Transport in PEMFCs

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Project ID #
FC054
Transport in PEMFCs

Timeline
- Project Start Date: 10/5/2009
- Project End Date: 4/30/2014
- Percent Complete: 95%

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
- AvCarb

Timeline
- Project Start Date: 10/5/2009
- Project End Date: 4/30/2014
- Percent Complete: 95%

Budget
- Funding in FY13: $560K
- Planned FY 14 DOE Funding $0K
- Total Project Funding
  - DOE Share $2.66M
  - Cost Share $678K (20%)
Outline

• Background and Introduction
• Hydrocarbon (HC) PEM development
• Membrane Transport Property Characterization
• HC Based PEM Fuel Cell Performance and Modeling
• Current Distribution Board Design and Modeling
• Fuel Cell Flow-Field Design and Modeling
• GDL Design and Modeling
• Summary
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. | 4/15/2011 | 4/1/2011
Extend Model to a variety of membranes, catalyst content, GDM's, and flow fields. The model should be able demonstrate prediction of the actual data within +/-20% of the experimental results. | 8/15/2012 | 90%
## Approach & Milestones

<table>
<thead>
<tr>
<th>Year</th>
<th>Techniques</th>
<th>Materials</th>
<th>Modeling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>New technique generation for static and dynamic diffusion, EODC, through plane conductivity confirmation with Baseline materials.</td>
<td>Baseline hydrocarbon PEM generated and down selected Baseline Gas diffusion Media Delivered First Etched Plates</td>
<td>Set-Up of Model Use of Baseline materials for Testing Model Sensitivity Testing</td>
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<tr>
<td></td>
<td>Current Distribution Board Demonstration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Year 1</td>
<td>Techniques applied to alternative materials. Diffusivity apparatus used to characterize alternative diffusion media (33%).</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 2</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>Year 3 (Period 2)</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Work on larger cells abandoned in favor of using GM “open source” hardware

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Use of Modeling in Fuel Cell Development is Widespread. Agreement on Fundamentals is not

- **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)


Relevance:

**PEM Development**

- Hundreds of PEMs developed for fuel cells
  - Would like to come up with design rules for PEMs
  - How does size/degree of Phase separation affect
    - Conductivity
    - EODC
    - Water Diffusivity
    - Gas Permeability
  - Similar Study done by *Gross et al* for side-chain polymers

**Modeling**

- Need to make sure we know how changes in transport numbers effect fuel cell performance
- Transport numbers and model are used to confirm each other
- How sensitive is fuel cell performance to these different parameters?
- What should we be working on?
Achievement 1: New Membranes

**BPSH100***

![Chemical structure of BPSH100]

Chemical Formula: C₁₈H₁₂O₁₃S₄⁻⁻
Molecular Weight: 560.57

IEC = 3.57 meq/g
*BiPhenol Sulfone, 100% sulfonated H⁺ form

**HQSH100***

![Chemical structure of HQSH100]

Chemical Formula: C₁₈H₁₂O₁₀S₃⁻⁻
Molecular Weight: 484.48

IEC = 4.13 meq/g
*Hydroquinone Sulfone, 100% sulfonated H⁺ form

**SQSH***

![Chemical structure of SQSH]

Chemical Formula: C₁₈H₁₂O₁₀S₃⁻⁻
Molecular Weight: 564.54

IEC = 5.31 meq/g
*Sulfonated Quinone-Sulfone, H⁺ form

- Goals:
  - Provide design guidelines for PEMs on impact of structure and segregation of charges
  - Provide materials for model test at various transport properties like conductivity, water uptake, diffusivity, and EODC
- 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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Copolymer Membrane Design

- **Matrix 1: Varied Block Lengths, Annealing Temperature and IEC**

![Chemical structure of 6FAEB-BPS100](image)

