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

Presenters: Rod Borup, Adam Weber

Tuesday, April 30th 2019

This presentation does not contain any proprietary, confidential, or otherwise restricted information.
FC-PAD Presentation Outline

- **FC-PAD Structure & Landscape**
- **Relevance, Overview & Objectives**
- **Approach: Revised Priorities, Milestones, Capabilities**
- **Durability:**
  - Durability loading comparison (0.15 to 0.05 mg Pt/cm²)
  - Voltage-Loss-Breakdown Modeling
  - Conditioning: Effect of Support & Alloys
- **Performance and Catalyst Layer (CL) Analysis:**
  - CL Agglomerate & Aggregate Ionomer Mapping: SAXS, AFM, STEM, Modeling
  - Mesoscale Transport & Water Management
    - Solvent and I/C effects, porous carbons
    - Cation migration, Ionomer thin films
    - Novel Catalyst Layer Structures: Array and nanowire
- **Collaborations**
- **Future Work**
### 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

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#### 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)

**3M**
**GM**
**United Technologies Research Center**
**Vanderbilt**

[www.fcpad.org](http://www.fcpad.org)

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

1. Electrocatalysts 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

Industry + Academia

Research Organizations

Lead: Rod Borup (LANL)
Deputy Lead: Adam Z. Weber (LBNL)
Couple national lab capabilities with future FOAs to foster innovative ideas and new research

Other collaborations continue outside the FOA process

Steering committee input
- Achieve consensus for no-cost, non-FOA collaborations within FC-PAD Core
- Input on AOP (Annual Operating Plan) tasks and milestones
FC-PAD Landscape

FC-PAD conducts research at pre-competitive development levels
Primarily TRL 2, 3, 4
FC-PAD directly interacts with OEMs, components suppliers and academia

FC-PAD
Understanding and science of integration
Performance optimization
Durability mitigation

Component Manufacturers
OEMs
Academia

Office of Science: User Facilities

Design Rules
Understanding Multi-component assemblies

Novel Materials
FC-PAD Consortium - Overview & Relevance

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

**Budget**
- FY19 project funding: ~ $3,500,000
- As proposed: 5-year consortium with quarterly, yearly milestones & Go/No-Go
- Total Expected Funding: Dependent upon yearly budget allocation

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

**Barriers (2025)**
- **Cost**: $35/kW system; $17.5/kW\textsubscript{net} MEA
- **Performance @ 0.8 V**: 300 mA/cm\textsuperscript{2} at < 0.1 mg PGM/cm\textsuperscript{2}
- **Performance**: 1,800 mW/cm\textsuperscript{2}
- **Durability with cycling**: 8,000 hours plus 5,000 SU/SD Cycles
- **Cost** targets not currently met; durability and performance being met at expense of cost; durability with system mitigation
- **Catalyst layer** is not fully understood and is key for lowering costs by meeting rated power
- Rated power @ low Pt loadings reveals unexpected losses
Overall Objectives:

- Advance performance and durability of polymer electrolyte membrane fuel cells (PEMFCs) and their components at a pre-competitive level
- Develop knowledge base for more durable and high-performance PEMFC materials & components
  - Understand science of component integration, e.g. ionomer interactions with carbon, interfaces between electrodes/GDL and/or electrodes/membranes
- Improve high-current density performance via:
  - 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: Highest Ranked Topics by FC-PAD/FCTT

Steering Committee

Catalyst-layer Structure
- Correlate electrode microstructure and performance using characterization results and modeling to determine, for example, electrode transport properties
- Develop/measure key CCL parameters using multiple methodologies with consistent results
- Show where the ionomer is for different systems
- Effect of ink composition, processing, and fabrication method on electrode microstructure

Performance/Durability (Characterization, Experimental, Modeling)
- Understand/improve durability of alloy catalysts: effect of leaching on ionomer properties
- Understand/improve high current performance: $R_{O_2}$, $R_{H_2}$, different ionomers/carbons

New Capability and Modeling Development
- Develop novel methods, cells, and analysis techniques for in situ, ex situ and operando characterization of electrode layers and components
- Develop new high-resolution ionomer imaging and spectroscopy methods and develop and apply algorithms for structural reconstructions
- Develop novel methods, cells, and analysis techniques for in situ, ex situ and operando characterization of electrode and membrane layers and components
- Develop new diagnostic methods to understand transport processes
- Develop and apply Integrated predictive models of coupled performance and durability
## FY2019 Q1 Milestone Status

<table>
<thead>
<tr>
<th>QTR</th>
<th>Lab(s)</th>
<th>Progress Measures, Milestones, Deliverables</th>
<th>Comments</th>
</tr>
</thead>
</table>
| Q1  | ANL    | Demonstrate the electrode reconstruction method by analyzing the nano-CT data for an alloy catalyst and publish a paper on statistics for electrode and agglomerate structures | ✓ Completed  
✓ Data included in AMR  
✓ Publication: Agglomerates in Polymer Electrolyte Fuel Cell Electrodes: Part I. Structural Characterization |
| Q1  | LANL   | Cation effect on thin layer ionomer structural changes with Ce and Co by NR | ✓ Completed  
✓ Data included in AMR |
| Q1  | LBNL   | Model developed and manuscript submitted for combined performance and membrane durability | ✓ Completed  
✓ Data included in AMR  
✓ Publication Submitted |
| Q1  | NREL   | Quantify bulk electrode and local transport resistance as a function of either ink composition, processing or fabrication method | ✓ Completed  
✓ Data included in AMR |
| Q1  | ORNL   | Complete conditioning study with NREL and ANL and report/publish results | ✓ Completed  
✓ Data included in AMR |
# FY2019 Q2 Milestone Status

