

**Development of Micro-Structural Mitigation  
Strategies for PEM Fuel Cells:  
Morphological Simulations and Experimental Approaches**

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**Ballard Materials Products**  
**11 May 2011**

**Project ID# FC049**

## Timeline

- Start Date: January 2010
- End Date: March 2013
- Percent Complete: 38%

## Barriers

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

## Budget

- Total Project: \$6,010,181
  - ▶ \$ 4,672,851 DOE + FFDRRC
  - ▶ \$ 1,337,330 Ballard
- Funding Received:
  - ▶ \$1,835,000 (Total)
    - FY 2010: \$ 1,435,000
    - FY 2011: \$ 400K to date, \$1M planned

## Project Partners

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

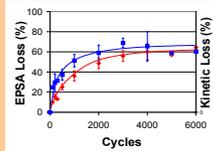
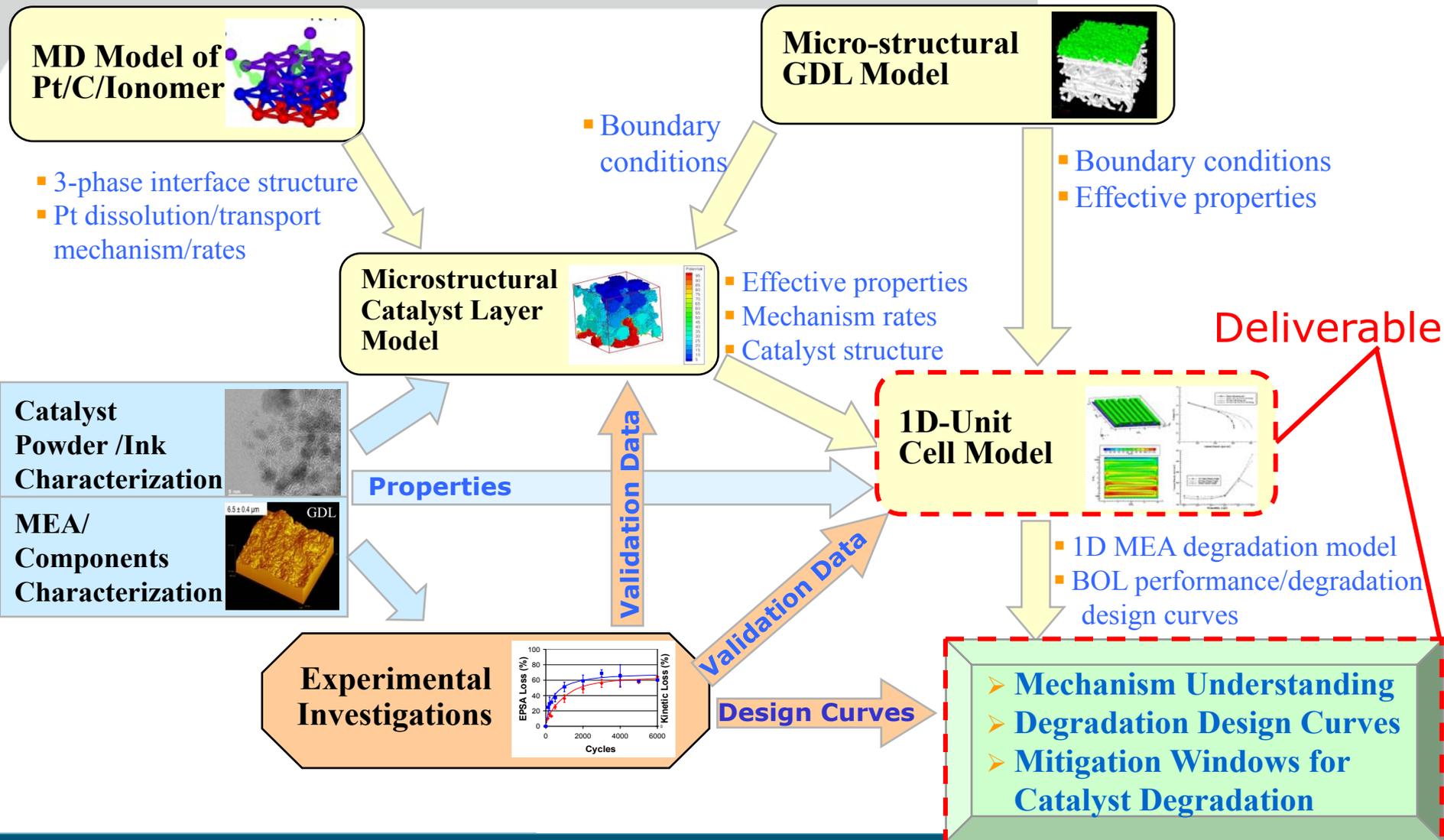
## ■ Objective

- ▶ 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

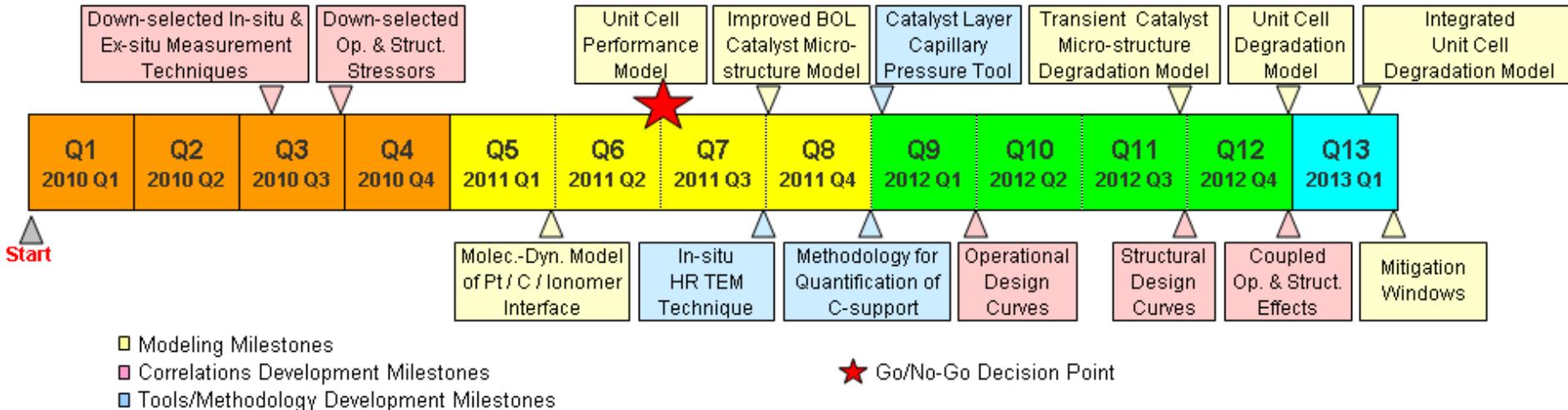
## ■ Impact

- ▶ Increasing catalyst durability
  - Based on understanding of the effect of structure and operating conditions
- ▶ Enabling achievement of DOE catalyst durability targets
  - Durability with cycling, i.e.  $\leq 40\%$  mass activity loss,  $< 10\%$  carbon support mass loss

# Approach



# Project Milestones & Timeline



## ★ Go/No-Go Decision Point

- Validation of statistically generated BOL UC-Model performance curves against experimental results

- Go: Model predictions are within the 95% statistical variability of the experimental data for the baseline MEA at standard conditions

# Milestones 2010/2011

**BALLARD®**

√ - Completed  
√ - In Progress

## ■ Model Development

- ▶ Molecular dynamic model of the Pt/C/ionomer system
  - √ • Determined cohesive energy of Pt cluster and interaction with H<sub>2</sub>O and O<sub>2</sub>, C and ionomer interactions are in progress
- ▶ Micro-structural catalyst model expansion for liquid water
  - √ • Implemented preliminary transient 2-phase flow
  - √ • Extraction of effective properties vs. catalyst layer composition and simulation of catalyst performance vs. effective properties is in progress
- ▶ BOL MEA/Cell macro-model development and validation
  - √ • Liquid water transport physics (from literature) has been added, under refinement
  - √ • Interfacial transport resistance model derived, implementation is in progress
  - √ • Statistical input modification and preliminary validation completed
  - √ • Final validation of Beginning of Life (BOL) Model is in progress.

