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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

Overview

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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 + FFDRC
  - $ 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

Relevance

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- **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. ≤40% mass activity loss, <10% carbon support mass loss

Approach

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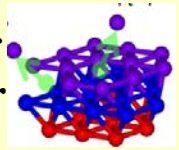
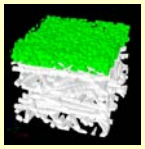
MD Model of Pt/C/Ionomer



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

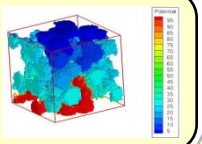
Micro-structural GDL Model



- Boundary conditions
- Effective properties

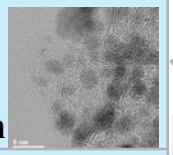
- Boundary conditions

Microstructural Catalyst Layer Model

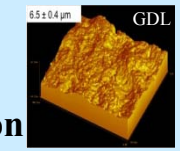


- Effective properties
- Mechanism rates
- Catalyst structure

Catalyst Powder /Ink Characterization



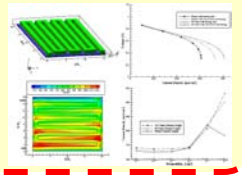
MEA/ Components Characterization



Properties

Validation Data

1D-Unit Cell Model

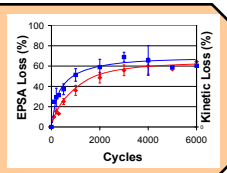


Deliverable

- 1D MEA degradation model
- BOL performance/degradation design curves

Validation Data

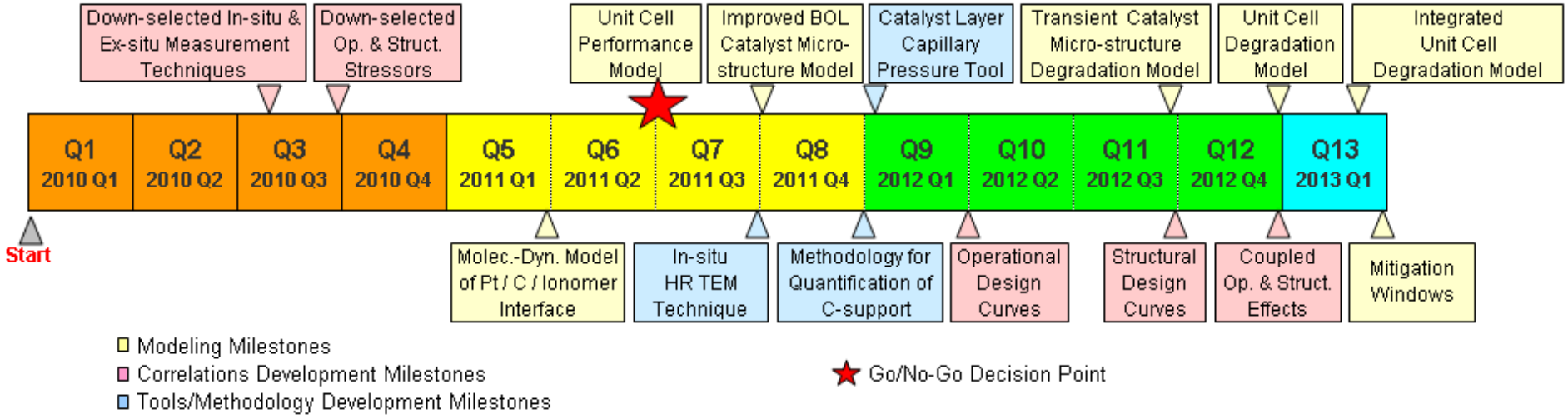
Experimental Investigations



Design Curves

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

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

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√ - Completed
√ - In Progress

- **Model Development**
  - Molecular dynamic model of the Pt/C/ionomer system
    - √ Determined cohesive energy of Pt cluster and interaction with H_2O and O_2, 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

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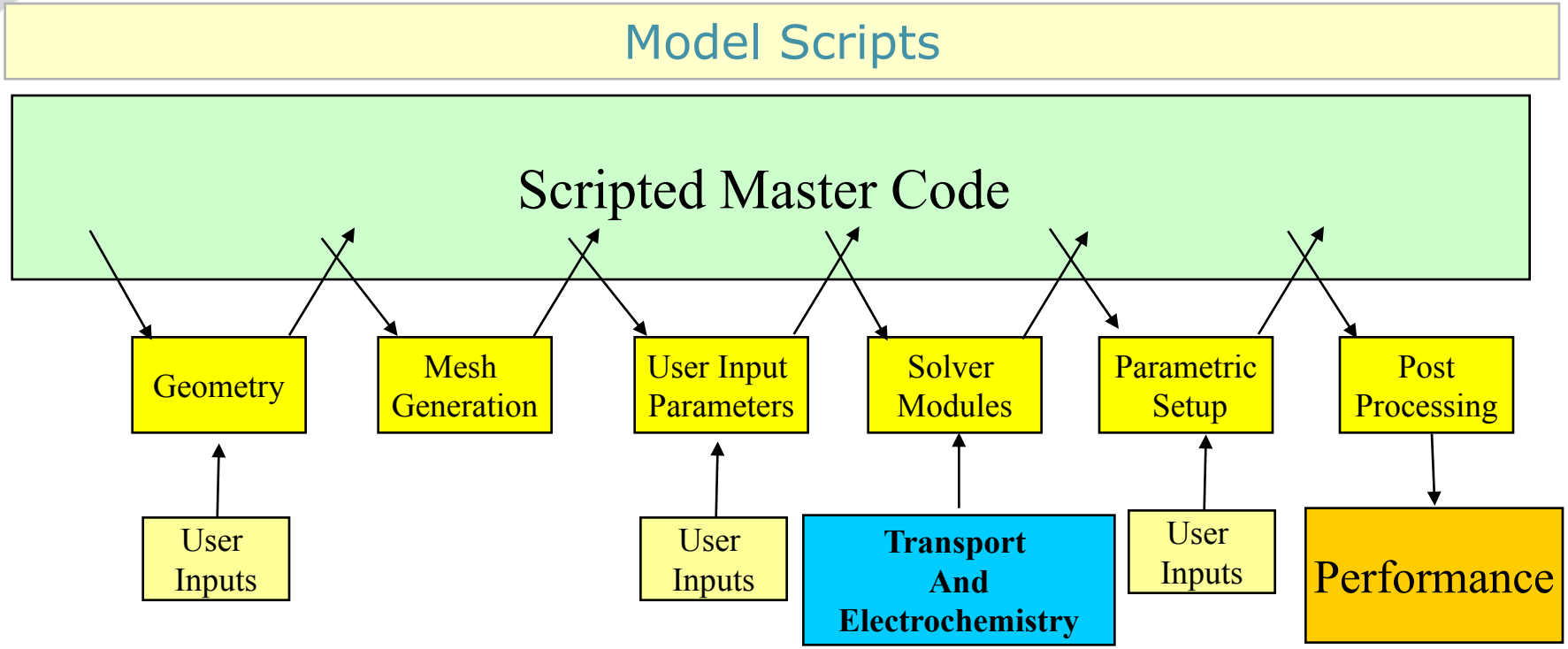

