Transport in PEMFCs

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Project ID # FC054

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Transport in PEMFCs

Timeline

- Project Start Date: 10/5/2009
- Project End Date: 10/31/2013
- Percent Complete: 80%

Budget

- Total Project Funding
  - DOE Share $2.66M
  - Cost Share $678K (20%)
- Funding Received in FY10: $915K
- Funding Received in FY11: $786K
- Funding Received in FY12: $400K
- Planned Funding in FY13: $560K

Barriers Addressed

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

Technical Targets

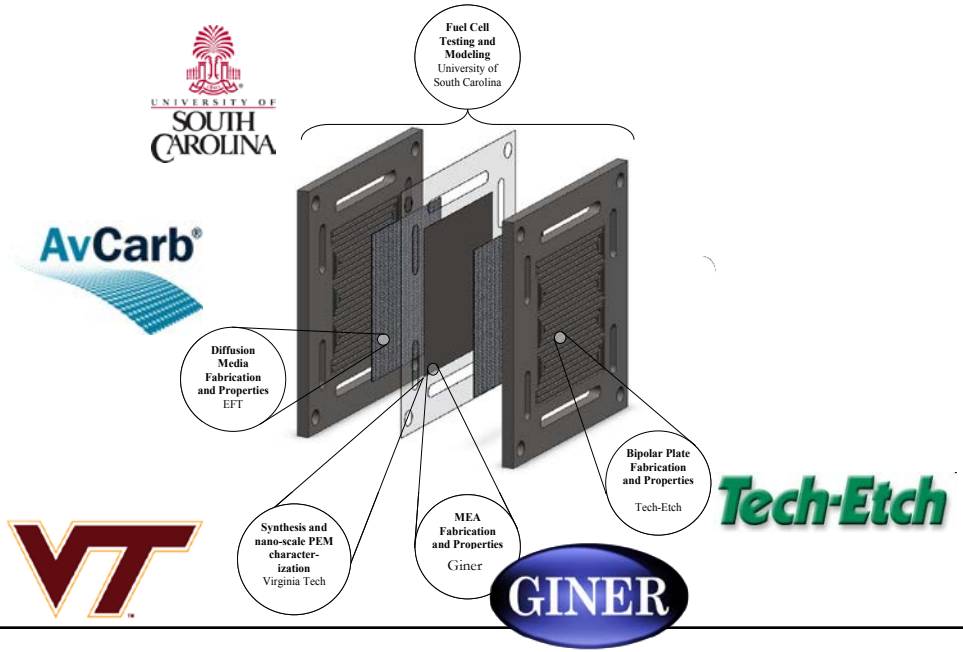
- *Cold Start-up Times*
- *Specific Power Density*
- *Stack Power Density*
- *Stack Efficiency*

Partners

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

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

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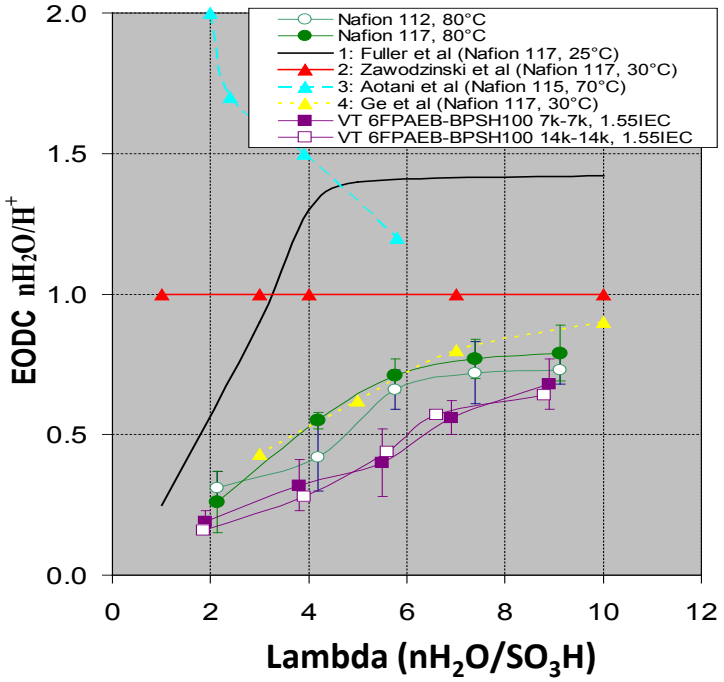
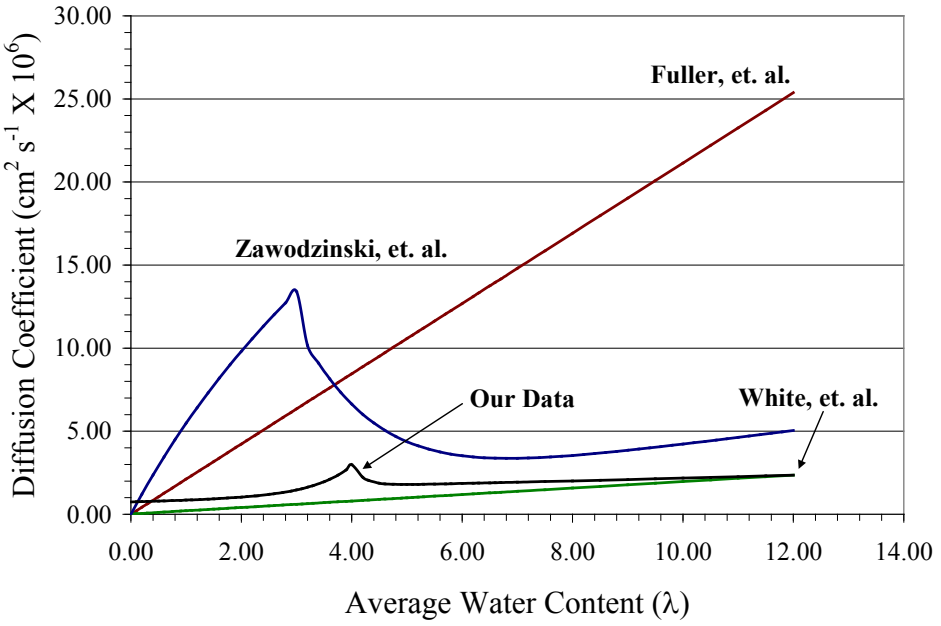
Relevance: Use of Modeling in Fuel Cell Development is Widespread. Agreement on Fundamentals *is not*





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

T.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)

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

Relevance:

PEM Development

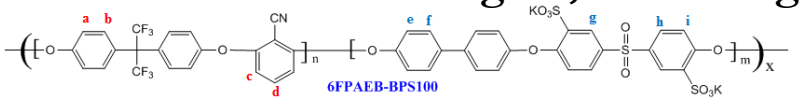
- Hundreds of PEMs developed for fuel cells
  - Would like to come up with design rules for PEMs
  - How does size/degree of Phase separation affect
    - Conductivity
    - EODC
    - Water Diffusivity
    - Gas Permeability
  - Similar Study done by *Gross et al* for side-chain polymers

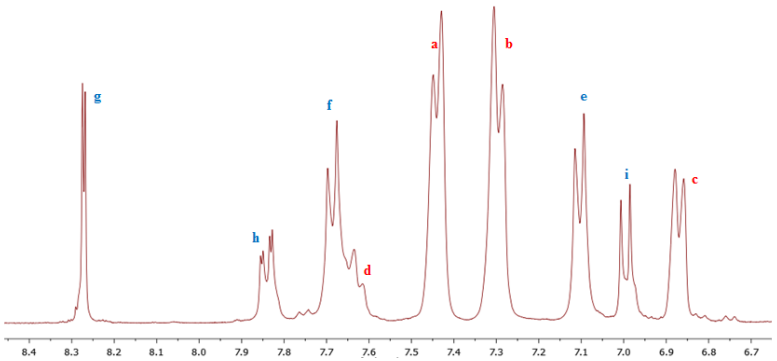
Modeling

- 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?

Achievements: Copolymer Membrane Design

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

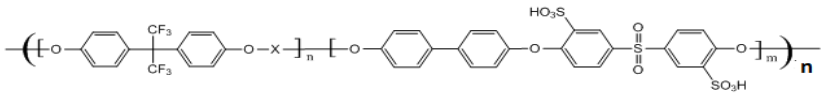




	Polymer	Thermal Treatment Temperature (°C)	IEC (meq/g)
1	6FPAEB-BPSH100 7k-7k	110	1.55
2	6FPAEB-BPSH100 15k-15k	110	1.55
3	6FPAEB-BPSH100 10k-18k	110	2.01
4	6FPAEB-BPSH100 7k-7k	220	1.55
5	6FPAEB-BPSH100 15k-15k	220	1.55
6	6FPAEB-BPSH100 10k-18k	220	2.01

- **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



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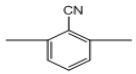
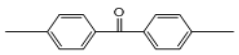
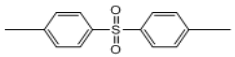
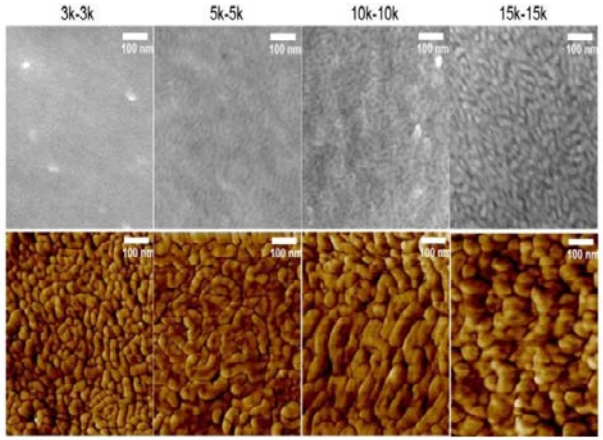

6FPAEB-BPSH


6FK-BPSH


6FBPS0-BPSH



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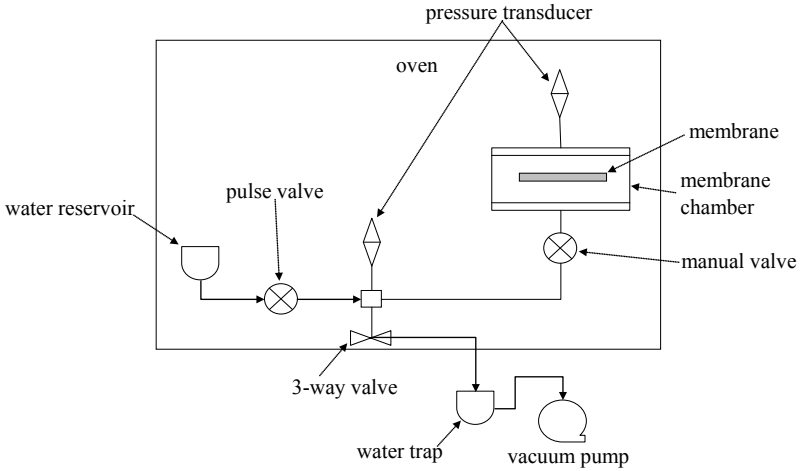
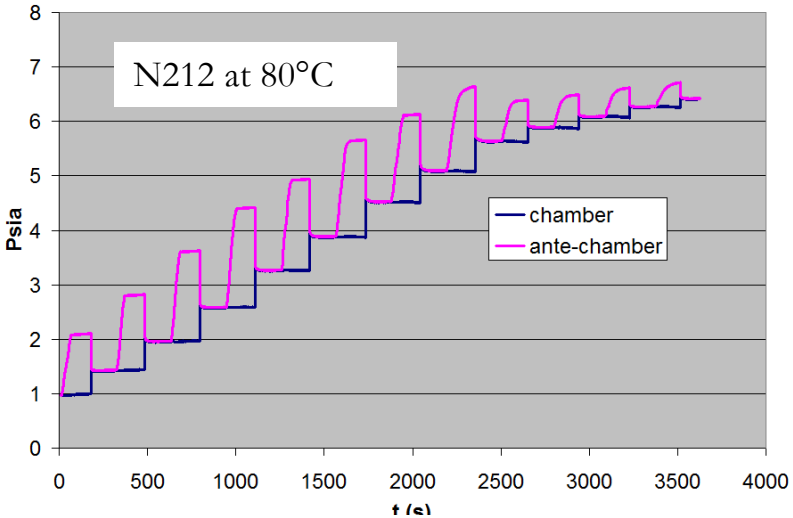
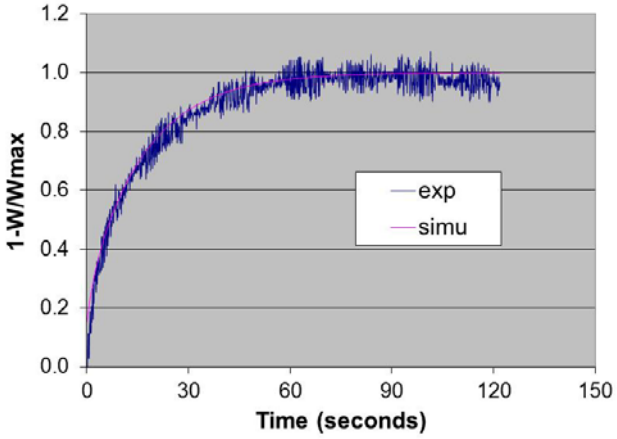
Achievements:

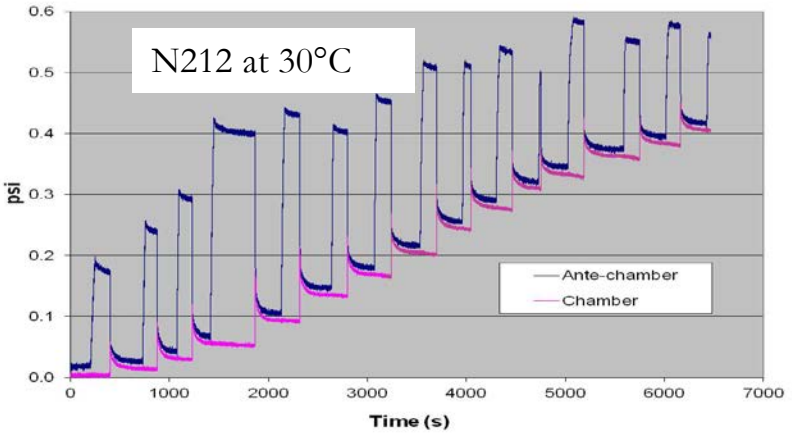
New Technique: Simultaneous Water Uptake and Diffusivity

Extended to Sub-Ambient Conditions

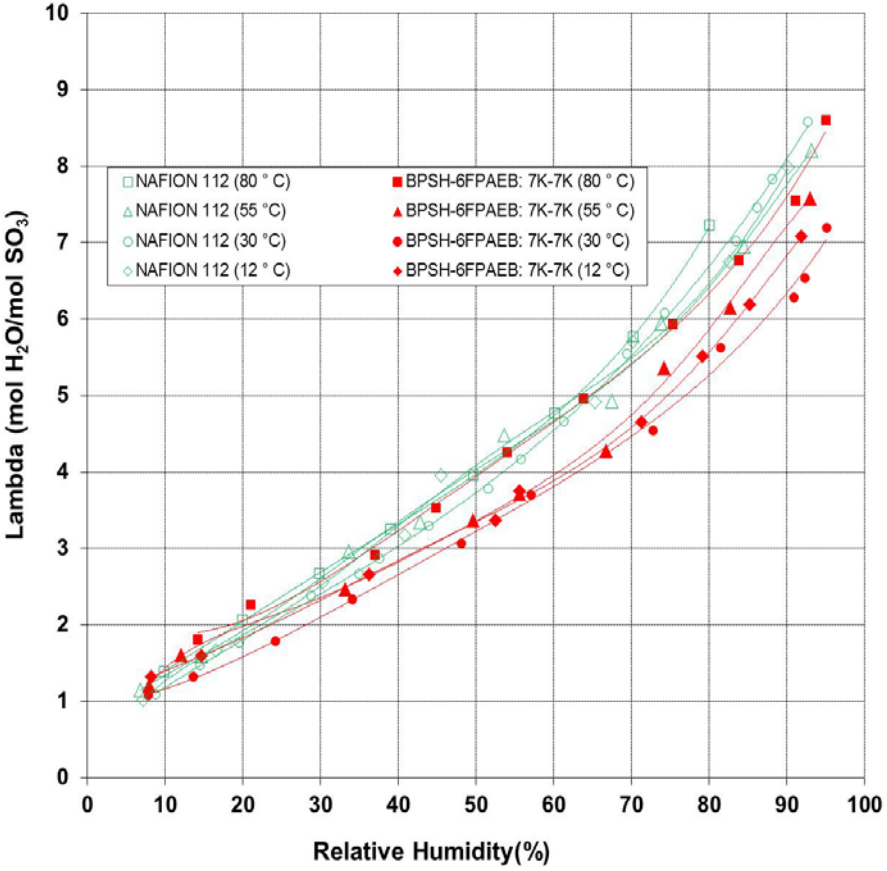


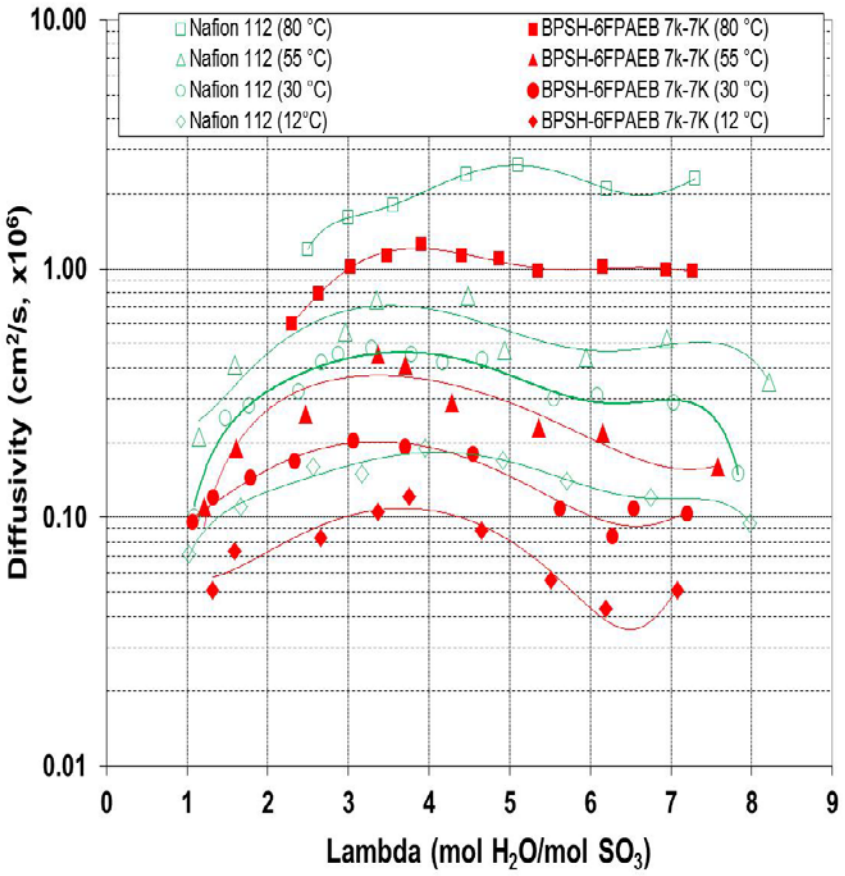






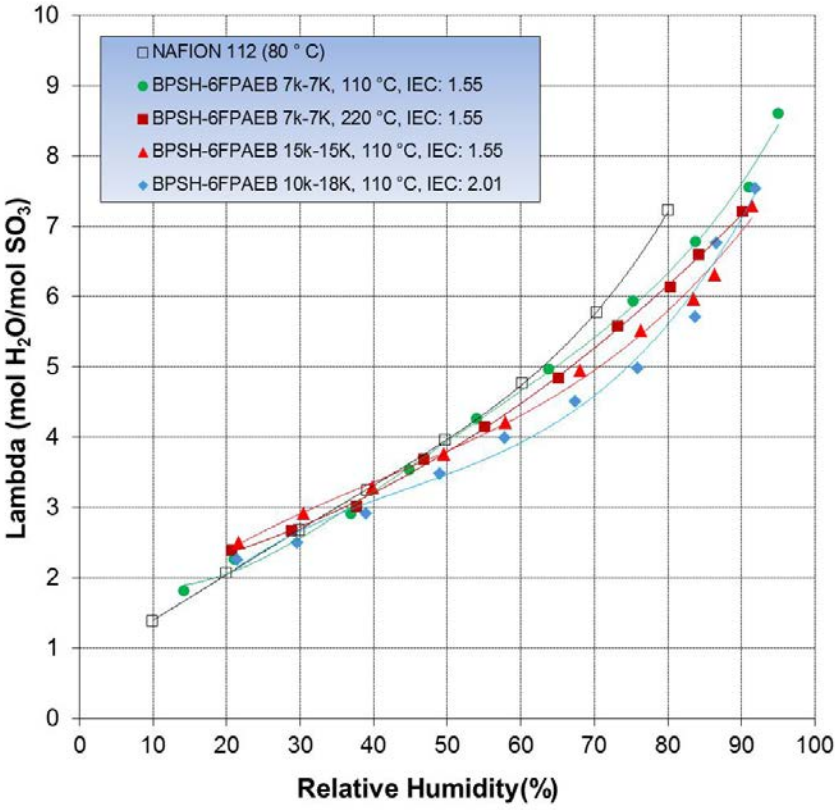
Achievements:
New Technique: Simultaneous Water Uptake and Diffusivity

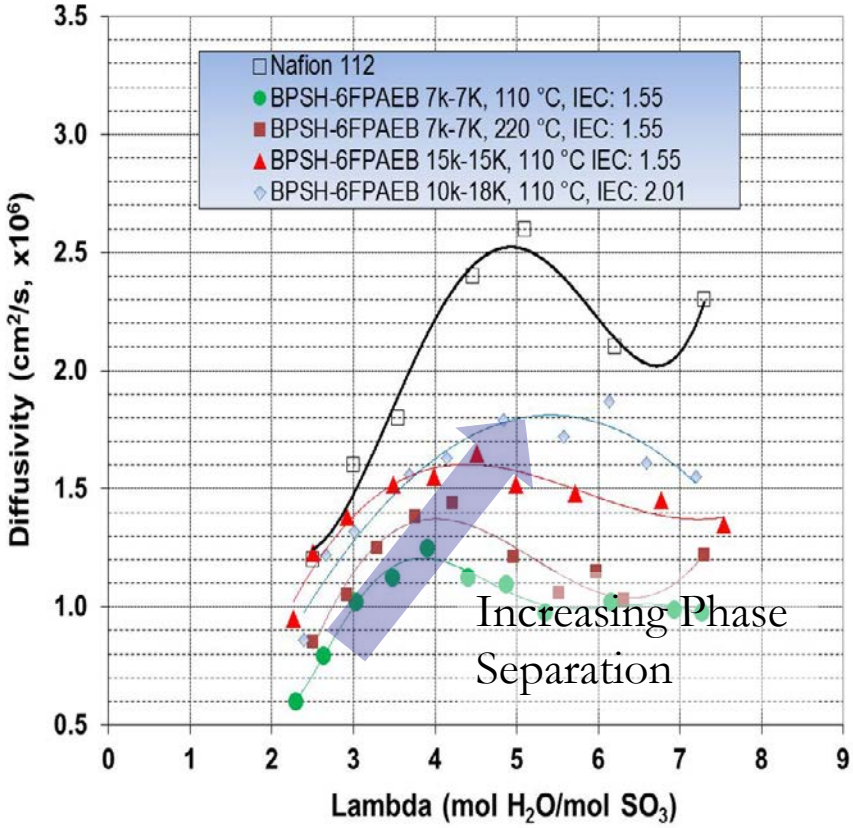




BPSH-6FPAEB Membranes show nearly identical water uptake with little temperature dependence
Water Diffusivity is ~ ½ that of Nafion® regardless of temperature.

