss Change</th></tr>
<tr><td rowspan="2">Pt Dissolution</td><td>Pt Loss:
PITM
Washout</td><td>Pt Content ↓</td><td rowspan="2">Pt Depletion at Membrane / Catalyst Interface</td><td rowspan="2">ECSA ↓</td><td rowspan="2">Kinetic Loss
CL Ionic Loss</td></tr>
<tr><td>Pt Agglomeration</td><td>Pt Size</td></tr>
<tr><td rowspan="3">Carbon Degradation</td><td>Carbon Oxidation</td><td>Oxygen Species on Carbon Surface</td><td></td><td>Ionomer Resistivity ↓</td><td>Kinetic Loss ↓
CL Ionic Loss ↓</td></tr>
<tr><td rowspan="2">Carbon Corrosion / Loss</td><td>Carbon Content ↓</td><td>Thickness ↓
Porosity ↓
Electronic Percolation* ↓
Ionomer Vol. Fraction
Tortuosity</td><td>Diffusivity ↓
Electronic Resistivity*</td><td>Kinetic Loss
CL Ionic Loss</td></tr>
<tr><td>Pt Content ↓</td><td></td><td>ECSA ↓</td><td>Kinetic Loss
CL Ionic Loss</td></tr>
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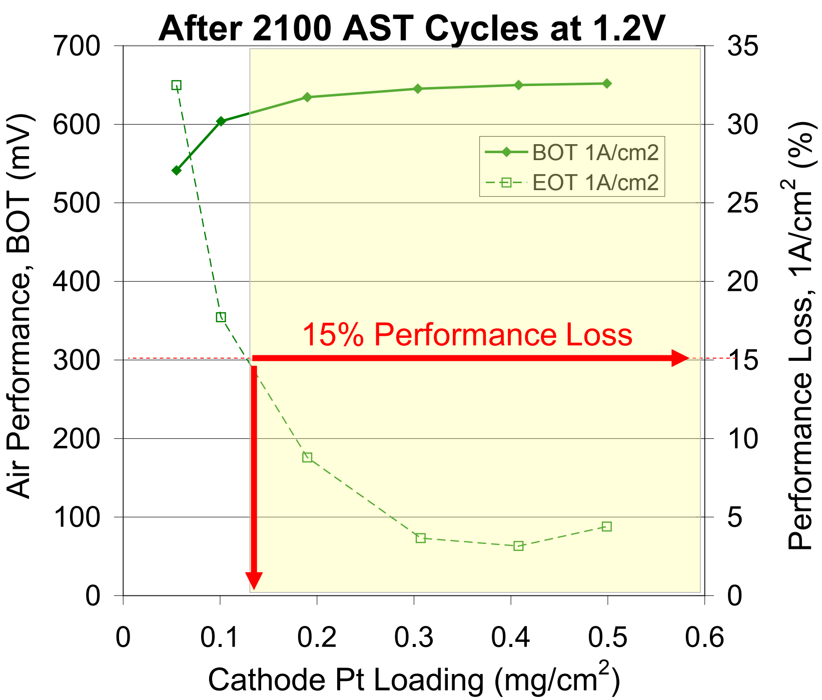
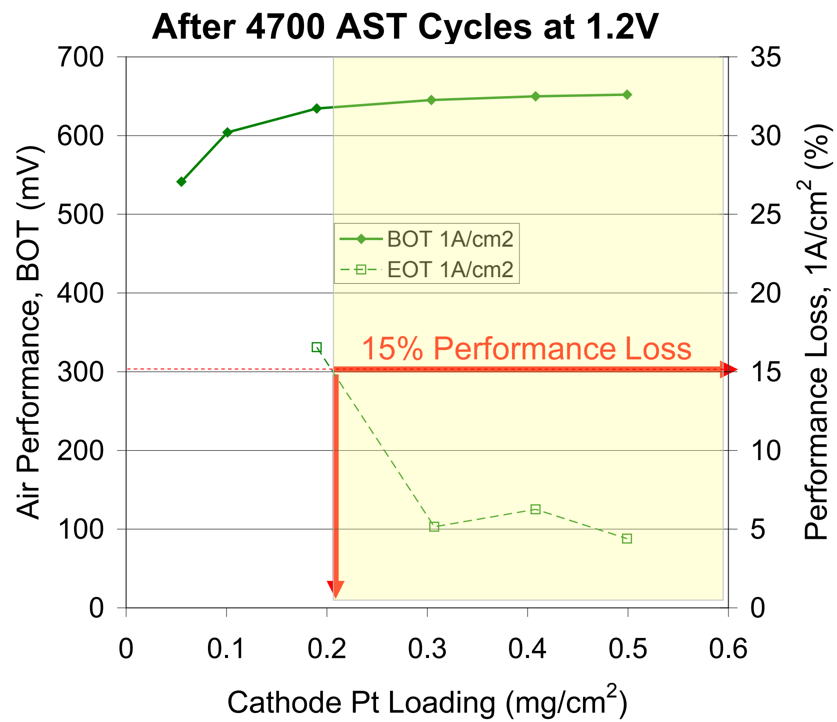
* Hypothesis

Durability Windows
Cathode Pt Loading (Pt50-LSAC Catalyst)