- 1-D - Unit Cell MEA model was re-derived for statistical inputs
  - Statistical inputs in geometry, transport/electrochemistry properties, and operational conditions
  - Moved to modular format to allow ease of physics modifications
  - Script based format allows automated parametric studies

Technical Progress – Modeling
BOL Simulations

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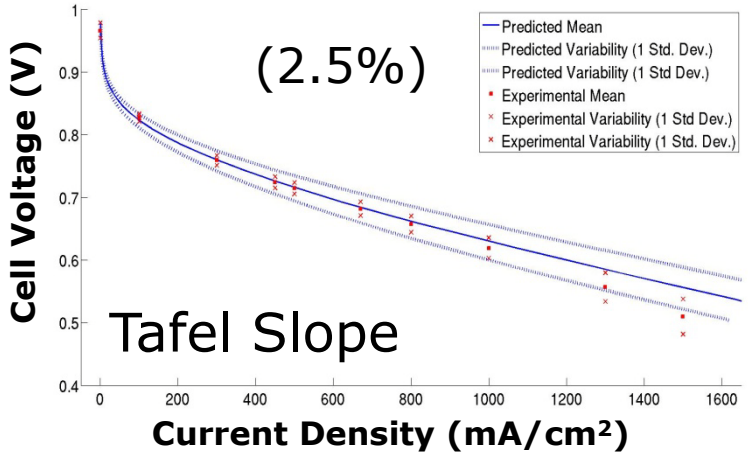
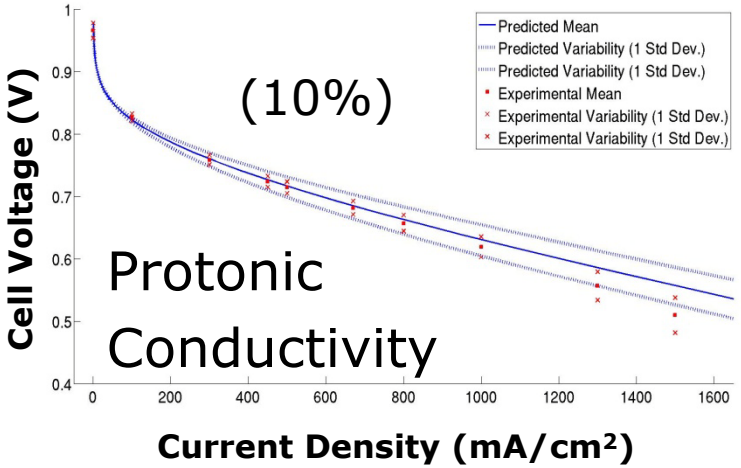
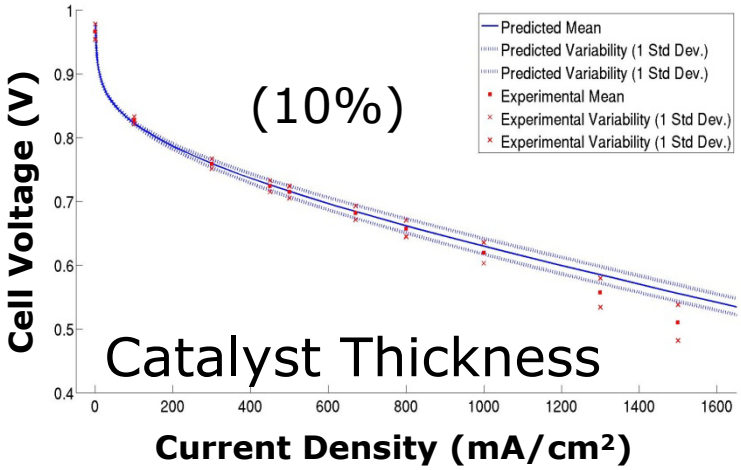
Statistical Sensitivity of Input Parameters







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

Technical Progress - Modeling
BOL Simulations

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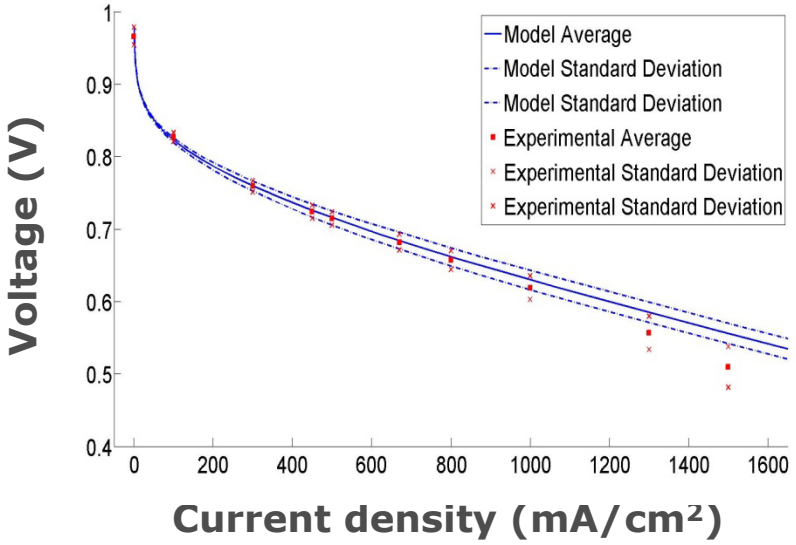
Statistical Input Options



Statistical Input

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%

- Comparison to Data
  - The average experimental results agree with model prediction to ~ 1.0A/cm² (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

