FC137 – FC-PAD: Electrode Layers and Optimization

Presenter: Adam Weber

Tuesday, June 6th 2017
**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. 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

Lead: Rod Borup (LANL)
Deputy Lead: Adam Z. Weber (LBNL)

www.fcpad.org
FC-PAD Consortium - Overview

Fuel Cell Technologies Office (FCTO)

• FC-PAD coordinates activities related to fuel cell performance and durability
  • The FC-PAD team consists of five national labs and leverages a multi-disciplinary team and capabilities to accelerate improvements in PEMFC performance and durability
  • The core-lab team consortium was awarded beginning in FY2016; builds upon previous national lab (NL) projects
• Provide technical expertise and harmonize activities with industrial developers
• FC-PAD serves as a resource that amplifies FCTO’s impact by leveraging the core capabilities of constituent members
Overall Objectives:

- Advance **performance** and **durability** of polymer electrolyte membrane fuel cells (PEMFCs) at a **pre-competitive** level
- Develop the knowledge base and optimize structures for more durable and high-performance PEMFC components
- Improve high current density performance at low Pt loadings
  - Loading: 0.125 mg Pt/cm² total
  - Performance @ 0.8 V: 300 mA / cm²
  - Performance @ rated power: 1,000 mW / cm²
- Improve component durability (e.g. membrane stabilization, self-healing, electrode-layer stabilization)
- Provide support to DOE Funded FC-PAD projects from FOA-1412
- Each thrust area has a sub-set of objectives which lead to the overall performance and durability objectives
FC-PAD Overview & Relevance

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

Budget
FY17 project funding: $5,150,000
As proposed: 5-year consortium with quarterly, yearly milestones & Go/No-Go
Total Expected Funding: $25M (NLs only)

Partners/Collaborations
(To Date Collaborations Only)

- EWii Fuel Cells, Umicore, NECC, GM, TKK, USC, JMFC, W.L. Gore, Ion Power, Tufts, KIER, PSI, UDelaware, 3M, CSM, SGL, NPL, NIST, CEA, Ulorraine, UTRC, U Alberta
- Partners added by DOE DE-FOA-0001412

Barriers

- Cost: $40/kW system (2020), $30/kW (ultimate); $14/kW_{net} MEA (2020)
- 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

- 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
Objective: How we get there

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

Understanding Electrode Layer Structure

Characterization

New Electrode Layer Design and Fabrication

Stratified (Spray, Embossed, Array), Pt - Deposition, Jet Dispersion

Defining/Measuring Degradation Mechanisms

Membrane, Catalyst Pt-alloy dissolution

FC-PAD Presentations

- FC135: FC-PAD: Fuel Cell Performance and Durability Consortium (Borup, LANL)
  - Overview, Framing, Approach, and Highlights/Durability
- FC136: FC-PAD: Components and Characterization (More, ORNL)
  - Concentrate on Catalysts and Characterization
- FC137: FC-PAD: Electrode Layers and Optimization (Weber, LBNL)
  - Concentrate on Performance - MEA construction and modeling
- FC155 (3M), FC156 (GM), FC157 (UTRC), FC158 (Vanderbilt) FOA-1412 Projects
Approach: Electrode Layers and Optimization

Film & Ink Characterization
- Dispersions
- Interactions
- Ionomer thin films
- Transport properties

Electrode Formation and Design
- Specific designs and components
- Preferential pathways

Component Characterization and Diagnostics
- Visualization
- GDL/flowfield droplets
- MPL properties
- Phase-change-induced flow

Optimization and Understanding

Cell Performance and Diagnostics
- Limiting current
- ∆V analysis
- Water and thermal management
- Mathematical modeling
Ink Stability

- **Inks are unstable**
  - Model and experiments demonstrate large carbon aggregates that drop out of suspension
  - Secondary peak forms after a couple of hours
  - Governed by collisions and interparticle forces
    - Settling
  - Ionomer helps to stabilize the ink
    - Depends on solvent ratio

