FC135: FC-PAD: Fuel Cell Performance and Durability Consortium

Presenters: Rod Borup, Karren More, Adam Weber

Thursday, June 14th 2018

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**FC-PAD: Consortium to Advance Fuel Cell Performance and Durability**

**Approach**

Couple national lab capabilities with funding opportunity announcements (FOAs) for an influx of innovative ideas and research

**Objectives**

- Improve component stability and durability
- Improve cell performance with optimized transport
- Develop new diagnostics, characterization tools, and models

**Consortium fosters sustained capabilities and collaborations**

**Core Consortium Team**

- Argonne National Laboratory
- Los Alamos National Laboratory
- NREL
- Oak Ridge National Laboratory

Prime partners added in 2016 by DOE solicitation (DE-FOA-0001412)

**Structured across six component and cross-cutting thrusts**

1. Electrocatylsts and Supports
2. Electrode Layer
3. Ionomers, GDL, Bipolar Plates
4. Modeling and Validation
5. Operando Evaluation
6. Component Characterization

**FC-PAD Fuel Cell Consortium for Performance and Durability**

- Foundational Science
- Industry + Academia
- Research Organizations

Lead: Rod Borup (LANL)
Deputy Lead: Adam Z. Weber (LBNL)
FC-PAD Organization

DOE Program Management:
Greg Kleen
D. Papageorgopoulos

• Couple national lab capabilities with future FOAs to foster innovative ideas and new research
• Other collaborations continue outside the FOA process
• Steering committee input
  o Achieve consensus for no-cost, non-FOA collaborations from FC-PAD Core
  o Input on AOP (Annual Operating Plan) tasks and milestones
**FC-PAD Thrusts, Coordinators, and NL Roles**

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<th>Thrust Areas</th>
<th>ANL</th>
<th>LBNL</th>
<th>LANL</th>
<th>NREL</th>
<th>ORNL</th>
<th>Coordinator</th>
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<tr>
<td>Electro catalysts and supports</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>Deborah Myers (ANL)</td>
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<td>Electrode Layers</td>
<td>X</td>
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<td>X</td>
<td>K.C. Neyerlin (NREL)</td>
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<td>Ionomers, gas diffusion layers, bipolar plates, interfaces</td>
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<td>X</td>
<td>X</td>
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<td>Ahmet Kusoglu (LBNL)</td>
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<tr>
<td>Modeling and validation</td>
<td>X</td>
<td>X</td>
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<td></td>
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<td>Rajesh Ahluwalia (ANL)</td>
</tr>
<tr>
<td>Operando evaluation: Benchmarking, ASTs, and contaminants</td>
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<td>X</td>
<td>X</td>
<td></td>
<td>Rangachary Mukundan (LANL)</td>
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<tr>
<td>Component characterization and diagnostics</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td>Karren More (ORNL)</td>
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</table>

**Moderate Activity**

**High Activity**

- Coordination between thrusts
  - Thrusts do not stand alone; standardization of materials
  - Input from DOE, associate steering committee members, FCTT, AMR reviews
  - Support to FOA projects
## FC-PAD Consortium - Overview & Relevance

### Timeline
- Project start date: 10/01/2015
- Project end date: 09/30/2020

### Budget
- FY18 project funding: ~ $4,000,000
- As proposed: 5-year consortium with quarterly, yearly milestones & Go/No-Go
- Total Expected Funding: Dependent upon budget allocation

### Partners/Collaborations
- **(To Date Collaborations Only)**
  - Partners added by DOE DE-FOA-0001412 (GM, 3M, UTRC, Vanderbilt)
  - See list at end of slides, no-cost collaborations

### Barriers
- **Cost:** $40/kW system; $14/kW_{\text{net}} MEA
- **Performance @ 0.8 V:** 300 mA / cm²
- **Performance @ rated power:** 1,000 mW / cm² (150 kPa abs)
- **Durability with cycling:** 5,000 (2020) – 8,000 (ultimate) hours, plus 5,000 SU/SD Cycles
- **Mitigation** of Transport Losses
- **Durability** targets have not been met without system mitigation

- The **catalyst layer** is not fully understood and **is key in lowering costs** by meeting rated power.
- Rated power @ low Pt loadings reveals unexpected losses
FC-PAD Consortium – Relevance & Objectives

Overall Objectives:

• Advance **performance and durability** of polymer electrolyte membrane fuel cells (PEMFCs) at a **pre-competitive** level

• Develop knowledge base for more durable and high-performance PEMFC components
  
  • Understand science of component integration
  
  • e.g. Ionomer interactions with carbon/interfaces between electrodes and GDL or membranes

• **Improve high current density performance**
  
  • Improved electrode structures
  
  • Reduced mass transport losses

• **Improve component durability** (e.g. membrane stabilization, self-healing, electrode-layer stabilization)

• *Provide support to DOE Funded FC-PAD projects from FOA-1412*
Approach: Overview

• Develop knowledge base and optimize structures for more durable and high-performance PEMFC components

• Structured in 6 Thrust areas
  
  o **Understand Electrode Layer Structures**
    – Advanced characterization techniques
    – Testing and diagnostics
    – Macroscale and Microstructure modeling
  
  o **Defining/Measuring Degradation Mechanisms**
    – Membrane: cation migration
    – Catalyst: Pt-alloy dissolution, carbon corrosion
  
  o **Novel Electrode Layer Design and Fabrication**
    – Ordered array electrode
    – Other concepts being investigated (not ready to report on)
Approach: Overview

FC-PAD Presentation: (One combined presentation)

– Overview, Framing, Objectives, Approach, Milestones
– Characterization of Commercial Components
– Durability: Membrane, Catalyst, Carbon Corrosion
– Performance – Novel MEA construction
– Thin film characterization
– Microstructural modeling

