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

Morphological Simulations and Experimental Approaches

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Project ID# FC049

Overview

Timeline

- Start Date: January 2010
- End Date: March 2013
- Percent Complete: 69%

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
- DOE FY11 Funding: $1385K
- Planned FY12 Funding: $1200K

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 thinning 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

Technical Targets/Barriers

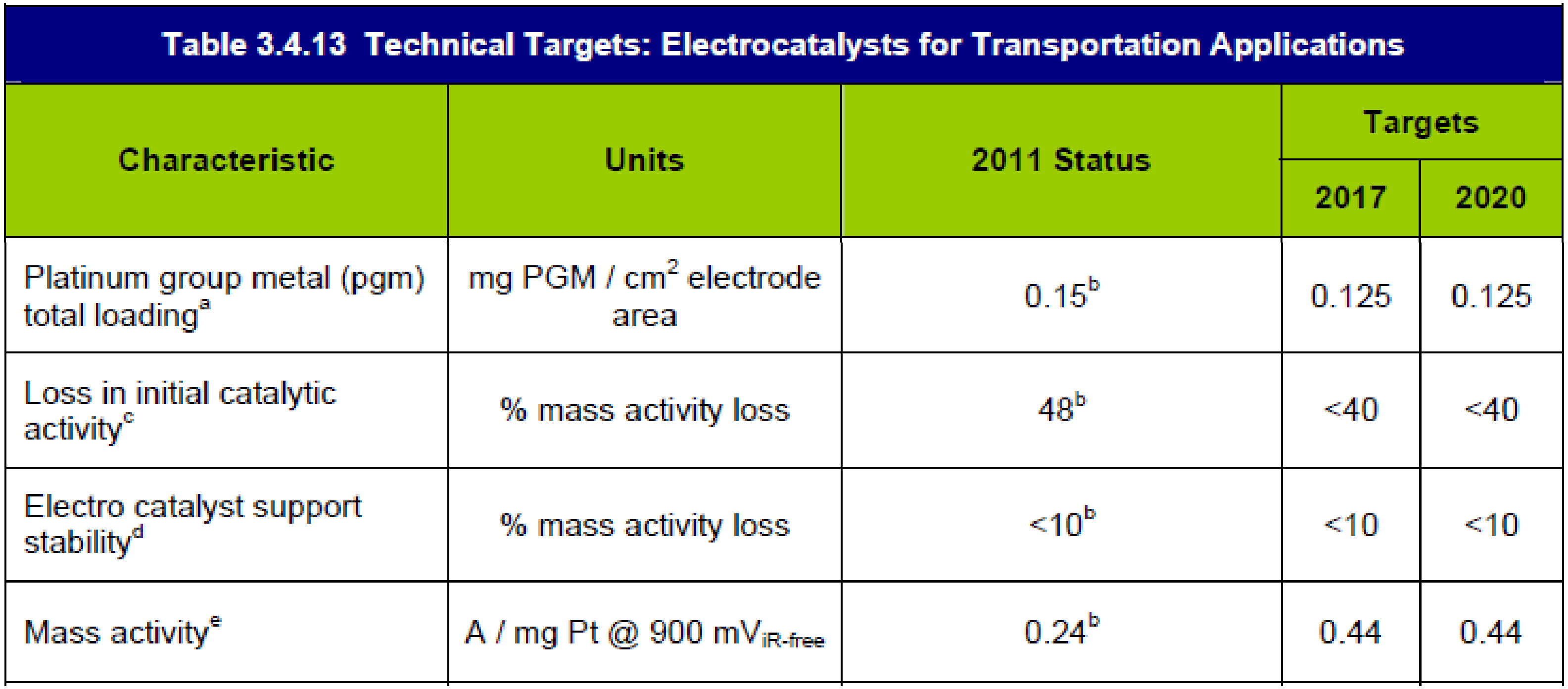


Table 3.4.13 Technical Targets: Electrocatalysts for Transportation Applications

Characteristic	Units	2011 Status	Targets	
			2017	2020
Platinum group metal (pgm) total loading[a]	mg PGM / cm^2 electrode area	0.15[b]	0.125	0.125
Loss in initial catalytic activity[c]	% mass activity loss	48[b]	<40	<40
Electro catalyst support stability[d]	% mass activity loss	<10[b]	<10	<10
Mass activity[e]	A / mg Pt @ 900 $mV_{iR\text{-}free}$	0.24[b]	0.44	0.44

Ref: http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

[c] Mass activity loss after triangle sweep cycles at 50 mV/s between 0.6 V and 1.0 V at 80°C, 100% RH

[d] Mass activity loss after 1.2V hold in H_2/O_2 at 80°C, 100% RH

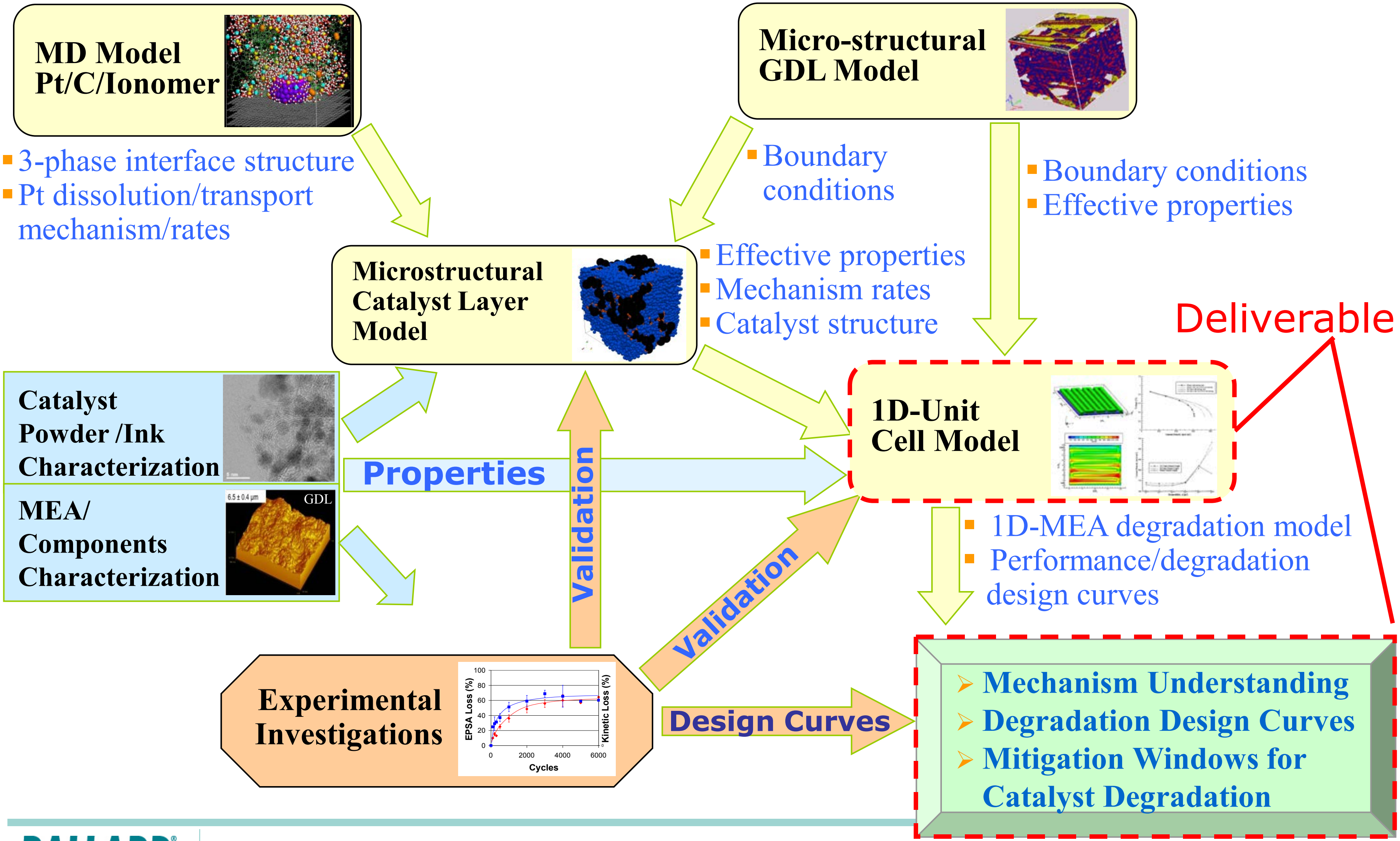
[e] MEA test at 80°C, 100% RH in H_2/O_2

- **2020 Durability Targets**
  - Automotive Drive Cycle: 5000 hours
  - CHP and Distributed Generation
    - 1 – $10kW_e$: 60,000 hours
    - 100 kW – 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



