BALLARD®
power to change the world

Open-source FCPEM-Performance and Durability Model (FC-APOLLO):

Consideration of Membrane Properties on Cathode Degradation

Silvia Wessel

Ballard Fuel Cell Systems

18 June 2014

Project ID# FC049

Project Overview

Timeline

- Start Date: January 2014
- End Date: October 2014

Barriers

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

B. Performance

C. Cost (indirect)

Budget

- Total Project: $552,464
  - Total Spent as of 3/31/14: ~$160,000
  - $ 429,264 DOE Contribution
  - $ 123,199 (22.3%) Ballard Cost Share

Project Partners

- K. Karan – University of Calgary
- P. Atanassov -University of New Mexico

Objective

- Enhancement of FC-APOLLO predictive capability
  - Include interaction effects of membrane transport properties (e.g. water transport, proton conductivity changes, water uptake,..) and catalyst layer local conditions to understand driving forces for Pt dissolution

Project Background

- **New project builds on the understanding gained in previous DOE project FC049**
  - We confirmed that platinum durability was impacted by the water content in the catalyst layer
  - RH was found to have a substantial effect on catalyst layer degradation
    - The membrane/ionomer is a critical part of the water management within the MEA (e.g. water sorption/ desorption hysteresis, proton conductivity)
      - FC-APOLLO is validated only for the Nafion® NR211 membrane
  - The majority of membrane models are not sufficient to capture the behavior of the MEA nor the linkage between membrane characteristic properties and its overall behavior (performance/water transport)

Project Objective

- **Objective**
  - **Modify membrane model to include:**
    - Interface interaction effects of water uptake/transport
    - Dissolved water transport mechanisms
    - Changes in water content vs. proton conductivity
    - Overall water uptake/adsorption effects of the membrane on the state of the cathode catalyst layer local conditions
  - **Understand the effect of membrane properties on cathode degradation (Pt dissolution)**
    - Correlate membrane properties with Beginning of Test (BOT) performance and cathode degradation
- **Impact**
  - **Increase catalyst durability**
    - Based on understanding of the effect of membrane properties on Pt dissolution
    - Enabling achievement of DOE catalyst durability targets
      - Durability with cycling, i.e. ≤40% ECSA loss

DOE Technical Targets

Electrocatalyst and Support Degradation

Metric	Target
Polarization curve from 0 to >1.5 A/cm2*	<30 mV loss at 0.8 A/cm2
ECSA/Cyclic Voltammetry**	<40% loss of initial area
Pt Dissolution Protocol: Triangle sweep cycle: 50 mV/s between 0.6 V and 1.0 V for 30,000 cycles. Single cell 25-50 cm^2, 80°C, H_2/N_2, 100/100%RH, ambient pressure	

* Polarization curve per Fuel Cell Tech Team Polarization Protocol

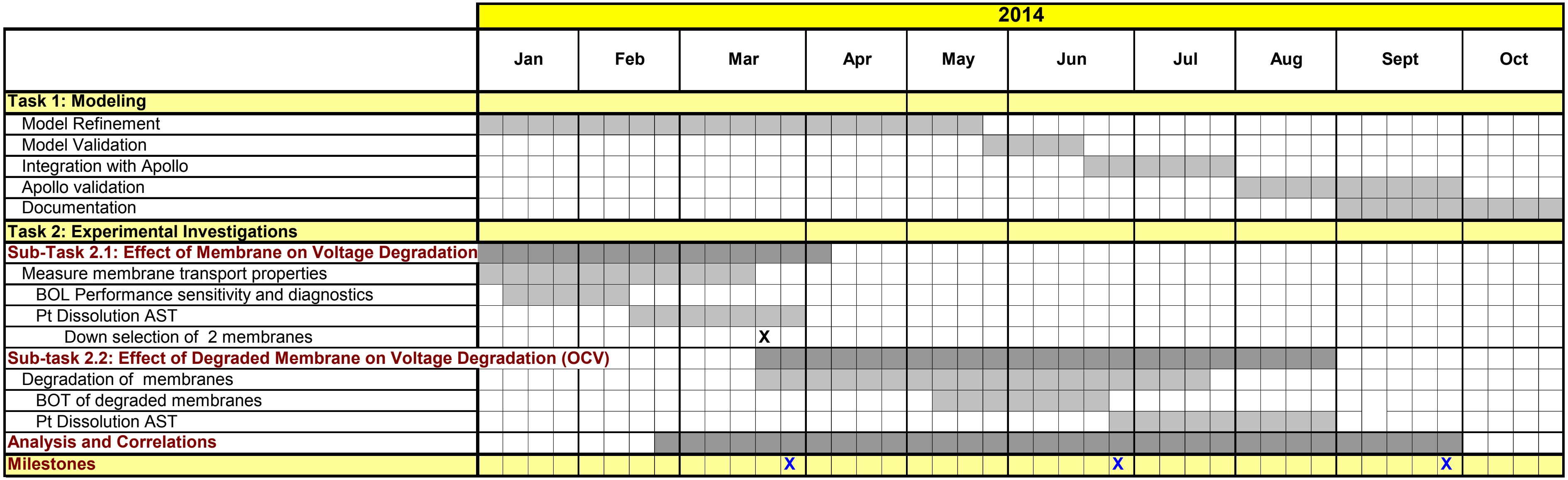
** Sweep from 0.05 to 0.6V at 20mV/s, 80°C, 100% RH.

- **2020 Durability Targets**
  - Transportation (80kW$_e$-net): 5000 hours
  - CHP and Distributed Generation
    - 1 – 10kW$_e$: 60,000 hours
    - 100kW – 3MW: 80,000 hours

Ref.: Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan
http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

2014/15 Project Plan & Milestones

Original Plan



	2014									
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct
Task 1: Modeling										
Model Refinement	▨	▨	▨	▨	▨					
Model Validation					▨	▨				
Integration with Apollo						▨	▨			
Apollo validation								▨	▨	
Documentation									▨	▨
Task 2: Experimental Investigations										
Sub-Task 2.1: Effect of Membrane on Voltage Degradation	▨	▨	▨	▨						
Measure membrane transport properties	▨	▨	▨							
BOL Performance sensitivity and diagnostics	▨	▨								
Pt Dissolution AST		▨	▨							
Down selection of 2 membranes			X							
Sub-task 2.2: Effect of Degraded Membrane on Voltage Degradation (OCV)			▨	▨	▨	▨	▨	▨		
Degradation of membranes			▨	▨	▨	▨	▨			
BOT of degraded membranes					▨	▨				
Pt Dissolution AST						▨	▨	▨		
Analysis and Correlations		▨	▨	▨	▨	▨	▨	▨	▨	
Milestones			X			X			X	

MS1 – Down-selection of a minimum of 2 types of membranes, i.e. NR211 (baseline membrane) and membranes that showed largest impact on catalyst degradation and that will within 3 weeks degrade to 60% of membrane end-of-life (EOL=membrane transfers) when subjected to membrane accelerated stress testing.

MS2 – Obtain preliminary correlations of BOT membrane properties with performance and polarization losses and show that at 60% RH one membrane type results in at least 20% greater loss than another membrane type.

