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U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

FUEL CELL TECHNOLOGIES OFFICE

FC-APOLLO

***F**uel*
***C**ell*
***A**pplication*
***P**ackage for*
***O**pen-source*
***L**ong-**L**ife*
***O**peration*

David Harvey, Alexander Bellemare-Davis

Introduction

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- **FC-APOLLO Simulation Suite Development**
  - Financial and technical support by the U.S. Department of Energy (DE-EE0000466)

- **What can FC-APOLLO simulate?**
  - Predictions for:
    - Cell polarizations (e.g. specified voltage, simulated current density)
    - Effective property distributions (e.g. ECSA, diffusivity, proton conductivity)
    - Local distributions (e.g. temperature, pressure, relative humidity, reactant and product concentrations, potential, overpotential, current)
    - Life cycle effects (e.g. loss in platinum surface area and loss in carbon support via AST)
  - Using the inputs of:
    - Operational Conditions (e.g. temperature, pressure, relative humidity, reactant concentration, cell voltage)
    - Material Properties (e.g. platinum loading, catalyst layer composition, material conductivities, component thickness, permeability)
    - Statistical variability of operational and/or material properties (Optional)

FC-APOLLO Agenda

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- FC-APOLLO Review
  - Multi-scale Methodology
  - Input Parameters and Design Variables
  - Physical Model
    - Transport
    - Reaction Kinetics and Oxide Formation
  - Validation
- FC-APOLLO Application
  - Model Graphic User Interface
    - Simulation Setup
    - Running the Simulation Suite
    - Post Processing
  - How to access the model
  - Release Schedule

FC-APOLLO Multi-scale Overview

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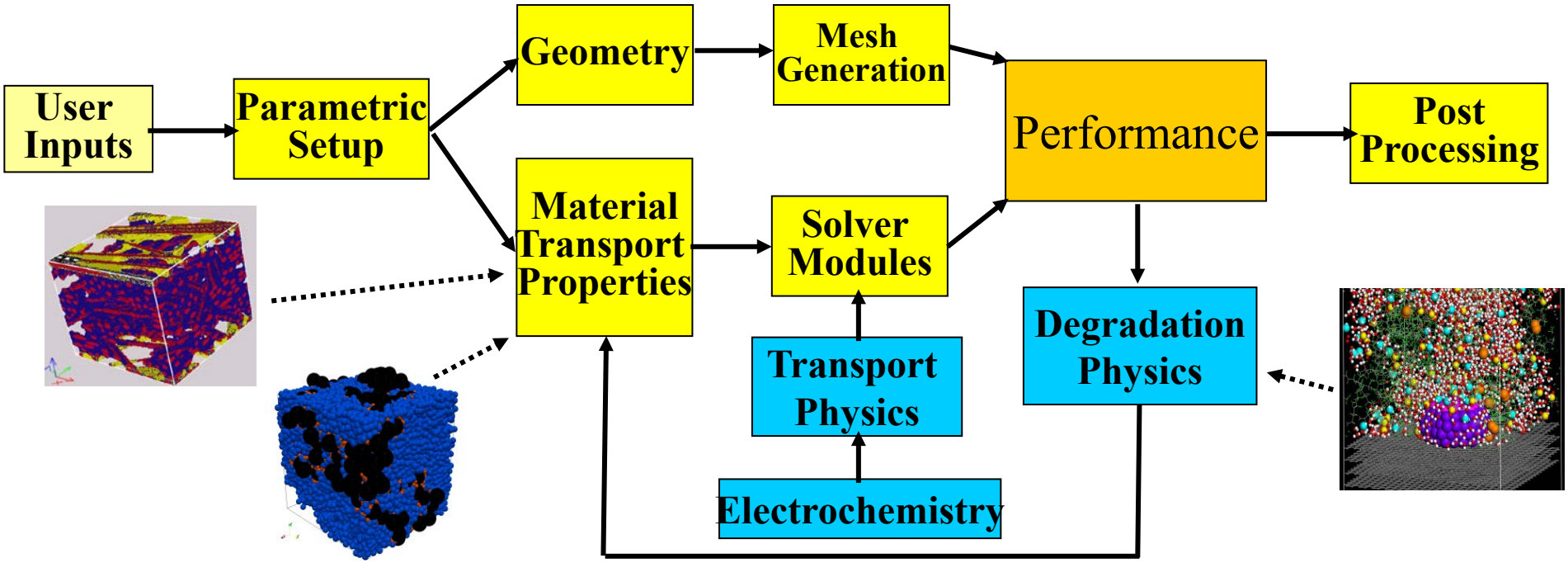

- Simulation Suite is separated into modular components
  - User inputs of operational conditions and material characteristics for each component
  - Statistical variation can be applied to all material characteristics in order to generate statistically significant data sets
- Electrochemistry, Transport Physics, and Degradation kinetics
  - Software is open-source which allows customization of the relevant modules
  - Improved Pt-oxide reaction model is applicable for oxygenated and low-oxygenated environments.

FC-APOLLO Mission Statement

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- Develop a simulation package for PEMFC
  - Performance
    - Describe the composition and loading of the cathode catalyst layer
    - Include capability for statistical descriptions of component properties
    - Capture the performance effects for a range of operational conditions
    - Capture performance of the baseline MEA at reference conditions
    - Predict baseline MEA at high current density

FC-APOLLO Mission Statement

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- Develop a simulation package for PEMFC
  - Durability
    - Develop a unified description for platinum oxide kinetics under Nitrogen and Oxygen atmospheres
    - Create a numerical cycling algorithm to describe arbitrary trapezoidal waves
    - Implement Platinum dissolution for an anodic mechanism
    - Implement a carbon surface oxidation and corrosion mechanism
    - Capture the performance of degrading MEAs at reference conditions

