Transport in PEMFCs

Giner, Inc.
Hui Xu
Junqing Ma
Shelly Brawn
Cortney Mittelsteadt (PI)

University of South Carolina
Sirivatch Shimpalee
Visarn Lilavivat

AvCarb
(Formerly Ballard Materials)
Don Connors
Guy Ebbrell
Jason Morgan

University of Alabama
John VanZee

Virginia Tech
James McGrath
Yu Chen
Jarrett Rowlett
Andy Shaver
Chang Hyun Lee

Tech Etch
Kevin Russell

Project ID # FC054

Transport in PEMFCs

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%)

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

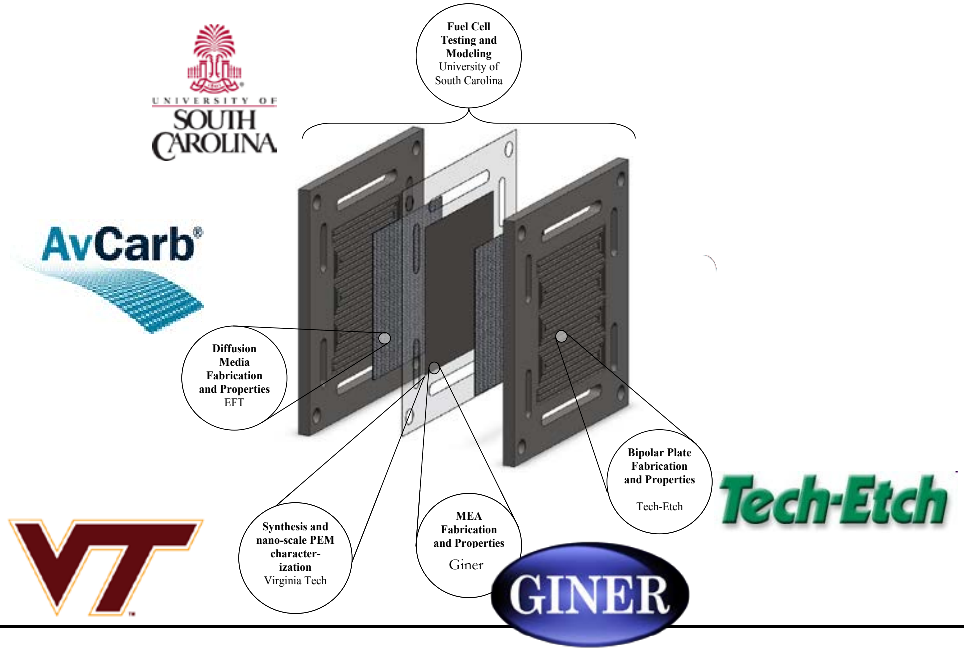
- University of South Carolina
- Virginia Tech
- Tech Etch
- AvCarb

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

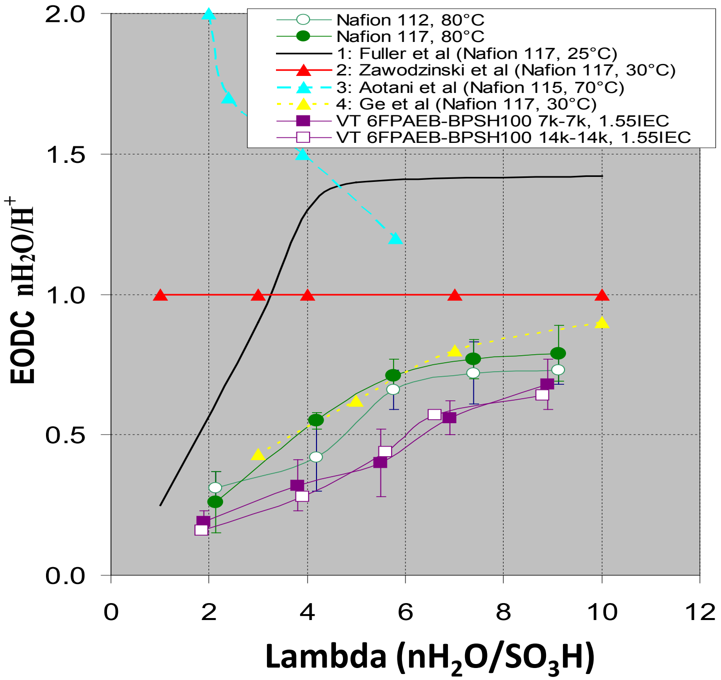
Milestone	Plan Complete	Actual Complete
Baseline PFSA model, with overall results correlating within +-20% of each other. Design the new apparatus for extending the range of electroosmotic drag and diffusivity.	4/15/2011	4/1/2011
Extend Model to a variety of membranes, catalyst content, GDM's, and flow fields. The model should be able demonstrate prediction of the actual data within +-20% of the experimental results.	8/15/2012	90%

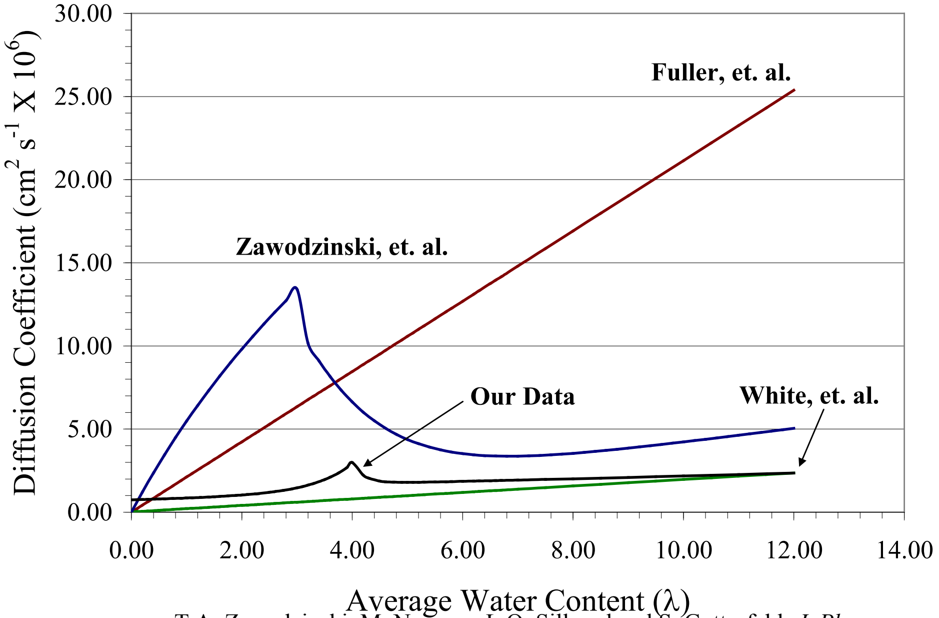
Approach & Milestones

	Techniques	Materials	Modeling
Year 1	New technique generation for static and dynamic diffusion, EODC, through plane conductivity confirmation with Baseline materials. Current Distribution Board Demonstration	Baseline hydrocarbon PEM generated and down selected Baseline Gas diffusion Media Delivered First Etched Plates	Set-Up of Model Use of Baseline materials for Testing Model Sensitivity Testing
Year 2	Techniques applied to alternative materials. Diffusivity apparatus used to characterize alternative diffusion media (33%).	Scale-up of Baseline PEM Integration of catalysts Modification of diffusion media Alternative Plates & Design of larger plates.	Performance and water balance modeled and confirmed with baseline materials and hydrocarbon PEM. (50%) Alternative diffusion media tested.
Year 3 (Period 2)	Low Temperature Studies	~~Delivery of Large PEMs~~ ~~Current Distribution board for larger plate~~ ~~Fabrication of larger plate and current distribution board~~	Modeling extended to larger cells. Effect of coolant/heat transfer. Model confirmation with current distribution and water balance.

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

Use of Modeling in Fuel Cell Development is Widespread. Agreement on Fundamentals *is not*





T.A. Zawodzinski, M. Neeman, L.O. Sillerud and S. Gottesfeld, *J. Phys. Chem.*, **95**, 6040 (1990)
T.F. Fuller, Ph.D. Thesis, University of California, Berkeley, CA (1992)
T.V. Nguyen and R.E. White, *J. Electrochem. Soc.*, **140**, 2178 (1993)
Equations of the form of: S. Motupally, A.J. Becker and J.W. Weidner, *J. Electrochem. Soc.*, **147**, 3171 (2000)

- *NOTHING EVEN RESEMBLING CONSENSUS ON THESE FUNDAMENTALS*
- Systematic approach of generating and developing various materials with better characterization methods is needed

Relevance:

PEM Development

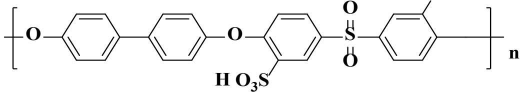
- Hundreds of PEMs developed for fuel cells
    - – Would like to come up with design rules for PEMs
    - – How does size/degree of Phase separation affect
        - Conductivity
        - EODC
        - Water Diffusivity
        - Gas Permeability
    - – Similar Study done by *Gross et al* for side-chain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

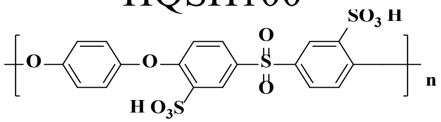


Chemical Formula: $C_{24}H_{16}O_{10}S_3^{\cdot\cdot}$
Molecular Weight: 560.57

IEC = 3.57 meq/g

**BiPhenol Sulfone, 100% sulfonated H^+ form*

HQSH100*

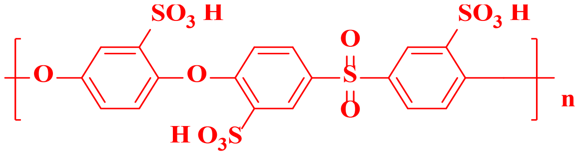


Chemical Formula: $C_{18}H_{12}O_{10}S_3^{\cdot\cdot}$
Molecular Weight: 484.48

IEC = 4.13 meq/g

**Hydroquinone Sulfone, 100% sulfonated H^+ form*

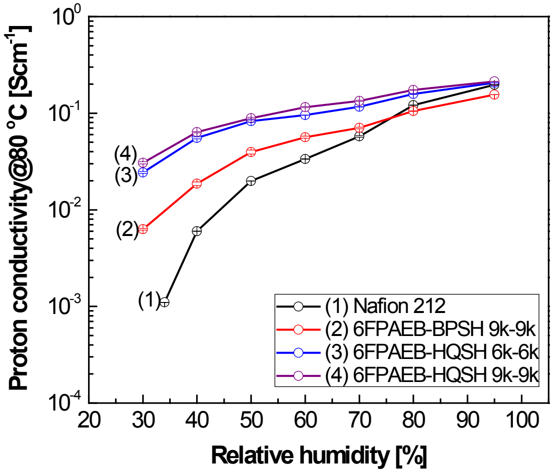
SQSH*



Chemical Formula: $C_{18}H_{12}O_{13}S_4^{\cdot\cdot}$
Molecular Weight: 564.54

IEC = 5.31 meq/g

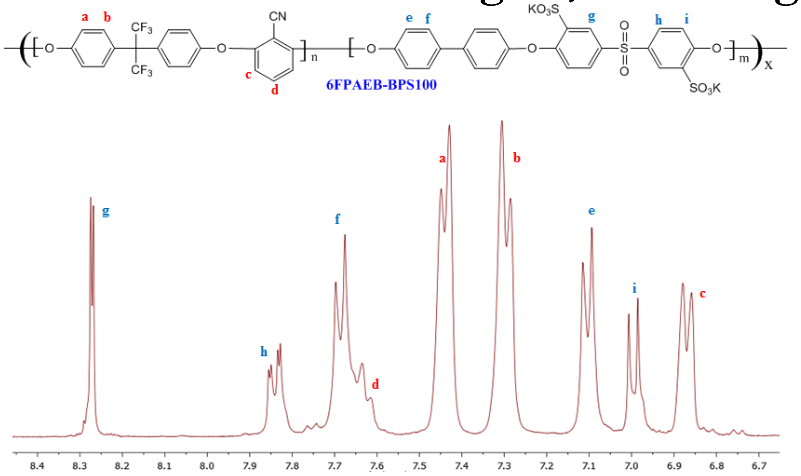
**Sulfonated Quinone-Sulfone, H^+ form*



- 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*

Copolymer Membrane Design

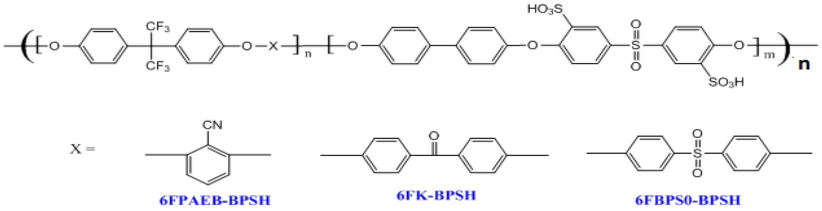
- **Matrix 1: Varied Block Lengths, Annealing Temperature and IEC**

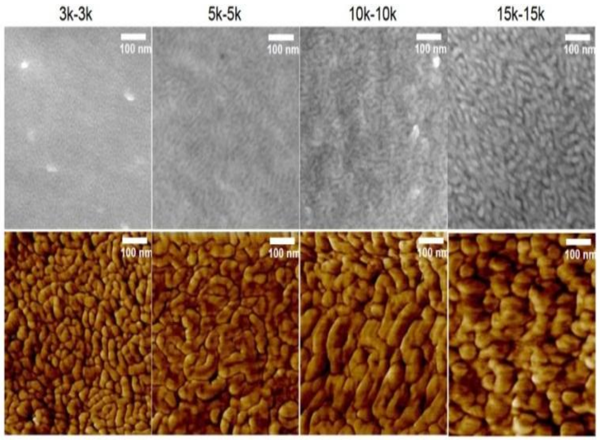


	Polymer	Thermal Treatment Temperature (°C)	IEC (meq/g)
1	6FPAEB-BPSH100 7k-7k	110	1.55
2	6FPAEB-BPSH100 15k-15k	110	1.55
3	6FPAEB-BPSH100 10k-18k	110	2.01
4	6FPAEB-BPSH100 7k-7k	220	1.55
5	6FPAEB-BPSH100 15k-15k	220	1.55
6	6FPAEB-BPSH100 10k-18k	220	2.01