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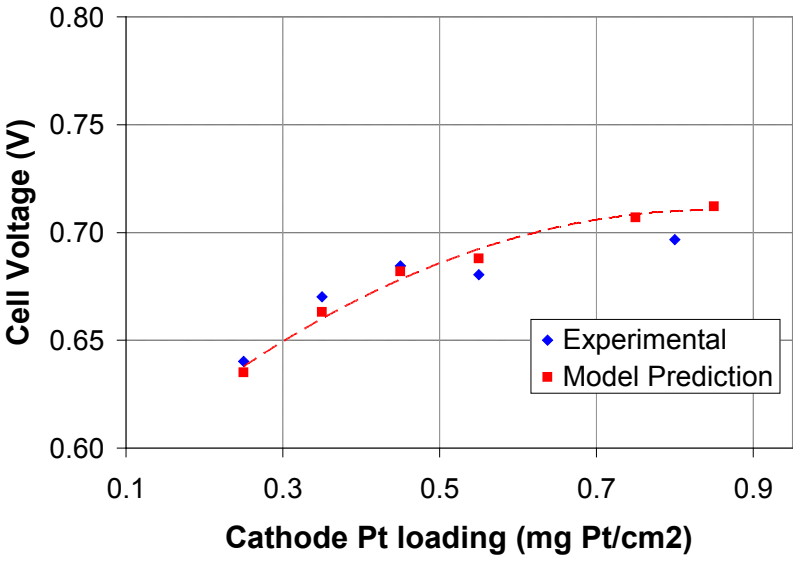
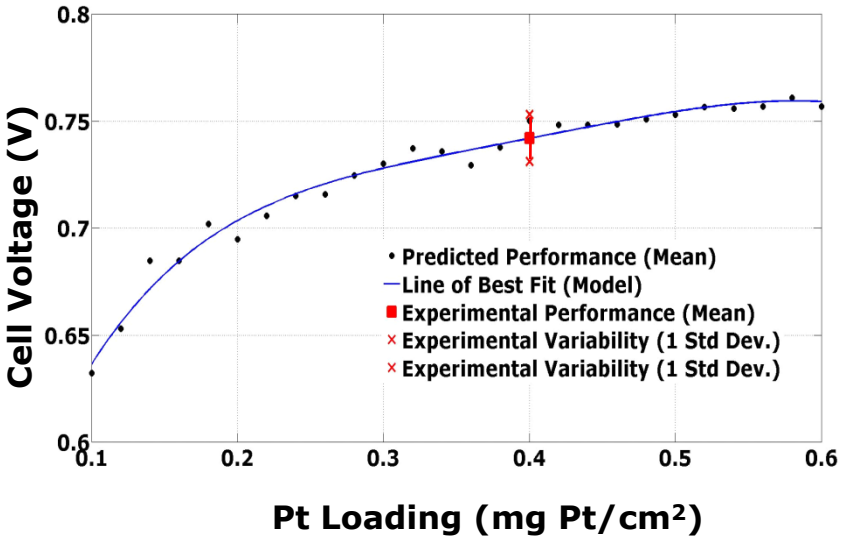
Statistical Parametric Study

Commercial Test Hardware



50 cm² Test Hardware



- Variation of Pt loading from 0.1 to 0.7mg/cm² in steps of 0.02mg/cm²
  - 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

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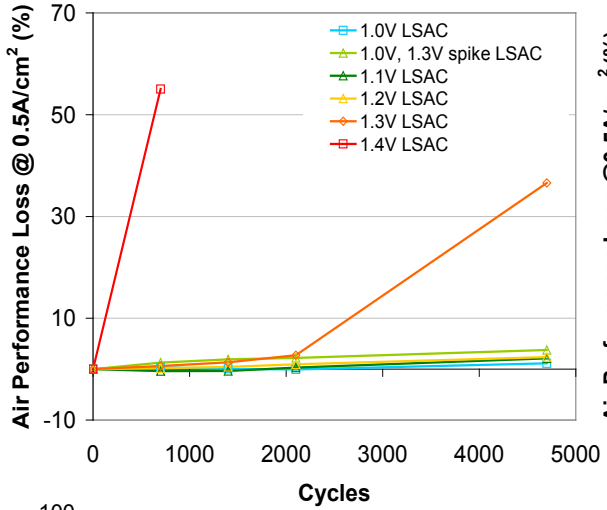
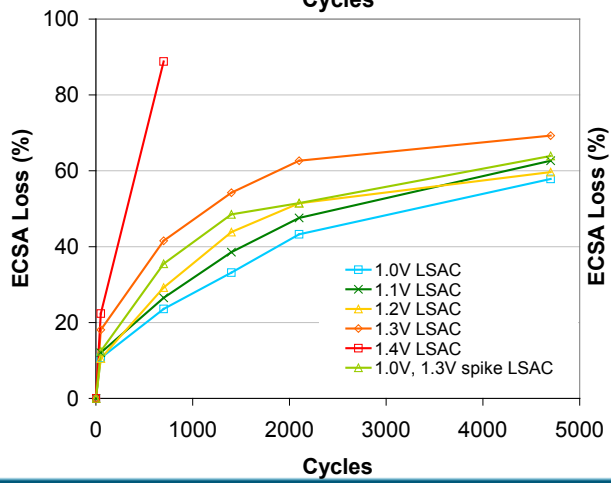
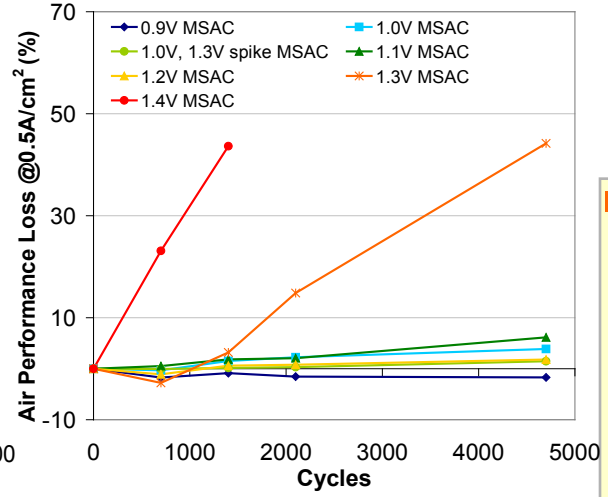
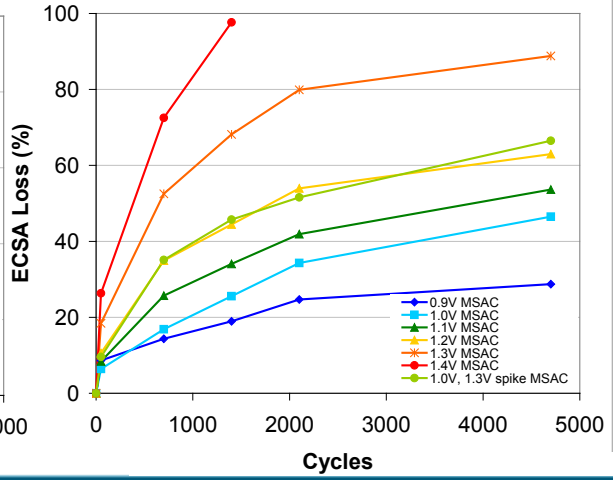
Pt50-LSAC
Low SA Carbon



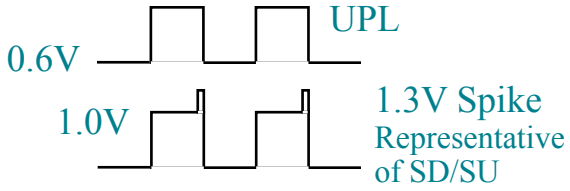


Pt50-MSAC
Medium SA Carbon





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/H2, 100% RH, 5 psig, 80°C, 0.6 V (30 sec)→ UPL (60 sec), 4700 cycles