MD Model Pt/C/Ionomer

- 3-phase interface structure
- Pt dissolution/transport mechanism/rates

Micro-structural GDL Model

- Boundary conditions

- Boundary conditions
- Effective properties

Microstructural Catalyst Layer Model

- Effective properties
- Mechanism rates
- Catalyst structure

Catalyst Powder /Ink Characterization

MEA/ Components Characterization

Properties

Validation

Deliverable

1D-Unit Cell Model

- 1D-MEA degradation model
- Performance/degradation design curves

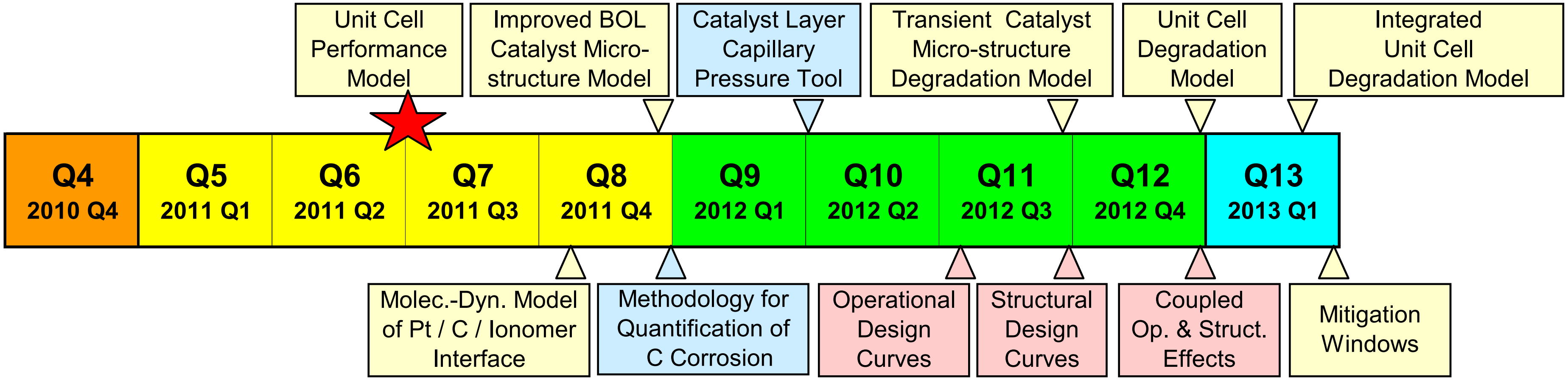
Validation

Experimental Investigations

Design Curves

- **Mechanism Understanding**
- **Degradation Design Curves**
- **Mitigation Windows for Catalyst Degradation**

Milestones & Timeline
FY 2011 to 2013



Unit Cell Performance Model

Improved BOL Catalyst Micro-structure Model

Catalyst Layer Capillary Pressure Tool

Transient Catalyst Micro-structure Degradation Model

Unit Cell Degradation Model

Integrated Unit Cell Degradation Model

Q4	**Q5**	**Q6**	**Q7**	**Q8**	**Q9**	**Q10**	**Q11**	**Q12**	**Q13**
2010 Q4	**2011 Q1**	**2011 Q2**	**2011 Q3**	**2011 Q4**	**2012 Q1**	**2012 Q2**	**2012 Q3**	**2012 Q4**	**2013 Q1**

Molec.-Dyn. Model of Pt / C / Ionomer Interface

Methodology for Quantification of C Corrosion

Operational Design Curves

Structural Design Curves

Coupled Op. & Struct. Effects

Mitigation Windows

★ Go/No-Go Decision Point

- 🟨 Modeling Milestones
- 🟥 Correlations Development Milestones
- 🟦 Tools/Methodology Development Milestones

Go/No-Go Decision Point (completed 30 June 2011)

- **Validation of statistically generated BOL UC-Model performance curves against experimental results**
  - Model predictions are within the 95% statistical variability of the experimental data for the baseline MEA at standard conditions

2011/2012 Milestones

Molecular Dynamics Model

- ✓ Completion of Pt/C/ionomer interface
- ◇ Molecular modeling of Pt dissolution

Micro-structural Model

- ◇ Completion of two-phase flow implementation
- ◇ Simulation of effective properties and performance with liquid water

1D-MEA Model

- ◇ Pt Dissolution, agglomeration
- ✓ Validation of statistical 1D-MEA model with experiment
  - **Go/No-Go decision June 30, 2011**
- ✓ Integration of electrical contact resistance model
- ✓ Implementation of Multi-step ORR

Experimental Investigations

- Carbon Types
  - ✓ Investigate lower upper voltage limits
  - ✓ Correlate degradation with material properties
- ✓ Ionomer equivalent weight
- ✓ Pt/C ratio study
- ✓ Carbon corrosion (potential hold) study

Material Characterization

- ✓ GDL wettability and capillary pressure
- ◇ Interface characterization
- ◇ Property changes of aged GDLs and catalyst layers

