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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

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Project ID# FC049

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Overview

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Timeline

- Start Date: January 2010
- End Date: March 2013
- Percent Complete: 7%

Barriers

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

B. Performance

C. Cost (indirect)

Budget

- Total Project: $6,010,181
  - $ 4,672851 DOE + FFDRC
  - $ 1,337,330 Ballard
  - Funding Received in FY10:
  - $ 935,000 Ballard
  - $ 243,000 LANL

Project Partners

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

Project Objective

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- **Identify/verify catalyst degradation mechanisms**
  - Pt dissolution, transport/ plating
  - Carbon-support oxidation and corrosion
  - Ionomeric thinning and conductivity loss
  - Mechanism coupling, feedback, and acceleration
- **Correlate catalyst performance & structural changes**
  - Catalyst layer and unit cell operational conditions
  - Catalyst layer morphology and composition
  - Gas diffusion layer (GDL) 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

Project Relevance

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Project Objectives

- Understanding of the degradation mechanisms
- Relationships to degradation rates
- Three-phase interface stability
- Component interface stability
- Development of degradation models
- GDL effect on catalyst layer degradation

Project Outcomes

- Verification of catalyst layer degradation mechanisms
- Performance and structural degradation correlations
- Predictive mechanistic models for catalyst layer degradation
- Mitigation 'windows' for catalyst layer degradation

Overall Technical Approach

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Overall Project Structure

Theoretical Modeling

Molecular Dynamics
- GIT (S. Jang)

Micro-scale Component
- Ballard
- QU (J. Pharoah)

Macro-scale MEA/Cell
- Ballard
- QU (K. Karan)

Degradation Investigations

Cell-level ASTs
- Ballard

Micro-cell ASTs
- UNM (P. Atanassov)

Neutron Imaging ASTs
- LANL (R. Borup, R. Mukundan)

Material & Component Characterization

MEA Components
- Ballard
- UNM (P. Atanassov)
- MTU (J. Allen)
- LANL (R. Borup)
- QU (K. Karan)

MEA Assembly
- Ballard
- MTU (J. Allen)
- UNM (P. Atanassov)

Approach - Modeling

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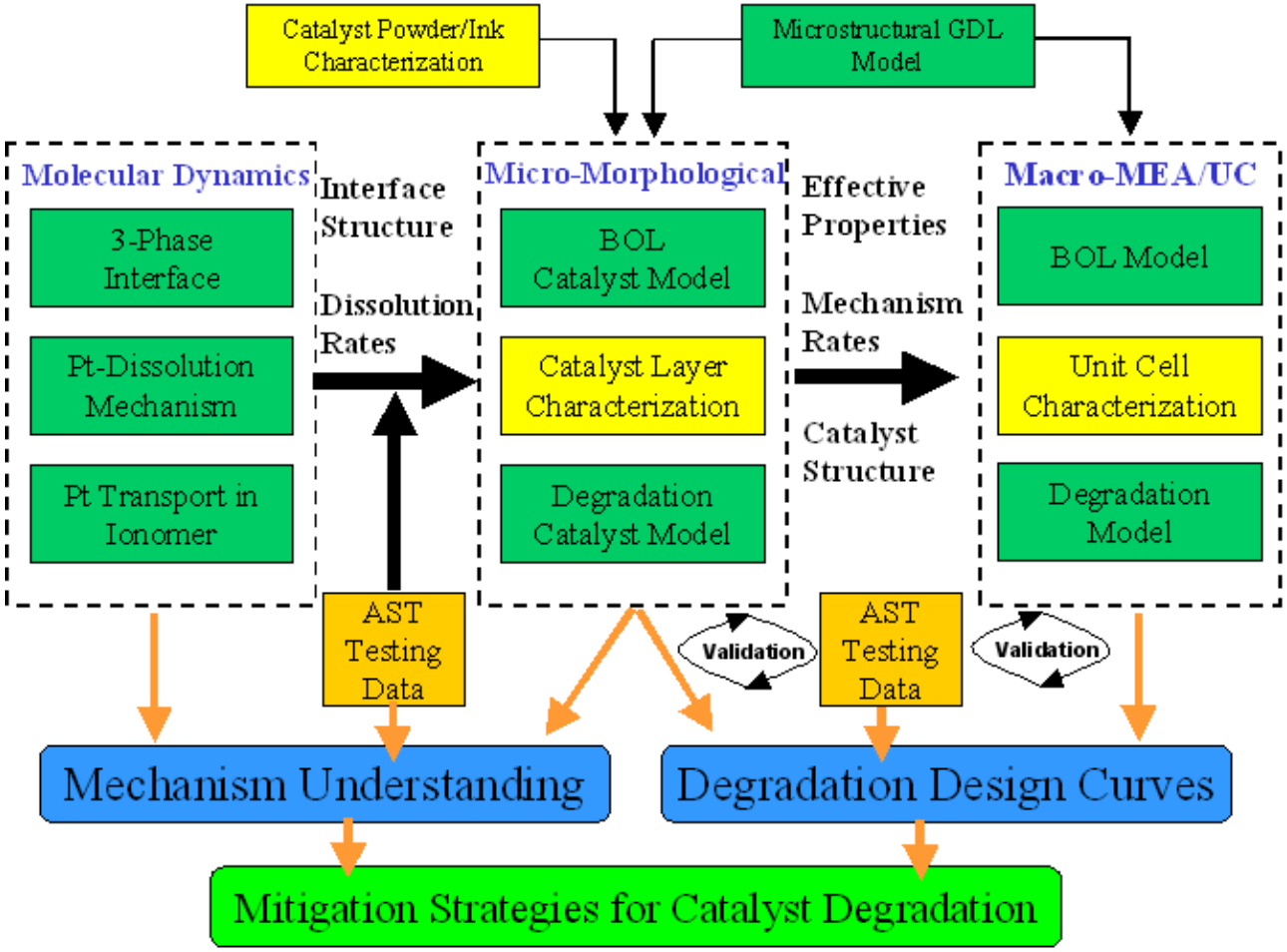
Theoretical Modeling Methodology



Modeling Approach
Molecular Dynamics

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Molecular Dynamics Model of the Pt/C/Ionomer Interface

- Develop model of a Pt/C particle covered with ionomer
- Investigate interaction effects at BOL in 3-phase interface

Molecular Dynamics Modeling of Pt Dissolution

- Expand Pt/C/ionomer model to include Pt dissolution
- Investigate role of ionomer hydration/equivalent weight, Pt size/shape, and preferential dissolution location

Molecular Dynamics Modeling for Pt Ion Transport

- Develop simulation for the transport of platinum ions in hydrated ionomer
- Predict the transport coefficients for platinum ions
- Validate transport coefficients against experimental data

Modeling Approach
Micro-Scale Component

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BOL Catalyst Layer Micro-structure Model

- Extension to include water management
- Validation of effective property/performance predictions at BOL

Transient Catalyst Layer Micro-structural Degradation Model

- Implement transient and degradation solvers
- Simulate AST cycles
- Validate predictions against experimental data

Micro-structural GDL Model

- Predict effective properties at BOL
- Validate BOL effective properties with experimental data
- Simulate measured changes of aged GDL microstructures
- Predict effect of aged microstructure on transport properties
- Validate aged transport properties with experimental data

Modeling Approach
Macro-scale MEA/Cell

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Unit Cell Performance Model (BOL)

- Include interface descriptions and statistical input options
- Validate against experimental data and statistical variability

Unit Cell Degradation Model (Aged)

- Include transient and degradation solvers
- Validate predictions using experimental data
- Simulate AST cycles for different operational conditions and morphologies

Model Integration

- Integrate micro-structural relationships
- Develop user guide/interface for simplified model application
- Release model for public dissemination

