High performance PEFC electrode structures

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United Technologies Research Center

FC PAD Consortia Project
Project ID: FC157
DE-EE0007652

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Polarization curve for an ultra-low-loaded PtNi/C cathode
- Raw in blue,
- Transport-corrected in red.

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Overview

Timeline
Project Start: October 2016
2016Q4 = “Q0”
Project Q1: Jan-March 2017
Project End: December 2019
39 months

Key Barriers
- Achieve DOE’s 2020 Targets for MEAs

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Units</th>
<th>2015 Status</th>
<th>2020 Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum-group metal (PGM) total loading (both electrodes)</td>
<td>mg PGM/cm²</td>
<td>0.13</td>
<td>≤ 0.125</td>
</tr>
<tr>
<td>Performance @ 0.8 V</td>
<td>mA/cm²</td>
<td>240</td>
<td>300</td>
</tr>
<tr>
<td>Performance @ rated power (150 kPa abs)</td>
<td>mW/cm²</td>
<td>810</td>
<td>1,000</td>
</tr>
</tbody>
</table>

Budget
Total Project Budget: $3,019K
- Federal Share $2,415K
- Cost Share (20%) $604K
Total DOE Funds Spent*: $23K
* as of 3/31/2017

Partners

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Relevance

Objective: Develop improved fundamental understanding of transport limitations in a SOA MEA and use this know-how to develop and demonstrate high-performance MEAs with ULCLs

• High-activity ORR catalysts have been developed & demonstrated
  – MEAs with ultra-low catalyst loadings (ULCLs) can meet activity targets
  – *Transport losses are major barrier*
    • Flux rate per catalyst site is increased
      – Transport losses increase
    • MEAs with ULCLs cannot yet meet power density (high current) targets

• Need to reduce transport losses in MEAs with ULCLs
  – *First step is to determine actual root-cause mechanisms* (e.g., not CCL thickness)
  – Fundamental understanding is currently lacking

New electrocatalysts require new MEA architectures to realize their full potential
Technical Approach

Develop Detailed Geometric (i.e., microstructure) Model of CCL

- Cathode catalyst layer (CCL) contains multiple length scales
- Agglomerates in CCL probably contain more than one carbon particle
- If there is an ionomer shell around agglomerates, then need to determine:
  - Thickness of ionomer shell and number of carbon (and catalyst sites) per agglomerate

**Different transport-limiting mechanisms result in different limiting currents**
- Use microstructure model to help discern different transport limitations
- Make CCLs that can help to probe these differences, as guided by model

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**Multiple possible transport-limiting mechanisms within CCL**
Project Approach

Roles of key participants

- Make electrodes to probe model
- Characterize electrodes
- MEAs that exceed DOE’s BOL Performance Targets
- Improve electrode design
- Cell diagnostics that highlight different losses
- Build increasingly sophisticated electrode model

Non conventional catalysts

Iterative process will enable improved understanding and performance

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Collaborations

Core Project Team (i.e., subcontractors)

- SOA MEAs
  1. C-supported catalysts
  2. Novel catalysts
- Novel catalyst structures
- Modeling
- Cell testing
- Cell diagnostics

Mike Perry (Project)
Rob Darling (Modeling)
J.V. Yang (Experimental)

Stephen Grot
Tansel Karabacak

Core team has capability to lead modeling and fabricate key materials required
Collaborations
FC-PAD Consortia roles

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FC-PAD (LBNL)

FC-PAD (LANL)

Make electrodes to probe model

Ion Power

Characterize electrodes

MEAs that exceed DOE’s BOL Performance Targets

FC-PAD (LANL)

FC-PAD (ORNL)

Durability Testing (ASTs)

FC-PAD (LANL & LBNL)

FC-PAD (NREL & LBNL)

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Non conventional catalysts

FC-PAD (ANL)

Build increasingly sophisticated electrode model

Improve electrode design

Cell diagnostics that highlight different losses

FC PAD can make significant contributions on every major project task

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Accomplishments & Progress

Key Project accomplishments in Q1:

- Completed sub-contracts (both done by 4/7/2017)
- Made progress on micro-structural CCL model
- Began to assess diagnostic methods at UTRC based on model cases
- Obtain MEAs from Ion Power and completed initial diagnostic testing in cells at UTRC
- Prioritized catalyst-architecture options with UALR
- Begin to engage appropriate FC PAD Consortia members
  - Assigned primary contact (R. Borup, LANL)
  - Completed FC-PAD SOW for this project
  - Obtained MEAs from LANL
  - Began to work with LBNL on modeling tasks

UTRC has recently begun to work with all of the project partners
Technical Progress: **Initial microstructure model has been developed**

- CCL geometry depends on multiple factors:
  - Composition of the component materials (*e.g.*, Pt/C wt%, Ionomer EW, I/C ratio)
  - Arrangement of these key components (*e.g.*, agglomerate size, ionomer film distribution)

**One possible arrangement** is an agglomerate structure with an outer shell of ionomer:
- For a assumed agglomerate size, can estimate number of C and Pt per agglomerate
- Can also estimate ionomer film and electrode thickness from I/C ratio
- These estimates can be verified with SEM and other electrode-characterization tools

**UTRC has begun to construct and verify some microstructure CCL models**

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- **Graph**: Number of carbon particles against agglomerate inner diameter for different conditions (30 nm C, 50 nm C, Pt on 30 nm C, Pt on 50 nm C).