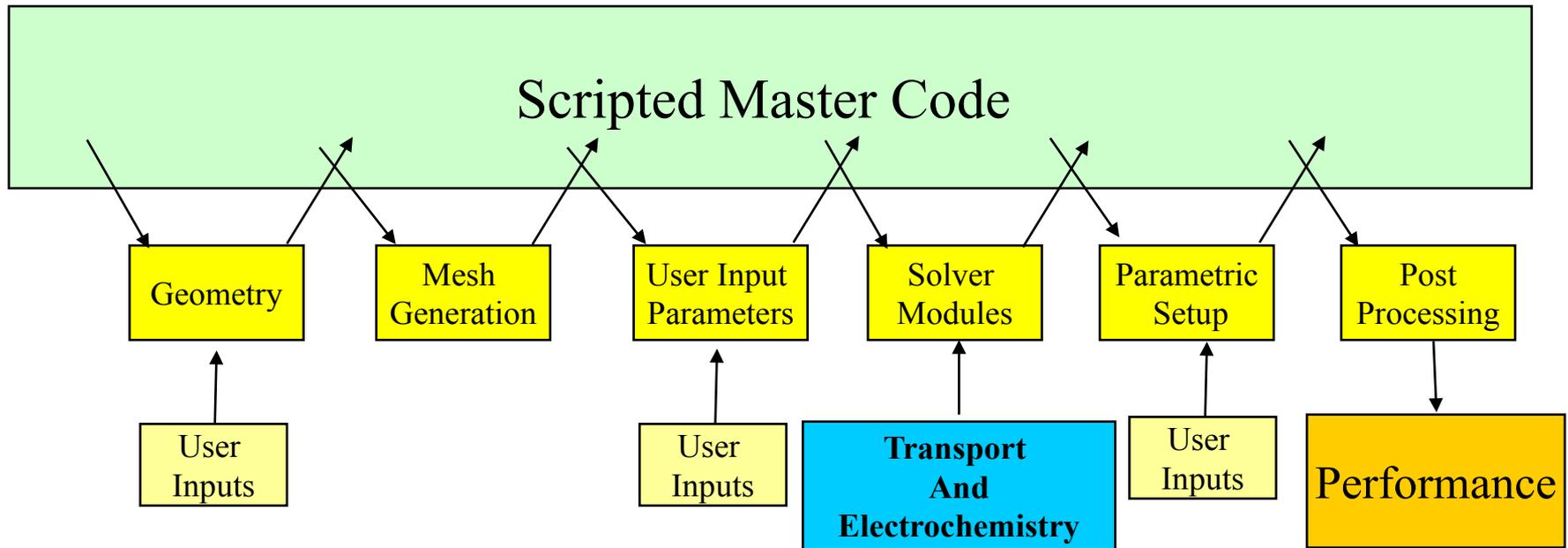
## ■ Experimental Investigations

- ▶ Operational and Structural Design Curves
  - √ • Carbon type study: Performance degradation rates established
  - √ • Ionomer content study: Performance degradation rates established
  - √ • Pt/C ratio study is in progress
  - √ • Upper Potential Limit study (two carbon supports) is completed
- ▶ Characterization
  - In-situ HRTEM Tool - planned
  - √ • Quantitative changes of the Pt surface and carbon support: Cathode powder characterization and correlation development is in progress

# Technical Progress - Modeling BOL Unit Cell Performance Model

## Model Scripts

### Scripted Master Code

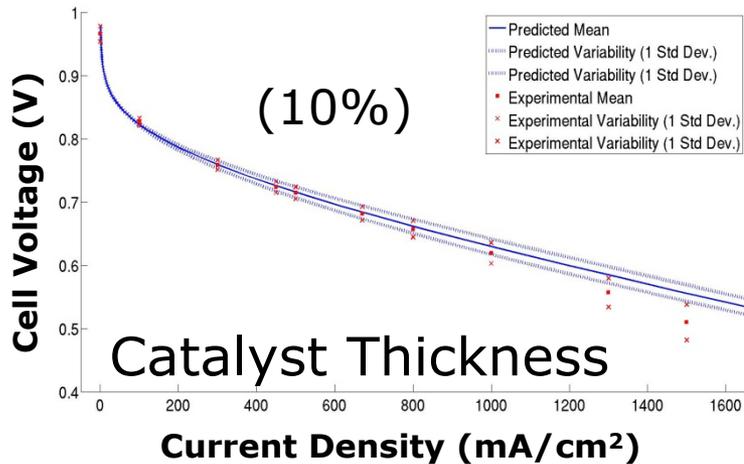
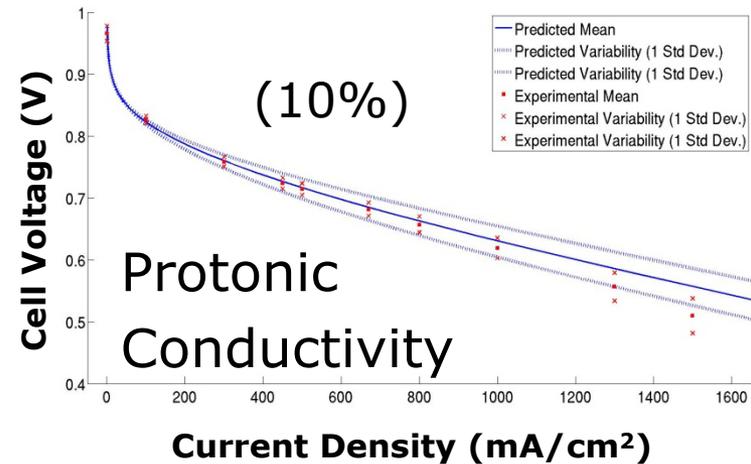
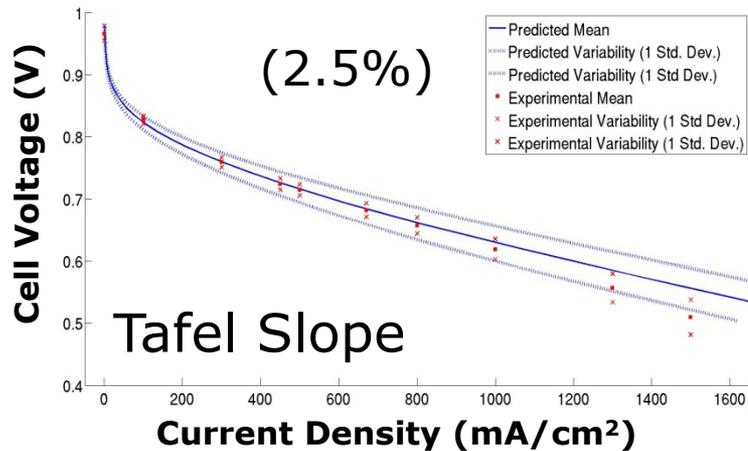


- 1-D - Unit Cell MEA model was re-derived for statistical inputs
  - Statistical inputs in geometry, transport/electrochemistry properties, and operational conditions
  - Moved to modular format to allow ease of physics modifications
  - Script based format allows automated parametric studies

# Technical Progress – Modeling BOL Simulations



## Statistical Sensitivity of Input Parameters

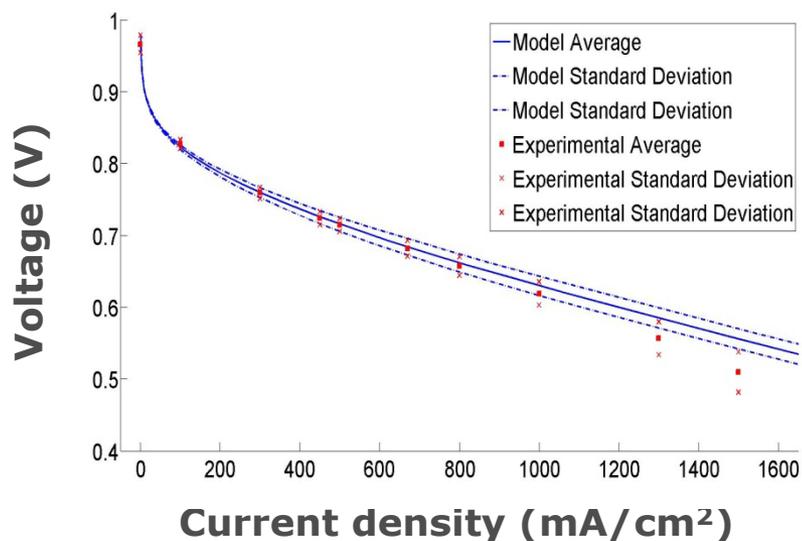


- Tested 1 – 10% variability in each input parameter.
  - Sensitive parameters are Tafel Slope, catalyst ionic resistance, catalyst thickness,  $j_0$ , ECSA, Pt loading, Pt:C ratio

# Technical Progress - Modeling BOL Simulations



## Statistical Input Options



## Statistical Input

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

## Comparison to Data

- ▶ The average experimental results agree with model prediction to ~ 1.0A/cm<sup>2</sup> (1Std Dev)
  - Experimental dataset of 20 (different MEA batches and test stands)
  - Differences between predicted and experimental at high current densities likely caused by water sensitivity
- ▶ Model is currently extended to include 2-phase flow