**Interparticle forces and interactions key towards understanding CL formation**
Catalyst Layer Structure

- Catalyst structures are heterogeneous
- Impacts analysis of transport phenomena
- Ionomer preferentially interacts with Pt/V
Electrode Microstructure Analysis

- Developed method to reconstruct electrode microstructure from multiple data
  - Nano-CT, TEM, USAXS data
  - C, Pt, pore size distributions
  - Ionomer visualized and computed

Simulate transport through the domain
- Elucidate transport bottlenecks

**Accomplishments**

- Cation (+) / anion (-) diffusion
- Tortuosity
- Ionomer thickness dependence

**Resulting Microstructure**

- 2.5 nm resolution
- 400 x 400 x 400 voxels
- $\varepsilon_v = 0.45$

**Graphs**

- **C Surface %**
  - vs. Ionomer Thickness, nm
  - $\ell_v = 0.45$

- **Tortuosity**
  - vs. $\tau$

- **Effective Diffusivity**
  - vs. $\varepsilon_v$
  - $D_{\text{eff}} / D_{\text{bulk}}$
  - $D_{\text{Ko}} = \frac{d_p}{3} \sqrt{\frac{8RT}{\pi M}}$
  - $D_{\text{local}} = \left( \frac{1}{D_b} + \frac{1}{D_{\text{Ko}}} \right)^{-1}$

- **Local Diffusivity**
  - model input:

- **Diagram**
  - Visualization of microstructure with annotations.
Local Transport Resistance

- Hydrogen limiting current can be used to yield more information

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>1.035</th>
<th>1.69</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (s/cm)</td>
<td>$R_{GDL}$</td>
<td>$R_{cl}$</td>
</tr>
<tr>
<td>Method</td>
<td>GDL stacking</td>
<td>8.79</td>
</tr>
<tr>
<td></td>
<td>local resistance</td>
<td>8.67</td>
</tr>
</tbody>
</table>

- Can use H$_2$ data to correct polarization curves for mass-transport resistance

- Stacking allows single loading testing
- Resistance values depend on technique
- Suggests not all Pt is active

80°C, 90% RH
H$_2$/air, 140 kPa$_{abs}$
Local Transport Resistance

- Use oxygen limiting current to measure the local transport resistance
  - Value depends on accurate measurement of ECA
  - Varies depending on carbon support
  - Pt/V is a better baseline for novel ionomers

Accomplishments

Greszler et al., JES, 159(12):F831-F840 (2013)
Comparison of hydrogen- and oxygen-derived local transport resistance

- Hydrogen is lower and less humidity and more temperature dependent than oxygen
  - Consistent with ionomer difference in bulk permeability
  - Driven by change in (bulk) diffusivity

Diagnostics suggest ionomer-related transport is limiting
Influence of Environment on Ionomer Thin Film

‘Real’ catalyst-layer phenomenon studied using Model experimental system

Water uptake of Nafion thin-film supported on Platinum substrate in reducing and oxidizing environments

GISAXS
Lower critical angle & film density
Higher critical angle & film density

Oxidizing gas (Air) facilitates Pt-O growth, while reducing gas (H₂) removes it
Reducers environment promotes Pt surface, resulting in ionomer densification
Reversible process, related to ionic and water interactions with the surface

Ionomer undergoes changes with local surface conditions and environment
Electrode Structure: Stratified

- Optimize catalyst-layer structure
  - Irregular thickness and porosity: enhanced gas and water transport in and out of MEA
    - Minimize local resistance effects?