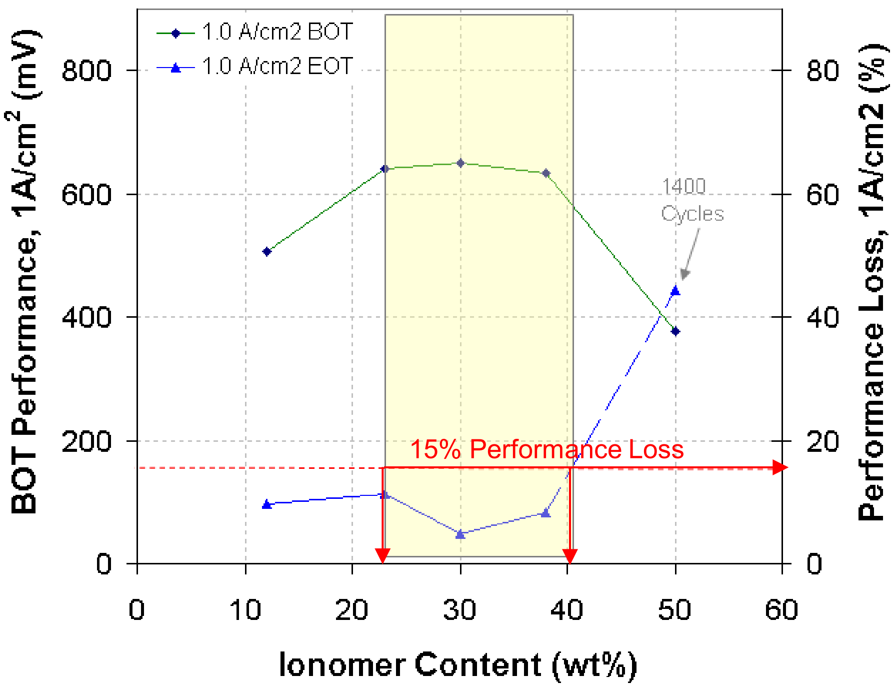


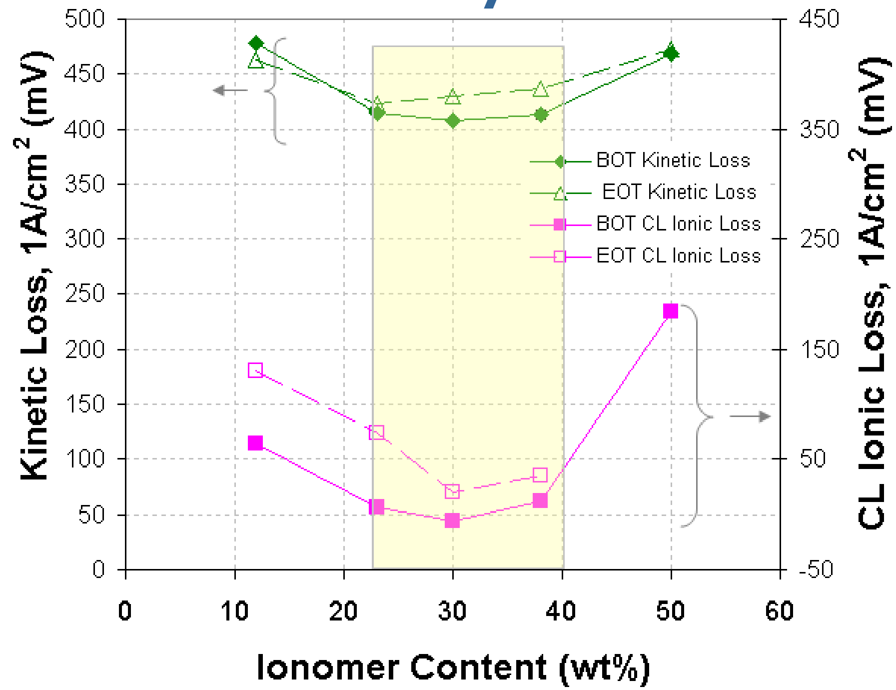
- A cathode Pt loading $\geq$ 0.13mg/cm² and 0.21 mg/cm² is needed to ensure a $\leq$ 15% performance loss after 2100 and 4700 AST cycles, respectively.

AST: 0.6 (30sec)→1.2V (60 sec), 100% RH, 80°C
Diagnostic Air Polarization: Air/H_2, 100% RH, 5 psig, 75°C

Durability Windows
Ionomer Content (Pt50-LSAC Catalyst)