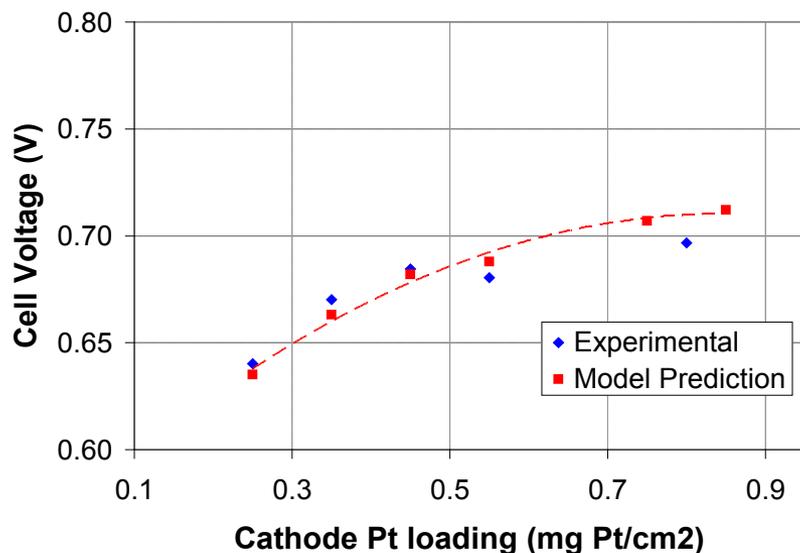


# Technical Progress - Modeling BOL Simulations

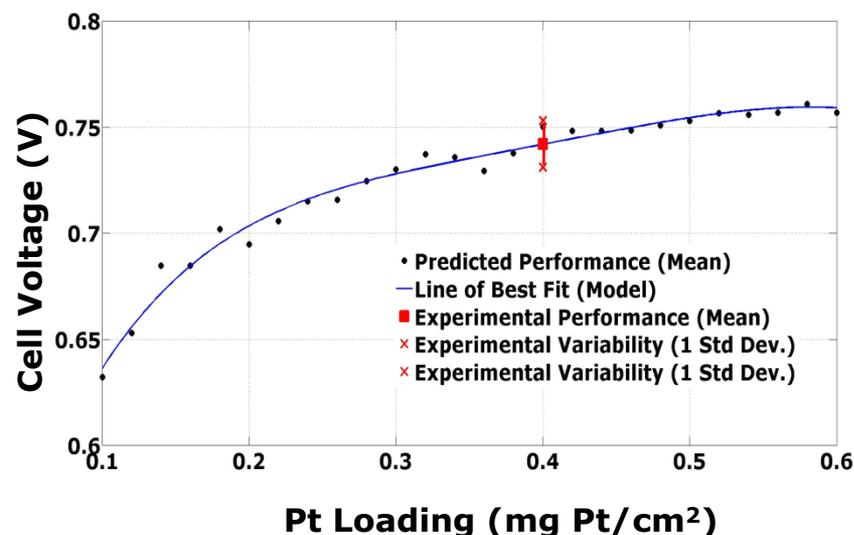


## Statistical Parametric Study

### Commercial Test Hardware



### 50 cm<sup>2</sup> Test Hardware



- Variation of Pt loading from 0.1 to 0.7mg/cm<sup>2</sup> in steps of 0.02mg/cm<sup>2</sup>
  - For each loading 15 polarization curves were generated
  - Model was validated against commercial test hardware, loading dependency is similar between the hardware.

# Technical Progress

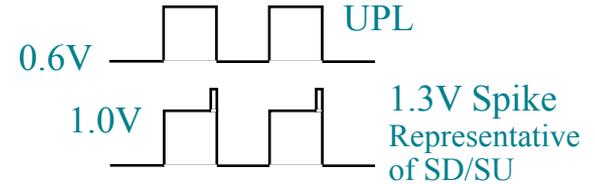
## Effect of Upper Potential Limit



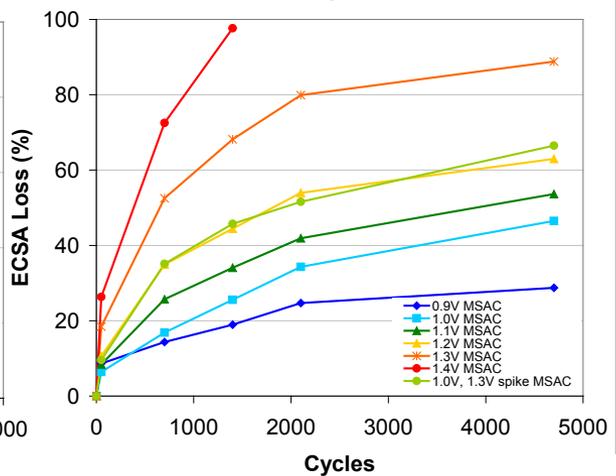
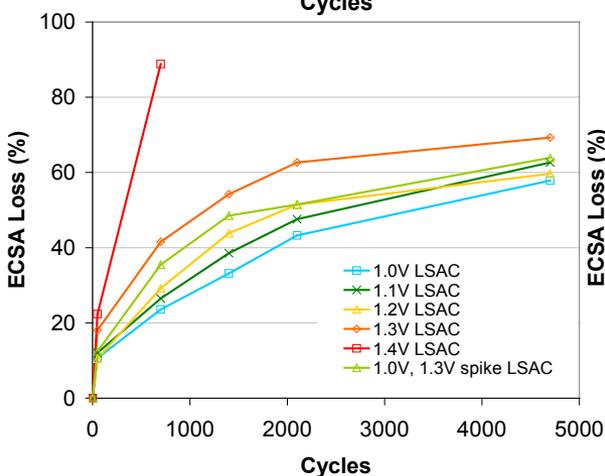
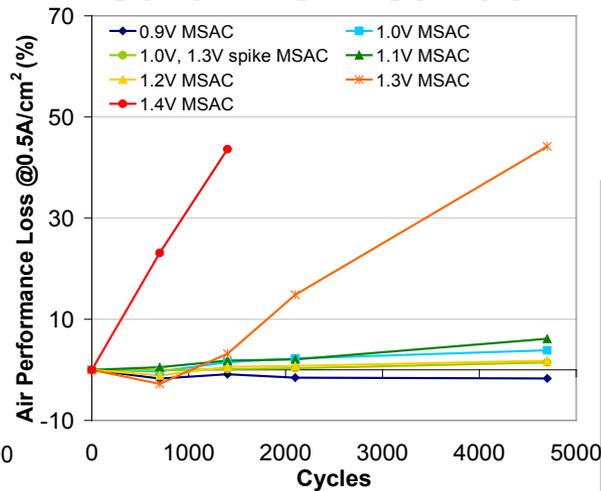
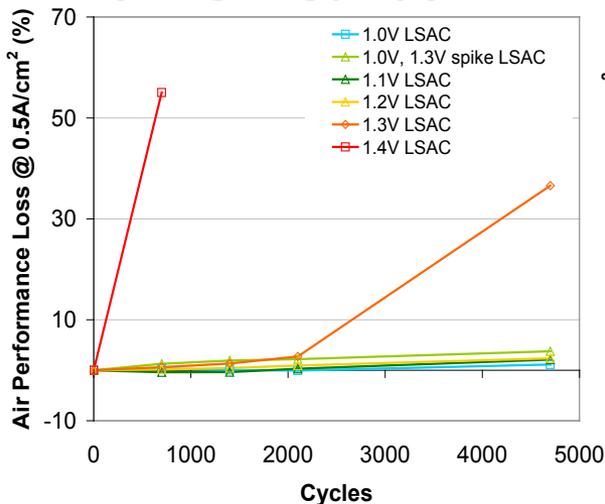
### Pt50-LSAC Low SA Carbon

### Pt50-MSAC Medium SA Carbon

### Cycling Profile



- Degradation signature is similar for both catalysts
  - Pt dissolution is the dominating mechanism at low cycle number and low UPL resulting in agglomeration and PITM
  - With increasing UPL and/or cycle number the dominant mechanism shifts to carbon corrosion
- Superimposed voltage spike does not cause significant degradation



AST: Air/H<sub>2</sub>, 100% RH, 5 psig, 80°C, 0.6 V (30 sec) → UPL (60 sec), 4700 cycles