✓= Completed ◇= In progress/on target

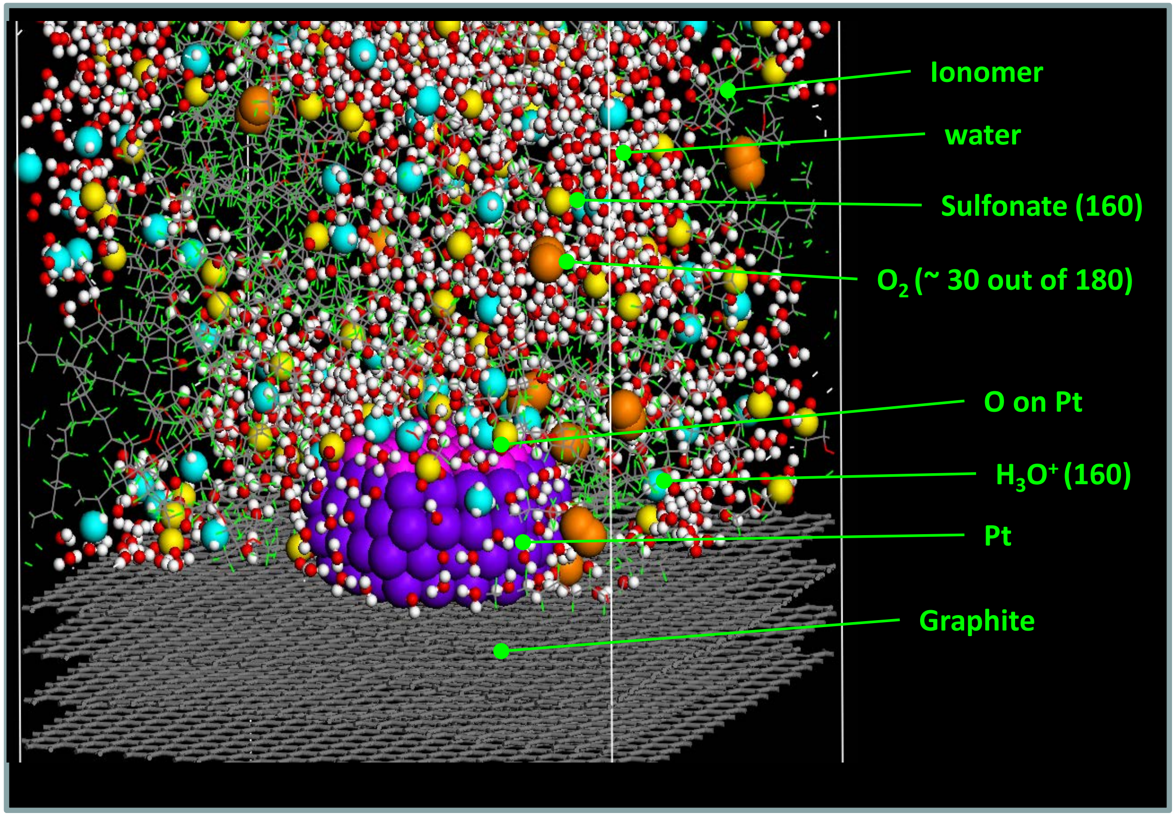
Accomplishments

Modeling Status

Molecular Dynamics Model
Three Phase Interface Model

Surface Area Analysis of O-covered Pt

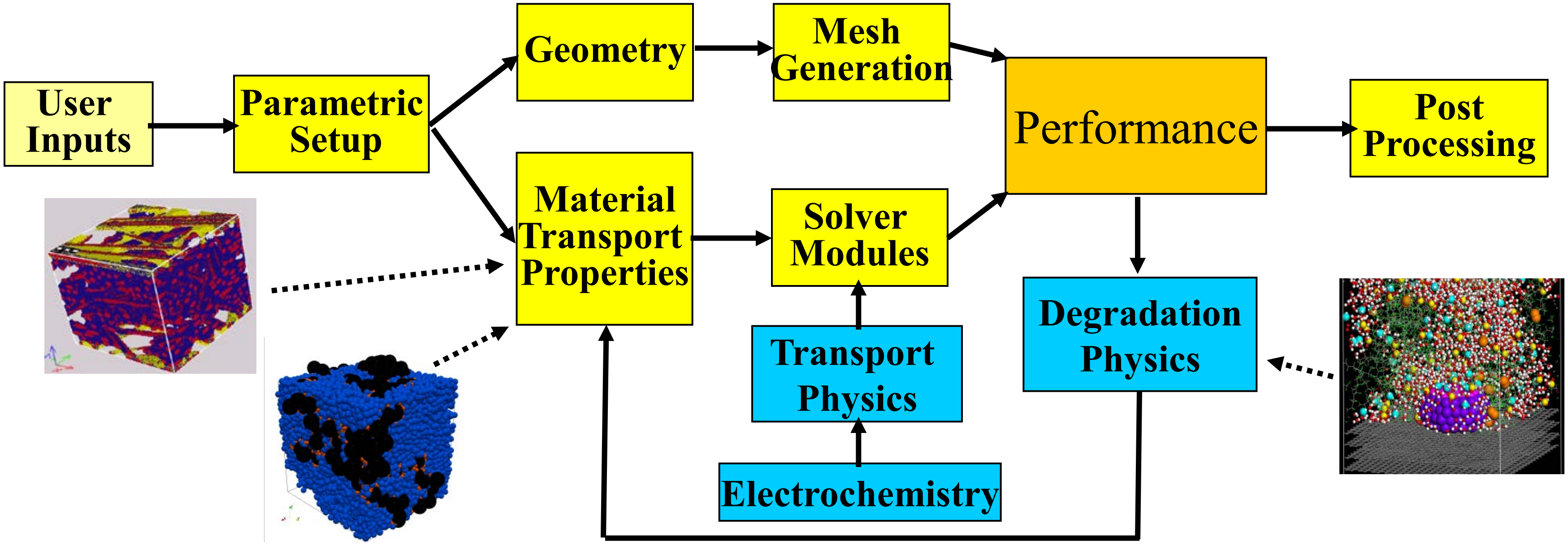
MD Simulation: Nafion®117 with 10 wt % H_2O @, 353 K, 1 atm



- Calculated species coverage of bare and oxide covered platinum
  - Determined active and inactive surface moieties (H_2O, H_3O^+, O_2, SO_3, and polymer)
- O_2 prefers polymer phase over H_2O
- SO_3 interacts strongly with Pt/PtO
  - SO_3 is well solvated by the water phase despite being connected to the hydrophobic chain

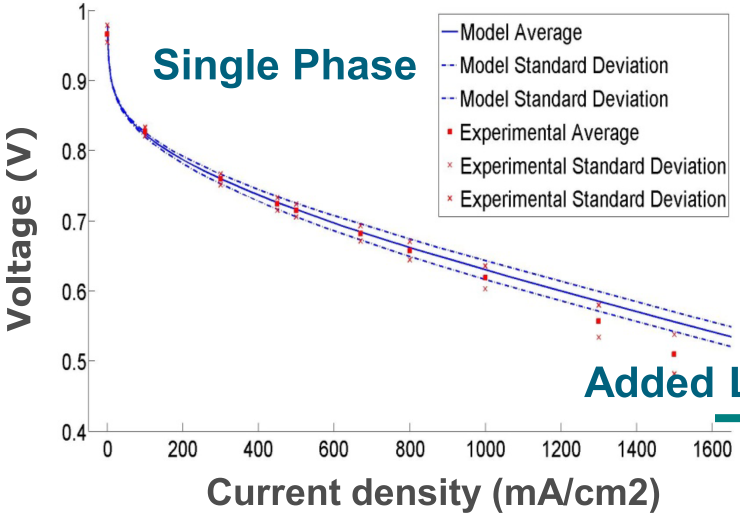
- Improved understanding of three-phase interface (coverages vs. ECSA)
  - Correction factor for ECSA estimation in micro-structural model
- Interaction between PtO, SO_3, and H_2O is important to understand dissolution

Unit Cell Model Development
Scripting and Statistical Input Options

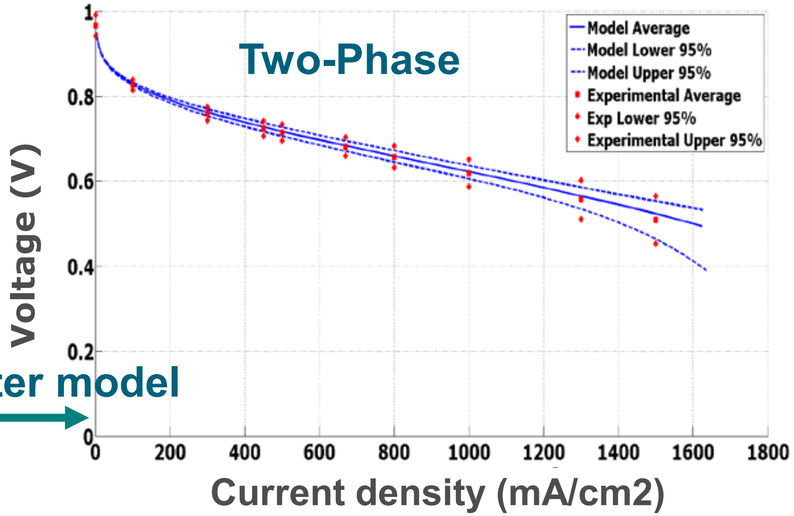


- **Model was separated into modular parts**
  - User inputs, transport properties, and physics
  - Statistical variation
    - User inputs (material constants or operational conditions)
    - Transport properties (effective properties vs. composition of porous media)
- **Effective transport properties from micro-structural models**
  - Catalyst layer (gas diffusivity, thermal conductivity)
  - Gas diffusion layer (gas diffusivity, permeability, thermal conductivity)

Unit Cell BOL Model
Validation (Baseline MEA, Standard Conditions)


Single Phase

Added Liq. Water model


Two-Phase

Statistical Model Inputs

Component Properties	% Deviation (1 Std Dev)
Catalyst/Catalyst Layer	
Thickness (microns)	+/- 8%
Weight Ratios (%)	
Pt:C	+/- 1%
(Pt:C):Ionomer	+/- 1%
Pt Loading [mg/cm^2]	+/- 1.25 %
Pt size	+/- 10%
Tafel Slope [mV/dec]	fixed
Jo [A/cm^2 pt]	+/- 10%
GDL	
Porosity	fixed
Tortuosity	+/- 3%
Thickness (microns)	+/- 4%
Membrane	
Thickness (microns)	+/- 2%

- **Sample to sample variation created using a normally distributed, random population**
- **Initial model validation, single phase**
  - Predictions were within 1 standard deviation up to 1.0 A/cm^2
- **Two-phase model validation**
  - Accurately captures effect of increasing water content
  - Experimental and model variation both increase with current density due to "noise" factors having increased effects on transport processes
- **Experimental dataset of 20 MEAs**

Accomplishments Modelling/Experimental Results

Effect of Cathode Catalyst Structure / Composition on Performance and Degradation

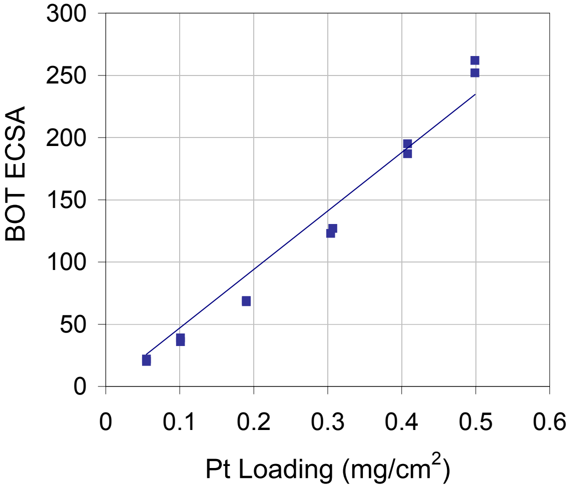
- **Pt Loading Study (Pt50-LSAC)**
- **Carbon Ratio Study (PtX-LSAC)**