- Model guided design
  - Need catalyst under channel
  - Strong HFR dependence
  - Model shows gains for stratified CL at high current densities
    - Best gains for ~2 stratified CL segments per channel

**H₂/Air Data**

<table>
<thead>
<tr>
<th>80°C, 100% RH, 10.5 psig</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂/Air Data</td>
</tr>
<tr>
<td>(0.07 mg/cm² 46.6 wt% Pt/C)</td>
</tr>
</tbody>
</table>

- Channels only
- Channels + Vulcan
- Lands only

**Accomplishments**

**Electrode Structure: Stratified**

- **Cathode**: 0.1 mg/cm² Pt/HSAC
- Improved kinetics
- Improved MT
- I/C\textsubscript{filler} 0.9
- I/C\textsubscript{filler} 0.6
- Baseline Flat CL
- 80°C, 100% RH & 10.5 psig

**Accomplishments**

- **Need filler to improve performance**
  - Kinetic improvement at high I/C ratio suggests higher Pt utilization
  - Mass-transport improvement with low I/C ratio is likely due to reduced water retention and better utilization of Pt
  - Carbon filler made of Ketjen 300J better than Vulcan

**Enhanced performance at high current densities compared to conventional layers**
Electrode Structure: Meso-Structured Array

Electrode functions separated into different elements with a ternary array

Controlled, low-tortuosity configuration enables transport limitations to be reduced or eliminated

Nafion nanofibers provide effective proton transport through these low-tortuosity percolating highways

Allows the catalyst domain to have a lower ionomer/catalyst ratio

SEM image of oriented Nafion nanofibers of 200nm diameter and 5 µm height
Electrode Structure: Controlled Deposition of Pt

Scanning Pt-XRF image of Pt deposited in a spiral on a GDL (catalyzed spiral region roughly 1 mm wide by 10 µm deep)

HAADF-STEM image within the spiral depicting Pt catalyst particles with uniform distribution and size (avg. 2 to 3 nm dia.)
Water Management: Hydrophilic MPLs

- Examine carbon nanotubes (SGL 25BN) in MPL
  - Observe liquid water in nanotubes
  - **Improved performance**
    - Less liquid water throughout the cell
    - Diagnostics demonstrate both easier breakthrough as well as lower adhesion force/detachment velocity from GDL

### Accomplishments

<table>
<thead>
<tr>
<th>Test</th>
<th>SGL 25BN</th>
<th>SGL 25BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detachment velocity</td>
<td>3 m/s</td>
<td>5 m/s</td>
</tr>
<tr>
<td>Adhesion Force</td>
<td>7 mN/m</td>
<td>8 mN/m</td>
</tr>
<tr>
<td>Breakthrough pressure</td>
<td>4.4 kPa</td>
<td>5.7 kPa</td>
</tr>
</tbody>
</table>

![Nano XCT](image1.png)

- 80°C, 100% RH, 1.2/2, 275 kPa
- SGL 25BN vs SGL 25BC
  - Detachment velocity: 3 m/s vs 5 m/s
  - Adhesion Force: 7 mN/m vs 8 mN/m
  - Breakthrough pressure: 4.4 kPa vs 5.7 kPa

![Neutron Imaging](image2.png)
Carbon nanotubes demonstrate *increased durability* performance under drive cycle.

- Mass-transport losses related to GDL develop during testing.
Water Management: Phase-Change-Induced Flow

PCI flow observed and quantified
- Slow until becomes disconnected then rapid evaporation
- Major role in water and thermal management
Modeling \( \Delta V \) Analysis Performance Diagnostic

- **Shape of the \( \Delta V \) curves, magnitude of \( \Delta V \), and reaction order may be used to uniquely identify limiting mechanism:**

<table>
<thead>
<tr>
<th>Limitation</th>
<th>Order</th>
<th>Sensitivity</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetics</td>
<td>1/2</td>
<td>High sensitivity to specific area</td>
<td>Logarithmic</td>
</tr>
<tr>
<td>CL diffusion</td>
<td>1</td>
<td>Low sensitivity to diffusivity</td>
<td>Exponential</td>
</tr>
<tr>
<td>GDL-MPL Diffusion</td>
<td>1</td>
<td>High sensitivity to diffusivity</td>
<td>Exponential</td>
</tr>
<tr>
<td>CL proton conductivity</td>
<td>0</td>
<td>High sensitivity to ionomer conductivity</td>
<td>Linear</td>
</tr>
</tbody>
</table>

Analysis of experimental \( \Delta V \) shows kinetic and transport limited Kinetic and transport parameters are adjusted to determine relative fractions and values.
Collaborations (From FOA-1412)