Performance Loss at 1.2V UPL and 4700 cycles



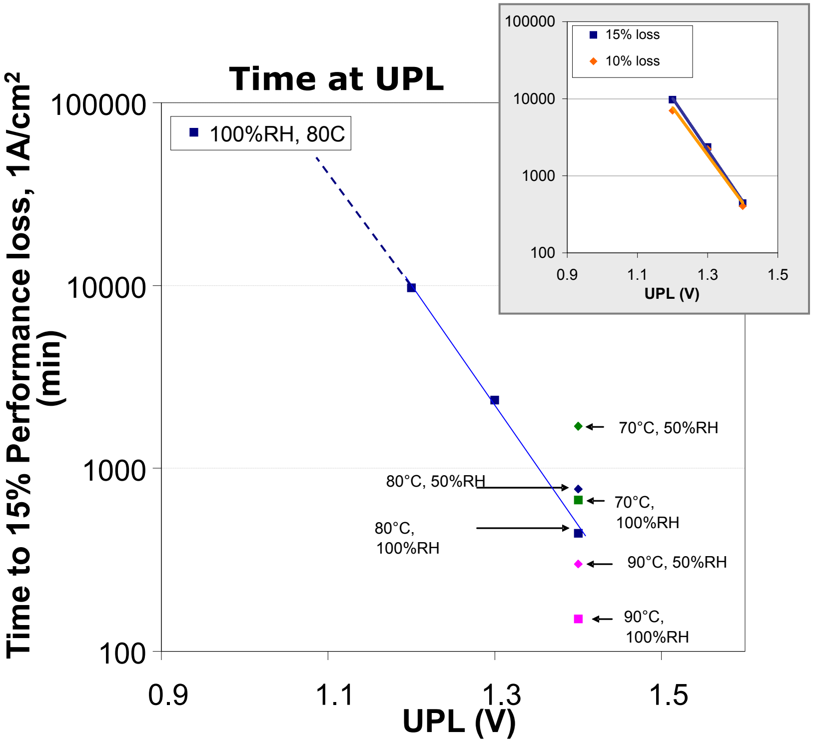


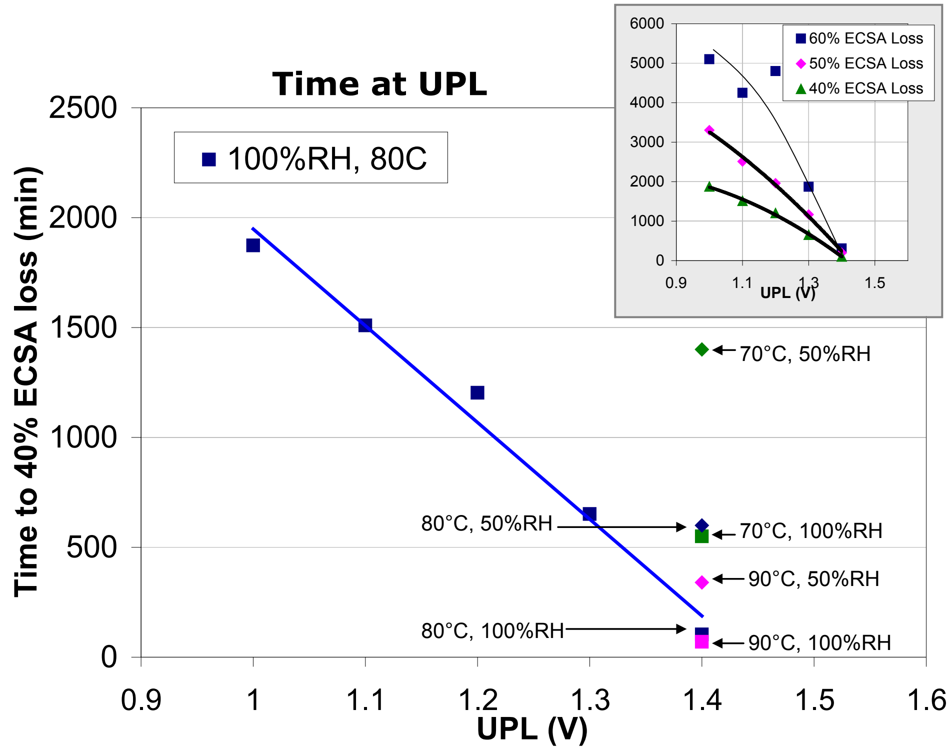
- A catalyst layer ionomer content of 23 to 40% would meet a durability target of 15% performance loss after 4700 AST cycles (30,000 DOE Pt dissolution cycles)

AST: 0.6 (30sec)→1.2V (60 sec, 100% RH, 80C
Diagnostic Air Polarization: Air/H_2, 100% RH, 5 psig, 75°C

Durability Windows
Upper Potential Limit (UPL)

LSAC Support, 0.4mg/cm² Pt Loading





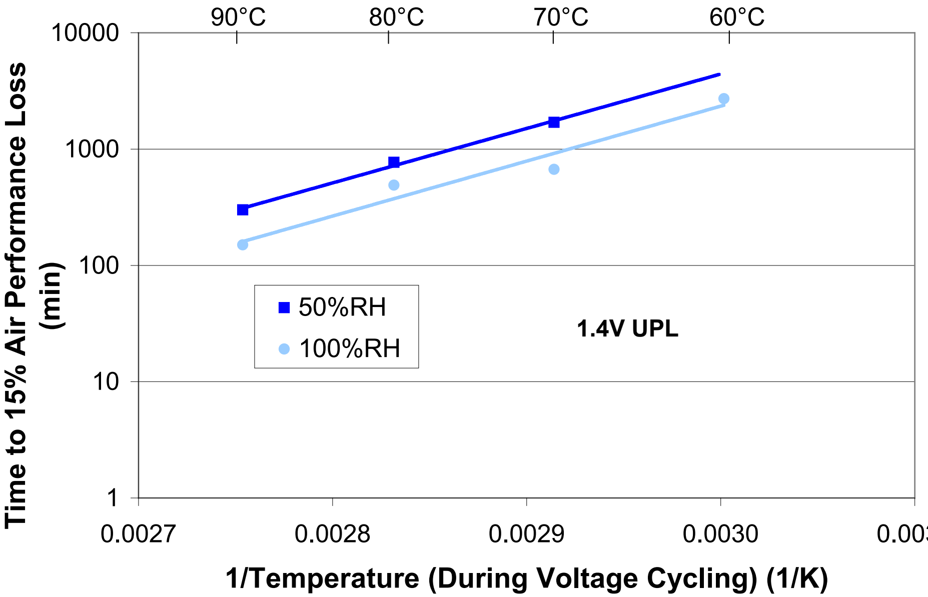
- The time at UPL to 15% air performance loss increases exponentially with decreasing upper potential limit due carbon corrosion
- The time at UPL to 40% ECSA loss is linearly dependent on the UPL
- ~20x increase in lifetime by reducing UPL of 1.4V to 1.2 V

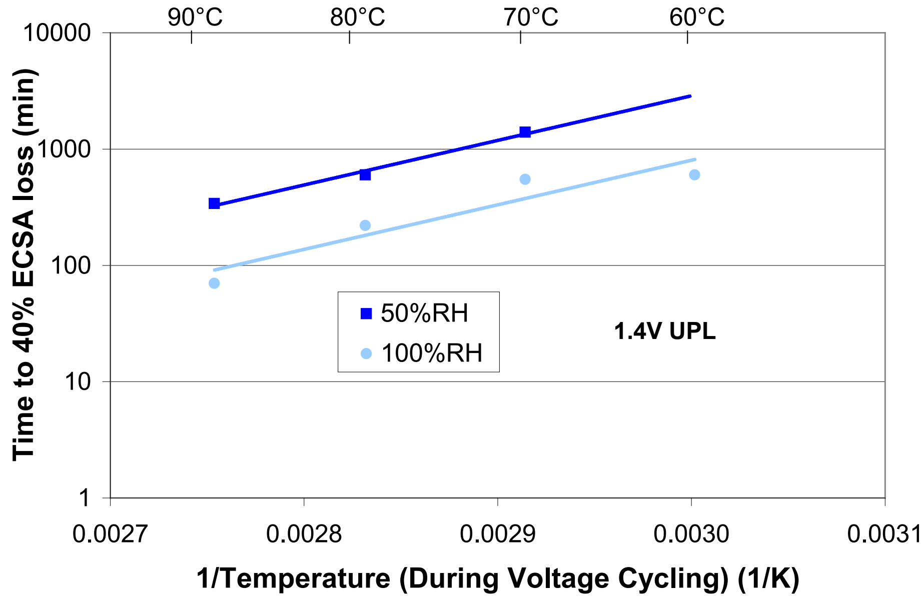
BALLARD®

AST: 0.6 (30sec)→UPL (60 sec), 100% RH, 80C
Diagnostic Air Polarization: Air/H_2, 100% RH, 5 psig, 75°C