<table>
<thead>
<tr>
<th>QTR</th>
<th>Lab(s)</th>
<th>Progress Measures, Milestones, Deliverables</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q2</td>
<td>ANL</td>
<td><strong>Direct numerical simulation demonstration:</strong> Demonstrate the direct numerical simulation technique by determining oxygen and liquid transport in primary and secondary pores and across ionomer films in electrodes and agglomerates.</td>
<td>✓ Completed &lt;br&gt; ✓ Data included in AMR &lt;br&gt; ✓ Publication: Agglomerates in Polymer Electrolyte Fuel Cell Electrodes: Part I. Structural Characterization</td>
</tr>
<tr>
<td>Q2</td>
<td>LANL</td>
<td><strong>Direct imaging of catalyst layer cross-section:</strong> Demonstrate electrochemical operation with direct imaging of catalyst layer cross-section (AFM) measuring ionomer layer thickness on carbon in dispersed catalyst layer structures.</td>
<td>✓ In progress &lt;br&gt; ✓ Data included in AMR</td>
</tr>
<tr>
<td>Q2</td>
<td>LBNL</td>
<td>In-situ casting of ionomer demonstrated with two different solvent mixtures and two different ionomers EWs.</td>
<td>✓ In progress &lt;br&gt; ✓ Q2 done for one EW. Waiting for next beam-time and also redesigning the casting stage.</td>
</tr>
<tr>
<td>Q2</td>
<td>NREL</td>
<td>Develop methodology for determining relative ionomer coverage on carbon and Pt. Demonstrate this capability as a function of either ink solvent ratio OR catalyst type (e.g. Pt/Vu vs Pt/HSC).</td>
<td>✓ In progress &lt;br&gt; ✓ Data included in AMR</td>
</tr>
<tr>
<td>Q2</td>
<td>ORNL</td>
<td>Coordinate microstructural analysis of at least three new catalyst alloy MEAs before and after catalyst-cycling and C-corrosion ASTs (LANL, ANL, ORNL).</td>
<td>✓ In progress &lt;br&gt; ✓ Data included in AMR</td>
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</table>
## Joint National Lab FC-PAD Annual Milestone

<table>
<thead>
<tr>
<th>Q4</th>
<th>9/30/2019</th>
<th>FC-PAD Overall Milestone</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Understand effect of catalyst ink properties in terms of catalyst-ionomer-ink-solvent-composition (solvent, I/C, mixing and application methods, catalyst morphology (implementing 3 different catalyst systems comparing surface accessible Pt versus Pt in pores using various shaped-controlled catalysts)) on initial performance, (O_2/H_2) limiting current, performance quantifying a 10% percentage improvement in initial performance in terms of high current density performance (current density at 0.675 V) reduction of limiting current and durability improvement (e.g. 30,000 cycles of the catalyst AST and/or DOE recommended drive cycle protocol).</td>
</tr>
</tbody>
</table>

### In progress:
Ink solvent effects presented in AMR, I/C and application methods have been examined (ongoing). Three catalyst systems have been examined with limiting currents. Catalyst AST examined for loading study. Conditioning/recovery protocols demonstrating improved performance. Demonstrated both increasing and decreasing the water content of the catalyst ink leads to 26% and 64% increases in non-Fickian transport resistance at 75% RH for water rich and nPA rich inks, respectively.
### Approach

<table>
<thead>
<tr>
<th>Reactions and Charge Transport</th>
<th>Mass Transport of Species</th>
<th>Kinetics and cell testing</th>
<th>Durability ASTs: RH, V, T cycling</th>
<th>Durability: Field Testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>nsec - msec local nanostructure</td>
<td>sec - min component function</td>
<td>sec - hrs membrane-electrode</td>
<td>hrs - days fuel-cell</td>
<td>lifetime stack/system</td>
</tr>
</tbody>
</table>

**Characterization/Diagnostics**

- **Catalyst**
  - Pt Edge XAFS
  - Probing water & ion transport
  - Normalized thickness
  - Operando imaging
  - Water content

**Modeling**

- Nanoscale
- Agglomerate analysis
- Component Transport

**Characterization of phenomena & performance-durability interplay:**

- Fundamental understanding
- Understanding and improvement

**Component Transport**

**Predicting life and decay**
Durability Approach:
Materials-based Solutions to Decrease Degradation

- Develop/new operando evaluation capability
  - Confocal XRF of cation migration
  - Surface coverage by CO displacement

- Develop/Refine ASTs

- Durability Testing/Evaluation
  - Catalysts
  - Membranes
  - GDLs
  - Catalyst Layer microstructure and stability
  - Impact of microstructure on durability
  - Identify degradation mechanisms & phenomena

- Characterization
  - Voltage-loss-breakdown
  - Degradation rate
  - Evolution of transport properties and phenomena