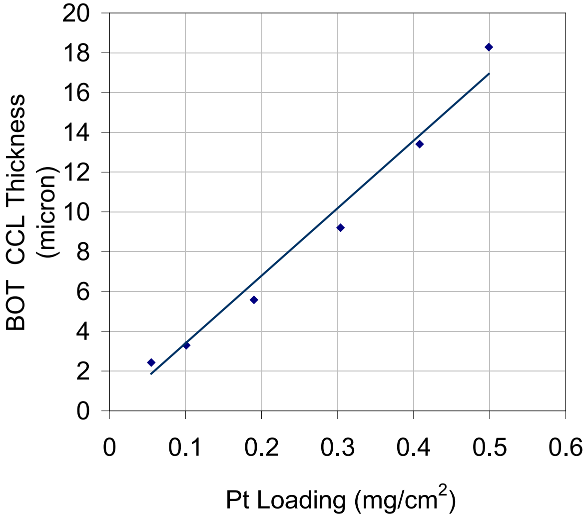
Reference MEA: 50:50 Pt/C, Nafion® ionomer, 0.4/0.1 mg/cm^2 (Cathode/anode), Ballard CCM, Nafion® NR211, BMP GDLs

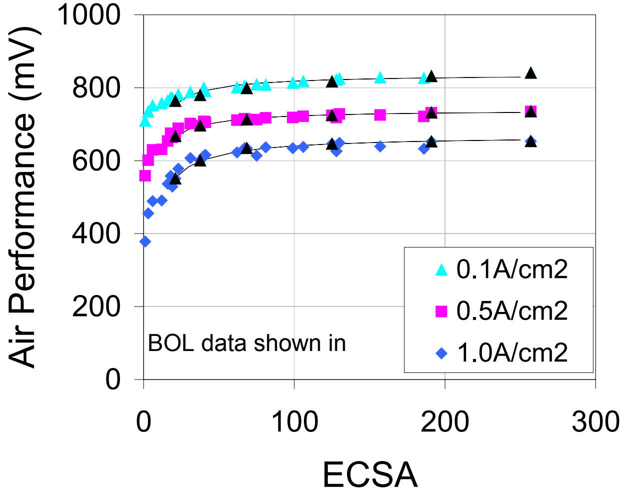
Ballard Test Cell: 1D, 45cm^2 active area

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

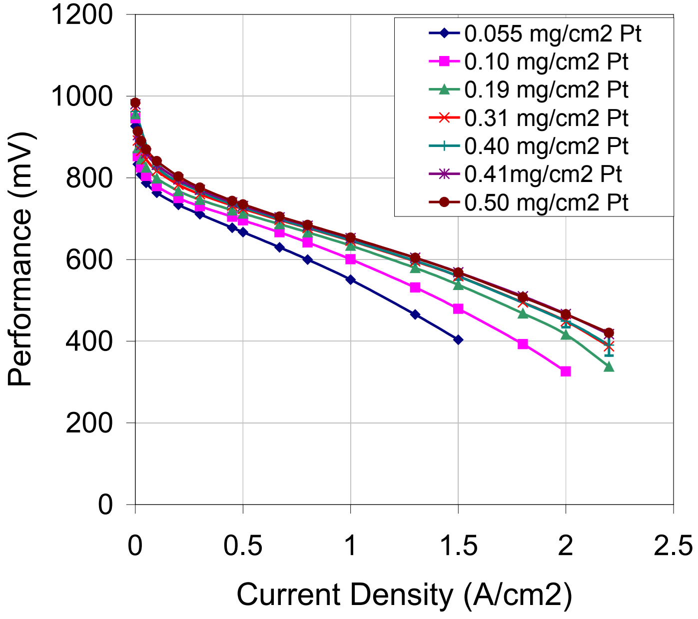
Effect of Pt Loading
Catalyst Layer Structure (Experiment)



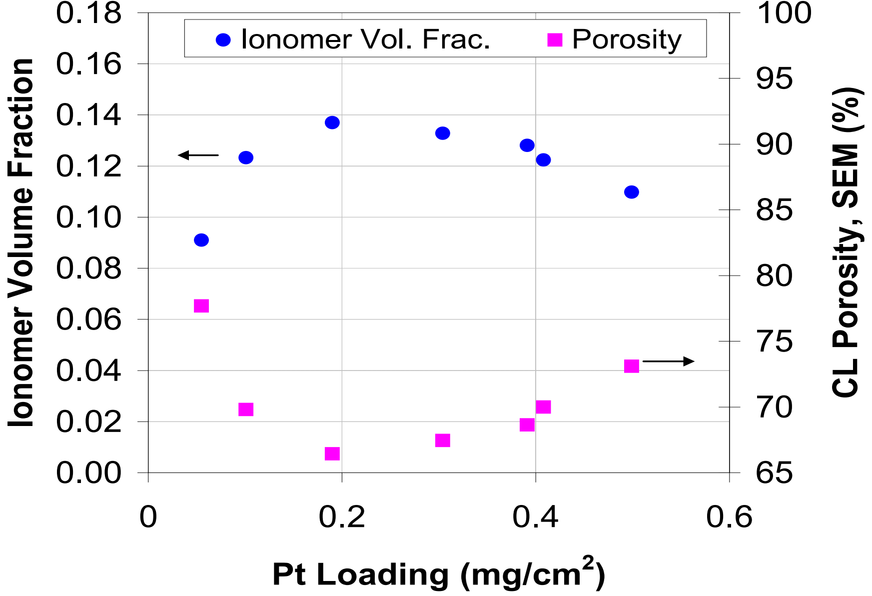


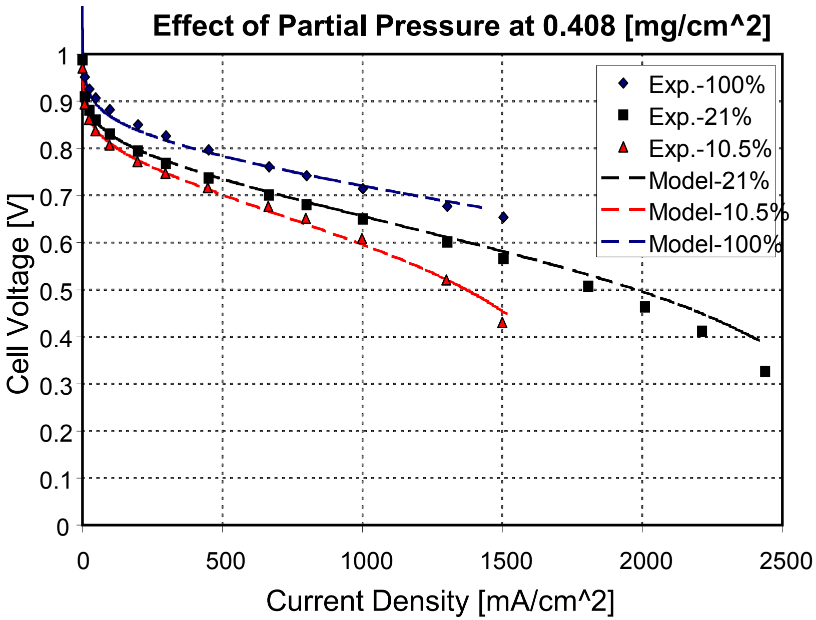


- **ECSA/Thickness vs. loading**
  - Relationships for macro-model
  - Validation data for micro-structural model
- **Performance loss increases with low loaded structures**
  - Below ECSA ~75
  - Loss increases with increasing current
  - Higher sensitivity to low oxygen concentration

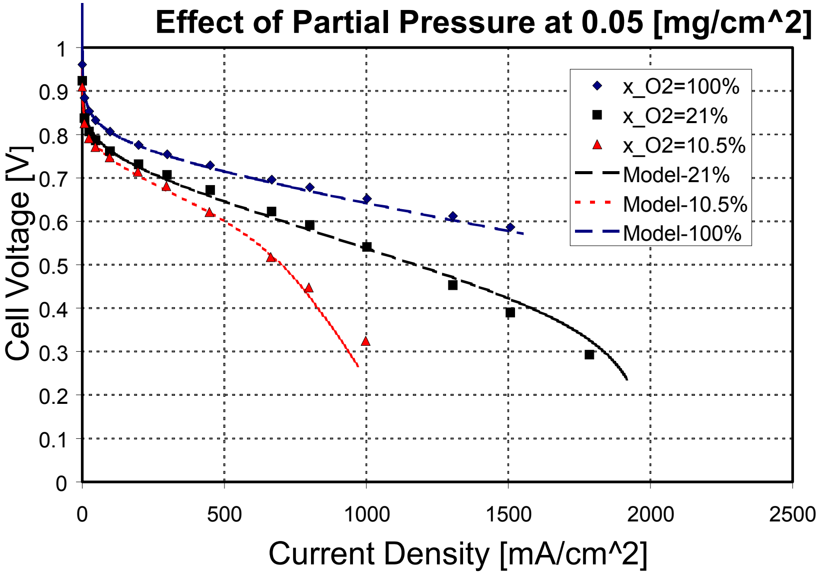


Platinum Loading Study
BOT Performance (Experiment & Predicted)