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

Sample	Block Copolymer	Block Length	IEC (meq/g)[a]	Water Uptake (%)[b]	Conductivity (S/cm)[c]
JR-143-2	6FK-BPSH	8K – 8K	1.45	21	0.10
JR-143-3	6FPAEB-BPSH	13K – 13K	1.63	37	0.14
JR-143-4	6FBPS0-BPSH	10K – 10K	1.47	35	0.10





New Membranes based MEA Fabrication

VA Tech: Polymer Synthesis

Solution Cast

4" x 4"

12" x 5"

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

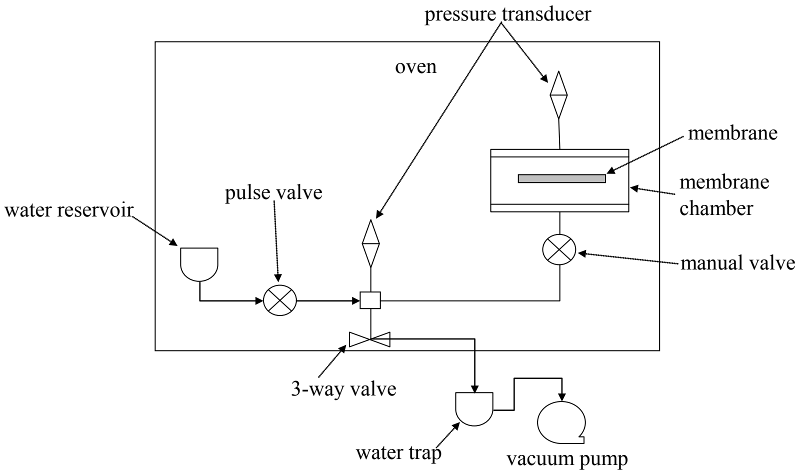
Decal Transfer

50cm^2 FCT plates

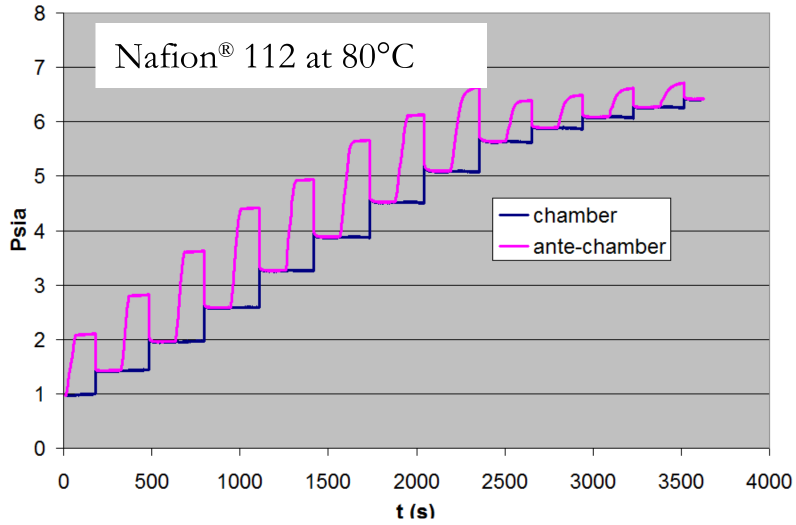
50cm^2 GM plates

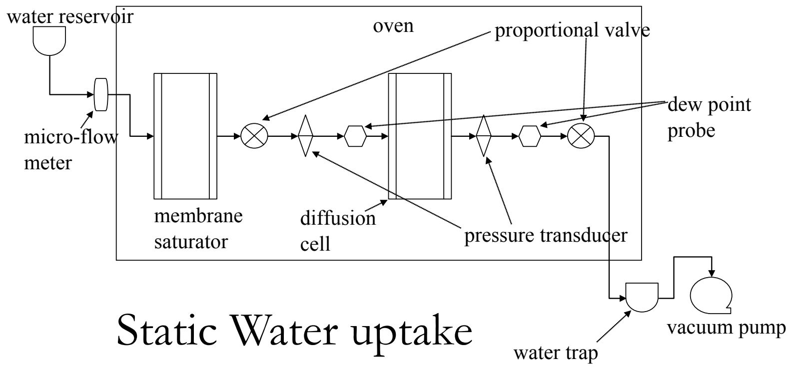
South Carolina: Performance evaluation and model validation

Achievement 2
New Technique for Water Uptake and Diffusivity

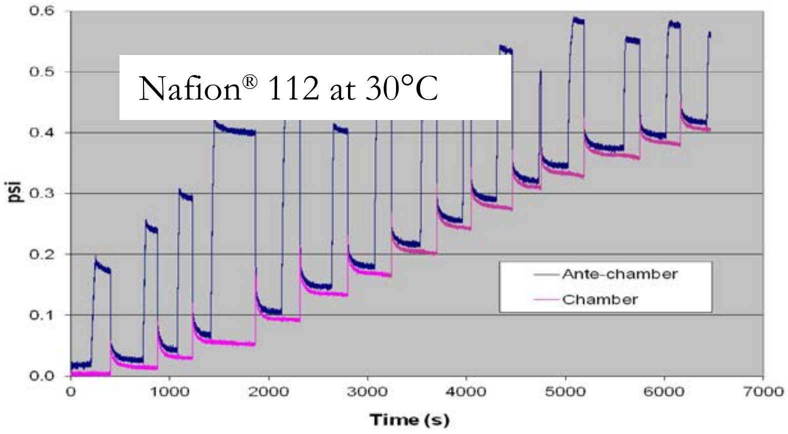


Dynamic Water uptake



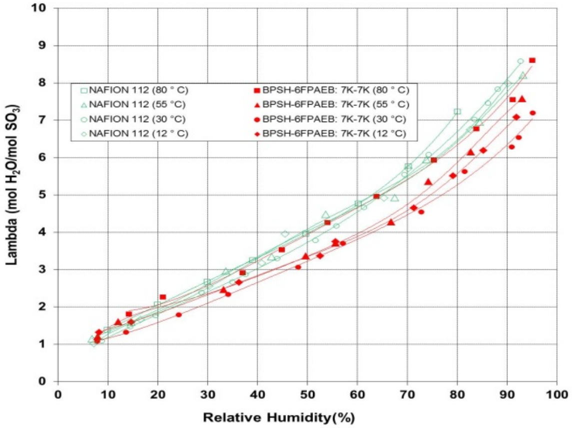


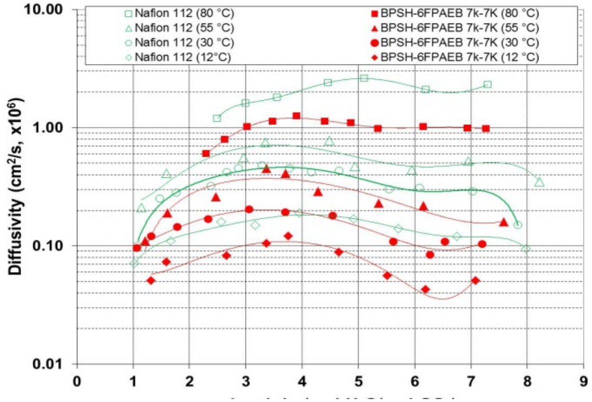
Static Water uptake

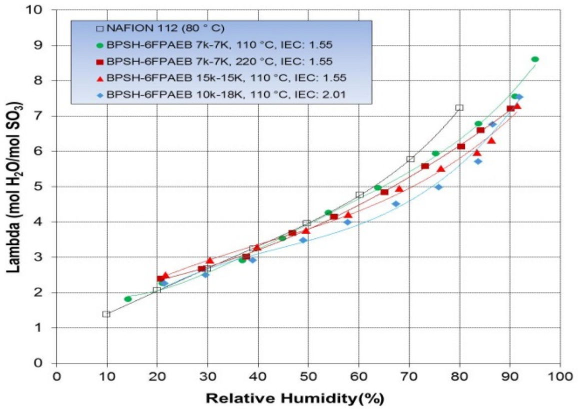


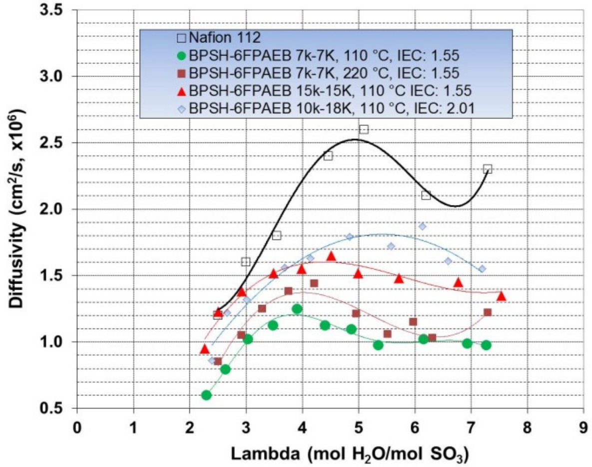
Operation T: 80°C

Simultaneous Water Uptake and Diffusivity



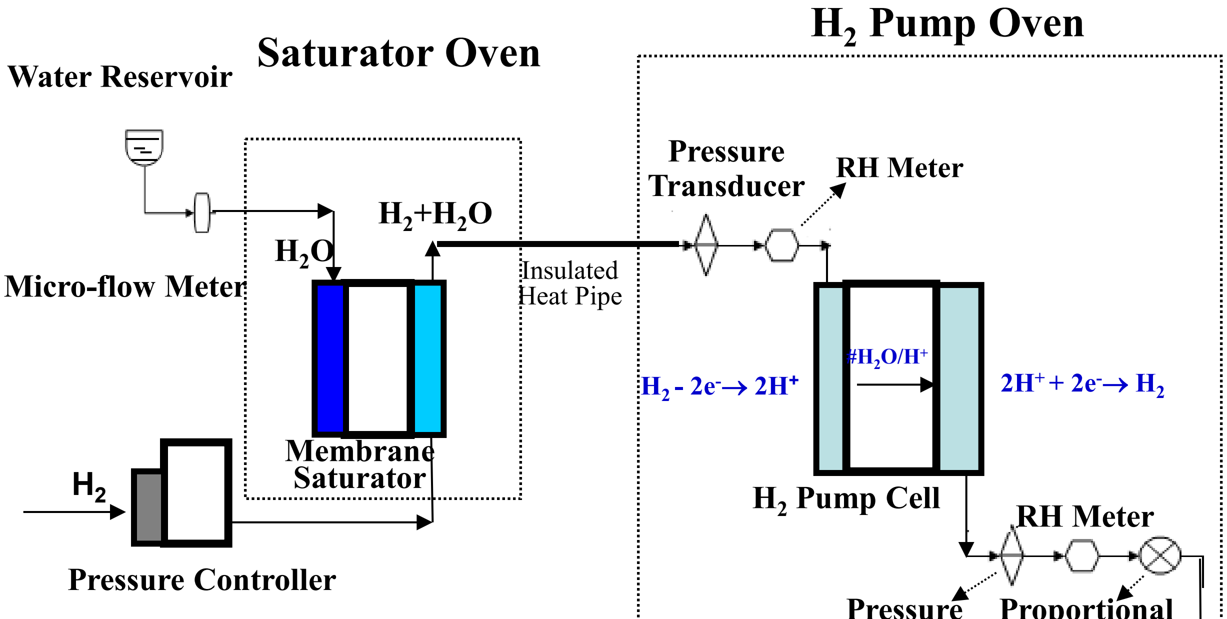


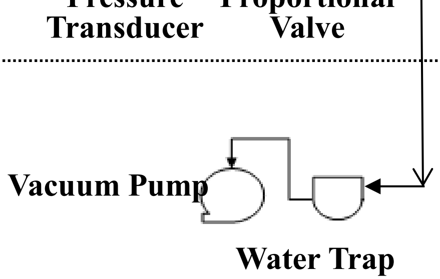


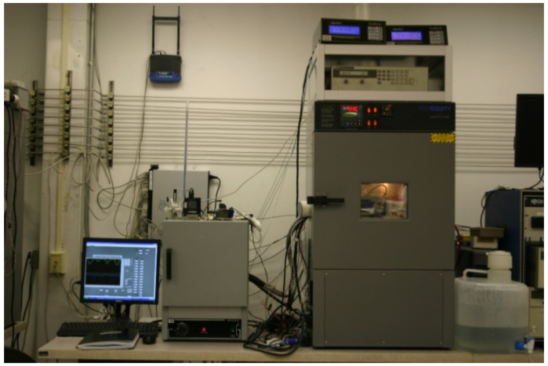


- BPSH-6FPAEB Membranes show nearly identical water uptake with little temperature dependence Water Diffusivity is ~ ½ that of Nafion® regardless of temperature;
- Phase separation on a smaller scale results in lower diffusivity. Annealing increases phase separation and diffusivity