Technical Progress
Effect of Upper Potential Limit

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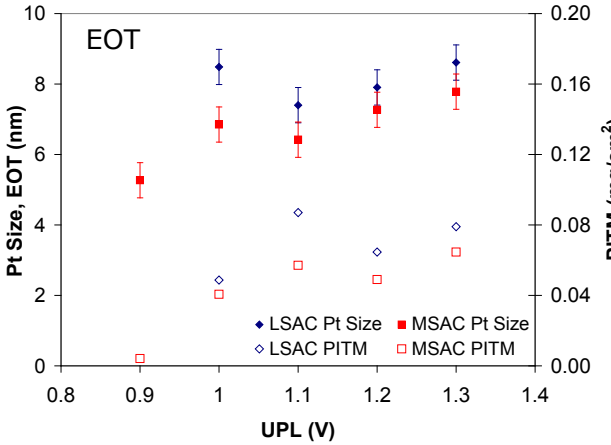
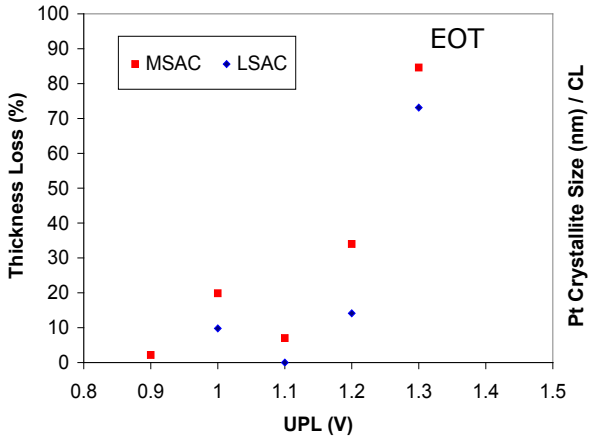
Pt Supported on Low/Medium Surface Area Carbon

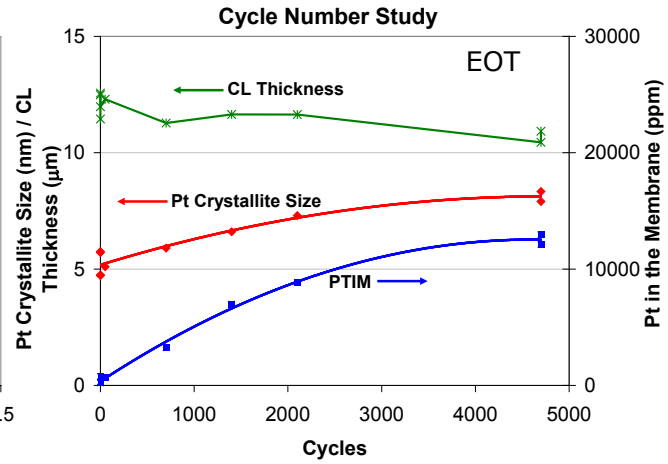
Pt Crystallite Size/PITM



Pt in the Membrane (PITM)



Pt-LSAC at 1.2V UPL

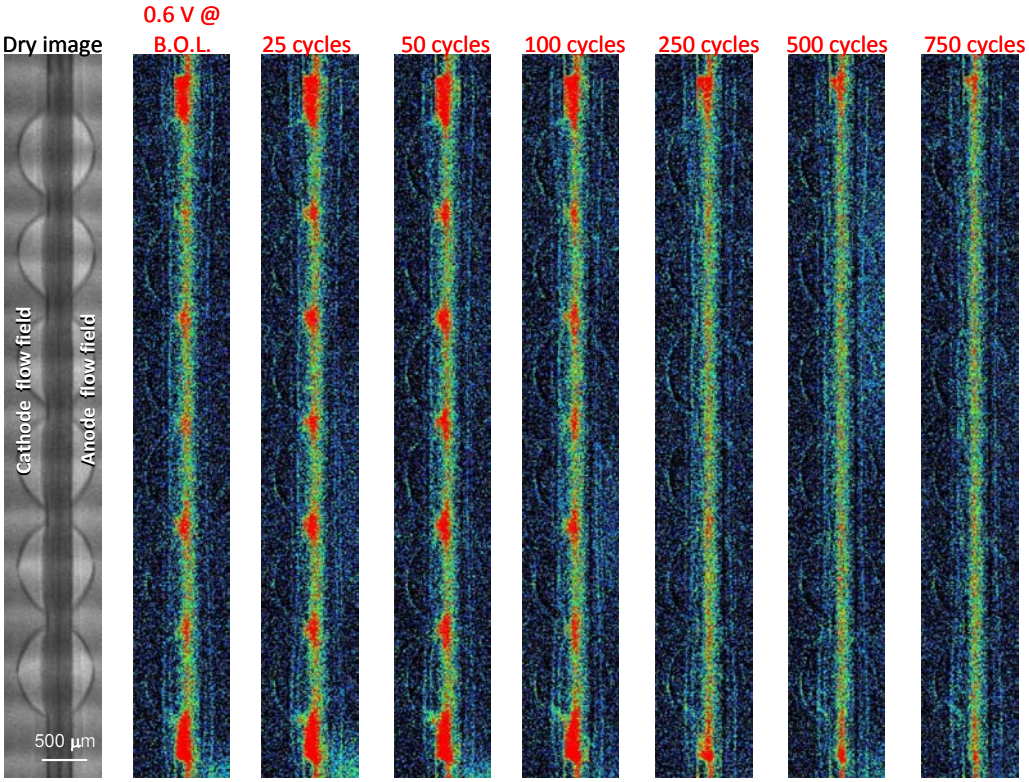


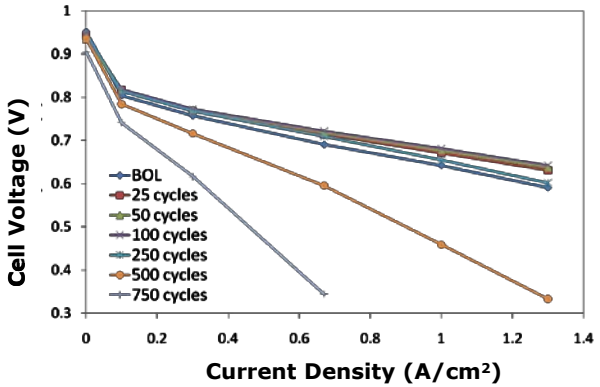
- Pt Agglomeration at EOT
  - Both catalysts have similar agglomeration at UPL≥1.0V
  - Pt50 LSAC has slightly larger Pt size
- PITM at EOT shows dependency on UPL
  - Similar PITM concentration for both catalysts
- Catalyst layer thickness at EOT is dramatically reduced for UPL>1.2V
  - Pt50-MSAC less corrosion resistant than LSAC

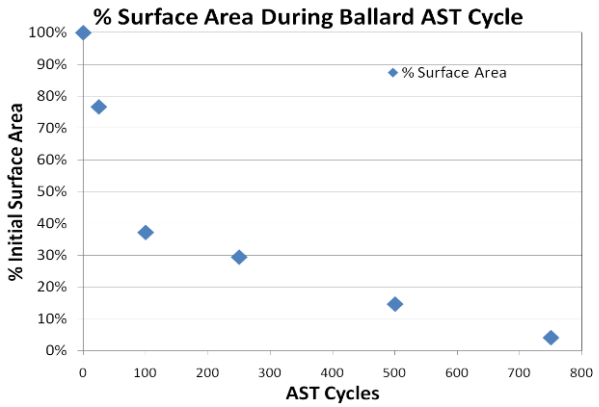
AST: Air/H2, 100% RH, 5 psig, 80°C, 0.6 V (30 sec)→ UPL (60 sec), 4700 cycles