Approach – Experimental Investigations

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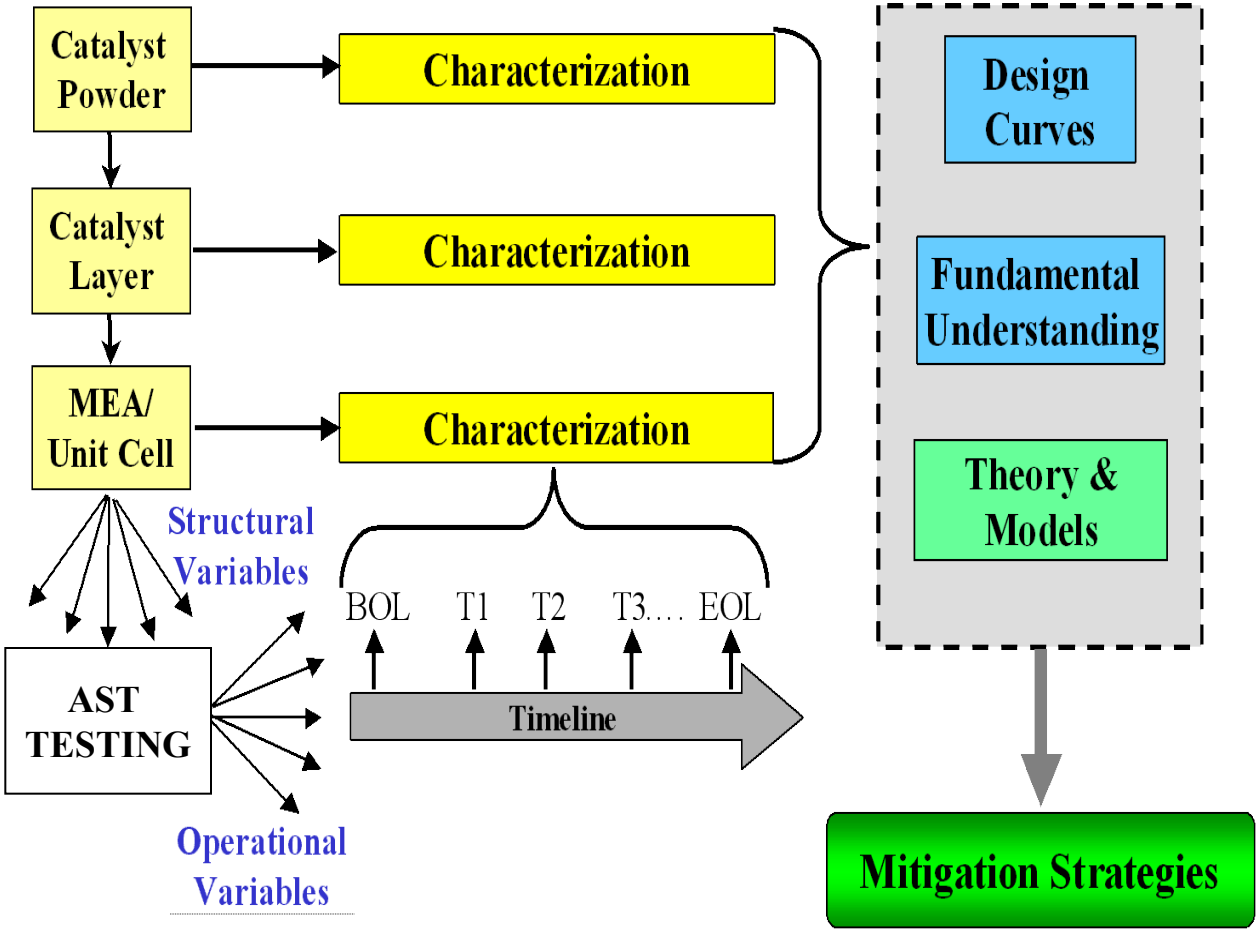
Experimental Methodology



Experimental Approach:
Cell Level Accelerated Stress Testing

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Experimental Benchmarking

- Review and down-select experimental techniques
- Compare degradation mechanisms for DOE and Ballard AST protocols
- Identify key operational and structural variables for degradation design curves, based on Ballard data and literature

Operational and Structural Design Curves

- Quantify the effect of operational stressors on degradation mechanisms and rates
- Quantify the effect of structural stressors on degradation mechanisms and rates
- Develop design curves for stressor effects

Operational and Structural Coupling

- Determine interactions between structural and operational stressors
- Quantify the coupling and feedback effects

Experimental Approach:
Micro-Cell and Neutron Imaging AST

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In-Situ HRTEM (BOL/Aged Catalyst Layers) (UNM)

- In-situ HR TEM methodology development and measurements of electro-catalysts changes in oxidative environment
  - Develop/refine measurement technique for analysis of Pt surface area loss
  - Characterize Pt loss mechanisms during AST cycling
    - Analysis of Pt size and distribution change during conditioning
    - Pt size change and distribution as a function of upper potential limit

Aged MEA Water Content Changes (LANL)

- Measure water content in cathode /anode GDL/membrane using Neutron Imaging
  - BOL
  - Progressively aged (from selected AST studies)
- Determine progressive changes in water content of MEA during AST testing using Neutron Imaging

Experimental Approach:
MEA Components Characterization

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Catalyst Powder (UNM, Queen's)

- Establish material characteristics using standard techniques
- Transfer data for model input and experimental design curve development

GDL Characterization (LANL, MTU)

- Characterize property changes with degradation, using standard techniques
- Cross-correlate property changes with AST degradation rates

Catalyst Layer Characterization (UNM, LANL, MTU, Queen's)

- Develop electrochemical corrosion measurement technique
- Quantify carbon-support changes with degradation
- Adapt capillary pressure technique for catalyst layers
- Determine capillary pressure changes with degradation

Experimental Approach:
MEA and Interface Characterization

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MEA Characterization (UNM)

- De-convolute performance losses using voltage loss breakdown techniques
- Cross-correlate voltage loss breakdown with measured property changes
- Quantify and cross-correlate failure modes

MEA Interface Characterization (MTU)

- Develop technique to quantify CCL/GDL interface characteristics
- Quantify interface changes with degradation
- Correlate voltage loss breakdown with interface and water content changes

Project Deliverables

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Unit Cell /MEA Macro-scale Model

- Integrated micro-structural relationships
- User guide/interface for simplified model application
- Model for public dissemination

Mitigation Windows

- Operational degradation mitigation 'windows' for catalyst layer designs using experimental data and model predictions
- Morphological degradation mitigation 'windows' for catalyst layer designs using experimental data and modeling predictions
- Recommendations for further research/modeling

Project Milestones & Timeline

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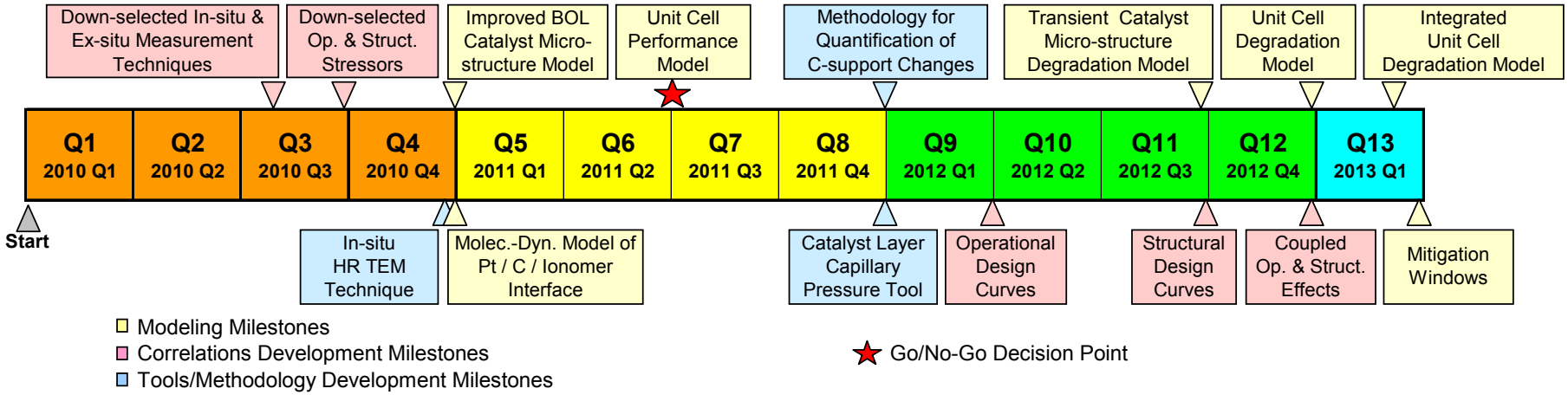