- **Matrix 2: Varied Oligomer Categories/Properties**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Block Copolymer</th>
<th>Block Length</th>
<th>IEC (meq/g)</th>
<th>Water Uptake (%)</th>
<th>Conductivity (S/cm)</th>
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</thead>
<tbody>
<tr>
<td>JR-143-2</td>
<td>6FK-BPSH</td>
<td>8K – 8K</td>
<td>1.45</td>
<td>21</td>
<td>0.10</td>
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<tr>
<td>JR-143-3</td>
<td>6FPAEB-BPSH</td>
<td>13K – 13K</td>
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<td>0.14</td>
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<tr>
<td>JR-143-4</td>
<td>6FBPS0-BPSH</td>
<td>10K – 10K</td>
<td>1.47</td>
<td>35</td>
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</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Thermal Treatment Temperature (°C)</th>
<th>IEC (meq/g)</th>
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</thead>
<tbody>
<tr>
<td>6FPAEB-BPSH100 7k-7k</td>
<td>110</td>
<td>1.55</td>
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<tr>
<td>6FPAEB-BPSH100 15k-15k</td>
<td>110</td>
<td>1.55</td>
</tr>
<tr>
<td>6FPAEB-BPSH100 10k-18k</td>
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<tr>
<td>6FPAEB-BPSH100 10k-18k</td>
<td>220</td>
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</table>

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New Membranes based MEA Fabrication

Solution Cast

4" x 4"

Decal Transfer

50cm² FCT plates

VA Tech: Polymer Synthesis

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

South Carolina: Performance evaluation and model validation

50cm² GM plates
Achievement 2
New Technique for Water Uptake and Diffusivity

Dynamic Water uptake

Static Water uptake

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Simultaneous Water Uptake and Diffusivity

Operation T: 80°C

- BPSH-6FPAEB Membranes show nearly identical water uptake with little temperature dependence.
- Water Diffusivity is ~½ that of Nafion® regardless of temperature;
- Phase separation on a smaller scale results in lower diffusivity. Annealing increases phase separation and diffusivity.
Achievement 3: New Technique for 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
Correlation EODC to Copolymer Structure

- All hydrocarbon membranes exhibit lower EODC than Nafion®;
- Higher thermal annealing, block lengths and IEC seem to increase EODC;
- Increasing hydrophobic difference between functional and non-functional group leads to higher EODC.
Achievement 5: Current Distribution Board (CDB) Design

- We run the test for 10 segments with 3 Amp DC current
- Condition
  - Whole H090 and silicone gasket
  - Cut 10 pieces H090 with silicone

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CDResult for Cut GDL

- Uniform current distribution along each segment with cut GDL with a maximum of 0.9% error to the true applied current of 3 Amps.
Achievement 4: VT Membrane Based Performance and Water Distribution

- VT’s Lower EODC leads to less flooding at high relative humidity;
- Model and exp. validation

80°C, 1.5/2.0 stoich, \( H_2/Air: \text{GDL - EP40T} \)

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Comparison of Simulated Water Uptake and Liquid Water Film

$\lambda_{AVG} = 9.8$

$\lambda_{AVG} = 9.4$

Nafion 112

Hydrocarbon (VT)

Liquid water film thickness (mm) on cathode MEA surface under high RH (95%/95%)
Local Distributions of Current Density & Water Transport on the Membrane Surface at low inlet RH at 0.4 A/cm²

At dry condition: no liquid water is presented in fuel cell

Current density (A/cm²)

Water flux across membrane (mg/cm²·s)

Operating condition:
- Anode Stoich. = 1.5
- Anode RH = 75%
- Tcell = 80°C
- Cathode Stoich. = 2.0
- Cathode RH = 25%
- System pressure = 101 kPa
- $i_{\text{avg}} = 0.4$ A/cm²

VT membrane shows slightly lower performance but more uniformity in distributions of both current density and water transport across membrane.
Achievement 6: Design of 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

50-cm² USC-parallel flow-field (In-progress)

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

Current Distribution Boards Designed for All 3
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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Model Verification: 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

Model Predicts Equally Well
• 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

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Achievement 7: Design 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.

\[ N_M = f(\tau, \varepsilon) = \frac{\tau^n}{\varepsilon^m} \]
MacMullin number as function of wet proofing in substrate and MPL

Difficult to make general relationship of \( N_M(\varepsilon) \)
Gas Diffusion Media Design