• FOA-1412 Projects
  • FC155 (3M)
  • FC156 (GM)
  • FC157 (UTRC)
  • FC158 (Vanderbilt)
## FY2018 Q1, Q2 Milestone Status

<table>
<thead>
<tr>
<th>QTR</th>
<th>Lab(s)</th>
<th>Progress Measures, Milestones, Deliverables</th>
<th>Comments</th>
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</thead>
<tbody>
<tr>
<td>Q1</td>
<td>ANL, LBNL</td>
<td>Macroscale modeling converged for polarization behavior using scaled up properties from microstructural model. (LBNL, ANL) [From Q2 originally]</td>
<td>✓ Completed</td>
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<td></td>
<td></td>
<td></td>
<td>✓ Data included in AMR</td>
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<tr>
<td>Q1</td>
<td>LANL</td>
<td>Carbon corrosion by direct CO&lt;sub&gt;2&lt;/sub&gt; measurement comparison of ‘identical’ Pt/C and PtCo/C and comparison with thermal analysis stability</td>
<td>✓ Completed</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>✓ Data included in AMR</td>
</tr>
<tr>
<td>Q1</td>
<td>NREL, ORNL</td>
<td>Measurement of the effect of break-in processes on Pt/HSC, Pt/GrC and state-of-the-art PtCo/C activity, performance and resistance as well as catalyst layer morphology (NREL, ORNL, LANL, ANL)</td>
<td>✓ Completed</td>
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<td></td>
<td></td>
<td></td>
<td>✓ Data included in AMR</td>
</tr>
<tr>
<td>Q2</td>
<td>ANL, LBNL, ORNL</td>
<td>Ionomer/solvent ink properties with 3M ionomer measured with three solvents of different dielectric constants and correlated to as-cast membrane film properties. Determine effects of three solvent compositions and sonication time of PtCo catalyst-ionomer inks on Co loss from catalyst, changes in catalyst atomic structure, and ink agglomerate structure. (ANL, LBNL, ORNL).</td>
<td>✓ Data included in AMR</td>
</tr>
<tr>
<td>Q2</td>
<td>LANL, NREL</td>
<td>Deliver/Deposit Pt by preferential CVD on at least three electrode templates (fabricated using electrospun nanofibers) to LANL from NREL. Characterize performance, access to active sites and local transport (NREL, LANL).</td>
<td>✓ Completed</td>
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### FY2018 Q3, Q4 Milestone Status

<table>
<thead>
<tr>
<th>QTR</th>
<th>Lab(s)</th>
<th>Progress Measures, Milestones, Deliverables</th>
<th>Comments</th>
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</thead>
</table>
| Q3  | ANL, LBNL, LANL, NREL, ORNL (All) | Establish correlation between in situ and ex situ examinations of cation effect on transport; quantify how applicable ex situ measurements are for in situ performance. Water uptake (ellipsometry), morphology (GISAXS and NR), and oxygen transport (microelectrode) measured for 2 different Nafion thin film thicknesses (between 10 and 150 nanometer) with 2 different Ce and Co doping levels determined by leaching rates and verified by microscopy. Measure O₂ and H₂ limiting current at 3 different RHs 25, 50, 100%. (LANL, ORNL, ANL, LBNL, NREL) | ✓ In Progress/on track  
✓ Data included in AMR |
| Q4  | ANL, LBNL, LANL, NREL, ORNL (All) | Definition of the allowable cation contaminant level (e.g. Ce or Co) to limit performance degradation to 10% due to reduction of either proton conduction or oxygen transport from the cation/ionomer interactions. Provide a method to keep cation related performance reduction to 10%. (LANL, ORNL, ANL, LBNL, NREL) | ✓ In Progress/on track  
✓ Data included in AMR |
Approach: Durability

• Results intended to guide component, cell, and stack development efforts to improve durability by identifying degradation mechanisms

• MEA durability is primary concern,
  – Durability of other stack components, including bipolar plates

• Materials-based solutions to decrease degradation

• Component microstructure stability in three-phase region of reactant gas, electrolyte, and catalyst and impact of microstructure on durability

• Catalyst layer stability, including support stability, and methods to decrease support corrosion and compaction while maintaining appropriate pore structures

• Durability/aging and evolution of transport properties and phenomena

• Characterization of degradation phenomena in state-of-the-art membranes

• Identifying and characterizing degradation mechanisms associated with contaminants (e.g. Co leaching from alloy catalysts)
  o Membrane/catalyst – cation migration (Co/Ce)
  o Catalyst – particle grown/alloying agent leaching/kinetic and transport losses
  o Catalyst support – alloying effect on carbon corrosion
PtCo Alloy Catalyst Degradation

- Small losses in low current region
- Larger losses in high current region
- ECSA loss due to particle size increase
- Mass activity loss due to Co leaching
- Local transport resistance increases
- BOT: 75% MT losses recoverable in HelOx
- EOT: 40% MT losses recoverable in HelOx
PtCo Alloy Catalyst Degradation

Accomplishments

- Minimal CL *thickness* change
- Minimal CL *porosity* change
- Pt in membrane increases with cycles; $\sim 2\mu m$ Pt-depleted zone after 30k cycles
- PtCo catalyst *size* (4.4nm vs. 5.5nm)
- Overall CL *composition* (Co:Pt 0.14 vs. 0.11)
- *Mass activity loss due to Co leaching* - *partially recoverable*
**Effect of Electrocatalyst Alloving on Carbon Corrosion**

- Corrosion rate of Pt/C and PtCo/C are identical
- Corrosion rate of 50% Cat/C < 30% Cat/C
- Rate adjusted for total carbon is similar in 30% and 50%
- Alloy catalyst loses more performance than Pt catalyst even though corrosion rate is similar
- Mass transport limitations of alloy catalysts are worse than Pt catalysts at BOL
  - Exacerbated by C-corrosion