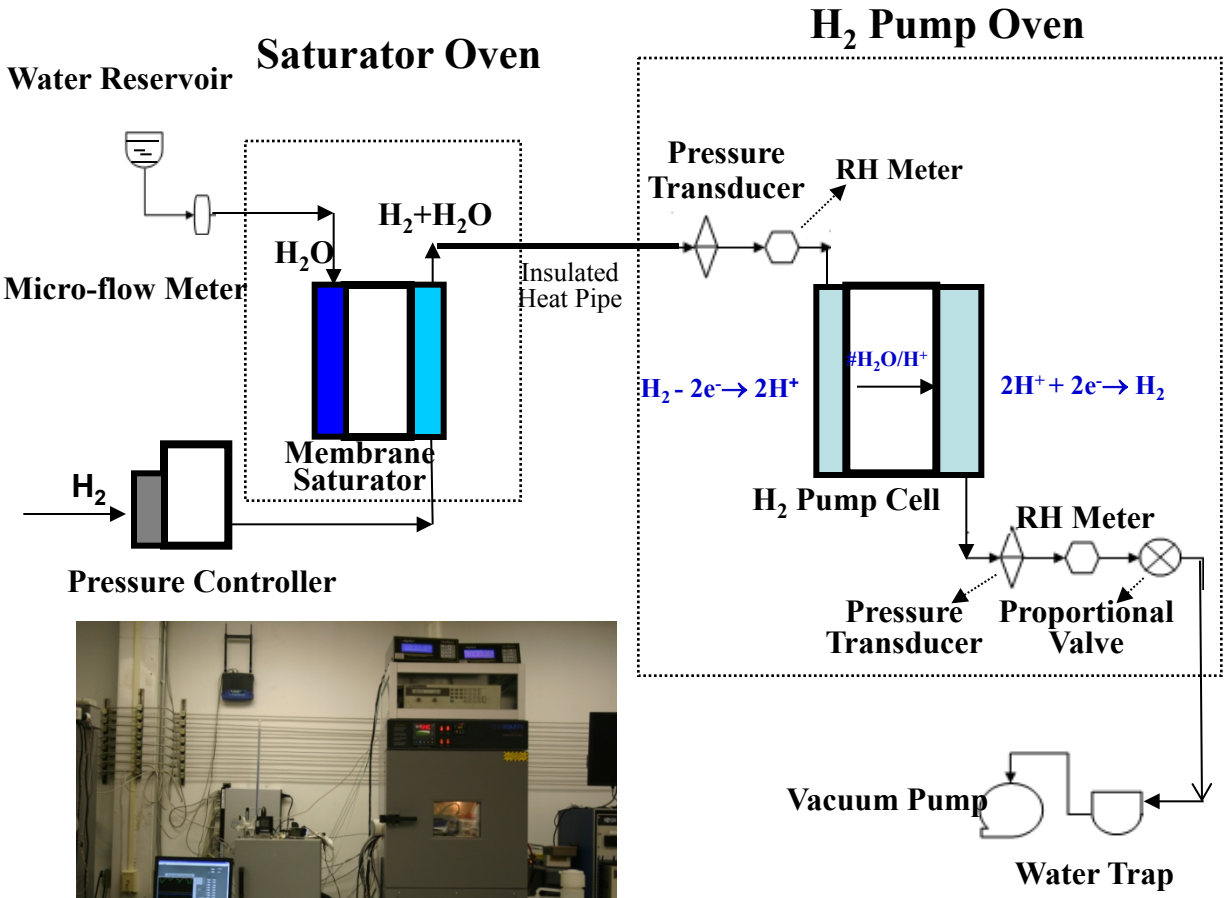
Achievements: Water Diffusivity of Various Membranes

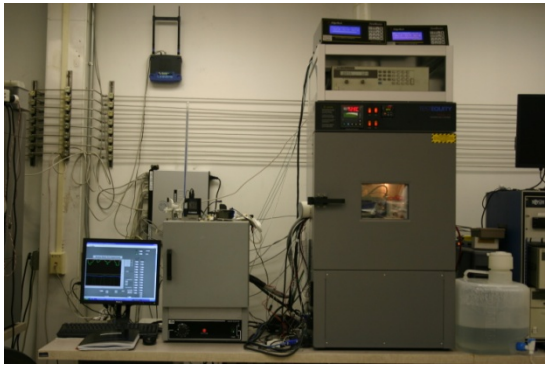




- Morphology does not affect water uptake at low RH
- Phase separation on a smaller scale results in lower diffusivity. Annealing increases phase separation and diffusivity

Achievements: New Technique: EODC

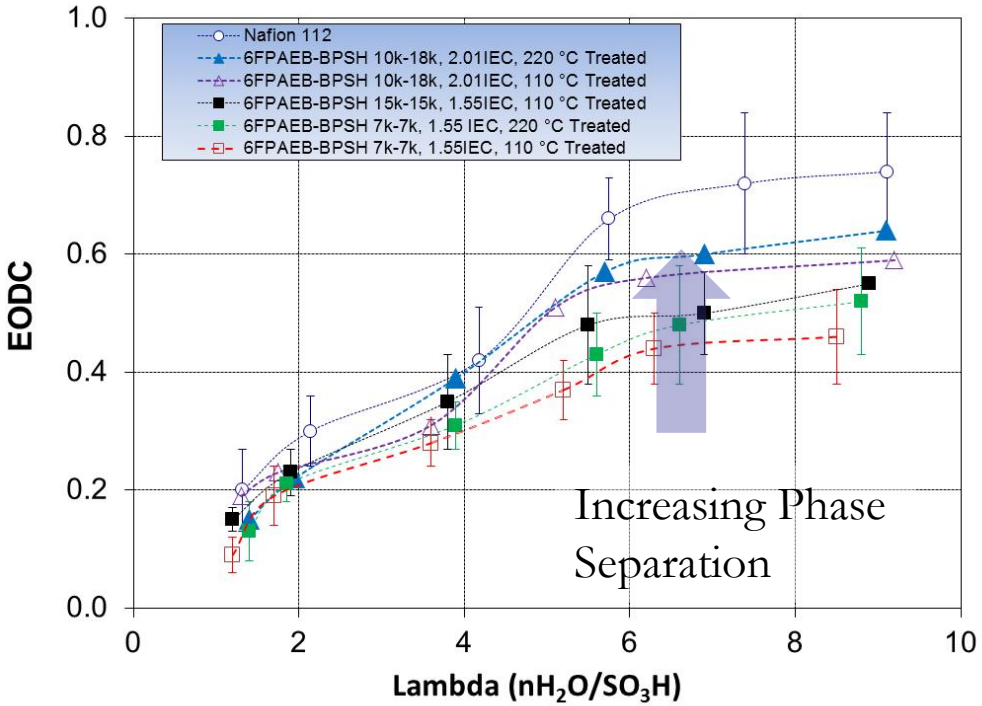




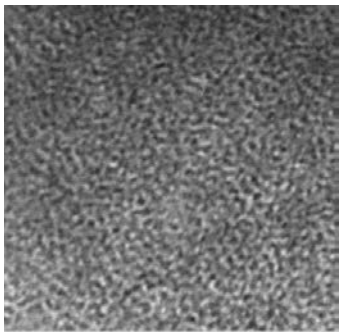
- Water/H_2 inlet ratio controlled by controlling saturator temperature and H_2 pressure
- If ratio is too high, not enough water is dragged across and cell floods and fails
- If ratio is too low, membrane dries out and cell fails
- At Water/H_2 = 2*EODC Cell operates in quasi-stable state

All gas/gas diffusion is eliminated

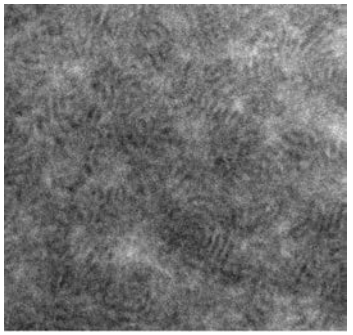
Correlation EODC to Copolymer Structure

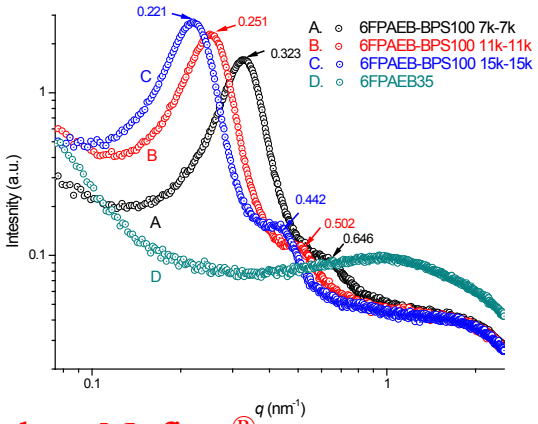


7K-7K



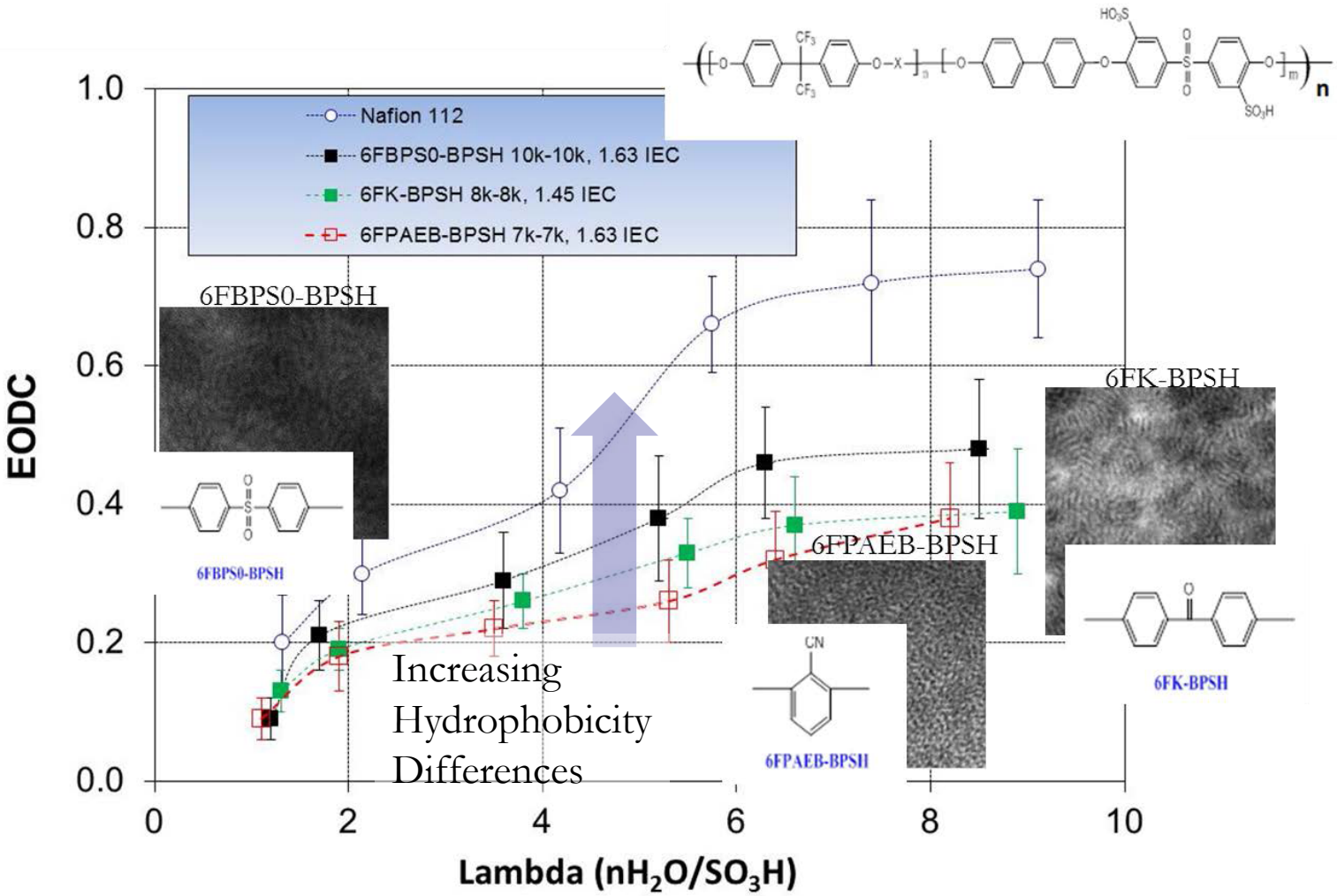
15K-15K





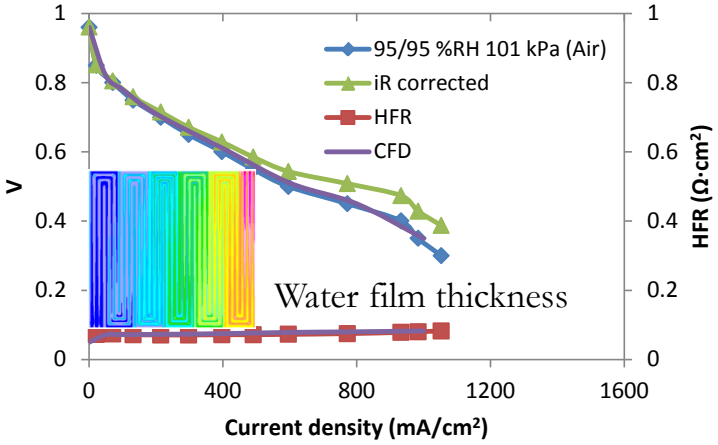
- All hydrocarbon membranes exhibit lower EODC than Nafion®
- Higher thermal annealing, block lengths and IEC seem to increase EODC

