Transport in PEMFC Stacks

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Project ID #
FC054
Transport in PEMFC Stacks

Timeline
• Project Start Date: 11/1/2009
• Project End Date: 8/31/2013
• Percent Complete: 60%

Budget
• Total Project Funding: $3.340M
  – DOE Share $2.662M
  – Cost Share $0.678M
• Funding Received in FY11: $786K
• Planned Funding for FY12: $300K

Barriers Addressed
• Performance
• Water Transport within Stack
• System Thermal and Water Management
• Start-Up and Shut Down

Technical Targets
• Cold Start-up Times
• Specific Power Density
• Stack Power Density
• Stack Efficiency

Partners
• University of South Carolina
• Virginia Tech
• Tech Etch
• Engineered Fiber Technologies
Approach: Team and Tasks

Objective: Improve Understanding/Correlation Between Material Properties and Model Equations

- Generate model
- Supply model relevant transport numbers
- Stress the model by developing different materials with different transport properties
- Determine sensitivity of fuel cell performance to different factors
- Guide research

Milestone Plan Complete Actual Complete

Baseline PFSA model, with overall results correlating within +/-20% of each other. Design the new apparatus for extending the range of electroosmotic drag and diffusivity.

Plan Complete: 4/15/2011
Actual Complete: 4/1/2011

Extend Model to a variety of membranes, catalyst content, GDM’s, and flow fields. The model should be able to demonstrate prediction of the actual data within +/-20% of the experimental results.

Plan Complete: 8/15/2012
Actual Complete: 60%
Approach & Milestones

<table>
<thead>
<tr>
<th>Year</th>
<th>Techniques</th>
<th>Materials</th>
<th>Modeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year 1</td>
<td>New technique generation for static and dynamic diffusion, EODC, through plane conductivity confirmation with Baseline materials. (90%) Current Distribution Board Demonstration (100%)</td>
<td>Baseline hydrocarbon PEM generated and down selected (80%) Baseline Gas diffusion Media Delivered (100%) First Etched Plates (100%)</td>
<td>Set-Up of Model Use of Baseline materials for Testing Model Sensitivity Testing</td>
</tr>
<tr>
<td>Year 2</td>
<td>Techniques applied to alternative materials. Diffusivity apparatus used to characterize alternative diffusion media.</td>
<td>Scale-up of Baseline PEM Integration of catalysts Modification of diffusion media Alternative Plates &amp; Design of larger plates.</td>
<td>Performance and water balance modeled and confirmed with baseline materials and hydrocarbon PEM. (50%) Alternative diffusion media tested.</td>
</tr>
<tr>
<td>Year 3</td>
<td>Low Temperature Studies</td>
<td>Delivery of Large PEMs Current Distribution board for larger plate Fabrication of larger plate and current distribution board</td>
<td>Modeling extended to larger cells. Effect of coolant/heat transfer. Model confirmation with current distribution and water balance.</td>
</tr>
<tr>
<td>(Period 2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Relevance: Use of Modeling in Fuel Cell Development is Widespread. Agreement on Fundamentals is Not.

- In developing a model for transport in fuel cell systems, the first thing that is needed is the key transport numbers
  - Diffusivity
  - Water Uptake
  - Electro-osmotic Drag
  - Through Plane Conductivity
- NOTHING EVEN RESEMBLING CONSENSUS ON THESE FUNDAMENTALS
- Systematic approach of generating and developing various materials with better characterization methods is needed

T.F. Fuller, Ph.D. Thesis, University of California, Berkeley, CA (1992)
Achievements: New Membranes: HQS100-6FPAEB

BPSH100* \[ \text{Chemical Formula: C}_{24}\text{H}_{16}\text{O}_{10}\text{S}_{3} \]  \[ \text{Molecular Weight: 560.57} \]  
IEC = 3.57 meq/g  
*BiPhenol Sulfone, 100% sulfonated H$^+$ form

HQSH100* \[ \text{Chemical Formula: C}_{18}\text{H}_{12}\text{O}_{10}\text{S}_{3} \]  \[ \text{Molecular Weight: 484.48} \]  
IEC = 4.13 meq/g  
*Hydroquinone Sulfone, 100% sulfonated H$^+$ form

