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

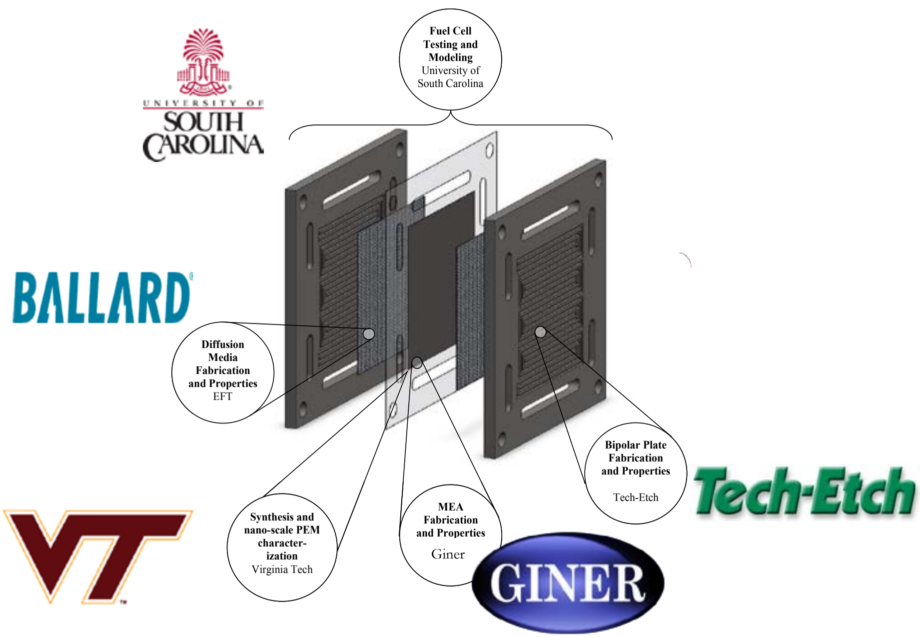
- *Cold Start-up Times*
- *Specific Power Density*
- *Stack Power Density*
- *Stack Efficiency*

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

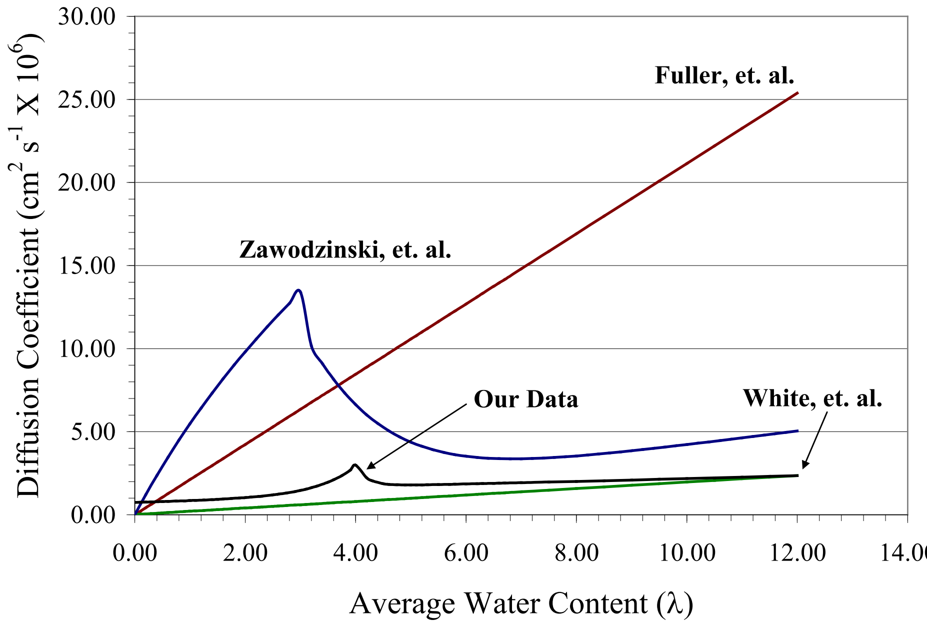
Milestone	Plan Complete	Actual Complete
Baseline PFSA model, with overall results correlating within +-20% of each other. Design the new apparatus for extending the range of electroosmotic drag and diffusivity.	4/15/2011	4/1/2011
Extend Model to a variety of membranes, catalyst content, GDM's, and flow fields. The model should be able to demonstrate prediction of the actual data within +-20% of the experimental results.	8/15/2012	60%

Approach & Milestones

Year	Techniques	Materials	Modeling
Year 1	New technique generation for static and dynamic diffusion, EODC, through plane conductivity confirmation with Baseline materials. (90%) Current Distribution Board Demonstration (100%)	Baseline hydrocarbon PEM generated and down selected (80%) Baseline Gas diffusion Media Delivered (100%) First Etched Plates (100%)	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.	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.

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

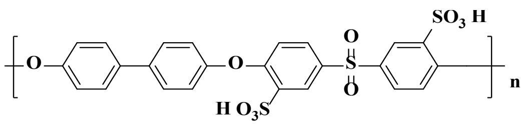


T.A. Zawodzinski, M. Neeman, L.O. Sillerud and S. Gottesfeld, *J. Phys. Chem.*, **95**, 6040 (1990)
T.F. Fuller, Ph.D. Thesis, University of California, Berkeley, CA (1992)
T.V. Nguyen and R.E. White, *J. Electrochem. Soc.*, **140**, 2178 (1993)
Equations of the form of: S. Motupally, A.J. Becker and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

GINER — BALLARD — UNIVERSITY OF SOUTH CAROLINA — VT — Tech-Etch — DOE Hydrogen Program

Achievements: New Membranes: HQS100-6FPAEB

BPSH100*

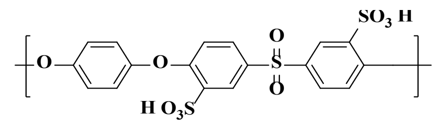


Chemical Formula: $C_{24}H_{16}O_{10}S_3$••
Molecular Weight: 560.57

IEC = 3.57 meq/g

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

HQSH100*

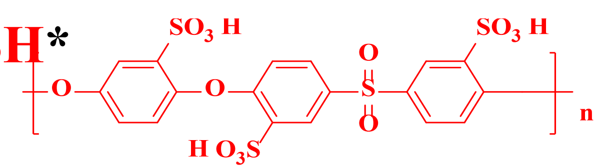


Chemical Formula: $C_{18}H_{12}O_{10}S_3$••
Molecular Weight: 484.48

IEC = 4.13 meq/g

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

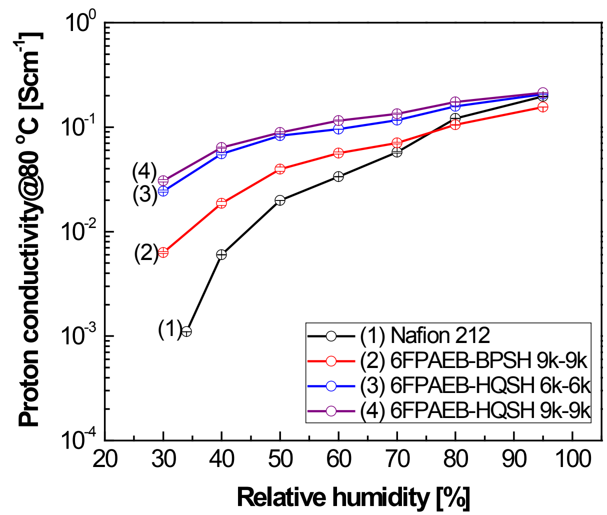
SQSH*



Chemical Formula: $C_{18}H_{12}O_{13}S_4$••
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*

Achievements: New Membranes: 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