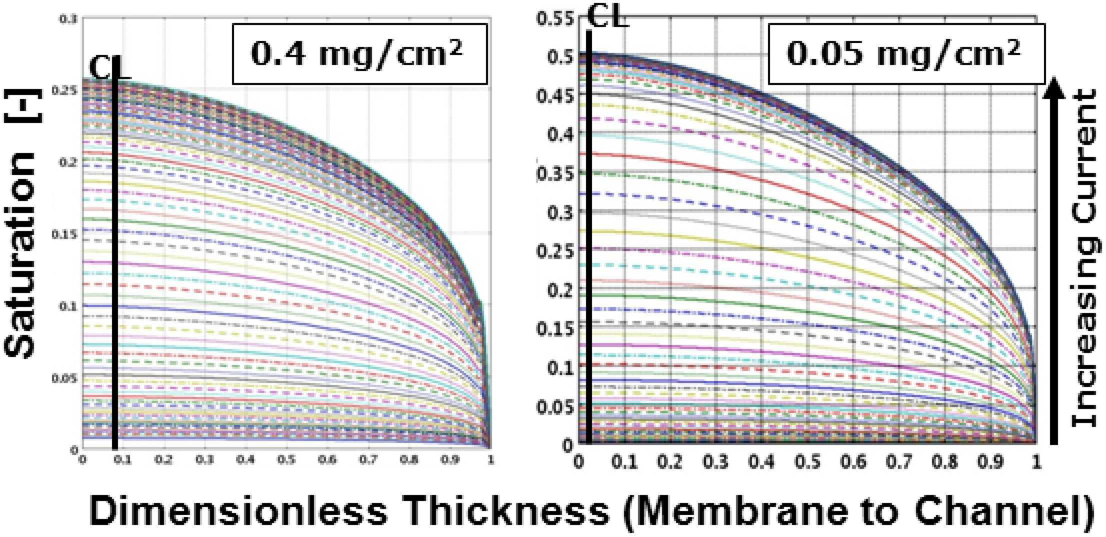


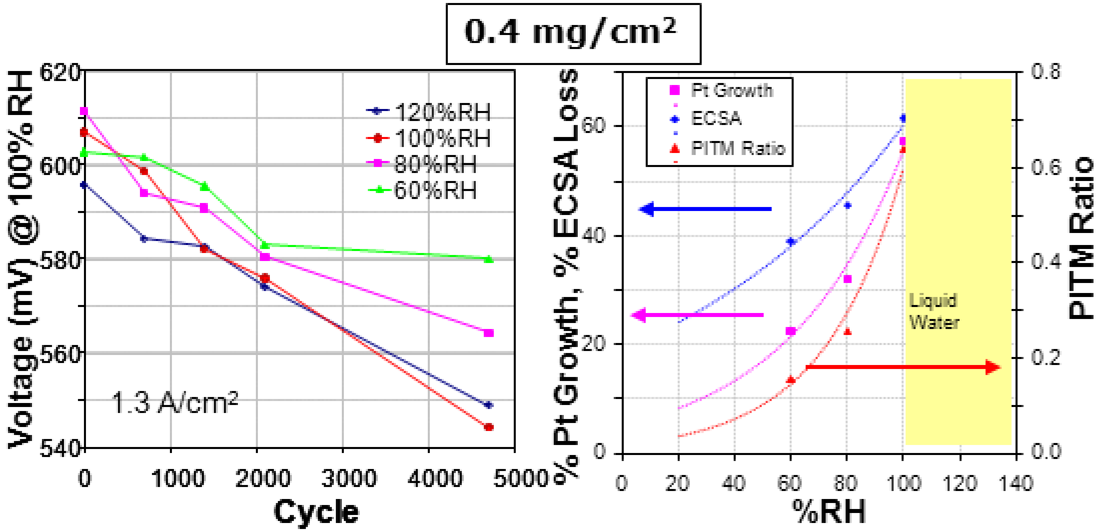


- **Model captures behaviour at low Pt loading and oxygen sensitivity**
  - Permeability is fitted at 21% O_2
- **Sensitivity to oxygen fraction**
  - Saturation vs. diffusivity relationship
  - Ionomer film behaviour?
- **Volume fraction variation with loading and thickness**
  - Important in capturing behaviour



Platinum Loading Study Effect of Water

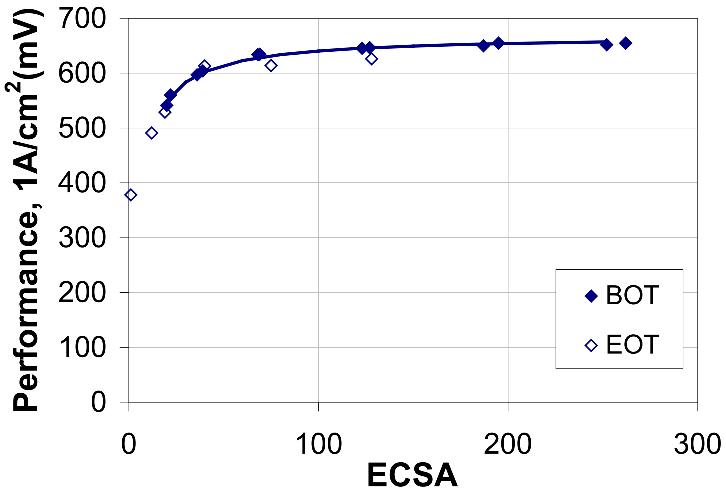


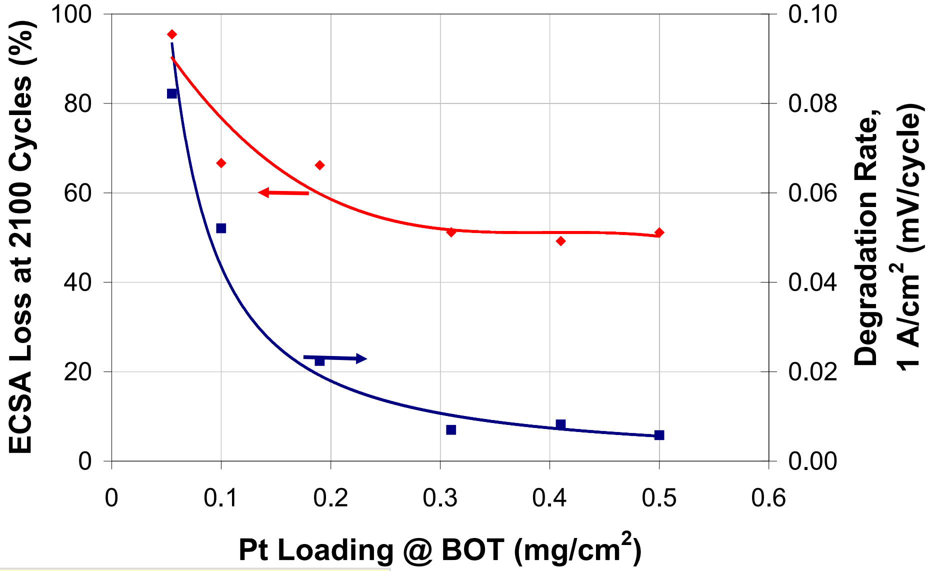


- **Saturation increases in low loaded structures**
  - For low Pt loading max H_2O content is ~2x higher than for high Pt loading
  - Relationship between saturation and diffusion causes additional sensitivity to O_2 transport at high water contents

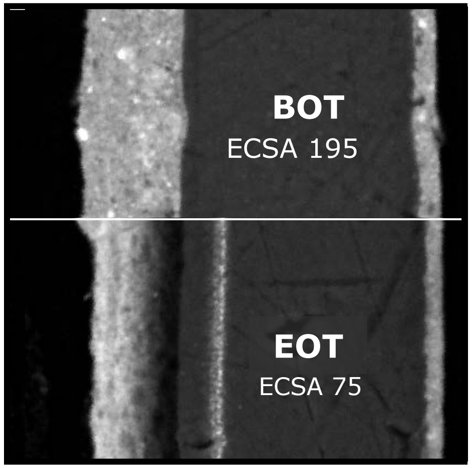
- **Voltage loss increases with increasing RH**
  - Similar performance loss for RH > 100% (plateau in PITM, Pt growth, and ECSA loss
- **Pt dissolution decreases with lower reactant RH (<100%)**
  - Decrease in PITM, Pt growth, ECSA