All carbons HSAC
**Catalyst Comparison during Carbon Corrosion**

**Accomplishments**

- Pt/HSAC is more stable than PtCo/HSAC over 1000 cycles

**Distributed ORR oxide coverage kinetic model**

- For Tafel kinetics, the ORR and CCL Ohmic overpotentials are separable

\[ \eta_c = \eta_s^c + iR_{\Omega}^C \left( \frac{i\delta_C}{\rho \sigma_i} \right) \]

\[ i = i_0 A_{Pt}(1 - \theta)e^{-\frac{\omega \theta}{RT}P_2} e^{\frac{\alpha n F}{RT} \eta_s^c} \]

**Losses after 1000 AST Cycles**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ECSA (%)</th>
<th>MA (%)</th>
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</thead>
<tbody>
<tr>
<td>PtCo/HSAC</td>
<td>52</td>
<td>71</td>
</tr>
<tr>
<td>Pt/HSAC</td>
<td>50</td>
<td>49</td>
</tr>
<tr>
<td>Pt/LSAC</td>
<td>21</td>
<td>8</td>
</tr>
</tbody>
</table>

*Molar composition of Co in Catalyst: BOT / EOT
Changes in Electrode Microstructure

Accomplishments

Moderate growth in catalyst particle size in HSAC electrode after 1000 cycles, but larger secondary pores have collapsed.
Mass activity and Performance Losses

- ECSA loss tracks particle size increase for Pt/C (3.5 to 4.2nm) and PtCo/C (4 to 4.8nm)
- Mass activity loss of PtCo is a lot higher due to Co leaching (Pt:Co changes from 76:24 to 84:16)

- Kinetic Resistance @ BOL: Pt/LSAC > Pt/C > PtCo/C (Open symbols)
- Kinetic resistance @ EOL: Pt/C (2000 cycles) > PtCo/C (1000 cycles) > Pt/LSAC (5000 cycles)
- Mass transport @ BOL PtCo/C > Pt/C > Pt/LSAC

- Kinetic region: PtCo/C has much higher resistance after corrosion experiment
- Mass transport region: Similar result but even at BOL Pt/C is better than PtCo/C
Breakdown of Electrode Losses

**Kinetic Losses**

![Graph showing kinetic losses over number of cycles for PtCo/HSAC, Pt/HSAC, and Pt/LSAC.]

- Kinetic losses during carbon corrosion due to Co leaching from active catalyst
- Increased local transport resistance due to loss in surface area (ECSA)
  - Pt and PtCo HSAC show additional transport losses
- Porosity as function of AST cycle estimated assuming constant carbon corrosion rate and knowing initial and final CCL thickness/porosity

**Mass-Transport Losses**

![Graph showing mass-transport losses versus roughness for Pt/LSAC and PtCo/HSAC.]

Closed symbols: 100% RH
Open symbols: 42% RH

**Porosity Loss During Corrosion**

![Graph showing porosity loss during AST cycles.]

Porosity, ε

AST Cycles
Modeling of Ionomer Film Resistance ($R_f$)

Assume small changes in CCL thickness in catalyst AST and support AST for Pt/LSAC

- Film resistance controls $O_2$ transport in CCL:
  \[ R_f \gg R_c \]
  \[ R_m = \frac{4F\dot{C}_{O_2}}{i_l} = R_g + R_d + R_f \]
  \[ R_f = 27.6 \text{ s cm}^{-1} \text{ Pt/LSAC}; 15.8 \text{ s cm}^{-1} \text{ PtCo/HSAC} \]

- GDL has remained stable
  \[ \frac{R_{g1} + R_{d1}}{P_1} = \frac{R_{g2} + R_{d2}}{P_2} = 63.5 \text{ s cm}^{-1} \text{ atm}^{-1} \]

Electrode resistance from 1D macro-homogenous model for $O_2$ transport in CCL

\[ R_{cf} = \left( \frac{R_c}{\beta} \right) \coth \beta \]
\[ R_c = \left( \frac{i_c}{D_{O_2}^{c}} \right) \]
\[ R_f = \left( \frac{i_f}{D_{O_2}^{f} S_{Pt}} \right) \]

\[ \beta = \sqrt{\frac{R_c}{R_f}} \]

$R_c = $ Pore resistance
$R_f = $ Film resistance [s cm$^{-1}$]
$l_{c/f} = $ Catalyst/film thickness [cm]
$D_{O_2}^{c} = $ Pore/film diffusivity [cm$^2$ s$^{-1}$]
Approach: Electrode Layers and Optimization

- **Film & Ink Characterization**
  - Dispersions
  - Interactions & pH
  - Ionomer thin films
  - Impact of cations

- **Component Characterization & Diagnostics**
  - Visualization
  - Microstructural modeling
  - Catalyst & alloy characterization

- **Electrode Formation and Design**
  - Formation process
  - Specific designs & components
  - Preferential pathways
  - Limiting current
  - Water & thermal management
  - Multiscale modeling
  - ASTs

- **Optimization and Understanding**

- **Cell Performance and Diagnostics**
Ordered Array Electrode

- **Array Electrode**
- **Nanowire Electrode**

Meso-structured electrode relies on vertically aligned ionomer channels for long-distance H+ transport.

Catalyzed elements can have reduced ionomer content.

*Carbon  Pt  Ionomer*  

*not to scale*
Ordered Array Electrode

Array Electrode

Nanowire Electrode

---

Loading (A/C) = 0.08/0.1 mg cm\(^{-2}\), Catalyst: TEC10E50E, Temperature: 80 °C, Pressure:150 kPa abs

Loading (A/C) = 0.1/0.15 mg cm\(^{-2}\), Catalyst: TEC10E50E, Temperature: 80 °C, Pressure:150 kPa abs
Approach: Establish SOA Commercial Components

Toyota Mirai Components Provided by USCAR

Analysis - inform current SOA material set in terms of composition, structure, performance, and durability. Set current benchmark that new materials can be compared with and may provide information about materials not previously explored in open literature.