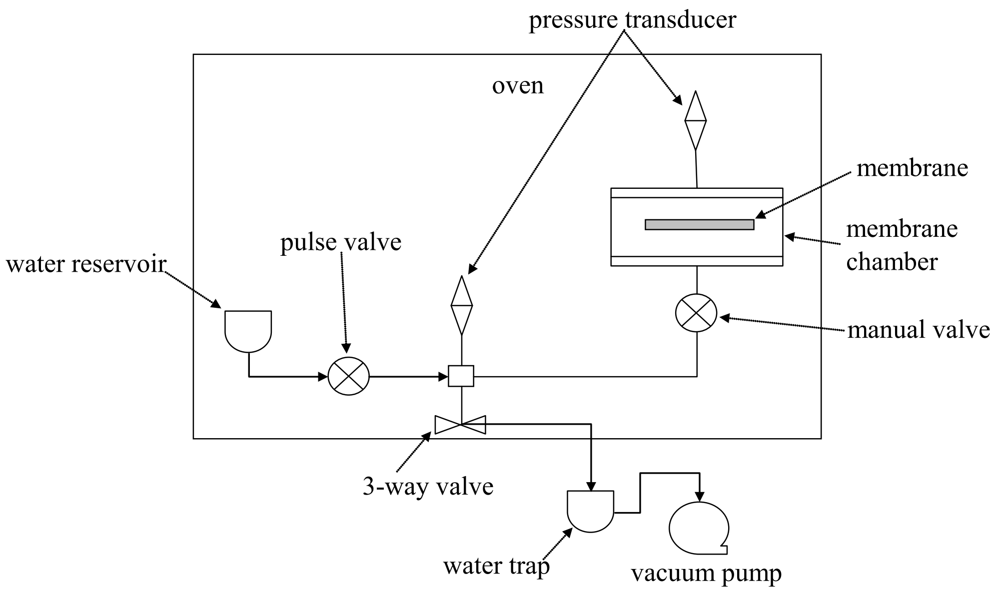
50cm^2 FCT plates

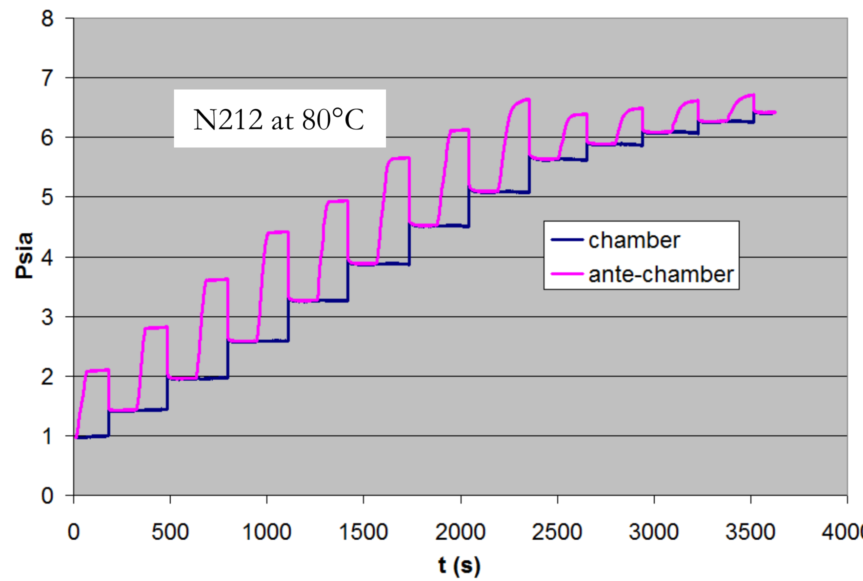
50cm^2 GM plates

South Carolina: Performance evaluation and model validation

7

Achievements: New Technique: Simultaneous Water Uptake and Diffusivity



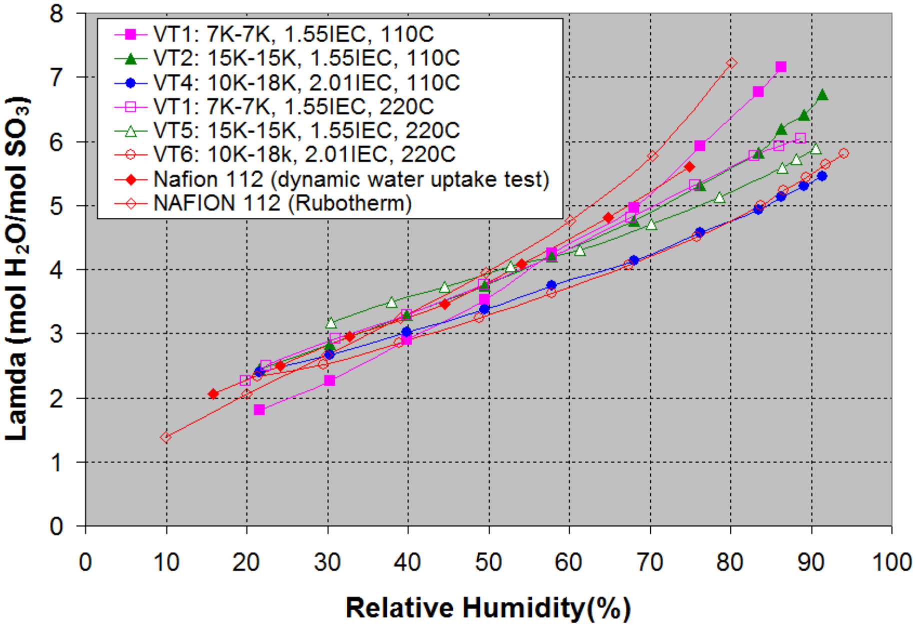


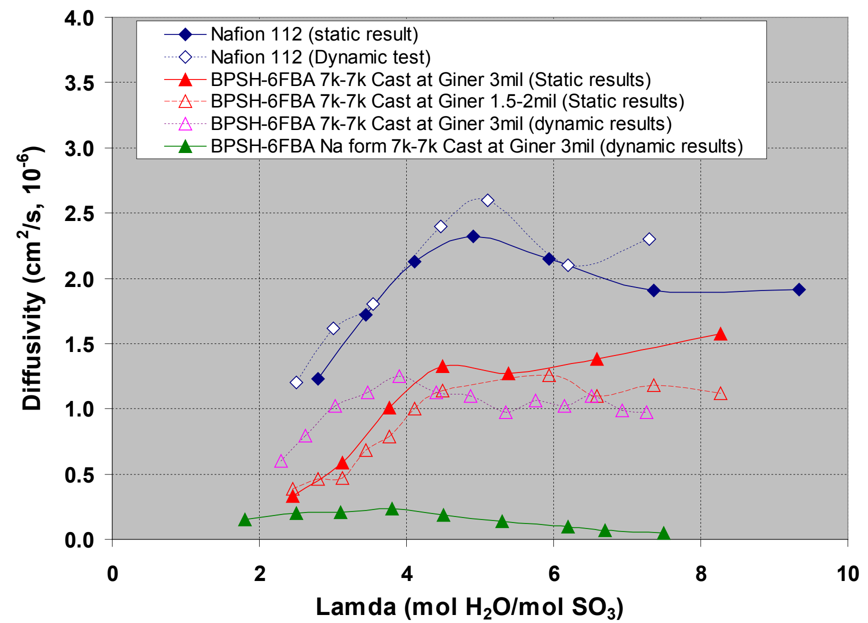
Non-membrane diffusion is eliminated by avoiding inerts in the system

- 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

Achievements: New Technique: Simultaneous Water Uptake and Diffusivity

Operation T: 80°C



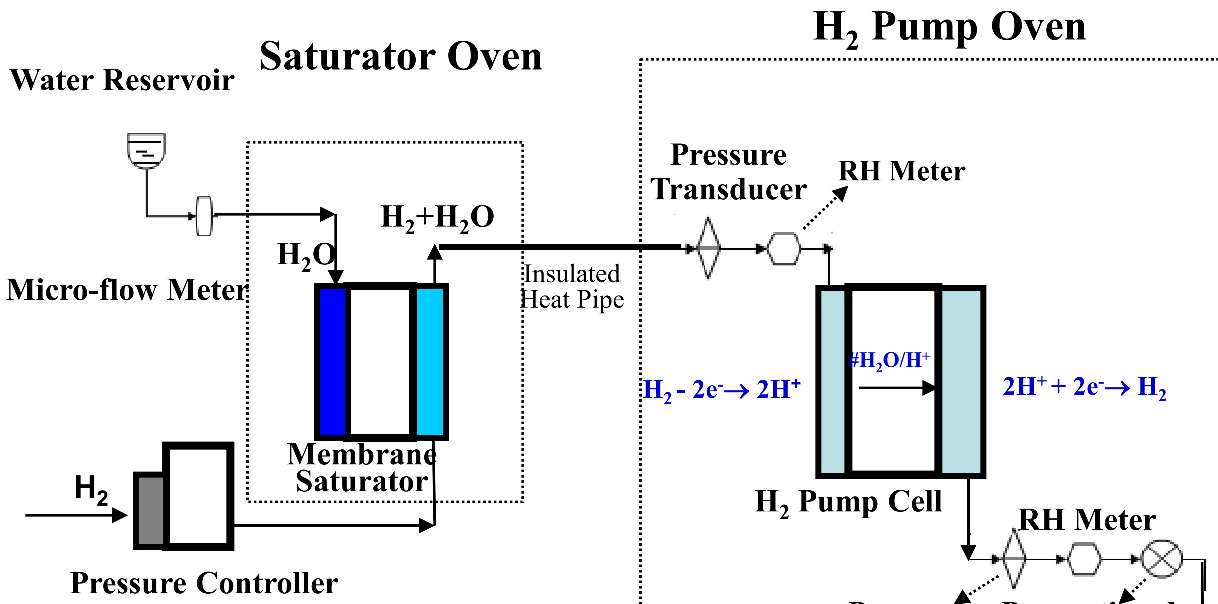


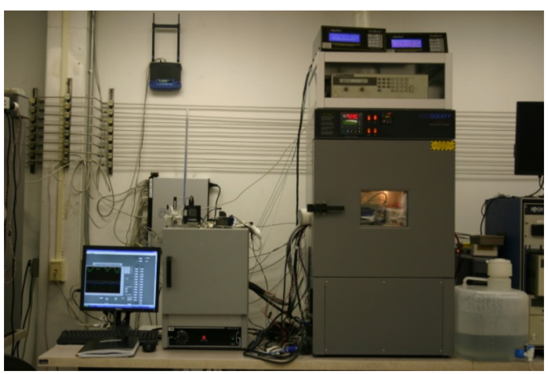
Nafion is a registered trademark of E.I. du Pont de Nemours and Company