FC-APOLLO
STC Hardware & Reference MEA

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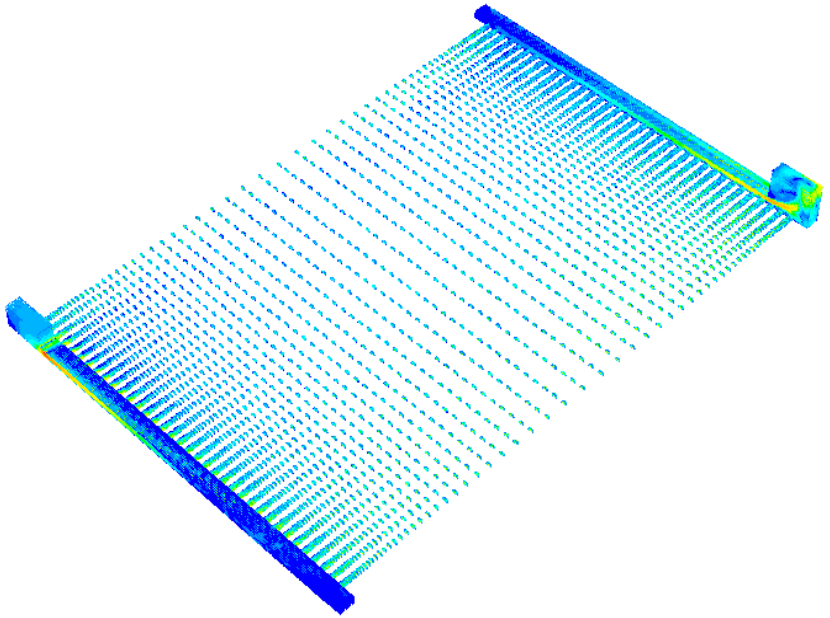
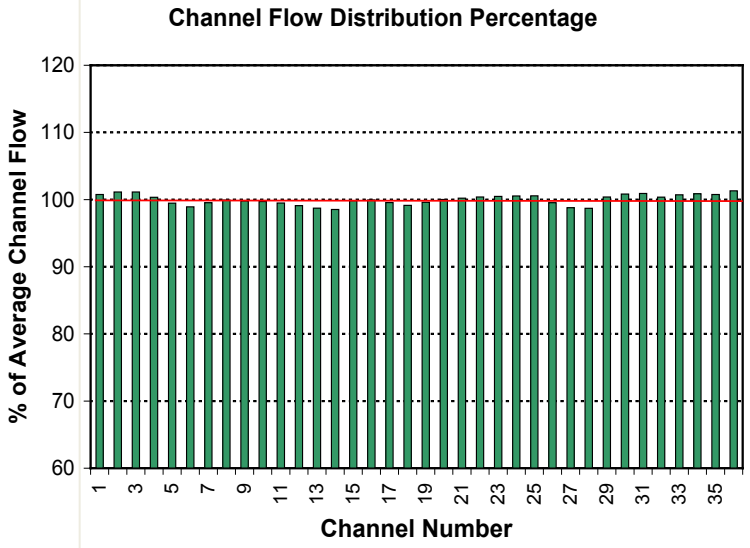
- Reference MEA
  - Pt Catalyst
    - Graphitized carbon-support
    - 50:50 Pt/C ratio
    - Nafion® ionomer
  - Catalyst Loading
    - Cathode/anode
    - 0.4/0.1 mg/cm2
  - Catalyst Coated Membrane
    - Ballard manufactured CCM
    - Nafion® NR211
  - Gas diffusion layer
    - BMP Continuous Process Product
- 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





FC-APOLLO Transport Physics

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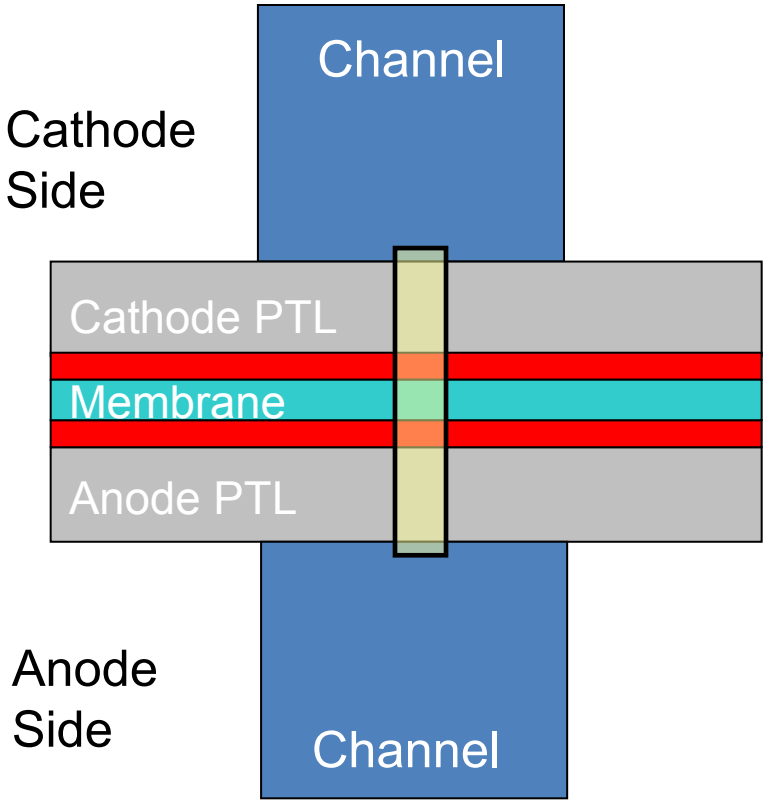

Physics	Variable
Electron Transport	(phi_e)
Proton Transport	(phi_p)
Species Transport	
Hydrogen	(w_H2)
Oxygen	(w_O2)
Nitrogen	(w_N2)
Water	(w_H2O_v)
Carbon Dioxide	(w_CO2)
Energy Transport	(T)
Mass Transport	(P_mix)
Liquid Water Transport	(saturation)
Dissolved Water Transport	(C_H2O_diss)
Dissolved Platinum Transport	(C_pt_diss)

****Note: Full details of all equations are available in the released documentation**

FC-APOLLO
Performance Transport Physics

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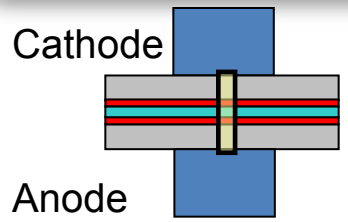

Physics	Variable
Electron Transport	(phi_e)
Proton Transport	(phi_p)
Species Transport	
Hydrogen	(w_H2)
Oxygen	(w_O2)
Nitrogen	(w_N2)
Water	(w_H2O_v)
Energy Transport	(T)
Mass Transport	(P_mix)
Liquid Water	(saturation)

Design Property	Variable
Electronic Conductivity	(sigma_e_eff)
Protonic Conductivity	(sigma_p_eff)
Species Transport	
Hydrogen Diffusivity	(D_H2_mix_eff)
Oxygen	(D_O2_mix_eff)
Nitrogen	(N-1 Species)
Water	(D_H2O_v_mix_eff)
Thermal Conductivity	(K_thermal_eff)
Relative Permeability	(K_p_g_relative)
Diffusivity of Water (l)	(D_H2O_l)

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Liquid Water Transport

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Anode and Cathode

The two-fluid model is used and is similar to the approach used by:

- Mazumder and Cole (J.ECS, 2003)
- Shah et al. (J.PS, 2006)
- Meng (J.PS, 2007)
- Wang and Cheng (Adv. Heat Transfer, 1997)

Liquid water models suffer from uncertainty around the transport mechanism…

Is it thermal??