★ Go/No-Go Decision Point

Unit Cell Performance Model (BOL Stage)

Go: Model BOL performance predictions are within statistical variation of the experimental data

Milestones and Progress FY 2010/11 (1/2)

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Milestones			
Task	**Description**	**Completion Date**	**Status % complete**
Model Development and BOL Simulations			
* BOL Catalyst Microstructure	Add governing physics/chemistry for liquid water production and movement, validate model using BOL experimental data from PHASE 1- Task 3.0	Dec-10	awaiting contract
* Molecular Dynamic Modeling of Pt/C/Ionomer Interface	Create a Molecular Dynamics Model of a carbon supported Pt particle that is activated via the ionomeric phase. Run model to study transport processes.	Dec-10	awaiting contract
Microstructural GDL Model	Simulate GDL microstructures using GeoDict software and extract effective properties. Compare/validate against data from Phase 1.0 - Task 3.0.		not started
Experimental Benchmarking			
* Down Selection of In-situ and Ex-situ Characterization Techniques	Evaluate and validate in-situ and ex-situ techniques that will enable characterization and quantification of the degradation mechanism	Jul-10	70% complete
Correlations of ASTs	Evaluate/correlate DOE voltage degradation ASTs using in-situ/ex-situ characterization	Jul-10	70% complete
* Evaluation of Structural and Operational Stressors	Evaluate literature, previous experimental results, and new AST data to prioritize key variables that affect degradation rates and mechanisms	Aug-10	50% complete

*** Milestone**

Milestones/Progress FY 2010/11 (2/2)

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Milestones			
Task	**Description**	**Completion Date**	**Status % complete**
Ex-situ Characterization			
Catalyst Powder Characterizations	Characterize catalyst powder using standard techniques, such as XRD, SEM, EDX, HRTEM, Brunauer-Emmett-Teller Surface Area (BET)	ongoing	
* BOL Catalyst Layer and Aged Catalyst Layer In-situ HRTEM Technique	Characterize catalyst layers using standard techniques, such as ex-situ HRTEM, XRD, SEM, (2). Establish the in-situ HRTEM technique and measure structural changes during AST testing.	Jan-11	awaiting contract
BOL GDL Characterization	Characterize GDL structures using standard techniques, such as Diffusivity, Mercury Intrusion Porosimetry (MIP), Thickness, Resistance, Capillary Pressure, Contact Angle.	ongoing	not started
Durability Model Development and Simulations			
* Unit Cell Performance Model – BOL	Include physics that describes the relevant transport properties for the component interfaces. Run model with statistical BOL input characterization results and effective properties generated by the micro-structural model.	Jun-11 **Go/No-Go**	20%

*** Milestone**

Accomplishments/Progress
Unit Cell Performance Model

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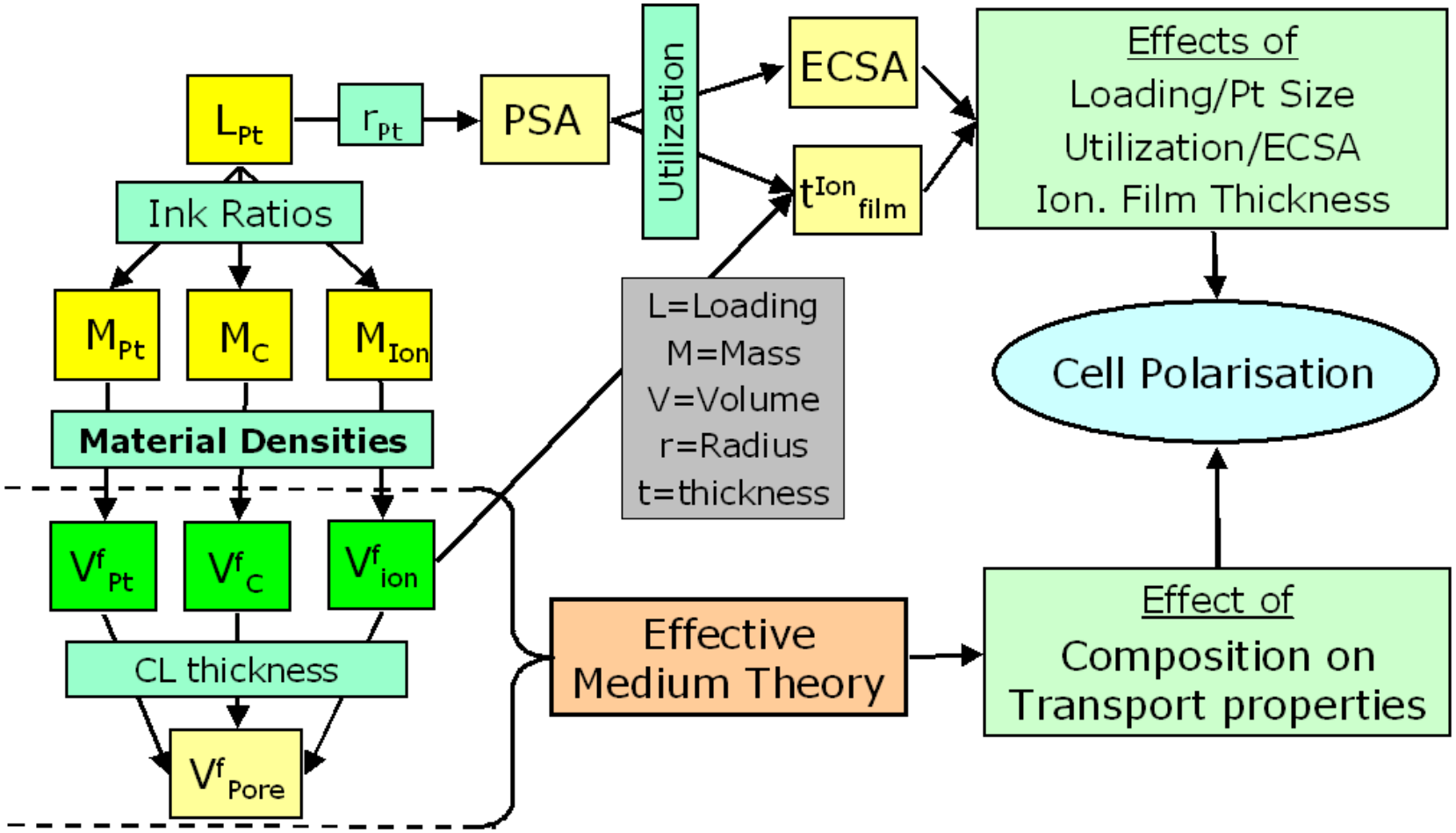
Linking Compositional Effects