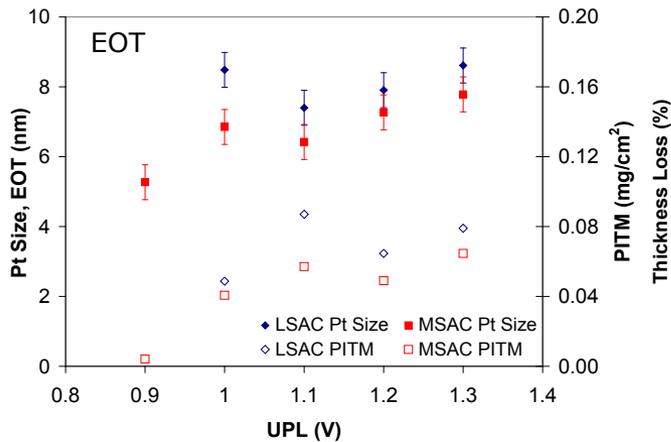
# Technical Progress

## Effect of Upper Potential Limit

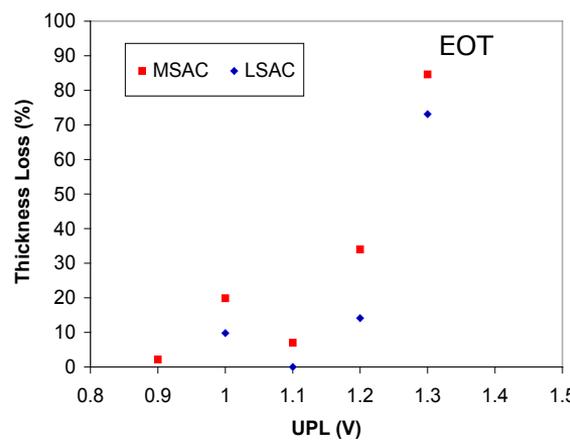


### Pt Supported on Low/Medium Surface Area Carbon

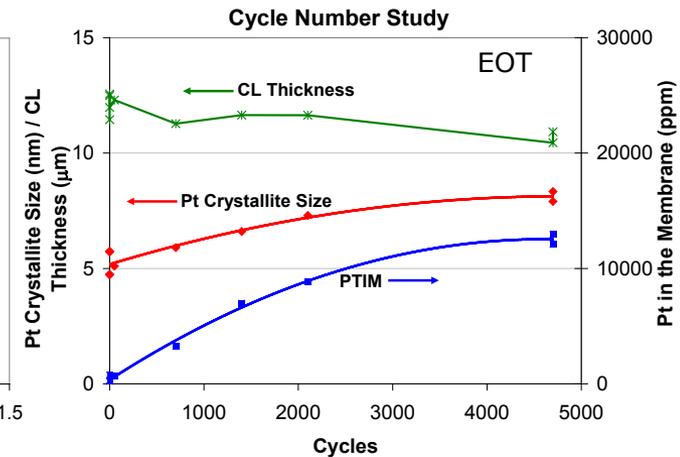
Pt Crystallite Size/PITM



Pt in the Membrane (PITM)



Pt-LSAC at 1.2V UPL



#### Pt Agglomeration at EOT

- Both catalysts have similar agglomeration at  $UPL \geq 1.0V$
- Pt50 LSAC has slightly larger Pt size

#### PITM at EOT shows dependency on UPL

- Similar PITM concentration for both catalysts

#### Catalyst layer thickness at EOT is dramatically reduced for $UPL > 1.2V$

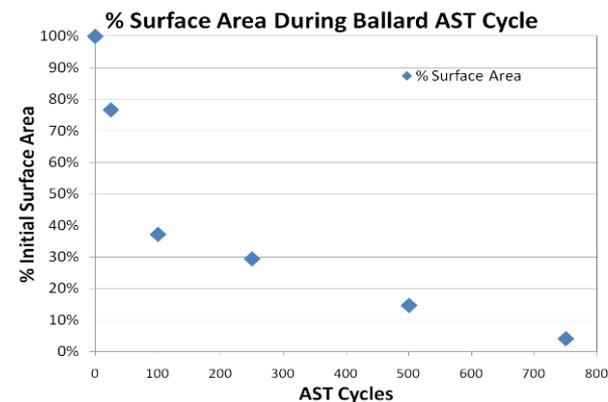
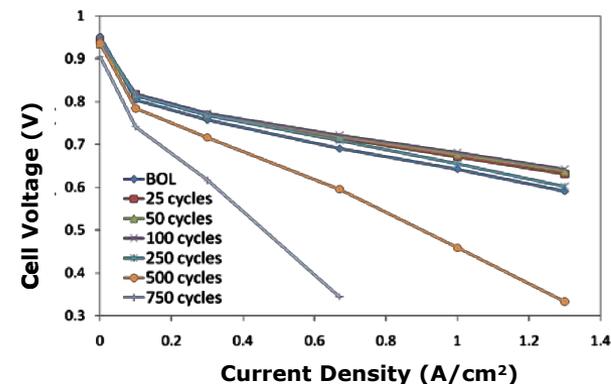
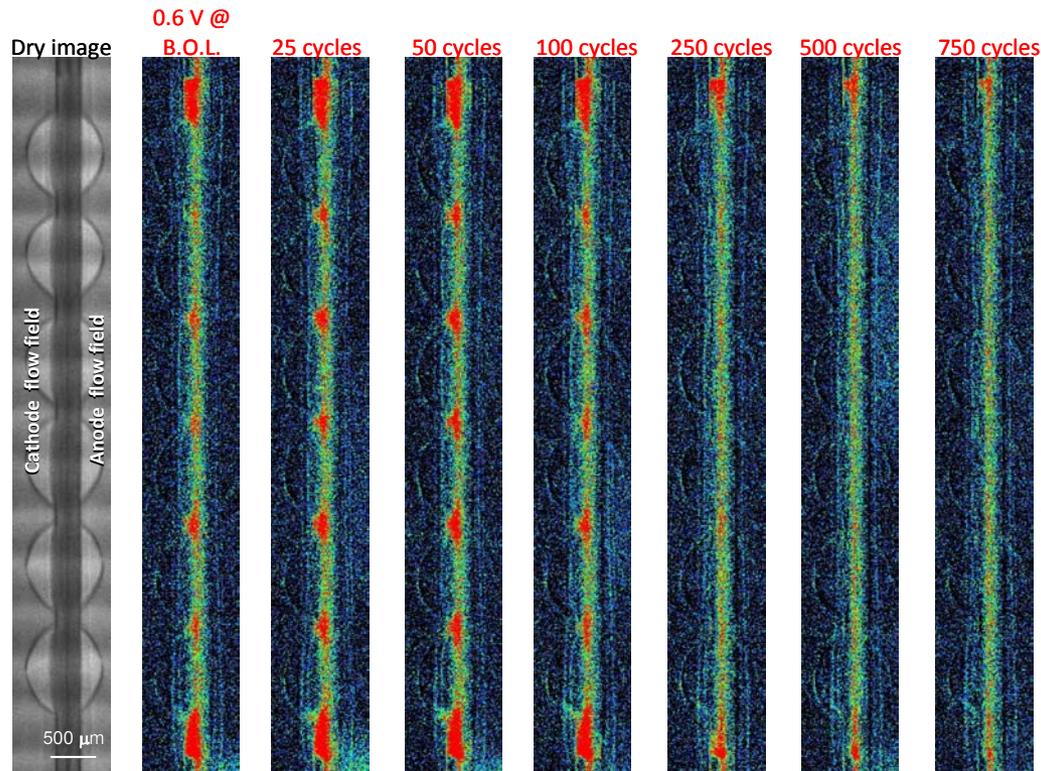
- Pt50-MSAC less corrosion resistant than LSAC