- Modeling
  - Catalyst-alloying; particle growth, kinetics losses with leaching
  - Catalyst-support corrosion
  - Membrane stabilizers and cation migration

- Feedback from Component thrusts

Approach
Durability Performance: Effect of Loading (0.15 to 0.05 mg Pt/cm²)

0.15 mg Pt/cm²

- After recovery @ 30,000 cycles, mainly kinetic losses observed

0.10 mg Pt/cm²

- ECSA and mass activity decrease
- Local transport still most significant loss at high current density

0.05 mg Pt/cm²

- ECSA loss due to particle size increase
- Mass activity loss due to Co leaching
- Durability losses (kinetic and transport) greatly exacerbated by lower loading

Square Wave Catalyst AST (0.6 – 0.95V)
80°C, 100% RH, 150kPa
Coupled Durability and Performance Modeling

Performance and mechanics interact synergistically

Evaluate membrane failure

Observe pinhole growth due to induced hydration dynamics and crossover

Simulation conditions: Nafion 211, T = 80ºC, P = 1 bar, \( \phi = 0.7 \) V, Feed stoichiometry = 1.2, Air Stoichiometry = 2

Modeling Voltage Loss During Catalyst AST Cycles

**O₂ Transport Resistance at Limiting Current Density (iₐ)**

![Graph showing O₂ transport resistance (Rₚ) vs. O₂ mole fraction (xₐ) at varying temperatures and current densities.](image)

O₂ transport resistance (Rₚ) increases at higher O₂ mole fraction: \( Rₚ = \frac{cO₂}{iₐ/4F} \)

**New Representation for Rₚ (Total Transport Resistance)**

\[
Rₚ = \left\{ R_g \frac{P}{P_r} + R_d \frac{P}{P_r} \right\}_{GC/DM} + R_{Kn} + \left\{ R_f + R_i \frac{i}{i_r} \right\}_{MPL/CCL/CCL}
\]

Microstructural simulations indicate that flooding of primary pores in CCL explain Rₚ increasing at higher current density.
Modeling Impedance Data for DC Impedance

Fitting impedance data and low frequency inductive loop: DC Resistance $(Z_r)$

**Dependence of DC impedance $(Z_r)$ on current density:**
- $Z_r$ decreases from 0.2 to 0.6 A/cm$^2$ because of decrease in kinetic resistance
- $Z_r$ increases from 0.6 to 2.1 A/cm$^2$ because of mass transfer effects
O₂ Transport Resistance ($R_m$) from Impedance (EIS) and Polarization (VI) Data

Model developed to determine Oxygen Transport Resistance ($R_m$) from EIS and VI data

\[ Z_r = -\frac{dE}{di} \]

- $Z_r$ (EIS) > $Z_r$ (VI)
- Trends are similar

- $R_m$ decreases at higher $i$
- Small increase in $R_m$ with AST
- Similar trends for $R_m$ (EIS) and $R_m$ (VI) at large $i$

Model used to determine $R_m$ as a function of current density and AST cycles
Catalyst Degradation Loss Breakdown

$R_m$ at Limiting Current Density ($i_L$): 1.5 atm, 4% $X(O_2)$, 80°C, 90% RH

**Accomplishments**

- **At BOL**, reducing Pt loading to 0.05 from 0.15 mg/cm² causes 30.6% increase in $R_m$

- **After 30k cycles**, $R_m$ increased by 12.3% for 0.15 mg/cm² loading and by 43.1% for 0.05 mg/cm² loading, and is 66.4% higher in the lower loaded cell

**Representation for $R_m$ (Total Transport Resistance)**

\[
R_m = \left( R_g \frac{P}{P_r} + R_d \frac{P}{P_r} \right) + R_{Kn} + \left( R_f + R_I \frac{i}{i_r} \right)
\]

- $R_f = \text{Ionomer Film Resistance}$
- $R_f = \frac{R_{O_2}}{S_{Pt}}$

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**BOL**

- **0.15 mg/cm²**
  - $i_L = 615$ mA/cm², $R_m = 0.937$ s/cm
  - $R_f = 0.142$
  - $R_g = 0.069$
  - $R_d = 0.357$
  - $iR_I = 0.189$
  - GC = 0.18

- **0.1 mg/cm²**
  - $i_L = 535$ mA/cm², $R_m = 1.077$ s/cm
  - $R_f = 0.187$
  - $R_g = 0.069$
  - $R_d = 0.428$
  - $iR_I = 0.214$
  - GC = 0.18

- **0.05 mg/cm²**
  - $i_L = 471$ mA/cm², $R_m = 1.224$ s/cm
  - $R_f = 0.359$
  - $R_g = 0.069$
  - $R_d = 0.518$
  - $iR_I = 0.099$
  - GC = 0.18

**30k Cycles**

- **0.15 mg/cm²**
  - $i_L = 548$ mA/cm², $R_m = 1.052$ s/cm
  - $R_f = 0.277$
  - $R_g = 0.069$
  - $R_d = 0.357$
  - $iR_I = 0.169$
  - GC = 0.18

- **0.1 mg/cm²**
  - $i_L = 473$ mA/cm², $R_m = 1.218$ s/cm
  - $R_f = 0.352$
  - $R_g = 0.069$
  - $R_d = 0.428$
  - $iR_I = 0.189$
  - GC = 0.18

- **0.05 mg/cm²**
  - $i_L = 329$ mA/cm², $R_m = 1.751$ s/cm
  - $R_f = 0.915$
  - $R_g = 0.069$
  - $R_d = 0.518$
  - $iR_I = 0.069$
  - GC = 0.18

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DOE FCTO FC PAD Webinar: March 28, 2019
Accomplishments

**Break-in**
- Reduction in Non-Fickian transport resistance ($R_{nf}$)
- Still figuring out the lack of polarization change
- Removing majority of contaminants

**Voltage recovery (VR)**
- Improvements in mass activity
- $H_2/O_2$-Air performance

Changes in $R_{nf}$ and mass activity seem to occur independent of each other.