Accomplishments/Progress
Unit Cell Performance Model

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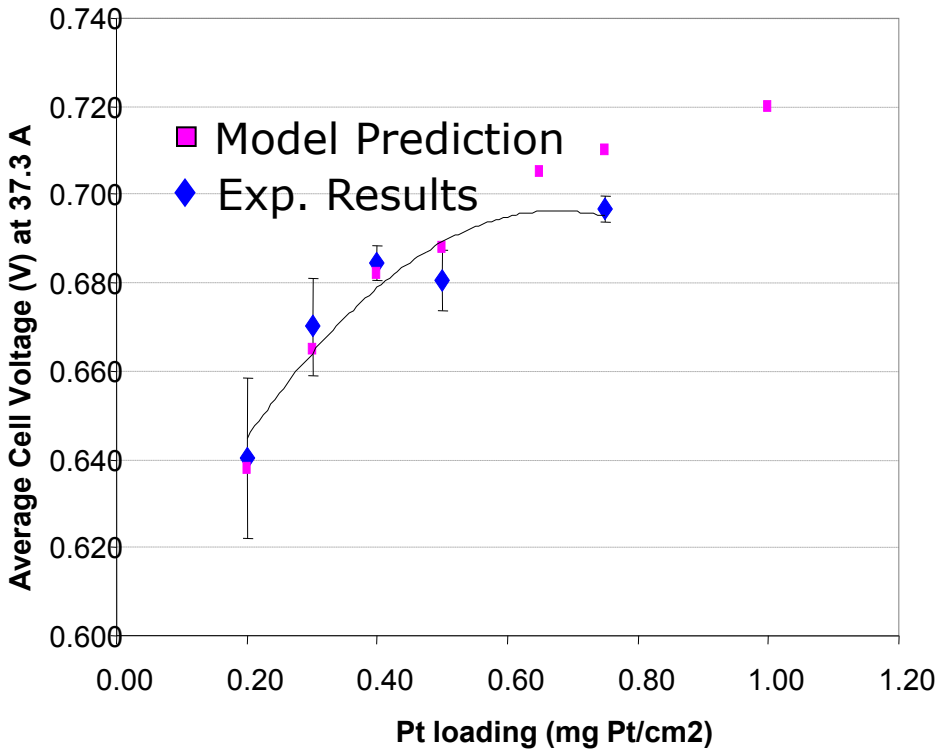
Pt Loading Comparison



- **Good agreement between model results and experiment for Pt loadings <0.5 mg/cm²**
- **Inability to capture higher loadings (also expected at extremely low loadings)**
  - Due to assumption of constant utilization in macro-model
  - Anticipated to be resolved using utilization predictions from the micro-structural model outputs

Accomplishments/Progress
Unit Cell Performance Model

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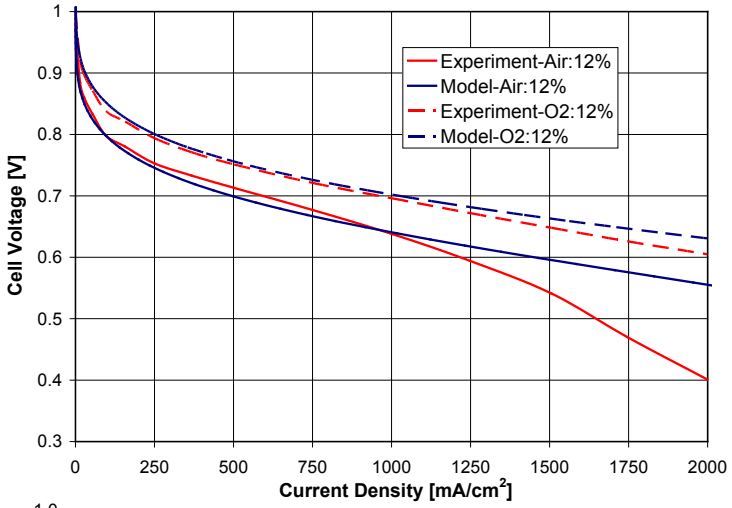
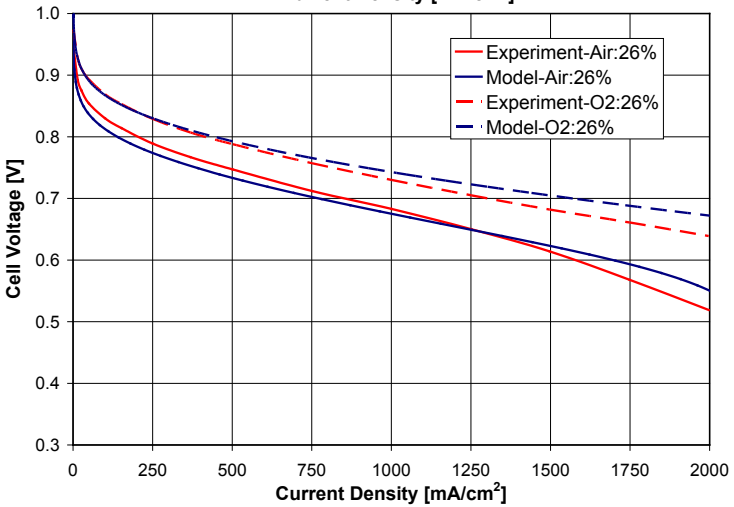
Compositional Effect: 12 and 26 wt.% Ionomer Ratio





- **Parameter set**
  - Held constant for both Air/Oxygen and 12/26% Ionomer simulations
- **Input Parameters**
  - ECSA, operational conditions, material ratios, and component dimensions
  - Material properties, e.g. density
- **Results**
  - Current density < 1 A/cm^2
    - good predictions j<1 A/cm^2)
    - Including Pt-O effects will further improve predictions
  - Current density > 1 A/cm^2
    - Liquid water transport model will improve predictions (vapor only results shown)
    - Component interface effects
    - Additional validation data will include statistical variation

Accomplishments/Progress
Unit Cell Performance Model

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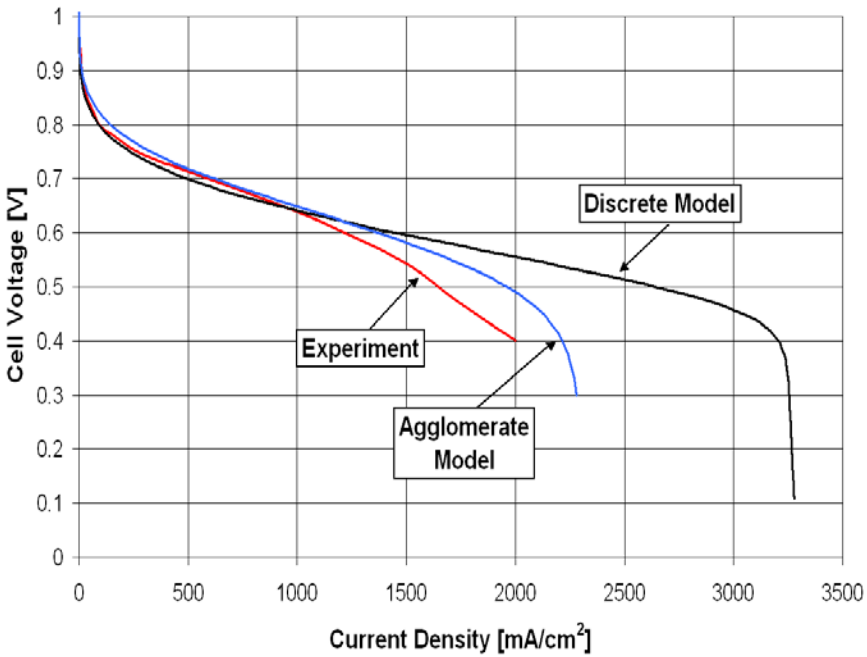
Macro Model Catalyst Effect



- **Macro-level simulations**
  - Very sensitive to the choice of catalyst model
- **Agglomerate models**
  - May provide a partial alternative explanation for mass transport losses at higher current density
    - liquid water + catalyst structure
- **Moving Forward**
  - Both models will continue to be evaluated
  - Micro-structural models will provide improved descriptions of the catalyst structure for BOL performance simulations
  - Model choice will have an impact on the understanding of degradation from model predictions

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State-of-the-Art Unit Cell Components & Hardware

- **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

- **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

Accomplishments/Progress
Experimental Benchmarking

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Diagnostics for Analyses of Cell-level Accelerated Stress Testing (AST)*