# Technical Progress

## MEA Characterization-Water Content

### Neutron Imaging - AST Test Pt50-LSAC

0.6 V images, 80°C, 100%RH; after cycles of 0.6 – 1.4 V in H<sub>2</sub>/air

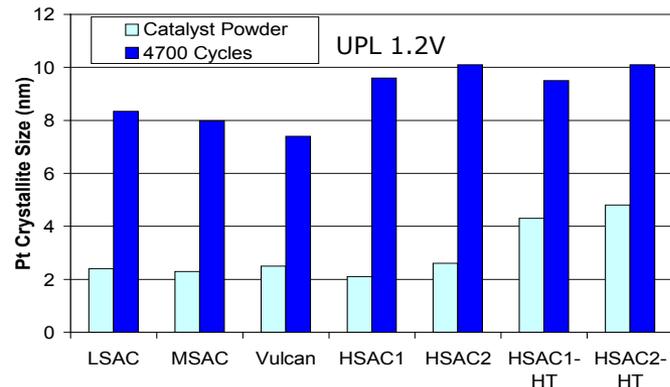
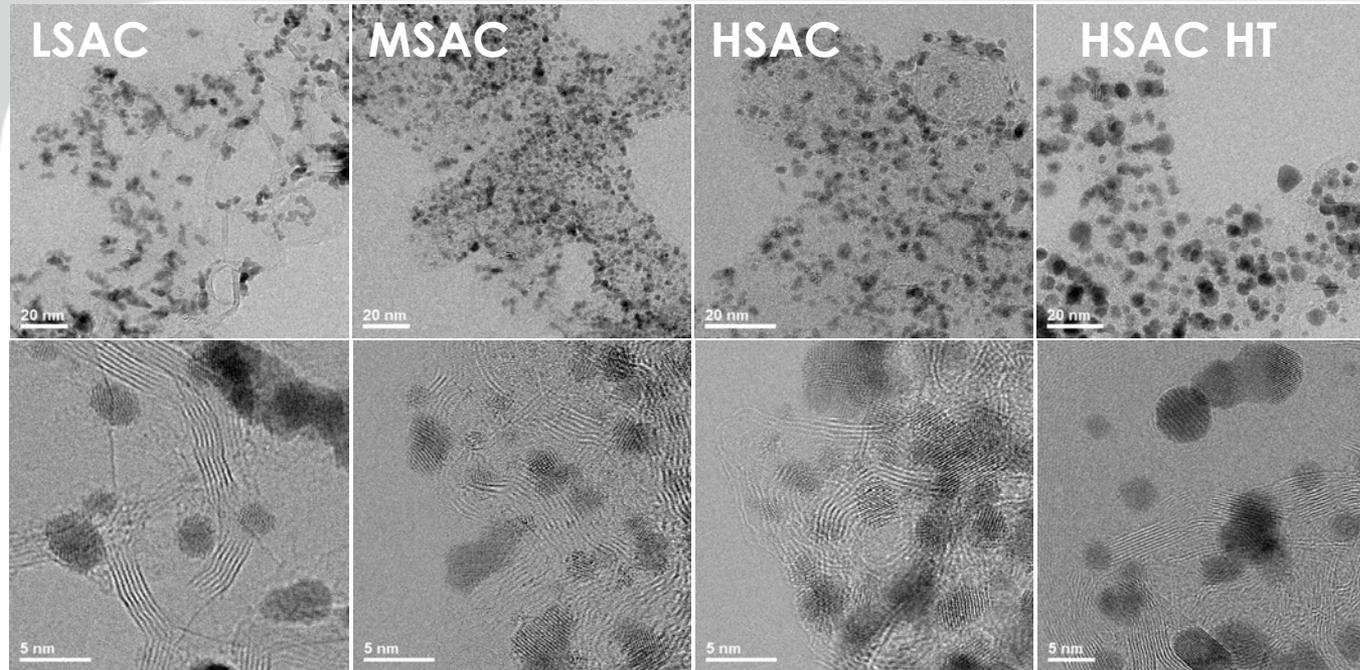
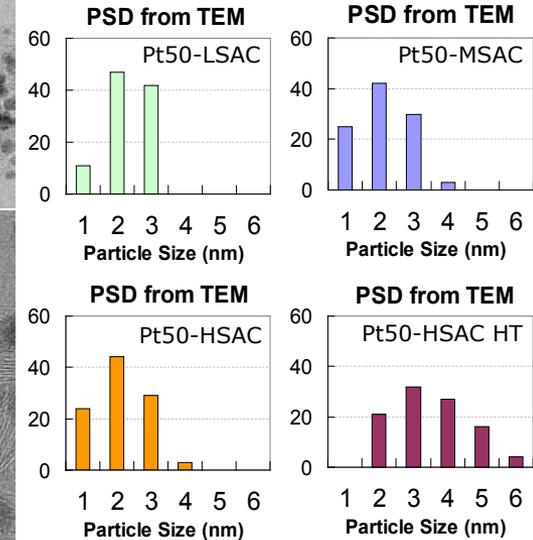


- Water content at 0.6V increases to 100 Cycles, decreases from 100 cycles to EOT
  - Performance loss is not observed until >250 cycles
- ECSA loss as observed in 50 cm<sup>2</sup> test hardware

# Technical Progress

## Effect of Carbon Type

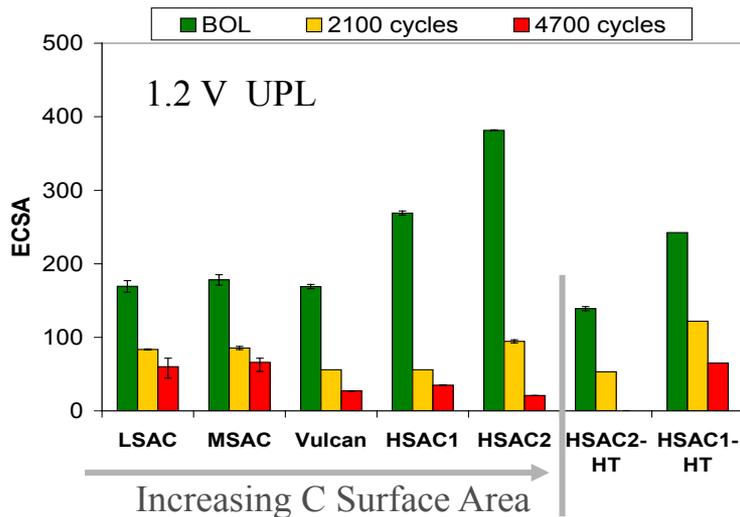
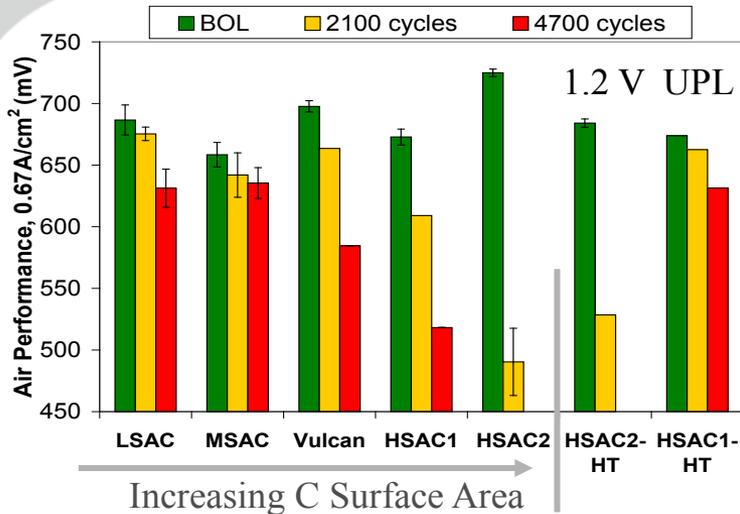
### Pt/C Catalyst Powders (50wt.%)



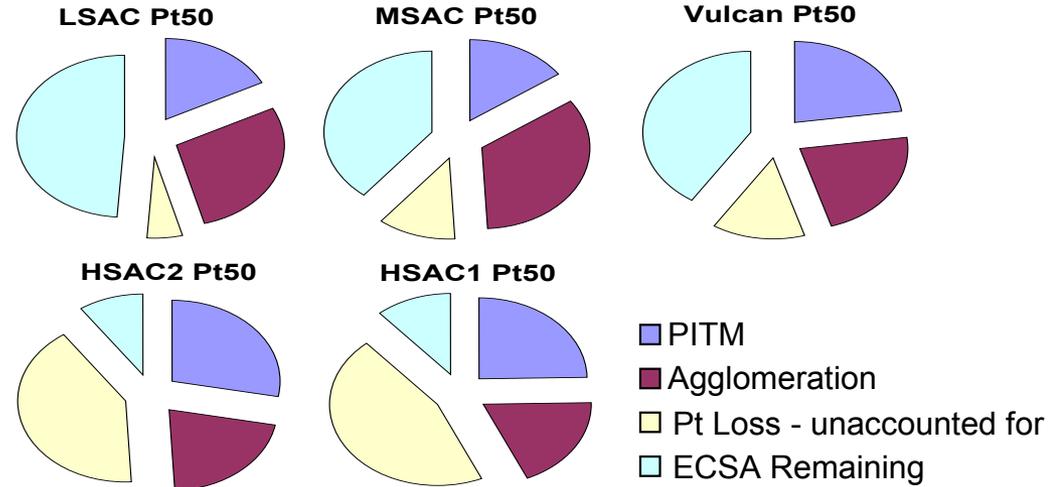
- Pt average crystallite size is similar for all non-heat treated Pt catalyst powders
- Heat treatment widens particle size distribution and increases average crystallite size
- EOT (1.2V UPL) crystallite size varies with carbon support structure

# Technical Progress

## Effect of Carbon Support Structure



### ECSA Breakdown @ EOT



- Catalysts supported on higher surface area carbons show in general improved performance but durability is greatly impacted
- Carbon support surface area is not the only measure of durability, the carbon structure and morphology impacts durability