Similar Isotherms seen for both PFSA and hydrocarbon-based ionomers

Diffusivity of PFSA > Block Hydrocarbons in H^+ form >> Na^+ form

Achievements: New Technique: EODC



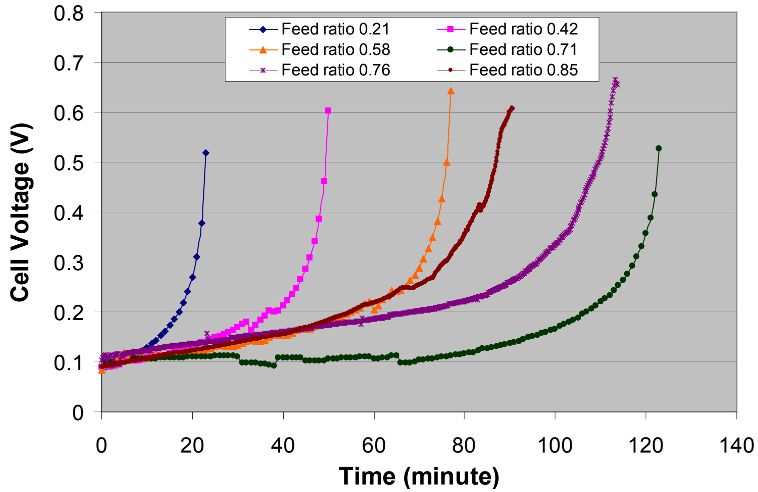


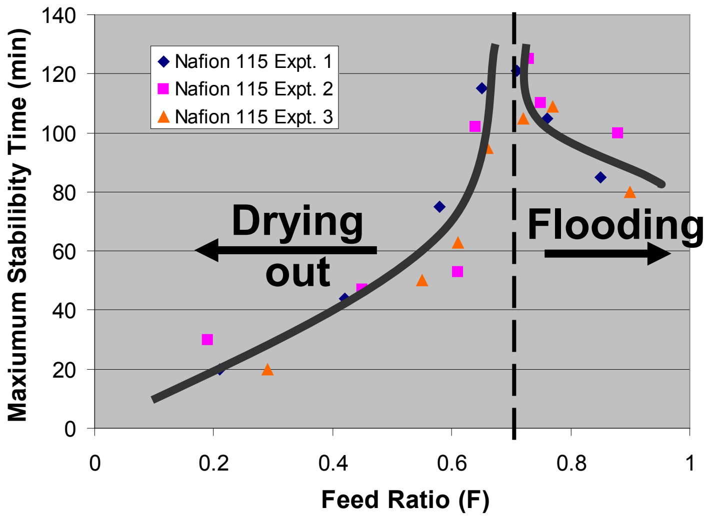
- Water/H_2 inlet ratio controlled by controlling saturator temperature and H_2 pressure
- If ratio is too high, not enough water is dragged across and cell floods and fails
- If ratio is too low, membrane dries out and cell fails
- At Water/H_2 = 2*EODC Cell operates in quasi-stable state

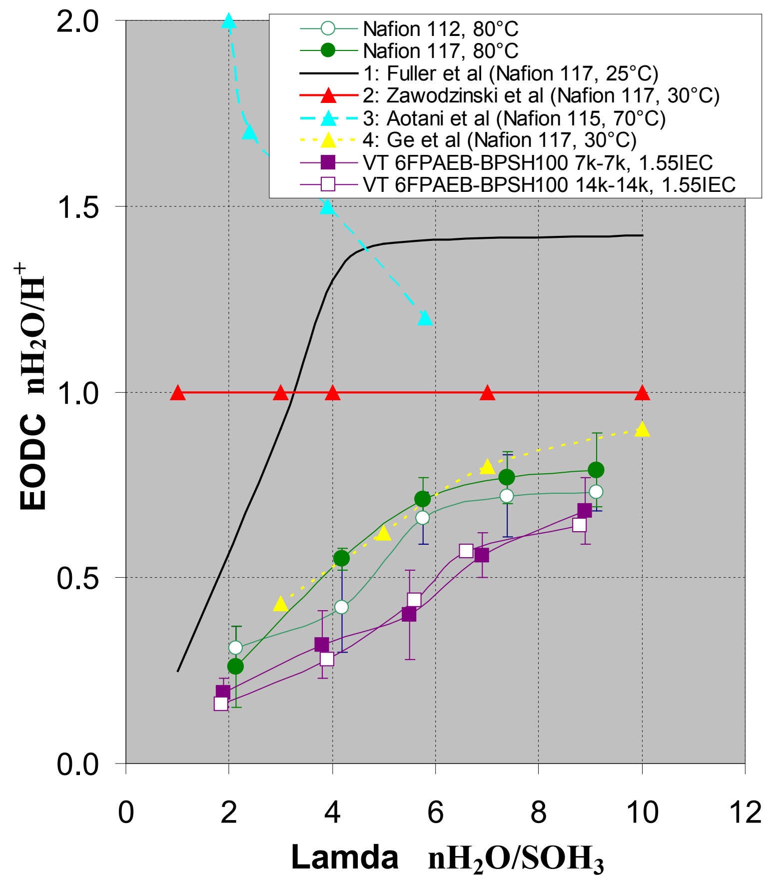
All gas/gas diffusion is eliminated

Achievements: New Technique: EODC

Nafion® 115, 80 °C and 82% RH, 100 mA/cm^2







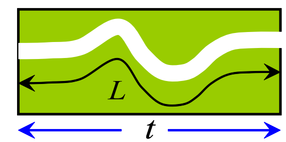
- EODC of hydrocarbon-based materials slightly lower, but similar trend
- Still working on consensus

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

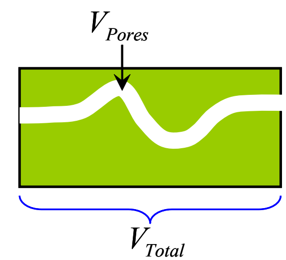
- Ratio of the actual path length through the pores to the shortest linear distance between two points.



$$\tau = \frac{L}{t}$$

•Porosity

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



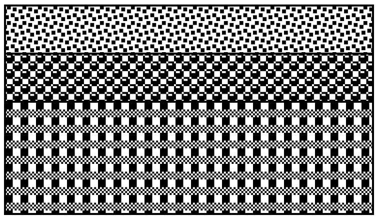
$$\varepsilon = \frac{V_{Pores}}{V_{Total}}$$

•MacMullin Number

- Function of tortuosity and pososity.