Achievement3: New Technique for EODC



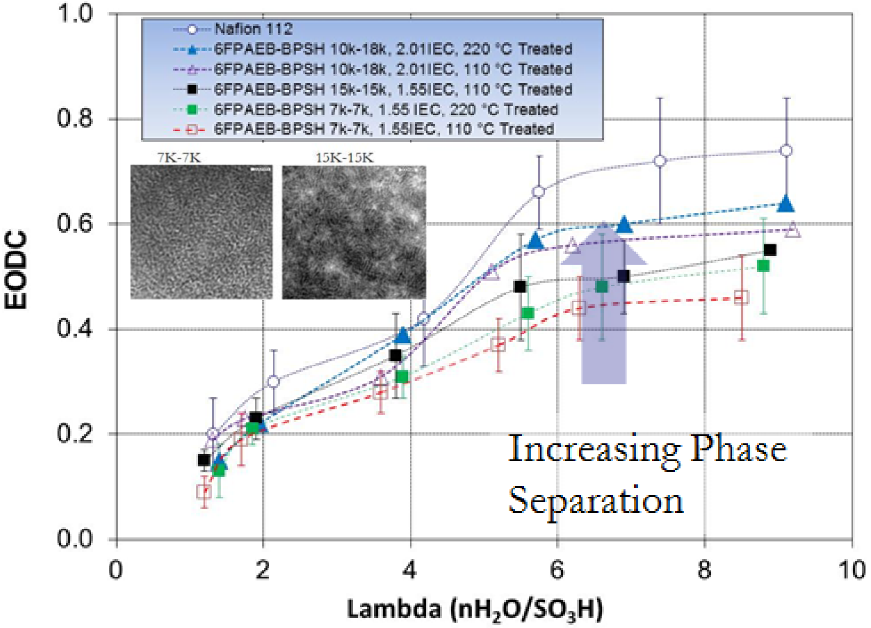




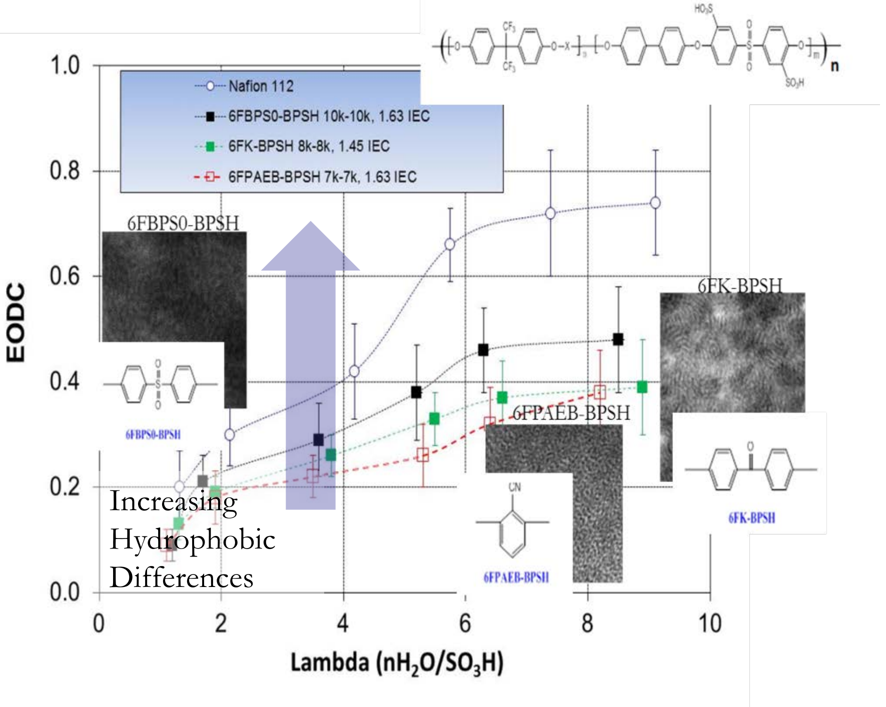
- Water/H_2 inlet ratio controlled by controlling saturator temperature and H_2 pressure
- If ratio is too high, not enough water is dragged across and cell floods and fails
- If ratio is too low, membrane dries out and cell fails
- At Water/H_2 = 2*EODC Cell operates in quasi-stable state

All gas/gas diffusion is eliminated

Correlation EODC to Copolymer Structure



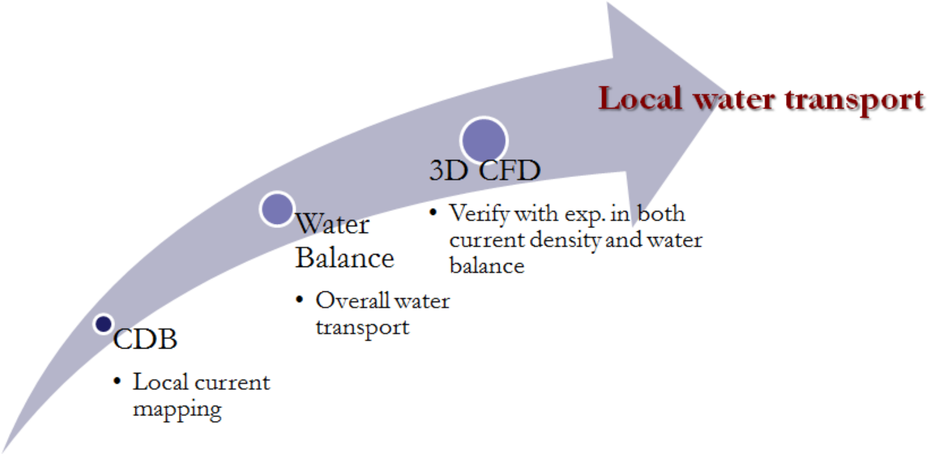
Increasing Phase Separation



Increasing Hydrophobic Differences

- 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 lead s to higher EODC

Achievement 5: Current Distribution Board (CDB) Design

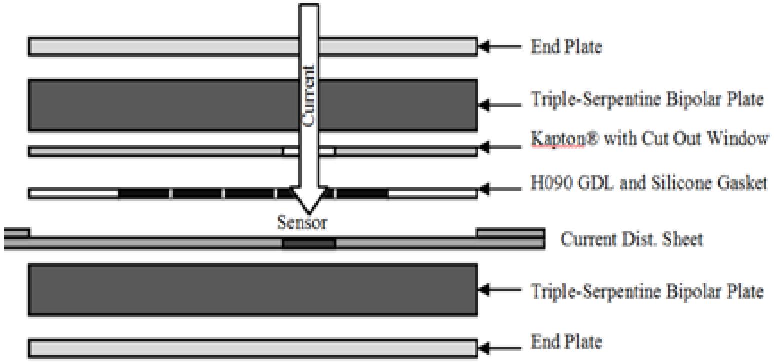


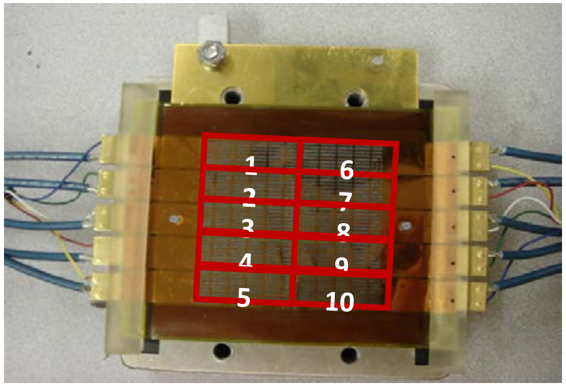
Local water transport

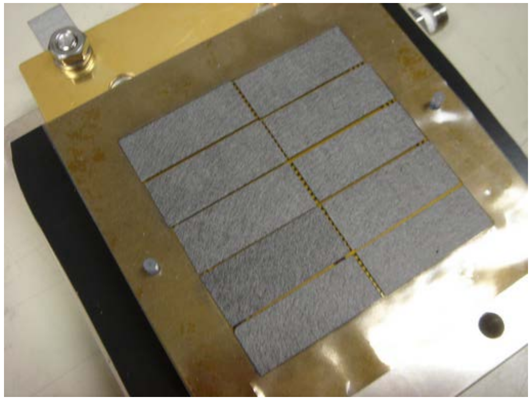
3D CFD
- Verify with exp. in both current density and water balance

Water Balance
- Overall water transport

CDB
- Local current mapping

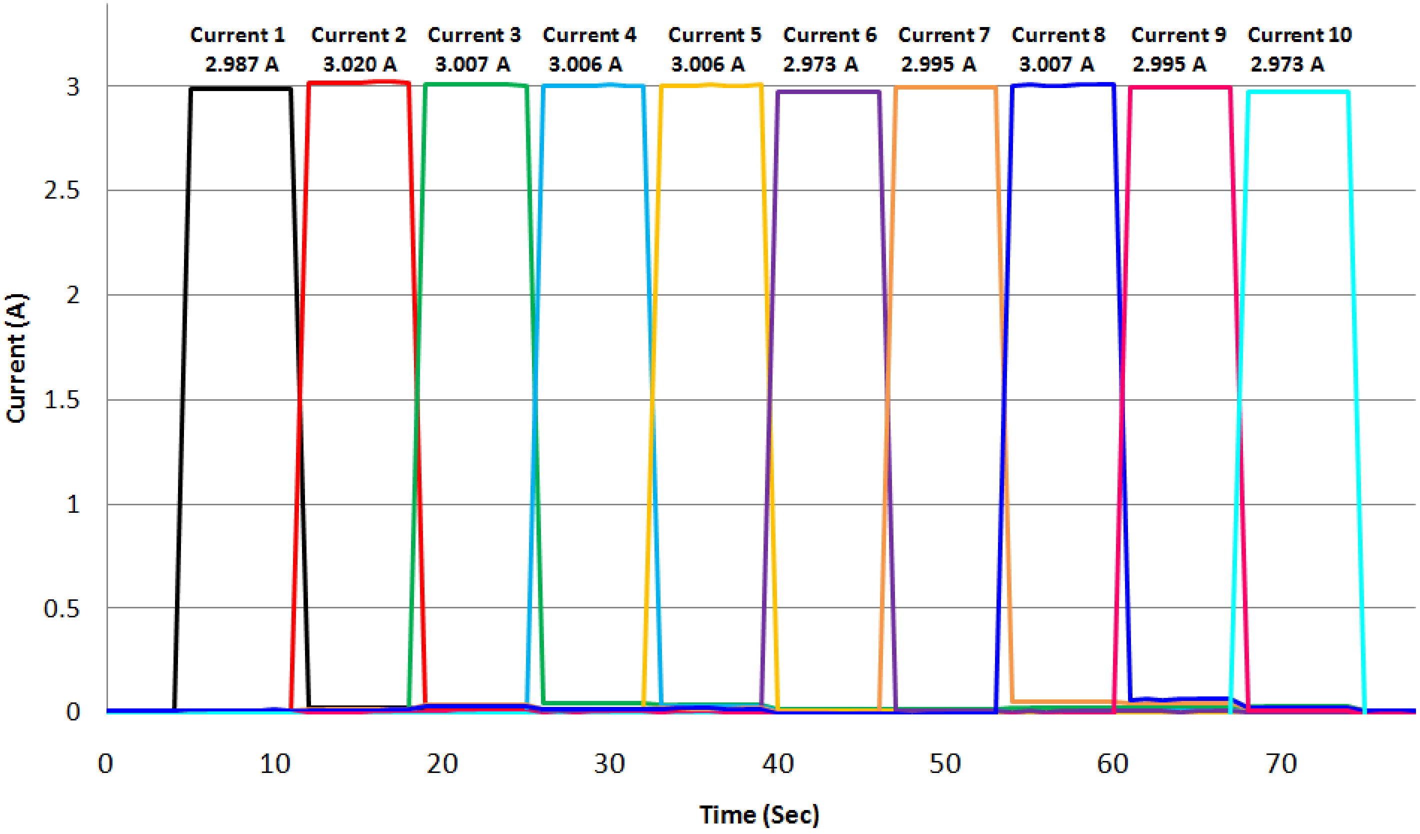






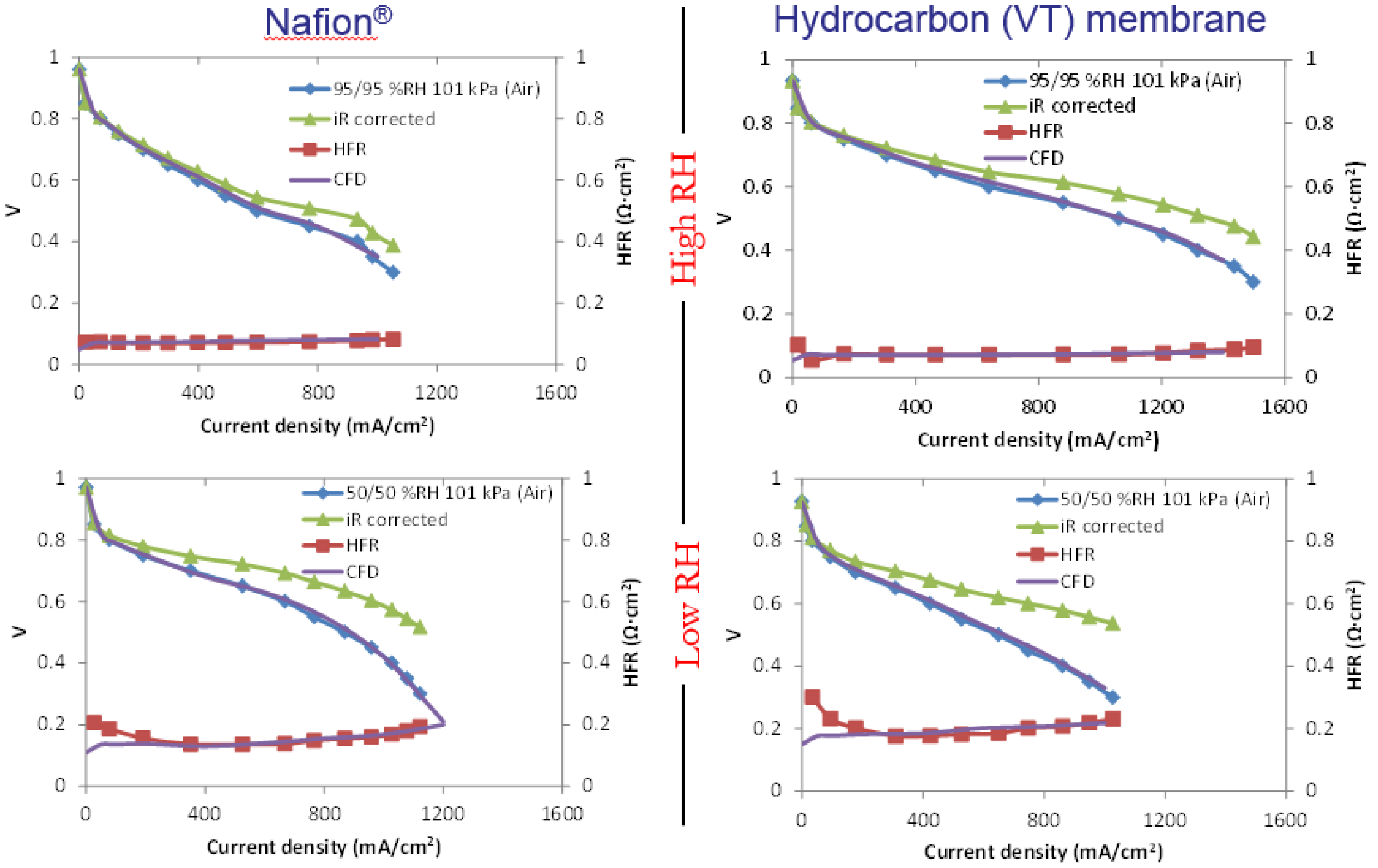
- We run the test for 10 segments with 3 Amp DC current
- Condition
  - Whole H090 and silicone gasket
  - Cut 10 pieces H090 with silicone

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.