- The 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)

Assigned a POC for each project to coordinate activities with project PI:

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

- 35% of the National Lab budget defined as support to the Industrial FOA projects
- Support to these projects is primarily just beginning
- Equal support to each project
- Agreed upon 1-year SOW by ~ Feb 2017

Support Distribution

<table>
<thead>
<tr>
<th>3M %</th>
<th>GM %</th>
<th>UTRC %</th>
<th>Vanderbilt %</th>
</tr>
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<tbody>
<tr>
<td>20%</td>
<td>LANL</td>
<td>LANL</td>
<td>LANL 64%</td>
</tr>
<tr>
<td>39%</td>
<td>LBNL</td>
<td>LBNL</td>
<td>LBNL 0%</td>
</tr>
<tr>
<td>10%</td>
<td>ANL</td>
<td>ANL</td>
<td>ANL 15%</td>
</tr>
<tr>
<td>19%</td>
<td>NREL</td>
<td>NREL</td>
<td>NREL 10%</td>
</tr>
<tr>
<td>12%</td>
<td>ORNL</td>
<td>ORNL</td>
<td>ORNL 12%</td>
</tr>
</tbody>
</table>
## Collaborations (non-FOA activities)

<table>
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<tr>
<th>Institutions</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Umicore</td>
<td>Supply SOA catalysts, MEAs</td>
</tr>
<tr>
<td>IRD Fuel Cells</td>
<td>Supply SOA catalysts and/or MEAs</td>
</tr>
<tr>
<td>Ford</td>
<td>Ionomer imaging studies</td>
</tr>
<tr>
<td>TKK</td>
<td>Supply SOA catalysts</td>
</tr>
<tr>
<td>Johnson Matthey</td>
<td>Catalysts and CCMs (as part of FC106)</td>
</tr>
<tr>
<td>GM</td>
<td>Supply SOA catalysts and/or MEAs</td>
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<tr>
<td>Ion Power</td>
<td>Supply CCMs</td>
</tr>
<tr>
<td>GM/W.L. Gore</td>
<td>Supply SOA catalysts, SOA Membranes,</td>
</tr>
<tr>
<td>ANL–HFCM Group</td>
<td>SOA catalyst</td>
</tr>
<tr>
<td>Tufts University</td>
<td>GDL, MPL imaging</td>
</tr>
<tr>
<td>KIER</td>
<td>Micro-electrode cell studies</td>
</tr>
<tr>
<td>U Delaware</td>
<td>Membrane durability</td>
</tr>
<tr>
<td>Vanderbilt U.</td>
<td>Ink studies</td>
</tr>
<tr>
<td>PSI – Paul Scherrer Institute</td>
<td>GDL imaging</td>
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<tr>
<td>NTNU – Norwegian Technical University</td>
<td>GDL imaging</td>
</tr>
<tr>
<td>UTRC</td>
<td>Cell diagnostics</td>
</tr>
<tr>
<td>3M</td>
<td>Ionomers</td>
</tr>
<tr>
<td>Colorado School of Mines</td>
<td>Membrane diagnostics</td>
</tr>
<tr>
<td>SGL Carbon</td>
<td>GDL Supplier</td>
</tr>
<tr>
<td>NPL - National Physical Laboratory</td>
<td>Reference electrodes for spatial measurements</td>
</tr>
<tr>
<td>NIST – National Inst. of Standards and Tech</td>
<td>Neutron imaging</td>
</tr>
<tr>
<td>U. Alberta</td>
<td>GDL and flowfield modeling; ink studies</td>
</tr>
</tbody>
</table>
Proposed Future Work

**Inks**
- Model study to elucidate interactions of ionomer with particle surfaces and solvents
  - Elucidate governing binary interactions
  - Direct observation of dispersions
- Measure ionomer thin-film properties under applied potential

**Catalyst-layer structure**
- Continue exploration of different catalyst-layer structures
  - Stratified, array, electrospun, HSC/VC layered, specific Pt deposition
- Microstructural modeling for catalyst layers
- Local resistance analysis
  - Limiting current under variety of conditions, techniques, ionomers, gases, temperature, humidity