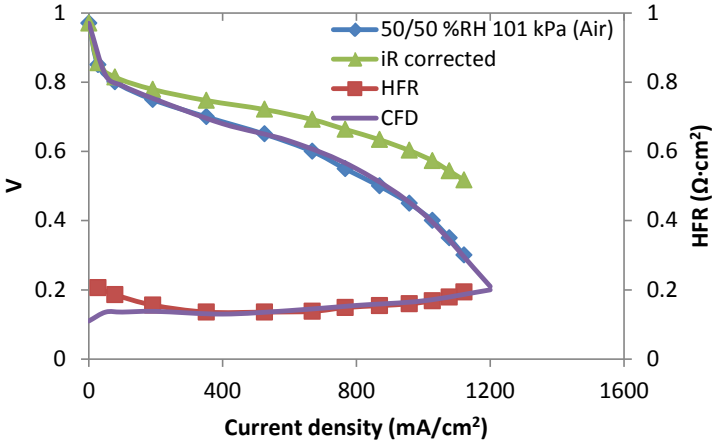
Relating EODC to Block Chemistry



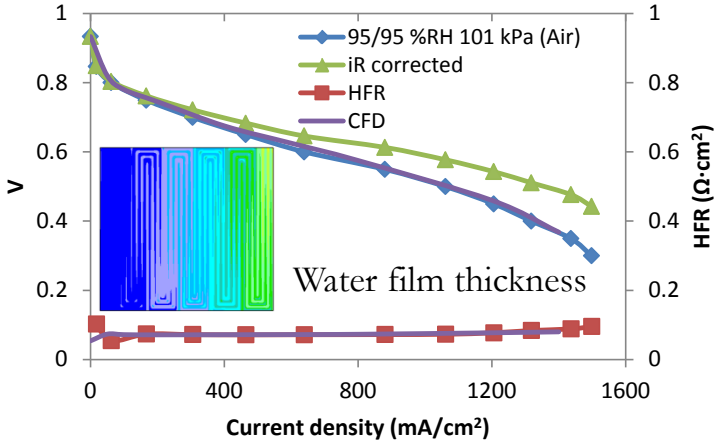
Polarization Curves: (co-current flow: 80°C, 1.5/2.0 stoich, H_2/Air: GDL - EP40T)

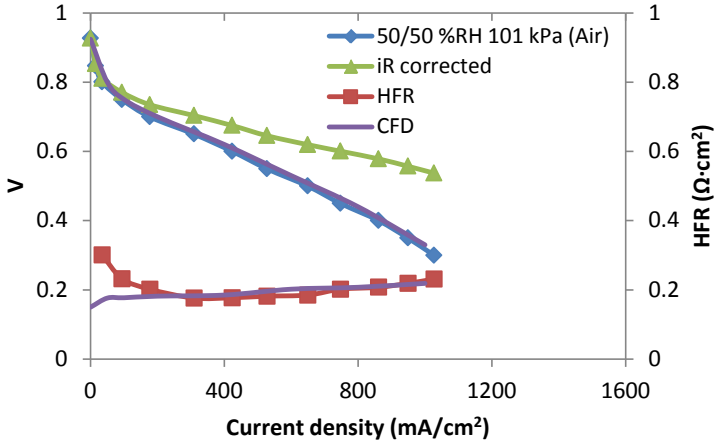
Nafion®





Hydrocarbon (VT) membrane





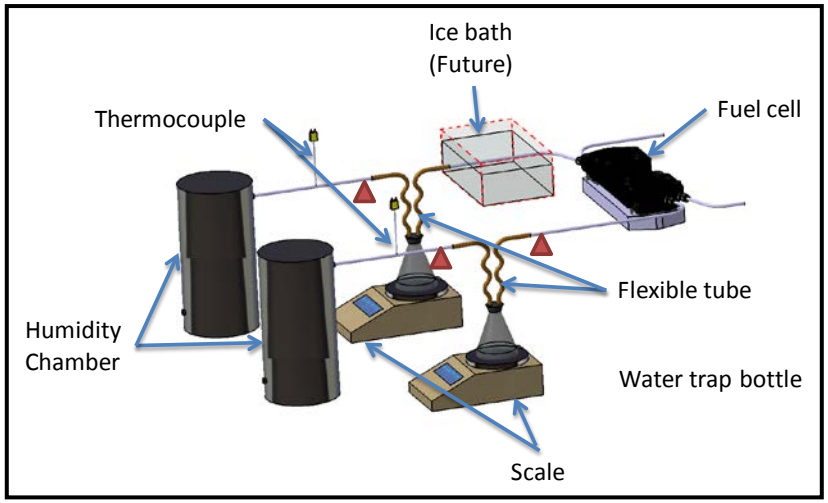
High RH

Low RH

HC's Lower EODC leads to less flooding **80% more H_2O** delivered to cathode (model and experimental validation)

Water Balance Measurement Under Different Conditions

Experimental vs. CFD (VT membrane)



Water Balance experiment and numerical result of new MEA

(80°C, 1.5/2.0 stoich H_2/O_2)

Water balance shows the transport of water inside fuel cell. For different operating conditions and membranes, the water transport inside fuel cell will also be different.

	i A/cm^2	RH	Anode Water Balance (mg/sec)			Cathode Water Balance (mg/sec)				Cross error (%)
			Water in	Water out	Cross to Cathode	Water in	Gen.	Water out	Cross from Anode	
EXP	**1.2**	80/80	1.40	0.071	1.32	0.95	2.80	4.82	1.25	5
CFD	**1.2**	80/80	1.40	0.055	1.34	0.95	2.80	5.10	1.36	1.5
EXP	**0.8**	100/100	1.27	1.42	-0.15	0.85	1.86	2.44	-0.17	11
CFD	**0.8**	100/100	1.28	1.44	-0.16	0.85	1.86	2.54	-0.17	6

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Water Balance Measurement Under Different Conditions

Water Balance experiment of VT MEA 6FPAEB-BPSH

(80°C, 1.5/2.0 stoich H_2/Air)

		i A/cm²	RH	Anode Water Balance (mg/sec)			Cathode Water Balance (mg/sec)				error (%)
				Water in	Water out	Cross to Cathode	Water in	Gen.	Water out	Cross from Anode	
Low current density	EXP	**0.4**	75/25	0.75	0.22	0.53	0.59	0.93	2.01	0.49	7.5
	CFD	**0.4**	75/25	0.75	0.23	0.52	0.59	0.93	2.03	0.51	2.0
	EXP	**0.4**	50/50	0.42	0.29	0.13	1.35	0.93	2.42	0.14	7.1
	CFD	**0.4**	50/50	0.42	0.29	0.13	1.35	0.93	2.40	0.12	8.3
	EXP	**0.4**	95/95	1.10	0.86	0.25	3.51	0.93	4.73	0.29	13.7
	CFD	**0.4**	95/95	1.10	0.90	0.20	3.51	0.93	4.66	0.22	9.0
	EXP	**0.6**	75/25	1.12	0.33	0.79	0.88	1.40	3.09	0.81	2.5
	CFD	**0.6**	75/25	1.12	0.31	0.81	0.88	1.40	3.13	0.85	4.7
High current density	EXP	**0.8**	50/50	0.85	0.55	0.30	2.70	1.87	4.88	0.31	3.2
	CFD	**0.8**	50/50	0.85	0.58	0.27	2.70	1.87	4.85	0.28	3.5
	EXP	**0.8**	95/95	2.21	1.68	0.53	7.03	1.87	9.44	0.54	1.8
	CFD	**0.8**	95/95	2.21	1.66	0.55	7.03	1.87	9.45	0.55	0.0
	EXP	**1.2**	95/95	3.32	1.99	1.34	10.55	2.80	14.60	1.25	7.5
	CFD	**1.2**	95/95	3.32	2.01	1.31	10.55	2.80	14.72	1.37	4.4

WIDE AGREEMENT BETWEEN CFD MODEL AND EXP RESULTS

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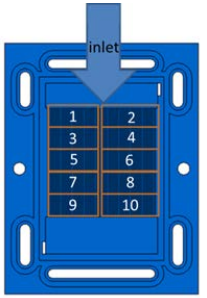
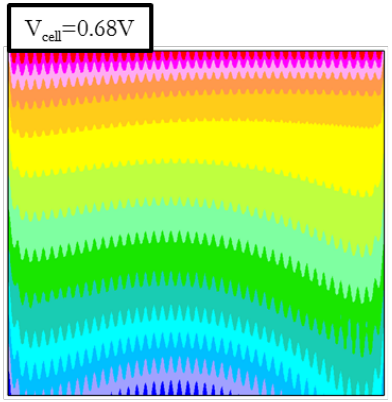
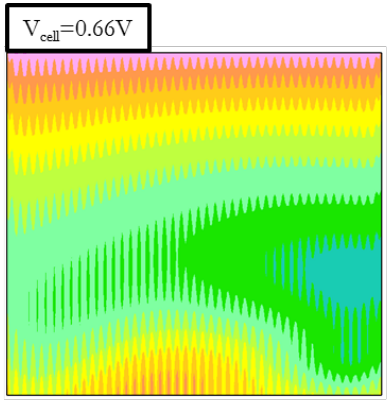
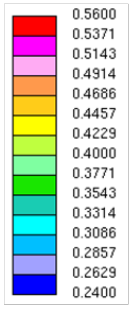
Local Distributions of Current Density & Water Transport on the Membrane Surface at low inlet RH at 0.4 A/cm^2





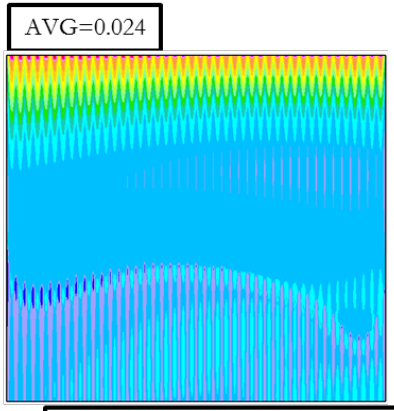


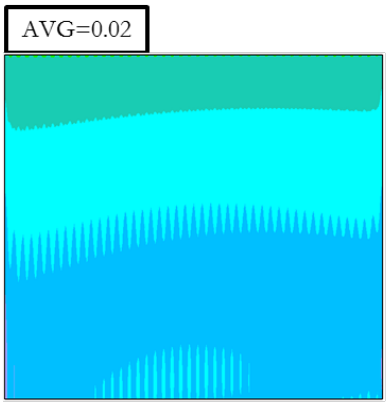


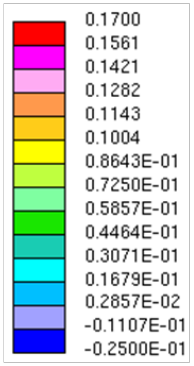
Current density (A/cm^2)

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





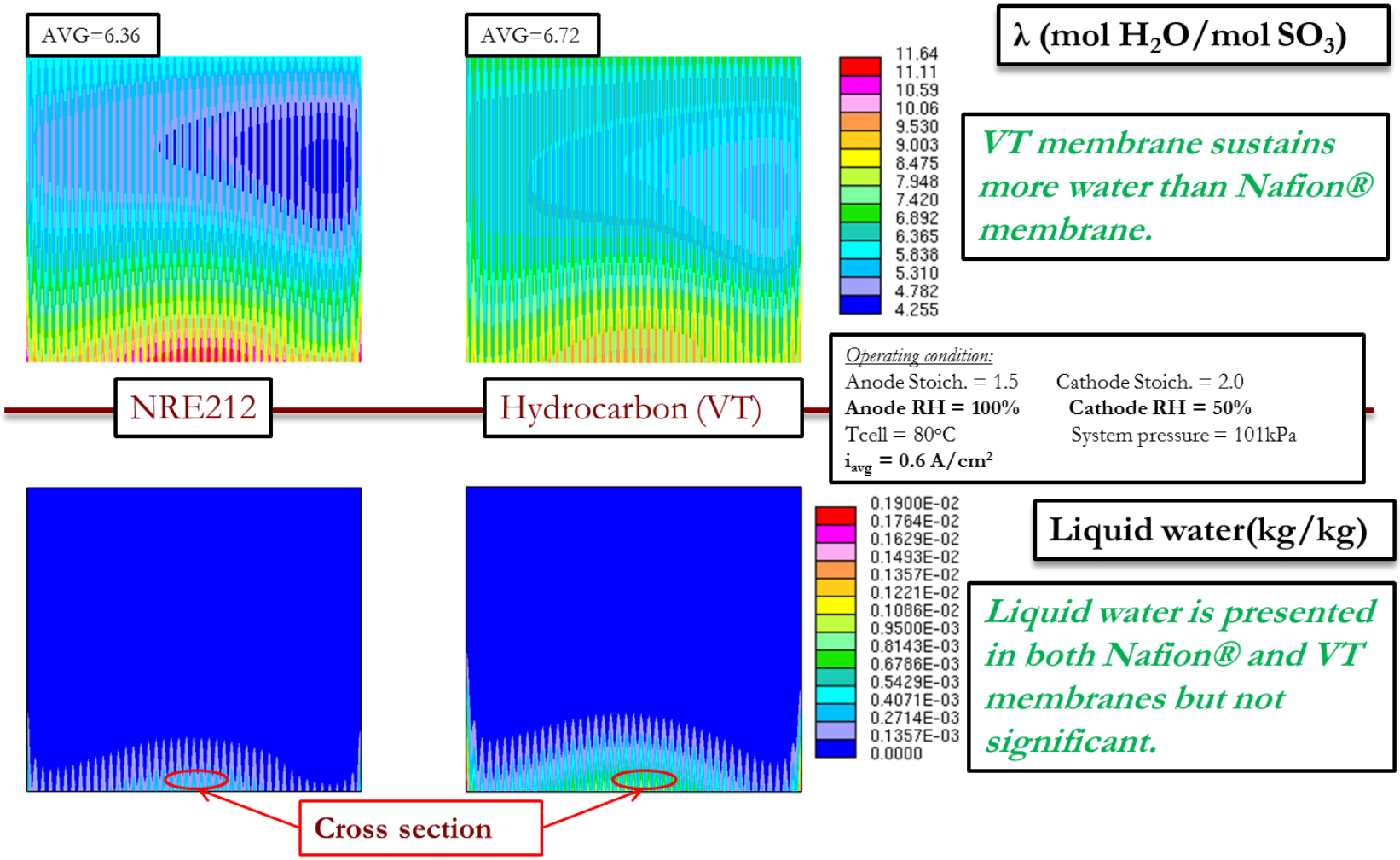


Water flux across membrane (mg/cm^2-s)