Durability Windows
Temperature

LSAC Support, 0.4mg/cm² Pt Loading, 1.4V UPL





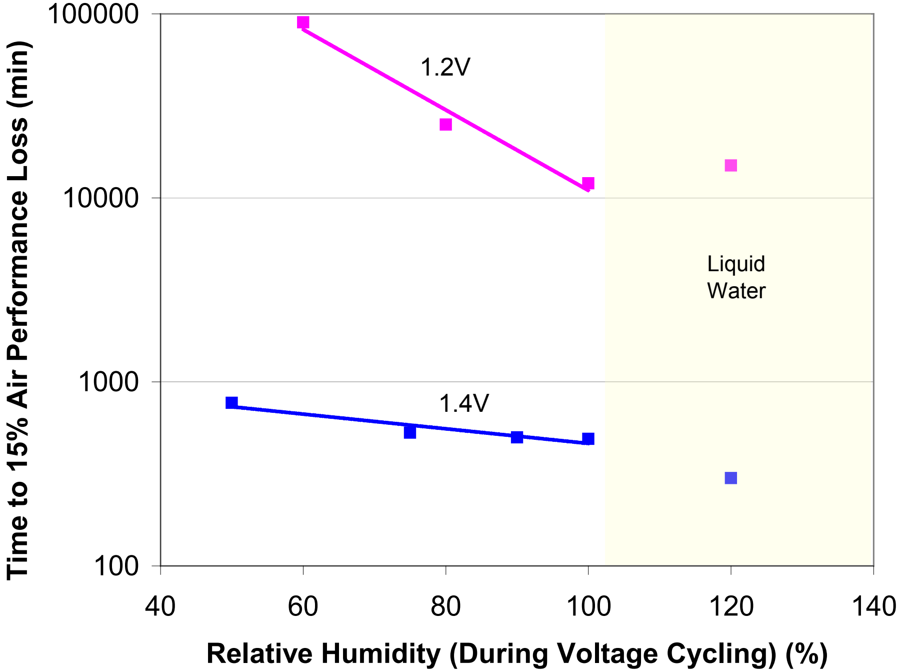
- The dependence on temperature follows an Arrhenius type behaviour under both wet (100%RH) and dry (50%RH) conditions
- ~15 times increase in lifetime at 1.4V UPL by reducing temperature from 90 to 60°C

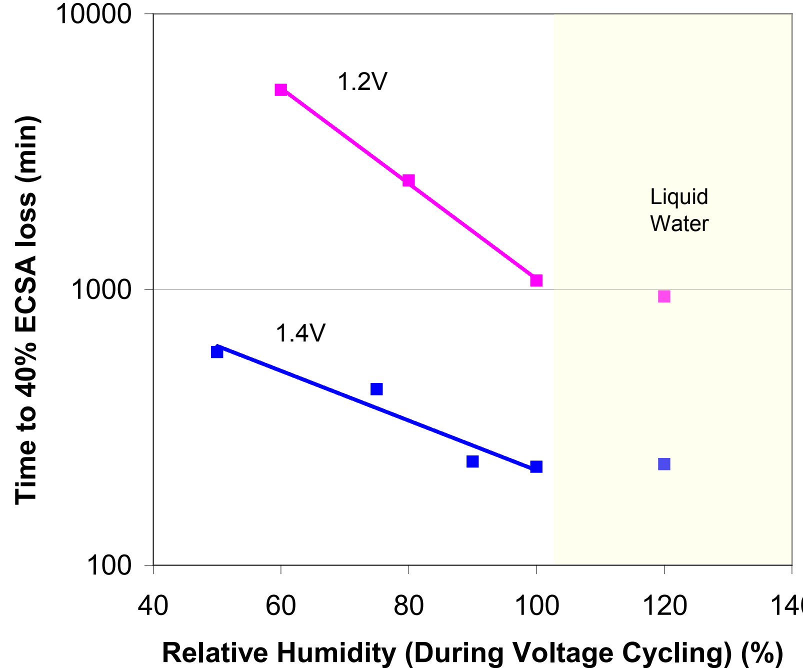
BALLARD®

AST: 0.6 (30sec) → 1.4V (600 sec), 4700 cycles, 100% RH, X°C
Diagnostic Air Polarization (STC): Air/H_2, 100% RH, 5 psig, 75°C

Durability Windows
Relative Humidity

LSAC Support, 0.4mg/cm² Pt Loading, 1.4V UPL





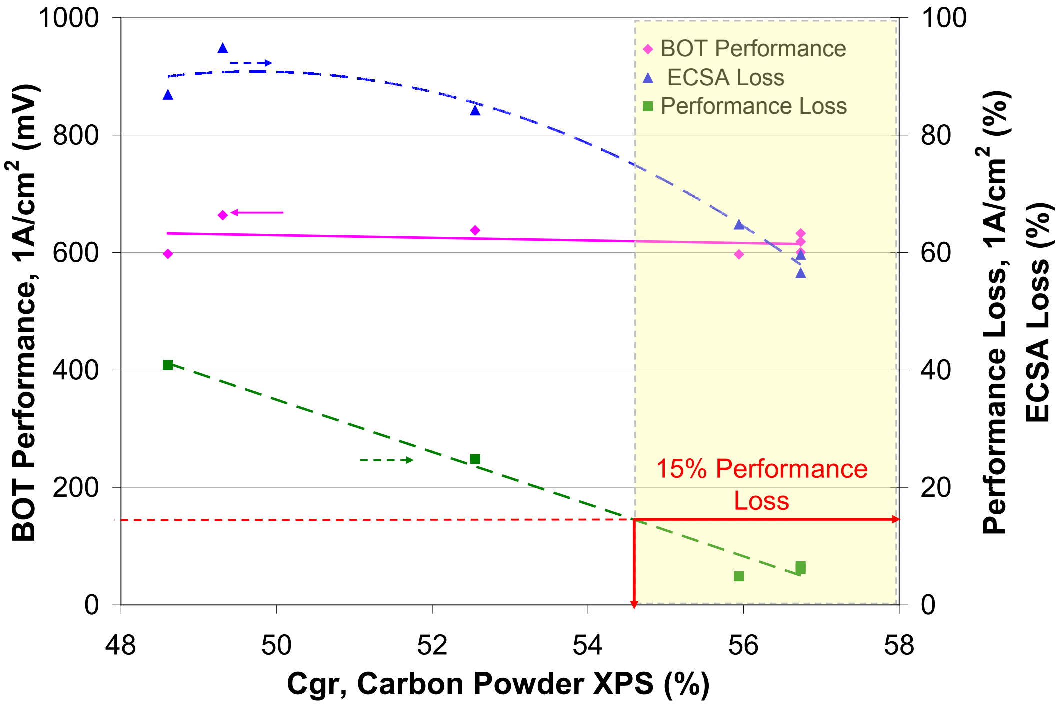
- Pt dissolution and corrosion increase with increasing RH (50%-100% RH)
- ~10 times increase in lifetime by reducing RH from 100% to 60% (1.2V UPL)