Is it capillary??

We assume it is capillary driven and that the saturation phase is continuous…

Strictly speaking that is not correct, however is it consistent with most approaches for liquid water transport used currently.

Room for improvement here!!

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Liquid Water Transport

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Saturation driven transport of the liquid phase:

$$\nabla \cdot \left(\frac{\rho_l \mathrm{K_{rl}}}{\mu_l} \frac{dP_c}{ds} \frac{ds}{dx} \right) - \nabla \cdot \left(\frac{\rho_l \mathrm{K_{rl}}}{\mu_l} \frac{dP}{dx} \right) = S_{vapour-liquid} M_w^{\mathrm{H2O}}$$

$$S_{vapour-liquid} = h_{pc} \left(P_{\mathrm{H2O}}^{vap} - P_{\mathrm{H2O}}^{sat} \right)$$

$$h_{pc} = \frac{k_{cond} V_f^{Pore} (1 - \mathrm{s}) x_{\mathrm{H2O}}^{vap}}{2RT} \left[1 + \frac{\left| P_{\mathrm{H2O}}^{vap} - P_{\mathrm{H2O}}^{sat} \right|}{p_{\mathrm{H2O}}^{vap} - P_{\mathrm{H2O}}^{sat}} \right] + \frac{k_{evap} V_f^{Pore} s \rho_l}{2\mathrm{M}_{\mathrm{w}}^{\mathrm{H2O}}} \left[1 - \frac{\left| P_{\mathrm{H2O}}^{vap} - P_{\mathrm{H2O}}^{sat} \right|}{p_{\mathrm{H2O}}^{vap} - P_{\mathrm{H2O}}^{sat}} \right]$$

FC-APOLLO
Liquid Water Transport

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Saturation-driven transport of the liquid phase:

$$h_{pc} = \frac{k_{cond} V_f^{Pore} (1-s) x_{H2O}^{vap}}{2RT} \left[1 + \frac{\left| P_{H2O}^{vap} - P_{H2O}^{sat} \right|}{p_{H2O}^{vap} - P_{H2O}^{sat}} \right] + \frac{k_{evap} V_f^{Pore} s \rho_l}{2 M_w^{H2O}} \left[1 - \frac{\left| P_{H2O}^{vap} - P_{H2O}^{sat} \right|}{p_{H2O}^{vap} - P_{H2O}^{sat}} \right]$$

$$p_c = \sigma_c \mathcal{J}(s), \quad \kappa_l(s) = \kappa_c s^3$$

$$\sigma_c = \sigma' \cos\theta_c^j \sqrt{\frac{\epsilon_p}{\kappa_c}}$$

and, assuming hydrophobic media:

$$\mathcal{J}(s) = 1.417s - 2.12s^2 + 1.262s^3$$

Liquid water models are still largely "fitted" empirically.

This model is no exception, the permeability (while taken from microstructural simulations) required adjustment for the "Type" of porous media used.

This is an area for future improvement and with open-source there is choice!

FC-APOLLO Reaction Kinetics Modules

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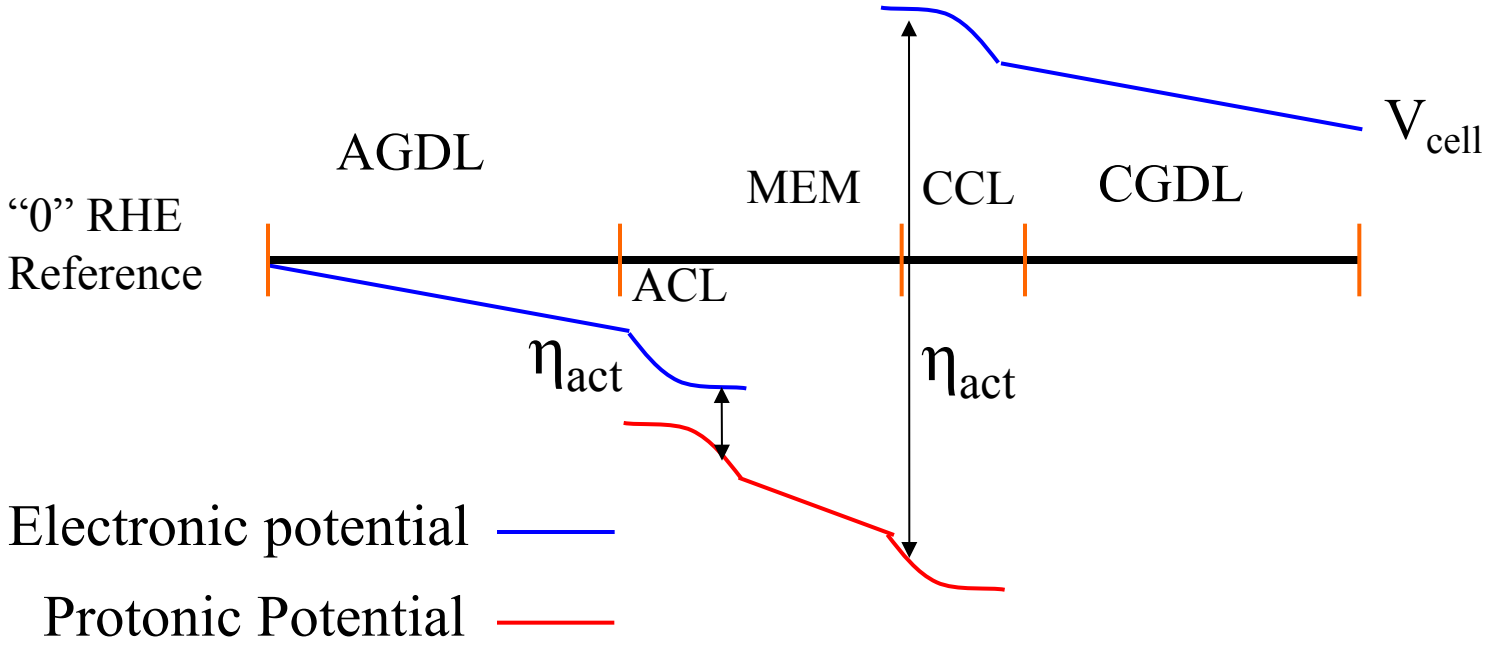
- **Oxygen Reduction Reaction**
  - Module #1 - Butler-Volmer kinetics with an agglomerate model
  - Module #2 – Multi-step ORR Kinetics (agglomerate model pairing is pending)
- **Anode**
  - Module #1 – Butler-Volmer kinetics with an agglomerate model
  - Module #2 - Tafel-Volmer-Heyrovsky kinetics (agglomerate model pairing is pending)



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Reaction Kinetics/Catalyst Activity

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Exchange Current Density:

$$i_{o,geom}^{(T,C,S)} = i_{o,pt}^{ref\,(T,C)} S_{pt} \left(\frac{C_{O2}}{C_{O2}^{ref}} \right)^{\gamma_{O2}} \exp\left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right]$$

“Platinum is Platinum” ….. ??