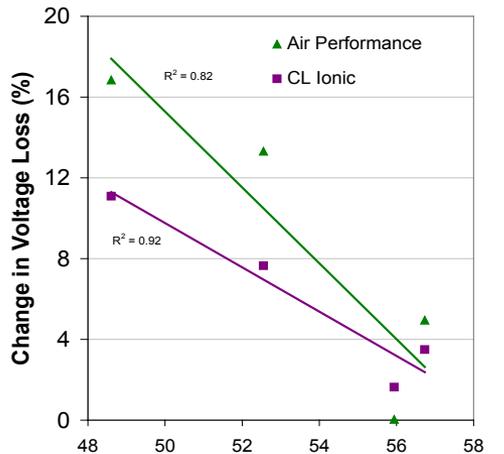
# Technical Progress Effect of Carbon Support Structure

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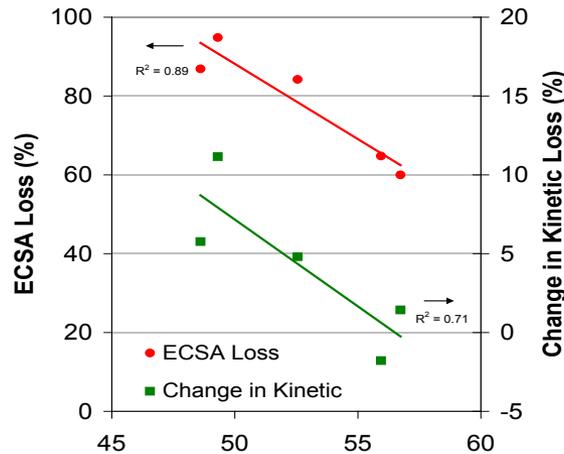


THE UNIVERSITY of  
NEW MEXICO

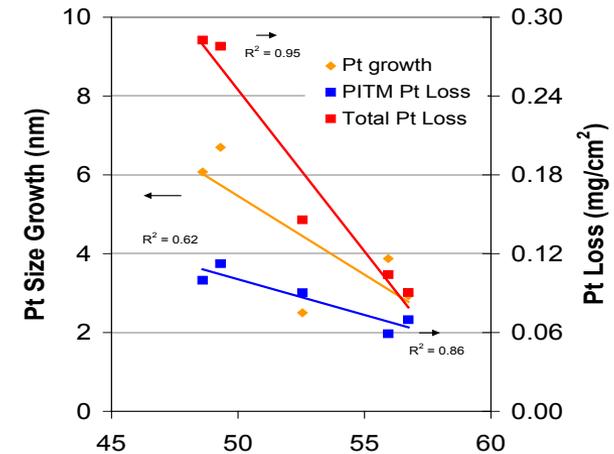
## Graphitic Carbon Content of Catalyst Support



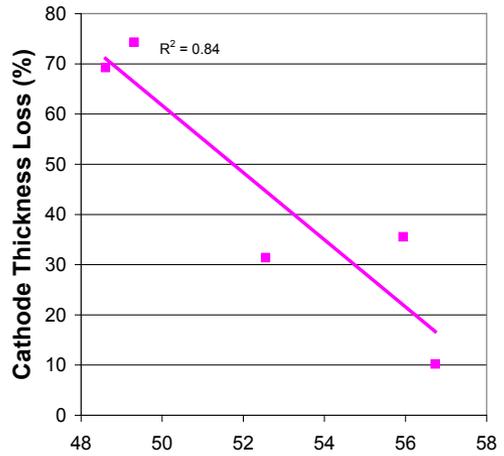
Graphitic Carbon, Carbon Powder (% of total C)



Graphitic Carbon, Carbon Powder (% of total C)



Graphitic Carbon, Carbon Powder (% of total C)



Graphitic Carbon, Carbon Powder (% of total C)

- **Graphitic carbon content of catalyst support is one measure of durability**
- **Degradation decreases with increasing graphitic content**
  - Voltage loss
  - Catalyst layer ionic voltage loss
  - ECSA, Pt dissolution
  - Carbon corrosion (cathode thickness change)



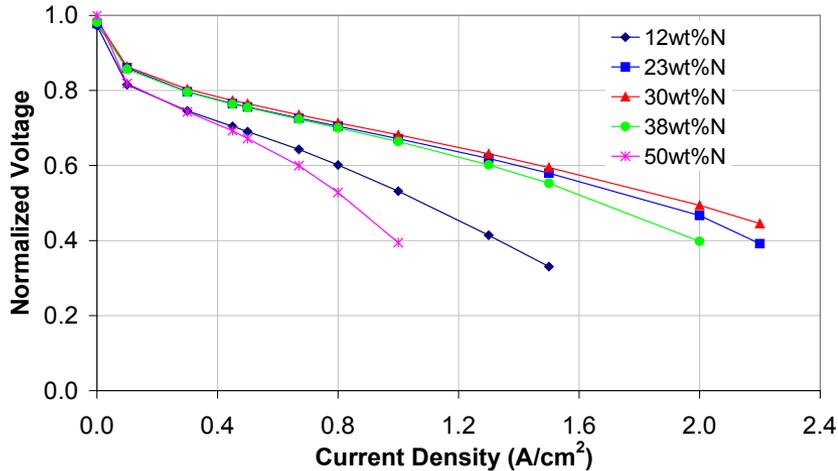
# Technical Progress

## Effect of Ionomer Loading

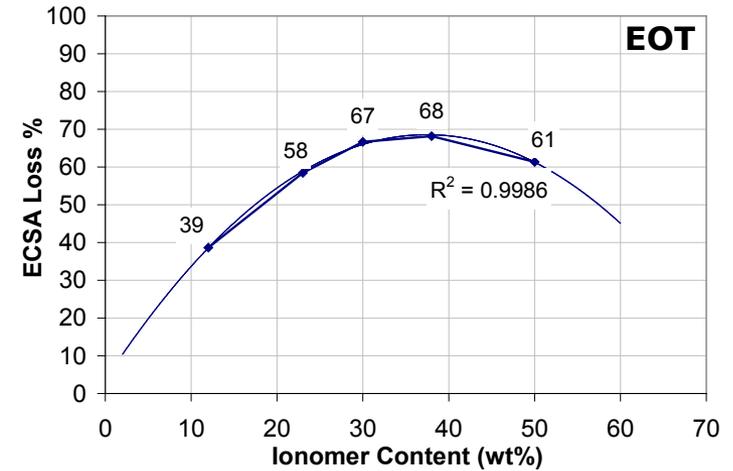


### Low Surface Area Carbon Catalyst (Pt50-LSAC)

Nafion Loading Study BOL Performance

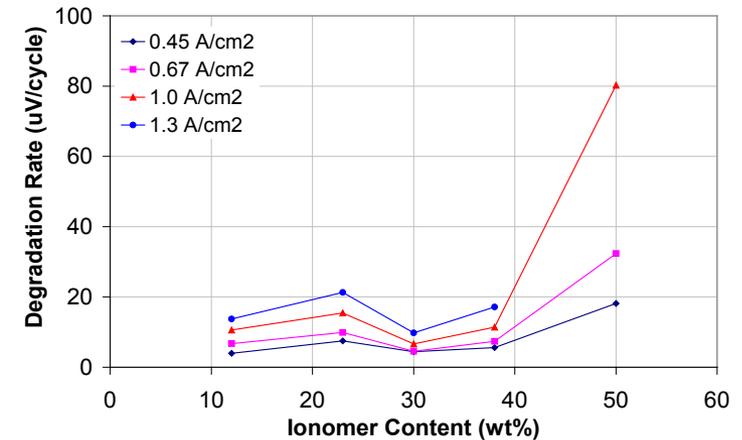


ECSA Loss vs. Ionomer Content



- Optimal performance for Nafion loading is ~30wt%
- Increased ionomer content results in:
  - increased catalyst layer ionic conductivity
  - increased ECSA loss (Pt dissolution)
- Excessive ionomer (50wt%) results in greater mass transport and catalyst layer resistance losses

Degradation Rate vs. Ionomer Content



- **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

# Plan Forward

## Experimental/Characterization



### ■ **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**

- Refinement of saturation model
- 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**

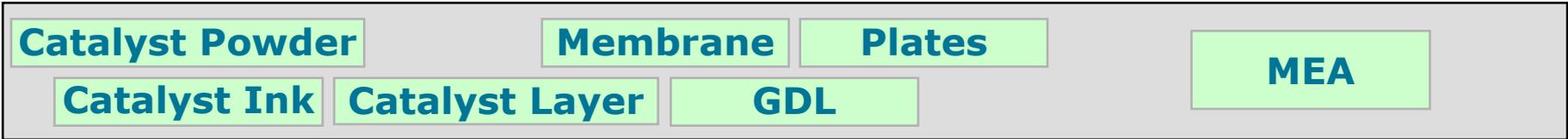
- GDL wettability and capillary pressure
- Interface characterization
- Property changes of aged GDLs and catalyst layers