Quantification of changes in

- Performance
  - kinetic, ohmic, mass transport
- Effective catalyst surface area (ECSA)
- Cell and ionomer resistance
- Double layer capacitance
- H_2 cross-over
- Mass and specific activity
- Pt agglomeration and crystallite orientation
- Morphology/thickness

* Ongoing evaluation, list of diagnostics may change subject to further analysis

In-situ diagnostics

- H_2/air polarization (performance, limiting current)
- H_2/O_2 polarization (V-loss break-down)
- Cyclic voltametry (CO stripping, ECSA, double layer charging current, H_2 cross-over, Pt surface)
- EIS (cell resistance, ionomer resistance, double layer charging current)

Ex-situ

- SEM (catalyst/membrane thickness)
- SEM/EDX (Pt content in membrane and catalyst layer)
- XRD (Pt crystallite size, orientation)

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Accelerated Stress Test Protocol Comparison

Attributes	DOE AST Adapted for BPS Hardware	Ballard AST
Cycle Profile	Triangular Wave 0.6V to 1.0V, 50mV/s	Square Wave 0.6V (30s) to 1.2V (60s)
Time / Cycle	16s	90s
Number of Cycles	30,000	5,000
Total Cycling Time	133 hours	125 hours
Temperature	80°C	80°C
RH Anode/Cathode	100% / 100%	100% / 100%
Fuel / Oxidant	H_2 4450 sccm N_2 9000 sccm	H_2 4450 sccm 21%O_2/N_2 9000 sccm
Pressure	5 psig	5 psig

Protocol Differences

- **DOE protocol adapted for Ballard hardware**
  - Low pressure
  - High flow
- **Triangular vs. square ramp**
- **1.0V vs. 1.2V upper potential**
- **N_2 vs. synthetic Air**
- **Total cycling time is similar**

Accomplishments/Progress
Experimental Benchmarking

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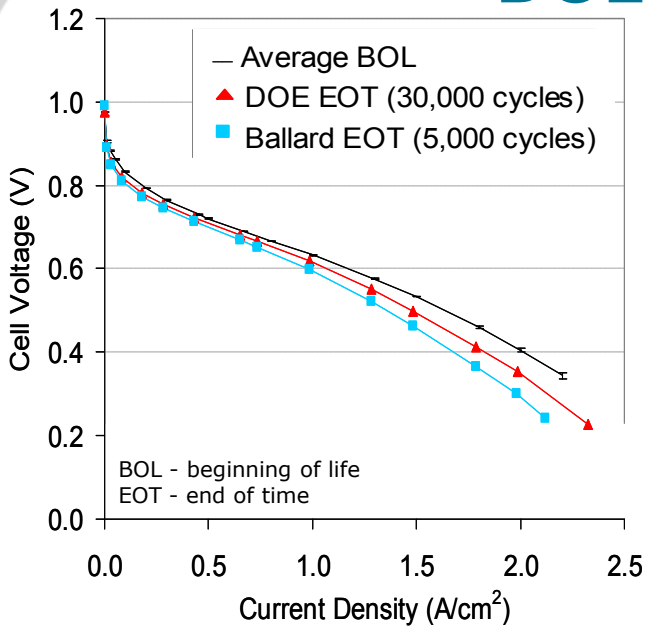
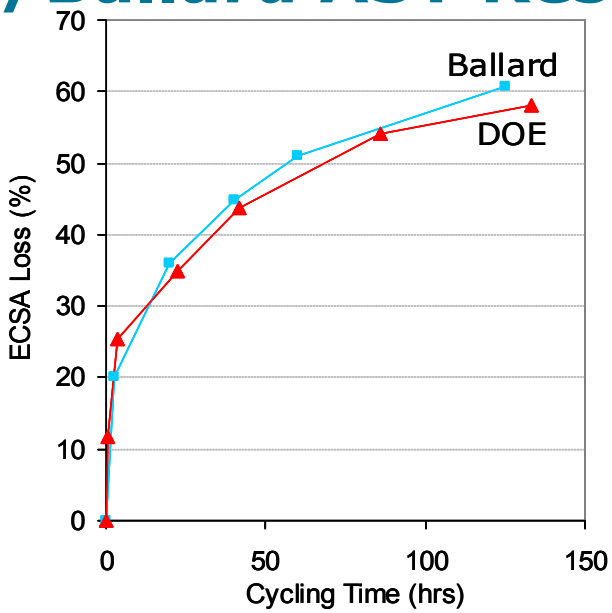
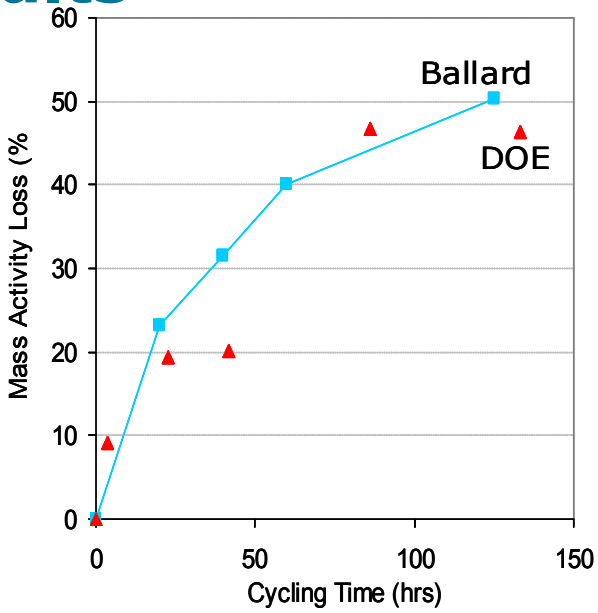
DOE/Ballard AST Results







- **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**
  - Performance losses at 0.8 A/cm^2 at End of Test (EOT) is ~14mV for DOE AST and ~29mV for Ballard ASTs indicating some contribution of non-kinetic related losses in both ASTs

Accomplishments/Progress
Experimental Benchmarking

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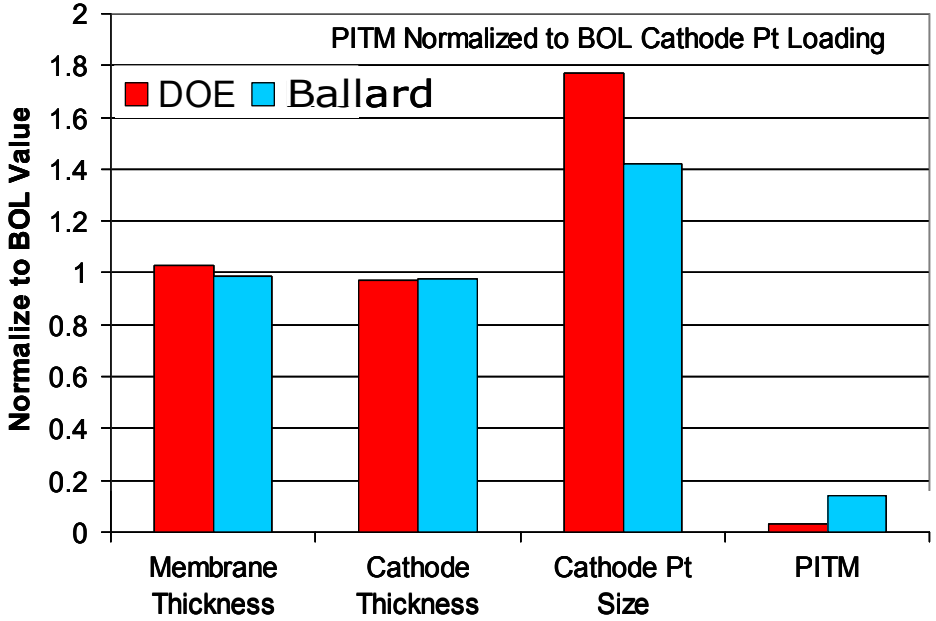
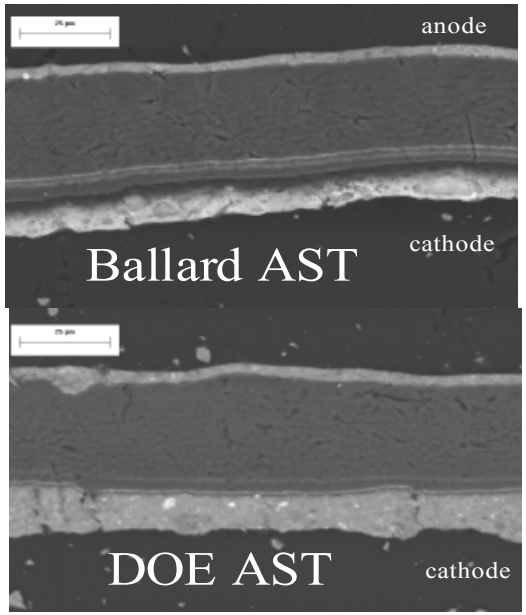
DOE/Ballard AST Results