MS3 - Comparison of FC-APOLLO performance simulations with experimental data for MEAs with different membrane types gives model predictions within 95% variability of the experimental data

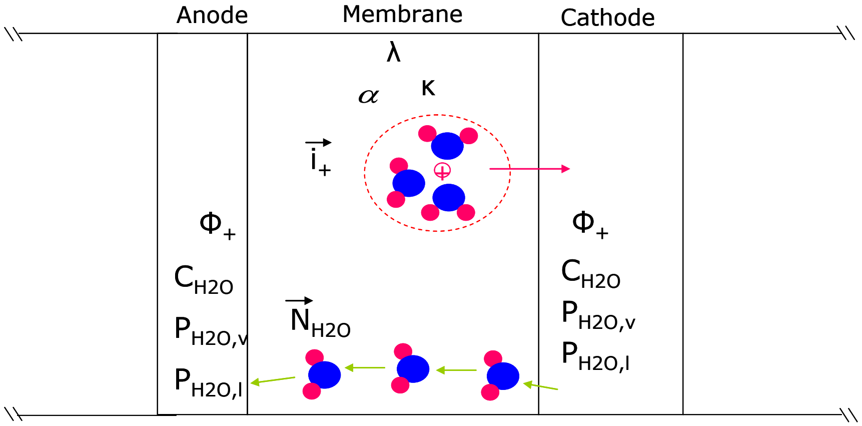
2014/15 Project Status

Task		Milestone Description	Status	% Complete
Model Development	Refinement of existing membrane model(s)	Assess capability of existing membrane model and modify model theory to describe changes in Transport properties (proton conductivity, and overall water uptake/adsorption effects) as a function of membrane type (material characteristics)	Basic ID Model description is completed	5%
	Integration of Membrane Model Integration with FC-APOLLO	Integrate refined membrane transport model into FC-APOLLO and demonstrate ability to capture MEA performance		
	Validation of Modified FC-APOLLO	Compare FC- APOLLO Performance and PT dissolution simulation with experimental data for MEAs with different membrane types		
Membrane Properties and MEA Evaluations	Ex-situ Membrane Properties	Measure ex-situ membrane transport properties (liquid water cross-over, gas permeability, proton conductivity)	Membrane property characterization for the baseline membrane and Reinforced PFSA membranes is in progress	10%
	Evaluate effect of membrane type / properties on MEA Performance	Measure in-situ MEA transport properties (liquid water cross-over, H2 cross-over)	MEA BOT performance of Baseline and Reinforced PFSA membranes is completed. Data analysis is in progress	20%
	Evaluate effect of membrane type / properties on MEA Performance	Evaluate the impact of membrane transport properties on performance (voltage loss mechanisms) for a range of operating conditions (current density, RH, T)	AST MEA performance of Baseline and Reinforced PFSA membranes is completed. Data analysis is in progress	20%
	Correlations of membrane transport properties and MEA performance and durability and catalyst/catalyst layer degradation	Link the membrane properties (EW, thickness, type, transport properties) with MEA performance/ voltage loss mechanisms		

Water Transport Model
Membrane Water: The Problem

- **Measurement Issues:**
  - Pressure & concentration poorly defined in membrane
  - Water & protons interact strongly
  - Theory & modelling often rely on coefficients that are inherently not measurable
  - Transport modes and BCs can be very different depending on liquid/vapour presence!

- **Membrane Component**
  - Determine Net Water Flux (Magnitude & Direction)
    - : For varying P, T, RH, and current density
  - Mixed Boundary Conditions
    - : Vapour
    - : Liquid
- **Adaptation of the Weber & Newman Membrane Model**
  - Insertion into Unit Cell Models
  - Use in Along-the-Channel Modelling

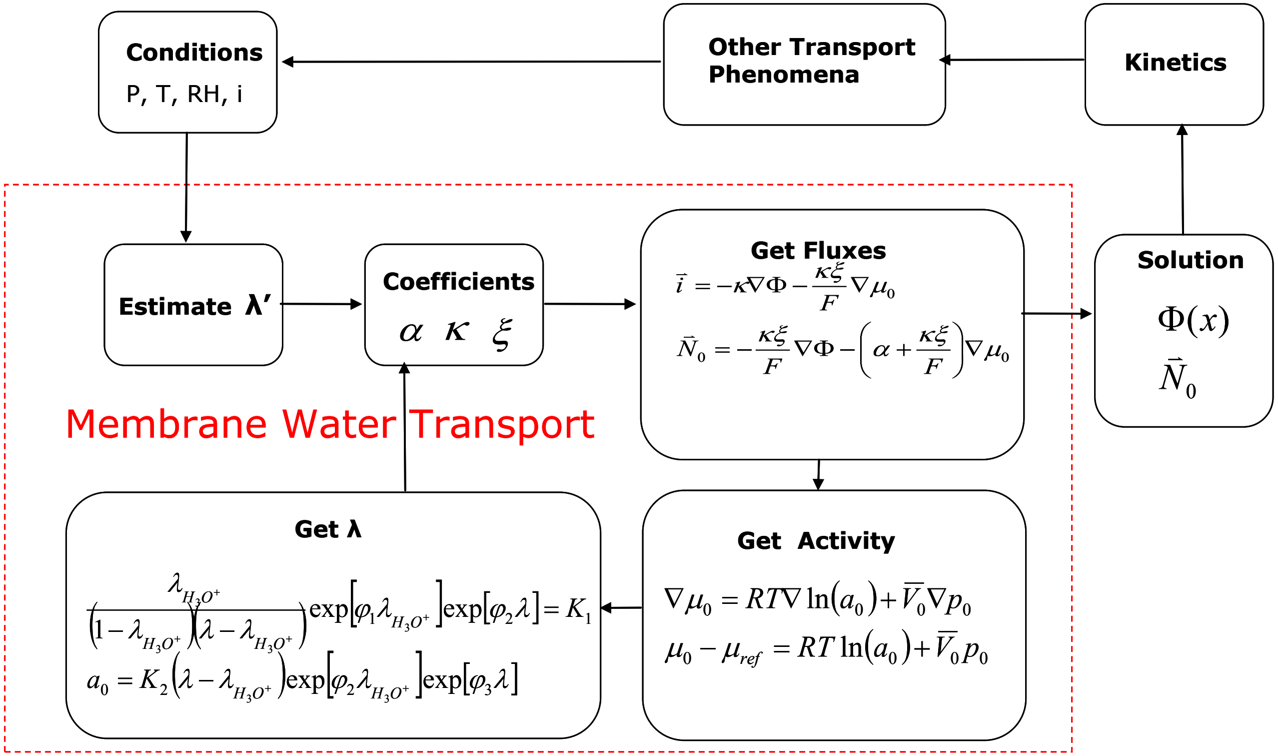


References

G.J.M. Janssen. “A phenomenological model of water transport in a proton exchange membrane fuel cell”, ECS 148 (12) A1313-A1323 (2001)

Weber, A.Z. & J. Newman. “Transport in Polymer-Electrolyte Membranes II. Mathematical Model”. ECS 151 (2) A311-A325 (2004)

Approach
Membrane Water Model



Conditions
P, T, RH, i

Other Transport Phenomena

Kinetics

Estimate λ'

Coefficients
$\alpha \ \kappa \ \xi$

Get Fluxes

$$\vec{i} = -\kappa \nabla \Phi - \frac{\kappa \xi}{F} \nabla \mu_0$$

$$\vec{N}_0 = -\frac{\kappa \xi}{F} \nabla \Phi - \left(\alpha + \frac{\kappa \xi}{F} \right) \nabla \mu_0$$

Solution
$\Phi(x)$
$\vec{N}_0$

Membrane Water Transport

Get λ

$$\frac{\lambda_{H_3O^+}}{\left(1-\lambda_{H_3O^+}\right)\left(\lambda-\lambda_{H_3O^+}\right)} \exp\left[\varphi_1 \lambda_{H_3O^+}\right] \exp\left[\varphi_2 \lambda\right] = K_1$$

$$a_0 = K_2 \left(\lambda - \lambda_{H_3O^+}\right) \exp\left[\varphi_2 \lambda_{H_3O^+}\right] \exp\left[\varphi_3 \lambda\right]$$