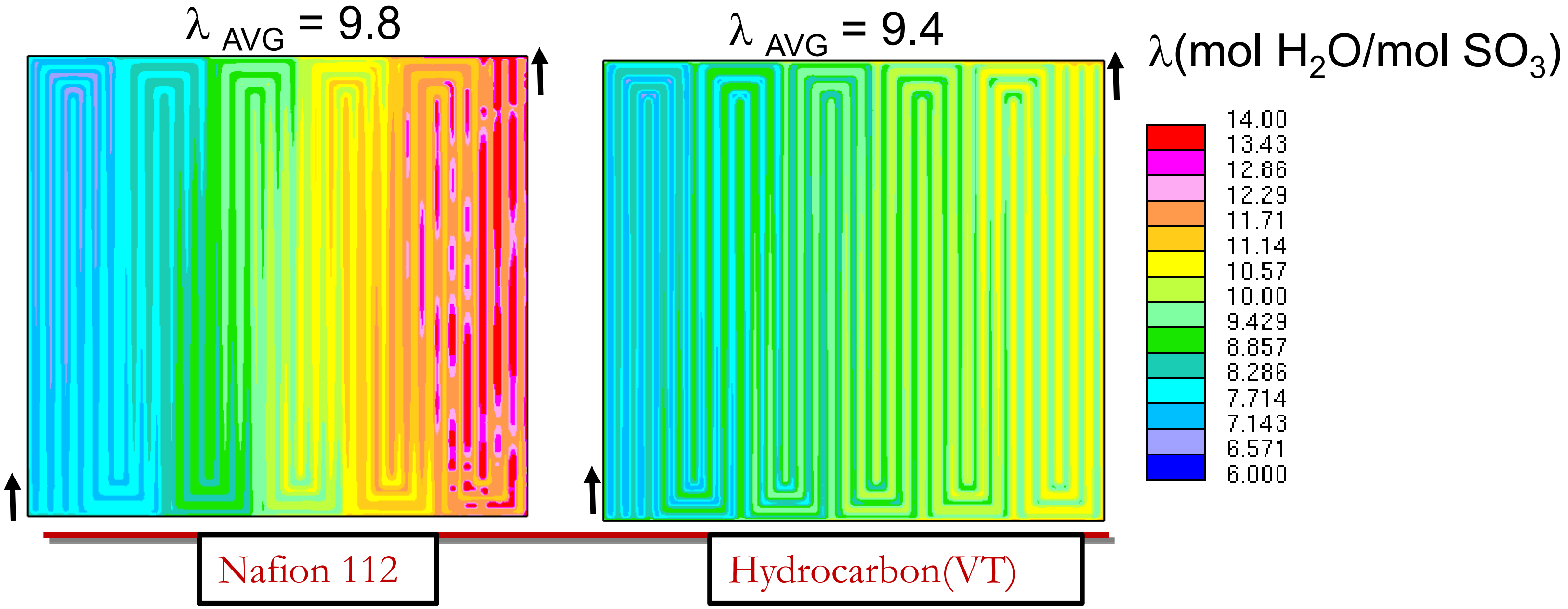
Achievement 4: VT Membrane Based Performance and Water Distribution



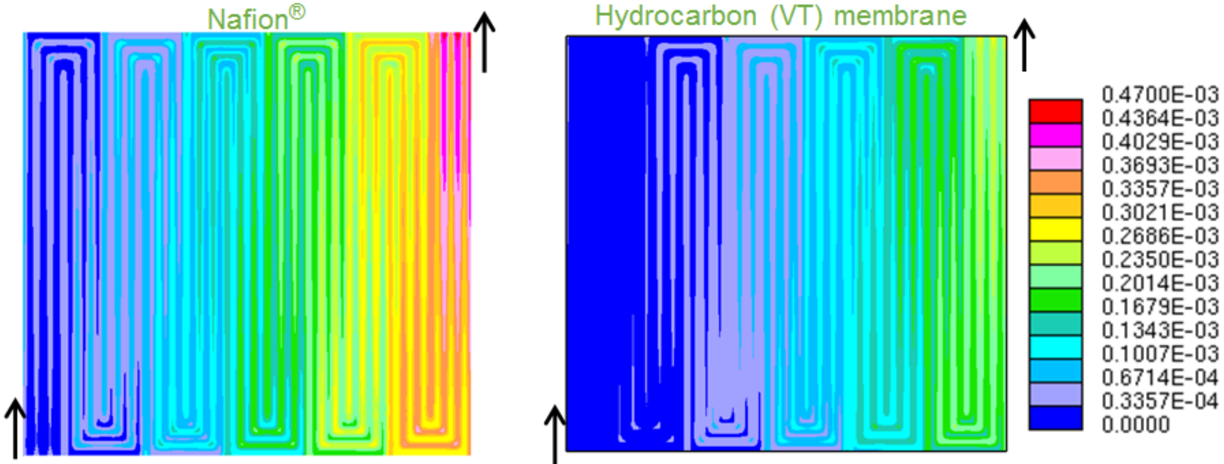
80°C, 1.5/2.0 stoich, H_2/Air: GDL - EP40T)

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

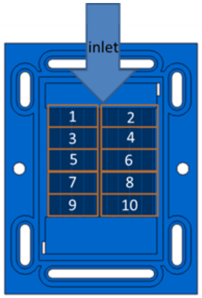
Comparison of Simulated Water Uptake and Liquid Water Film

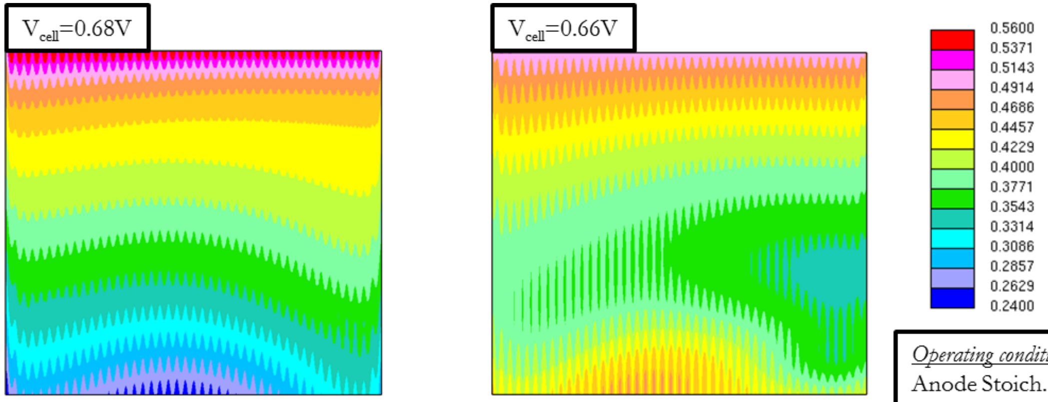


Liquid water film thickness (mm) on cathode MEA surface under high RH (95%/95%)



Local Distributions of Current Density & Water Transport on the Membrane Surface at low inlet RH at 0.4 A/cm^2





Current density (A/cm^2)

NRE212

Hydrocarbon (VT)

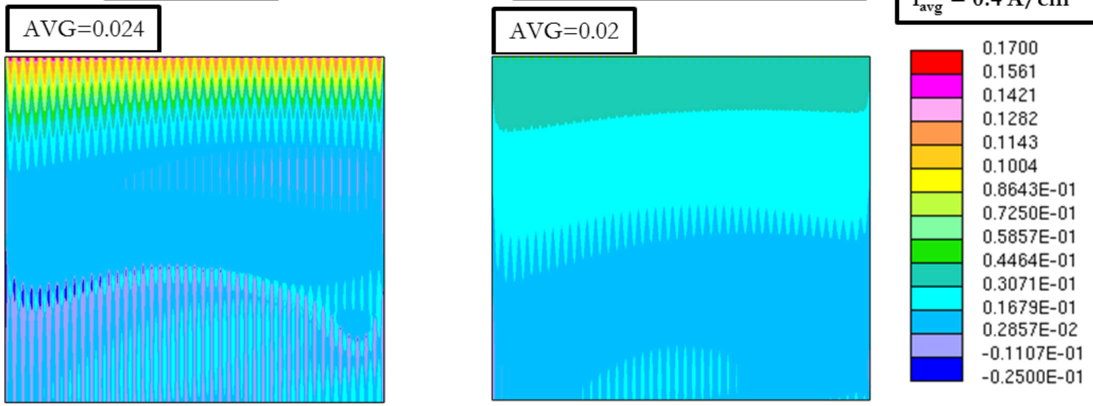
Operating condition:

Anode Stoich. = 1.5 Cathode Stoich. = 2.0

Anode RH = 75% **Cathode RH = 25%**

Tcell = 80°C System pressure = 101kPa

i_{avg} = 0.4 A/cm^2

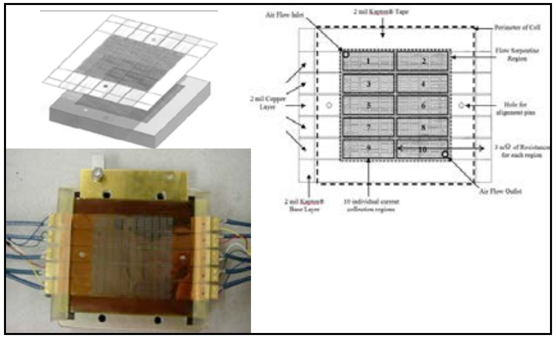


Water flux across membrane (mg/cm^2-s)

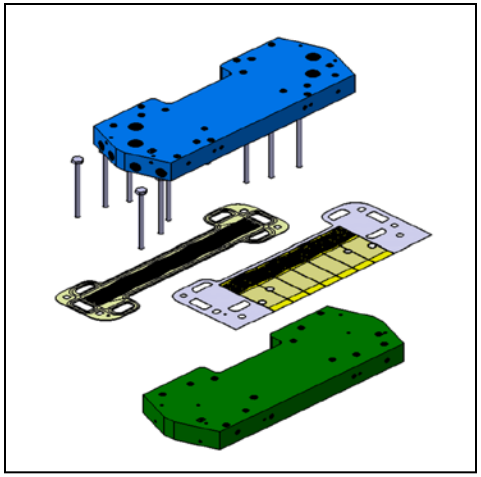
VT membrane shows slightly lower performance but more uniformity in distributions of both current density and water transport across membrane.

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

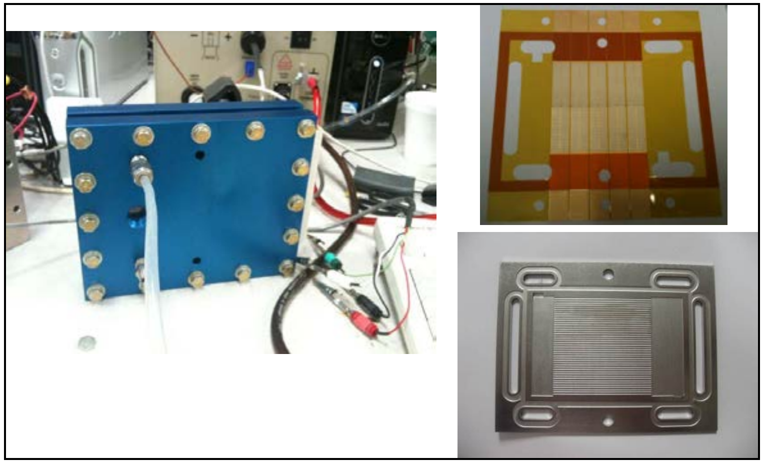
Achievement 6: Design of Fuel Cell Flow-Fields



50-cm^2 USC-serpentine flow-field



50-cm^2 GM-Down-the-Channel flow-field (In-progress)



50-cm^2 USC-parallel flow-field (In-progress)

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

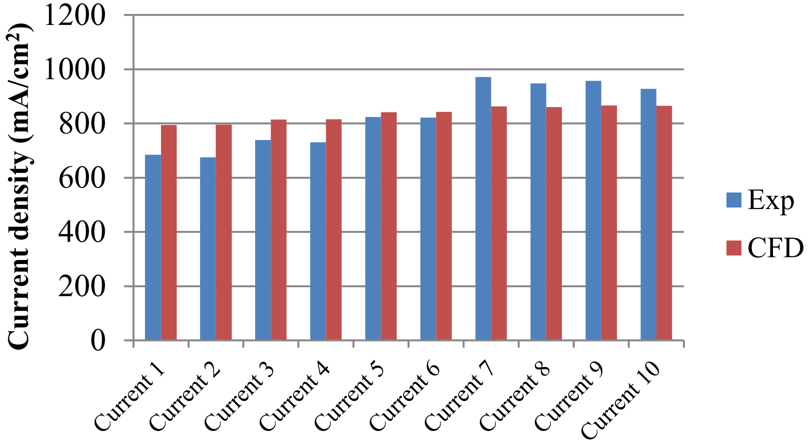
Thin Metal Plates (Tech Etch USC Design)
- Closer to Automotive
- Allows minimization of pressure drop to flow fields