- **DOE AST exhibits Pt accumulation at the cathode/membrane interface, Ballard AST results in Pt in the membrane (PITM)**
- **No significant changes in membrane nor cathode thickness were observed in either AST**
- **DOE AST results in larger average Pt crystallite size (XRD) compared to Ballard AST (9.3 nm vs. 7.4 nm)**

Accomplishments/Progress
Experimental Benchmarking

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AST Summary and Recommendation

Oxidant	Failure Modes	Advantages	Limitations
Nitrogen	▪ Pt Agglomeration ▪ Carbon Surface Oxidation ▪ Carbon Corrosion	▪ Relationships can be established without interference of other degradation modes ▪ RH can be controlled (No product water effects)	▪ Does not simulate PITM ▪ Does not take into account possible interference of membrane degradation bi-products
Air	▪ Pt Agglomeration ▪ PITM ▪ Carbon Surface Oxidation ▪ Carbon Corrosion	▪ Effect of Membrane Degradation (bi-products) on voltage degradation are captured ▪ Will capture effect of ionomer degradation ▪ More realistic to field data	▪ More difficult to control RH due to water production ▪ May be more difficult to separate failure modes ▪ More difficult to control/ set-up equipment (potentiostat & loadbank)

- **Recommendation: Continue using Ballard AST**
  - Ability to quantify Pt in the membrane failure mode
  - 1.2V upper potential limit enables better comparison with state-of-the-art catalysts and minimizes membrane degradation
  - Membrane thinning is not observed

Collaborations

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

Proposed Future Work
Modeling (FY2010/11)

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- **Molecular modeling of the Pt/C/ionomer system**
  - Investigation of defining features/characteristics of the Pt/C/Ionomer interface
- **Micro-structural catalyst model expansion for liquid water**
  - Extraction of effective properties vs. catalyst layer composition
  - Simulation of catalyst performance vs. effective properties
- **BOL MEA/Cell macro-model development and validation**
  - Addition of liquid water transport physics (from avail. literature)
  - Addition of Pt-O/OH pathway for ORR kinetics
  - Simulation/validation using cyclic voltammetry
  - Description for interfacial transport resistance between components
  - Capability to input statistical characterization data

Proposed Future Work
Experimental (FY2010/11)

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- **Operational and Structural Design Curves**
  - Structural Stressors
    - Establish performance degradation rates for different carbon supports
      - Effect of carbon surface area and graphitization levels
    - Establish performance degradation rates for different ionomer content
      - 10 to 50% ionomer by weight in catalyst layer
    - Establish performance degradation rates for different Pt/C ratios
      - 20% to 100% (subject to availability)
  - Operational Stressors
    - Establish performance degradation rates for two carbon supports
      - Effect of upper potential limit (0.8V to 1.4V)
- **Characterization**
  - In-situ HRTEM Tool
    - Methodology development
  - Quantitative changes of the Pt surface and carbon support
    - Degradation species/chemistry

Summary

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- **Relevance**
  - Improving understanding of durability for fuel cell materials and components
  - Providing 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**
  - Recommendation of AST protocol for going forward based on comparison of DOE and BPS protocols
  - Inclusion of composition effects into BOL MEA performance model and initial experimental validation.
- **Collaborations**
  - High levels of interaction between all project participants
  - Project participants have complementary expertise and capabilities
- **Proposed future research**
  - Further development of MEA model and statistical validation (Go/No-Go)
  - Effect of the carbon support and ionomer content on AST degradation rates

Supplemental Slides

Accomplishments/Progress
Unit Cell Performance Model

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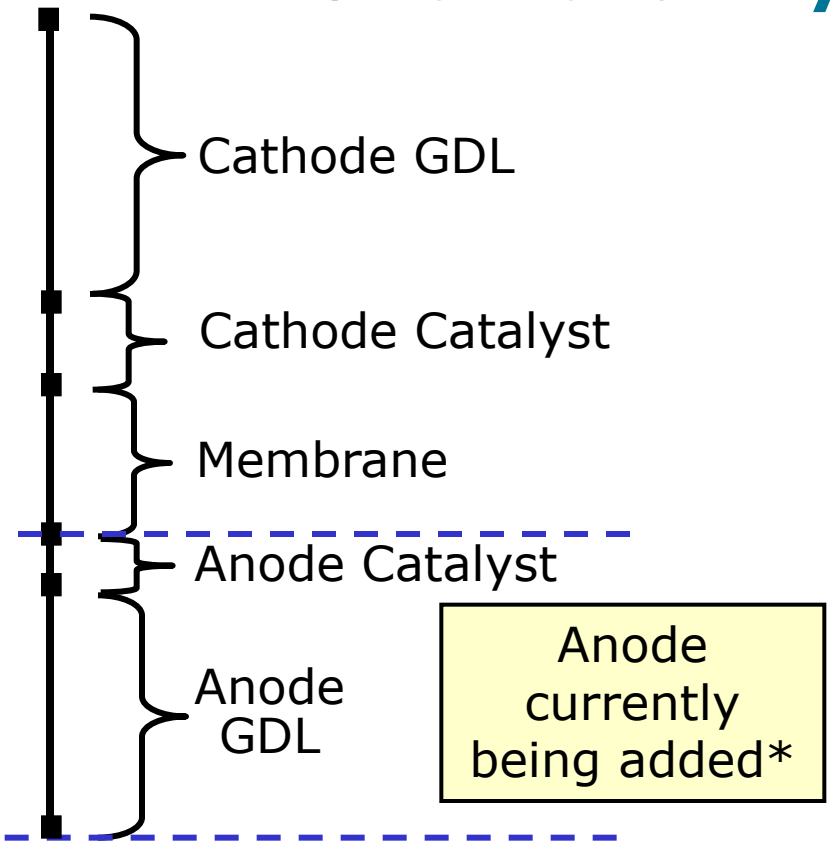
Domain and Physics Description*



- **1-D Model Physics***
  - Conservation of
    - Mass (species)
    - Charge (protonic/electronic)
  - Diffusive transport
    - Fickian-based
    - Multi-component (in-progress)
  - ORR electrochemistry
    - Butler-Volmer equation
    - Agglomerate or discrete structure description.

*Status as of March 2010, additional features currently under development to extend the model and refine the physics.