Get Activity

$$\nabla \mu_0 = RT \nabla \ln\left(a_0\right) + \bar{V}_0 \nabla p_0$$

$$\mu_0 - \mu_{ref} = RT \ln\left(a_0\right) + \bar{V}_0 p_0$$

- **The Membrane Model includes:**
  - Water in solvated, vapour, or liquid form
  - Water transport via diffusion, osmotic drag, and pressure
  - Transport modes are related and incorporated within an electrochemical potential description

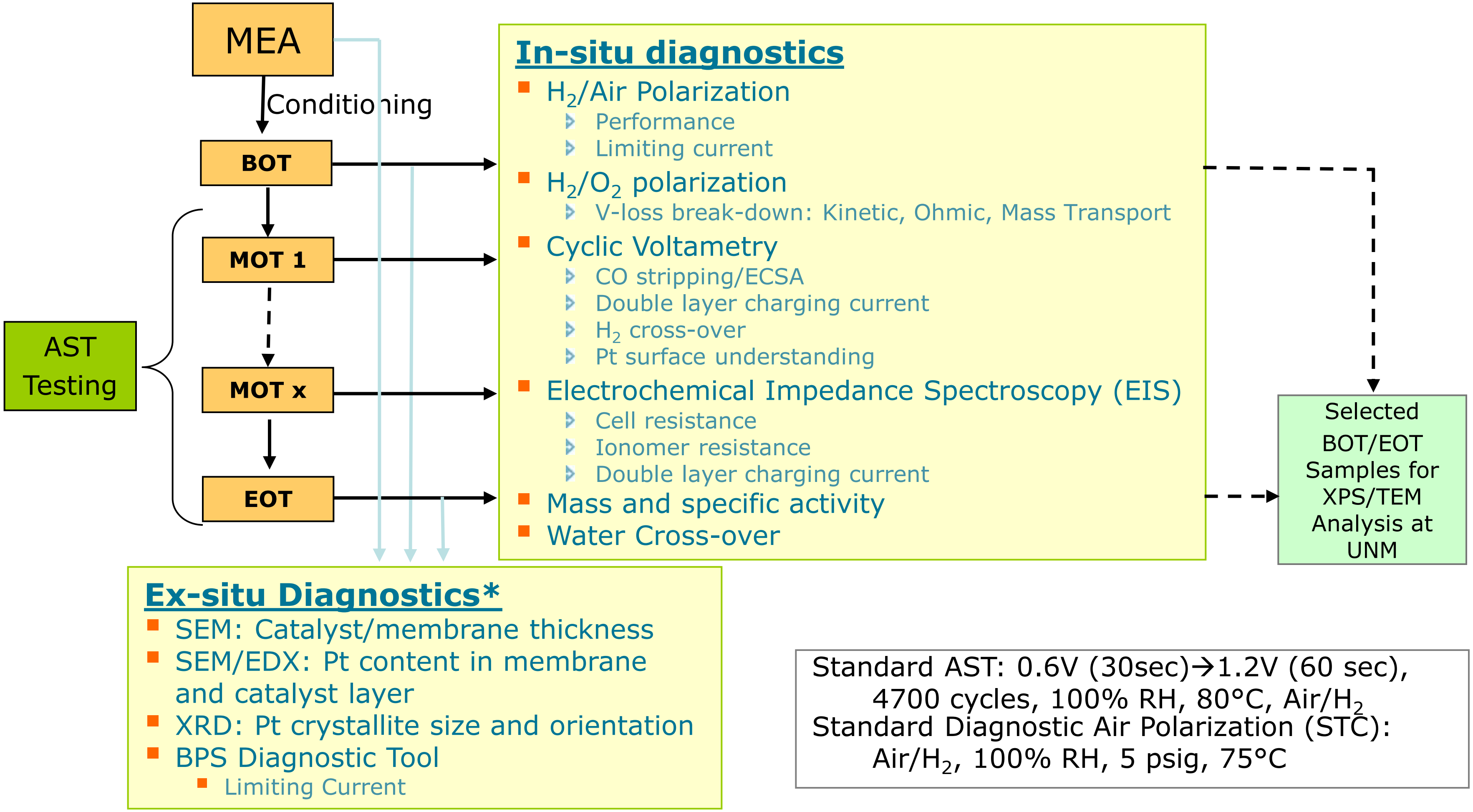
Membrane Parameters

Membrane Properties	**versus**	**Required**	**Optional**
Ion Exchange Capacity (EW)		x	
Density	dry, RH	dry	RH
Thickness	dry, RH	dry, RH	
Water Uptake/Content	T, RH, EW, time (rate of from dry state)	RH, time	T, EW
Proton Conductivity	T, RH, time (rate of from dry state)	RH, time	T, EW
O2, H2 Gas/Dissolved Gas Diffusivity	dry, T, RH, EW		T, RH, EW
O2, H2 Solubility	T, RH, EW		T, RH, EW
PtOH solubility/Diffusivity	T, RH, EW		T, RH, EW
Reactant Cross-over	T, RH	T, RH, system pressure	EW
Water flux (Constant System Pressure Anode/Cathode)	T, RH, EW, Pressure (cathode/anode)	RH, T, Pressure	EW
Water Permeation (Differential Pressure Anode/Cathode)	V/V, V/L, L/V, L/L		V/V, V/L, L/V, L/L
Thermal Relaxation			x
Interfacial Ionic Resistance (Between Ionomeric Materials)	T, RH, EW		RH, T, EW

RH calclated from P_total, P_H2O, T

- Data is leveraged from manufacturers where possible
- Measurements will be conducted at S. Holdcroft’s research lab in Simon Fraser University (SFU)
- Limited measurements conducted at Ballard

Experimental Approach



MEA

Conditioning

BOT

MOT 1

MOT x

EOT

AST Testing

In-situ diagnostics

- H_2/Air Polarization
  - Performance
  - Limiting current
- H_2/O_2 polarization
  - V-loss break-down: Kinetic, Ohmic, Mass Transport
- Cyclic Voltametry
  - CO stripping/ECSA
  - Double layer charging current
  - H_2 cross-over
  - Pt surface understanding
- Electrochemical Impedance Spectroscopy (EIS)
  - Cell resistance
  - Ionomer resistance
  - Double layer charging current
- Mass and specific activity
- Water Cross-over

Selected BOT/EOT Samples for XPS/TEM Analysis at UNM

Ex-situ Diagnostics*

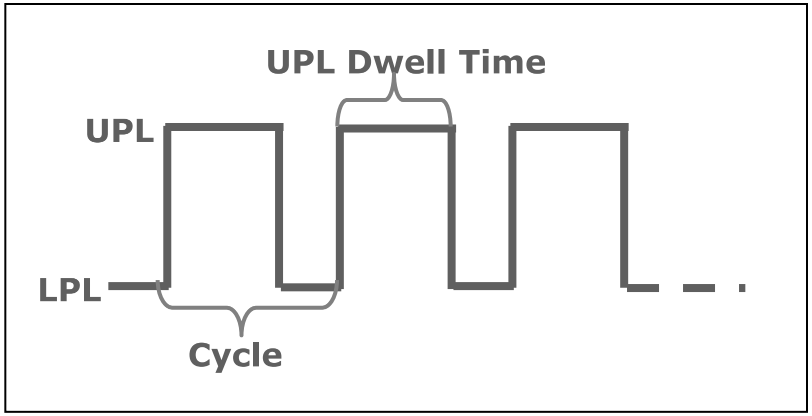
- SEM: Catalyst/membrane thickness
- SEM/EDX: Pt content in membrane and catalyst layer
- XRD: Pt crystallite size and orientation
- BPS Diagnostic Tool
  - Limiting Current