- **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 and cell operational conditions
- **Technical Accomplishments and Progress to date**
  - Implemented statistical input option for macro model
  - Quantified Pt/C catalyst performance degradation with UPL, carbon support type, ionomer loading
  - Composition effects included in BOL MEA performance model and validated with experimental results
- **Collaborations**
  - Project team partners GIT, LANL, MTU, Queen's, UNM
  - Participation in DOE Durability Working Group
- **Proposed Future Research**
  - Validate 2-phase flow micro-structural model and expand to full catalyst layer thickness
  - Complete MD model of Pt/C/ionomer, develop MD description of Pt dissolution
  - Refinement of liquid water transport physics, validate statistical capability (Go/No-Go)
  - Effect of the carbon ratio and ionomer type on AST degradation rates

# Project Applicability to Industry



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



## 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

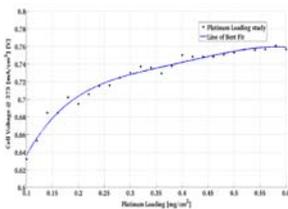
- EW
- Thickness

## BOL Performance

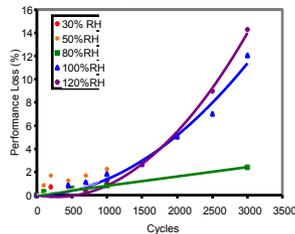
- ECSA
- Exchange current density
- Tafel slope
- Mass activity
- HFR

## Operating Conditions

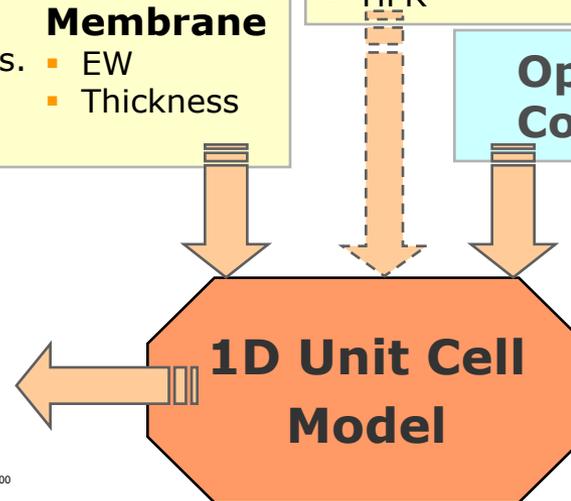
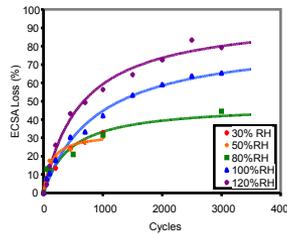
Parametric Performance Study



Predicted Voltage Degradation



Predicted ECSA Loss



# Acknowledgement



## ■ Thank you:

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

## Acronyms/Abbreviations

AST	Accelerated Stress Test	LSAC	Low Surface Area Carbon
BOL = BOT	Beginning of Life = Beginning of Test	MD	Molecular Dynamics
CB	Carbon Black	MEA	Membrane Electrode Assembly
CCL	Cathode Catalyst Layer	MOL = MOT	Middle of Life = Middle of Test
CL	Catalyst Layer	MPL	Micro-porous Layer
Cond	Conductivity	MSAC	Mid-range Surface Area Carbon
CV	Cyclic Voltammetry	NAA	Neutron Activated Analysis
ECSA	Effective Catalyst Surface Area	OER	Oxygen Evolution Reaction
EDX	Energy Dispersive X-ray Analysis	ORR	Oxygen Reduction Reaction
EIS	Electrode Impedance Spectroscopy	PSD	Particle Size Distribution
EOL = EOT	End of Life = End of Test	Pt/C	Platinum/Carbon Ratio
EPSA	Effective Pt Surface Area (cm <sup>2</sup> Pt/cm <sup>2</sup> geom)	PITM	Platinum in the Membrane
EW	Equivalent Weight	RH	Relative Humidity
FA	Failure Analysis	SA	Surface Area
GDL	Gas Diffusion Layer	SEM	Scanning Electron Microscopy
HFR	High Frequency Resistance	TEM	Transmission Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy	UPL	Upper Potential Limit
HSAC	High Surface Area Carbon	XPS	X-ray Photoelectron Spectroscopy
HSAC-HT	High Surface Area Carbon - Heat Treated	XRD	X-ray diffraction



# Technical Backup Slides

## ■ **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**

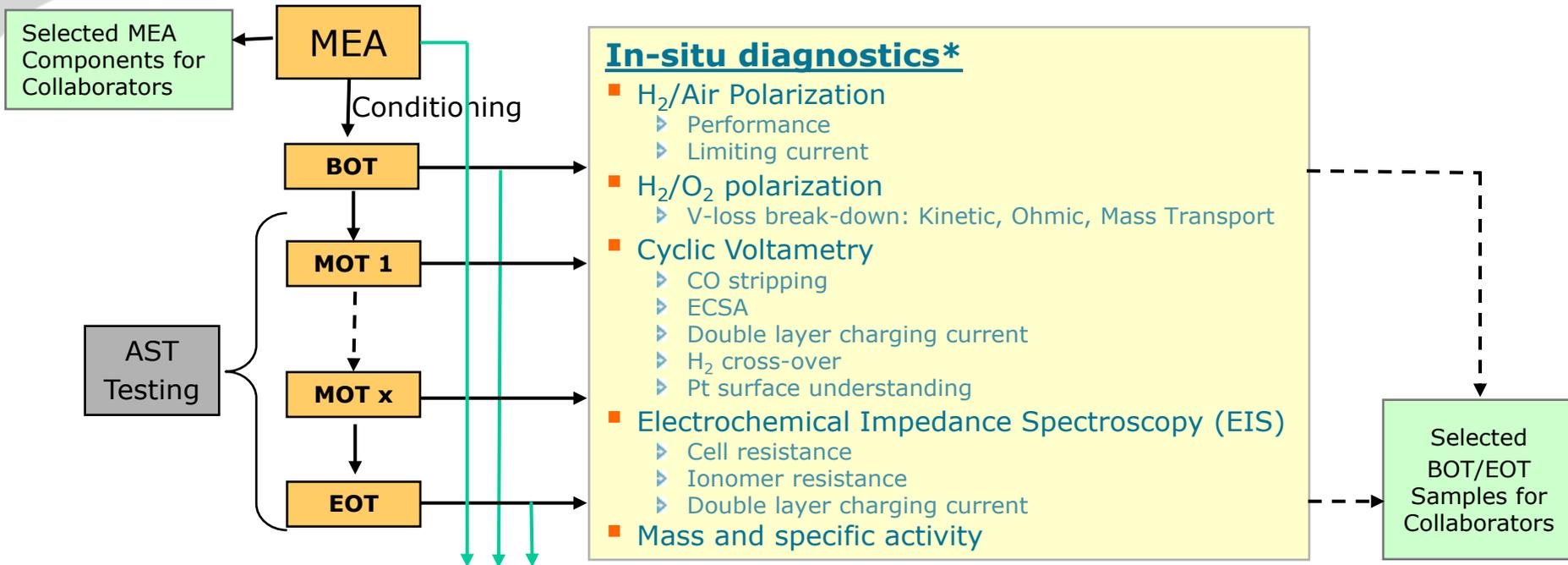
### ‣ Systematic evaluation of performance loss, catalyst layer structural and compositional changes of different catalyst layer structures/compositions under a variety of operational conditions

- Carbon support type, Pt/C ratio, ionomer content, ionomer EW, catalyst loading
- Potential, RH, O<sub>2</sub> 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