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 H2/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 cm² test hardware**

Technical Progress
Effect of Carbon Type

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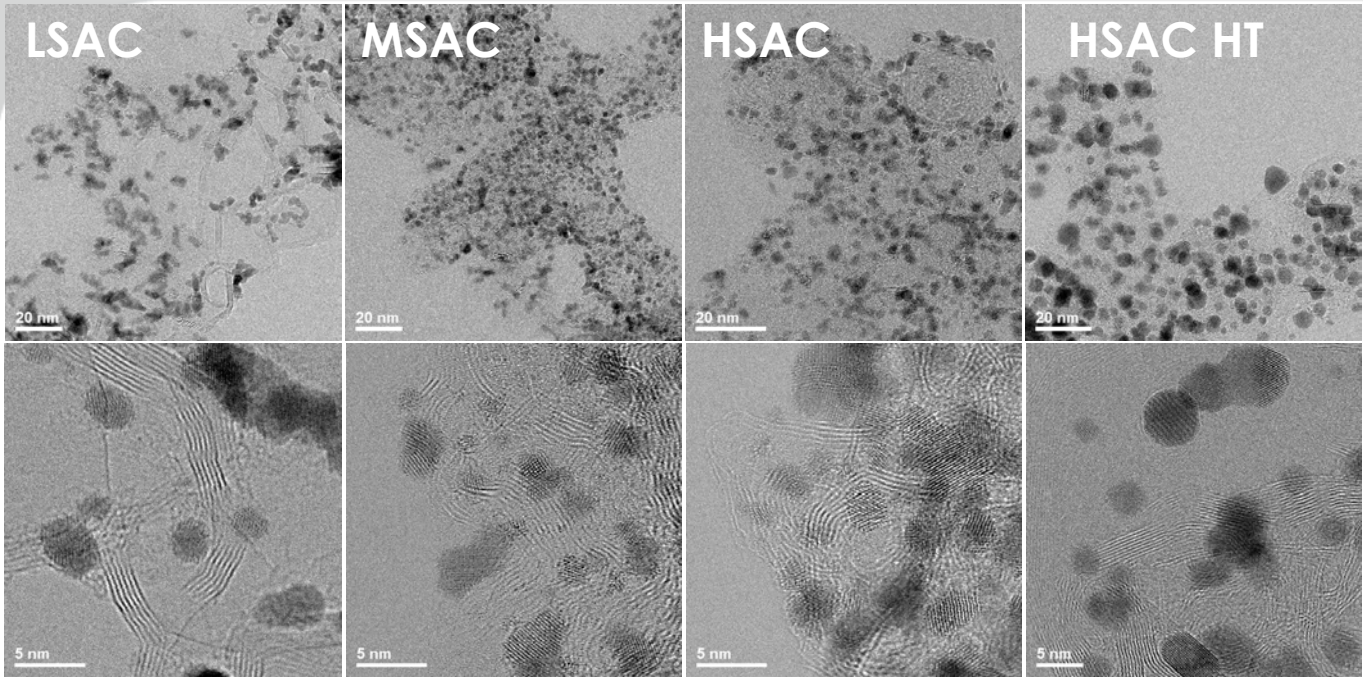
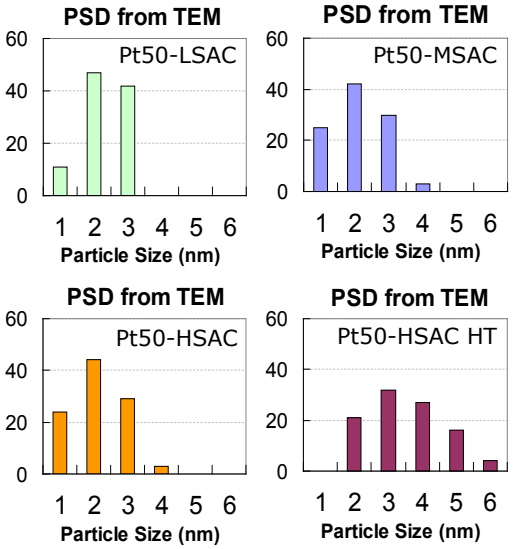
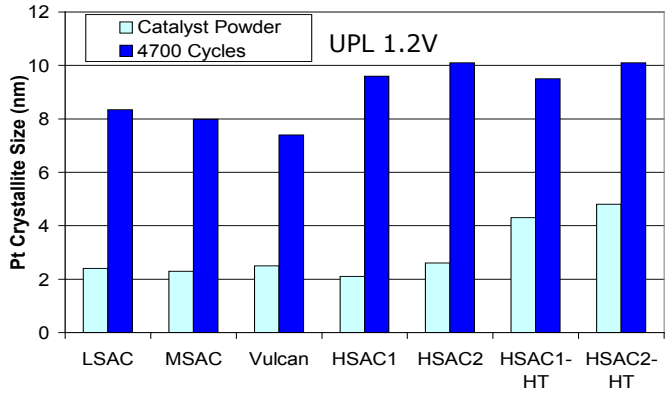


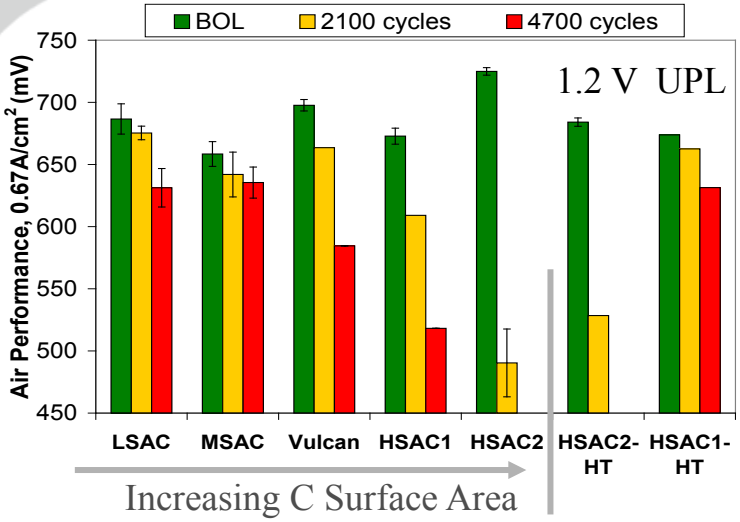
Pt/C Catalyst Powders (50wt.%)