Effect of Pt Loading
Degradation - Pt Dissolution

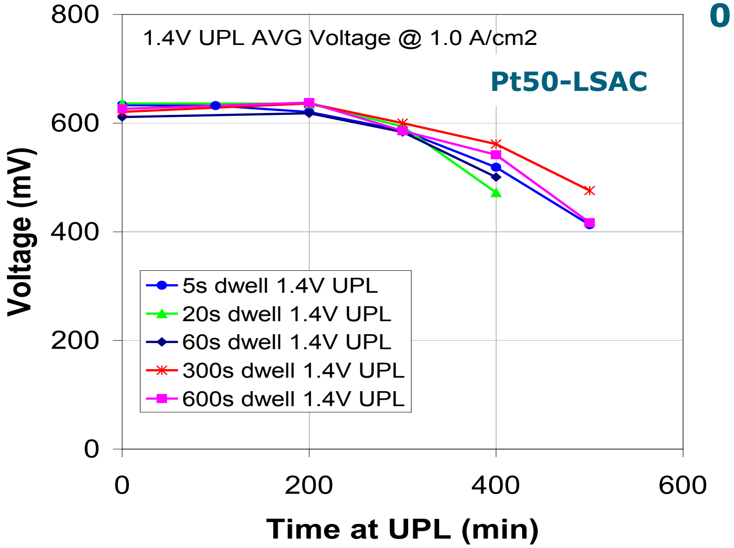




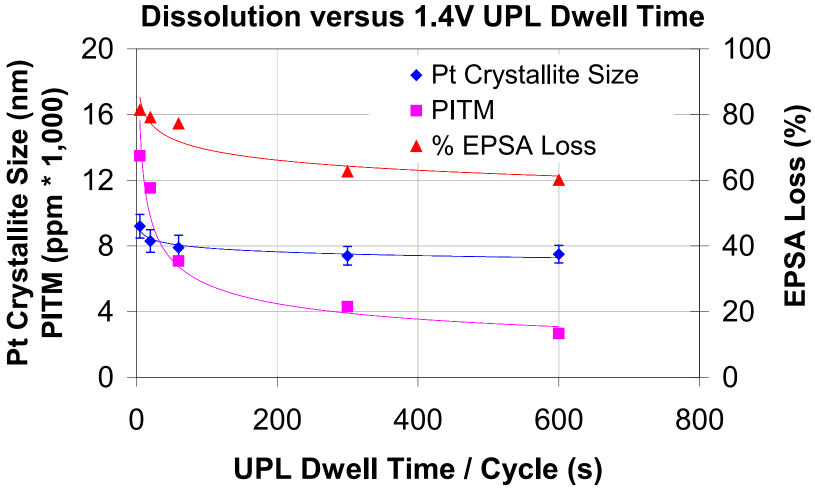
- Performance correlates to ECSA for BOT and degraded samples
- Degradation rate increases for <0.3 mg/cm^2 Pt loading
- Pt dissolution changes structure of catalyst layer
  - Depletion of Pt at membrane interface, PITM, increased Pt size, lower surface area
  - No significant change in catalyst layer thickness

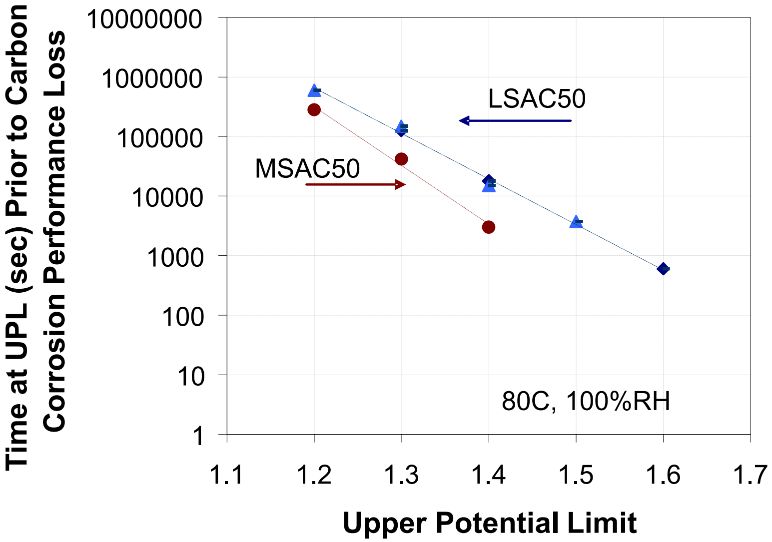


Carbon Corrosion Degradation Impact of Dwell time



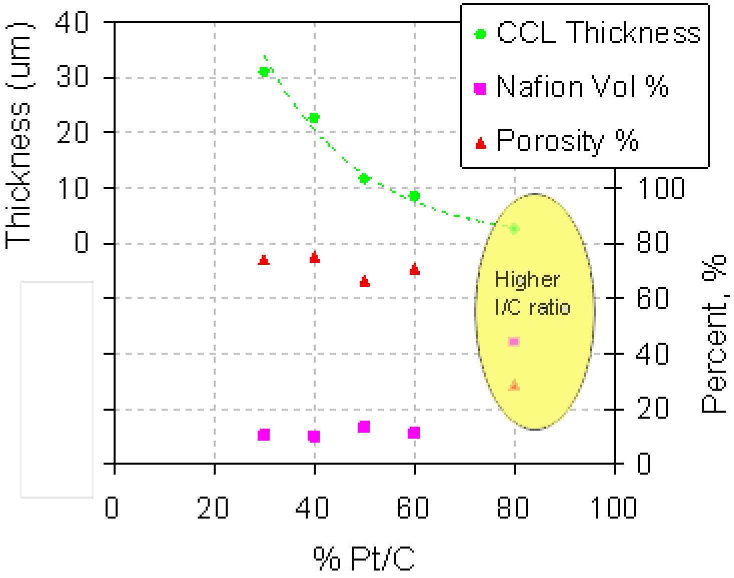
0.4 mg/cm² Loading



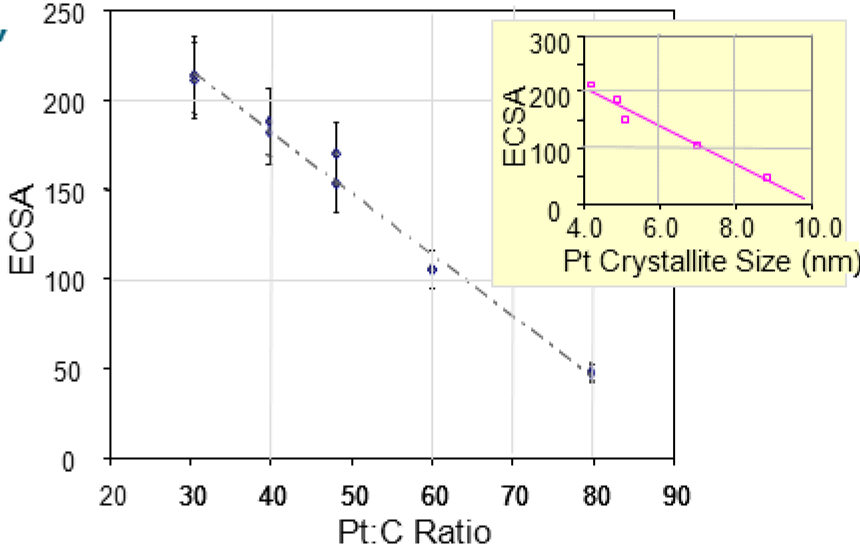


- **Onset of observable performance loss due to corrosion is dependent on time spent at UPL (total)**
  - Critical carbon oxidation threshold dependent on the carbon type
  - Pt dissolution is affected by oxide build-up with increased particle size with shorter dwell times
  - PITM formation impacted by amount of dissolved Pt, also increases with shorter dwell times
- **Time to corrosion onset is dominated by the UPL and graphitisation level of the support**

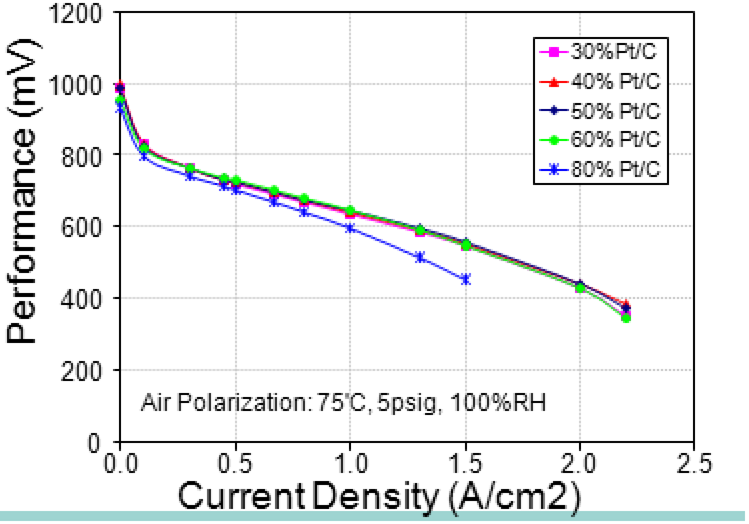
Effect of Pt/C Ratio
BOT Catalyst Layer Structure