Accomplishments/Progress
Unit Cell Performance Model

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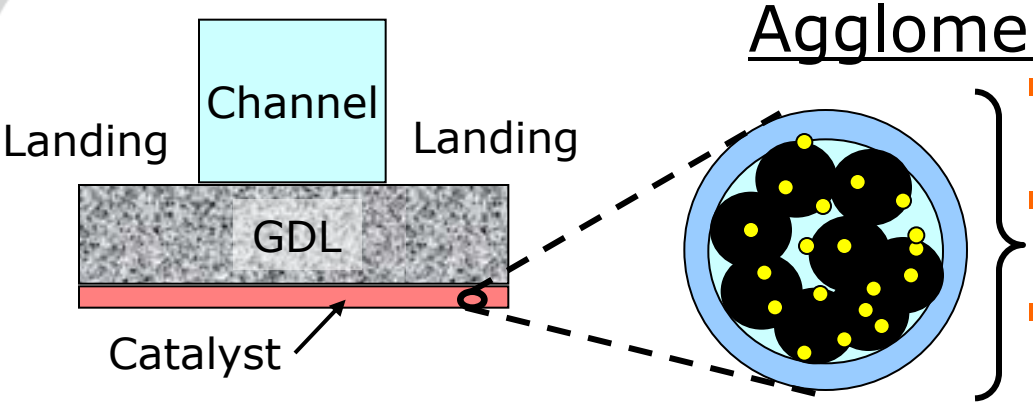
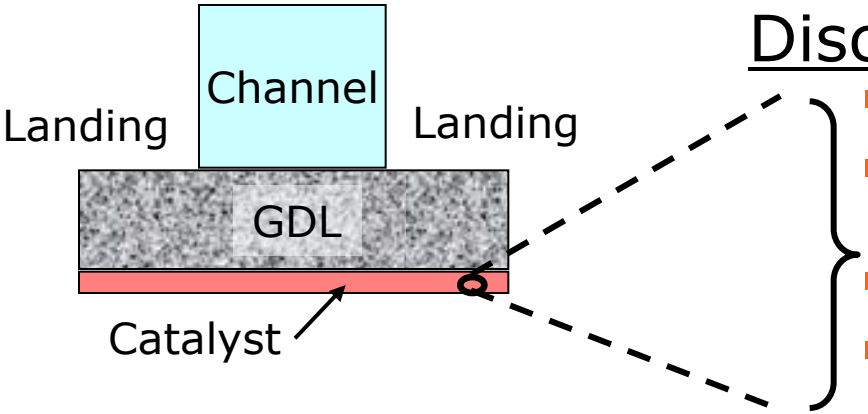
Catalyst Model Description*

Agglomerate Model



- Physical catalyst layer with additional sub-structure description
- Protonic, electronic, and diffusive resistance for layer
- Transport resistance and utilization within agglomerate structure
- Layer distributed ORR reaction

Discrete Model



- Physical catalyst layer
- Protonic, electronic, and diffusive resistance for layer
- Resistances via Effective Medium Theory
- Layer distributed ORR reaction

*Status as of March 2010, additional features currently under development to extend the model and refine the physics.

Accomplishments/Progress
Unit Cell Performance Model

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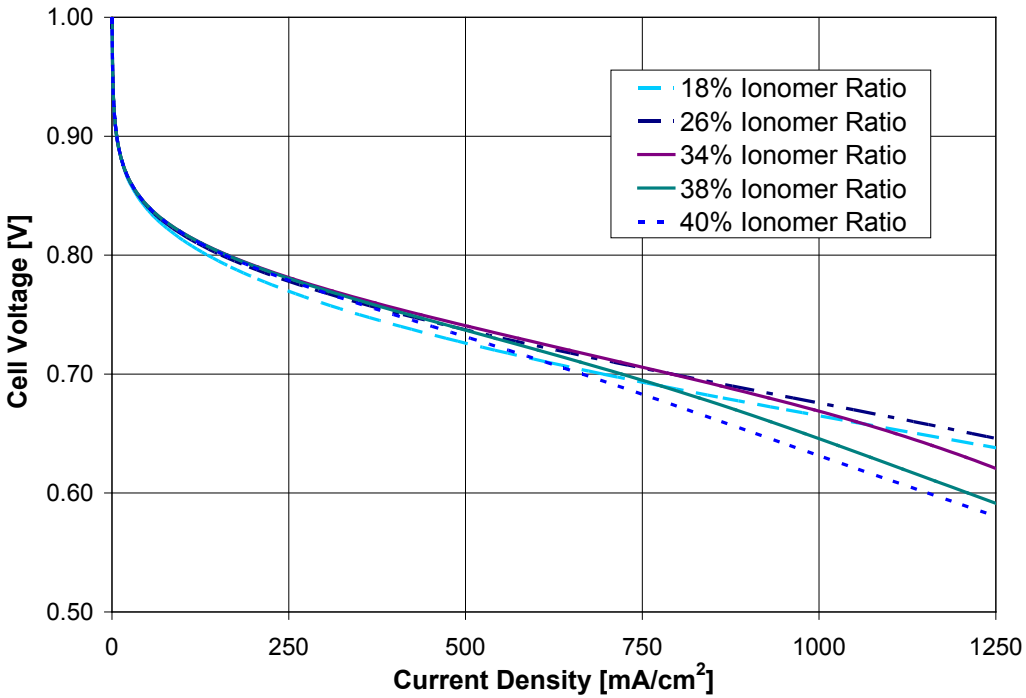
Compositional Effect
Parametric Study of Ionomer:(Pt:C) Ratio



- **Performance is sensitive to ionomer content**
  - Trade-off between ohmic resistance and mass transport effects
  - Effects over-potential distribution and limiting current
- **Transition point in performance**
  - Ohmic improvement is surpassed by high mass transport resistance (mass transport loss onset >34% ratio)

Accomplishments/Progress
Unit Cell Performance Model

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Status Summary

- **Features required at Go/No-Go point:**
  - Effect of structure (compositional)
    - Pt loading
    - Pt:C ratio
    - Ionomer ratio
    - Operational conditions (concentration, RH, T, etc.)
  - Liquid water transport
    - Catalyst layer
    - Gas diffusion layer
    - Membrane
  - Component interface resistance
    - GDL/flow field
    - GDL (MPL)/catalyst
  - Statistical polarization
    - Statistical property inputs

Capability exists, further validation required.

Air/O_2 demonstrated, physics development proceeding as planned.

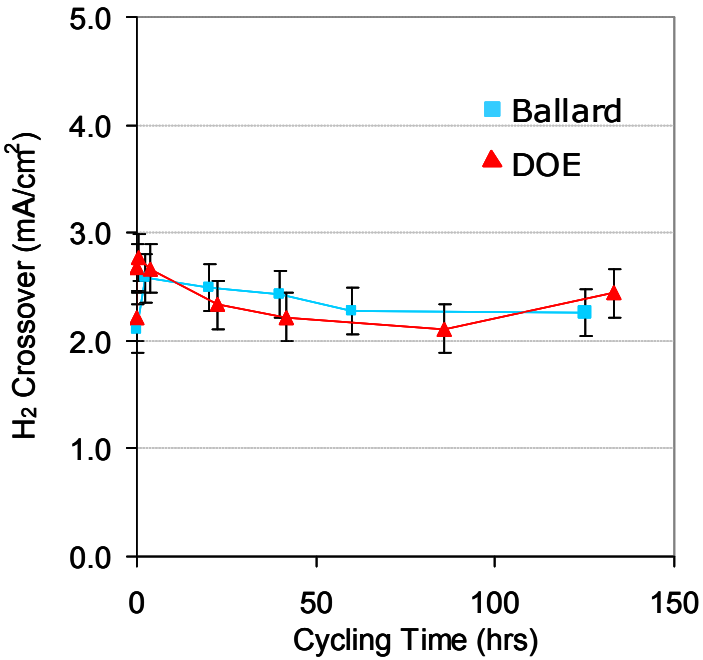
Pending completion structure-based linkages, the role of water with structure will be assessed