Platinum behaves according to its base physico-chemical characteristics regardless of the scale of the system (i.e. RDE, STC, Stack) and, if the transport processes are properly understood, those base physico-chemical characteristics are capable to describe the observed performance of a given system without requiring re-characterization on the new scale.

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Improved Multi-step ORR Kinetics

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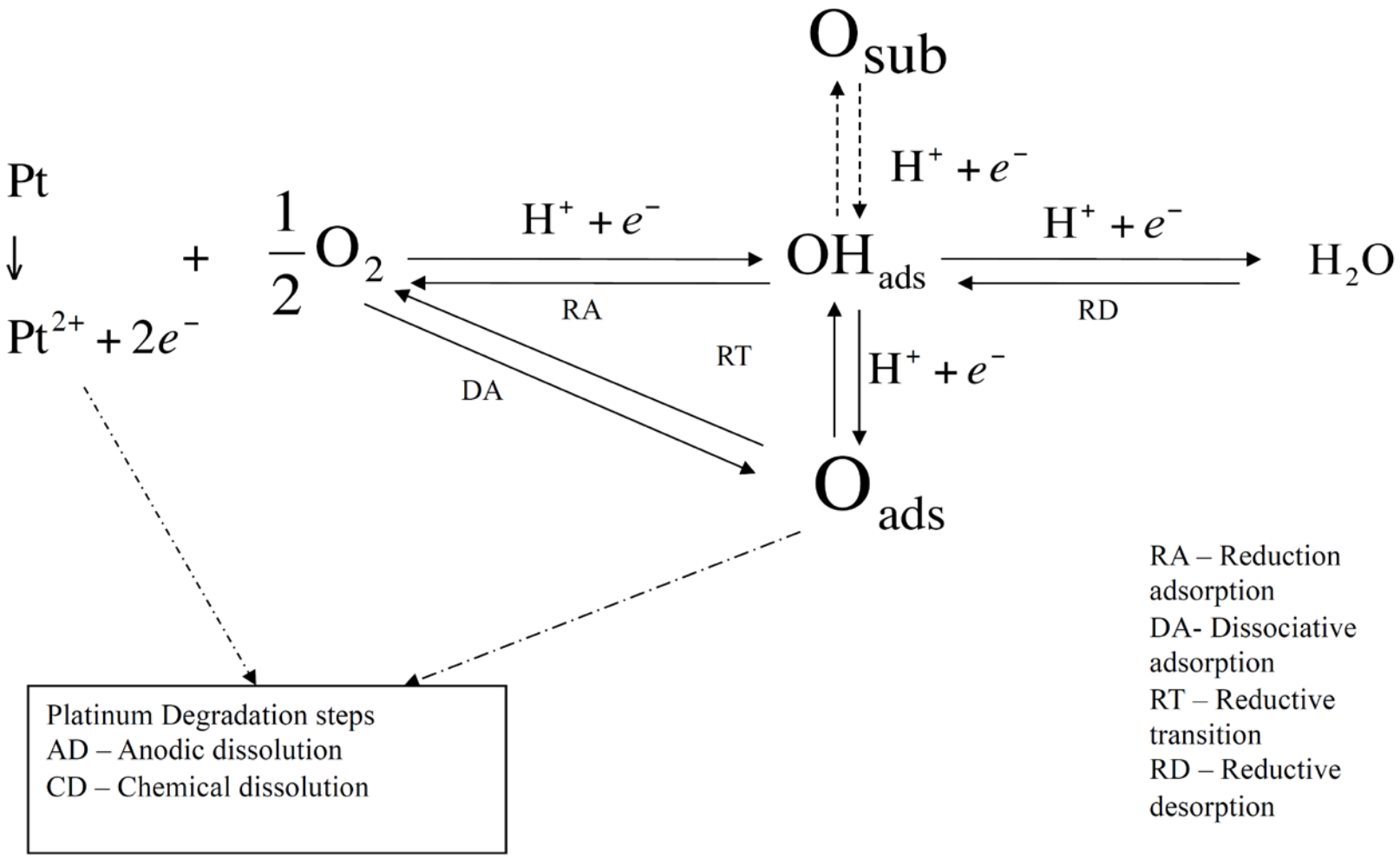

FC-APOLLO
Pt-Oxide and Reaction Kinetics

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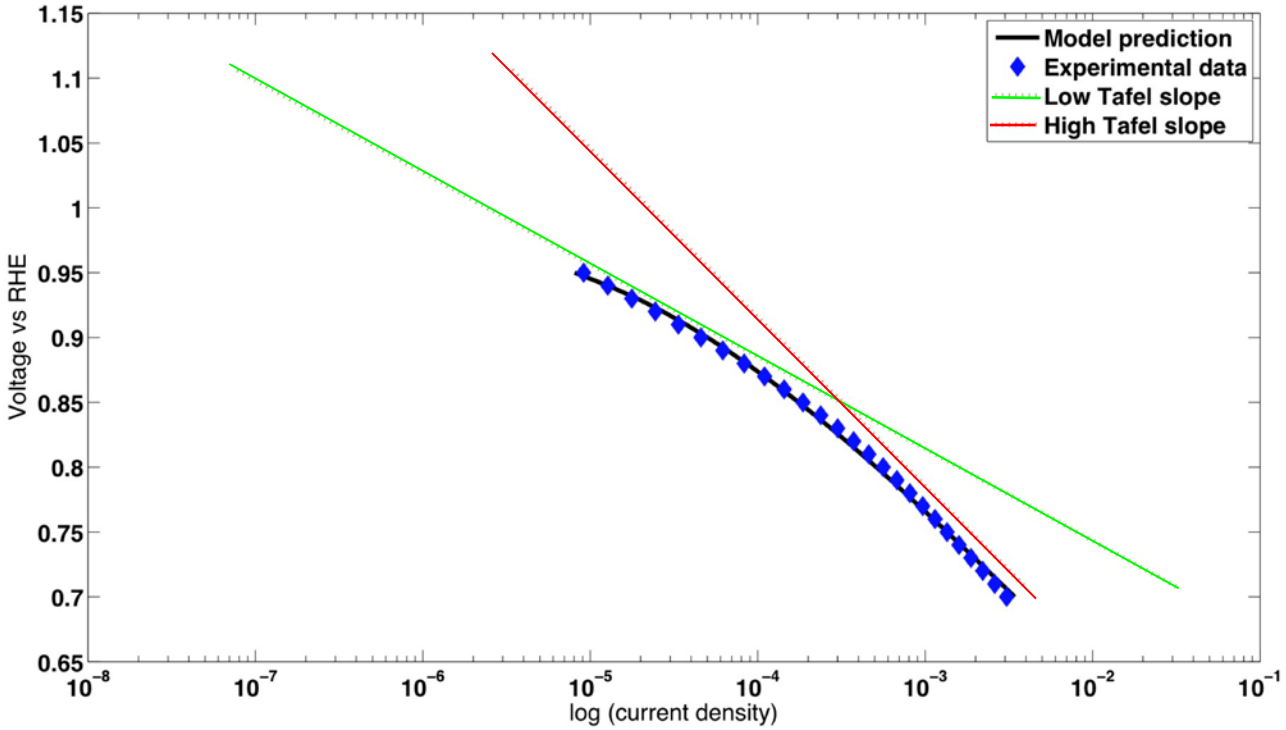
Polarization behavior