• **Cell sections provided by USCAR**
  – 300 hr operation (not “fresh”)
  – 3000 hr operation (“real-world” drive)

• **Task 1: Materials Analysis**
  – Task 1a: Catalyst and support
  – Task 1b: Electrode layer
  – Task 1c: Membrane and Ionomer
  – Task 1d: GDL/MPL
  – Task 1e: Metal Bipolar Plate

• **Task 2: Performance Analysis**
  – Task 2a: Water management in flowfield
  – Task 2b: Material durability performance
## Mirai: A case study in FC-PAD Characterization Capabilities

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<th>Component</th>
<th>Material Data/Information</th>
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<td>MEA dimensions, composition, structure</td>
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<td>TEM-cross-sections</td>
<td>MEA</td>
<td>MEA dimensions, composition, structure, ionomer mapping</td>
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<td>TEM-Particle size distributions</td>
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<td>XRF</td>
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<td>XRF Mapping</td>
<td>MEA</td>
<td>Elemental mapping</td>
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<td>XCT</td>
<td>MEA</td>
<td>MEA structure</td>
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<td>TGA-MS</td>
<td>Catalyst Layer</td>
<td>catalyst wt %/ I/C ratio</td>
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<td>SAXS</td>
<td>Catalyst</td>
<td>catalyst particle distribution</td>
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<td>EXAFS</td>
<td>Catalyst</td>
<td>Pt-Pt, Pt-Co bonding distances</td>
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<td>XRD</td>
<td>Catalyst</td>
<td>catalyst particle distribution</td>
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<td>FTIR</td>
<td>Membrane</td>
<td>Membrane composition</td>
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<td>NMR</td>
<td>Membrane/Ionomer</td>
<td>Membrane composition/eq. wt</td>
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<td>Membrane</td>
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<td>Testing - O2/Air Polarization</td>
<td>MEA</td>
<td>Catalyst layer performance</td>
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<td>Testing - Catalyst AST</td>
<td>Catalyst</td>
<td>Catalyst durability</td>
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<td>Testing - Carbon Corrosion AST</td>
<td>Catalyst Support</td>
<td>Catalyst support durability</td>
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<td>NDIR- Carbon Corrosion</td>
<td>Catalyst Support</td>
<td>Carbon corrosion measurements</td>
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<td>MIP</td>
<td>GDL/MEA</td>
<td>Component porosity</td>
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<td>BET</td>
<td>GDL/MEA</td>
<td>Component surface area/pore-size distribution</td>
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<td>Contact Angle - Sessile Drop</td>
<td>GDL/Bipolar Plate</td>
<td>Component Hydrophobicity</td>
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<td>Contact Resistance</td>
<td>Bipolar Plate</td>
<td>Contact Resistance</td>
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<tr>
<td>XPS</td>
<td>Bipolar Plate</td>
<td>Bipolar plate elemental analysis</td>
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<tr>
<td>XPS - Depth profiling</td>
<td>Bipolar Plate</td>
<td>Bipolar plate coating structure</td>
</tr>
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</table>
Mirai: MEA Component Summary

- **Cathode**
  - PtCo/C: Pt = 87mole%, 0.315 mg<sub>Pt</sub>/cm<sup>2</sup>
  - Cathode layer ~ 10µm
  - GDL separates from catalyst layer

- **Anode**
  - Anode layer ~ 2.3 µm; 0.050 mg<sub>Pt</sub>/cm<sup>2</sup>
  - GDL does not separate from catalyst layer

- **GDLs**
  - Anode: ~ 150 µm total with ~ 60 µm MPL
  - Cathode: ~ 160 µm total with ~ 40 µm MPL
  - High concentration of CeO<sub>x</sub> particles in MPLs; ~ 60 µg/cm<sup>2</sup> on cathode; ~ 120 µg/cm<sup>2</sup> on anode

- **Membrane**
  - ~ 10 – 10.5 µm reinforced with ePTFE; Nafion side chain
  - EW of the membrane ionomer ~ 901 ± 1 g/meq by acid-base titration

- **Bipolar Plate**
  - Cathode Ti foil with Ti porous mesh; ~ 80 nm carbon coating by XPS depth profile
  - Anode serpentine; ~ 80 nm carbon coating by XPS depth profile
**Mirai: MEA Component Summary - CCL**

**CCL observations after 300hr:**
- Cathode CL ~ 9-10 µm thick and relatively dense
- Ionomer distribution non-uniform within CL
- Localized regions of highly agglomerated PtCo/C
- Agglomerated PtCo/C not well infiltrated by ionomer
- Rough CL/membrane interface
Mirai: MEA Component Summary - Electrocatalyst

- Carbon support is acetylene black (AB)
- Smaller Pt-Co particles on “inside” of AB - typically ~2-3 nm
- Larger Pt-Co particles on “surface” of AB - particles range in size from 5-10 nm - large particles decorate surfaces of secondary pores

Average Pt-Co nanoparticle diameter = 4.7 nm
• Avg. equivalent secondary pore diameter = 75 nm
• Green outlined regions show two “dense” Pt-Co/AB agglomerates that exhibit smaller pore sizes
• Larger secondary pores are between agglomerates (with most of ionomer)
• Rough CL/membrane interface (~1 µm)
• Pt-Co/AB agglomerate protrusions extend into membrane
• Very large ~20 nm dia. “Pt-only nanoparticles” present at interface but do not form a continuous layer

Uniform, continuous enrichment of F at CL/membrane interface ~100nm thick
Mirai Component Summary: Bipolar Plate/GDL

Depth Profile of Bipolar Plate

Depth (nm)

Composition (at.%)