- **Equation**: \(2\delta = d_{a,o} - d_{a,i}\)
**Technical Progress:** Some Limiting Cases have been identified

- Different transport-limiting mechanisms result in different limiting currents
  - Can make CCLs that help to probe these differences

\[
I_{L,1} = \frac{4F \varepsilon_b D_P y}{\tau lRT} = \frac{4F \varepsilon_b (1 - \varepsilon) D_P y}{\tau RL_{Pt} G(\omega, \gamma)}
\]

\[
I_{L,2} = I_f r_a = \frac{24F D_P y L_{Pt} G(\omega, \gamma)}{\delta d_a}
\]

\[
I_{L,3} = I_f r_{Pt} u_{Pt} = \frac{24F H D_P y L_{Pt} u_{Pt}}{\tau_f \delta \rho_{Pt} d_{Pt}}
\]

\[
I_{L,4} = I_a r_a = \frac{48F D c L_{Pt} G(\omega, \gamma)}{d_a^2}
\]

- \(L_{Pt}\) = amount of platinum in electrode, mg/cm\(^2\)
- \(\omega\) = mass fraction Pt in Pt/C catalyst
- \(\gamma\) = ionomer to carbon ratio by mass

<table>
<thead>
<tr>
<th>Case</th>
<th>Limiting transport through</th>
<th>Limiting current varies as</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Electrode thickness in gas pores</td>
<td>(L_{Pt}^{n}, n= -1)</td>
</tr>
<tr>
<td>2</td>
<td>Ionomer film, uniform consumption in agglomerate</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Ionomer film, consumption near perimeter</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>Agglomerate</td>
<td>1</td>
</tr>
</tbody>
</table>

* The diffusion coefficient increases with agglomerate diameter.

**UTRC has already begun to engage FC-PAD (LBNL) on modeling work**

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Technical Progress: Established relevance of Pt-only MEAs

- Have utilized key results from previous DOE project to assess:
  - Best in-cell diagnostic techniques
  - Initial MEA compositions
- Comparison of Pt/Ni to Pt-only MEAs with ultra-low loadings:
  - Pt/C catalyst with similar catalyst-particle size as Pt-Ni/C exhibit very similar mass-transport losses
  - Pt-only MEAs offer simple path for initial transport studies

<table>
<thead>
<tr>
<th>BOL</th>
<th>#1 PtNi</th>
<th>#2 Pt (HSA)</th>
<th>#3 Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECA</td>
<td>58</td>
<td>82</td>
<td>56</td>
</tr>
<tr>
<td>(m²/g-Pt)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass activity</td>
<td>0.53</td>
<td>0.37</td>
<td>0.28</td>
</tr>
<tr>
<td>(A/mg-Pt)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Technical Progress: Initial Results with *Ion Power* MEAs

- Comparison with state-of-the-art (SOA) Pt-only MEA
- **Ion Power** MEA exhibited:
  - Similar Pt catalyst activity
  - Superior performance at low current densities
    - Higher catalyst loading
  - Lower $iR$-drop, but higher H2-pump resistance
    - Indicative of lower proton-conductivity in electrodes
  - Slightly lower limiting currents at low O$_2$ concentrations
    - Appears to indicate slightly lower oxygen-transport

Very good initial result, some further work required to match SOA performance
**Technical Progress: Non-Conventional Catalysts**

**Density-modulated Pt and Pt-alloy thin film electrocatalysts**

Tansel Karabacak's Group, University of Arkansas at Little Rock  
Collaboration with Deborah Myers' Group at ANL

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**Goal:**
- Developing an ORR electrocatalyst with high performance and durability.

**Approach:**
- High pressure sputtering (HIPS) to modulate the density of the thin film (TF) catalyst. Pressure change results in a change in porosity, density, and strain.
- High density bottom: Strong adhesion to the substrate leading to enhanced physical and electrochemical stability of the TF by preventing leaching of Pt at the bottom and the detachment of large regions of TF from the substrate.
- Porous top: Effective transportation of oxygen, improved catalyst utilization, reduced Pt-loading, and enhanced ORR activity.

**Preliminary results:**
- Electrochemical activity of Pt-TFs with different densities/porosities is shown. UALR will investigate the effect of density, thickness, strain, and crystal structure on the ORR activity.

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**Preliminary Results:**

**Pt TFs of different porosity/density:**

- Higher porosity (lower density)

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**Graph:**

- Cyclic voltammetry curves of Pt-TFs with different densities after 3000 cycling between 0.05-1 V in N₂ saturated 0.1 M HClO₄.

- RDE profile of Pt-TFs with different densities in O₂ saturated 0.1 M HClO₄ at sweep rate 20 mV/s and rotation rate 1600 rpm.