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

Achievements: Design of Gas Diffusion Media



Baseline Material at start of program was Toray H060

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

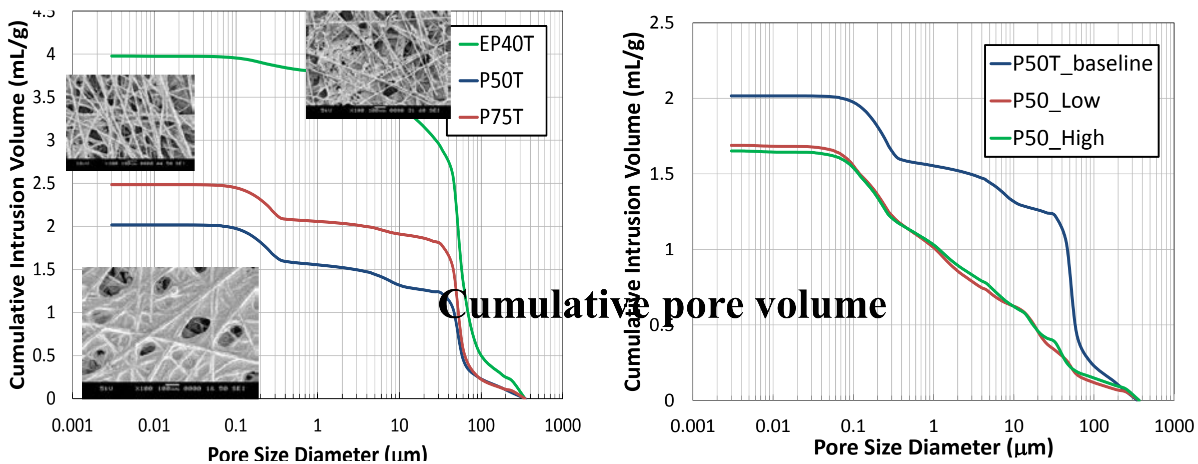
The new design of GDLs have been modified from standard Ballard GDLs by adding two micro porous layers. Each set has been treated with two different methods in order to provide two different values of diffusivity.

Total of 12 new papers generated
5 characterized ex-situ to date

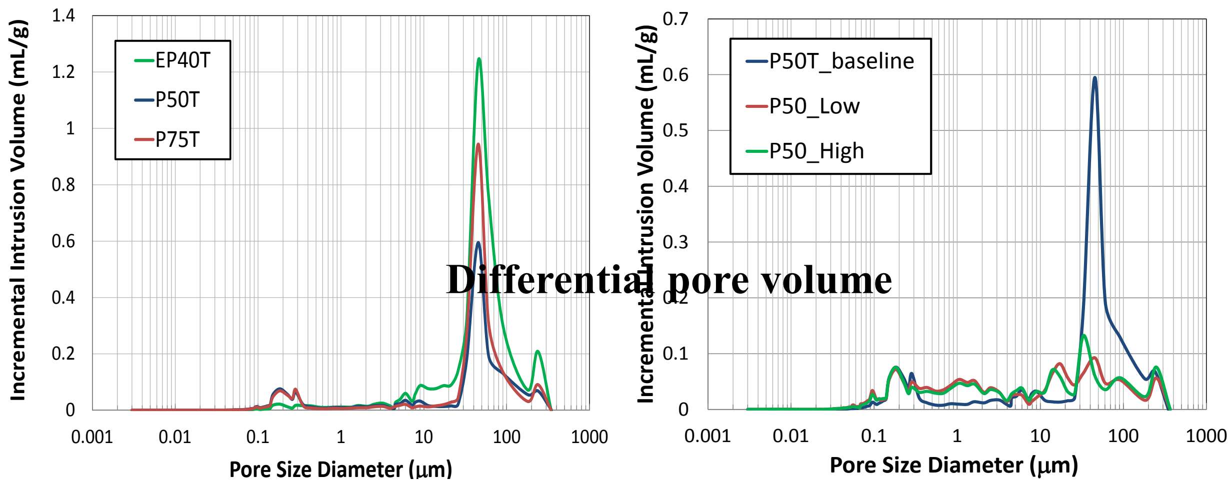
Achievements: Design of Gas Diffusion Media

Comparison of Mercury pore size distributions of new design GDLs

Baseline Substrates   Modified Substrates



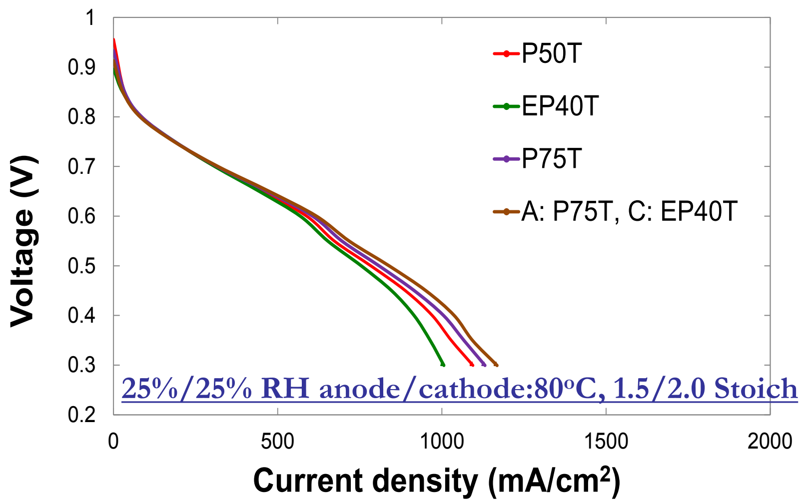
EP40T has largest pore volume, concentrated at 50 μm

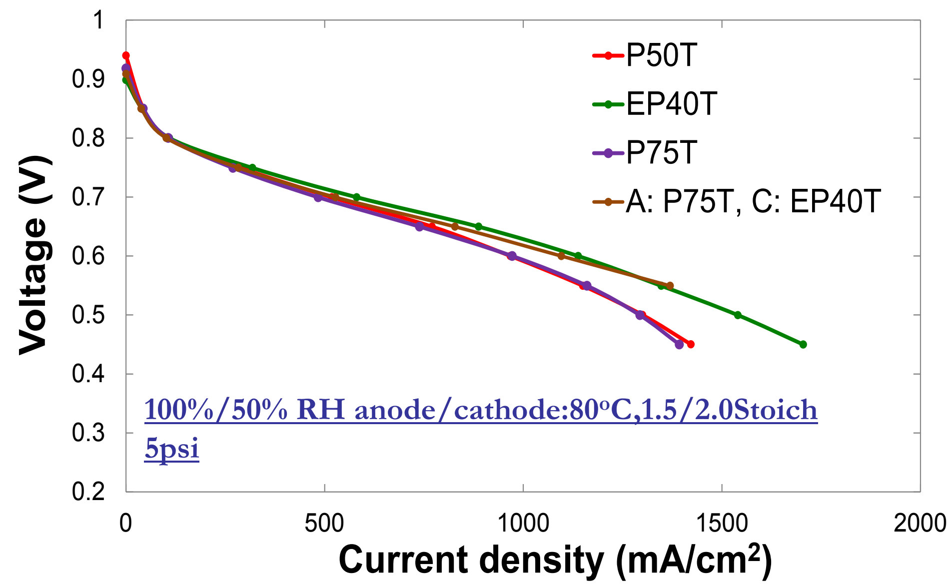


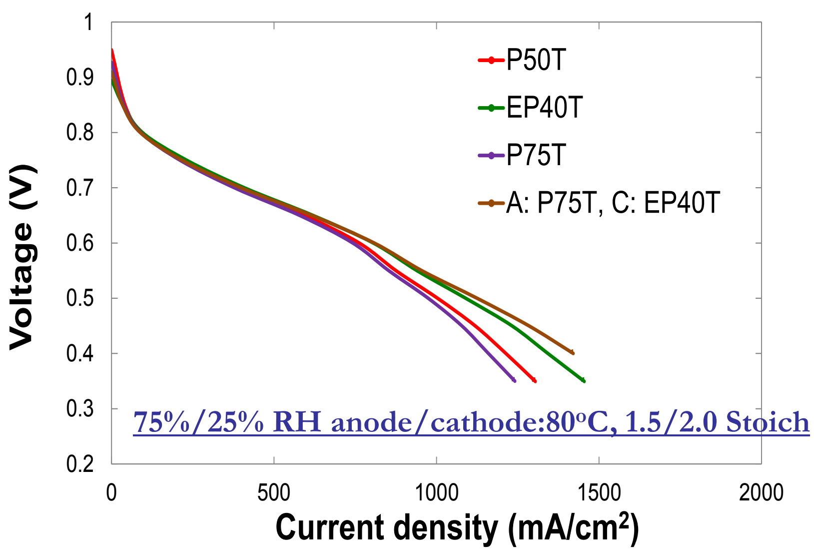
Modification greatly reduces volume of large pores