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

Current Distribution Boards Designed for All 3

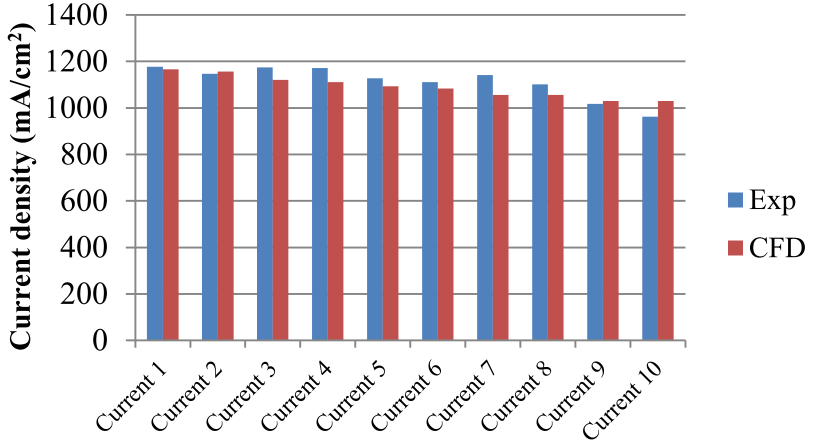
Model Verification: Serpentine

At potential=0.3V



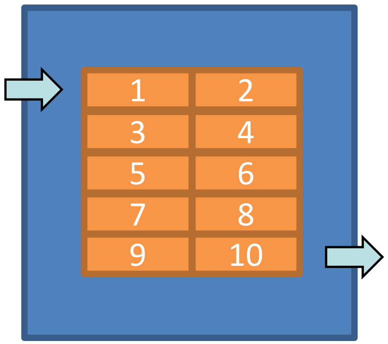
Anode 25%RH, Cathode 25%RH

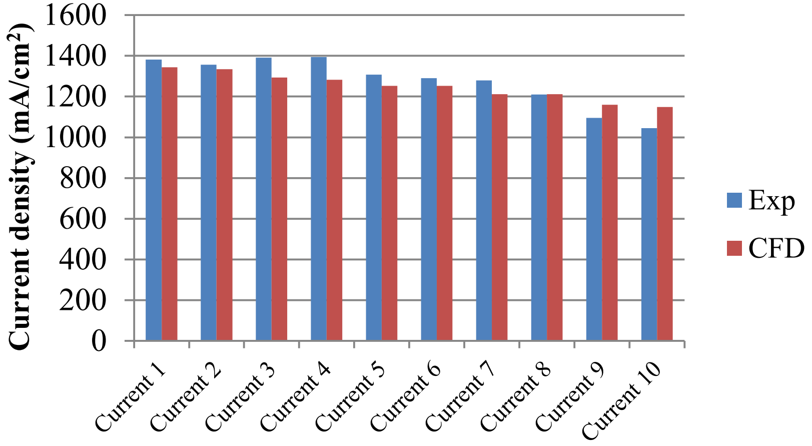
Average current density = 809 mA/cm²



Anode 75%RH, Cathode 25%RH

Average current density = 1094 mA/cm²

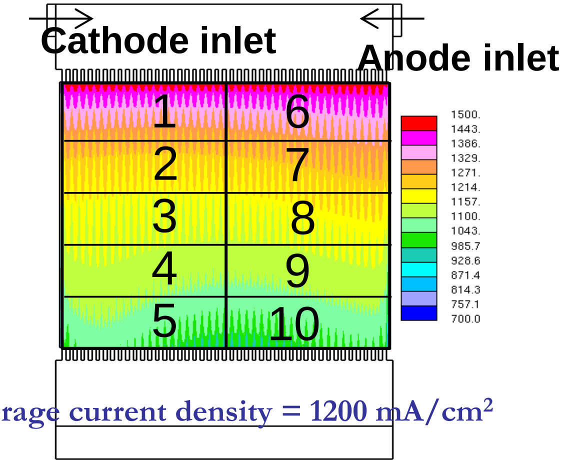




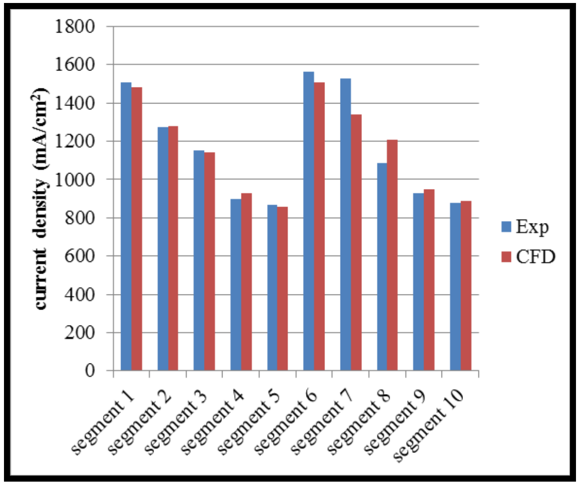
Anode 100%RH, Cathode 50%RH

Average current density = 1250 mA/cm²

Model Verification: Thin Metallic Plates



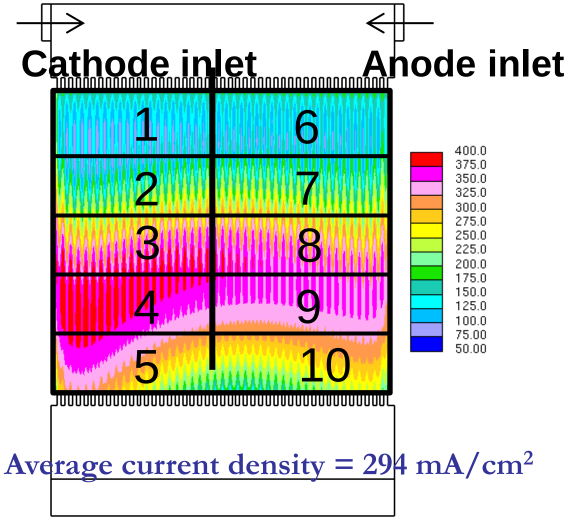
Average current density = 1200 mA/cm^2



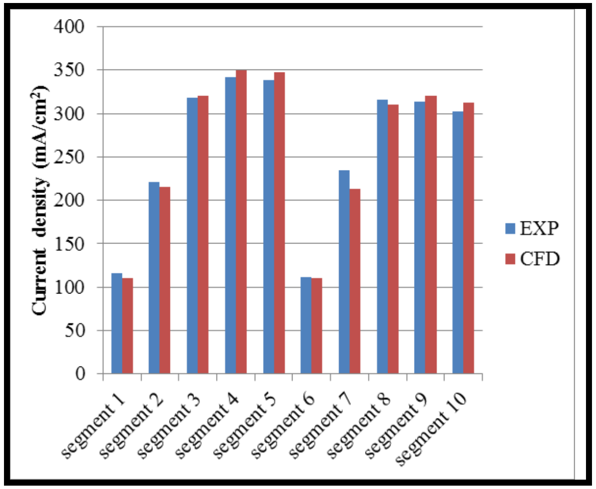
Operating condition:
Anode Stoich. = 1.5
Anode RH = 100%
Cathode Stoich. = 2.0
Cathode RH = 50%
Tcell = 80^{o}C
System pressure = 136kPa

High Current Wet

Model Predicts Equally Well
- *High i/Wet*
- *Low i/Dry*



Average current density = 294 mA/cm^2



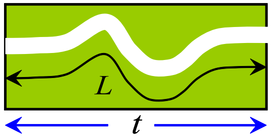
Low Current Dry

Operating condition:
Anode Stoich. = 1.5
Anode RH = 25%
Cathode Stoich. = 2.0
Cathode RH = 25%
Tcell = 80^{o}C
System pressure = 101kPa

Achievement 7: Design Diffusion Media

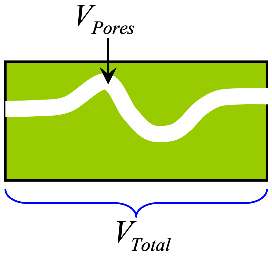
- Ballard added to the program recently
- Started with Toray Materials
  - Variable Wet-Proofing
  - Microporous Layer
- Ballard will provide more custom materials
- Want to generate differences in:
  - MacMullin Number
    - Porosity
    - Tortuosity
  - Hydrophobicity

- 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.

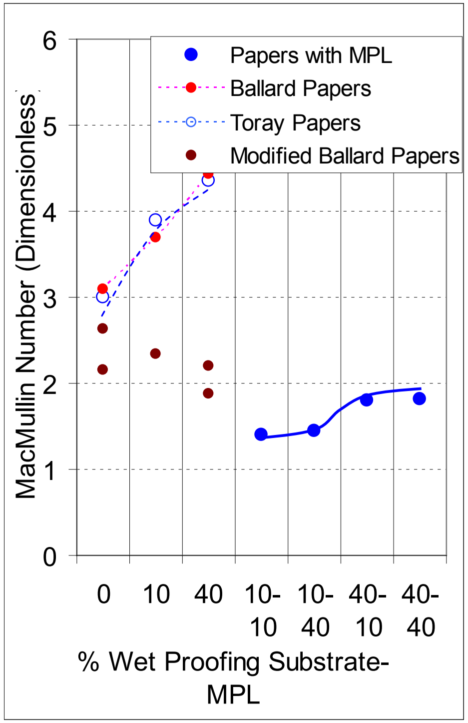


$$\varepsilon = \frac{V_{Pores}}{V_{Total}}$$

- MacMullin Number
  - Function of tortuosity and pososity.

$$N_M = f(\tau, \varepsilon) = \frac{\tau^n}{\varepsilon^m}$$

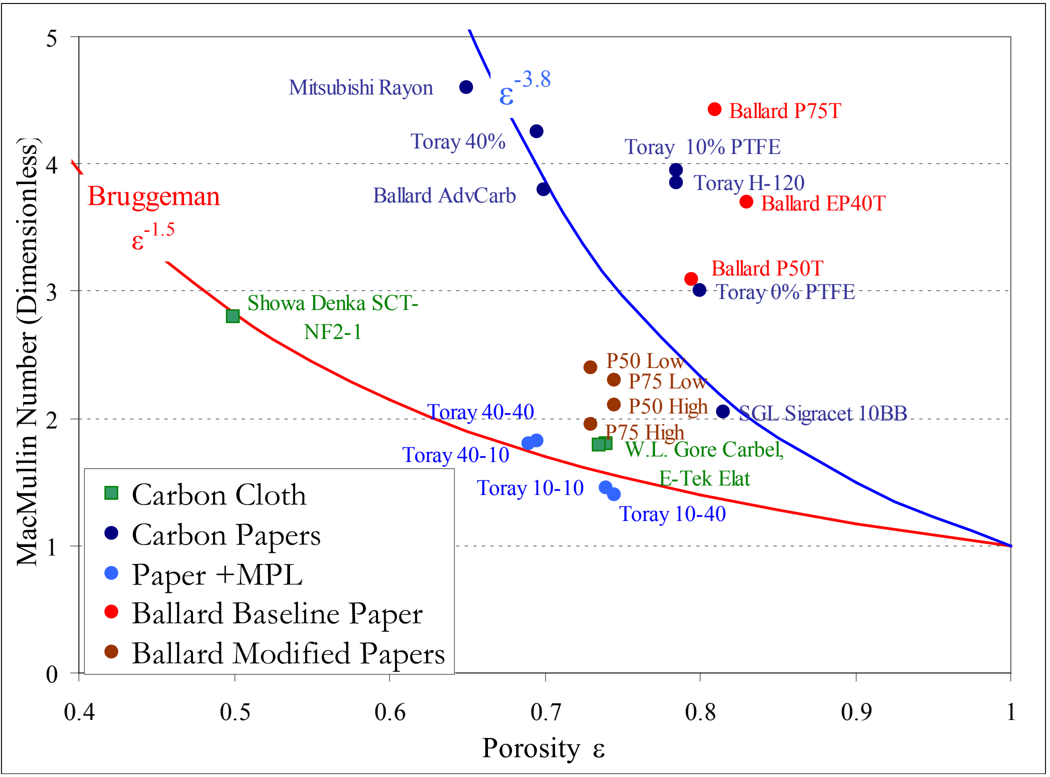
Wet Proofing



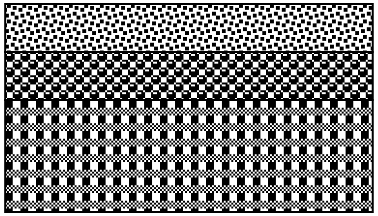
MacMullin number as function of wet proofing in substrate and MPL

MacMullin number as function of porosity

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



Gas Diffusion Media Design

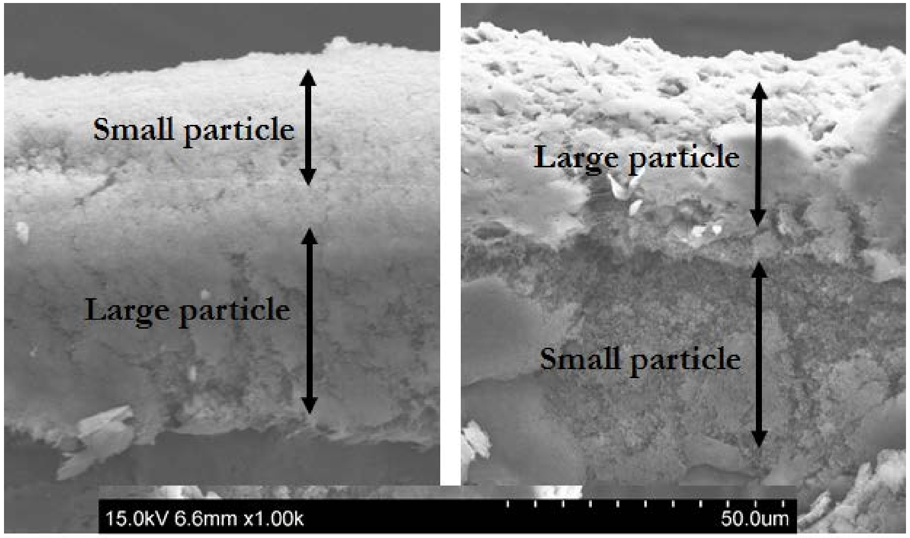


MPL 2

MPL 1

Carbon Substrate

Substrate	Diffusivity Modification	MPL 1/MPL2 (carbon particle size)
P50	Low	Small/Large
EP40		
P75	High	Large/Small



MPL 1 = Large
MPL 2 = Small

MPL 1 = Small
MPL 2 = Large

- 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.