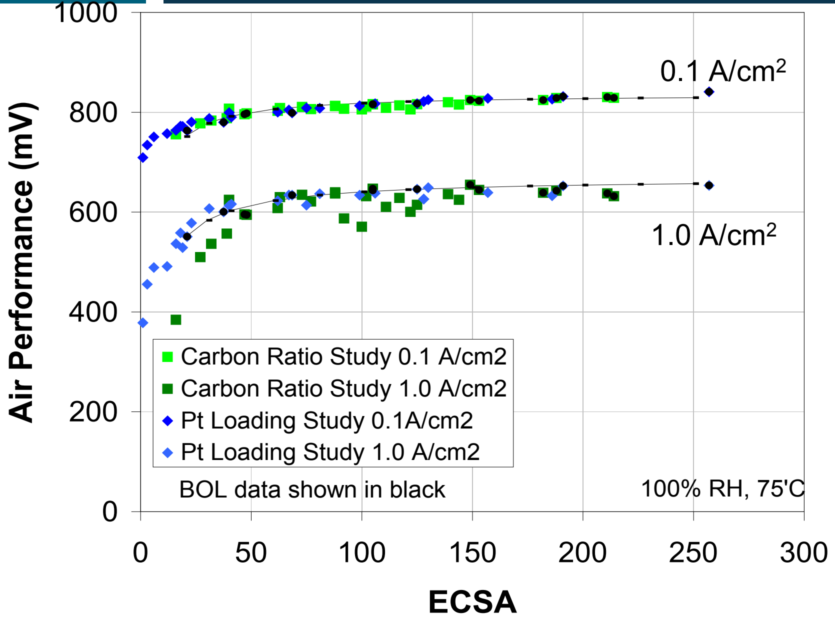
LSAC Support, 0.4 mg/cm² Loading

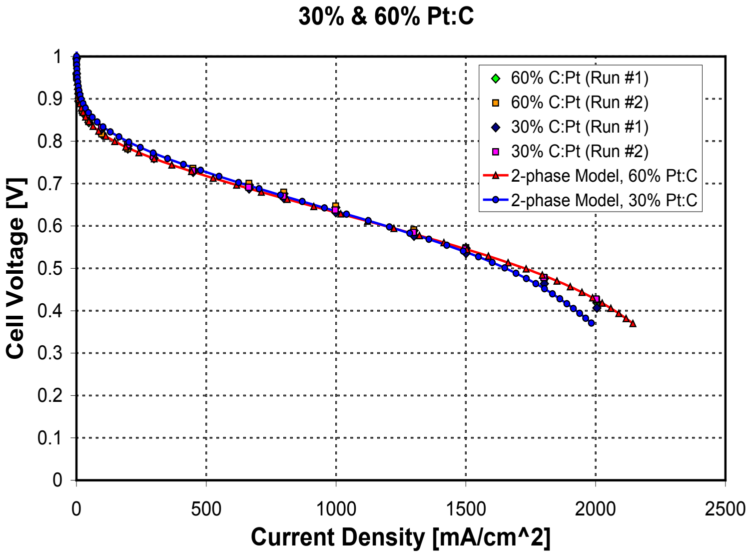


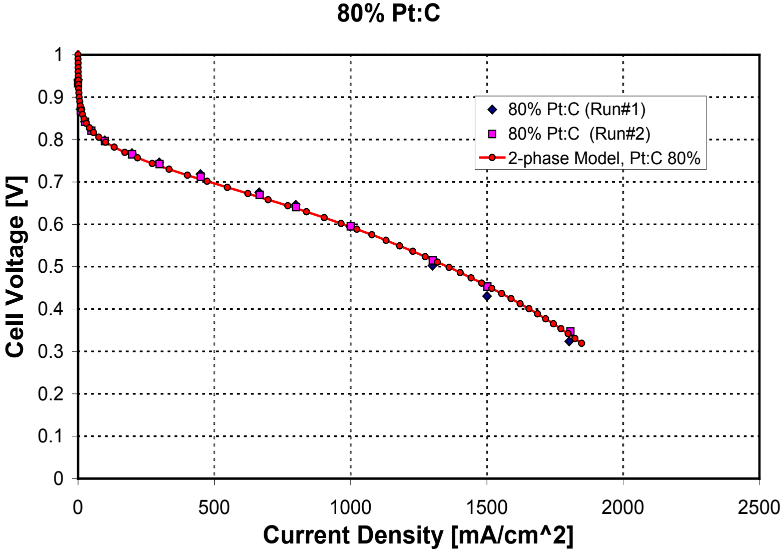
- **Cathode catalyst layer thickness decreases with increasing Pt/C ratio**
- **Porosity is not affected by the Pt/C ratio**
  - Ionomer/Carbon ratio is 2.5x higher for 80% Pt/C
- **ECSA deceases with increasing Pt/C ratio**
  - Pt crystallite size increases with Pt/C ratio



Effect of Pt/C Ratio
BOT Performance (Experiment & Predicted)



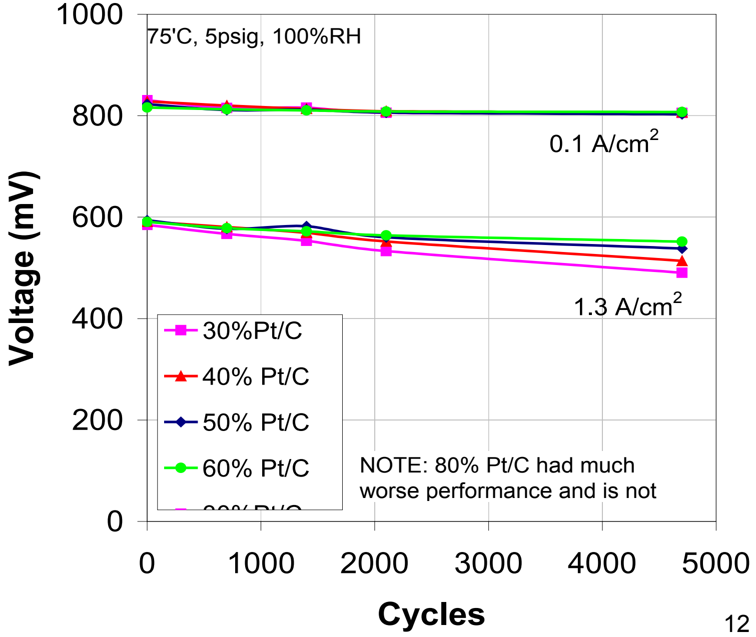




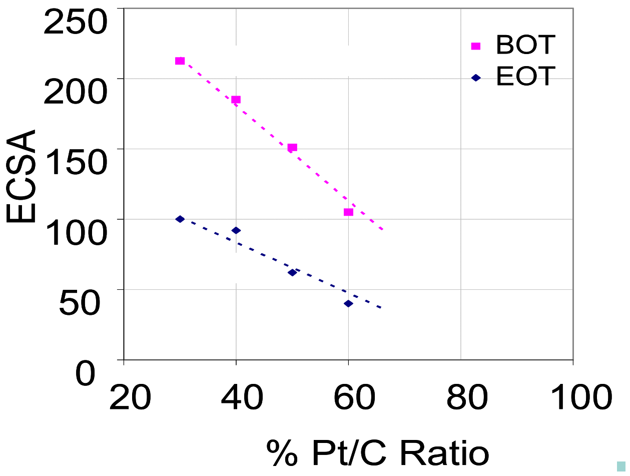
- **ECSA vs. Performance**
  - Similar behavior in kinetic region with Pt loading study
  - Pt dispersion effect at high ratios
- **80% Pt/C has lower performance**
  - Increased CL ionic resistance and reduced porosity
- **Model predictions**
  - Similar move in kinetics, liquid water effects with layer thickness changes
  - Able to capture effect of higher I/C ratio