Platinum behaves according to its base physico-chemical characteristics regardless of the scale of the system (i.e. RDE, STC, Stack) and, if the transport processes are properly understood, those base physico-chemical characteristics are capable to describe the observed performance of a given system without requiring re-characterization on the new scale.

FC-APOLLO
Pt-Oxide and Reaction Kinetics

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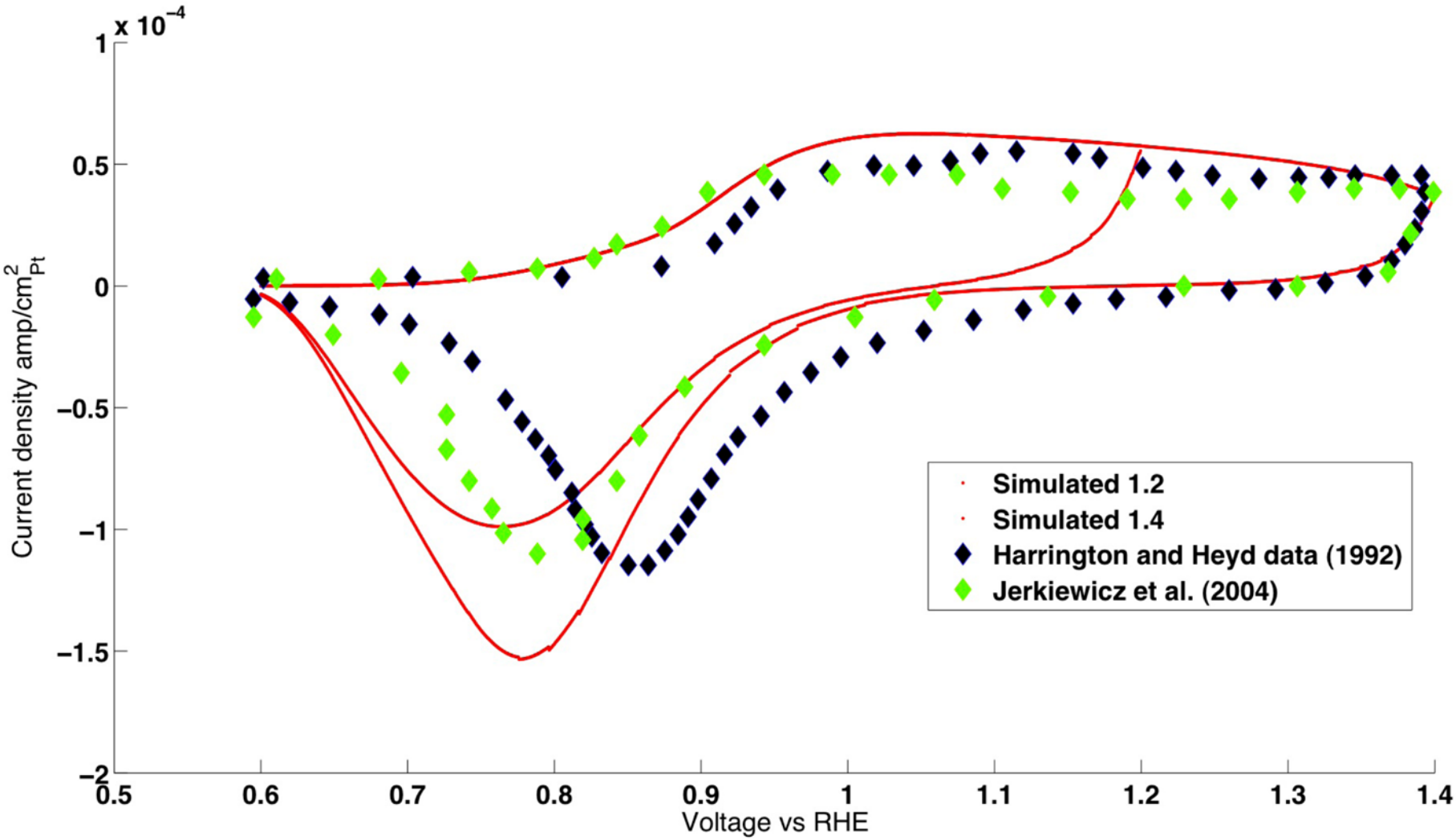
Cyclic voltammetry



FC-APOLLO
Platinum Dissolution

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Anodic dissolution reaction $\mathrm{Pt} \rightarrow \mathrm{Pt}^{2+} + 2e^-$

$$E^{Eq} = E^{o} - \frac{RT}{nF}\log\left(\frac{a_{Pt^{2+}}}{a_{Pt}}\right)$$

Gibbs Thompson effect

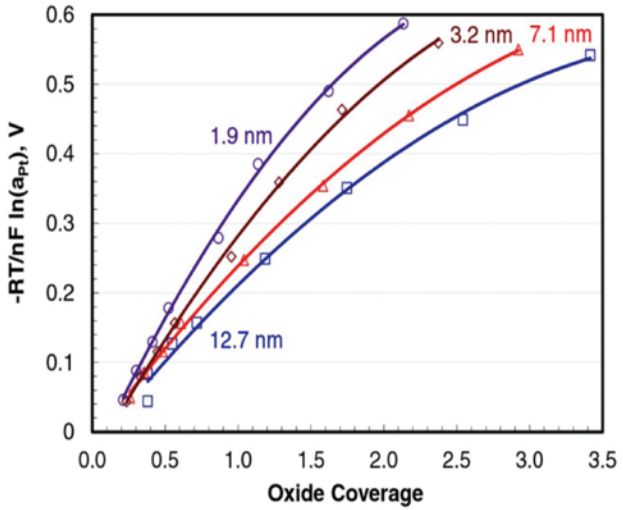
$$E^{Eq} = E_{\infty}{}^{Eq} - \frac{\overline{V}_{Pt}\gamma_{Pt}}{F \,.\, r}$$