- Ti
- O-Ti (x5)
- N-Ti (x5)
- N-surf (x5)
- C (x5)

Cathode GDL Porosity

- 29BC
- 300 hrs
- 3000 hrs

Small porosity < 5 µm
Large porosity > 5 µm

Porosity / %

Small
Large
Total

C 1s XPS

Profile Depth
88 nm
72 nm

Binding Energy (eV)

288 286 284 282 280
C-C
C-Ti
Mirai: Catalyst/Catalyst-Support ASTs

No changes to structure or chemistry observed (catalyst, support, ionomer, membrane) observed after 3000 hr “real-world driving”

Mitigation strategies implemented were successful

DOE FCTT–recommended durability protocols applied to assess stability under more aggressive conditions:

• **Catalyst AST (0.6 – 0.95V square wave)**
  – Loss of ~ 25% of ECSA; CL thinning to 6µm
  – VIR performance loss of ~ 25 mV at 1.0 A/cm²
  – XRD/TEM show particle growth and loss of Co
  – Particle growth from 4.7 to 6.7 nm

• **Catalyst Support AST (1.0 – 1.5V cycle)**
  – ~ 50 mV loss at 1200 cycles (HSAC shows large performance loss at this point)
  – Little performance remaining after 5000 cycles
  – ECSA 60% loss at 5000 cycles; particle growth from 4.7nm to 5.3nm
  – CL thinning from ~ 10 to 3µm
Mirai: Catalyst/Catalyst-Support ASTs

No changes to structure or chemistry observed (catalyst, support, ionomer, membrane) observed after 3000 hr “real-world driving”

Materials are not stable during DOE FCTT–recommended durability protocol ASTs
Conditioning: Testing Protocol

Voltage Cycling Break-in
80°C, 150 kPa, 0.8/2.5 SLPM

ECSA: H₂/N₂
30°C, 150 kPa, 100% RH
- 20 mV/s (0-0.6 V, 0 – 1.2 V)
- 50 mV/s (0-0.6 V, 0-1.2 V)

Conditioning/Voltage Recovery (H₂/Air)
40°C, 150/150% RH; 150/150 kPa
- 2 hour
- 0.1 V

H₂/O₂ Polarization Curves
80°C, 150 kPa O₂, 100% RH
- Constant Voltage: 0.750 – OCV (Anodic)
- Constant Voltage: OCV – 0.750 (Cathodic)

H₂/Air Polarization Curves
80°C, 150 kPa Air
1.5 – 0.05 A/cm²
- 100% RH
- 80% RH
- 40% RH

ECSA: H₂/N₂
30°C, 150 kPa, 100% RH

H₂ Crossover
80°C 100% RH
150 kPa H₂/N₂
- 20 mV/s (0-1.6 V, 0 – 1.2 V)
- 50 mV/s (0-1.2 V, 0-1.6 V)
Conditioning: Cathodic Mass Activities

Up to 2-3x variation between “initial” and peak $i_m^{0.9V}$

General Conclusions:

Rigorousness of conditioning required to reach maximum performance does not appear to depend exclusively on generic nature of carbon support or presence of an alloy.

Superficial observation would be that variables during the catalyst synthesis process may play a role.

When compared to higher loadings, lower loadings exhibit their largest disparity in performance in first conditioning cycle.
Conditioning: Effect of Carbon Support

**Accomplishments**

**Particle size change greater for Pt/V during conditioning:**

>30% change in Pt particle size on Vulcan during conditioning

vs.

~20% change in Pt particle size on HSAC
PtCo catalyst particle size increases after conditioning (EOT)

- Carbon agglomerates are larger after conditioning: negligible for Pt but notable for PtCo
XAFS - Co Leaching During Conditioning

- % Compression of Pt-Pt bond in Pt-Co wrt Pt-only catalyst: Powder: 1.9%; BOL: 1.5%; EOT: 1.3%
- 30 wt.% Pt/HSAC Umicore Pt-Pt bond length:
  - BOL MEA: 2.758 Å
  - EOT MEA: 2.760 Å

Pt-Pt coordination number increase, combined with less substantial decrease of Pt-Co coordination indicates Pt particle growth and/or Pt shell formation.

- For PtCo/HSAC Umicore Pt-Pt bond distance becoming more “Pt-like” while $i_m^{0.9V}$ increases
- For PtCo/HSAC Umicore Pt-Pt bond distance relatively unchanged while $i_m^{0.9V}$ increases
$R_{nf} \ f(\text{conditioning}) \ 80^\circ \text{C}, \ 75\% \text{ RH}$

- **50 wt.% Pt/Vulcan**

- **50 wt.% Pt HSC TKK**

- **30 wt.% Pt HSC Umicore**

- **30 wt.% PtCo HSC Umicore**

- Pt/pore accessibility appears to significantly improve after the first conditioning cycle.
Input for Electrode Microstructure Reconstruction

Method to reconstruct electrode microstructure from multiple datasets

Nano-CT data for morphology of the secondary pores

TEM and USAXS data for C particle size distribution

Validation against MIP and BET

TEM and USAXS data for Pt particle size distribution

Resulting Microstructure

Calculated ionomer size distribution is independent of random C and Pt placement – does not directly correspond to ionomer film coverage
Catalyst effectiveness is generally smaller if particles are closer to agglomerate center, at higher current density, and if pores are flooded.
Multiscale Modeling

Effectiveness Factor, $E_r = \frac{\text{Actual reaction rate}}{\text{Rate if not slowed by diffusion}}$

\[ E_r = \frac{\phi \{ r(x) \} E_r \{ r(x) \} A_v \{ r(x) \} i_0 \left( \frac{c_{O_2}}{c_{O_2}^{ref}} \right) \exp \left( -\frac{\alpha F}{RT} \eta \right) \left[ 1 - \epsilon_v(x) \right]}{\sum_r \phi \{ r(x) \} E_r \{ r(x) \} A_v \{ r(x) \} i_0 \left( \frac{c_{O_2}}{c_{O_2}^{ref}} \right) \exp \left( -\frac{\alpha F}{RT} \eta \right) \left[ 1 - \epsilon_v(x) \right]}