SQSH* \[ \text{Chemical Formula: C}_{18}\text{H}_{12}\text{O}_{10}\text{S}_{3} \]  \[ \text{Molecular Weight: 564.54} \]  
IEC = 5.31 meq/g  
*Sulfonated Quinone-Sulfone, H$^+$ form

- Provide design guidelines for PEMs on impact of structure and segregation of charges
- Giner to use polymer powders to determine fundamental properties, generate MEAs
- USC to use model to predict performance based on fundamental properties

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Achievements: New Membranes: MEA Fabrication

Solution Cast

Giner: Membrane cast & characterization: water uptake, diffusivity, electro-osmotic drag coefficient (EODC), MEA fabrication

Decal Transfer

VA Tech: Polymer Synthesis

50cm² GM plates

50cm² FCT plates

South Carolina: Performance evaluation and model validation
Achievements: New Technique: Simultaneous Water Uptake and Diffusivity

Non-membrane diffusion is eliminated by avoiding inerts in the system

• Automation of dynamic system assures continuous diffusivity measurements at a variety of relative humidity;
• Process simple, effective, and accurate, open to other researchers in fuel cell community

N212 at 80°C
Achievements: New Technique: Simultaneous Water Uptake and Diffusivity

Operation T: 80°C

Similar Isotherms seen for both PFSA and hydrocarbon-based ionomers
Diffusivity of PFSA > Block Hydrocarbons in H⁺ form >> Na⁺ form

Nafion is a registered trademark of E.I. du Pont de Nemours and Company
Achievements: New Technique: EODC

- Water/H₂ inlet ratio controlled by controlling saturator temperature and H₂ pressure
- If ratio is too high, not enough water is dragged across and cell floods and fails
- If ratio is too low, membrane dries out and cell fails
- At Water/H₂ = 2*EODC Cell operates in quasi-stable state

All gas/gas diffusion is eliminated
Achievements: New Technique: EODC

Nafion® 115, 80 °C and 82% RH, 100 mA/cm²

- EODC of hydrocarbon-based materials slightly lower, but similar trend
- Still working on consensus

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Achievements: New Materials: Diffusion Media

- Ballard added to the program recently
- Started with Toray Materials
  - Variable Wet-Proofing
  - Microporous Layer
- Ballard will provide more custom materials
- Want to generate differences in:
  - MacMullin Number
    - Porosity
    - Tortuosity
  - Hydrophobicity

**Tortuosity**
- Ratio of the actual path length through the pores to the shortest linear distance between two points.

\[
\tau = \frac{L}{t}
\]

**Porosity**
- Ratio of void volume (volume of pores) to the total volume.

\[
\varepsilon = \frac{V_{\text{Pores}}}{V_{\text{Total}}}
\]

**MacMullin Number**
- Function of tortuosity and porosity.

\[
N_M = f(\tau, \varepsilon) = \frac{\tau^n}{\varepsilon^m}
\]
Achievements: Design of Gas Diffusion Media

Baseline Material at start of program was Toray H060

The new design of GDLs have been modified from standard Ballard GDLs by adding two micro porous layers. Each set has been treated with two different methods in order to provide two different values of diffusivity.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Diffusivity Modification</th>
<th>MPL 1/MPL2 (carbon particle size)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P50</td>
<td>Low</td>
<td>Small/Large</td>
</tr>
<tr>
<td>EP40</td>
<td>Low</td>
<td>Small/Large</td>
</tr>
<tr>
<td>P75</td>
<td>High</td>
<td>Large/Small</td>
</tr>
</tbody>
</table>
Achievements: Design of Gas Diffusion Media
Comparison of Mercury pore size distributions of new design GDLs

Baseline Substrates

Modified Substrates

EP40T has largest pore volume, concentrated at 50 µm

Modification greatly reduces volume of large pores

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Achievements: Design of Gas Diffusion Media