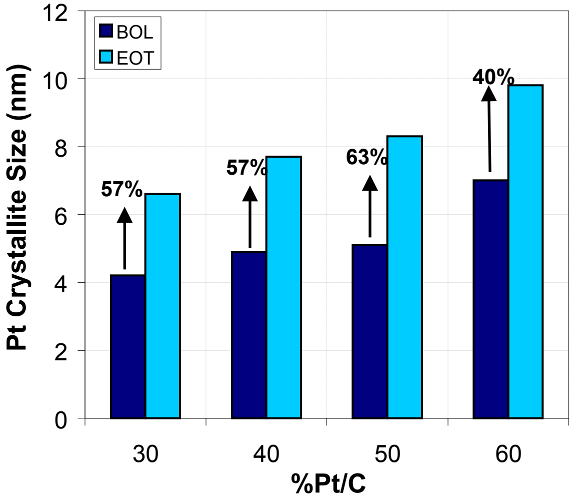
Effect of Pt/C Ratio

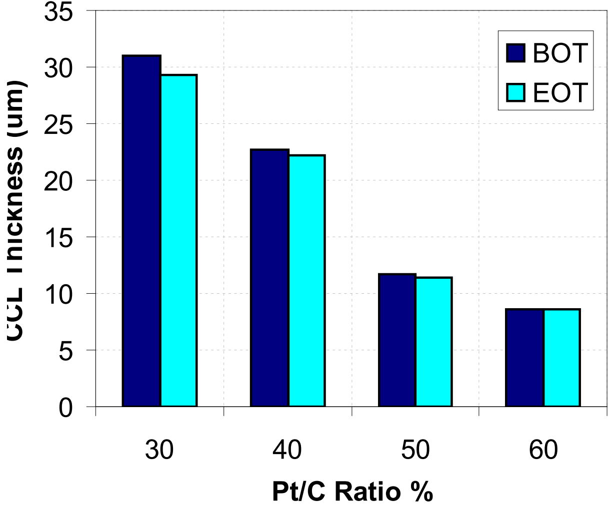
Degradation



- **Voltage Degradation decreases with increasing Pt/C Ratio**
  - Improved performance at higher current densities after degradation cycling
- **% ECSA loss at EOT is similar for all Pt ratios**
  - Each sample losing ~ 50% of the initial EPSA
- **BOT crystallite sizes increase with Pt/C ratio**
- **No electrode thickness changes (change is within variation at BOL)**







Plan Forward

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

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

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 layer/GDL
- **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
  - Carbon corrosion mechanism, characterization of catalyst powder/layers

Summary

- **Relevance**
  - Improve understanding of durability for fuel cell materials and components
  - Provide 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 and Progress to date**
  - Completed BOL 1D-MEA model, simulations of composition and operational effects on BOL performance were validated with experimental results
  - Quantified Pt/C catalyst performance degradation mechanisms with catalyst loading, Pt/C ratio, carbon type, ionomer EW , UPL , RH, time at UPL
- **Collaborations**
  - Project team partners GIT, LANL, MTU, Queen’s, UNM
  - Participation in DOE Durability and Modeling Working Group
- **Proposed Future Research**
  - Extend micro-structural model to include degradation and validate Complete MD model of Pt dissolution and transport mechanisms
  - Complete experimental investigation and correlations
  - Develop durability design windows using experimental results and the 1-D MEA model

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

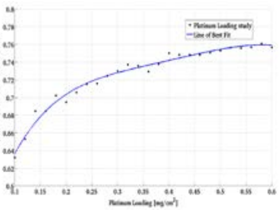
Membrane
- EW
- Thickness

BOL Performance

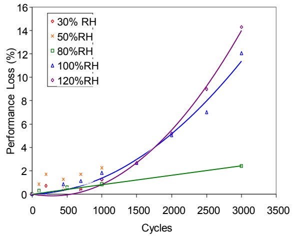
- ECSA
- Exchange current density
- Tafel slope
- Mass activity
- HFR

Operating Conditions

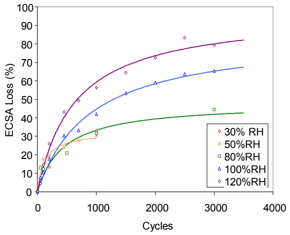
Parametric Performance Study

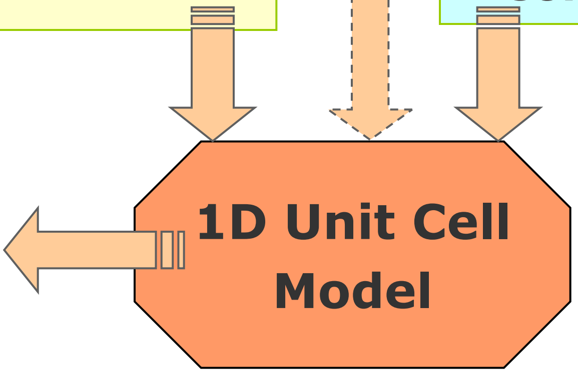


Predicted Voltage Degradation



Predicted ECSA Loss





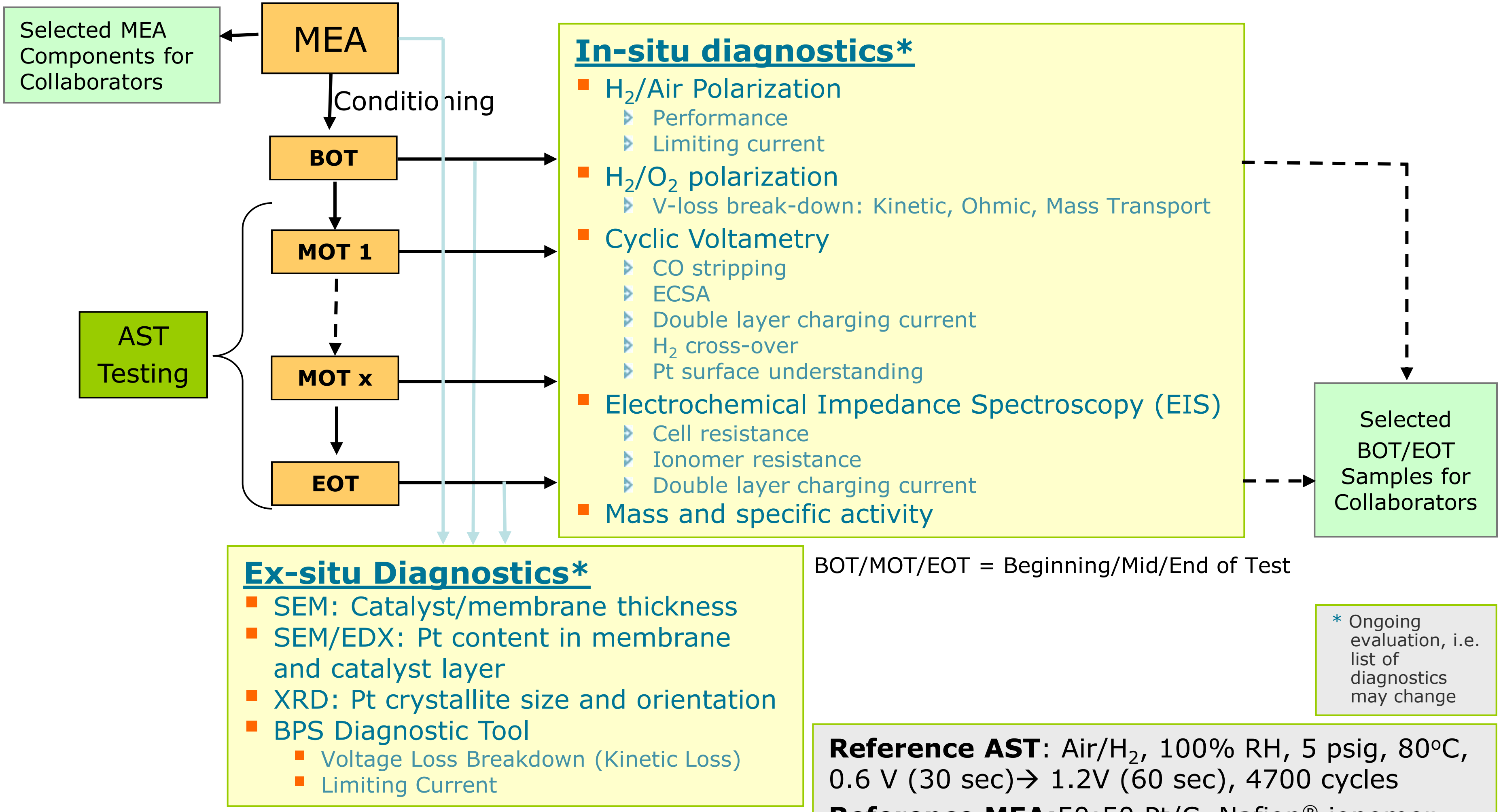
1D Unit Cell Model

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



Selected MEA Components for Collaborators

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

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

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)
	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)
	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)