- Incorporated microscale modeling and features in macroscale model
- CL structure is highly heterogeneous
Multiscale Modeling

**Accomplishments**

- Incorporated microscale modeling and features in macroscale model
- Local reductions in porosity results in transport bottleneck and underutilization of CL
  - Most of current is produced by smaller agglomerates
- Accounting for heterogeneities can be critical for computing performance accurately
  - No well-defined representative elementary volume (REV)
  - Conventional agglomerate models can underpredict/overpredict depending on estimated ionomer thickness
Differential to Integral Cell

- Develop 1+2D model to examine going from differential to integral cells
  - 2D model trained on differential cell data
  - Once above 3 stoich. start approaching differential cell conditions
    - Similar predictions at low current densities
    - Intermediate currents, integral model shows slightly higher performance due to better membrane hydration

- Predictions for integral cell model
  - Accurate predictions at 40% RH
  - Discrepancy at 80% RH and high current
    - Model predicts sooner flooding
Pore-scale Modeling

Model water in GDLs using direct simulation or lattice Boltzmann

Water invasion in SGL compared with micro-XCT data*

At 2 A/cm², water is transported through cracks in MPL leading to 50% lower saturation

Cannot define a through-plane REV

Impact of Ionomer EW on Local Resistance

Examine local resistance with H₂ limiting current and varying I/C

- At I/C 0.6:
  - 30% interfacial for 825 EW
  - 25% interfacial for 1100 EW
- Activation energy suggests transport through water or ionomer is limiting
- Phenomena agrees with thin-film analysis

I/C from reconstruction correlates to thicker ionomer film

Accomplishments

Impact of Ionomer EW on Local Resistance

- More alignment near the substrate
- Better phase separation with lower EW

Transport Resistance

Interfacial Resistance

Ionomer Thin Films on Si | 40-55 nm Thick

Lower EW

Higher swelling with low EW
Effect of Ink Solvent and Dispersion Nature

Nafion dispersions have an inherent pH
- Higher nafion loadings lead to higher aggregation and less accessible protons
- pH affects electrostatic interactions controlling ink aggregation, which can be removed by removing inherent pH
- Pt-Co, Co-Pt coordination numbers decrease with increasing water content and Co leaches into ionomer/solvent
- Co leaching increases with water content

Umicore PtCo (27.5 wt% Pt, 3 wt% Co/HSAC
3M 825 EW ionomer (I/C=0.7). Solid content: 0.33 wt%
Solvent Effects on PtCo/Ionomer Ink Dispersion

Accomplishments

- Scattering intensity at q<0.01 Å⁻¹ increases with sonication time - break-up of agglomerates >2 µm
- Agglomerate break-up reaches steady-state after 20 min of sonication
- Agglomerate break up is faster and yields smaller particle sizes with higher water content inks (5/5 and 3/7, nPA/Water)
- In-plane conductivity of ionomer films cast from ionomer dispersions increases with increasing water content and sonication time
- Connectivity of ionomer strands increases with water content
Operando Measurement of Cation Migration (Co)

Convection effects: dry cathode/50% RH anode

- Humidified anode/dry cathode causes Co transport from anode CL/PEM into cathode and MPL
- Fast equilibration into PEM/CL ionomers after exposure to humidified N₂/N₂
- Exposure to dry N₂/N₂ locks profile into place
- Co goes into anode CL when RHs are switched

Potential effects: 80% RH in H₂/air at 0.05 mA/cm²

- Significant migration from anode CL/PEM into cathode CL/MPL under load
- No evidence for migration beyond 50 μm cathode MPL
Pt Microelectrode Studies

Schematic of set-up

- Ionomer solution (0.05 wt.% Nafion) mixed with contaminants Co (as CoClO₄, target Co 5 mg/cm³) and Ce (as Ce(SO₄)₂, target Ce 15 mg/cm³) and allowed to exchange overnight
- Submicron (ca. 500 nm) thin-film of ionomer solution spin-cast onto 100 µm electrode at 1000 rpm
- Co-contaminated Nafion layer reduces limiting current for both HOR and ORR
- Ce-contaminated Nafion layer does not affect limiting current, but inhibits reaction until mass transport limited

Significant decrease in Pt surface area (observed in both HOR and ORR) with presence of Co contaminant in ionomer

Accomplishments

- 100% RH (20°C)
Impact of Cation on Ionomer Thin Films

- Different salt solutions employed to investigate impact of cation

- Impacted by cationic exchange, hydration dynamics depend on:
  - Coordination number and shell
    - Strength of binding ($\Delta H_{hyd}$): $\text{Cs}^+ < \text{Na}^+ << \text{H}^+ << \text{Co}^{2+} \sim \text{Ni}^{2+}$
  - Ionic radius: $\text{H}^+ << \text{Ni}^{2+} < \text{Co}^{2+} < \text{Na}^+ < \text{Cs}^+$

- Ionomer thin-film uptake impacted by processing:
  - Increases with water soaking (PB)
  - Increases with acidic re-exchanging (PT)
Impact of Cation on Ionomer Thin Films

- Water uptake below 50 nm increased due to anisotropic ionomer structure
  - Agrees with d-spacing from GISAXS

- Increase in Co\(^{2+}\) fully doped films possible due to CO\(^{2+}\) higher
  - Hydration energy (~1000 vs 2000 kJ/mol)
  - Water bond length (~250 vs 200 pm)
  - Residence time of water with Co\(^{2+}\) [*]

[*]Chem. Rev. 1993, 93, 1157-1204

Water Content, \(\lambda = [\text{H}_2\text{O/}[\text{SO}_3^{-}]\]