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

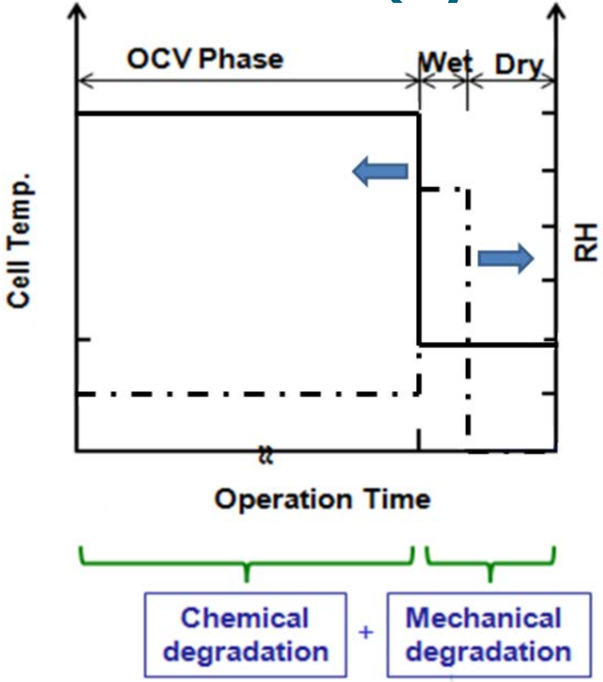
BOT/MOT/EOT = Beginning/Mid/End of Test

Experimental Approach
Accelerated Stress Tests

Cathode AST



Membrane AST (Cyclic OCV)



- Cathode AST
  - Air/H_2, 80°C, 100% RH,
    0.6 V (30s) to 1.2 V (150s) cycles

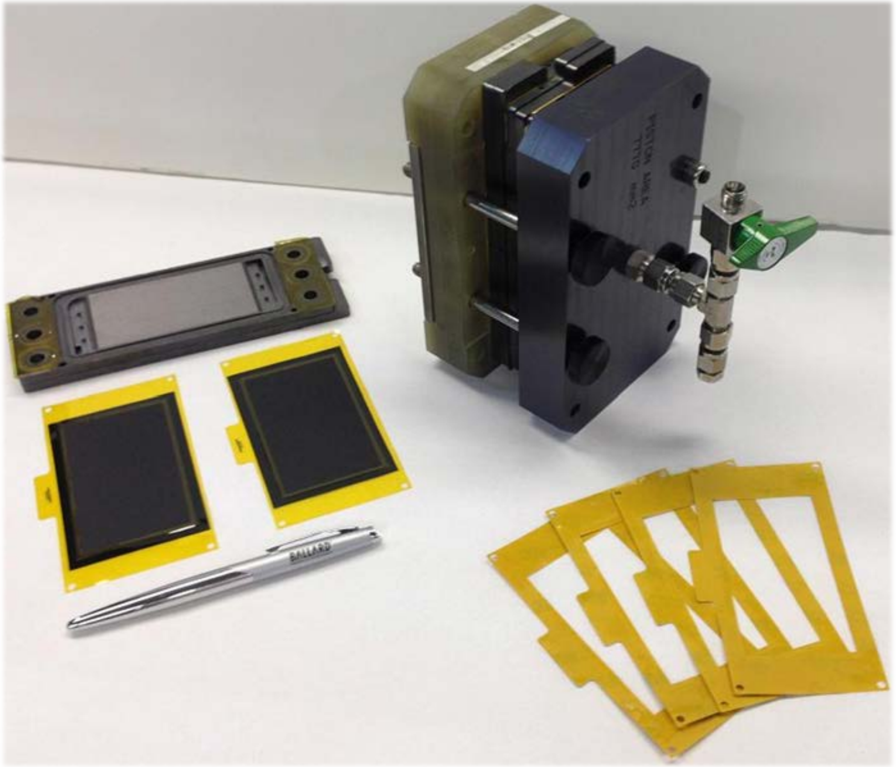
- Cyclic OCV AST combines chemical and mechanical degradation
  - Chemical Phase: OCV operation at increased T, low RH, increased oxygen concentration
  - Mechanical Phase: N_2 operation, wet/dry cycling

Membrane Electrode Assemblies

- **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**
    - AvCarb Product
    - Continuous Process

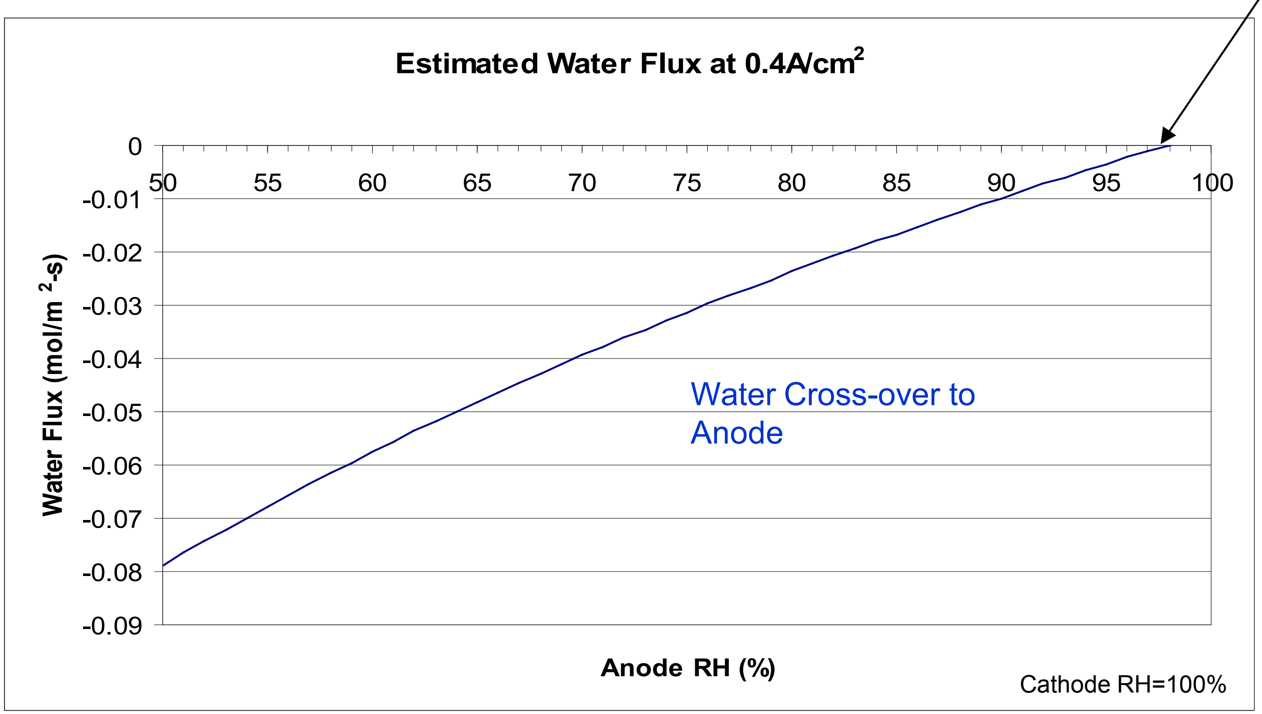
- **Membranes under Consideration**
  - **Dense Nafion® Membrane**
    - NR211 – Baseline
    - NR212 - optional
  - **Reinforced PFSA Membrane**
    - Low EW
    - High EW
  - **Reinforced Partially Fluorinated Hydro Carbon Membrane (experimental)**
    - Low EW
    - High EW

State-of-the-Art Unit Cell



- **1D Test Hardware**
  - Bladder compression
  - High flow rates
  - Temperature control
    - Liquid cooling
  - Carbon Composite Plates
    - Low pressure
    - Parallel flow fields
    - Designed for uniform flow
  - Framed MEA
    - 45 cm^2 active area