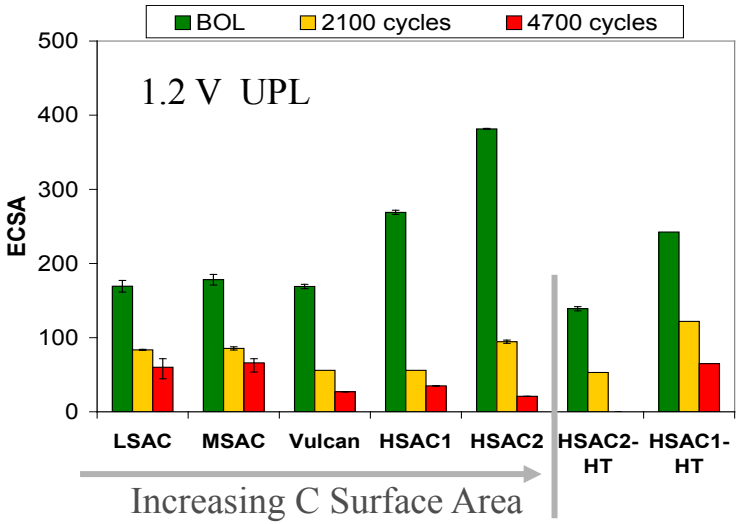




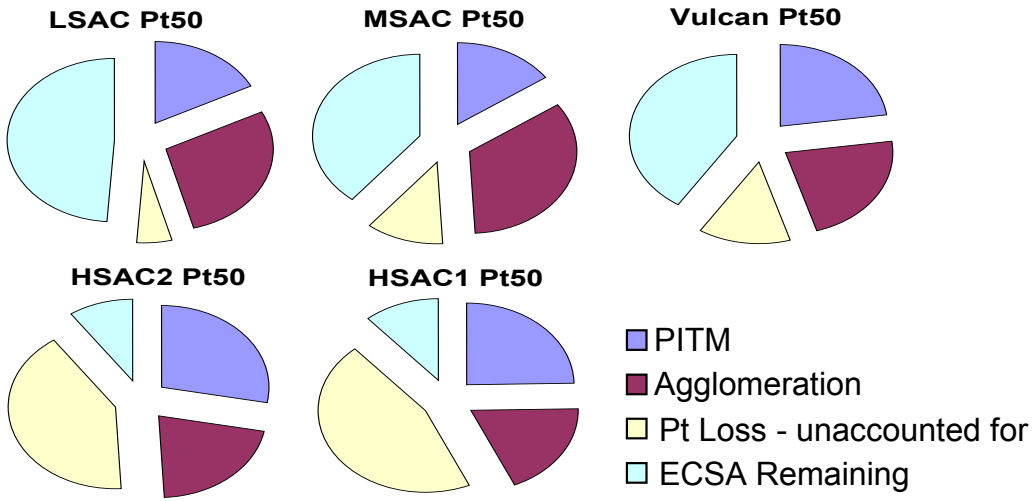
- Pt average crystallite size is similar for all non-heat treated Pt catalyst powders
- Heat treatment widens particle size distribution and increases average crystallite size
- EOT (1.2V UPL) crystallite size varies with carbon support structure

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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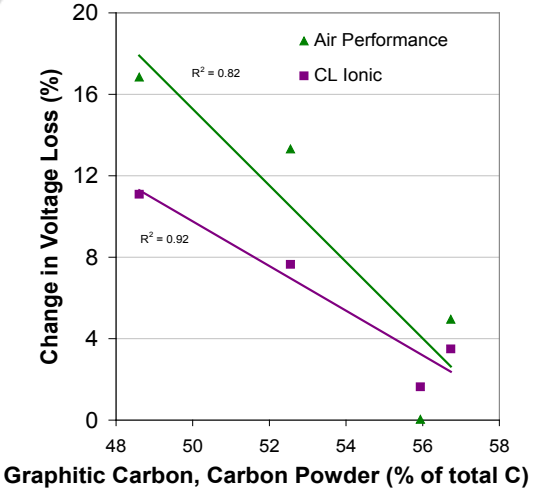
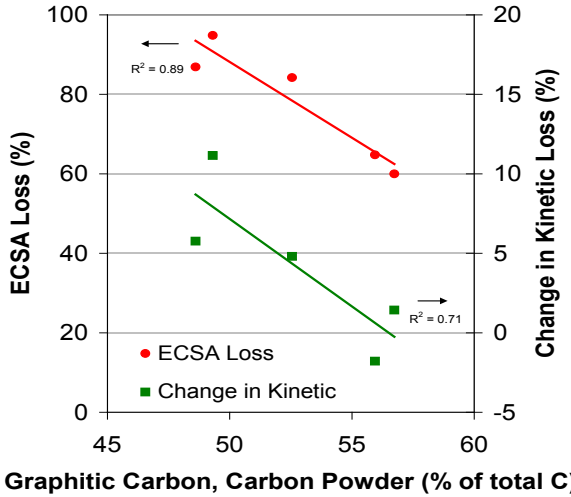
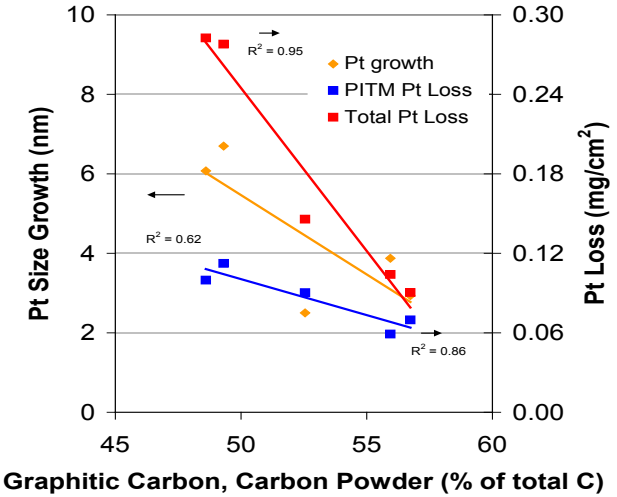
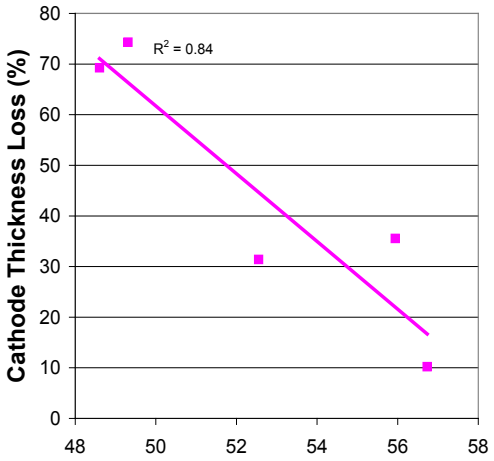
Graphitic Carbon Content of Catalyst Support