AST: 0.6 (30sec) → 1.2V(60 sec) / 1.4V (600 sec), 4700 cycles, X% RH, 80C
Diagnostic Air Polarization (STC): Air/H_2, 100% RH, 5 psig, 75°C

BALLARD

Durability Windows
Carbon Support

AST Cycle Performance Loss at 1.2V UPL and 4700 cycles

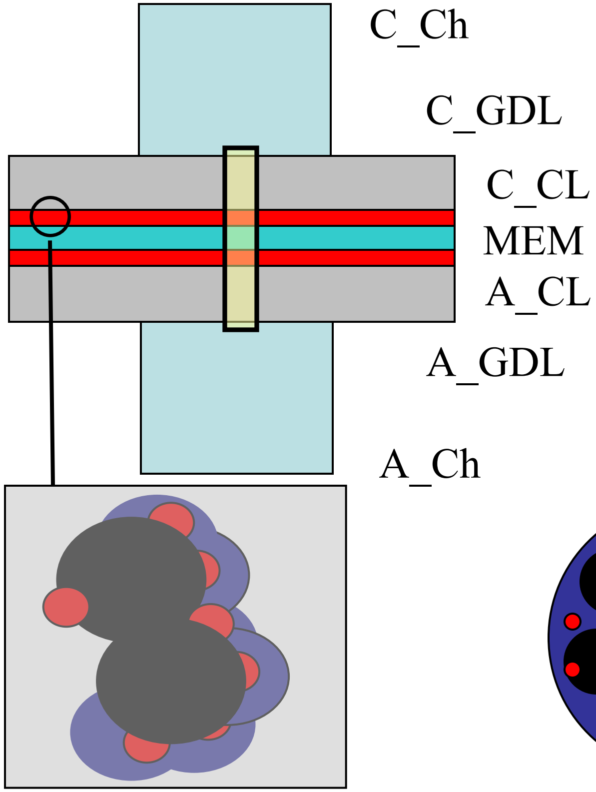


Pt/C ratio of 50 wt% supported on low, medium, and high surface area carbon powders.

- Surface graphite content of ≥55% will meet a durability target of 15% performance loss.

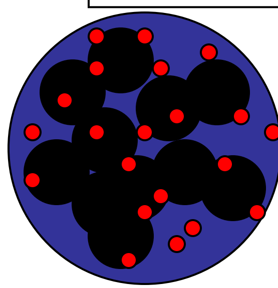
AST: 0.6 (30sec)→1.2V (60 sec), 100% RH, 80C
Diagnostic Air Polarization: Air/H_2, 100% RH, 5 psig, 75°C

Unit Cell Model Framework



Transport Equation Summary:

- Charge transport (electrons and protons)
  - Ohm`s Law
- Gas transport (H_2, O_2, N_2, and H_2O)
  - Mixture-based Fickian approach
- Dissolved water transport (membrane and catalyst)
- Energy transport (Ohmic heating, entropic waste heat)
  - Conductive transport
- Liquid water transport
  - Capillary driven with phase change



Discrete Catalyst Model:

- No sub structure
- Effective properties only
- Gas transport in bulk pores
- Utilization through layer

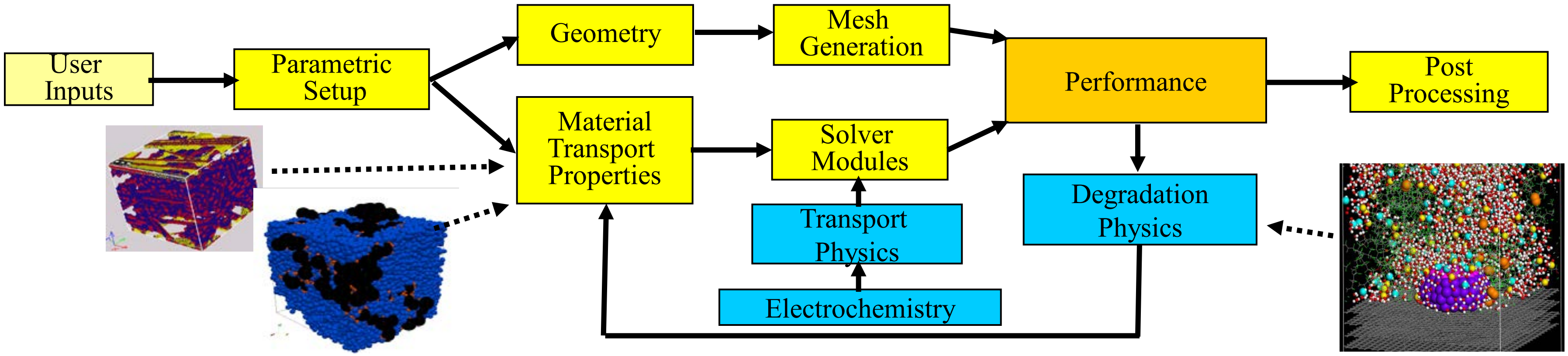
Agglomerate Catalyst Model:

- Sub structure
  - water-filled
  - ionomer filled
- Effectiveness factor in the volume of the structure

Assumptions

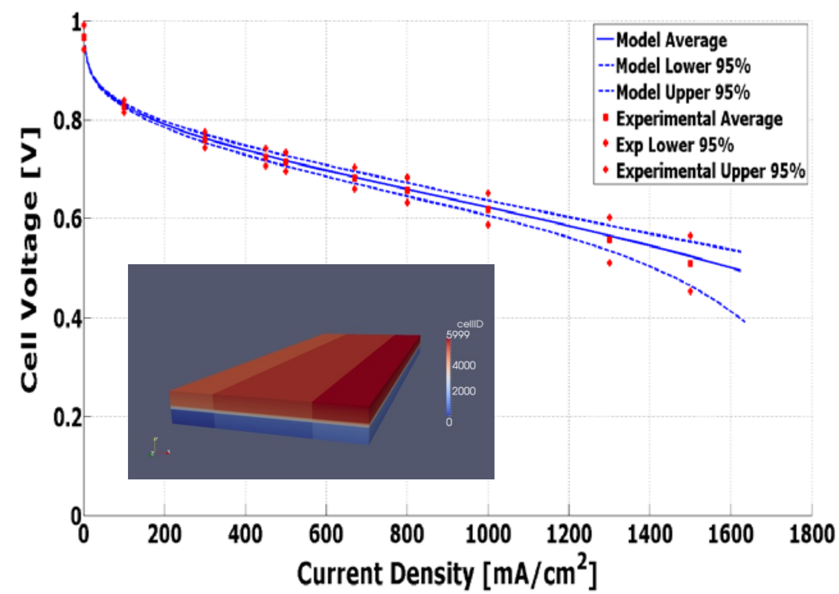
- Membrane is impermeable
- Channel flow is uniform from channel to channel
- Channel flow along the length has constant composition
- Pressure drop along the cell is negligible