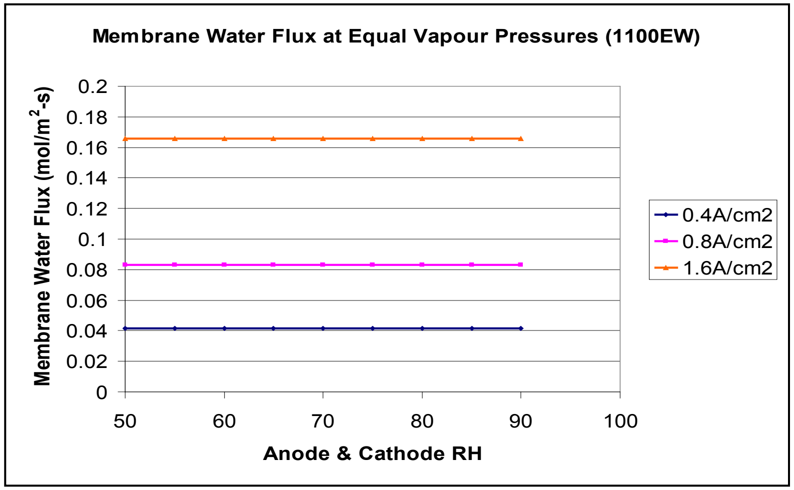
1D Membrane Water Model
Initial Water Flux Simulations

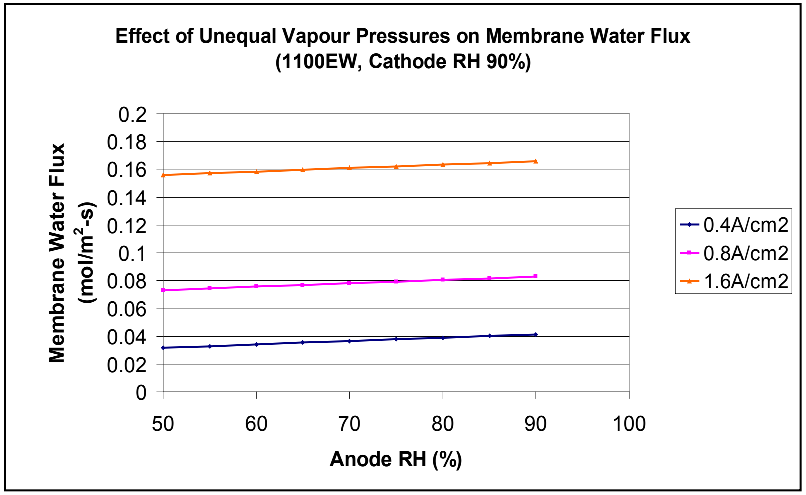


Electro-osmotic drag overpowers chemical potential

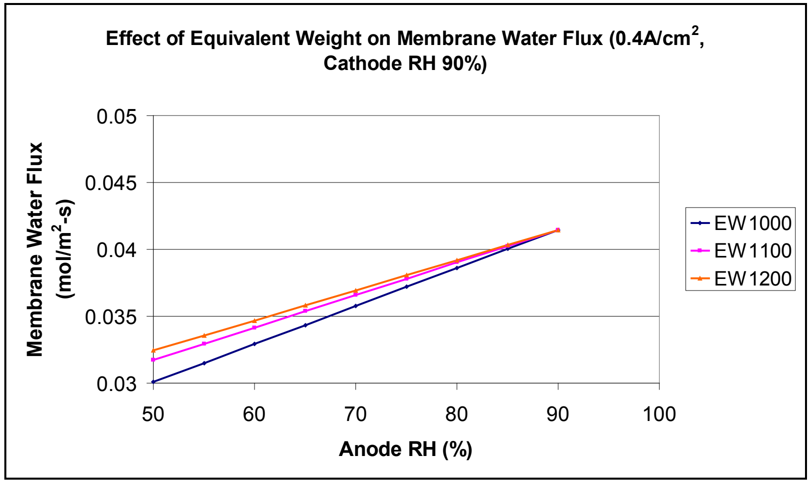
- Initial membrane model simulations to understand competing water fluxes in the membrane based on operating point and conditions, or at different points in the channel.