- **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

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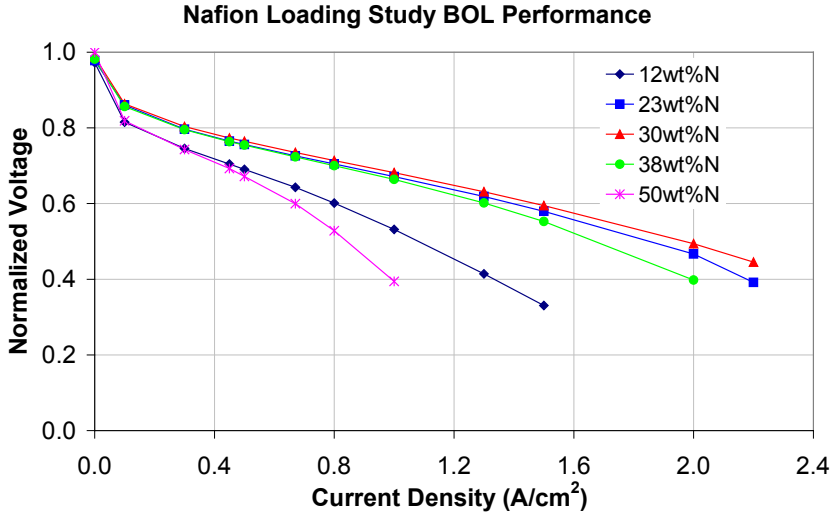
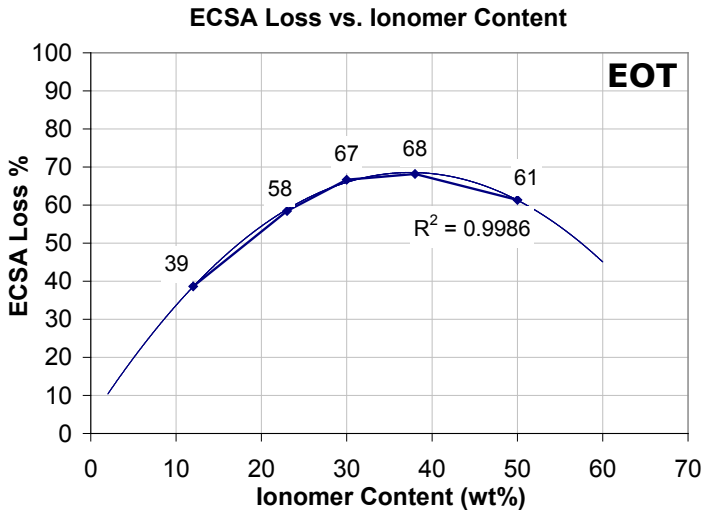
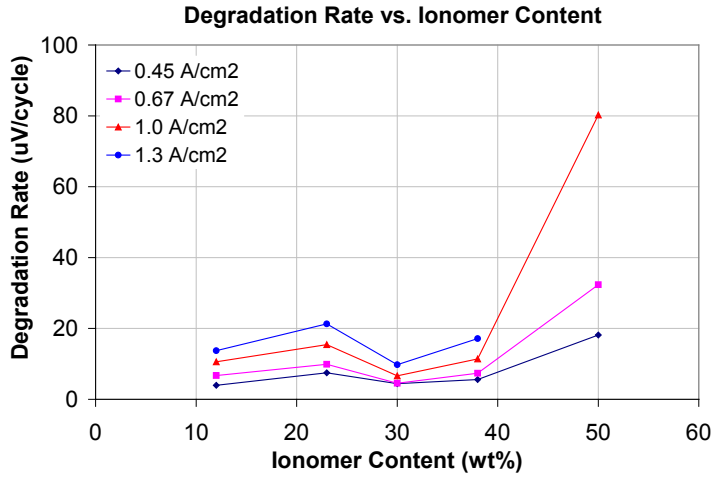
Low Surface Area Carbon Catalyst (Pt50-LSAC)





- 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



Organizations /Partners

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- **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

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- **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

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 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

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

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

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)

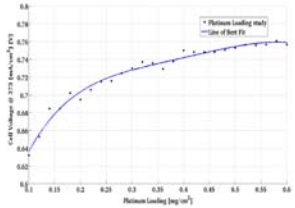
Plate
- Cond. (e-,T)
- Geometry

Membrane
- EW
- Thickness

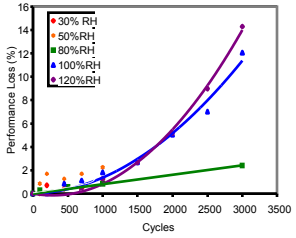
BOL Performance
- ECSA
- Exchange current density
- Tafel slope
- Mass activity
- HFR

Operating Conditions

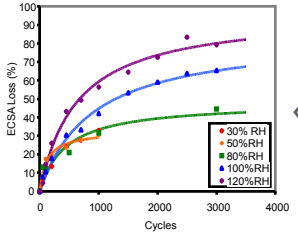
Parametric Performance Study



Predicted Voltage Degradation



Predicted ECSA Loss



1D Unit Cell Model

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 (cm2 Pt/cm2 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

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Technical Backup Slides

Approach

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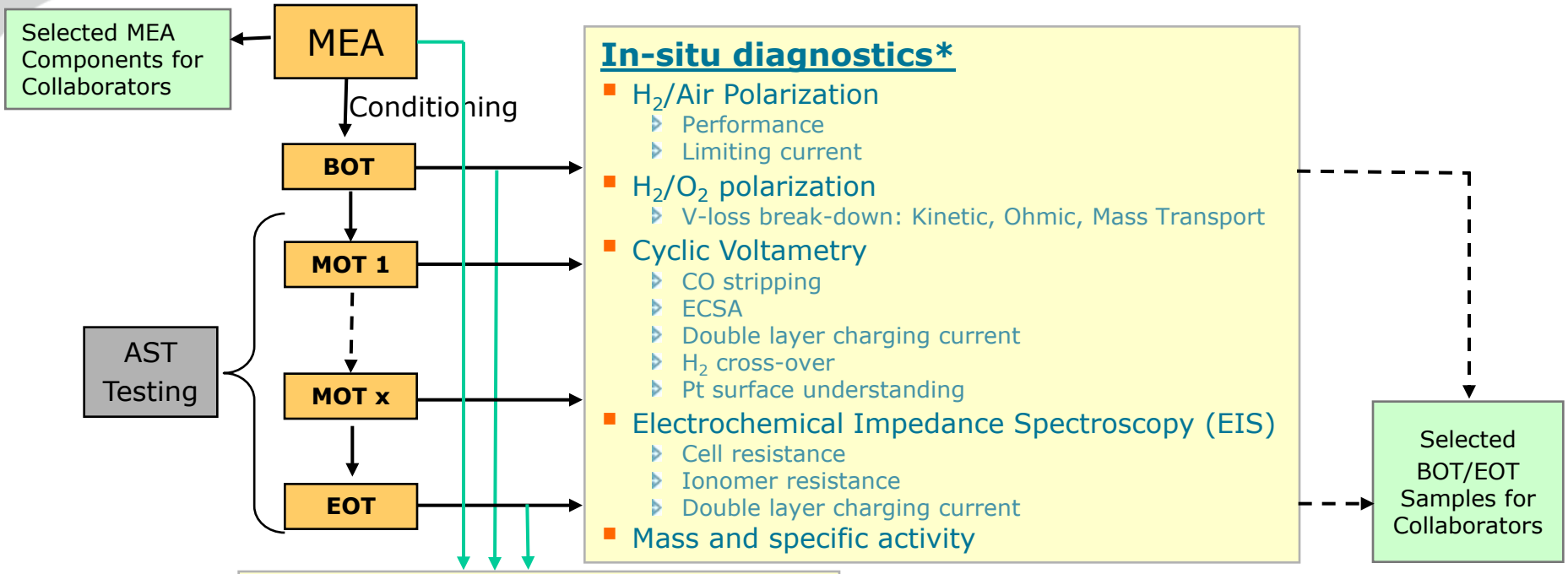
- **Model Development**
  - 3 scale modeling approach
    - Molecular dynamics model of the Pt/ carbon/ionomer interface, Pt dissolution and transport process
    - Microstructural catalyst layer model to simulate the effect of local operational conditions and effective properties on performance and 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
- **DOE Working Group (Durability and Modeling)**
  - Interaction and data exchange with other projects