Accounting for Pt activity

$$a_{Pt} \rightarrow (1 - \theta_O - \theta_{OH})$$

$$a_{Pt^{2+}} = \frac{C_{Pt^{2+}}}{C_{Pt^{2+},\,ref}}$$

$$C_{Pt_{ref}{}^{2+}} = \frac{a^{o}_{Pt}}{C^{o}_{Pt^{2+}}} \longrightarrow$$ Fixed from experimental data



Ahluwalia R K et al. J. Electrochem. Soc. 2013;160:F447-F455

Anodic dissolution kinetic model

$$r_{AD} = k_{AD} * ((1 - \theta_O - \theta_{OH}) * \exp\left(\frac{\beta nF}{RT}(E - E^{Eq})\right) - \frac{C_{Pt^{2+}}}{C_{Pt^{2+}{}_{ref}}} * \exp\left(-\frac{\beta nF}{RT}(E - E^{Eq})\right))$$

FC-APOLLO Validation

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- **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)
    - Operational Conditions
      - Relative Humidity (60% and 100% on the baseline MEA)
      - Oxidant Fraction (5 – 100%)
      - Temperature (60, 70, and 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)*
    - Carbon Corrosion (square wave/triangle wave)
      - *AST cycle (0.6 – 1.4V) (pending)*
- **Validation data is included in the documentation**

FC-APOLLO Performance Validation

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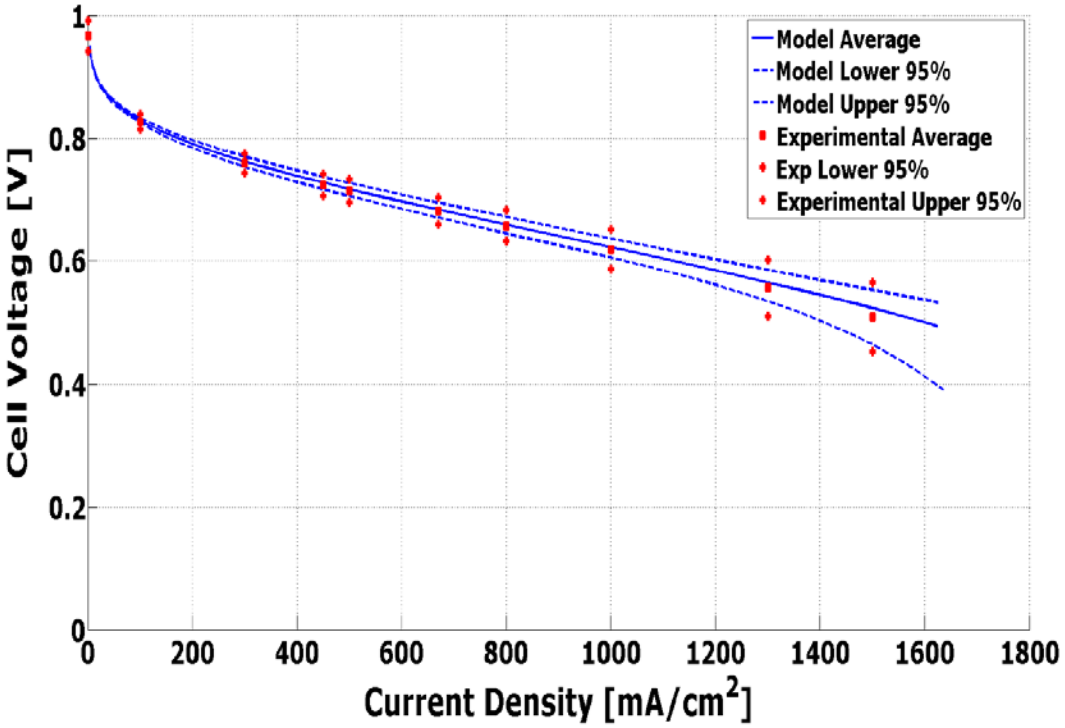

Statistical Model Inputs

Component Properties	% Deviation (1 Std Dev)
Catalyst/Catalyst Layer	
Thickness (microns)	+/- 8%
Weight Ratios (%)	
Pt:C	+/- 1%
(Pt:C):Ionomer	+/- 1%
Pt Loading [mg/cm^2]	+/- 5 %
Pt size	+/- 10%
Tafel Slope [mV/dec]	fixed
Jo [A/cm^2 pt]	+/- 10%
GDL	
Porosity	fixed
Tortuosity	+/- 3%
Thickness (microns)	+/- 5%
Membrane	
Thickness (microns)	+/- 2%

2-Phase Model Validation

- Model predictions were *within 95% variability* of the experimental data
  - The two phase model accurately captures the effect of increasing water content coupled with an agglomerate catalyst model
  - Experimental variation and model variation both increase with current density as “noise” factors have increased effects on the transport processes