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

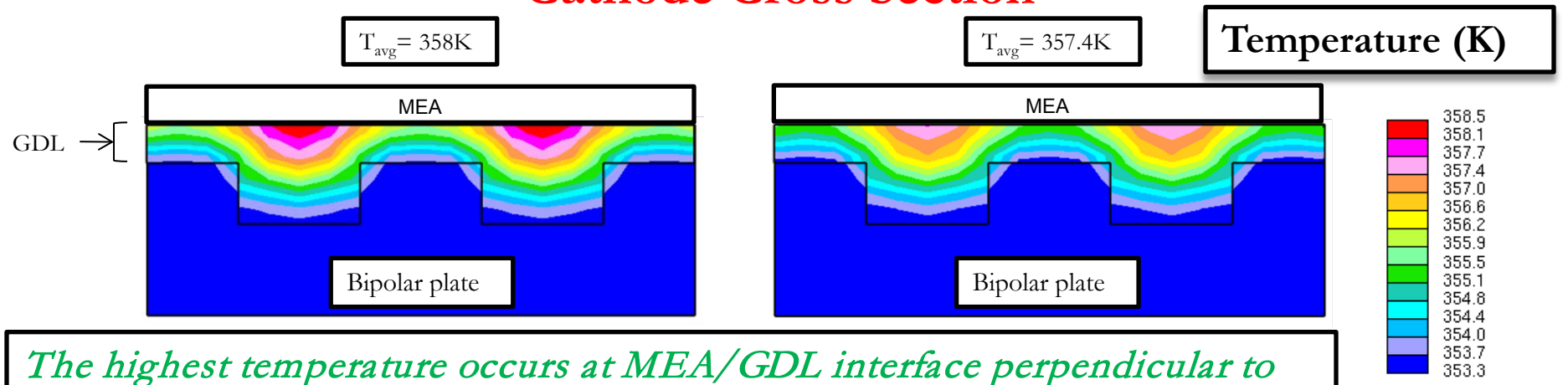
At dry condition: no liquid water is presented in fuel cell

Local Distributions of Water Content in Membrane & Liquid Water on Cathode MEA/GDL Interface at high inlet RH at 0.6 A/cm^2



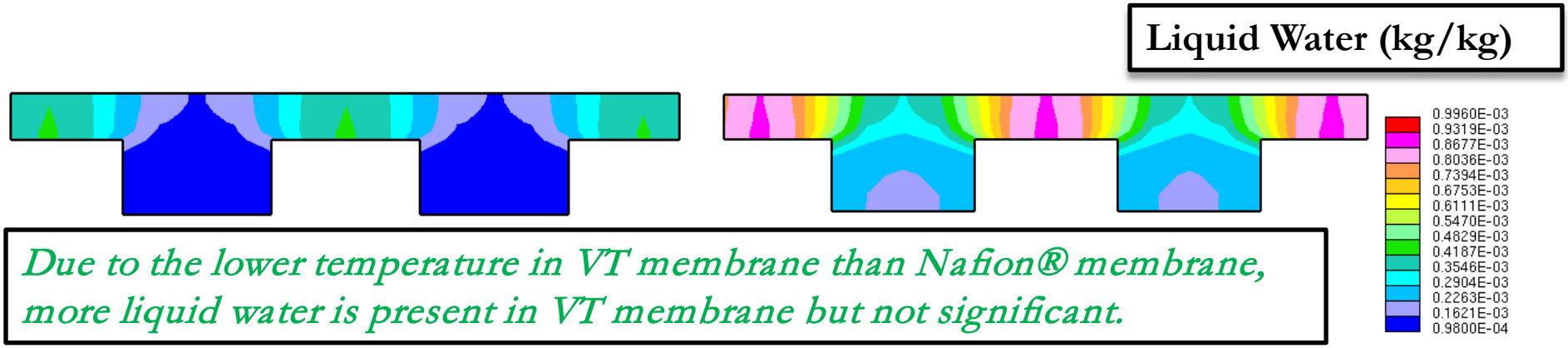
Local Distributions of Temperature and Liquid Water at High RH

Cathode Cross Section



The highest temperature occurs at MEA/GDL interface perpendicular to the flow channel. The temperature gradient across GDL ~ 3°C

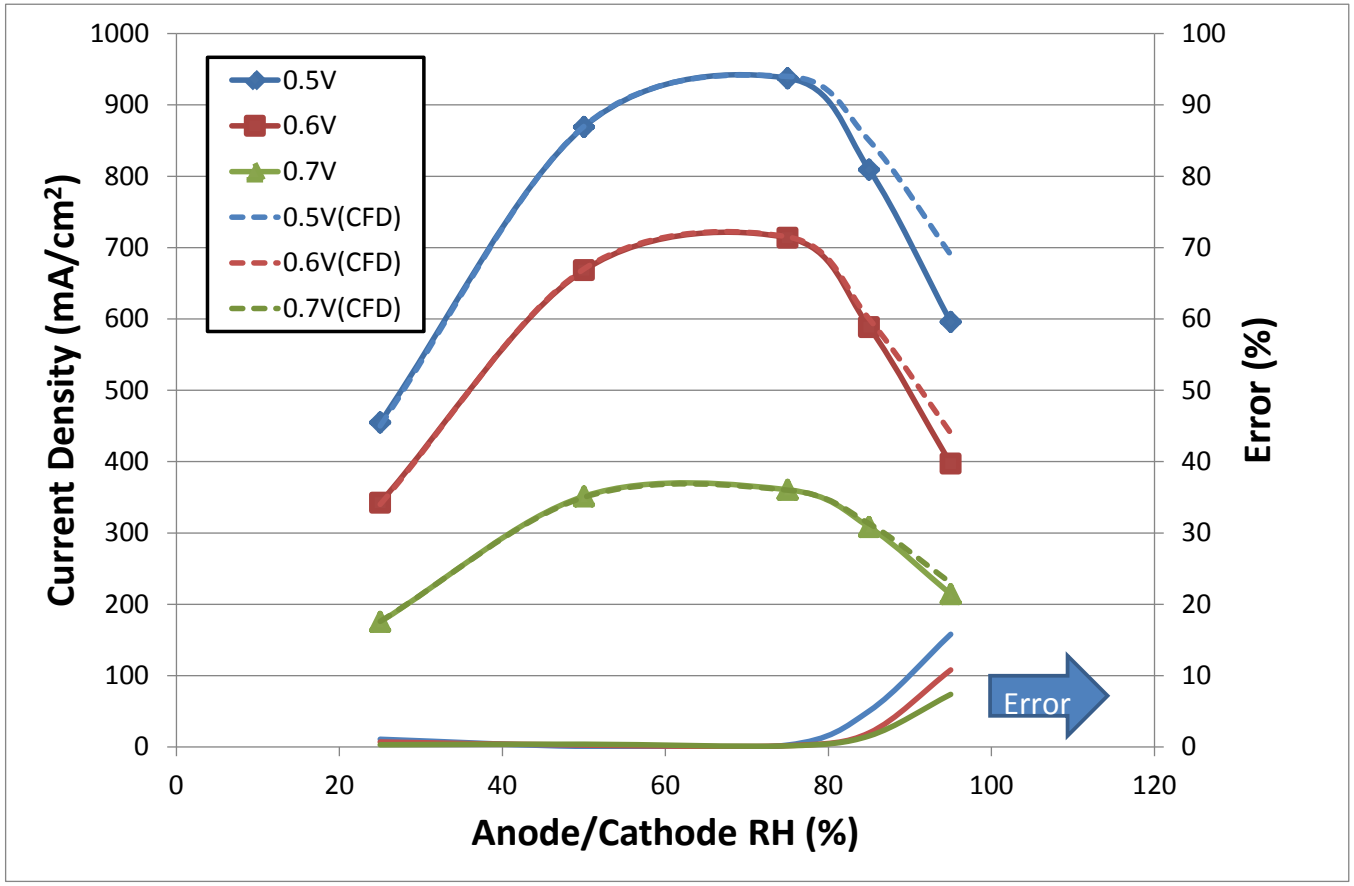
NRE212 | Hydrocarbon (VT)



Due to the lower temperature in VT membrane than Nafion® membrane, more liquid water is present in VT membrane but not significant.

Effect of Inlet Humidity on Current Density at Different Potentials

(80 °C, 1.5/2.0 stoich H_2/Air : Memrbrane – NRE212: GDL – EP40T)

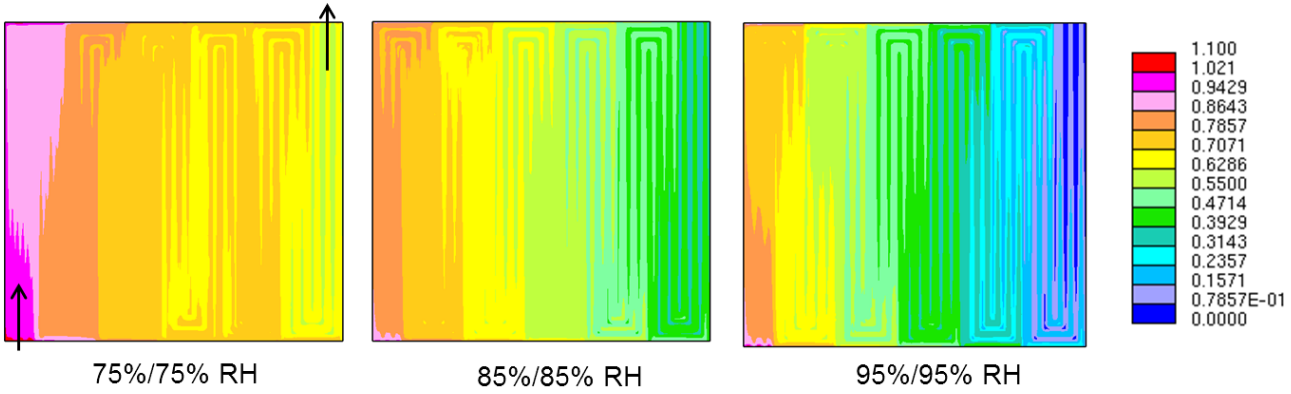


Using to probe/characterize efficiency of diffusion media to remove liquid water

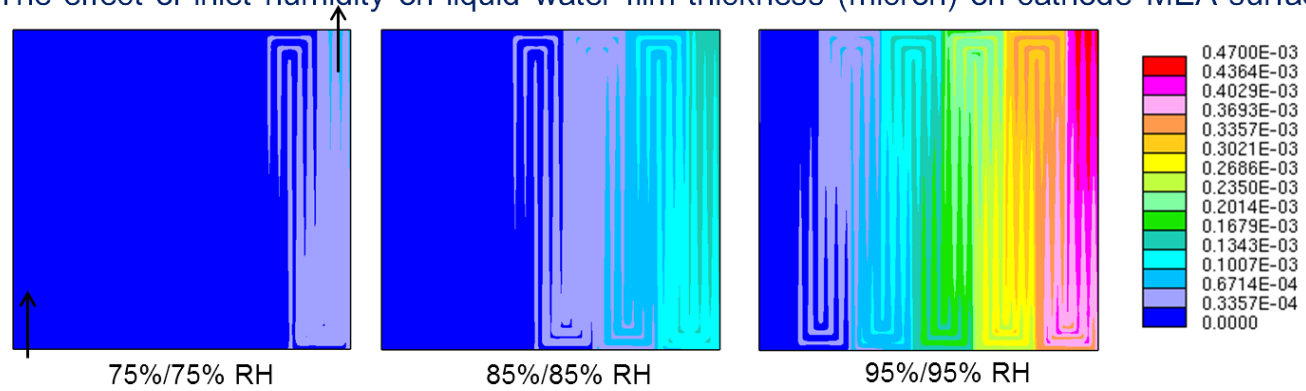
Will try to relate to porosity, hydrophobicity McMullin Number

Effect of Inlet RH on CDD (A/cm^2) on MEA Surface

at Vcell = 0.6V (80°C, 1.5/2.0 stoich H_2/Air : Membrane – NRE212: GDL – EP40T)



The effect of inlet humidity on liquid water film thickness (micron) on cathode MEA surface



Model does a good job of handling flooding by assuming accumulation of water film.