## ■ **DOE Working Group (Durability and Modeling)**

### ‣ Interaction and data exchange with other projects

# Experimental Approach



## 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

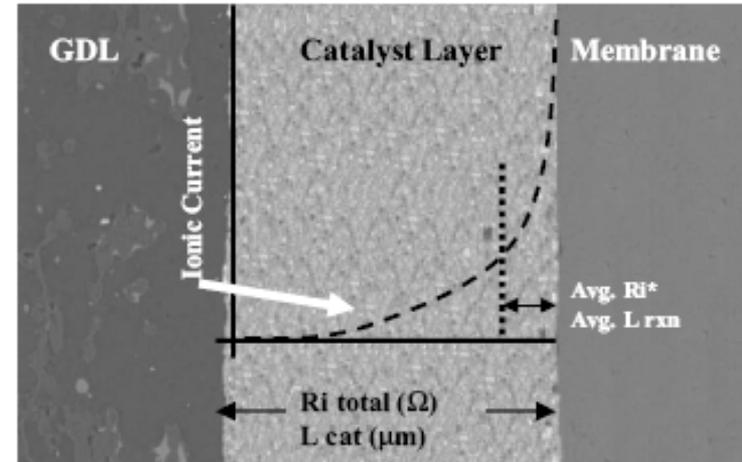
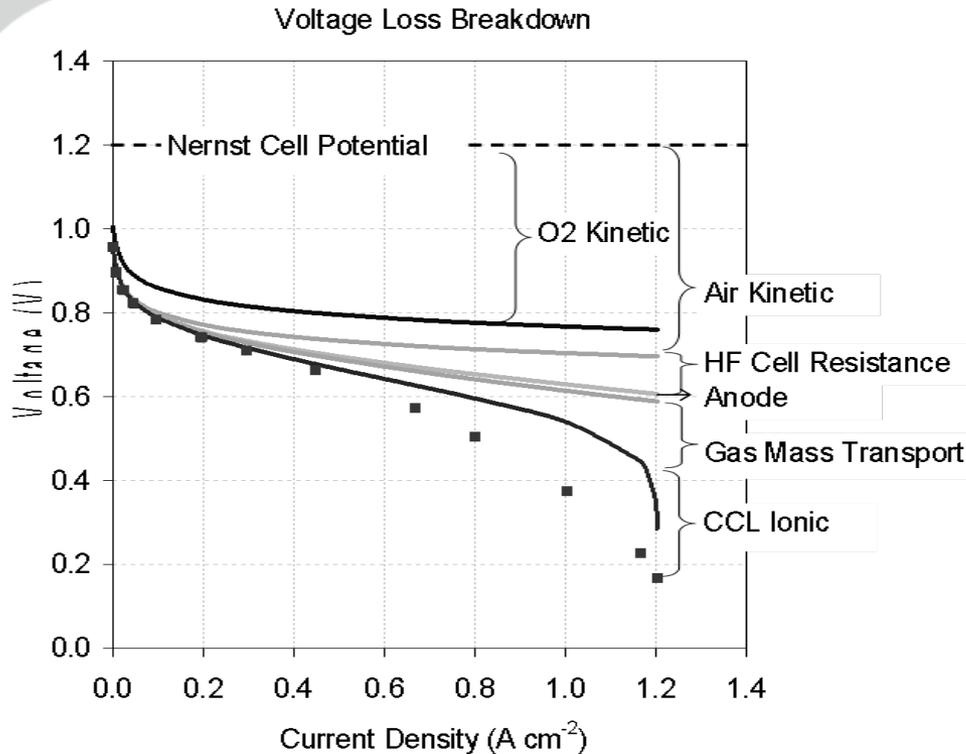
\* Ongoing evaluation, i.e. list of diagnostics may change

**Reference AST:** Air/H<sub>2</sub>, 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/cm<sup>2</sup> (Cathode/anode), Ballard CCM, Nafion® NR211, BMP GDLs

**Ballard 1D Test Cell, 45cm<sup>2</sup> active area**

# Experimental Approach Voltage Loss Breakdown Method



*A. Young et al, Journal of The Electrochemical Society, 157 3 B425-B436 2010*

- **Separation of voltage loss based on Air/O<sub>2</sub> and EIS**
  - ▶ Kinetic/ohmic/mass transport loss
  - ▶ Cathode catalyst layer ionic loss and estimated reaction penetration depth
- **Model validation of transport processes**
  - ▶ Kinetic rates for ORR
  - ▶ Component resistances
  - ▶ Mass transport losses at high and low current conditions

# Experimental Benchmarking

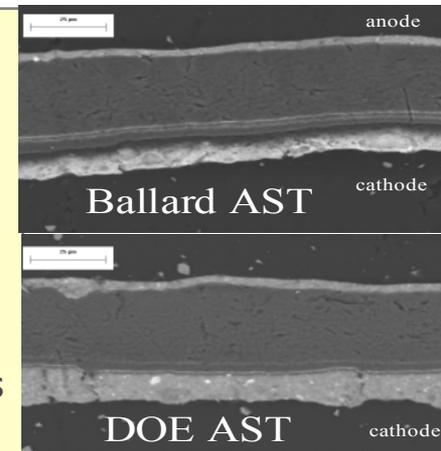


## Compare degradation mechanisms for AST protocols

Oxidant	Failure Modes	Advantages	Limitations
<b>Nitrogen (Water)</b>	<ul style="list-style-type: none"> <li>■ Pt Agglomeration</li> <li>■ Carbon Surface Oxidation</li> <li>■ Carbon Corrosion</li> <li>■ PITM (?)</li> </ul>	<ul style="list-style-type: none"> <li>■ Under N<sub>2</sub>, membrane degradation is nominal</li> <li>■ No product water effects</li> </ul>	<ul style="list-style-type: none"> <li>■ Platinum deposition occurs near the membrane/catalyst interface and is not separable from catalyst agglomeration.</li> </ul>
<b>Air</b>	<ul style="list-style-type: none"> <li>■ Pt Agglomeration</li> <li>■ PITM</li> <li>■ Carbon Surface Oxidation</li> <li>■ Carbon Corrosion</li> </ul>	<ul style="list-style-type: none"> <li>■ More realistic to field data due to separable platinum in the membrane.</li> <li>■ Potential to capture effect of ionomer degradation</li> </ul>	<ul style="list-style-type: none"> <li>■ More difficult to control RH due to water production</li> <li>■ Membrane degradation may occur at 1.0V UPL</li> <li>■ More difficult to control/ set-up equipment (potentiostat &amp; loadbank)</li> </ul>

### Primary Protocol Differences (DOE vs. Ballard)

- ▶ Triangular vs. square ramp
  - Square cycling profile enables better control/understanding of mechanisms
- ▶ N<sub>2</sub> vs. synthetic Air
  - Ability to quantify Pt in the membrane failure mode
  - Failure modes representative of products
- ▶ 1.0V vs. 1.2V upper potential limit (UPL)
  - 1.2V UPL enables better comparison with state-of-the-art catalysts
  - UPL will be investigated in operational and structural studies



# Experimental Benchmarking



## Ranking of Stressors

### Operational

Operational Stressor	Range Studied	Mechanism Shift
UPL	0.8>>>1.2V	≥1.2V
	0.8>>>1.3 V	≥1.2V
	0.8>>>1.5 V	≥1.2V
Dwell Time Cycle #	30-5000sec (10,000-1 cycle)	
Temp (UPL 1.3V)	60>>>80C	≥70
Temp (UPL 1.2V)	60>>>80C	≥75
RH	50>>>120%	≥100%
LPL	0.5>>>0.8V	

#### Legend

<b>Negligible Effect:</b> No Significant Change
<b>Small Effect:</b> 2 to 5 times increase in deg. rate
<b>Medium Effect:</b> 5 to 10 times increase in deg. rate
<b>Large Effect:</b> >10X increase in deg. rate

\*Based on LSAC

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### Structural

Structural Stressor	Impact on Degradation
Carbon Support Type	High
Pt/C Ratio	High
Ionomer loading	Medium
Pt Particle size	Medium
Membrane	Low-Medium
Pt Loading	Low
GDL Type	Low

\*Based on literature and experimental results

\*Relative Ranking

## Catalyst Samples Being Investigated

	Sample ID	Sample Specifics
Carbon	Vulcan	Vulcan
	LSAC	Low Surface Area Carbon
	MSAC	Mid-range Surface Area Carbon
	HSAC #1	High Surface Area Carbon #1
	HASC #2	High Surface Area Carbon #2
	Catalysts	Pt50-Vulcan
Pt50-LSAC		50/50 Pt/Low Surface Area Carbon
Pt50-MSAC		50/50 Pt/Mid-range Surface Area Carbon
Pt50-HSAC #1		50/50 Pt/High Surface Area Carbon #1
PT50-HSAC#1 -HT		50/50 Pt/High Surface Area Carbon #1 -Heat Treated
Pt50-HSAC #2		50/50 Pt/High Surface Area Carbon #2
Pt50-HSAC #2 HT		50/50 Pt/High Surface Area Carbon #2 - Heat Treated
Pt30-LSAC		30/70 Pt /Low surface Area Carbon
Pt40-LSAC		40/60 Pt /Low surface Area Carbon
Pt60-LSAC		60/40 Pt /Low surface Area Carbon
Pt80-LSAC	80/20 Pt /Low surface Area Carbon	