Baseline and Advanced GDLs

Substrate	Diffusivity	MPL1	MPL2	MacMullin No.	Status
P50T				3.09	Done
P50	Low	Large	Small	2.63	Done
P50	High	Large	Small	2.18	Done
P50	Low	Small	Large	4.04	Done
P50	High	Small	Large	2.73	Done
P75T				4.43	Done
P75	Low	Large	Small	2.14	Done
P75	High	Large	Small	1.92	Done
P75	Low	Small	Large	11.11	Done
P75	High	Small	Large	2.63	Done
EP40T				3.70	Done
EP40	Low	Large	Small	5.18	Done
EP40	High	Large	Small	2.34	Done
EP40	Low	Small	Large	3.18	Done
EP40	High	Small	Large	2.62	Done

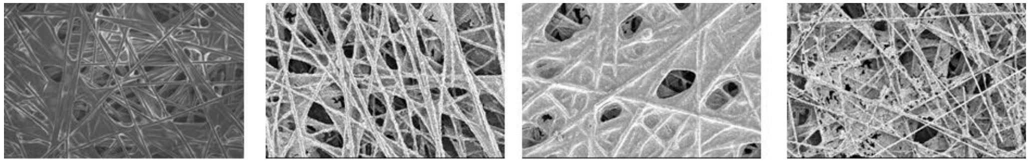


Photo micro-graphs of surface substrate

TGP-H-60 P50T P75T EP40T

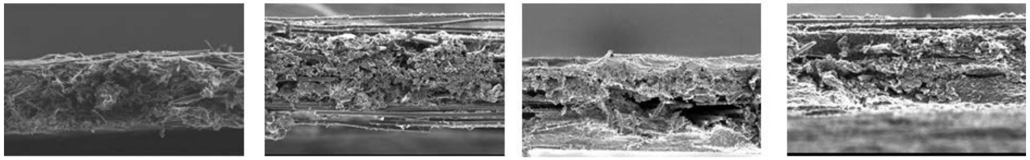
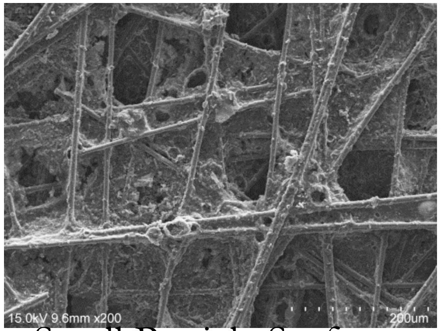


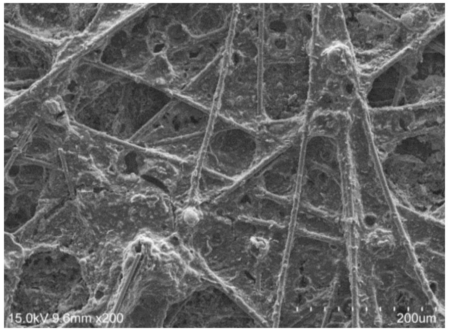
Photo micro-graphs of cross-section

Structure of EP40T-based GDLs

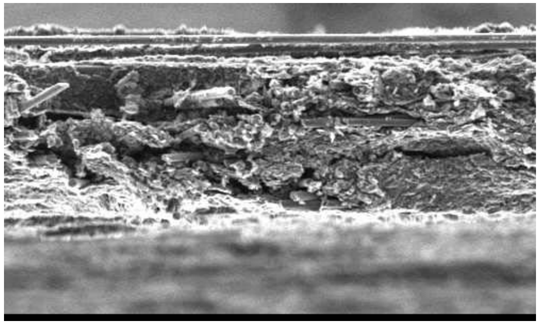
High-diffusivity Substrate Surface



low-diffusivity substrate surface

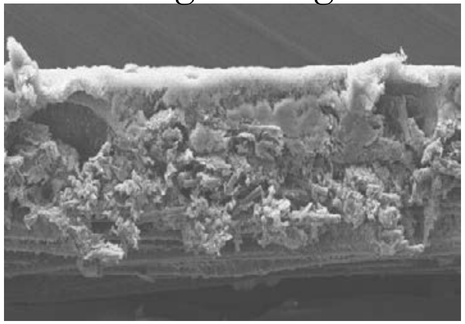


EP40T - standard

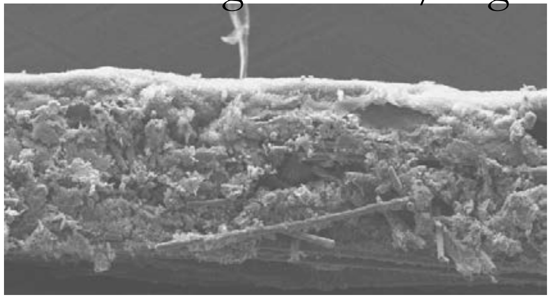


Small Particle Surface

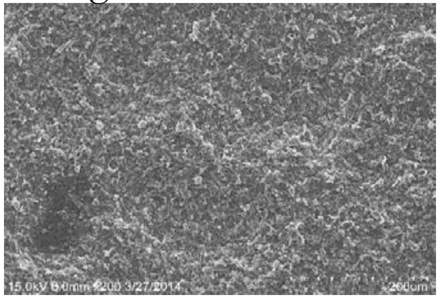
EP40 High – Large/Small



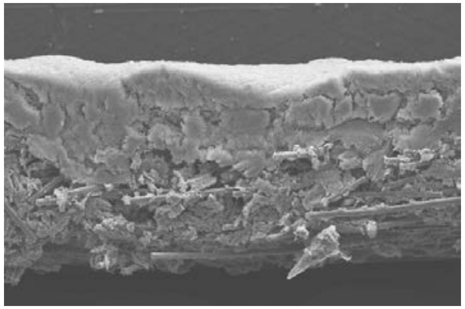
EP40 High – Small/large



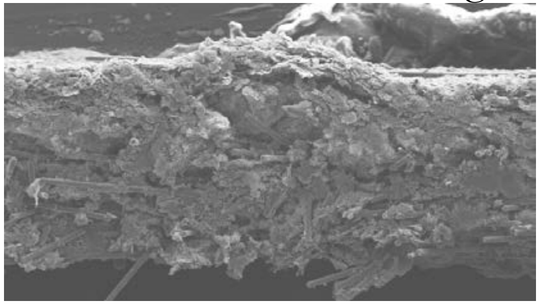
Large Particle Surface



EP40 Low – Large/Small

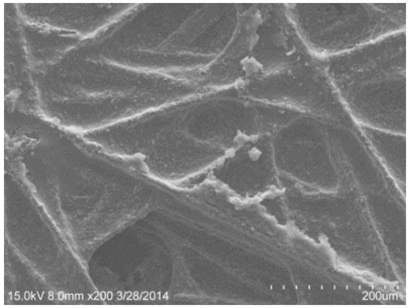


EP40 Low – Small/large

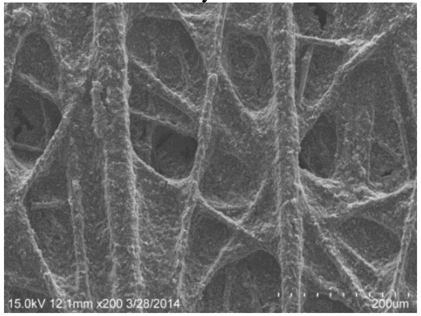


Structure of P75T-based GDLs

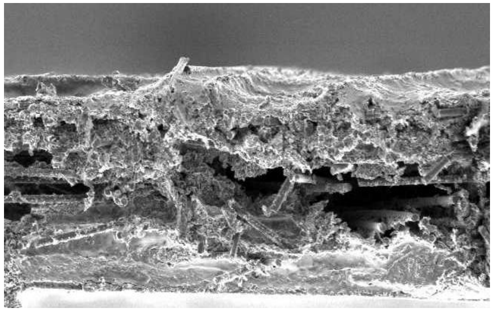
High-Diffusivity Substrate Surface



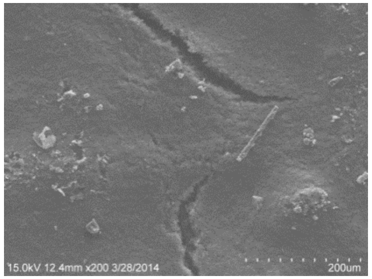
Low-Diffusivity Substrate surface



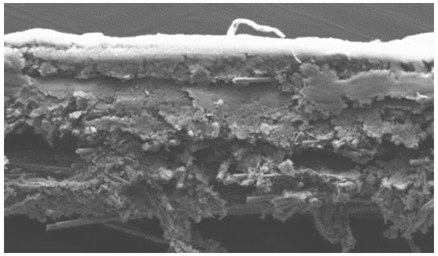
P75T - Standard



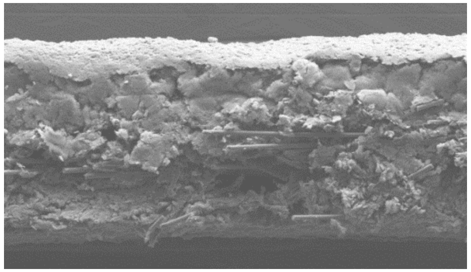
Small particle surface



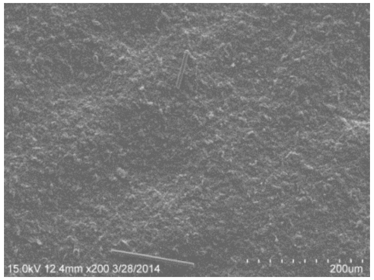
P75 High – Large/Small



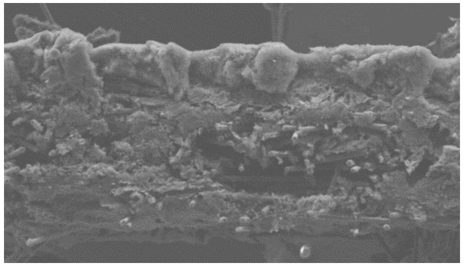
P75 High – Small/large



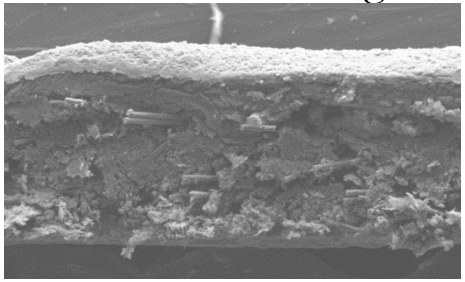
Large particle surface



P75 Low – Large/Small



P75 Low – Small/large

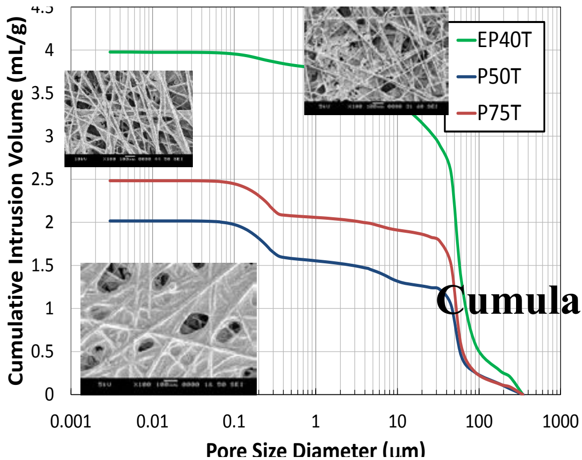


15.0kV 6.2mm x200 3/27/2014 200um

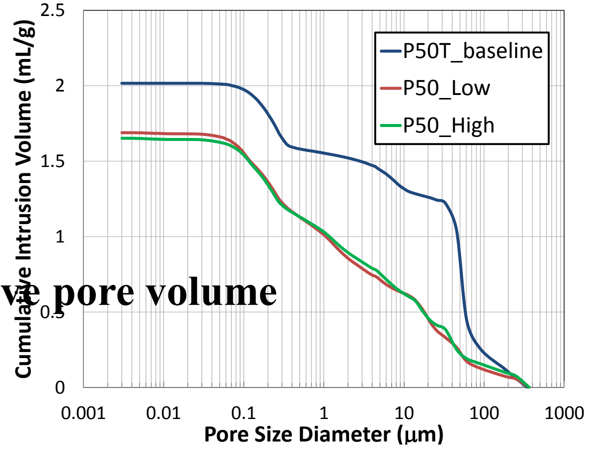
Achievements: Design of Gas Diffusion Media