**Baseline Material**: Toray H060

**New design of GDLs** modified from standard AvCarb 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>
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<tbody>
<tr>
<td>P50</td>
<td>Low</td>
<td>Small/Large</td>
</tr>
<tr>
<td>EP40</td>
<td>High</td>
<td>Large/Small</td>
</tr>
<tr>
<td>P75</td>
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</table>

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## Baseline and Advanced GDLs

<table>
<thead>
<tr>
<th>Substrate</th>
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<th>MPL1</th>
<th>MPL2</th>
<th>MacMullin No.</th>
<th>Status</th>
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<tr>
<td>P75</td>
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<td>Small</td>
<td>Large</td>
<td>2.63</td>
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<tr>
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<td>High</td>
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<td>Large</td>
<td>2.62</td>
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</tbody>
</table>

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Structure of EP40T-based GDLs

High-diffusivity Substrate Surface

low-diffusivity substrate surface

EP40T - standard

Small Particle Surface

EP40 High – Large/Small

Large Particle Surface

EP40 High – Small/large

EP40 Low – Large/Small

EP40 Low – Small/large

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Structure of P75T-based GDLs

High-Diffusivity Substrate Surface

Small particle surface

Large particle surface

Low-Diffusivity Substrate surface

P75 High – Large/Small

P75 Low – Large/Small

P75T - Standard

P75 High – Small/large

P75 Low – Small/large

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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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The Effect of GDL Structure

- **0.8V**
- **0.6V**
- **0.4V**

25/25RH 75/25RH 100/50RH with 5PSI
The Effect of Different Substrate

Diffusivity: High MPL1: Large MPL2: Small

Diffusivity: Low MPL1: Large MPL2: Small

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The Effect of Different Substrate

Diffusivity: High MPL1: Small MPL2: Large

![Graph showing potential vs. current density for different conditions.]

Diffusivity: Low MPL1: Small MPL2: Large

![Graph showing potential vs. current density for different conditions.]

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The Effect of Different Substrate

Diffusivity: High MPL1: Large MPL2: Small – $I_{avg} = 1A/cm^2$

Current density distribution ($A/cm^2$)

EP40

P50

P75

Membrane water content

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The Effect of Different Substrate

Diffusivity: Low MPL1: Large MPL2: Small – Iavg = 1A/cm²

Current density distribution (A/cm²)

EP40

P50

P75

Membrane water content

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Summary

- Membrane design and development (VA Tech) & Characterization (Giner):
  - Membranes with similar charge densities but different
  - Increased hydrophobicity of the non-functional group, longer block lengths and annealing all lead to a more distinct separation of phases, on a larger length scale

- Design of Current Distribution Board, Flow Field, GDL (Giner and USC) towards transport property improvement and better characterization

- Modeling of GDL, current distribution board, and flow fields successfully predicts:
  - Dry, Wet Conditions. Hydrocarbon and PFSA membranes
  - Performance and Water Balance
  - Increased flooding for PFSA membranes compared to hydrocarbon membranes
Publications/Presentations

- **Cortney Mittelsteadt et al.**
  - Simultaneous Water Uptake, Diffusivity and Permeability Measurement of Perfluorinated Sulfonic Acid Polymer Electrolyte Membranes, ECS Transactions, 41 (1) 101-121 (2011)
  - Novel Current Distribution Board for PEM Devices, ECS Transactions, 41 (1) 549-559 (2011)
  - Novel System for Characterizing Electro-Osmotic Drag Coefficient of Proton Exchange Membranes”, presented in 220th meeting of ECS, Abstract #1304, Honolulu, October 2012
  - Characterizing Water Transport Properties of Hydrocarbon Block Copolymer Proton Exchange Membranes”, in 222th meeting of ECS, Abstract #1344, San Francisco, October 2013

- **John VanZee et al.**
  - A novel current distribution board to understand local transport in PEMFCs, presented in 220th meeting of ECS, Abstract #1545, Honolulu, October 2012

- **James McGrath et al.**
  - Synthesis and characterization of multiblock semi-crystalline hydrophobic poly(ether ether ketone)-hydrophilic disulfonated poly(arylene ether sulfone) copolymers for proton exchange membranes, Chen, Yu; Lee, Chang Hyun; Rowlett, Jarrett R.; McGrath, James E. *Polymer* (2012), 53(15), 3143-3153.