Suggests that break-in impacts local effects and voltage recovery more than macroscopic effects.

First voltage recovery cycle is crucial for improved $H_2$/Air performance.
Accomplishments

Changes During Conditioning: Effect of Carbon Support

Ostwald Ripening

Coarsening  ΔECSA = -14%

Pt/VulcanTKK vs. Pt HSCTKK

Differences in ECSA losses due to mechanisms contributing to particle growth (e.g., contributions due to particle coarsening, Pt-dissolution, and Ostwald Ripening)
Conditioning Effect of Carbon Support Variation

### 50 wt% Pt TKK Catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading [mg$_{Pt}$/cm$^2$]</th>
<th>ECSA [m$^2$/g$_{Pt}$]</th>
<th>δ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BOL</td>
<td>EOT</td>
<td>Δ</td>
</tr>
<tr>
<td>Pt/V$_{vul}$TKK</td>
<td>0.054</td>
<td>44.5</td>
<td>37.9</td>
</tr>
<tr>
<td>Pt/HSCP$_{TKK}$</td>
<td>0.058</td>
<td>72.6</td>
<td>56.9</td>
</tr>
</tbody>
</table>

- Both Pt/V$_{vul}$TKK and Pt/HSCP$_{TKK}$ exhibit ECSA loss and particle growth
- Pt/V$_{vul}$TKK exhibited larger particle size growth compared to Pt/HSCP$_{TKK}$

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**Vulcan**

- Pt nanoparticles on surface have higher mobility, nucleation and growth

**HSC**

- Pt Nano particles within HSC micropores have preferential nucleation and limited mobility
Accomplishments

# Conditioning Effect on Catalyst Alloys: Pt vs. PtCo/HSC

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading [mgPt/cm²]</th>
<th>ECSA [m²/gPt]</th>
<th>δ [nm]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>BOL</td>
<td>EOT</td>
<td>Δ</td>
</tr>
<tr>
<td>Pt/HSCₚₜᵯ</td>
<td>0.051</td>
<td>60.4</td>
<td>57.6</td>
</tr>
<tr>
<td>PtCo/HSCₚₜᵯ</td>
<td>0.048</td>
<td>56.3</td>
<td>56.5</td>
</tr>
</tbody>
</table>

- Minimal reduction in ECSA during conditioning
- PtCo: wider particle size distribution than Pt
- Catalyst compositional changes occur during ink/MEA fabrication and conditioning

Pt-Pt coordination number increase combined with less substantial increase of Pt-Co coordination indicates Pt particle growth and/or Pt enrichment due to Co dissolution
Approach: Electrode Layers and MEA Exploration

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

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

**Electrode Formation and Design**
- Formation process
- Specific designs & components
- Preferential pathways

**Optimization and Understanding**
- Limiting current
- Water & thermal management
- Multiscale modeling
- ASTs

**Cell Performance and Diagnostics**
- Interactions & pH
- Visualization & diagnostics
- Ionomer thin films
- Thickness and structure
- Impact of cations
Agglomerates: Dispersions

Ionomer solutions: colloidal dispersions with multiple solvents and ionomer

- Precursor to ionomer interactions

<table>
<thead>
<tr>
<th></th>
<th>50% H₂O, 0.2 wt-%</th>
<th>90% H₂O, 0.2 wt-%</th>
<th>90% H₂O, 2 wt-%</th>
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<tbody>
<tr>
<td>Aggregation</td>
<td></td>
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Aggregation from single strands to multi-strands with increasing water and solid amounts studied via cryo-SEM

Operando casting shows evolution of domain formation with crystallites then formation and growth of ionomer domains
Ionomer and Pt/C exhibit different aggregation behavior, resulting in various heterogeneities within electrode that can be detected with various methods.

- Multiple techniques used to measure ionomer and carbon aggregates and agglomerates:
  - Ionomer thin films plus larger agglomerates (globules)
  - Carbon aggregates 50 to 200 nm; larger agglomerates

**Nano X-ray tomography**

**AFM**

**STEM**

**X-ray Scattering**

**USAXS**

**SAXS**
Accomplishments

Ionomer and Agglomerate Imaging of Catalyst Layers

AFM Height Imaging

- Higher resolution shows individual particles in aggregates
- Differences in aggregates measured with spray coated vs painted
- Particle diameter ranges fit previous data from TEM/SAXS
- Large variability in particle diameter & ionomer thickness

To measure ionomer thickness:

I/C = 1 at 1µm

MEAs made by Spraying

Measured Ionomer Thickness

I/C = 1.2

1µm

500nm
Measurements of Pt/C Aggregate Measurements (AFM & SAXS) and Ionomer Layer Thickness (AFM)