Comparison of Mercury pore size distributions of new design GDLs

Baseline Substrates

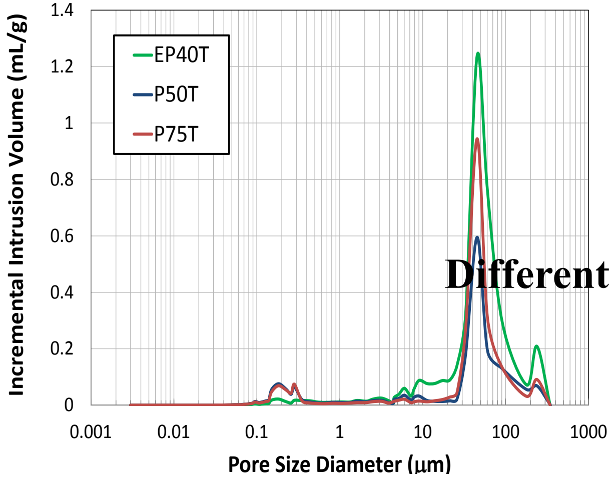


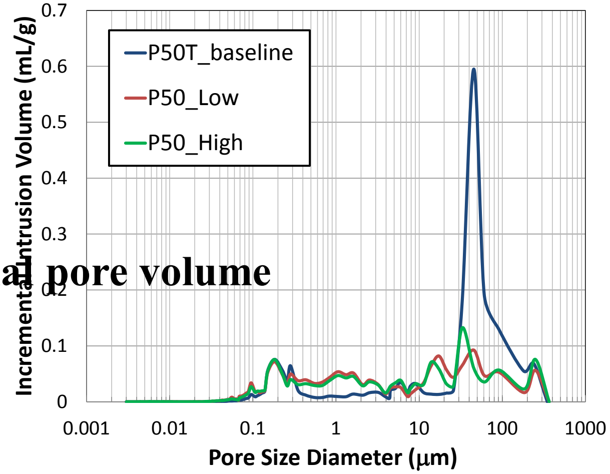
Modified Substrates



Cumulative pore volume

EP40T has largest pore volume, concentrated at 50 μm

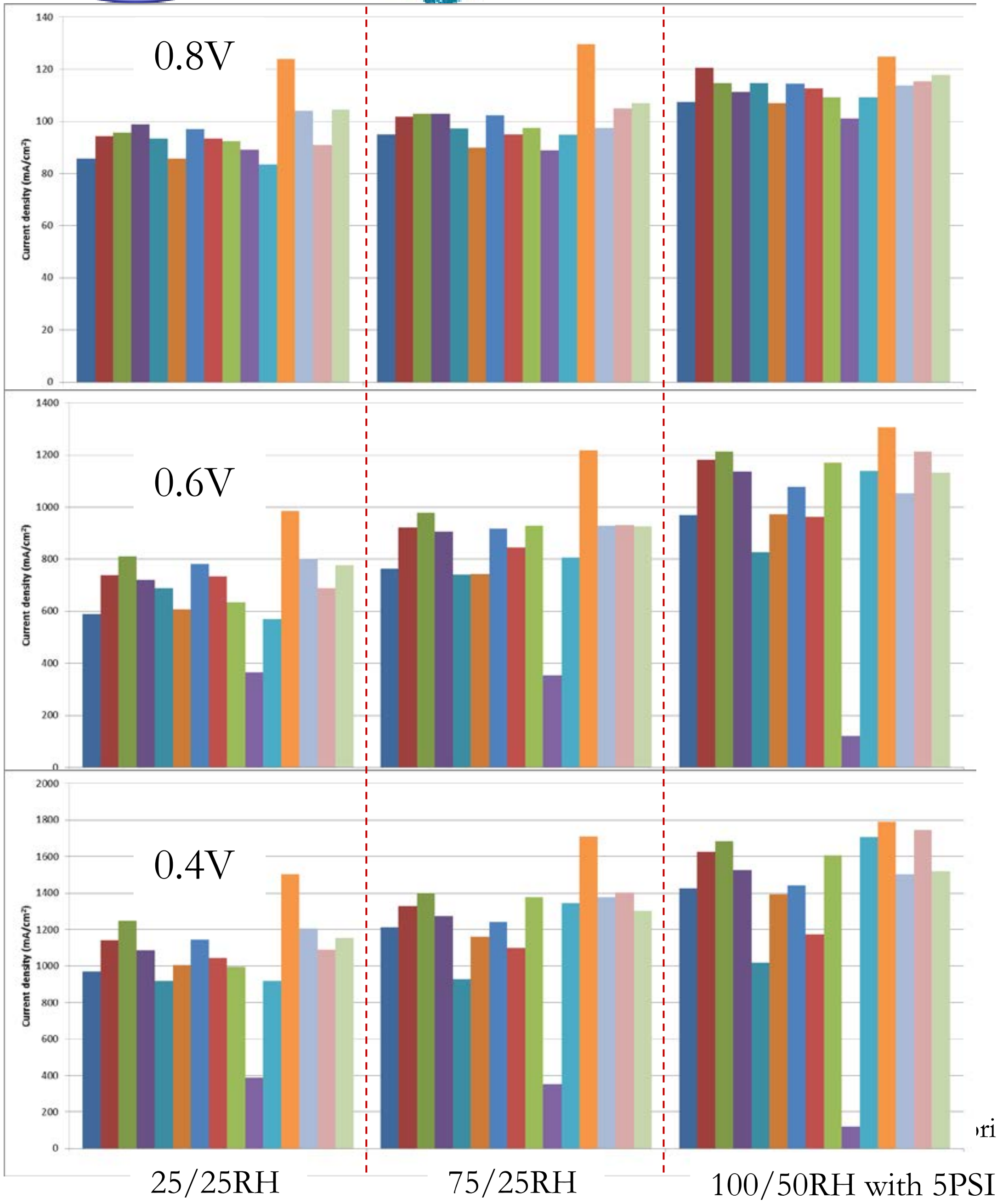




Differential pore volume

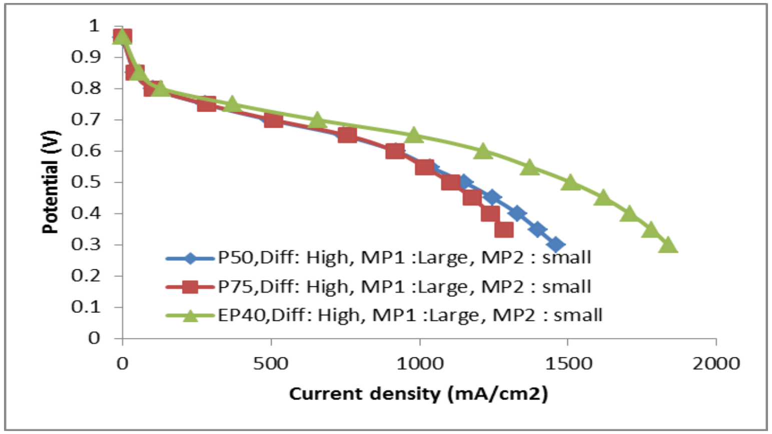
Modification greatly reduces volume of large pores

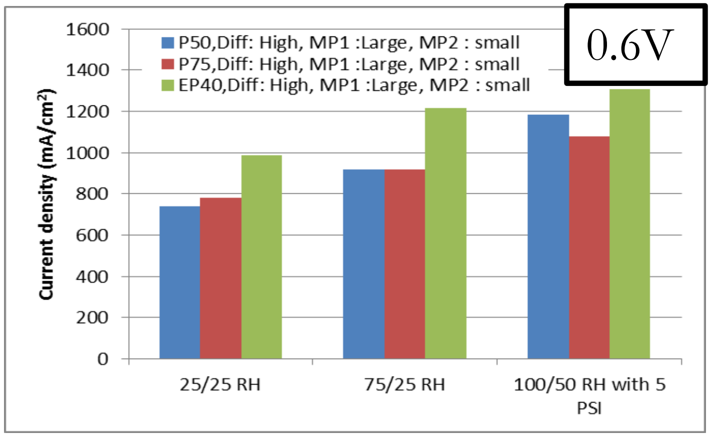
The Effect of GDL Structure



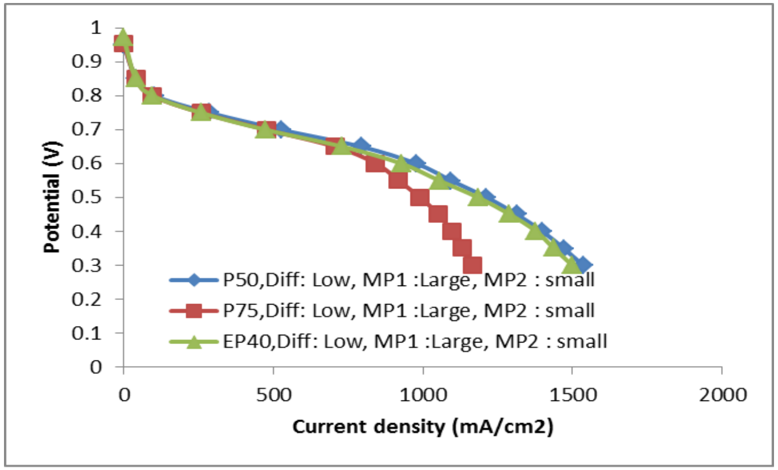
The Effect of Different Substrate

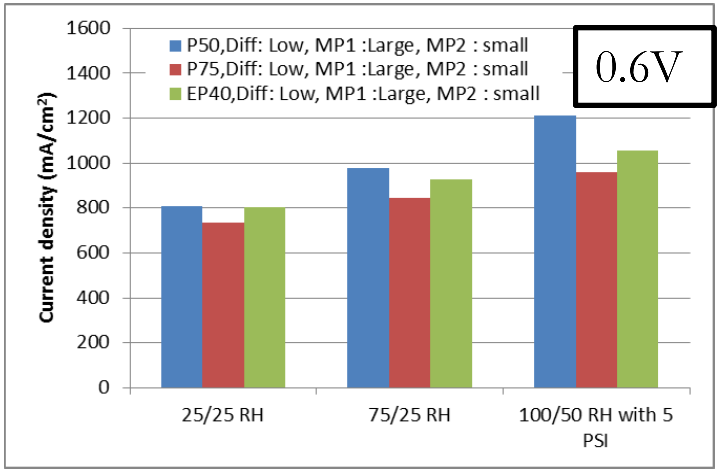
Diffusivity: High MPL1: Large MPL2: Small





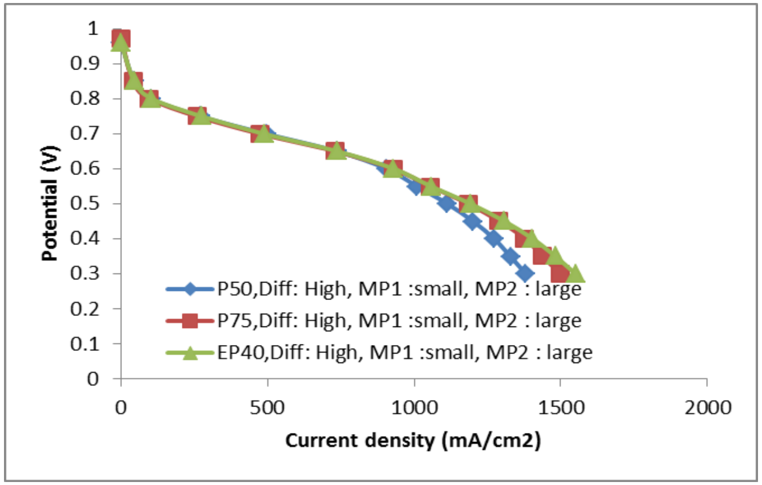
Diffusivity: Low MPL1: Large MPL2: Small

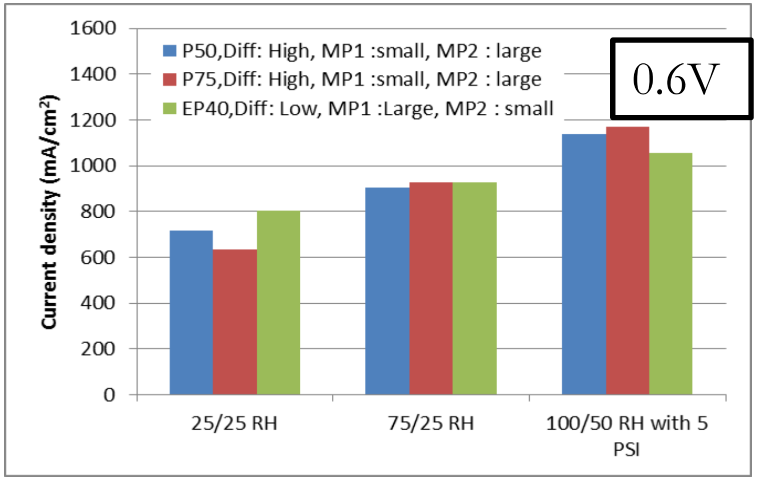




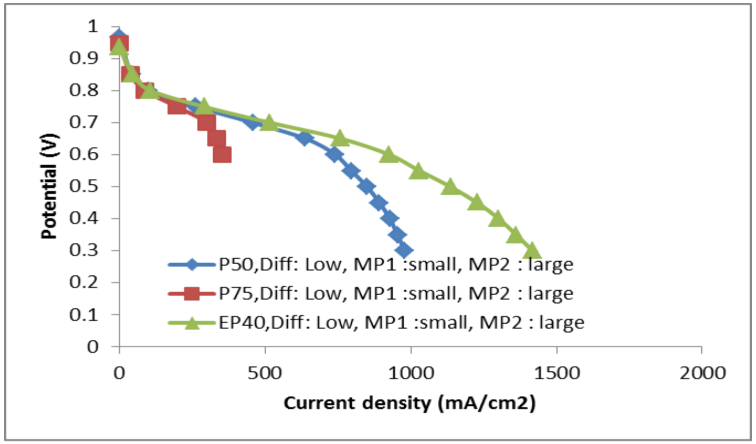
The Effect of Different Substrate

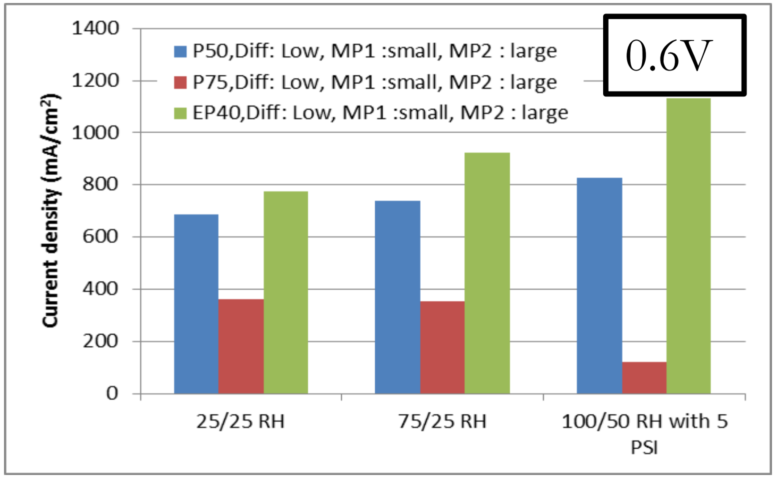
Diffusivity: High MPL1: Small MPL2: Large