54nm H\(^{+}\) (as cast)
15nm H\(^{+}\) (as cast)
54nm Co\(^{2+}\) 0.5M
20nm Co\(^{2+}\) 0.5M

fully exchanged, dried @ 100\(^{\circ}\)C

Ionomer

c

Water bond length (~250 vs 200 pm)
Residence time of water with Co\(^{2+}\) [*]
Impact of Cation on Ionomer Thin Films

Cation form impacts thin-film transition temperature ($T_T$), which represents mobility:
- Increase in cation charge $\rightarrow$ increase in $T_T$ due to ionic crosslinking
- $M^{2+}$ correlated better with ionic radius than $M^{1+}$

Thickness dependence of $T_T$ in $M^{1+}$ is not strong, indicating dominating influence of ion-dipole interaction between $M^+ - \cdot\cdot SO_3$ moieties over adsorption with substrate.
Understanding Ionomer Thin-Films

Ionomer thin-films experience:
- Finite size effects (confinement)
- Substrate impacts (physical adsorption & polymer chain interaction with substrate)
- Free surface interactions (higher configurational freedom near air/polymer interface)

Transition temperature ($T_T$) increases with decreasing thickness
- Greater impact of substrate
- Demonstrates less mobility and hence expected worse transport properties

Need to design polymers with free volume to counteract tendencies
Ionomer Thin-film Characterization

Grazing-incidence X-ray Scattering
- GISAXS beamline – ALS, LBNL
- 2D GIWAXS probes in-plane and out-of-plane ordering → Confinement induced anisotropic domain ordering

Neutron Reflectivity (NR)
- Asterix Beamline – LANSCE, LANL
- Through-plane scattering length density
- Sensitive to local density fluctuations
- Local hydration at the substrate-film interface is evident
Collaborations (FOA-1412 Partners)

- Core FC-PAD team consists of five national labs
- Each lab has one or more thrust roles and coordinators

**Interactions with DOE Awarded FC-PAD Projects (FOA-1412)**

**POC assigned for each project to coordinate activities with PI**

- 3M - PI: Andrew Haug – FC-PAD POC: Adam Weber
- UTRC - PI: Mike Perry – FC-PAD POC: Rod Borup
- Vanderbilt - PI: Peter Pintauro – FC-PAD POC: Rangachary Mukundan

- 35% of National Lab budget supports FOA projects
  - Equal support to each project across FC-PAD
- Two in-person FC-PAD meetings held annually - include FOA members with individual sessions held to discuss interactions and progress
- Project-by-project details vary, but some hold bi-weekly conference calls with FOA project member and national labs
## Collaborations (Non-FOA activities)

<table>
<thead>
<tr>
<th>Institutions</th>
<th>Role</th>
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</thead>
<tbody>
<tr>
<td>Umicore</td>
<td>Supply SOA catalysts, MEAs</td>
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<tr>
<td>EWii</td>
<td>Supply SOA catalysts, MEAs</td>
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<tr>
<td>University Carlos III of Madrid</td>
<td>Microscale simulations</td>
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<tr>
<td>TKK</td>
<td>Supply SOA catalysts</td>
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<tr>
<td>Johnson Matthey</td>
<td>Catalysts and CCMs</td>
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<tr>
<td>GM</td>
<td>Supply SOA catalysts, MEAs</td>
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<tr>
<td>Ion Power</td>
<td>Supply CCMs</td>
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<tr>
<td>W.L. Gore</td>
<td>SOA Membranes (in collaboration with GM)</td>
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<tr>
<td>ANL–Materials Science Division Group</td>
<td>SOA catalyst</td>
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<td>Tufts University</td>
<td>GDL imaging</td>
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<td>KIER</td>
<td>Micro-electrode cell studies</td>
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<td>University of Delaware</td>
<td>Membrane durability</td>
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<tr>
<td>Vanderbilt University</td>
<td>Ink studies</td>
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<tr>
<td>PSI – Paul Scherrer Institute</td>
<td>GDL imaging</td>
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<td>GDL modeling</td>
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<tr>
<td>University of Alberta</td>
<td>GDL and flowfield modeling; ink studies</td>
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<tr>
<td>3M</td>
<td>Ionomers</td>
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<tr>
<td>Colorado School of Mines</td>
<td>Membrane diagnostics</td>
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<tr>
<td>SGL Carbon</td>
<td>GDL Supplier</td>
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<tr>
<td>NPL - National Physical Laboratory</td>
<td>Reference electrodes for spatial measurements</td>
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<tr>
<td>NIST – National Institute of Standards and Tech.</td>
<td>Neutron imaging</td>
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<tr>
<td>University of Arkansas-Little Rock</td>
<td>Catalysts</td>
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<tr>
<td>Simon Fraser University</td>
<td>Ionomer</td>
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<tr>
<td>Chemours</td>
<td>Ionomer</td>
</tr>
<tr>
<td>NREL-EFTECS project</td>
<td>Catalyst</td>
</tr>
</tbody>
</table>
Proposed Future Work

**Inks and thin films**
- Examine carbon interactions with different solvents and ionomer chemistry
  - Direct observation of dispersions
- Measure ionomer thin-film properties under applied potential
- Evaluate interfaces and impact of carbon type including durability protocols
- Examine impact of cation doping level
- Casting and evolution of ionomer thin-film structure
- Gas permeability measurements

**Catalysts**
- Re-examine intrinsic potential-dependent kinetics
  - Elucidate governing binary interactions
  - Direct observation of dispersions

**Catalyst-layer structure**
- Continue exploration of different catalyst-layer structures
  - Array, electrospun, HSC/VC layered
- Incorporation and characterization of novel electrocatalyst materials
- Microstructural reconstruction and modeling for catalyst layers including multiphase flow
  - Impact of Pt/C agglomerates
- Directly measure ionomer film/carbon in operating electrodes
- Local resistance analysis
  - Limiting current under variety of conditions, techniques, ionomers, gases, temperature, humidity