Summary

- Membrane design and development (VA Tech) & Characterization (Giner):
  - Membranes with similar *charge densities* but different
    - Chemistries (different hydrophobicity of the non-functional block)
    - Morphologies
      - Block length
      - Annealing
  - 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
    - Increases conductivity at low RH
    - Increases diffusivity
    - Increases EODC

- Transport Modeling, GDL & Current Distribution Board Characterization (USC & Giner):
  - Model successfully predicts:
    - *Dry, Wet Conditions. Hydrocarbon and PFSA membranes*
    - *Performance and Water Balance*
    - *Increased flooding for PFSA membranes compared to hydrocarbon membranes*

Future Work

- Emphasis on Saturated Conditions
  - Diffusion Media
  - Membrane Transport Properties

- Electrode Effects
  - High Current Density at Low Catalyst Loading
  - Flooding of NSTF layers

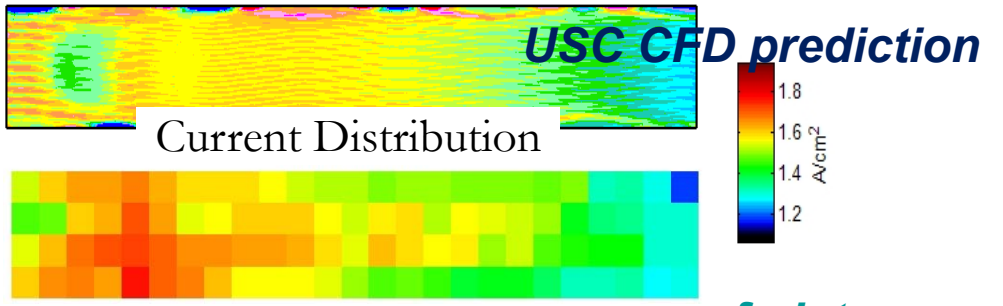
Technical Back Up Slides

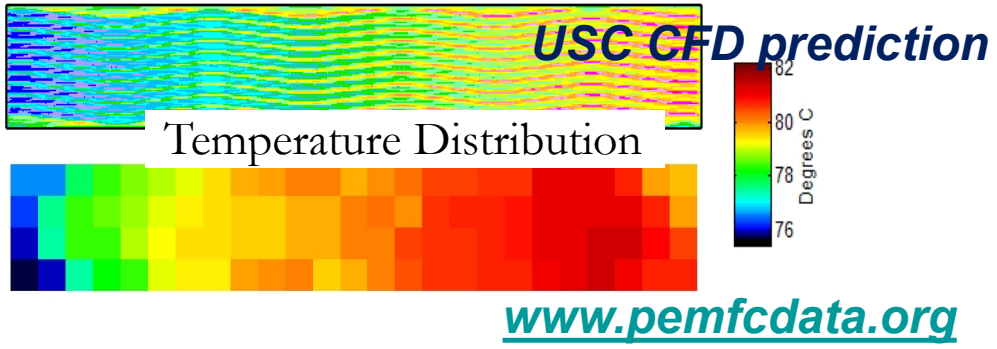
- Not Discussed:
  - Current Distribution Boards
  - Verification of Model with GM Open Data
  - Diffusion Media

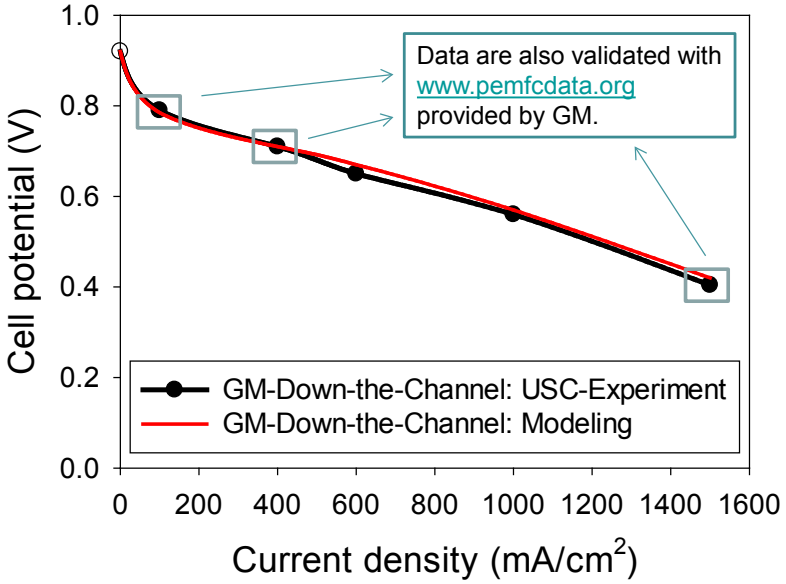
Achievement: Model Verification:

Distributions of current density and temperature of 50-cm^2 GM-Down-the-Channel flow-field compared with www.pemfcdata.prg

(I_{avg} = 1.5 A/cm^2, counter-current flow: 50/50%RH, 150/150kPa, 80^{o}C, 1.5/2.0 stoich)

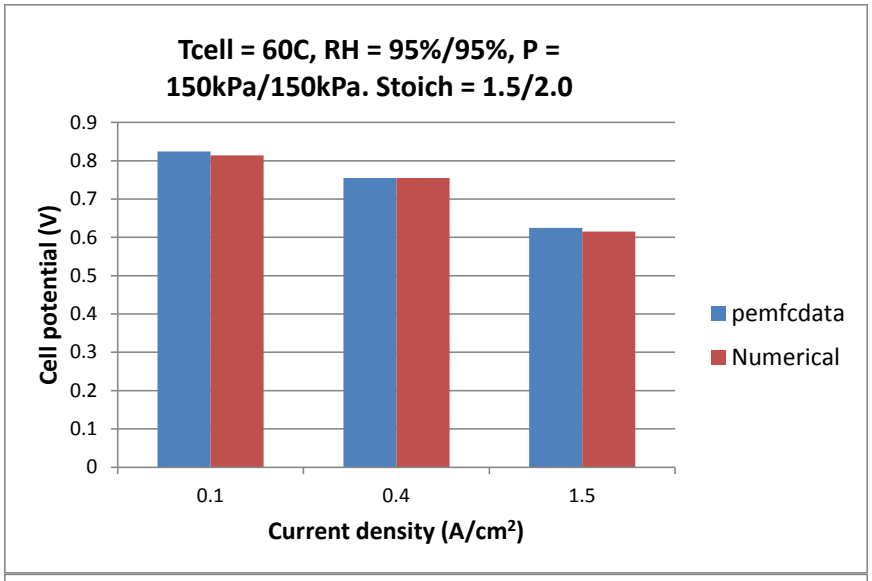


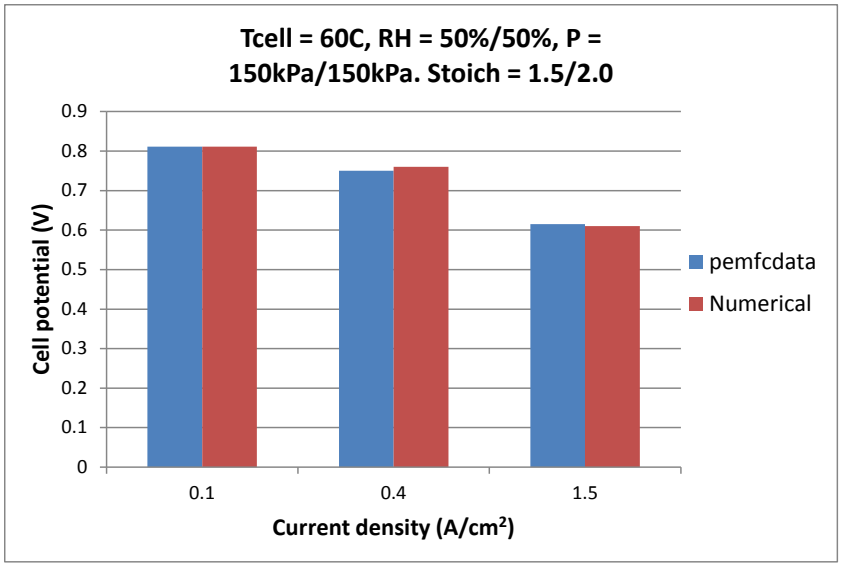


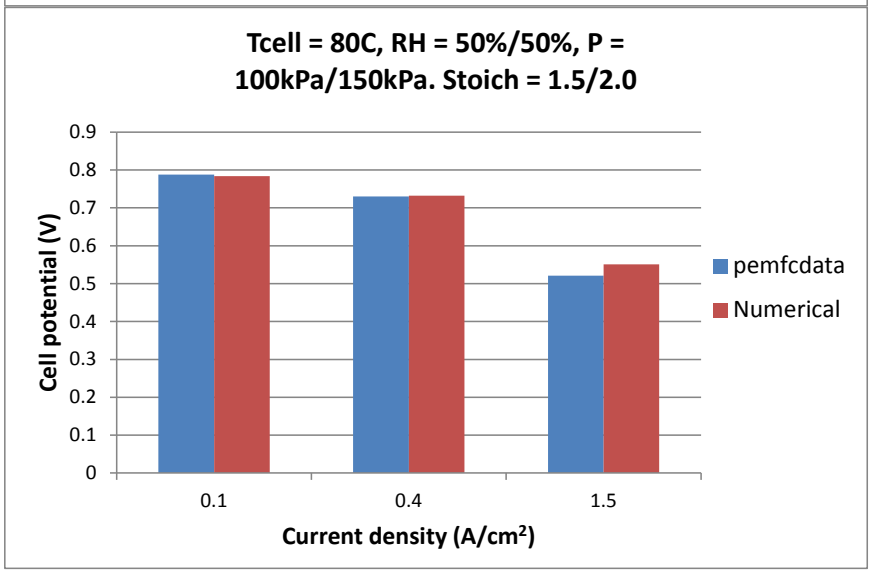


USC data matches published data very well, both with performance and model results