FC-APOLLO
Pt-Dissolution Validation

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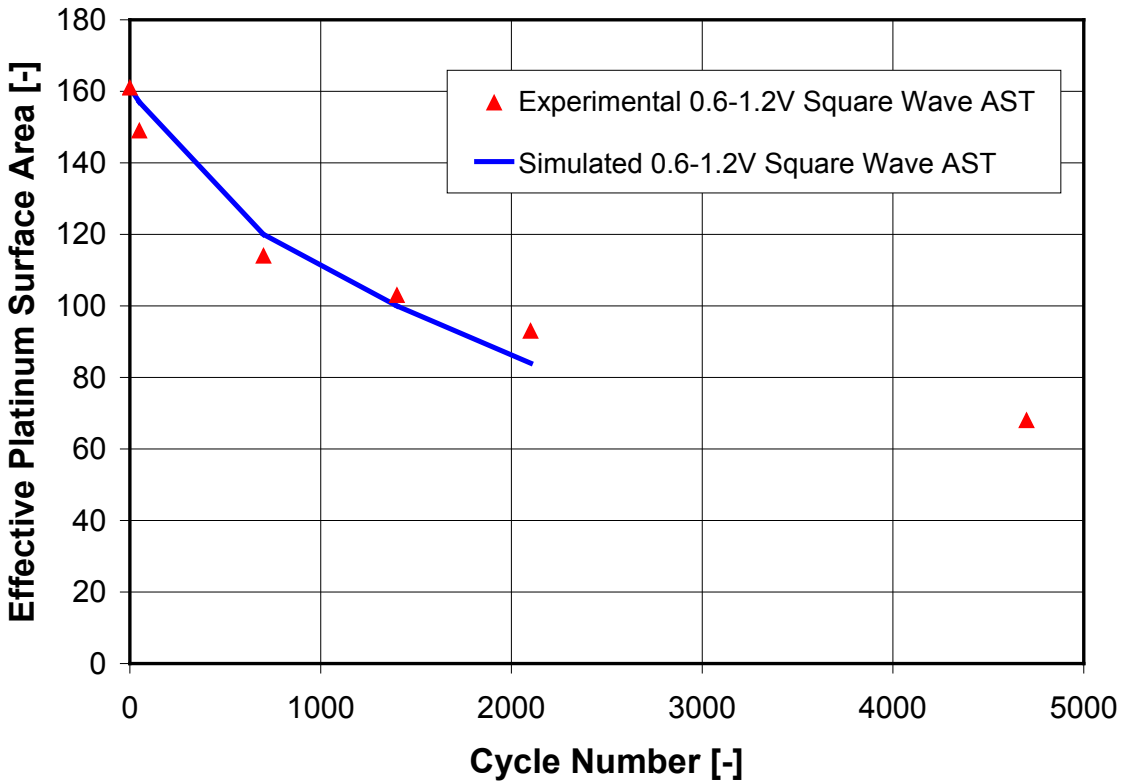

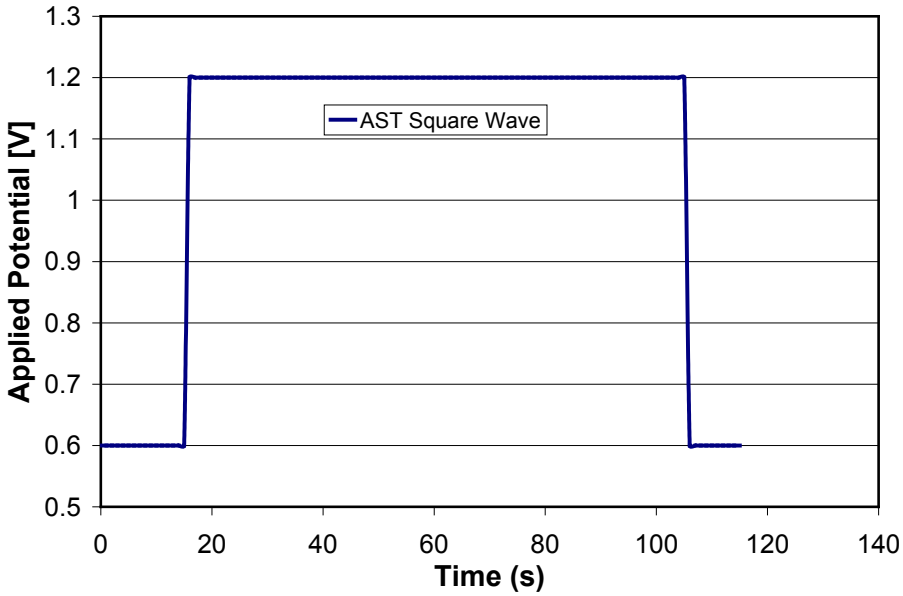

Pt-Dissolution Model Validation

- Simulation results are promising against the baseline AST cycle data for 1.2V
  - Platinum dissolved adjacent to the membrane/catalyst interface initially
  - Platinum particle growth occurs further into the catalyst layer, as opposed to in the dissolved “adjacent region”
- Simulations and further validation points continues to run, data management is essential to running durability simulations
- Full validation sets included in the documentation guide

FC-APOLLO
Graphic User Interface

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- Comprehensive front-end to FC-APOLLO
  - Includes interfaces for
    - Mesh Generation
    - Operational and Material properties
    - AST Cycling
    - Post-Processing (via Paraview)
  - Graphic User Interface and Module Customization is available
- Demonstration of Model Setup and Graphic User Interface

Access to FC-APOLLO

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- Linux
  - Model run 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 Paraview release
- SourceForge
  - www.sourceForge.net/projects/fcapollo
- GitHub
  - Pending, currently a “private” repository

FC-STC Hardware
Standard Test Cell

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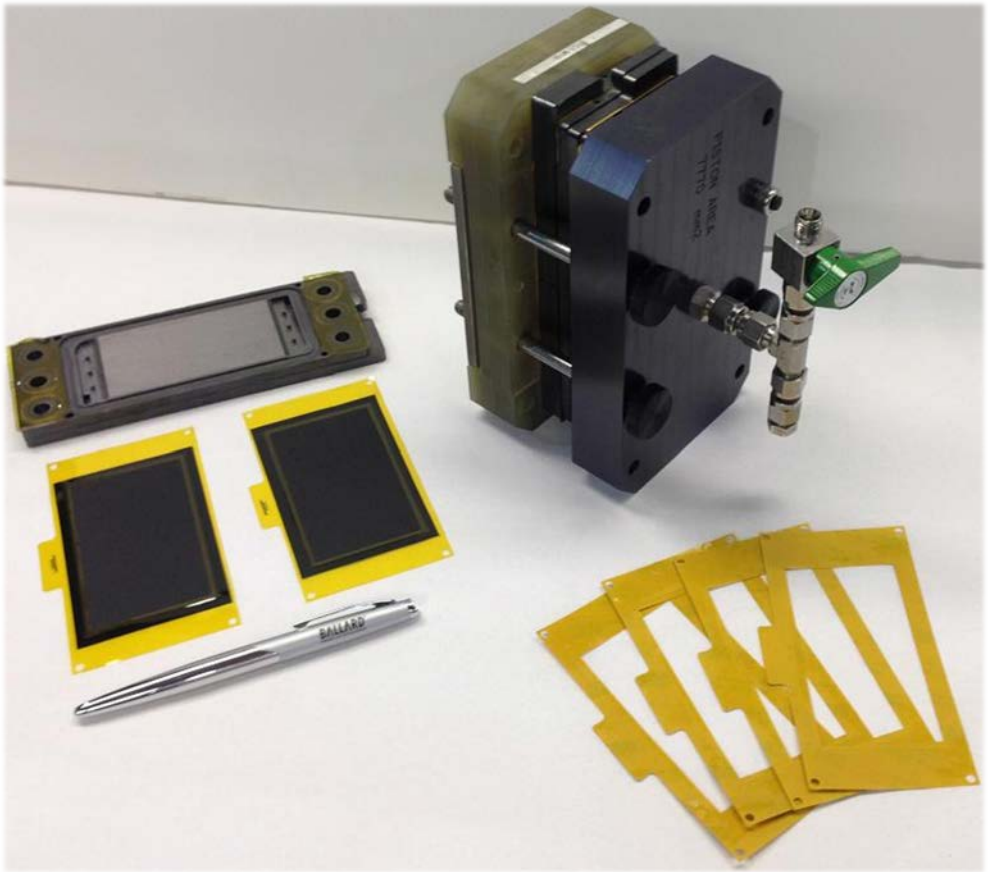
- FC-APOLLO Simulation Suite Validation
  - Validation was performed using data generated on reference MEAs in the FC-STC Hardware
  - FC-STC Hardware was used to generate both performance and durability data
  - Key features of the hardware enabled validation of the simulation suite