Open-source FC-PEM Performance and Durability Model



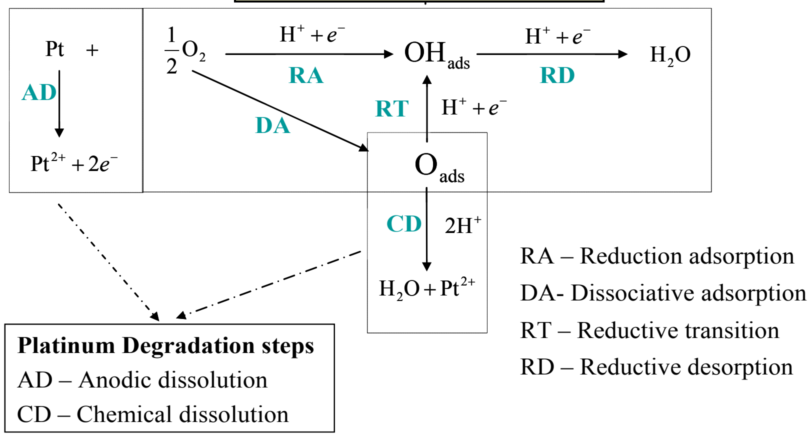
Open-source FC-PEM Package

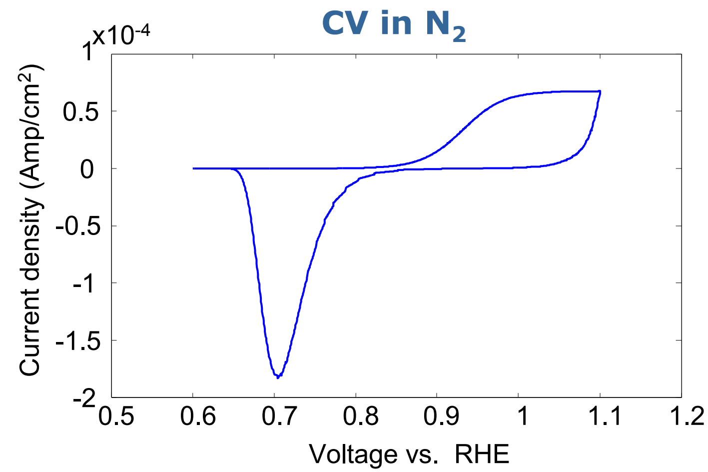
- Developed in the Open-source package OpenFOAM®
- Beginning of Life Performance
  - Multi-step kinetics (HOR/ORR)
  - Modifiable Materials and Composition (statistical)
  - Modifiable Operating Conditions (statistical)
- Validation across operational conditions and material data sets (i.e. RH, T, loading, ionomer content etc.)



Open-source FC-PEM Performance and Durability Model

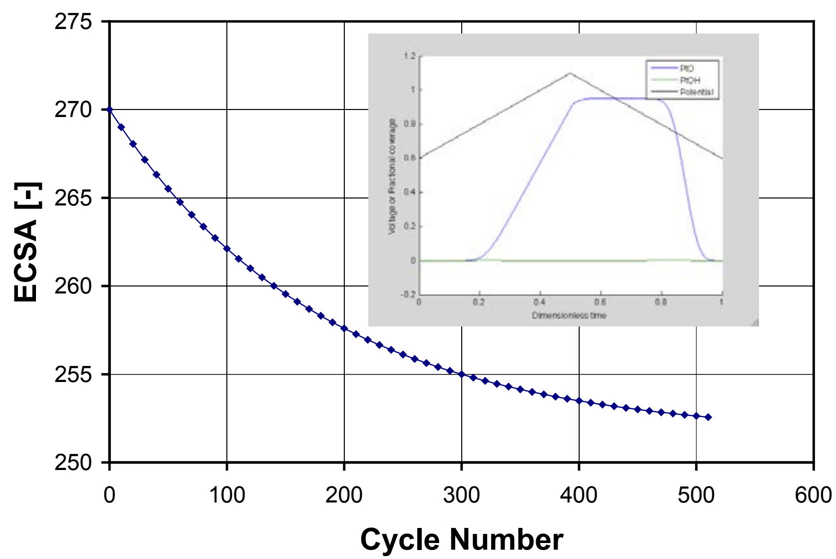
Multi-Pathway Pt ORR





Open-source FC-PEM Package

- Durability and AST Cycling Model
  - Platinum Dissolution processes
    - Modified Pt Oxide Model
    - Dissolution Pathway adapted into multi-step pathway
  - Carbon oxidation and corrosion
    - Two Surface Oxidation and Corrosion Steps
    - Layer collapse and composition change



Future Work
Plan Forward to June 2013

- **Deliver 1D-MEA Model and Final Report**
  - **OpenFoam® 1D MEA model codes, validation data, and model documentation**
  - **Design curves and correlations linking cathode catalyst layer degradation with structure, composition and operational conditions**
  - **Durability design windows**

Organizations /Partners

- **Prime: Ballard Material Products/Ballard Power Systems**
  S. Wessel, D. Harvey, V. Colbow
  - Lead: Micro-structural/MEA/Unit Cell modeling, AST correlations, characterization, durability windows
- **Queen's University – Fuel Cell Research Center**
  K.Karan, J. Pharoah
  - Micro-structural Catalyst Layer/Unit Cell modeling, catalyst characterization
- **Georgia Institute of Technology**
  S.S. Jang
  - Molecular modeling of 3-phase interface & Pt dissolution/transport
- **Los Alamos National Laboratory**
  R. Borup, R. Mukundan
  - Characterization of catalyst, MEA (NI)
- **Michigan Technological University**
  J. Allen, R. S. Yassar
  - Capillary pressure and interface characterization, catalyst layer capillary pressure tool development
- **University of New Mexico**
  P. Atanassov, K. Artyushkova
  - Carbon corrosion mechanism, characterization of catalyst powder/layers