Gore 57 Series 80°C

- P75T GDL shows the highest performance at lower humidity condition whereas EP40T shows the highest performance at higher humidity condition.
- P75T will be used in the anode and EP40T will be used in the cathode in following baseline testing.
Achievements: Design of Gas Diffusion Media: Wet Proofing

MacMullin number as function of wet proofing in substrate and MPL

MacMullin number as function of porosity

Difficult to make general relationship of $N_M(\varepsilon)$

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Achievements: Fuel Cell Flow-Fields

50-cm² USC-serpentine flow-field

Serpentine Hardware (Fuel Cell Technologies)
- Legacy Hardware
- Most Common

Thin Metal Plates (Tech Etch USC Design)
- Closer to Automotive
- Allows minimization of pressure drop to flow fields

Thin Graphite Plates (GM)
- Also common
- Open design allows comparison/collaboration

Current Distribution Boards Designed for All 3
Achievement: Model Verification: Serpentine

At potential=0.3V

Anode 25%RH, Cathode 25%RH
Average current density = 809 mA/cm²

Anode 75%RH, Cathode 25%RH
Average current density = 1094 mA/cm²

Anode 100%RH, Cathode 50%RH
Average current density = 1250 mA/cm²

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Achievements: Flow Field Modeling: Thin Metallic Plates

Operating condition:
Anode Stoich. = 1.5
Anode RH = 100%
Cathode Stoich. = 2.0
Cathode RH = 50%
Tcell = 80°C
System pressure = 136kPa

High Current Wet
- High $i$/Wet
- Low $i$/Dry

Low Current Dry
- Operating condition:
  Anode Stoich. = 1.5
  Anode RH = 25%
  Cathode Stoich. = 2.0
  Cathode RH = 25%
  Tcell = 80°C
  System pressure = 101kPa

Average current density = 1200 mA/cm²
Average current density = 294 mA/cm²

This presentation does not contain any proprietary, confidential, or otherwise restricted information.
Achievement: Model Verification:
Distributions of current density and temperature of 50-cm² GM-Down-the-Channel flow-field compared with www.pemfcdata.org

(I_{avg} = 1.5 \, A/cm², \textit{counter-current flow}: 50/50\%RH, 150/150kPa, 80°C, 1.5/2.0 \textit{stoich})

Current Distribution

Temperature Distribution

USC data matches published data very well, both with performance and model results
Achievement: Model Verification:

Water Balance experiment and numerical result of GM Down-the-Channel flow-field
(counter-current flow: 50/50%RH, 101/101kPa, 80°C, 1.5/2.0 stoich)

New Transport Numbers Greatly Improve Prediction of Water Mass Balance

<table>
<thead>
<tr>
<th></th>
<th>i A/cm²</th>
<th>RH</th>
<th>Anode Water Balance (mg/sec)</th>
<th>Cathode Water Balance (mg/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Water in</td>
<td>Water out</td>
</tr>
<tr>
<td>EXP</td>
<td>0.4</td>
<td>50</td>
<td>0.86</td>
<td>0.34</td>
</tr>
<tr>
<td>CFD(new)</td>
<td>0.4</td>
<td>50</td>
<td>0.90</td>
<td>0.33</td>
</tr>
<tr>
<td>CFD(old)</td>
<td>0.4</td>
<td>50</td>
<td>0.90</td>
<td>0.37</td>
</tr>
<tr>
<td>EXP</td>
<td>0.8</td>
<td>50</td>
<td>1.7</td>
<td>1.26</td>
</tr>
<tr>
<td>CFD(new)</td>
<td>0.8</td>
<td>50</td>
<td>1.72</td>
<td>1.30</td>
</tr>
<tr>
<td>CFD(old)</td>
<td>0.8</td>
<td>50</td>
<td>1.72</td>
<td>0.86</td>
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</table>
Future Work

• Period 1 (8/31/12)
  – Membrane Synthesis
    • Finish Characterization of SQS Based Materials
    • Scale up production of select membranes
  – Materials Characterization
    • Diffusion and water transport of various GDL
    • Continue Characterization of new materials
  – Modeling/Performance
    • New Membranes
    • New Diffusion Media
    • Concentrate on mixed flow conditions

• Period 2
  – Generate larger membranes
  – Extend characterizations to sub-ambient regions
  – Finish characterizations of alternative materials, develop non-empirical models
  – Utilize GM hardware for short stack performance/modeling
SUMMARY

• Membrane design and development, McGrath’s group at VA Tech:
  - Completed the synthesis of a full list of hydroquinone based hydrophilic-hydrophobic block copolymers (HQSH-6FPAEB).
  - Provided ~20g of the 6FPAEB-BPSH and 6FPAEB-HQS100 polymer powders to Giner for member casting and testing.