Achievements: Design of Gas Diffusion Media

Gore 57 Series 80°C

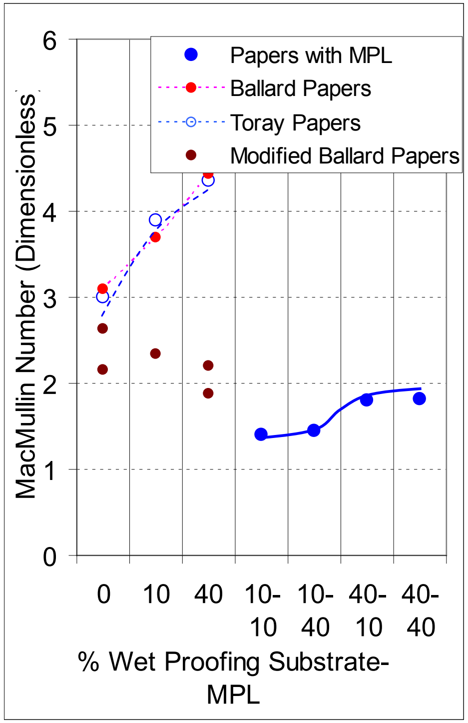






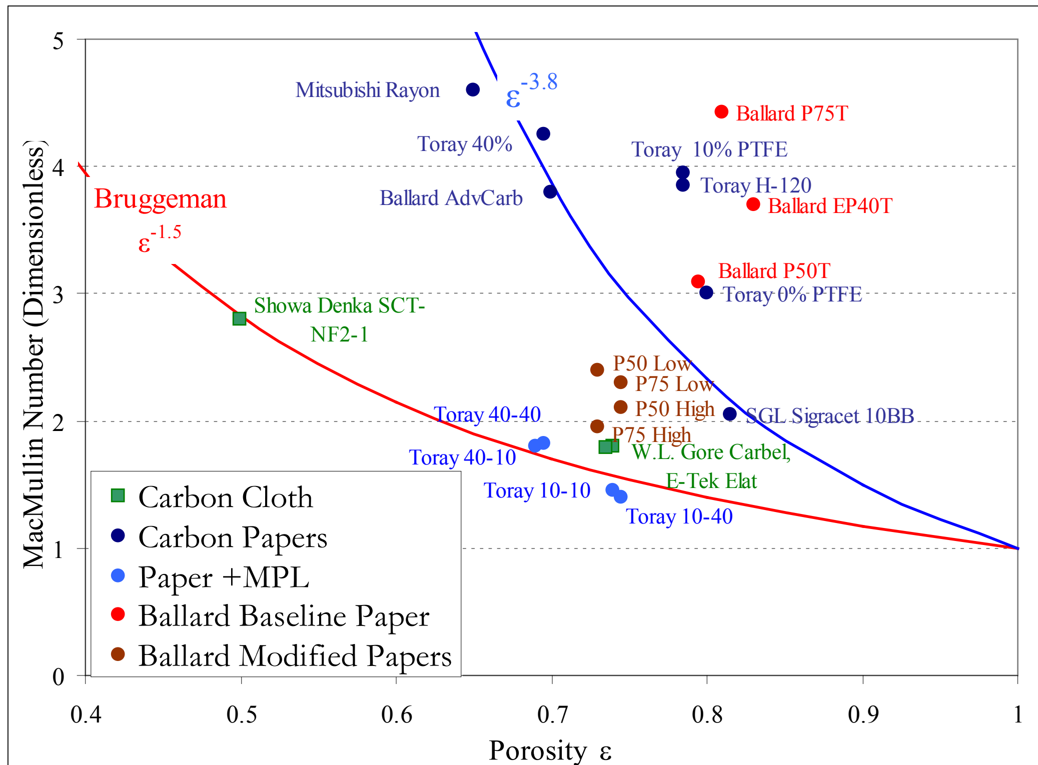
- P75T GDL shows the highest performance at lower humidity condition whereas EP40T shows the highest performance at higher humidity condition.
- P75T will be used in the anode and EP40T will be used in the cathode in following baseline testing

Achievements: Design of Gas Diffusion Media: Wet Proofing



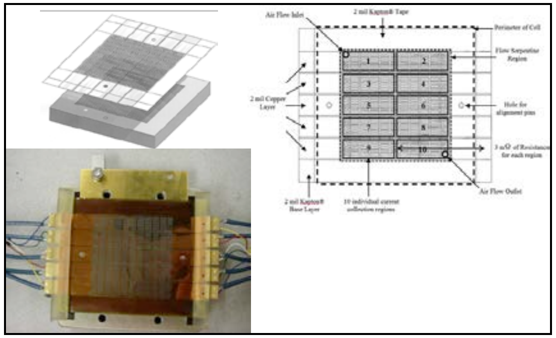
MacMullin number as function of wet proofing in substrate and MPL

MacMullin number as function of porosity

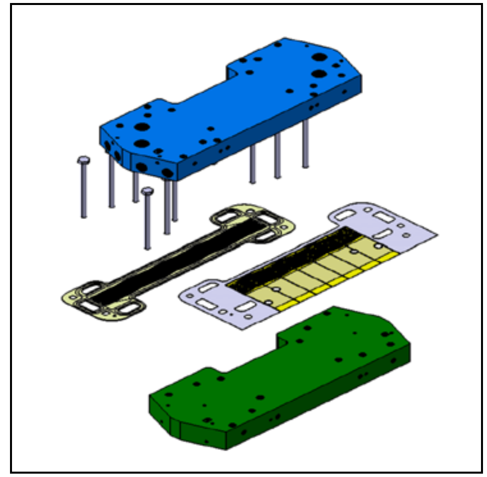


Difficult to make general relationship of $N_M(\varepsilon)$

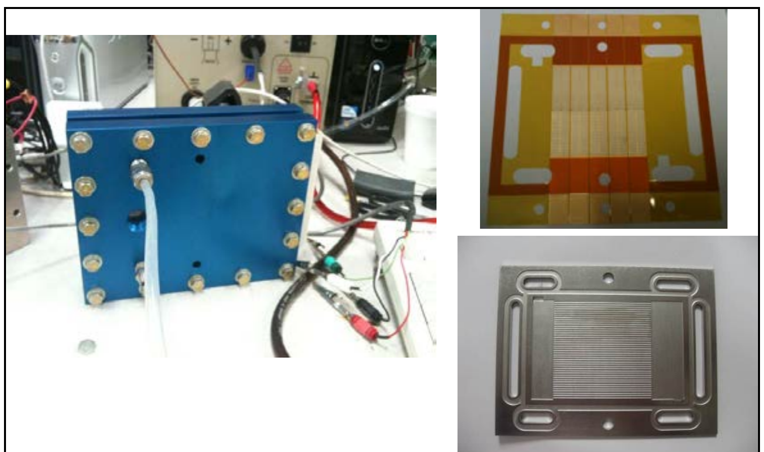
Achievements: Fuel Cell Flow-Fields



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

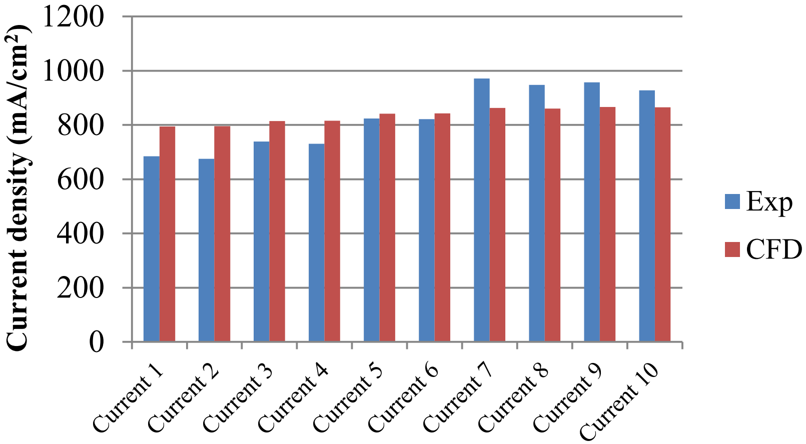
Thin Graphite Plates (GM)

- Also common
- Open design allows comparison/collaboration

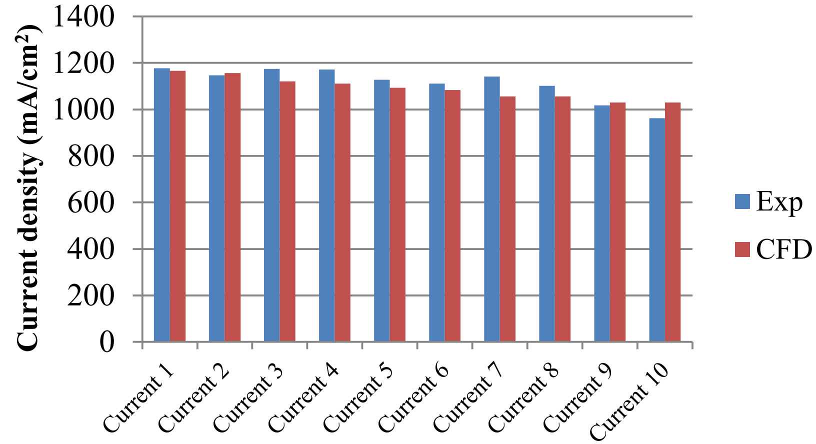
Current Distribution Boards Designed for All 3