Mean Pt/C Aggregate Diameter

Particle size Distribution

PSD by SAXS: Carbon aggregates $0.02 > q > 0.001$

I/C = 1.0
Mean = 99.2 nm

Ionomer Thickness

• Large variability in particle diameter and ionomer thickness
• Positive correlation between I/C ratio and ionomer thickness

MEAs made by hand painting

Height w/ adhesion overlay

Average Ionomer Thickness (nm)
Ionomer Dispersion within Catalyst Layers
Comparing Ionomer+C and Ionomer+Pt/C

- Increased interactions between ionomer + Pt/C compared to ionomer + carbon
- Evidence that ionomer is predominantly associated with Pt/C regions
  - Pt/ionomer interactions dominate aggregation in inks (by dynamic light scattering)

**Accomplishments**

**Pt/HSAC (50%) + HSAC-only (50%) in CL**

**Ink**

**CL**

**Higher agglomeration without Pt**
Modeling of Microscale Transport-Catalyst Layer Agglomerates

Explore agglomerate structures and understand mechanisms limiting of transport

Agglomerates identified by applying binary separation algorithm to segmented phase contrast images

Reconstructed agglomerate includes porous C, Pt, and ionomer distributions from absorption contrast images

Cylindrical agglomerates show lower O₂ transport resistance than spherical agglomerates of same equivalent diameter (500 nm), especially if flooded

\[
\frac{R}{R_s}
\]

Accomplishments

\[\frac{c}{c_s}\]

\[\begin{array}{c}
\text{flooded} \\
\text{dry}
\end{array}\]

\[
\begin{array}{c}
\text{cylindrical Ar:0.39} \\
\text{spherical Ar:0.76}
\end{array}
\]

\[R_p, \text{s.cm}^{-1}\]

\[\text{O}_2 \text{ concentration in ionomer phase (flooded agglomerates)}\]
Catalyst layer modeling at microscale is critical to resolve accurate trends

- Tortuosity has different dependence than expected
- Lattice Boltzmann simulation on constructed CL with local transport effects

- Ionomer thin film must be about 4% of bulk ionomer properties to agree with limiting-current data
  - Simulations show good agreement with data
  - Local transport resistance is limiting but some effects of ion adsorption as well
Water Management

- Anode can flood since harder to remove water due to $H_2$/droplet interactions
  - Experiments show more He than $N_2$ needed to remove droplet

- Simulations agree that gas density plays critical role for droplet detachment

![Graph showing droplet volume vs. gas velocity](image1)

![Liquid water on anode in Mirai](image2)

Coupled flow and deformation model

![Graph showing velocity vs. CA hysteresis](image3)
Case Study: Ink Solvents

Performance improvement with water-rich ink

- Reduction in non-Fickian and MW dependent transport percentage of resistance
- Decrease in agglomerate size both ink and CL

Accomplishments
For both inks and CLs, carbon aggregates show similar PSDs for all solvent ratios.

For both inks and CLs, water-rich solvent results in smaller agglomerates.
Case Study: Ink Solvent

- Higher Θ with increased ink water content
  - Aggregates grow due to increased ionomer/particle interactions
- Slightly water-rich ink exhibits best performance due to trade-off between coverage and structure
  - High water contents - aggregation of side-chains and looser structure, whereas with
  - High propanol contents - clustering and reverse-micelle structure

Case Study: Ink Solvent

- Higher Θ with increased ink water content
  - Aggregates grow due to increased ionomer/particle interactions
- Slightly water-rich ink exhibits best performance due to trade-off between coverage and structure
  - High water contents - aggregation of side-chains and looser structure
  - High propanol contents - clustering and reverse-micelle structure
- Larger solvent effects in O₂ transfer-limited region
  - Better aggregate break-up in water rich inks
  - Additional ionomer leads to thicker films on or near Pt
  - Similar to that observed for non-limiting case
With increasing I:C, more carbon agglomeration and larger agglomerates

- Observed in both ink (ex situ) and catalyst layer (in situ)

**Ink** (Dynamic light scattering)

**Catalyst Layer** (X-ray computed tomography)

- Results in more resistance
  - Higher interfacial and lower transport for lower EW
    - Impacted more by side-chain spacing and density than side-chain length
  - Agrees with *ex situ* film results

<table>
<thead>
<tr>
<th>Ionomer</th>
<th>Interfacial (s/m)</th>
<th>Transport (s/m)</th>
</tr>
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<tbody>
<tr>
<td>Nafion 1100</td>
<td>~0 ± 1.3</td>
<td>46.2 ± 2.0</td>
</tr>
<tr>
<td>3M 1000</td>
<td>0.2 ± 1.3</td>
<td>37.3 ± 2.2</td>
</tr>
<tr>
<td>3M 825</td>
<td>8.7 ± 1.0</td>
<td>24.6 ± 2.1</td>
</tr>
</tbody>
</table>
Increased Complexity: Porous Carbons

- Multi-mechanisms - water filling of porous carbons
  - Increasing RH results in higher ECSA
  - Adsorption and capillary condensation must occur

Water adsorption
Irregular shaped pores
Preferential Pt location

PSD in carbon from BET

![Graph showing water uptake vs. RH](image1)