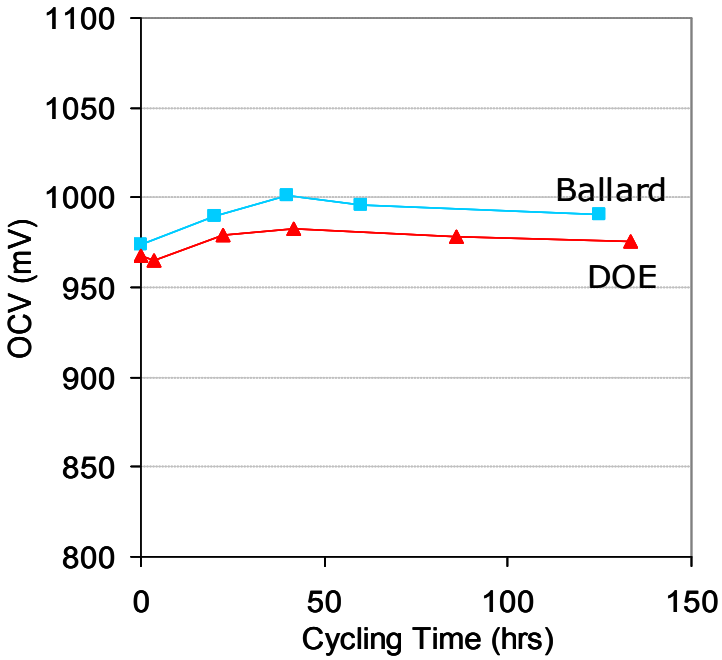
Not yet started

Accomplishments/Progress
Experimental Benchmarking

BALLARD®

DOE/Ballard AST Results





- **Both ASTs exhibit H_2 cross-over rates that are similar within experimental error over the test**
- **The open circuit voltage (OCV) increased by ~15 to 20mV over the initial 50 hours of AST cycling, likely due to cleaning of the PT surface and surrounding environment**

Accomplishments/Progress
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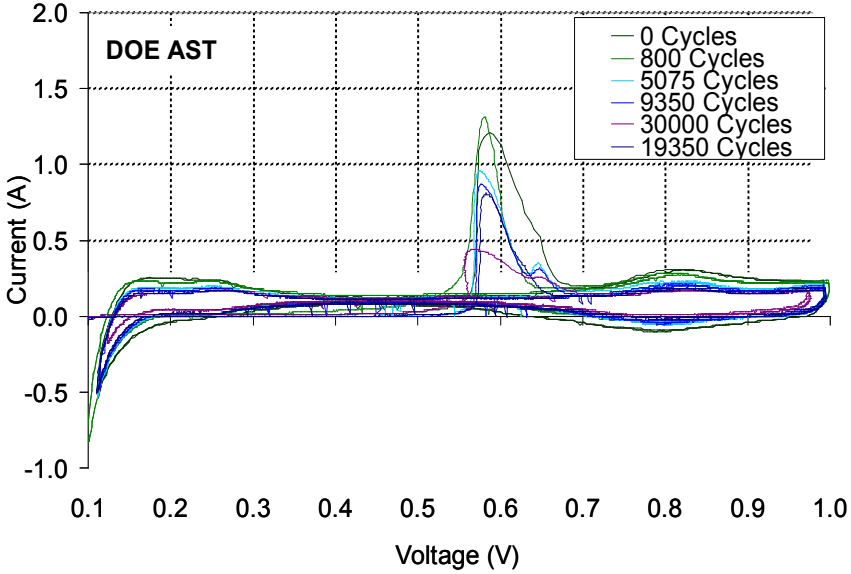
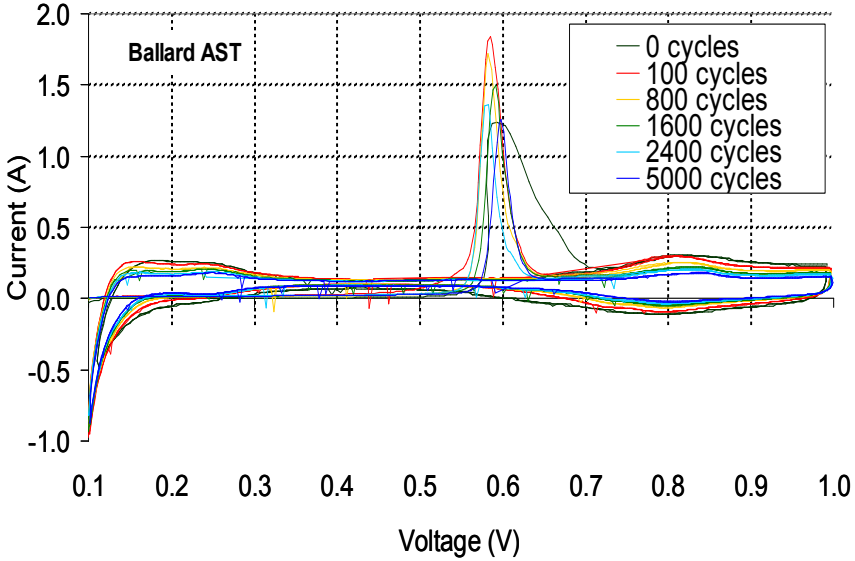
DOE/Ballard AST Results



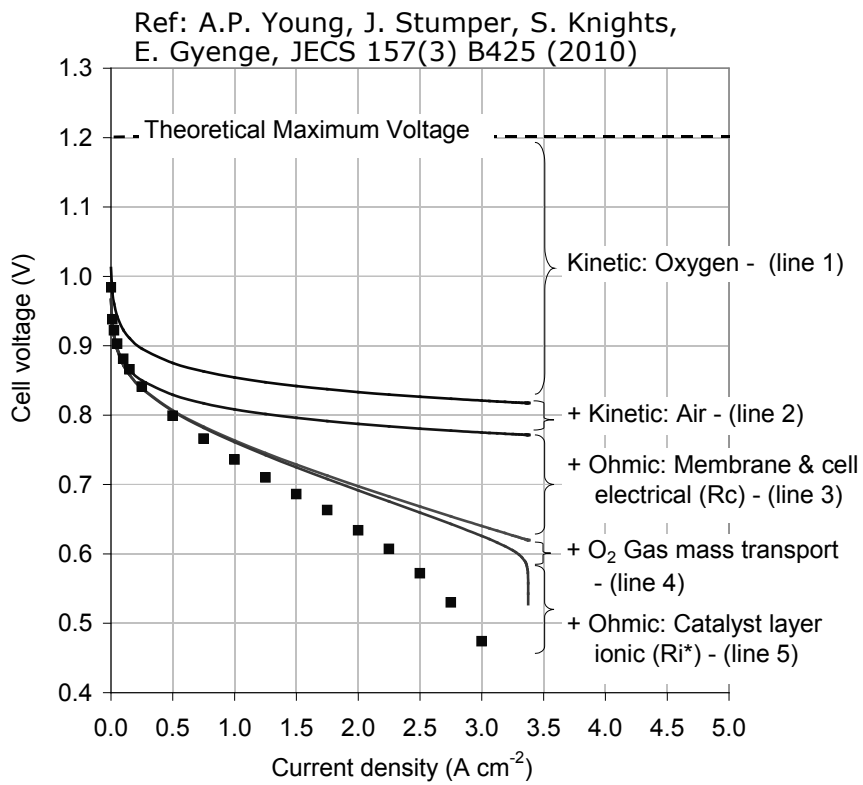


- **Cyclic Voltametry - CO stripping reveals some differences between DOE and Ballard ASTs**
  - DOE AST shows wide CO peaks that shift to lower voltage with increasing number of cycles
    - Peak broadening consistent with increased Pt agglomeration observed with DOE AST
  - Ballard AST causes narrowing of CO peak with cycling, but peak does not shift

Accomplishments/Progress
Experimental Benchmarking

BALLARD®

Voltage Loss Breakdown (VLB) Technique



- Oxygen and air polarization curves are fitted to Tafel equation and corrected for H_2 crossover and iR losses to give lines 1 & 2.
- EIS high frequency resistance was added to line 2 to give line 3.
- Nernst mass transport loss (calculated from limiting current) is added to line 3 to give line 4.
- Difference between line 4 and line 5 is assumed to be catalyst layer ionomer losses (primarily ohmic with additional porous layer mass transport limitations)

* Assumption: Anode loss is negligible; however, the VLB includes a linear anode loss component derived from anode electrode measurements using a dynamic reference electrode.