- FC-STC Features:
  - Custom transition region minimizing channel to channel flow sharing
  - Parallel flow field for low pressure drop and uniform flow (quasi - 1D)
  - Pressure bladder for uniform compression
  - Liquid cooling (cathode/anode plates)
  - Framed membrane electrode assemblies (MEAs)
  - 45 cm2 active area



FC-APOLLO Simulation Suite

Application Package using Open-source for Long Life Operation

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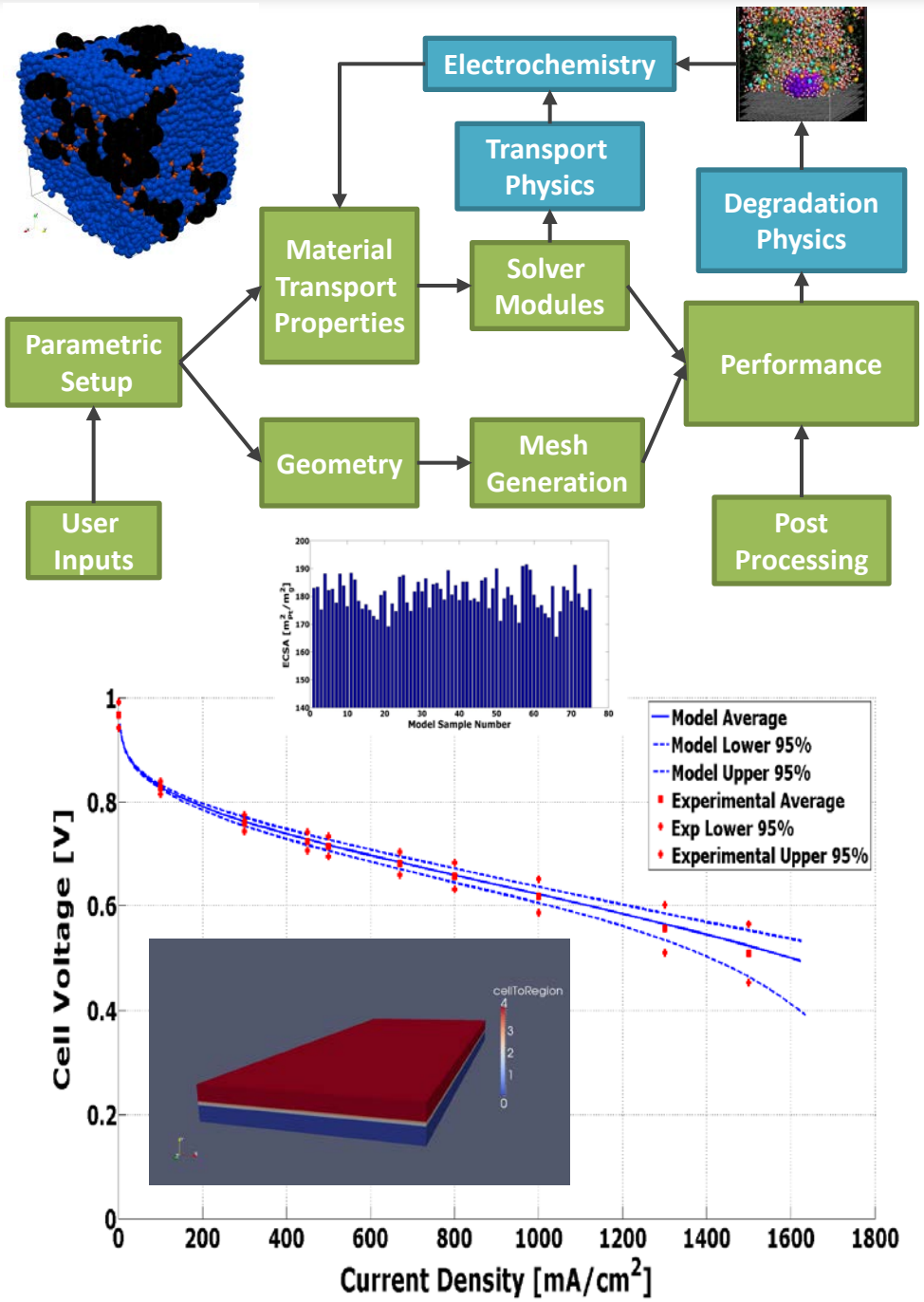

- Features:
  - Performance and durability simulation model
  - Optimize electrode composition and loading
  - Assess operational windows and Accelerated Stress Test (AST) behaviour
  - Scalable from 1D to 3D simulations
  - Validation data using FC-STC hardware is included in documentation within the Sourceforge repository
- Fuel Cell Community:
  - Ability to add or modify physics modules
  - Customize the user interface to meet specific needs
  - Transparent bug tracking system
  - Technical assistance is available through the developers, if requested.

Acknowledgements and Contact

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We most gratefully acknowledge:

- Financial and technical support from the Dept. of Energy's Fuel Cell Technologies Office

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FUEL CELL TECHNOLOGIES OFFICE

- Technical contributions from our collaborators,

Georgia Institute of Technology

Los Alamos National Laboratory

Michigan Technological University

Queen's University

University of New Mexico

- Technical discussion within DOE supported working groups
  - Transport Modelling Work Group
  - Durability Work Group
  - Fuel Cell Tech Team (FCTT)

For more information on the content of this webinar including FC-APOLLO or FC-STC Hardware please contact

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