![Graph showing NECA vs. RH](image2)

![Graph showing model vs. data](image3)
Increased Complexity: Porous Carbons

- Multi-mechanism - water filling of porous carbons
  - Adsorption and capillary condensation
  - Particles inside carbon pores result in 2 - 3 s/cm higher local resistance compared to solid carbon
  - Low ECSA manly responsible for high resistance at low RH
    - Reduction in local resistance, $R_{pt}$, with higher RH slows down after 65% RH due to flooding
  - Decreased diffusivity due to longer path-length to reach active Pt site

\[
\frac{D_{\text{Pt}}}{D_{\text{Pt, RH=100}}} = 0.8 \quad \text{for RH = 100%}
\]

Ce Migration: Experiments

Observing Ce migration during and after applied potential

**NR-212 w/ 13% Ce(III); 0.05/0.1 mg/cm² 10% Pt/V**

- **Scan length (µm)**
- **Ce fluorescence**
- **Avg. Ce (165-195 µm)**
- **Cath. An.**
- **0.45 V → migration**
- **0 min**
- **3.5 min**
- **7 min**
- **10.5 min**
- **14 min**

**Removing load redistributes Ce ~ 5 minutes; half that of migration**

**Ce moves towards cathode during operation - balance between diffusion and migration**
Ce Migration: Membrane Properties

- Ce impacts membrane water uptake properties but only at higher RHs
  - Decreased water uptake
    - Opposite of that in thin films
  - Dramatic decrease in conductivity in liquid water with Ce doping
  - Increased activation energy with loading
  - No master curve, suggesting conductive network differences
Ce Migration: Modeling

- Utilize interactions for Ce transport and examine transport at multiple scales
  - Concentrated solution theory model shows balance between migration and diffusion that push Ce to the cathode and water convection that pushes Ce to the anode
  - Heterogeneous ion distributions also change proton and water transport
**Ionomer Thin Films: Impact of Ageing**

- **Hygrothermal ageing of ionomer films**
  - Films are held at 70°C, 85% RH for 2 and 4 days

- **Swelling**
  - Fresh film: \( \text{Si} > \text{Pt} \)
  - Aged film: \( \text{Si} >> \text{Pt} \, \downarrow \)

- **Swelling Kinetics**
  - \( \text{Si} > \text{Pt} \)
  - \( \text{Si} >> \text{Pt} \, \downarrow \)

- **Domain Orientation**
  - Fresh: \( \text{Si} < \text{Pt} \)
  - Aged: \( \text{Si} << \text{Pt} \, \uparrow \)

---

M Tesfaye, D. Kushner, A. Kusoglu, *ACS Applied Polymer Materials* (Accepted Manuscript)
Ionomer Thin Films: Impact of Ageing

- Reduced rate of swelling is inversely proportional to nanodomain orientation
- Hold at RH/T intensifies ionic interactions impacting orientation
- Critical for cell operation and performance decay
- Implications for conditioning

Time constant ~ Orientation
- Thickness swelling slows down when domains are preferentially aligned

M Tesfaye, D. Kushner, A. Kusoglu, *ACS Applied Polymer Materials* (Accepted Manuscript)
Ionomer Thin films: Cerium Doping

Connection between structure and thermodynamic/mechanical properties is altered by cation exchange

- Similar structures in the dry state - manifests in similar mechanical response and swelling at low RH
- At high water content, more interspersed water results in higher stress and modulus for Ce-exchanged film
- Nafion thin films on Pt also demonstrate complicated water/surface structure which Ce modifies

Swelling response agrees with more water in Ce-exchanged film

Accomplishments

\[ G_{H} = 304 \text{ Mpa} \]
\[ G_{Ce} = 323 \text{ Mpa} \]
Optimizing CL Structure (Ionomer Distribution)

Control ionomer content & distribution

- Too Little
  - Poor H⁺ Transport
  - Lower Pt utilization

- Too Much
  - Decreased O₂ transport
  - Site and Pore Blockage

Ionomer Inhibits ORR

- ECA (m²/gₚ)
- Specific Activity (μA/cm²·Pt)
- Mass Activity (mA/mgₚ)

Challenge: Difficult to control and characterize

SEM elemental map

Umicore 0.1 mg PtCo/HSC - Bulk I:C 0.9

Pt/HSC Ionomer

4 μm
Ordered Array Electrode

- Meso-structured electrode relies on vertically aligned ionomer channels for long-distance H+ transport
- Catalyzed elements can have reduced ionomer content
Nanowire Electrode: Carbon Filler in Void Space

Carbon filler - Vulcan (XC-72)

Carbon filler used to fill void space and provide mechanical support.

Cross-sections reveal that filler helps prevent nanowire collapse during cell compression.