Queen's University FCRC

Georgia Institute of Technology

Summary

- **Relevance**
  - Improved understanding of durability for fuel cell materials and components
  - Recommendations for the mitigation of MEA degradation that facilitates achieving the stationary and automotive fuel cell targets
- **Approach**
  - Develop forward predictive MEA degradation model using a multi-scale approach
  - Investigate degradation mechanisms and correlate degradation rates with catalyst microstructure, material properties, and cell operational conditions
- **Technical Accomplishments**
  - 1D-MEA degradation model, validated BOL simulations with experimental results for catalyst layer composition, structure and operational conditions
    - Validated Pt dissolution model using AST cycles
  - Developed model for mixed Pt oxide formation from water and air for performance and Pt dissolution
  - Correlated performance and voltage loss breakdown with cathode catalyst layer structure and composition and catalyst properties
  - Developed catalyst layer durability windows and design curves
- **Collaborations**
  - Project team partners GIT, LANL, MTU, Queen's, UNM
  - Participation in DOE Durability and Modeling Working Group

Acknowledgement

- **Thank you:**
  - Financial support from the U.S. DOE-EERE Fuel Cells Technology Program
  - Support from project managers/advisor Kathi Epping Martin, David Peterson, and John Kopasz
  - Project Collaborators

Technical Backup Slides

Project Applicability to Industry

Model Predictions of Performance & Degradation based on MEA Components, Composition, and Processing (Structure)

Catalyst Powder | Membrane | Plates | MEA
Catalyst Ink | Catalyst Layer | GDL

Component Properties and Structure

Cat. Powder
- BET SA
- Mass activity
- ECA

Cat. Ink
- Pt/C/Ionomer Vol. fractions

Catalyst Layer
- Mass activity
- ECSA
- Utilization
- Thickness
- Conductivity (H^+, e^-,T)
- Capillary pressure
- Porosity.

GDL
- Thickness
- Tortuosity
- Diffusivity
- Porosity
- Capillary Press.
- Cond. (e^-,T)

Plate
- Cond. (e-,T)
- Geometry

Membrane
- EW
- Thickness

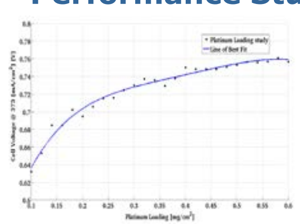
BOL Performance

- ECSA
- Exchange current density
- Tafel slope
- Mass activity
- HFR

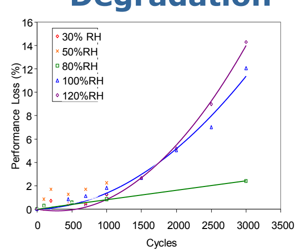
Operating Conditions

1D Unit Cell Model

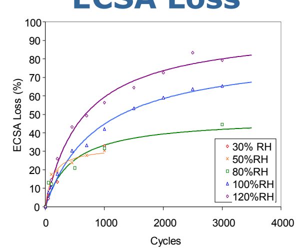
Parametric Performance Study



Predicted Voltage Degradation



Predicted ECSA Loss



State-of-the-Art Unit Cell

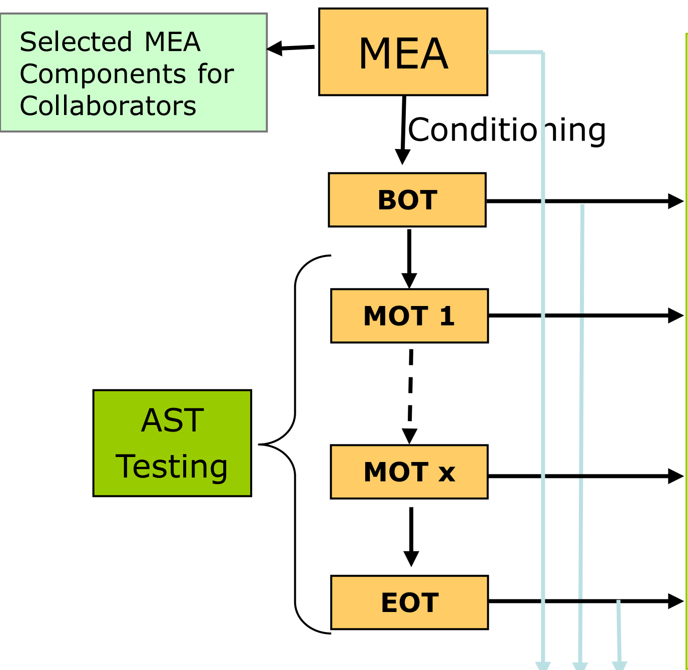
1D Test Hardware

- Bladder compression
- High flow rates
- Temperature control
  - Liquid cooling
- Carbon Composite Plates
  - Low pressure
  - Parallel flow fields
  - Designed for uniform flow
- Framed MEA
  - 45 cm^2 active area

Reference MEA

- Pt Catalyst
  - Graphitized carbon-support
  - 50:50 Pt/C ratio
  - Nafion® ionomer
- Catalyst Loading
  - Cathode/anode
  - 0.4/0.1 mg/cm^2
- Catalyst Coated Membrane
  - Ballard manufactured CCM
  - Nafion® NR211
- Gas diffusion layer
  - BMP Product
  - Continuous Process

Experimental Approach



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

Selected BOT/EOT Samples for Collaborators

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
  - Voltage Loss Breakdown (Kinetic Loss)
  - Limiting Current