Achievement: Model Verification: Serpentine

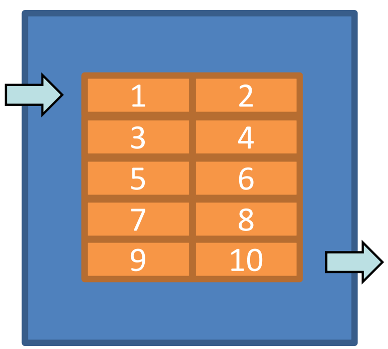
At potential=0.3V

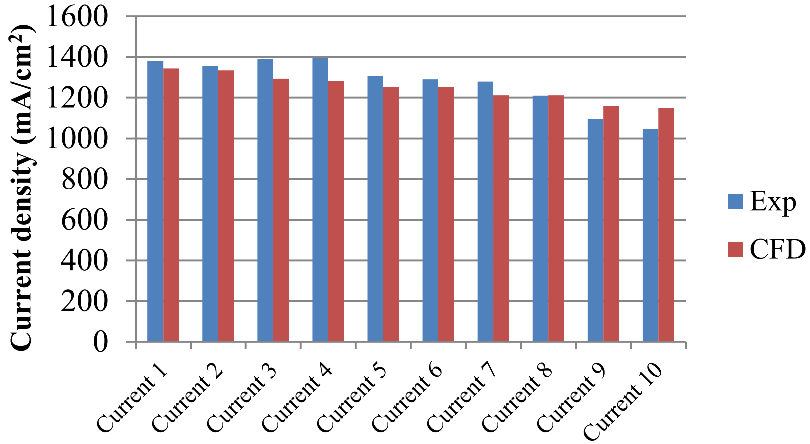


Anode 25%RH, Cathode 25%RH
Average current density = 809 mA/cm^2



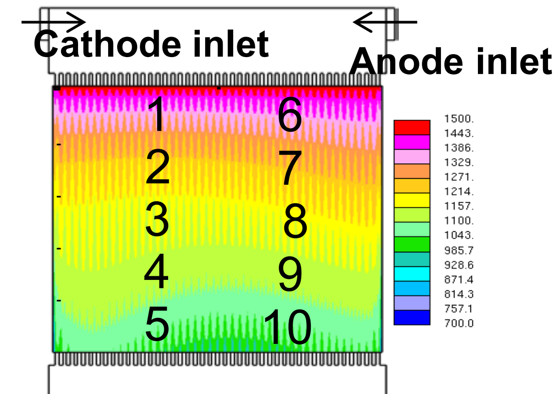
Anode 75%RH, Cathode 25%RH
Average current density = 1094 mA/cm^2



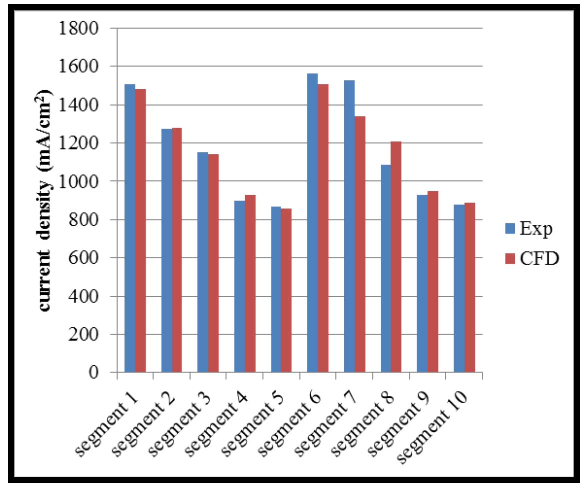


Anode 100%RH, Cathode 50%RH
Average current density = 1250 mA/cm^2

Achievements: Flow Field Modeling: Thin Metallic Plates



Average current density = 1200 mA/cm²

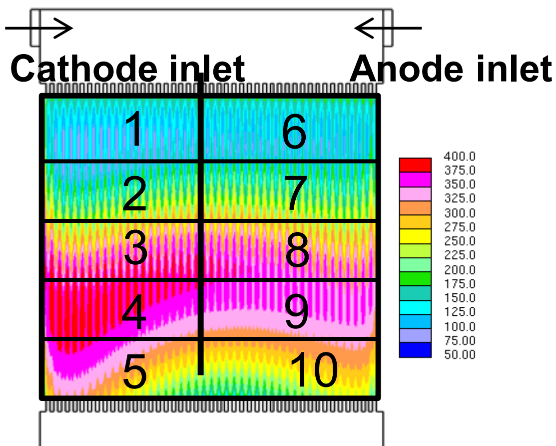


Operating condition:
Anode Stoich. = 1.5
Anode RH = 100%
Cathode Stoich. = 2.0
Cathode RH = 50%
Tcell = 80°C
System pressure = 136kPa

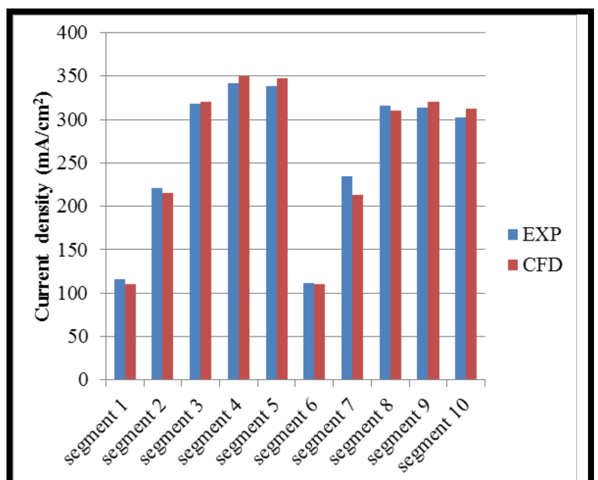
High Current Wet

Model Predicts Equally Well

- *High i/Wet*
- *Low i/Dry*



Average current density = 294 mA/cm²



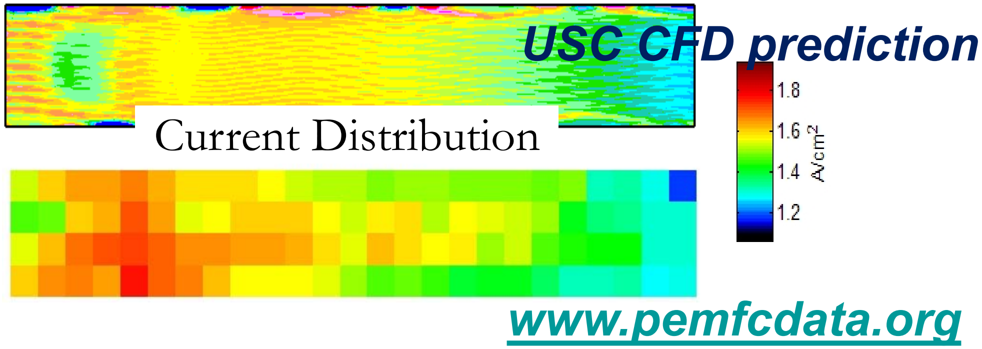
Low Current Dry

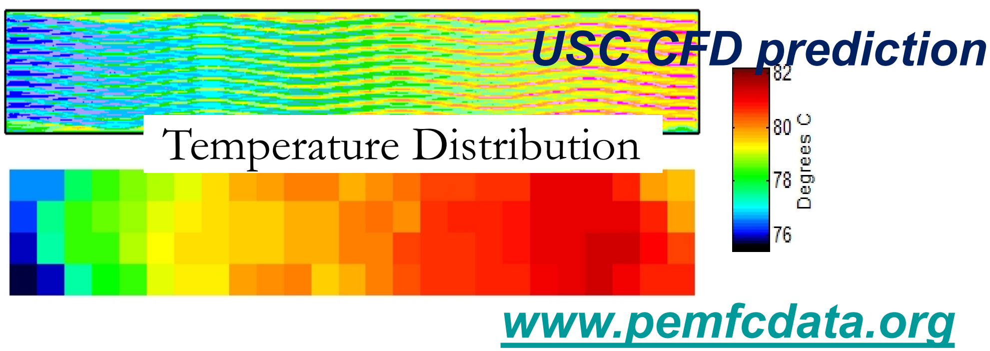
Operating condition:
Anode Stoich. = 1.5
Anode RH = 25%
Cathode Stoich. = 2.0
Cathode RH = 25%
Tcell = 80°C
System pressure = 101kPa