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**Graph:**

- Electrochemical activity of Pt-TFs with various densities  
  * Mass and specific activity of Pt-TFs are compared only for three films (19, 15 and 14 g/cm³).
## Proposed Future Work

### Major goals for the next year of this project:
- Completion and validation of microstructural model using state-of-the-art MEAs with ultra-low catalyst loading (Pt/C)
- Use improved understanding of mass-transport loss mechanisms to improve CCLs & fabricate MEAs with improved performance

<table>
<thead>
<tr>
<th>Milestone I.D.</th>
<th>Tasks</th>
<th>Task Title</th>
<th>Brief Milestone Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>1</td>
<td>Program Management</td>
<td>All subcontracts completed</td>
</tr>
<tr>
<td>Q2</td>
<td>3, 4</td>
<td>Carbon-supported MEA Fabrication</td>
<td>Demonstrate SOA performance at low PGM loading</td>
</tr>
<tr>
<td>Q3</td>
<td>2</td>
<td>Model development and validation</td>
<td>Microstructural electrode model framework complete</td>
</tr>
<tr>
<td>Q4 Go/No-Go</td>
<td>2</td>
<td>Model development and validation</td>
<td>Initial carbon-supported catalyst-layer model complete and validated with SOA MEA data</td>
</tr>
<tr>
<td>Q5</td>
<td>6</td>
<td>Novel catalyst MEA Fab</td>
<td>Fabricate thin-film graded catalyst</td>
</tr>
<tr>
<td>Q6 (2Q2018)</td>
<td>3, 4</td>
<td>Carbon-supported MEA Fabrication</td>
<td>Meet 2020 performance targets with high stoichiometric flow rates</td>
</tr>
</tbody>
</table>

**Major focus in first year will be on MEAs/CCLs with conventional electrocatalysts**
Summary

- **Major barrier** to meeting DOE’s 2020 MEA Targets is *mass-transport losses in CCL*
- Sources of these losses are *currently not well understood*
- This project should enable improved understanding
- Utilize this understanding to develop MEAs that meet all of DOE’s performance targets
- Both conventional and thin-film catalysts are included

*Polarization curve for an ultra-low-loaded PtNi/C cathode*
- Raw in **blue**,
- Transport-corrected in **red**.

**Develop MEAs w/ ultra-low catalyst loadings & minimal transport losses**
TECHNICAL BACK-UP SLIDES
Technical Background: **Non-Conventional Catalysts**

**Fabrication Technique:**

**High Pressure Sputtering (HIPS)**

- **Obliquely incident sputtered atoms**
- **Ionized working-gas (e.g. Ar plasma)**
- **Sputtered atoms**
- **Substrate**
- **Sputter target**

**Enhanced Shadowing Effect:**

*Lower density (higher porosity)*

- **High working gas pressure**
- Higher number of atom-atom collisions and shorter mean free-paths
- Flux of source atoms with higher angular distribution:
  - **Obliquely incident atoms**

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Technical Progress: **Non-Conventional Catalysts**

Summary of electrochemical activity vs. porosity/density

<table>
<thead>
<tr>
<th>Density (g/cm³)</th>
<th>Porosity %</th>
<th>Mass Activity (A/mg)</th>
<th>Specific Activity (µA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>9</td>
<td>0.023</td>
<td>1159</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>0.046</td>
<td>1311</td>
</tr>
<tr>
<td>14</td>
<td>36</td>
<td>0.034</td>
<td>1331</td>
</tr>
</tbody>
</table>

Additional Preliminary results:

- Electrochemical activity of Pt-TFs with different densities/porosities.
- UALR is currently investigating the effect of density, thickness, strain, and crystal structure on the ORR activity.
Key Risk

- **Fabrication of CCLs** with *sufficient differentiation* to uniquely identify model parameters and/or sufficiently uniform ULCLs

- **FC PAD Consortia** has additional capabilities that can be used here
- LANL has already provided UTRC with ULCL MEA samples
- NREL also has MEA-fabrication capabilities
  - Thrust 2: “Electrode Layers”
  Coor: Shyam Kocha

Figure from: R. Borup, 2016 AMR: “FC-PAD Consortium Overview” (FC135)
Key Risk

- Capability to **adequately characterize structures** for accurate input into the geometric models

- **FC PAD Consortia** has world-class capabilities that can be used here

- Especially valuable in assessing:
  - Ionomer-film dimensions and primary pore sizes & volume
    - Example: HAADF-STEM
  - Pt particle sizes and pore structures in thin-film catalysts
    - Ex: Electron Tomography

Figures from: K. More, 2016 AMR Presentation (FC020) showing ionomer dispersion in CCLs
Key Risk

- Availability of **sufficient quantities of alternative catalysts** (e.g., thin-film and/or nanoframe structures) to support the fabrication of MEAs by conventional techniques
- FC PAD Consortia has world-class capabilities that can be used here
- NREL has experience in fabricating MEAs with Thin-Film catalysts
  - Use MEA fabrication methods that work with relatively small quantities of catalysts
- ANL also has extensive capabilities to make alternative electrocatalysts
  - This is **not** part of FC-PAD Consortia, but is still a possible source of materials

Figure from: V. Stamenkovic, 2016 AMR (FC140)