Experimental Approach



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

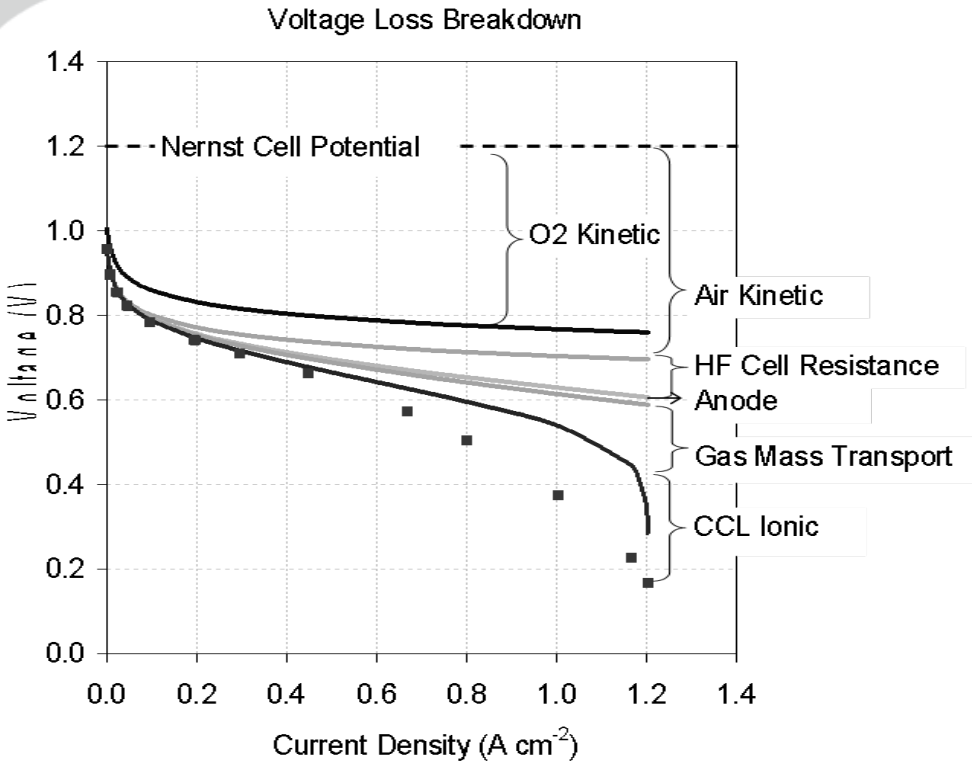
* Ongoing evaluation, i.e. list of diagnostics may change

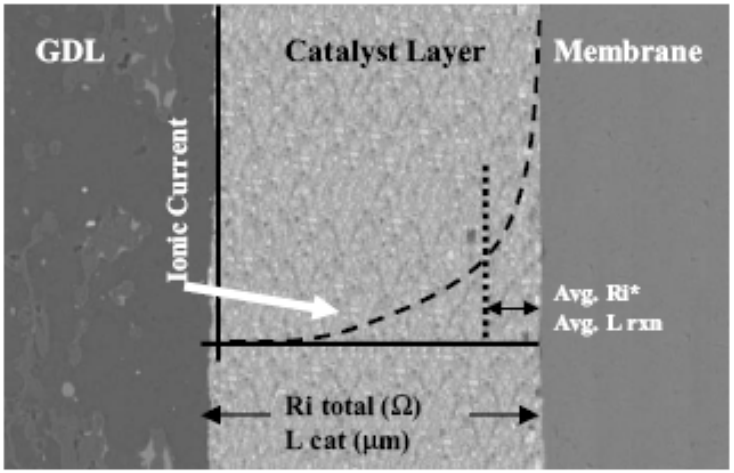
Reference AST: Air/H_2, 100% RH, 5 psig, 80°C, 0.6 V (30 sec)→ 1.2V (60 sec), 4700 cycles

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

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_2 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

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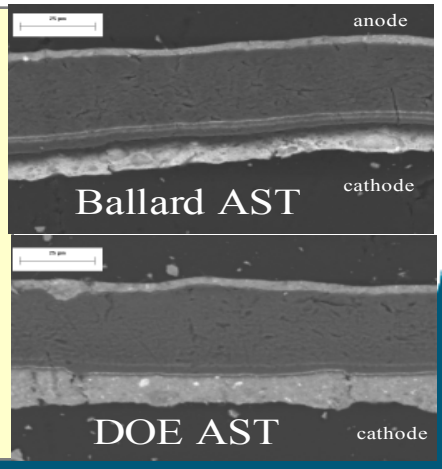
Compare degradation mechanisms for AST protocols

Oxidant	Failure Modes	Advantages	Limitations
Nitrogen (Water)	▪ Pt Agglomeration ▪ Carbon Surface Oxidation ▪ Carbon Corrosion ▪ PITM (?)	▪ Under N_2, membrane degradation is nominal ▪ No product water effects	▪ Platinum deposition occurs near the membrane/catalyst interface and is not separable from catalyst agglomeration.
Air	▪ Pt Agglomeration ▪ PITM ▪ Carbon Surface Oxidation ▪ Carbon Corrosion	▪ More realistic to field data due to separable platinum in the membrane. ▪ Potential to capture effect of ionomer degradation	▪ More difficult to control RH due to water production ▪ Membrane degradation may occur at 1.0V UPL ▪ More difficult to control/ set-up equipment (potentiostat & loadbank)

- **Primary Protocol Differences (DOE vs. Ballard)**
  - Triangular vs. square ramp
    - Square cycling profile enables better control/understanding of mechanisms
  - N_2 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

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

*Based on LSAC

Results funded by Natural Resources Canada,
Project ID: 414-CETC-526/823

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
Cartalysts	Pt50-Vulcan	50/50 Pt/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