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

* Ongoing evaluation, i.e. list of diagnostics may change

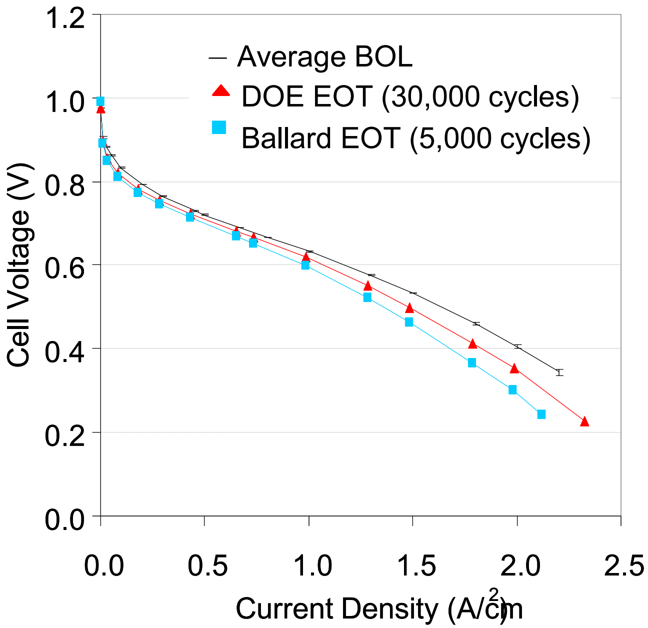
Reference AST: Air/H_2, 100% RH, 5 psig, 80°C, 0.6 V (30 sec)→ 1.2V (60 sec), 4700 cycles

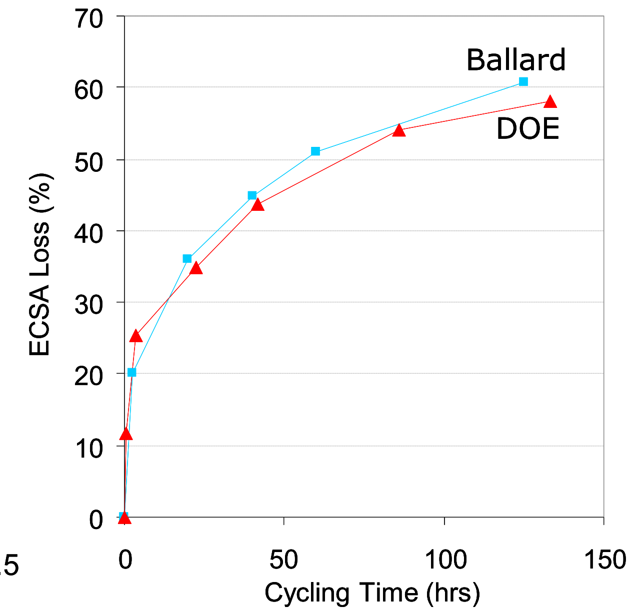
Reference MEA: 50:50 Pt/C, Nafion® ionomer, 0.4/0.1 mg/cm² (Cathode/anode), Ballard CCM, Nafion® NR211, BMP GDLs

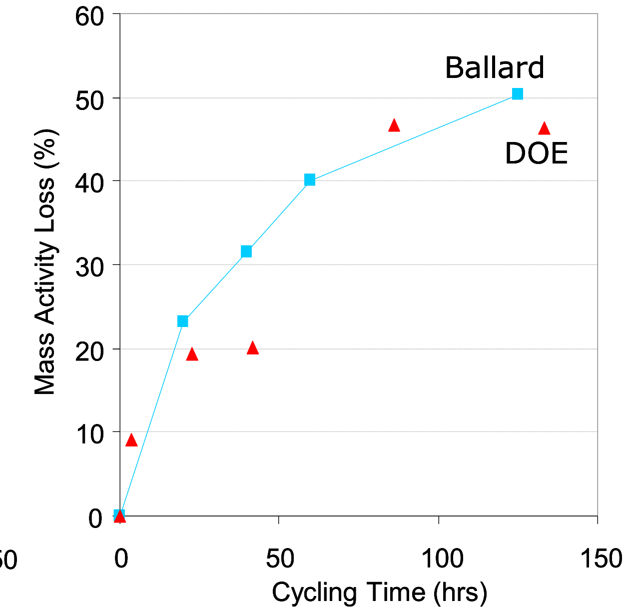
Ballard 1D Test Cell, 45cm² active area

Pt Dissolution AST Comparison
BPS and DOE Protocols

Previous Results







- **Low current density**
  - Performance losses are very similar and consistent with predominately kinetic changes for both ASTs
  - ECSA and mass activity losses vs. cycle time are very similar between ASTs
- **High current density**
  - End of Test (EOT) performance loss at 0.8 A/cm2 is ~14mV for DOE AST and ~29mV for Ballard ASTs

DOE AST: Triangle sweep @ 50 mV/s 0.6 V→1.0 V, 30,000 cycles, 80C, H2/N2, 100%RH,
Ballard AST: Square wave @ 0.6 (30sec)→1.2V (60 sec), 4700 cycles, 80C, H2/Air, 100%RH
Diagnostic Air Polarization: Air/H_2, 100% RH, 5 psig, 75°C

Ex-situ Characterization
Component Structure/Property Changes

	Properties	Purpose	Technique
Carbon Support	• Structure/morphology • Pore size distribution • Surface species	• Model input • Correlation dev.	• HRTEM (UNM) • BET (LANL/BPS) • XPS (UNM)
Catalyst Powder	• Pt crystallite size • Pt size distribution • Pt agglomerate size • Porosity • Pore size distribution • Surface species	• Model input • Dev. of correlations	• XRD (BPS) • HRTEM (UNM) • HRTEM (UNM) • BET/MIP (LANL/BPS) • XPS (MTU)

		Not Run	Conditioned	Degraded	Purpose	Technique
MEA	**Membrane**	**Membrane Changes** • Thickness • PTIM			• Determine if memb. degrades • Model validation	• SEM/EDX (BPS)
MEA	**GDL**	**Water Management Changes** • Capillary pressure • Contact angle • Surface energy/species • PSD			• Model input • Determine if GDL degrades	• Pseudo Hele-Shaw (MTU) • Sessile Drop • FTIR, X-ray Fluores. (LANL) • MIP(BPS)
MEA	**Cathode Cat Layer**	**Structure/ Property Changes** • Pt crystallite size • Pt content, Thickness • Porosity • Crack density, depth and width • Surface species • Surface roughness • Capillary pressure • Electrical conductivity • Cohesive strength			• Mechanism understanding • Model input • Model validation • Structure/material properties - BOL/ EOL performance correlations	• XRD (BPS) • SEM/EDX (BPS) • MIP/BET (BPS/LANL) • SEM/FESEM (BPS/MTU) • XPS (UNM) • Laser Profiliometry (MTU) • Hele-Shaw (MTU) • cAFM (MTU) • AFM (MTU))
	CL/Membrane Interface	**Structure/Property Changes** • Cohesive strength/adhesion • Chemical bond			• Model input • Correlation dev.	• AFM (MTU) • Raman/FTIR (MTU)