CFD comparison with pemfcdata.org at different operating conditions

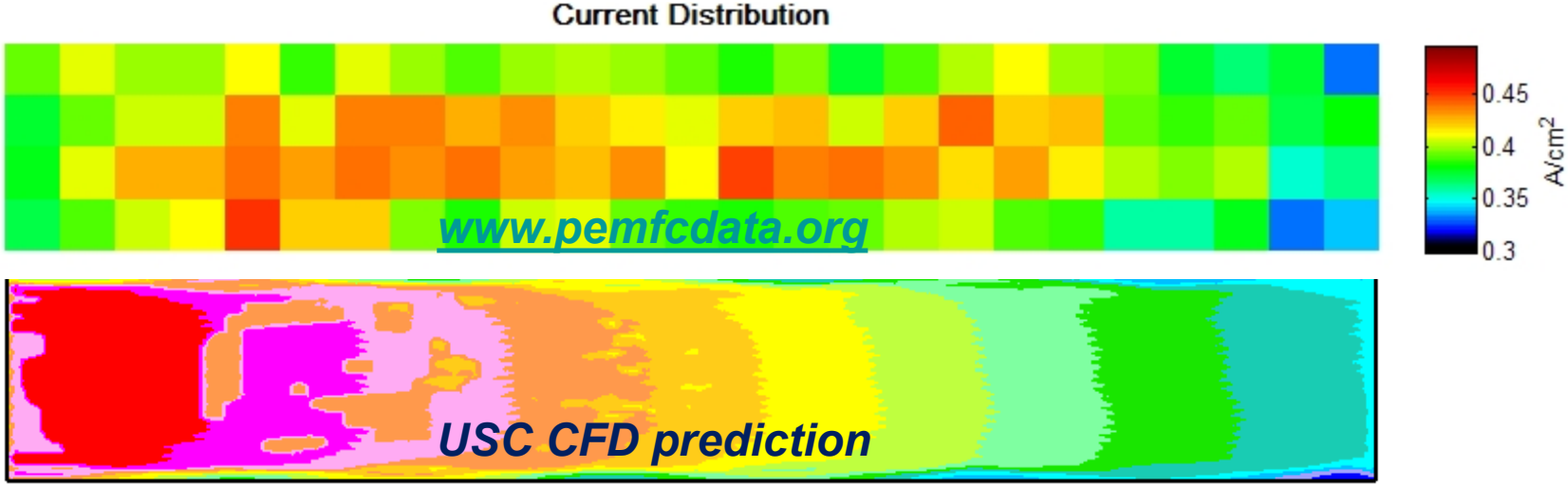


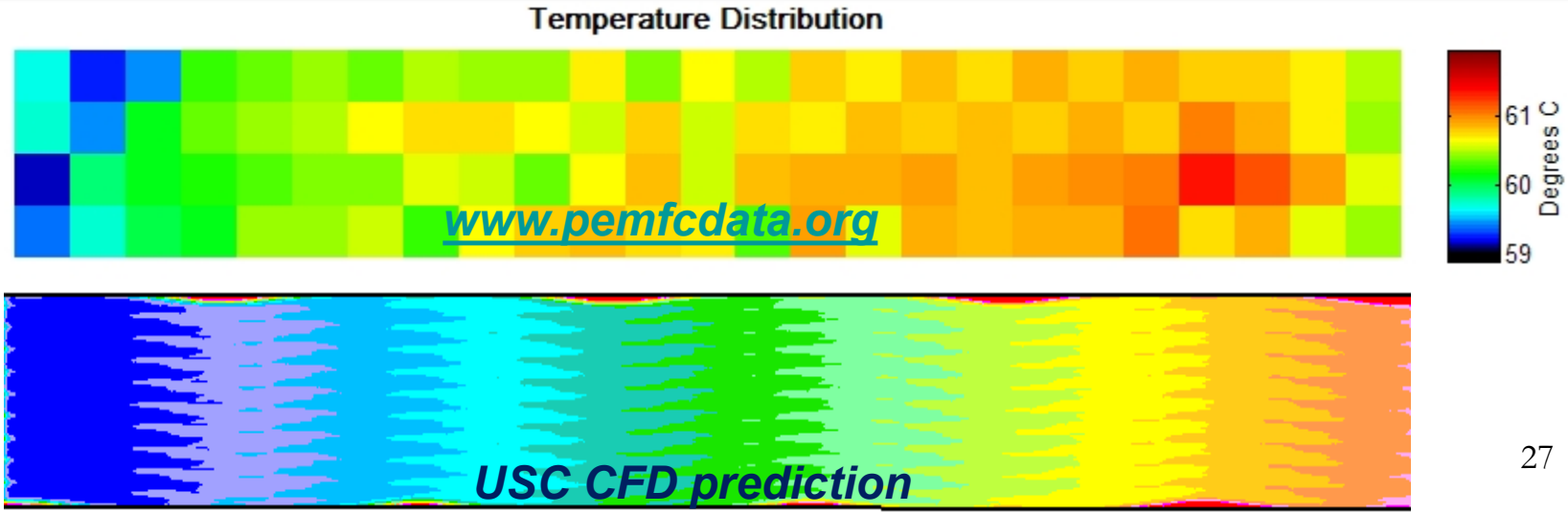




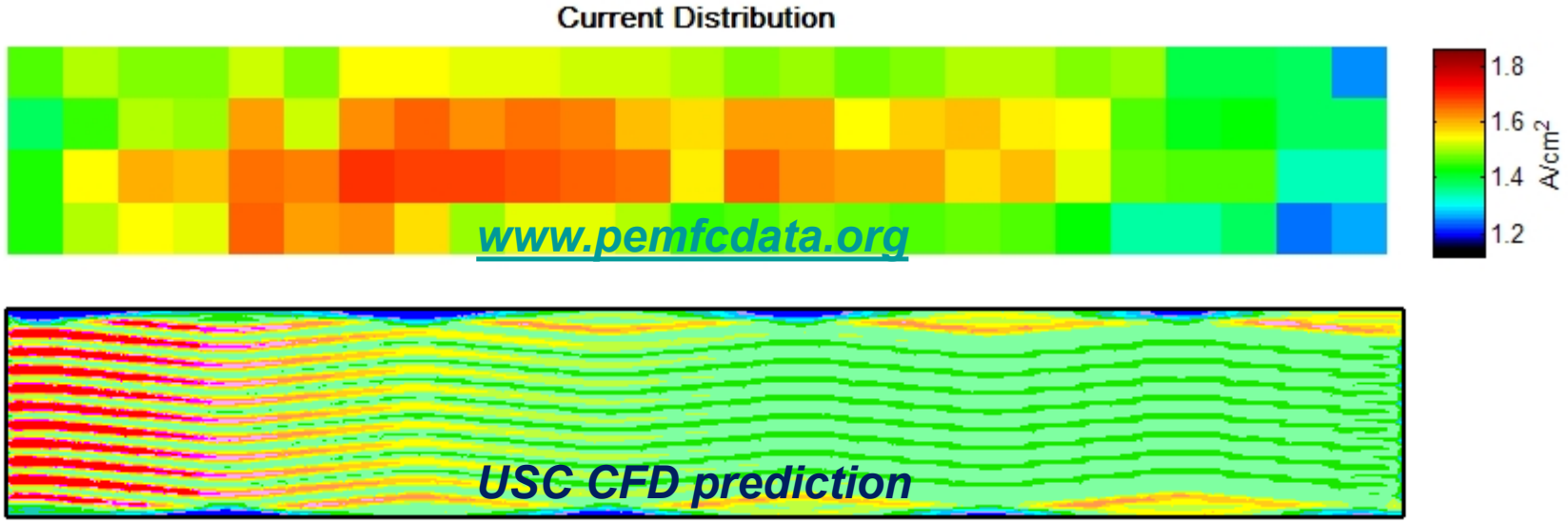
USC's CFD predictions compare well with published data from pemfcdata.org

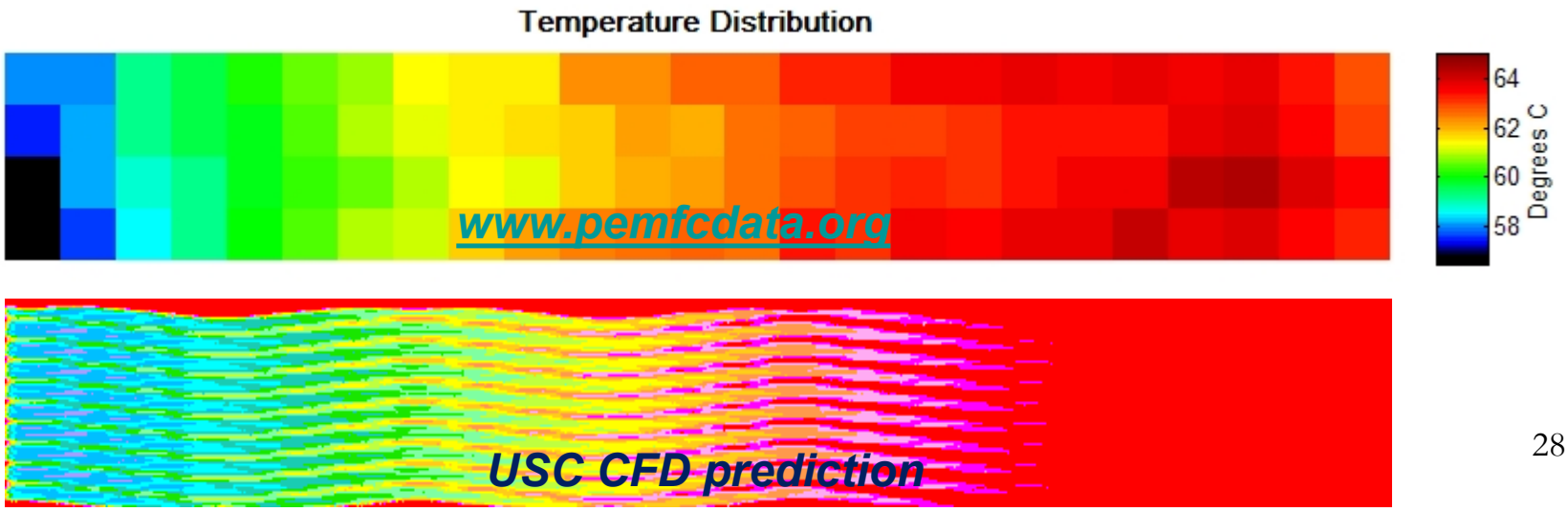
Local distributions of current density and temperature on membrane surface at I_{avg} = 0.4 A/cm^2
T_{cell} = 60C, RH = 95%/95%, P = 150kPa/150kPa. Stoich = 1.5/2.0





Local distributions of current density and temperature on membrane surface at I_{avg} = 1.5 A/cm^2
T_{cell} = 60C, RH = 95%/95%, P = 150kPa/150kPa. Stoich = 1.5/2.0

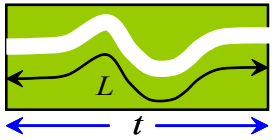




Achievements: New Materials: Diffusion Media

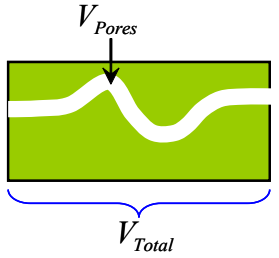
- AvCarb added to the program recently
- Started with Toray Materials
  - Variable Wet-Proofing
  - Microporous Layer
- AvCarb will provide more custom materials
- Want to generate differences in:
  - MacMullin Number
    - Porosity
    - Tortuosity
  - Hydrophobicity

•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.

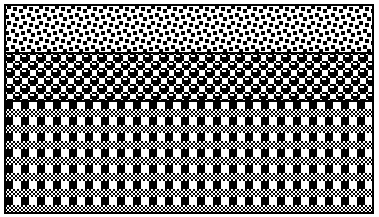


$$\varepsilon = \frac{V_{Pores}}{V_{Total}}$$

•MacMullin Number
- Function of tortuosity and pososity.

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

Achievements: Design of Gas Diffusion Media



MPL 1

MPL 2

Carbon Substrate

Baseline Material at start of program was Toray H060

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

The new design of GDLs have been 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.

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

AvCarb GDLs Status

5 sets of 12 assigned new design of GDLs with two different micro porous layers

Substrate	Diffusivity	MPL 1	MPL 2	# of Samples	MacMullin No.
P50	low (<0.15)	Small	Large	5	
P50	low (<0.15)	Large	Small	2	2.63
P50	high (>0.25)	Small	Large	5	
P50	high (>0.25)	Large	Small	2	2.16
EP40	low (<0.25)	Small	Large	5	
EP40	low (<0.25)	Large	Small	5	
EP40	high (>0.35)	Small	Large	5	
EP40	high (>0.35)	Large	Small	2	2.34
P75	low (<0.20)	Small	Large	5	
P75	low (<0.20)	Large	Small	2	2.26
P75	high (<0.3)	Small	Large	5	
P75	high (<0.3)	Large	Small	2	1.88

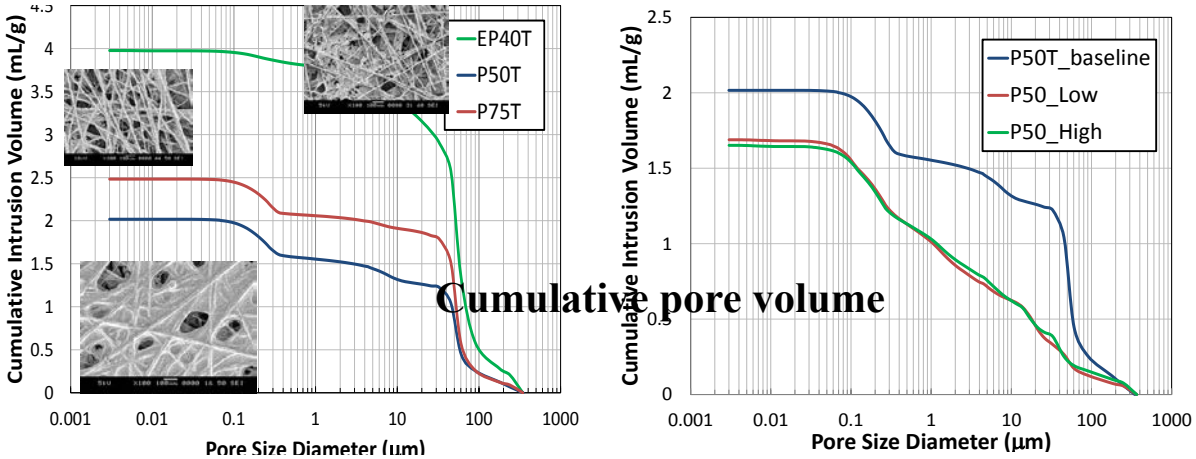
The new design of GDLs have been modified from standard Ballard GDLs by adding two micro porous layers. Each set has been treated with two different methods in order to provide two different values of diffusivity.