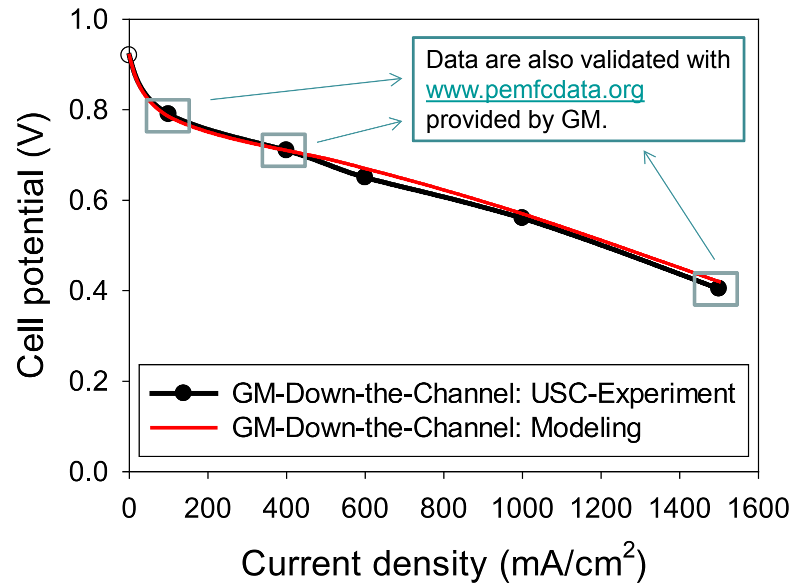
Achievement: Model Verification:

Distributions of current density and temperature of 50-cm² GM-Down-the-Channel flow-field compared with www.pemfcdata.prg

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

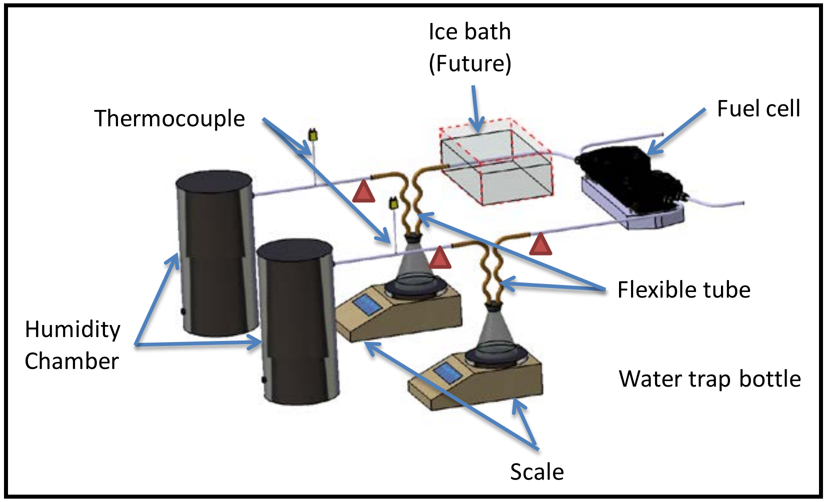






USC data matches published data very well, both with performance and model results

Achievement: Model Verification:



Water Balance experiment and numerical result of GM Down-the-Channel flow-field

(<u>counter-current flow</u>: 50/50%RH, <u>101/101kPa</u>, 80°C, 1.5/2.0 stoich)

New Transport Numbers Greatly Improve Prediction of Water Mass Balance

	i A/cm^2	RH	Anode Water Balance (mg/sec)			Cathode Water Balance (mg/sec)			
			Water in	Water out	Cross to Cathode	Water in	Gen.	Water out	Cross from Anode
EXP	**0.4**	50	0.86	0.34	0.51	2.68	1.87	5.02	0.47
CFD(new)	**0.4**	50	0.90	0.33	0.57	2.70	1.87	5.08	0.51
CFD(old)	**0.4**	50	0.90	0.37	0.53	2.70	1.87	5.12	0.55
EXP	**0.8**	50	1.7	1.26	0.43	5.36	3.73	9.40	0.31
CFD(new)	**0.8**	50	1.72	1.30	0.32	5.37	3.73	9.43	0.33
CFD(old)	**0.8**	50	1.72	0.86	0.86	5.37	3.73	9.99	0.89

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

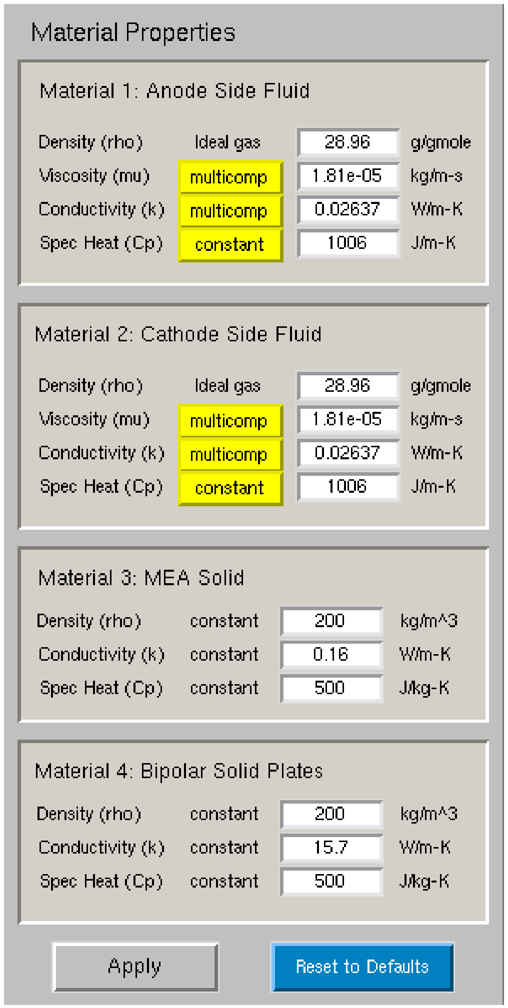
- **Membrane design and development, McGrath's group at VA Tech:**
  - Completed the synthesis of a full list of hydroquinone based hydrophilic-hydrophobic block copolymers (HQSH-6FPAEB).
  - Provided ~20g of the 6FPAEB-BPSH and 6FPAEB-HQS100 polymer powders to Giner for member casting and testing.

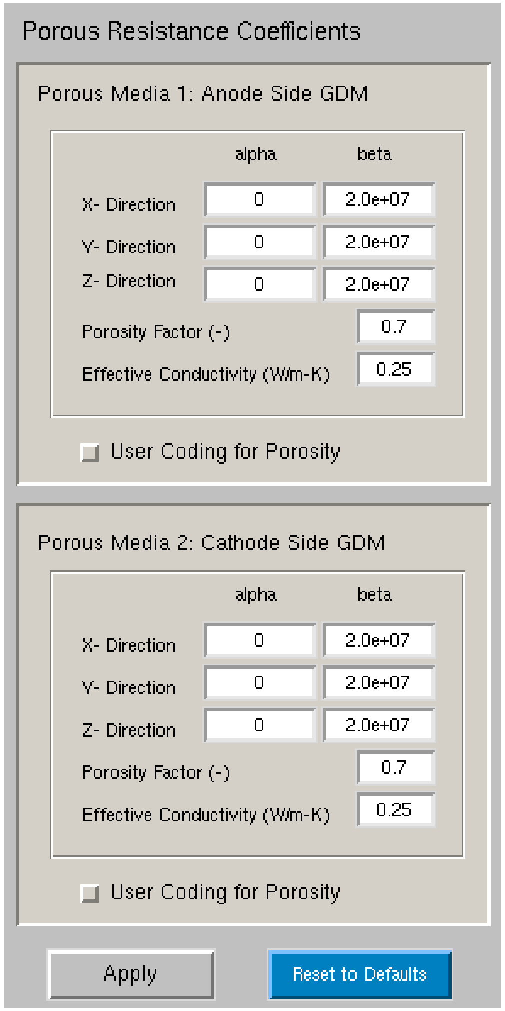
- **Membrane Characterization And Performance Testing at Giner**:
  - Successfully casted copolymer powders from VA Tech to membranes
  - Automated dynamic water uptake/diffusivity test system
  - Completed diffusivity measurements of VA Tech membranes
  - Measure EODC measurements of Nafion® membrane using dead-ended H_2 pump
  - Obtained GM plates and flow paths and provided MEAs for testing