• Membrane Characterization And Performance Testing at Giner:
  - Successfully casted copolymer powders from VA Tech to membranes
  - Automated dynamic water uptake/diffusivity test system
  - Completed diffusivity measurements of VA Tech membranes
  - Measure EODC measurements of Nafion® membrane using dead-ended H₂ pump
  - Obtained GM plates and flow paths and provided MEAs for testing

• Transport Modeling, GDL & Current Distribution Board Characterization at USC:
  - Designed new GDLs and completed pore size distributions with fuel cell performance test;
  - Simulated cell performance and current distribution at various water uptake, membrane diffusivity and electro-osmotic drag coefficient (EODC);
  - Compared modeling results with segmented cell data for both serpentine and parallel flow-fields;
  - Completed simulation of GM Down-the-Channel fuel cell and compared with available data
  - Validated modeling result with water balance experiment.
Technical Back Up Slides
Modeling Input Parameters

Material Properties

Material 1: Anode Side Fluid
- Density (ρ): 23.36 g/mole
- Viscosity (μ): 1.81e-05 kg/m-s
- Conductivity (k): 0.02637 W/m-K
- Spec. Heat (Cp): 1006 J/kg-K

Material 2: Cathode Side Fluid
- Density (ρ): 23.36 g/mole
- Viscosity (μ): 1.81e-05 kg/m-s
- Conductivity (k): 0.02637 W/m-K
- Spec. Heat (Cp): 1006 J/kg-K

Material 3: MEA Solid
- Density (ρ): 200 kg/m³
- Conductivity (k): 0.16 W/m-K
- Spec. Heat (Cp): 500 J/kg-K

Material 4: Bipolar Solid Plates
- Density (ρ): 200 kg/m³
- Conductivity (k): 15.7 W/m-K
- Spec. Heat (Cp): 500 J/kg-K

Porous Resistance Coefficients

Porous Media 1: Anode Side GDM
- α (X-Direction): 0
- β (X-Direction): 2.0e+07
- α (Y-Direction): 0
- β (Y-Direction): 2.0e+07
- α (Z-Direction): 0
- β (Z-Direction): 2.0e+07
- Porosity Factor (-): 0.7
- Effective Conductivity (W/m-K): 0.25

Write Operating Conditions Input File

Operating Parameters
- Initial Cell Voltage for all Cells (V): 0.72
- Membrane Thickness (mm): 0.018
- Anode GDM Thickness (mm): 0.260
- Cathode GDM Thickness (mm): 0.260
- Cell Temperature (°C): 80
- Dry Membrane Density (g/cm³): 2
- Equiv Wt. of Dry Membrane (g/mmol): 1106

Electrochemical and Kinetic Parameters
- Open Circuit Voltage (V): 0.92
- Oxygen Diff. Current Density (Am²): 500
- Anode Transfer Coefficient (-): 2
- Cathode Transfer Coefficient (-): 0.717
- Hydrogen Inlet Mole Fraction (-): 0.763
- Oxygen Inlet Mole Fraction (-): 0.160

Other Parameters
- Evaporation / Condensation Rate (s⁻¹): 1.0
- Starting Iteration for Reacting Flow: 50
- No. of Cells in z-dir in the Anode GDM: 5
- No. of Cells in z-dir in the Cathode GDM: 5
- No. of Fuel Cells in the Model: 1
- Average Current Density (Am²): 0.4

Auto-adjust Cell Voltage (V/CEL)

Write Operating Conditions Input File
Modeling Input Parameters (Cont.)