**Water and thermal management**
- Explore conditioning protocols and understand how each step impacts performance
- Model interactions and examine scale coupling
  - Compare to segmented cell data
  - Detail model for GDL/Channel interface and droplets
- Water visualization in various components
- Explore impact of carbon type in MPLs

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:
- Examined water transport throughout MEA
- Developed new catalyst-layer architectures
  - Stratified and array electrodes with variations in loadings
  - Pt deposition where it is needed
- Unraveling origin of local resistance
  - Hydrogen and oxygen limiting current suggests ionomer film and its local morphology are dominant cause
- Developed new diagnostics and models for interpreting critical phenomena and data
- Explored ink stability and dispersions and fabrication methods

Future Work:
- Optimize catalyst-layer structure for high performance at low loadings
- Elucidate critical bottlenecks for performance and durability from ink to formation to conditioning to testing
- Multiscale modeling of cell and components
- Explore genesis of membranes and thin films and their associated properties
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, ALS-LBNL, APS-ANL, LBNL-Molecular Foundry, CNMS-ORNL, CNM-ANL
- NIST: BT-2
Technical Back-Up Slides
Reaction order analysis at BOL

- Kinetics limitations are kept same at BOL & EOL
- Other limitations are increased from BOL to EOL
- The reaction order is different from BOL to EOL due to changing contribution of kinetics and other limitations
  - Kinetic effects are prominent at BOL, skewing the reaction orders towards 1/2. Other effects become more prominent at EOL.
- See change in order due to different mechanisms at different potentials
- Different effects need to be decoupled to be uniquely identified
- Need for mathematical model
Accomplishments

Droplets in Channel

- Develop model for water droplet movement in channels
- Need to couple to physics within the domain
- Look at different flow regimes and interactions

Droplet growth with $Q_w = 2.5$ SLPM, $Q_{air} = 8$ SLPM

$t = 0\text{ ms}$  
$t = 2\text{ ms}$  
$t = 4\text{ ms}$  
$t = 9\text{ ms}$
Accomplishments

From Differential Data to Integral Cell Model

- Determine resistances from differential cell data
- Develop governing correlations
- Predict integral cell performance using differential-trained correlations
GISAXS under flowing hydrogen to reduce Pt-oxides

- Peak at $\sim 0.5$ 1/nm is the paracrystalline peak of the platinum surface
  - Strong in N$_2$, it disappears upon purging chamber with H$_2$. This would indicate x-rays are not penetrating all the way through the film
  - Reappears in air, showing a reversibility
- H$_2$ is interacting with Nafion and/or Pt substrate, increasing the film density and therefore the critical angle
Accomplishments

Impact of Fabrication Method

NREL Fabrication: Spray Coating

- Stratified

CL thickness non-uniform – ranging from 2µm to 10µm thick

Umicore Fabrication: Proprietary non-spray

CL thickness very uniform - 6µm

<table>
<thead>
<tr>
<th>MEA</th>
<th>Loading [mg Pt/cm²]</th>
<th>ECSA [m²/g Pt]</th>
<th>( i_m ) [μA/mg Pt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NREL Fab, test MEA- PtCo 0.9 I:C</td>
<td>0.10</td>
<td>37 ± 2</td>
<td>514 ± 40</td>
</tr>
<tr>
<td>NREL Fab, test MEA- PtCo 0.7 I:C</td>
<td>0.10</td>
<td>36 ± 1</td>
<td>388 ± 47</td>
</tr>
<tr>
<td>Umicore Fab, NREL test MEA- PtCo 0.95 I:C</td>
<td>0.10</td>
<td>40 ± 1</td>
<td>336 ± 18</td>
</tr>
<tr>
<td>Umicore Fab, test MEA- PtCo 0.95 I:C</td>
<td>0.14</td>
<td>50 ± 1</td>
<td>475 ± 35</td>
</tr>
</tbody>
</table>