Accomplishments

- Low carbon loading
- High carbon loading

Pt-coated Nafion Nanowire
Carbon Filler

Nafion nanowire
STEM and TEM images reveal thin conformal coating of Pt surrounding Nafion nanowires

Pt forms separate crystallites during deposition; crystallites merge as loading increases
**Filler Carbon Stabilizes Structure – Transport not limiting**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>ECSA ($m_{Pt}^2 g_{Pt}^{-1}$)</th>
<th>Roughness ($cm_{Pt}^2 cm_{geo}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Filler</td>
<td>15.1±0.07</td>
<td>25.6±0.12</td>
</tr>
<tr>
<td>Vulcan Filler (0.28)</td>
<td>15.0±0.16</td>
<td>22.4±0.24</td>
</tr>
<tr>
<td>Vulcan Filler (0.60)</td>
<td>13.5±0.05</td>
<td>25.9±0.01</td>
</tr>
<tr>
<td>Vulcan Filler (0.10)</td>
<td>10.7±0.21</td>
<td>21.0±0.42</td>
</tr>
</tbody>
</table>

- **Accomplishments**
  - Carbon filler enables improved performance
  - Further development of electrode structure to prevent nanowire bundling is needed

- Cathode loading: 0.15 mg$_{Pt}$ cm$^{-2}$
- Vulcan (XC-72) with I/C = 0.28
Collaborations (FOA-1412 Partners)

- Core FC-PAD team consists of five national labs
  - Argonne, Lawrence Berkeley, Los Alamos, Oak Ridge and NREL
  - Materials, data and students frequently travel between labs

Interactions with DOE-awarded FC-PAD Projects (FOA-1412)

POC assigned for each project to coordinate activities with PI

FC-PAD work related to those presented in those AMRs

- FC155: 3M - PI: Andrew Haug – FC-PAD POC: Adam Weber
- FC157: UTRC - PI: Mike Perry – FC-PAD POC: Rod Borup
- FC158: Vanderbilt - PI: Peter Pintauro – FC-PAD POC: Rangachary Mukundan

- 30% of National Lab budget supports FOA projects
  - Equal support to each project
- Two in-person FC-PAD meetings held annually - include FOA members with individual sessions held to discuss interactions and progress
## Collaborations (Non-FOA activities)

<table>
<thead>
<tr>
<th>Institutions</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Umicore</td>
<td>Supply SOA catalysts, MEAs</td>
</tr>
<tr>
<td>UC Irvine</td>
<td>GDL imaging</td>
</tr>
<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>
</tr>
<tr>
<td>Johnson Matthey</td>
<td>Catalysts and CCMs</td>
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<tr>
<td>CEA (and ID-FAST EU Consortium)</td>
<td>Membrane studies</td>
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<tr>
<td>Ion Power</td>
<td>Supply CCMs</td>
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<tr>
<td>Xi'an Jiaotong University</td>
<td>CL mesoscale modeling</td>
</tr>
<tr>
<td>NIST – National Institute of Standards and Tech.</td>
<td>Neutron imaging</td>
</tr>
<tr>
<td>Simon Fraser University</td>
<td>Ionomer</td>
</tr>
<tr>
<td>University of Alberta</td>
<td>GDL and flowfield modeling; ink studies</td>
</tr>
<tr>
<td>US Drive</td>
<td>Mirai analysis</td>
</tr>
<tr>
<td>Xi'an Jiaotong University</td>
<td>CL mesoscale modeling</td>
</tr>
<tr>
<td>LEMTA, CNRS/Université de Lorraine</td>
<td>Shut-down/Start-up testing</td>
</tr>
</tbody>
</table>
Future Work: Heavy-Duty Applications

Heavy-Duty Deviations from Light-Duty (Durability & Efficiency)

- Much longer lifetimes (1,000,000 miles; 25,000-30,000 hrs)
- Different drive cycles compared with light-duty
  - Long-haul and delivery also have substantially differing drive cycles
- Focus on improved efficiency - higher operating temperatures (better kinetics), higher emphasis on lower stack power density (higher voltage)
- Cost targets are less stringent depending upon efficiency and durability payback

Initial FC-PAD Workscope

- Understand the heavy-duty fuel cell operating space and prioritize research directions
  - Examples include: more idle time, fewer start/stops (long haul), more time at high voltage, minimizing voltage clipping, understand efficiency hit due to gas crossover through membrane for extended idle, low-power operation with high-power extended spikes. Understand the effect of membrane additives, membrane thickness, catalyst particle size and catalyst alloying under heavy duty operating modes.
- Refine applicable models, characterization, and diagnostics to heavy-duty operating conditions & materials
- Develop refined ASTs for extended life-time prediction with appropriate heavy-duty materials and operating conditions

Planned activities on understanding of component properties, structures and transport phenomena is applicable to both light- and heavy-duty

Any proposed future work is subject to change based on funding levels
Future Work: Component and Cell Understanding

**Material and characterization studies**
- Catalyst alloy studies including dissolution and high-potential kinetics
- Directly measure ionomer film properties and morphology on operating electrodes
  - TEM (EELS, EDS and tomography (4D STEM), GiSAXS, NR

**Catalyst layer studies**
- Continue exploration of different catalyst layer structures; low and moderate Pt loadings
  - Microstructural reconstruction and modeling for catalyst layers including multiphase flow
  - Understanding the size and impact of Pt/C aggregates and agglomerates
- Translational studies from ink to catalyst-layer structure
- Low-voltage cryo-STEM, AFM

**Durability**
- Evaluate external system component contaminants (e.g. Fe++) and mechanism for transport to MEA
- Characterize electrode microstructural changes as a result of ageing
- Local resistance analysis (e.g. O\textsubscript{2} and H\textsubscript{2} limiting current) related to impact of metal alloy catalyst leaching on ionomer transport resistance
- Evaluate catalyst loading comparison between light-duty and heavy-duty on MEA durability