1D Membrane Water Model
Initial Water Flux Simulations

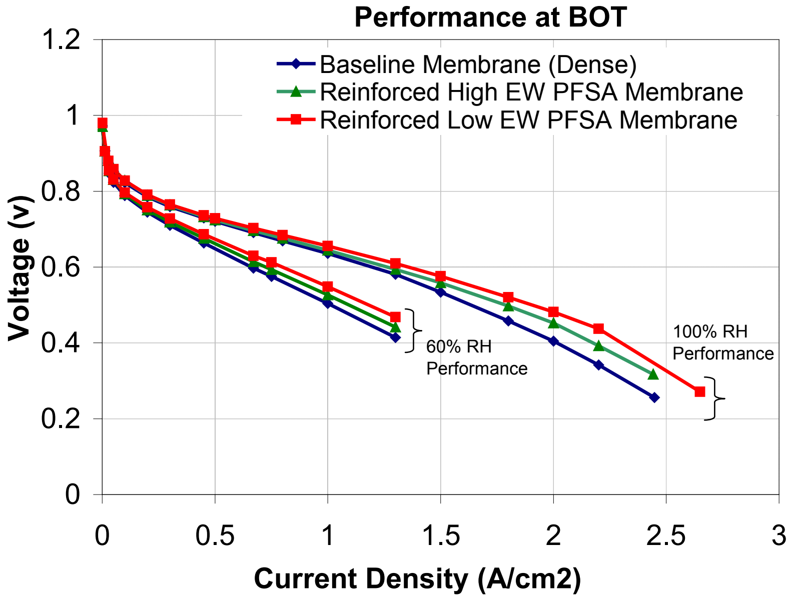


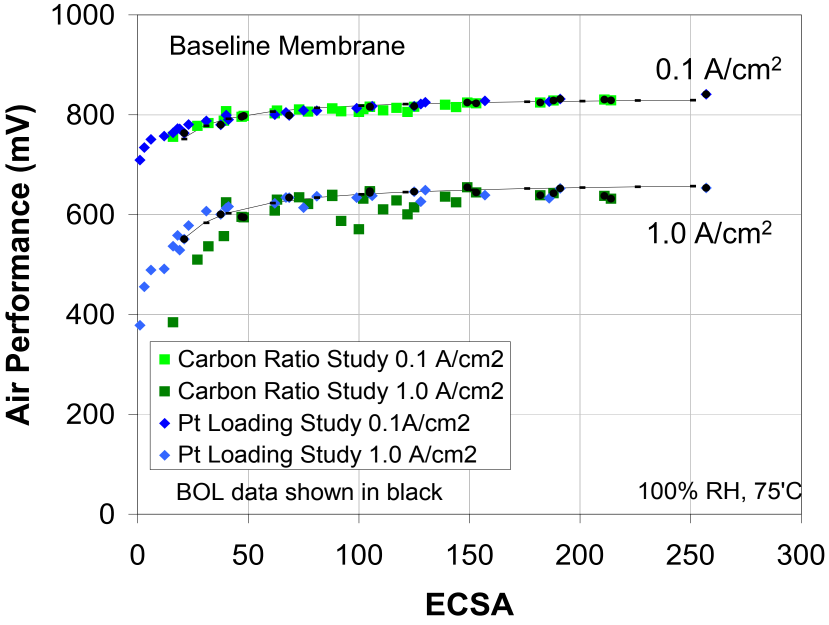


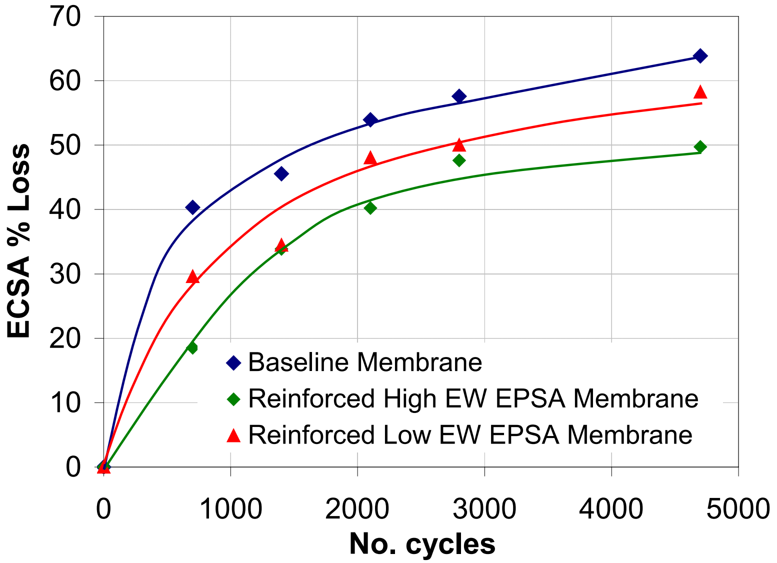
- Positive water flux → anode to cathode
- Effect of RH
  - Equal anode/cathode RH gives flux from electro-osmotic drag
  - Inequality in RH between anode and cathode causes small extra flux
- Effect of EW
  - EW affects transport due to RH imbalance
  - Pivot point at balanced Anode/Cathode RH
  - EW effect on membrane water flux is small



Experimental Status Update
Performance (Preliminary Results)

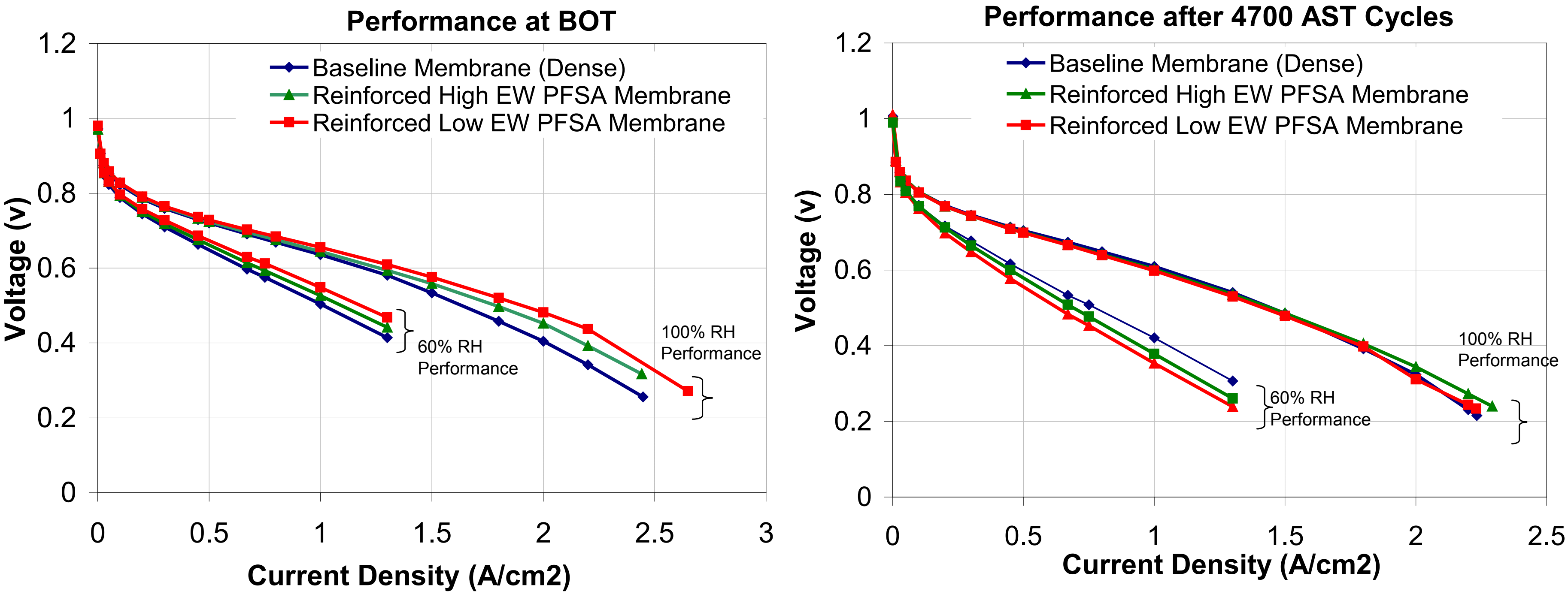






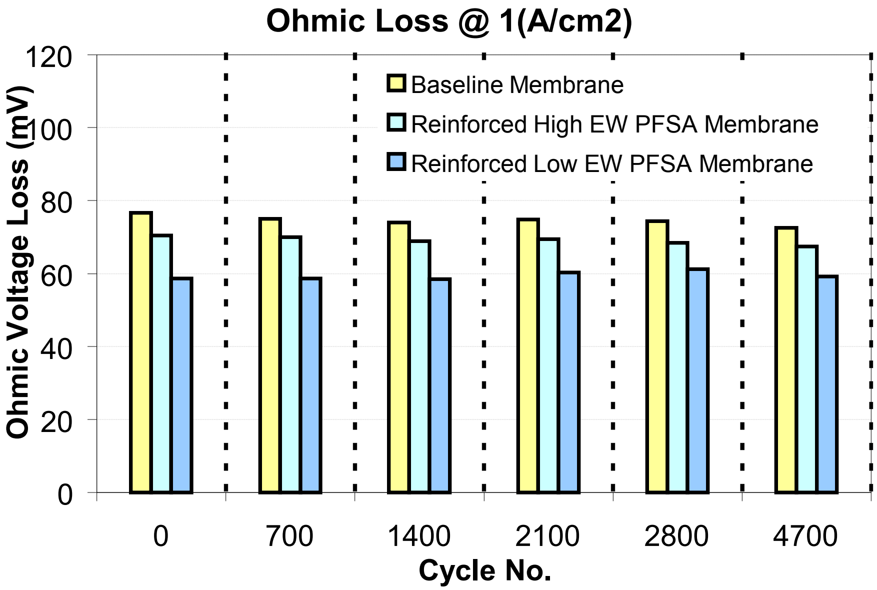
- Beginning of Test
  - Low current performance (<1 A/cm^2) appears to be insensitive to EW
  - High current performance (>1 A/cm^2) may reflect difference in water content of the MEA
- ECSA loss <70% may not be significant in terms of performance impact

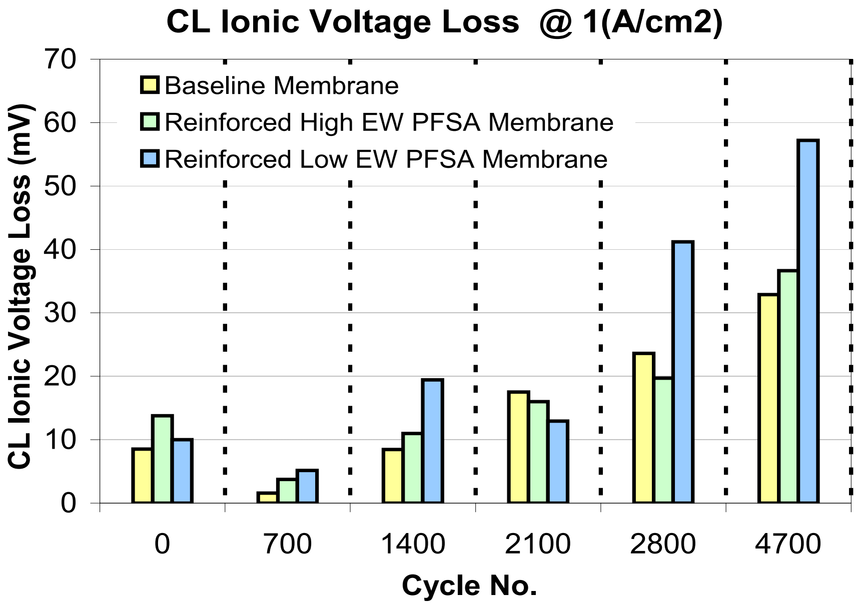
Experimental Status Update
Performance & Degradation (Preliminary Results)