**Constitutive Equation Panel (Advanced)**

**Input of Coefficients of Parametric Constitutive Equations**

- **Main Equations**
- **Water Diff. Equation**
- **Overpot. Equation**
- **Electrical Properties**

**Membrane Properties** are a function of:
- Anode water activity
- Cathode water activity
- Average between anode and cathode water activities

**Water Content in the Membrane (λnba)**
- \(B_1 = 0.043\)
- \(B_2 = 17.81\)
- \(B_3 = -33.65\)
- \(B_4 = 36.0\)

**Electro-osmotic Drag Coefficient (η)**
- \(E_1 = 0.05\)
- \(E_2 = 0.0029\)

**Local Membrane Conductivity (σnba)**
- \(H_0 = 0.0\)
- \(H_1 = 0.514\)
- \(H_2 = 0.326\)

**Water Diffusion Coefficient (D)**
- \(G_0 = 2416.0\) (K)
- \(G_1 = 1\times10^{-10}\) (m²/s)
- \(G_2 = 1\times10^{-10}\) (m²/s)
- \(G_3 = 1.25\times10^{-10}\) (m²/s)
- \(G_4 = 303.0\) (K)

**Membrane Water Content Range (λnba)**
- \(L_1 = 1.67\)
- \(L_2 = 2.0\)
- \(L_3 = 3.0\)
- \(L_4 = 4.5\)

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Modeling Outputs

### Scalars

#### Active Scalars
- Description: Description of the scalar.
- No.: Number identifier of the scalar.
- Name: Name of the scalar.

<table>
<thead>
<tr>
<th>Description</th>
<th>No.</th>
<th>Name</th>
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<tbody>
<tr>
<td>Nitrogen Gas</td>
<td>1</td>
<td>N2</td>
</tr>
<tr>
<td>Hydrogen Gas</td>
<td>2</td>
<td>H2</td>
</tr>
<tr>
<td>Oxygen Gas</td>
<td>3</td>
<td>O2</td>
</tr>
<tr>
<td>Water Vapor - Anode</td>
<td>4</td>
<td>WVA</td>
</tr>
<tr>
<td>Water Vapor - Cathode</td>
<td>5</td>
<td>WVC</td>
</tr>
<tr>
<td>Liquid Water - Anode</td>
<td>6</td>
<td>LWA</td>
</tr>
<tr>
<td>Liquid Water - Cathode</td>
<td>7</td>
<td>LWC</td>
</tr>
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</table>

#### Passive Scalars

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Current Density</td>
<td>8</td>
<td>CD</td>
</tr>
<tr>
<td>Net Water Flux per Proton</td>
<td>9</td>
<td>ALPHA</td>
</tr>
<tr>
<td>Kinetic Overpotential</td>
<td>10</td>
<td>KOP</td>
</tr>
<tr>
<td>Anode Overpotential</td>
<td>11</td>
<td>AOP</td>
</tr>
<tr>
<td>Cathode Overpotential</td>
<td>12</td>
<td>COP</td>
</tr>
<tr>
<td>Membrane Conductivity</td>
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<td>MC</td>
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<tr>
<td>Water Diffusivity</td>
<td>14</td>
<td>WDC</td>
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<tr>
<td>Water Content Inside MEA</td>
<td>15</td>
<td>LAMBDA</td>
</tr>
<tr>
<td>Anode Activity</td>
<td>16</td>
<td>AA</td>
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<td>Cathode Activity</td>
<td>17</td>
<td>CA</td>
</tr>
<tr>
<td>MEA Liquid Film Thickness</td>
<td>18</td>
<td>LFT</td>
</tr>
</tbody>
</table>

| Local MEA Voltage*           | 20  | MEA_POTENT, |
| * Only used when Electron Transport is On |

#### Generic Scalars

<table>
<thead>
<tr>
<th>Description</th>
<th>No.</th>
<th>Name</th>
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</thead>
<tbody>
<tr>
<td>Potential*</td>
<td>19</td>
<td>POTENTIAL</td>
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</table>

* Only used when Electron Transport is On