**Water and thermal management**
- Modeling of water droplet detachment and GDL/channel interface
- Water visualization in operating cell components
- Integrate and evaluate various components to elucidate emergent phenomena
- Translational modeling going from ex-situ property data to operando performance

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

- Measurements and modeling effect of loading with durability potential cycling
- Transport measurements during MEA conditioning evaluating carbon support effect
- Evaluation of aggregate and agglomerates in catalyst layer by multiple complimentary techniques and their impact by microscale transport modeling
- Evaluation of catalyst-ink solvent effect on catalyst layer structure and performance
- Measured thin film ionomer structural changes in ionomer/water structure with cations
- Operando measurements and modeling of Ce and Co profiles with applied potential
- Developed catalyst-layer architectures with better transport and structural stability

Future Work:

- Greater focus on heavy duty applications, with greater emphasis on efficiency and durability
- Continue to develop the knowledge base to improve catalyst layer structures and component integration for fuel cell performance, efficiency, and durability
What (Who) is FC-PAD? National Lab Contributors

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- 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
Models can be used to obtain critical parameters

Comparison of integral vs differential demonstrates that gas flow is important in integral and humidity changes are exacerbated.

Impedance analysis allows for determination of local resistance

Only small growth after catalyst AST.

Functional form of surface area as a function of RH is elucidated.
Water Imaging of Operating Short Stack (Mirai) 
USCAR Matrix of Operating Conditions

- Liquid water primarily on Anode side; Stack water is primarily sensitive to anode flowrate
- All conditions show some water; especially at 2/3 serpentine interface and cathode outlet weld area
- Anode Inlet/outlet (and Cooling serpentine returns) show water build-up.

High Current & Flowrates show much less liquid water than low current/flowrates

50A

70A

125A

225A

312A
Effect of ECSA, $\Delta \delta_{pt}$ & Specific Activity on $i_m^{0.9V}$

- Highest Mass Activity ($m^2/g$): optimal no. of active sites and activity per site

- Particle growth and detachment

- Removal of contaminants, adsorbed species, oxides or changes to carbon structure improved pore accessibility

- Effect of ECSA, $\Delta \delta_{pt}$, & Specific Activity on $i_m^{0.9V}$

- Pt/Vulcan$_{TKK}$

- Pt/HSC

- Mass Activity, $i_m^{0.9V}$ (A mg$_{Pt}^{-1}$)

- Mass Activity, $i_m^{0.9V}$ (A mg$_{Pt}^{-1}$)
Effluent Emission Rates During Conditioning and Recovery Steps – Pt/V_{TKK} and Pt/HSC_{TKK}

- Majority of the sulfate and fluoride contaminants are released during the break-in
- Continual removal of total contaminants with consecutive VR cycles can have a positive impact on Specific activity --> lead to potential improvements in mass activity of the catalysts
Ce Modeling Details Backup Slide

Driving forces: cerium, solvent (subscript 0) gradient and migration

\[ N_{Ce} = -\alpha_{CeCe} \nabla \mu_{Ce,H} - \alpha_{Ce0} \nabla \mu_0 + \frac{t_{Ce}}{z_{Ce}} \frac{i}{F} \]

\[ N_H = -\alpha_{CeH} \nabla \mu_{Ce,H} - \alpha_{H0} \nabla \mu_0 + \frac{t_{H}}{z_{H}} \frac{i}{F} \]

\[ N_0 = -\alpha_{Ce0} \nabla \mu_{Ce,H} - \alpha_{00} \nabla \mu_0 + \xi \frac{i}{F} \]

Transport coefficients derived from Stefan-Maxwell treatment with bulk solution diffusion coefficients and hydrodynamic theory of flow in pores.

Chemical potentials (ideal cerium and proton thermodynamics)

\[ \mu_0 - \mu_0^{ref} = RT \ln RH \]

\[ \mu_{Ce,H} - \mu_{Ce,H}^{ref} = \mu_{Ce} - \mu_{Ce}^{ref} - \frac{z_{Ce}}{z_{H}} (\mu_H - \mu_H^{ref}) \]

\[ = RT \ln \frac{f_{Ce}}{\lambda} - \frac{z_{Ce}}{z_{H}} RT \ln \frac{1 - f_{Ce}}{\lambda} \]

Relative humidity boundary condition on water

Zero flux of cerium

Applied potential

<table>
<thead>
<tr>
<th>Variable</th>
<th>Variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_i )</td>
<td>Species molar flux</td>
</tr>
<tr>
<td>( z_i )</td>
<td>Valance</td>
</tr>
<tr>
<td>( \alpha_{ij} )</td>
<td>Transport coefficient</td>
</tr>
<tr>
<td>( F )</td>
<td>Faradays constant</td>
</tr>
<tr>
<td>( \mu_i )</td>
<td>Chemical potential</td>
</tr>
<tr>
<td>( \xi )</td>
<td>Electroosmotic coefficient</td>
</tr>
<tr>
<td>( i )</td>
<td>Current density</td>
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<tr>
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<td>( t_i )</td>
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<tr>
<td>( \lambda )</td>
<td>Water content</td>
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<tr>
<td>( f_{Ce} )</td>
<td>Fraction cerium loading</td>
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</tbody>
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