- End of Test Performance
  - Under low humidity condition, performance sensitivity appears to increase
  - Preliminary results do not show a systematic trend with EW

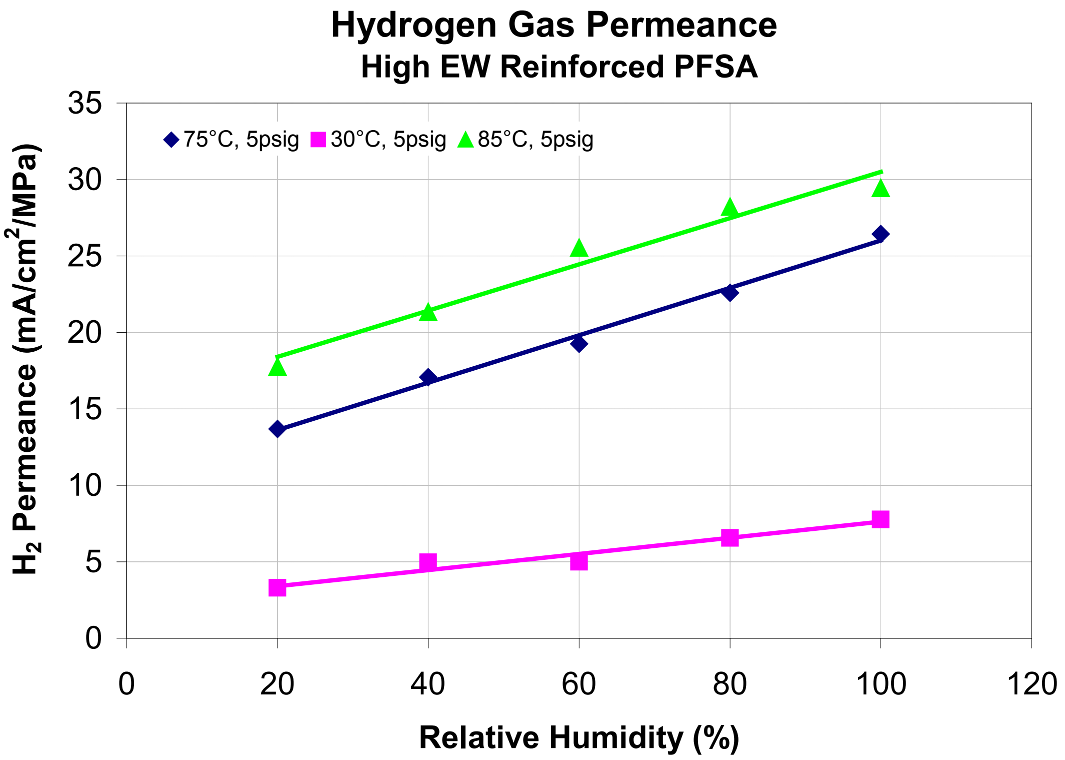
Experimental Status Update
Performance & Degradation (Preliminary Results)





- Ohmic voltage loss
  - Does not seem to be affected by membrane EW (may be dependent on test conditions)
  - Affected by membrane thickness
- Ionic Voltage loss increases towards EOT
  - Catalyst ionomer is the same between samples, suggesting perhaps that water management/water content has changed

Experimental Status Update
In-situ Hydrogen Cross-over at BOT



- H_2 Cross-over increases largely with temperature
- Crossover also increases with RH within a temperature family.
  - Permeability is a function of diffusivity and solubility

Organizations /Partners

- **Prime: Ballard Fuel Cell Products / Ballard Power Systems (S. Wessel, D. Harvey)**
  - Lead: Membrane Model adaptation, performance/degradation-membrane property correlations
- **University of Calgary (K. Karan)**
  - Pt dissolution mechanisms
- **University of New Mexico (P. Atanassov)**
  - Surface characterization of catalyst layers/membrane interface
- **Membrane suppliers and Simon Fraser University**
  - Characterization of membrane transport properties

Summary

- **Relevance**
  - Improve understanding of the Pt dissolution mechanism, with respect to water content and the role of the membrane.
  - Enhance FC-APOLLO performance and durability predictions
- **Approach**
  - Adapt/expand physical membrane model published by Weber and Newman
  - Investigate the effect of membrane transport properties on Pt dissolution
- **Technical Accomplishments and Progress to date**
  - Description of 1D membrane transport model
  - Initial performance and durability results for Nafion® NR211 and reinforced PFSA membranes
- **Collaborations**
  - Project team partners University of Calgary and University of New Mexico
  - DOE Durability and Modeling Working Groups
- **Future Research**
  - Expand membrane water transport model to 3-D
  - Validate FC-Apollo membrane sub-model against experimental results
  - Evaluate partially fluorinated hydrocarbon membranes
  - Correlate membrane properties with MEA performance losses and Pt dissolution