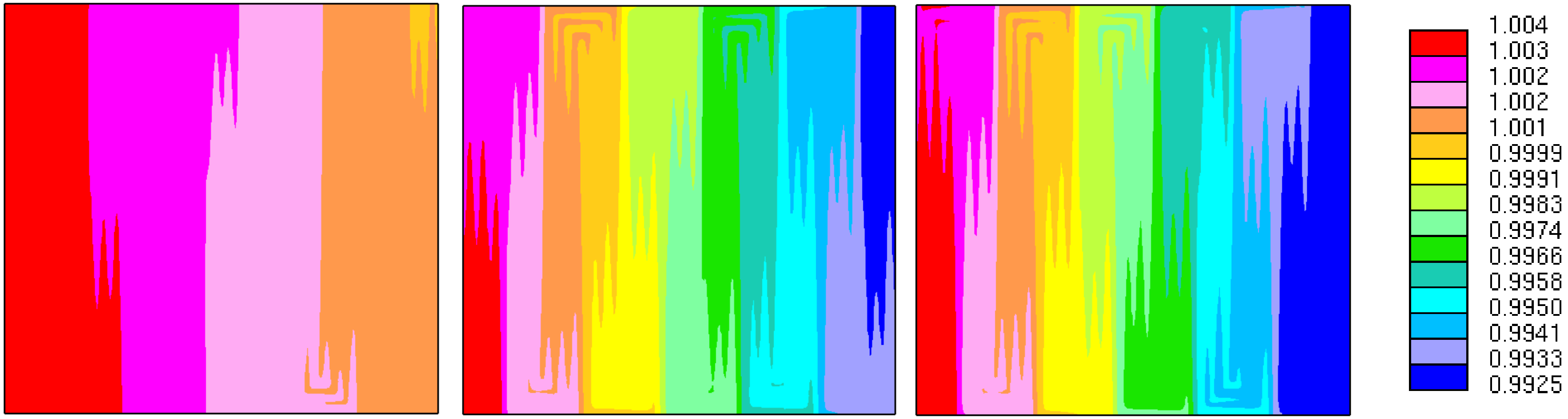
Diffusivity: Low MPL1: Small MPL2: Large





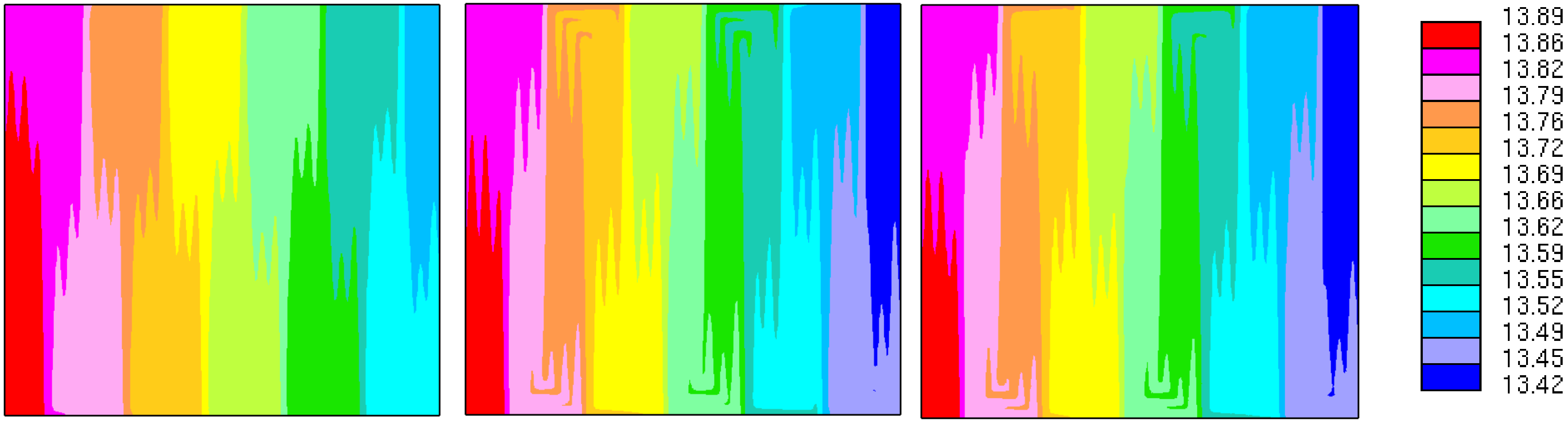
The Effect of Different Substrate

Diffusivity: High MPL1: Large MPL2: Small – Iavg = $1 A/cm^2$



Current density distribution (A/cm^2)

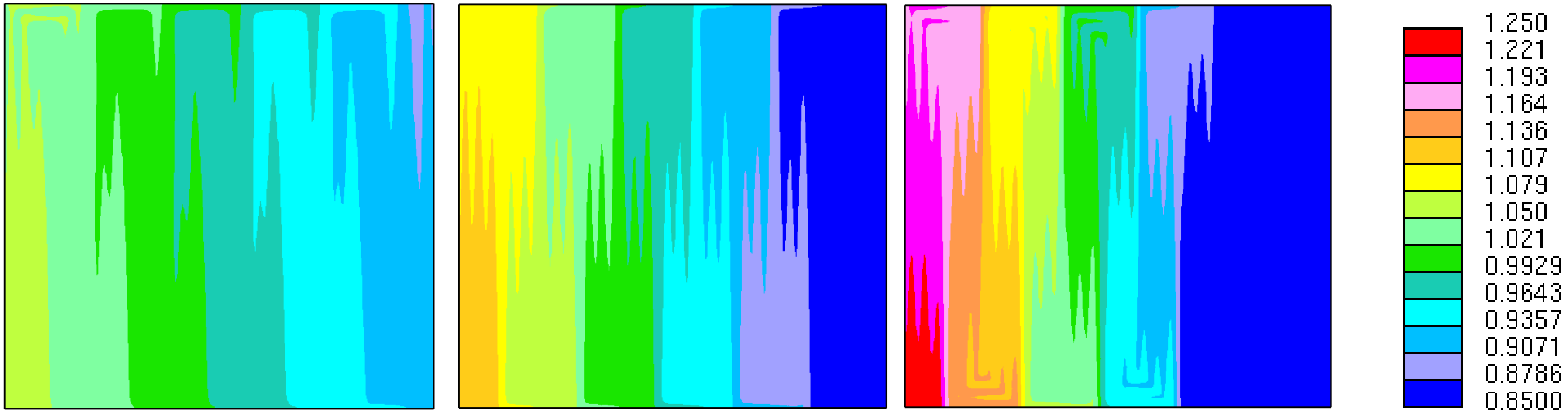
EP40 P50 P75



Membrane water content

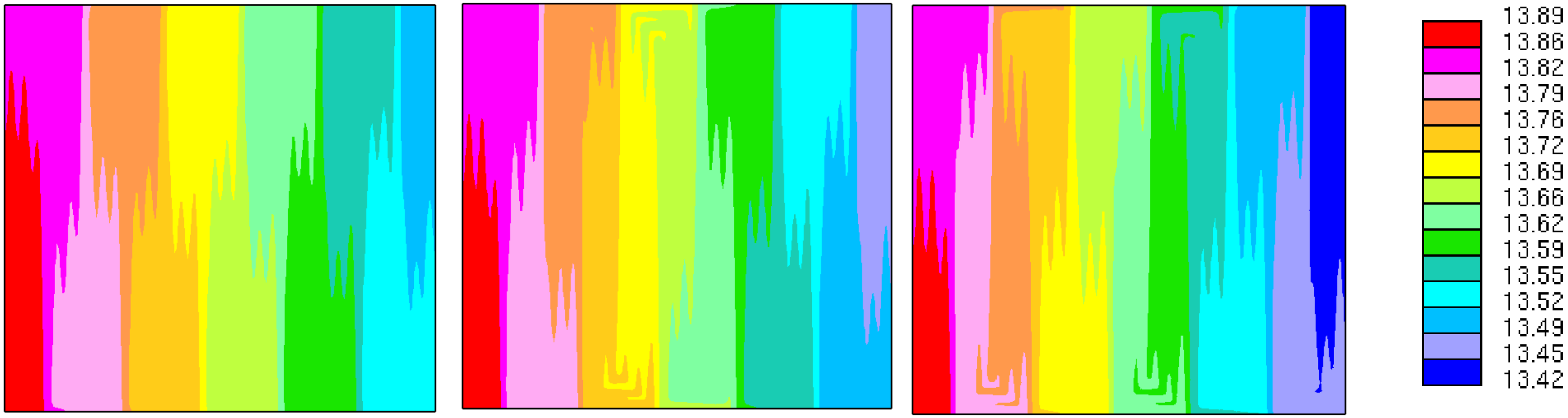
The Effect of Different Substrate

Diffusivity: Low MPL1: Large MPL2: Small – Iavg = 1A/cm^2



Current density distribution (A/cm^2)

EP40 P50 P75



Membrane water content

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)
  - Transport in PEMFC Stacks, Present in DOE Hydrogen and Fuel Cell merit review meeting, Arlington, VA, May 2011, 2012 and 2013
  - 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.***
  - M.J. Martinez-Rodriquez, C. Tong, S. Shimpalee, and J.W. Van Zee, "Characterization of Microporous Layers in Carbon Paper GDL for PEM Fuel Cell", in ECS Transactions Vol. 33 (1), Polymer Electrolyte Fuel Cells 10, The Electrochemical Society, pp. 1133-1141 (2010).
  - S. Shimpalee, V. Lilavivat, H. McCrabb, A. Lozano-Morales, J.W. Van Zee, "Understanding the effect of channel tolerances on performance of PEMFCs," Intl. J. of Hydrogen Energy, 36/19, 12512-12523, 2011.
  - M. Martinez, S. Shimpalee, T. Cui, B. Duong, S. Seraphin, J.W. Van Zee, "Effect of microporous layer on MacMullin number of carbon paper gas diffusion layer," J. of Power Sources, 207/1, 91-100, 2012.
  - A novel current distribution board to understand local transport in PEMFCs , presented in 220th meeting of ECS, Abstract #1545, Honolulu, October 2012
  - V. Lilavivat, S. Shimpalee, H. Xu, J. W. Van Zee, and C. K. Mittelsteadt, "Novel current distribution board for PEMFC," submitted to Intl J. of Hydrogen Energy (2013).
  - V. Lilavivat, S. Shimpalee, H McCrabb, and J. W. Van Zee, "Fundamental Analyses, Observations, and Predictions of Liquid Droplet Movement on Etched-Metal Surfaces for PEMFC," submitted to Electrochimica Acta (2013).
- **James McGrath *et al.***
  - Hydrophilic-Hydrophobic Multiblock Copolymer Electrolyte Membranes, Progress in MEA 2010, La Grande Motte, France, 19-22 September 2010.
  - Disulfonated Poly(Arylene Ether) Copolymers as Proton Exchange Membranes for H2/Air and DMFC Fuel Cells, Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2011, Asilomar Conference Grounds, Pacific Grove, CA. February 20 - 23, 2011.
  - Synthesis and characterization of multiblock partially fluorinated hydrophobic poly(arylene ether sulfone)-hydrophilic disulfonated poly(arylene ether sulfone) copolymers for proton exchange membranes, Chen, Yu; Rowlett, Jarrett R.; Lee, Chang Hyun; Lane, Ozma R.; Van Houten, Desmond J.; Zhang, Mingqiang; Moore, Robert B.; McGrath, James E. (2013) *Journal of Polymer Science, Part A: Polymer Chemistry*, published online: DOI: 10.1002/pola.26618.
  - 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.
  - Partly fluorinated poly(arylene ether ketone sulfone) hydrophilic-hydrophobic multiblock copolymers for fuel cell membranes, Chen, Yu; Guo, Ruilan; Lee, Chang Hyun; Lee, Myoungbae; McGrath, James E. *International Journal of Hydrogen Energy* (2012), 37(7), 6132-6139.
  - The effect of block length upon structure, physical properties, and transport within a series of sulfonated poly(arylene ether sulfone)s, Y. Fan, C.J. Cornelius, H.S. Lee, J.E. McGrath, M. Zhang, R.B. Moore and C.L. Staiger, *Journal of Membrane Science* (2013), 430, 106-112.
  - Rowlett, J.R., Chen, Y., Shaver, A.T., Lane, O., Mittelsteadt, C., **Xu, H.**, Zhang, McGrath, J.E., "Multiblock poly(arylene ether nitrile) disulfonated poly(arylene ether sulfone) copolymers for proton exchange membranes: Part 1 synthesis and characterization", ***Polymer (United Kingdom)*** 54 (23) PP. 6305 - 6313 (2013)