Any proposed future work is subject to change based on funding levels
Proposed Future Work

**Advanced Characterization**
- Multimodal characterization of thin films
- New low-voltage cryo-STEM
  - Combinatorial EELS and EDS and tomography (4D STEM)
  - Customized in situ cryo-holder to enable improved soft-matter imaging

**Water and thermal management**
- Complete impact of conditioning and changes during break-in
- Detail model for GDL/channel interface and droplets
- Water visualization in various components
- Explore impact of carbon type in MPLs
- Integrate and evaluate various components to elucidate emergent phenomena
- Translational modeling going from ex situ property data to operando performance

**Durability**
- Model synergistic mechanical degradation with crossover and performance
- Model and measure the movement of chemical scavengers and/or other ions
- Examine the effect of aging on electrode microstructure
- Develop stabilized systems of radical scavengers

Any proposed future work is subject to change based on funding levels
Summary

Relevance/Objective:

- Optimize performance and durability of fuel-cell components and assemblies

Approach:

- Use synergistic combination of modeling and experiments to explore and optimize component properties, behavior, and phenomena

Technical Accomplishments:

- Developed new catalyst-layer architectures
- Utilized characterization and experimental diagnostics to delineate catalyst layer interactions
- Experimentally evaluated degradation mechanisms and conditioning effects
- Completed analysis of Mirai SOA components
- Developed diagnostics and models for interpreting critical phenomena and data
- Explored impact of cations from inks to MEAs

Future Work:

- Develop the knowledge base to improve catalyst-layer structures for higher fuel cell performance and durability
Acknowledgements


Fuel Cells Program Manager & Technology Manager:

- Dimitrios Papageorgopoulos
- Greg Kleen

Organizations we have collaborated with to date

User Facilities

- DOE Office of Science: SLAC, LBNL-Advanced Light Source, ANL-Advanced Photon Source, LBNL-Molecular Foundry, ORNL-Center for Nanophase Materials Sciences, ANL-Center for Nanostructured Materials
- NIST: BT-2
Technical Back-Up Slides
Transport Activation Energy Analysis

- Diffusional activation energy of CL ionomer thin films higher than bulk hydrated Nafion values

<table>
<thead>
<tr>
<th>CL Ionomer</th>
<th>Activation Energy $(10^{-20} \text{ J})$</th>
</tr>
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<tbody>
<tr>
<td>1000 EW</td>
<td>4.58</td>
</tr>
<tr>
<td>725 EW</td>
<td>4.29</td>
</tr>
<tr>
<td>Nafion (wet)$^1$</td>
<td>3.32</td>
</tr>
<tr>
<td>Nafion (dry)$^1$</td>
<td>6.20</td>
</tr>
<tr>
<td>Water$^2$</td>
<td>3.33</td>
</tr>
<tr>
<td>Argon$^3$</td>
<td>0.67</td>
</tr>
<tr>
<td>Knudsen</td>
<td>0.22</td>
</tr>
</tbody>
</table>

* Linear fit curve equations are color coded with legend

2. Wilke-Chang correlation
3. Chapman-Enskog correlation
Development of 1+2D Integral Cell Model

- 1+2D stepping based model
  - 2-D MEA cross section model in COMSOL
  - Along the channel stepping in MATLAB
  - Can account for down the channel changes in concentration, RH, pressure and temperature
  - In-plane transport not incorporated
  - Suitable for low stoich (integral) cell conditions

![Diagram of MEA and channel](image)

### Matlab

- Read PEFC geometry
- Estimate Step sizes
- Inlet conditions

---

![Diagram of simulation flow](image)

### Matlab

- Inlet mass fractions
- Inlet RH
- Inlet temperature
- Inlet pressure

---

![Diagram of outlet mass fractions](image)

### Matlab

- Outlet mass fractions
- Outlet RH
- Outlet temperature

---

![Diagram of channel inlet and outlet](image)

### Matlab

- Channel inlet:
  - $N_{R,in}$
  - $N_{D,in}$
  - $N_{V,in}$
  - $N_{L,in}$

- Channel outlet:
  - $N_{R,out}$
  - $N_{D,out}$
  - $N_{V,out}$
  - $N_{L,out}$

---

**Note:** The diagram includes a flowchart for the simulation process, showing the steps from reading geometry, estimating step sizes, and inlets to outlet conditions and mass fractions.
Development of 2D Differential MEA Model

- 2-D MEA cross-section model
- Doesn’t account for along the channel variations
- Suitable for differential conditions (high stoich/flow rate)
- Incorporated physics:
  - Non-isothermal, two-phase model
  - Multicomponent diffusion
  - Electronic and protonic conduction
  - BV kinetics in anode, Tafel with PtOH coverage in Cathode
  - Agglomerate model in cathode

Validation Studies

- Oxygen concentration sensitivity:
  - Model able to match experimental trends accurately

- RH sensitivity:
  - Can predict cell behavior with RH change
  - Quantitative predictions accurate at higher RH
  - Higher error at lower RH values and high currents

80C, 100% RH, Oxygen concentration sensitivity validation

80C, Air/H₂, RH sensitivity validation
Mesoscale Modeling

- Formalism to bridge nanoscale chemistry to macroscale properties

- Nanoscale model:
  - Concentrated solution transport theory
  - Mean-field interactions
  - Ion dissociation through solvation
  - Swelling

- Mesoscale upscaling model:
  - Resistor network model
  - Heterogeneous domain size distribution
  - Predicts conductivity, water diffusion, and electro-osmosis

- Macroscale predictions:
  - Macroscopically relevant transport properties
  - Account for emergent behavior

Accomplishments