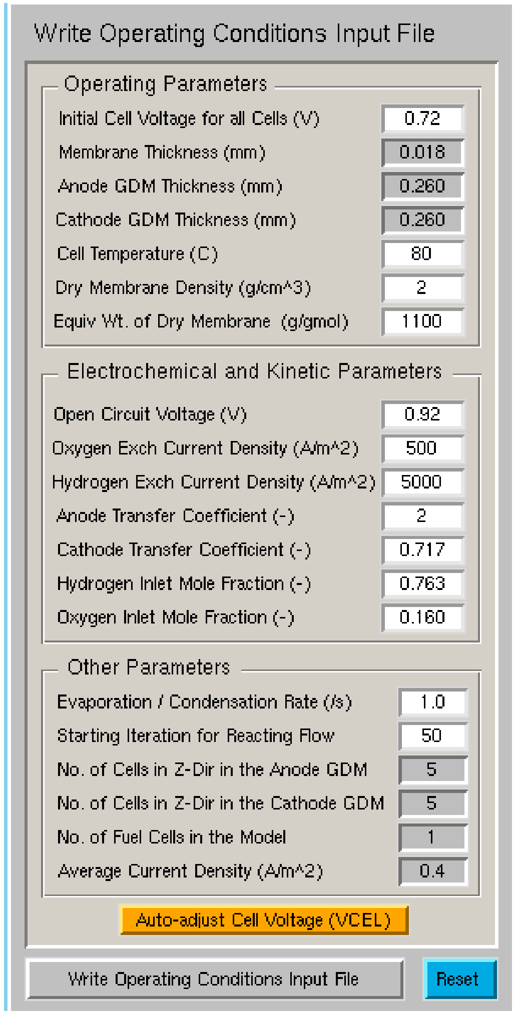
- **Transport Modeling, GDL & Current Distribution Board Characterization at USC:**
  - Designed new GDLs and completed pore size distributions with fuel cell performance test;
  - Simulated cell performance and current distribution at various water uptake, membrane diffusivity and electro-osmotic drag 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

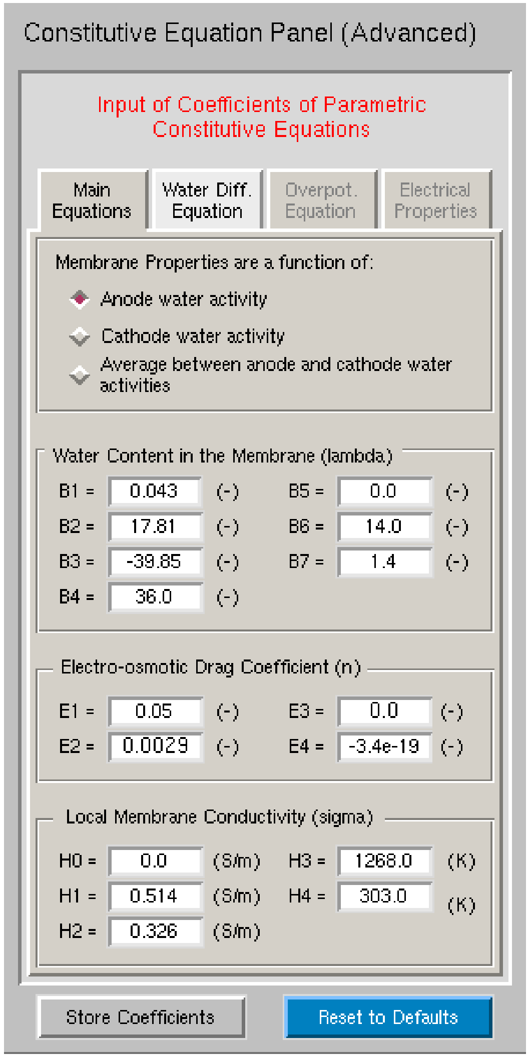
Modeling Input Parameters

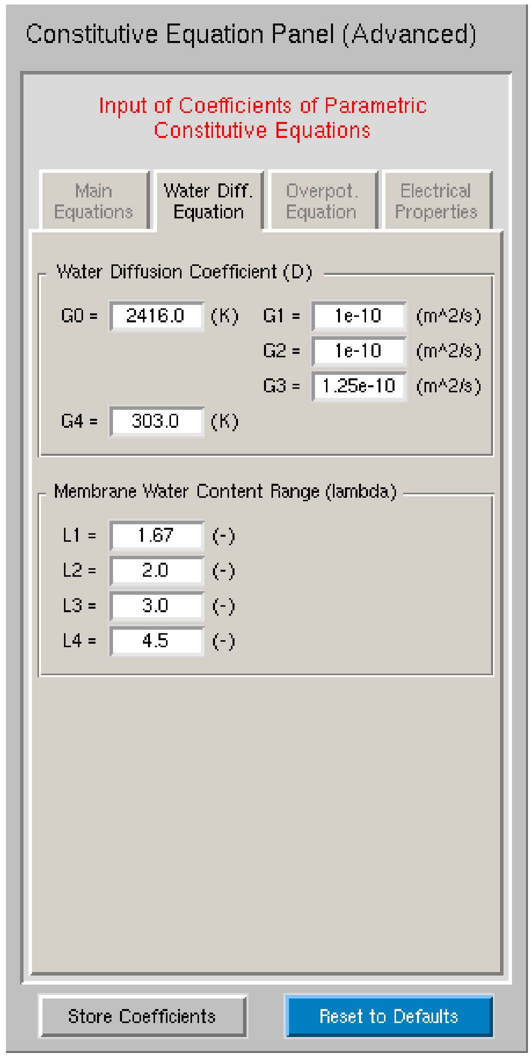


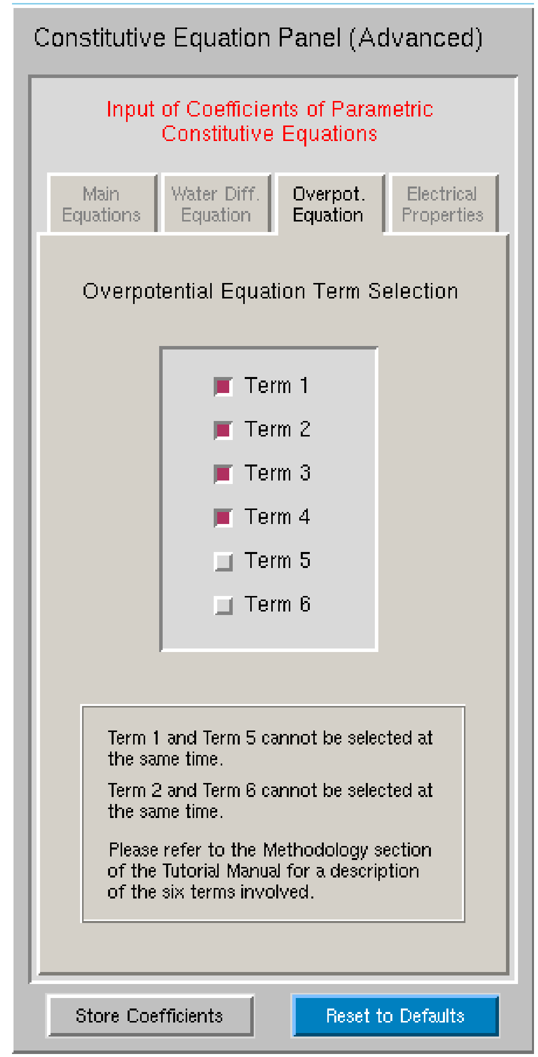




Modeling Input Parameters (Cont.)







Modeling Outputs

Scalars — Active | Passive | Generic

Active Scalars

Description	No.	Name
Nitrogen Gas	1	N2
Hydrogen Gas	2	H2
Oxygen Gas	3	O2
Water Vapor - Anode	4	WVA
Water Vapor - Cathode	5	WVC
Liquid Water - Anode	6	LWA
Liquid Water - Cathode	7	LWC

Apply

Scalars — Active | Passive | Generic

Passive Scalars

Description	No.	Name
Current Density	8	CD
Net Water Flux per Proton	9	ALPHA
Kinetic Overpotential	10	KOP
Anode Overpotential	11	AOP
Cathode Overpotential	12	COP
Membrane Conductivity	13	MC
Water Diffusivity	14	WDC
Water Content inside MEA	15	LAMBDA
Anode Activity	16	AA
Cathode Activity	17	CA
MEA Liquid Film Thickness	18	LFT
Local MEA Voltage*	20	MEA_POTENT.

* Only used when Electron Transport is On

Apply

Scalars — Active | Passive | Generic

Generic Scalars

Description	No.	Name
Potential*	19	POTENTIAL

* Only used when Electron Transport is On

Apply