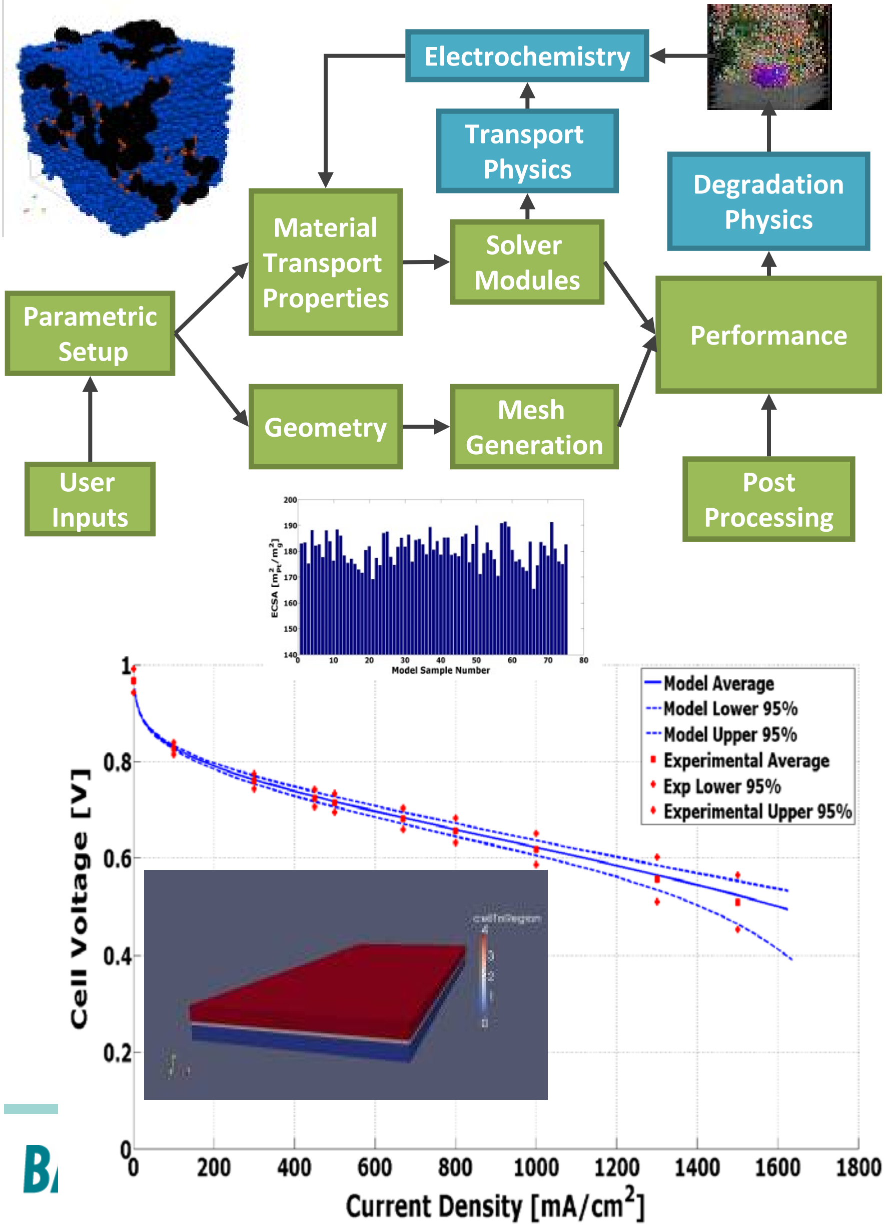
Acknowledgement

- **Thank you:**
  - Financial support from the U.S. DOE-EERE Fuel Cells Technology Program
  - Support from DOE project managers/advisor Donna Ho, David Peterson, John Kopasz
  - Valuable discussions with the Fuel Cell Tech Team
  - Discussions and collaboration within the DOE Transport Modelling Working Group
  - Project Collaborators
  - Ballard Colleagues

Technical Back-up Slides

FC-APOLLO Simulation Suite

Fuel Cell Application Package Open Source for Long Life Operation



Electrochemistry

Transport Physics

Material Transport Properties

Solver Modules

Degradation Physics

Parametric Setup

Performance

Geometry

Mesh Generation

User Inputs

Post Processing

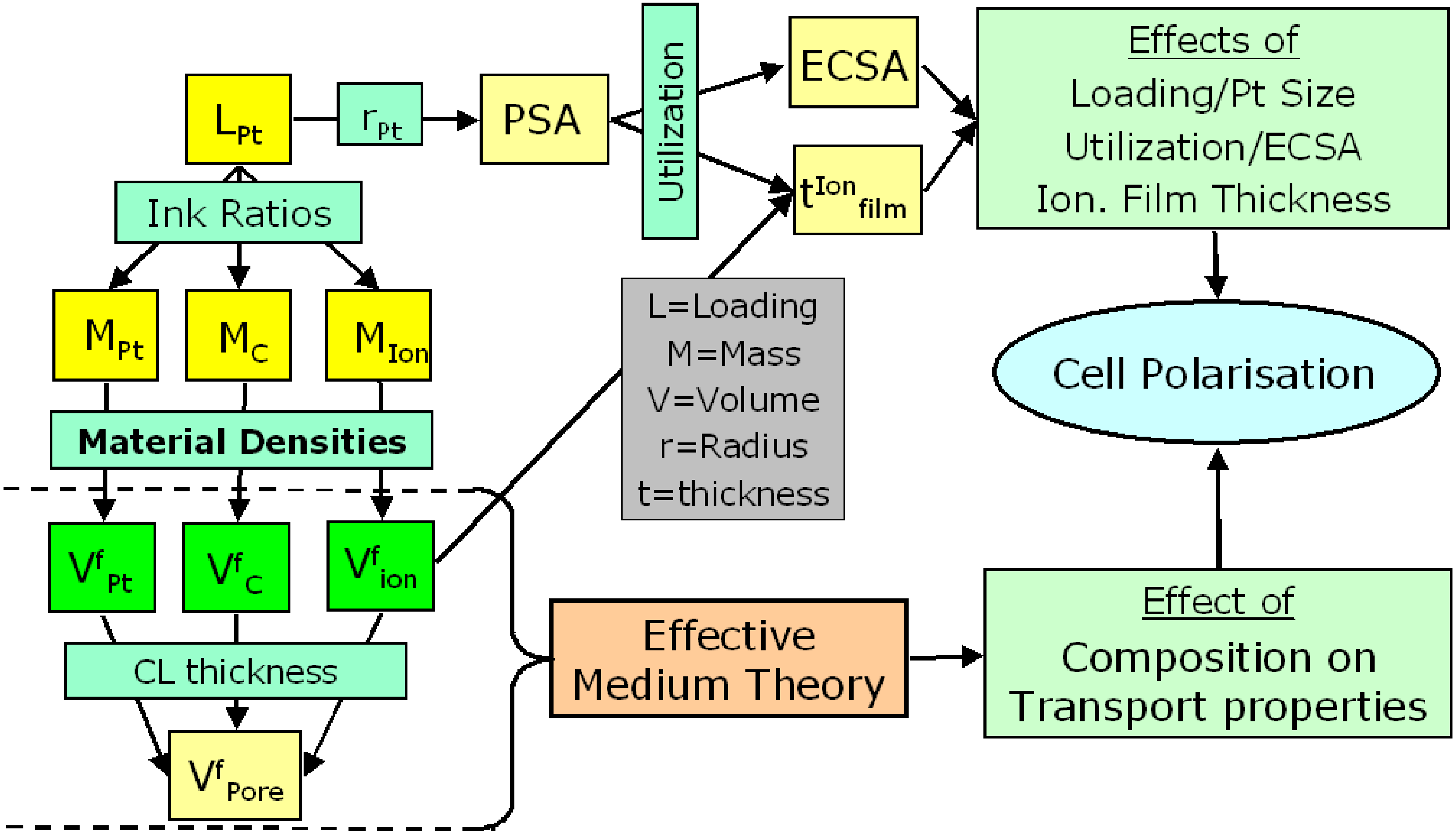
Features:

- Performance and durability simulation
- Catalyst layer optimization
- Accelerated Stress Test (AST) behaviour
- Scalable simulations (1D → 3D)
- Fully open source package

Simulation Validation

- Performance - Material Composition
  - Pt Loading (0.05 – 0.4 mg/cm^2)
  - Pt:Carbon Ratio (0.3 – 0.8)
  - Pt:Ionomer Ratio (0.13 – 0.43)
- Performance - Operational Conditions
  - Relative Humidity (60% and 100%)
  - Oxidant Fraction (5 – 100%)
  - Temperature (60, 70, 80°C)
- Durability – Pt-Dissolution (square wave/triangle wave)
  - AST cycle (0.6 – 1.2V) up to 2000 Cycles
  - AST cycle (0.6 – 1.0/1.1/1.2/1.3/1.4) up to 4700 cycles (pending)
- Durability - Carbon Corrosion (square wave/triangle wave)
  - AST cycle (0.6 – 1.4V) (pending)

Linking Catalyst Compositional Effects



L_{Pt}

r_{Pt}

PSA

Utilization

ECSA

t^{Ion}_{film}

Effects of
Loading/Pt Size
Utilization/ECSA
Ion. Film Thickness

Ink Ratios

M_{Pt}

M_C

M_{Ion}

Material Densities

L=Loading
M=Mass
V=Volume
r=Radius
t=thickness

Cell Polarisation

V^f_{Pt}

V^f_C

V^f_{ion}

CL thickness

V^f_{Pore}

Effective
Medium Theory

Effect of
Composition on
Transport properties

Access to FC-APOLLO

- **Linux**
  - Model runs in a Linux based environment
  - Hosting internally is done via cluster and remote login
  - Local installs are done using a Git repostitory
- **OpenFoam**
  - Simulation suite was built using OpenFoam-2.2.x nightly build
  - FC-APOLLO builds will remain current against the nightly build
- **Paraview**
  - www.paraview.org
  - FC-APOLLO is built against the latest Parkview release
- **SourceForge**
  - www.sourceForge.net/projects/fcapollo
- **GitHub**
  - Pending, currently a “private” repository