Achievements: Design of Gas Diffusion Media

Comparison of Mercury pore size distributions of new design GDLs

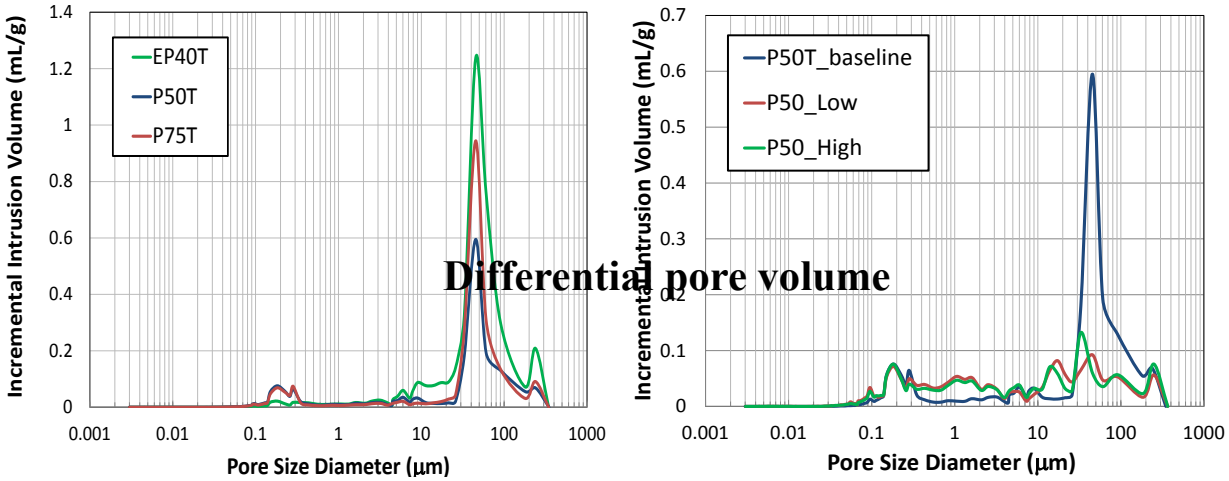
Baseline Substrates

Modified Substrates



Cumulative pore volume

EP40T has largest pore volume, concentrated at 50 µm



Differential pore volume

Modification greatly reduces volume of large pores

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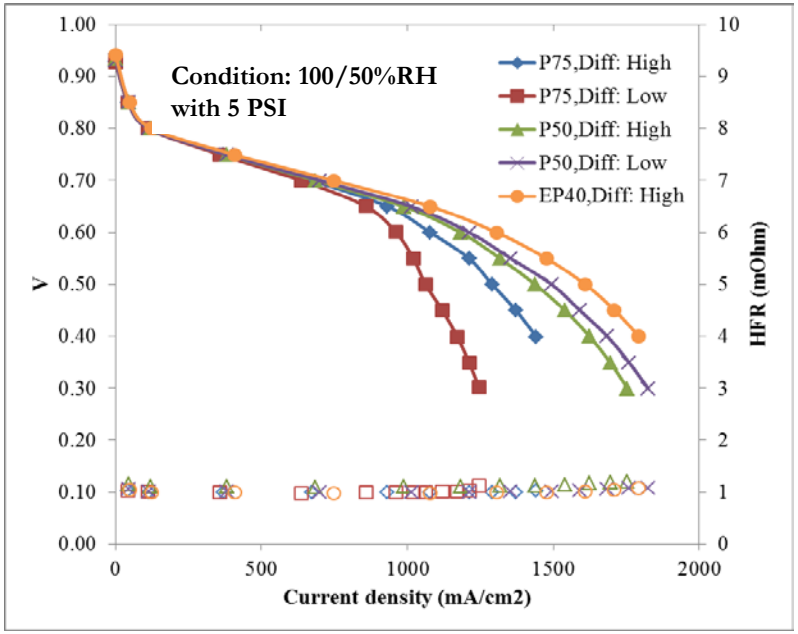
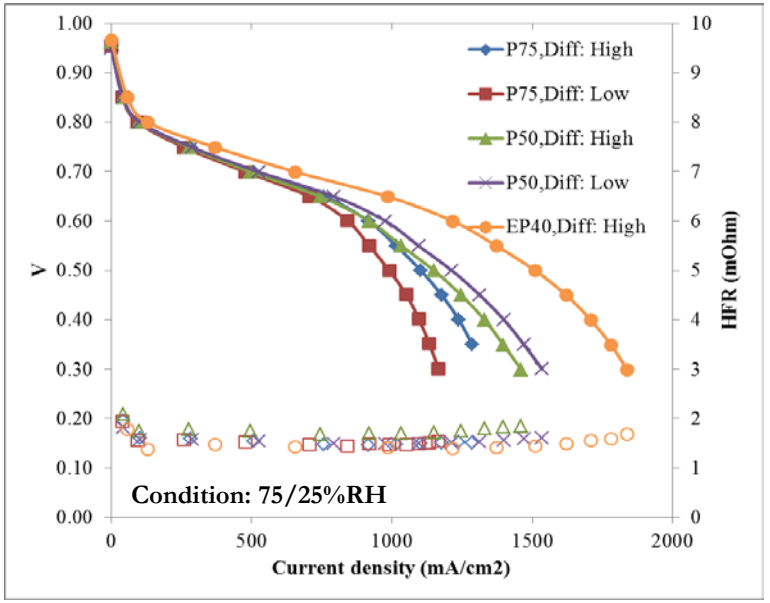
AvCarb GDLs Status

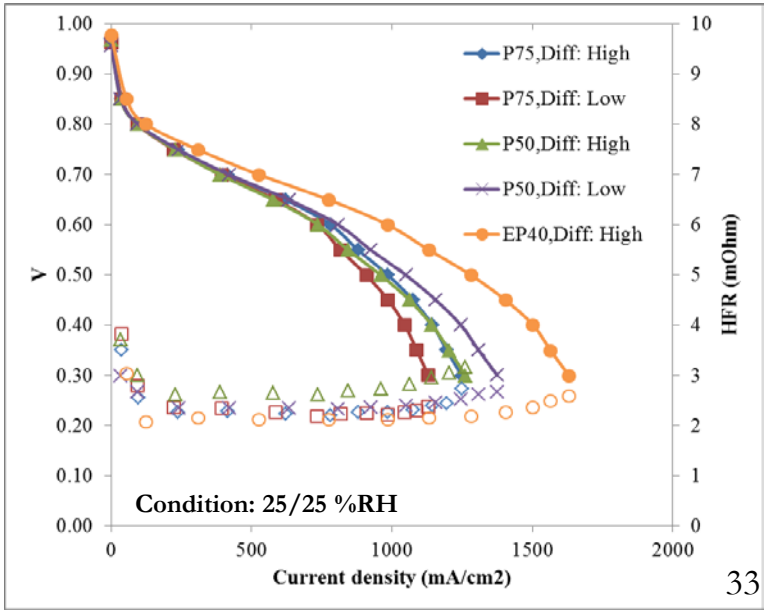
Baseline performance at Tcell = 80°C MEA = Gore™ 57; Serpentine

Substrate	Diffusivity	MPL1	MPL2	Macmullin#	Status
P50	Low (<0.15)	Large	Small	2.63	Done
P50	High (>0.25)	Large	Small	2.18	Done
EP40	High (>0.25)	Large	Small	2.34	Done
P75	Low (<0.20)	Large	Small	2.14	Done
P75	High (<0.30)	Large	Small	1.92	Done



- *EP40,Diff: high shows the highest performance for all three cases*
- *P75, Diff: low shows the lowest performance for all three cases*
- *Both P50, Diff: high and Diff: low show similar performance*



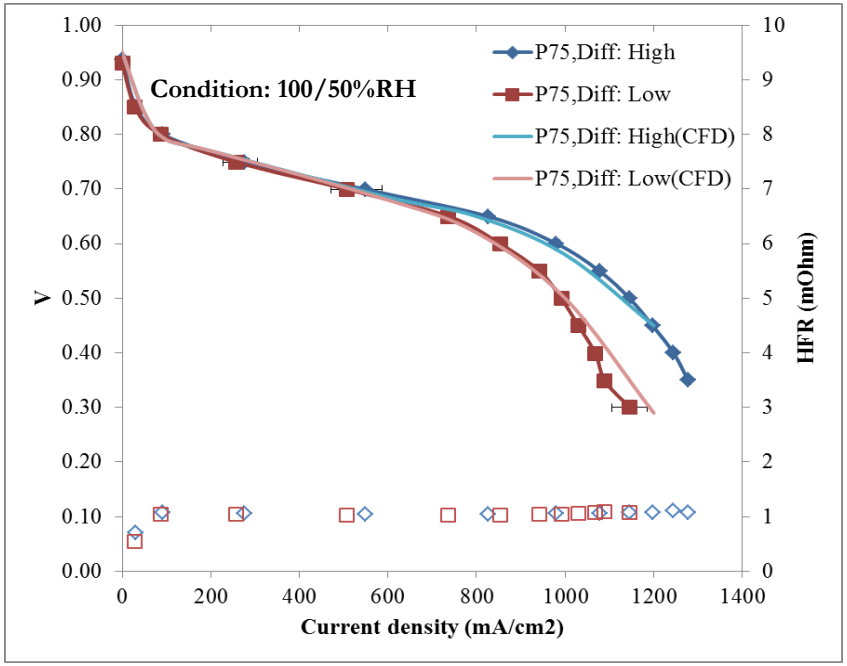


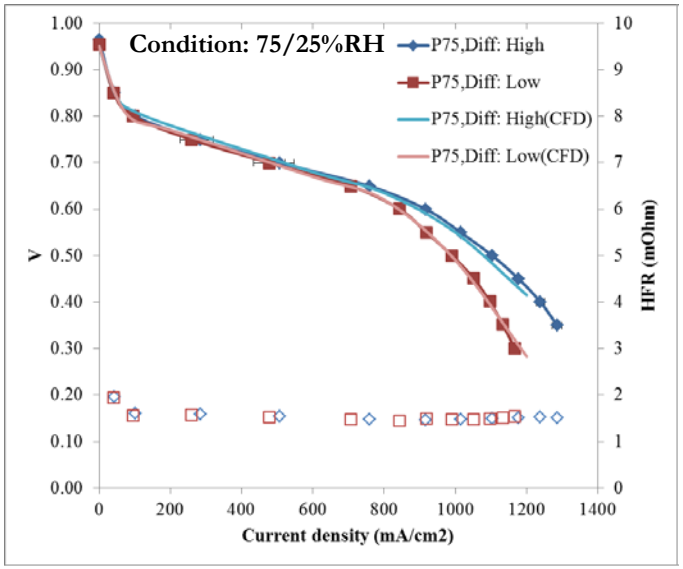
AvCarb GDLs Status

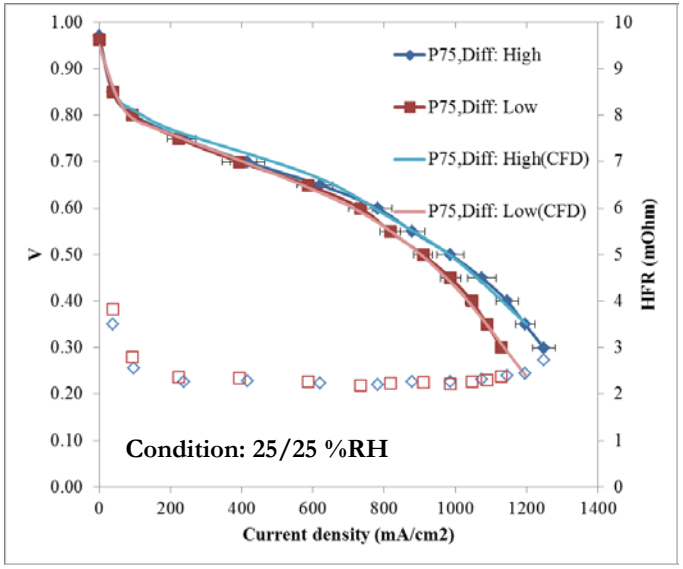
CFD comparison at T_{cell} = 80°C

MEA = Gore™ 57; Serpentine cell

GDL: P75 Diffusivity low and High







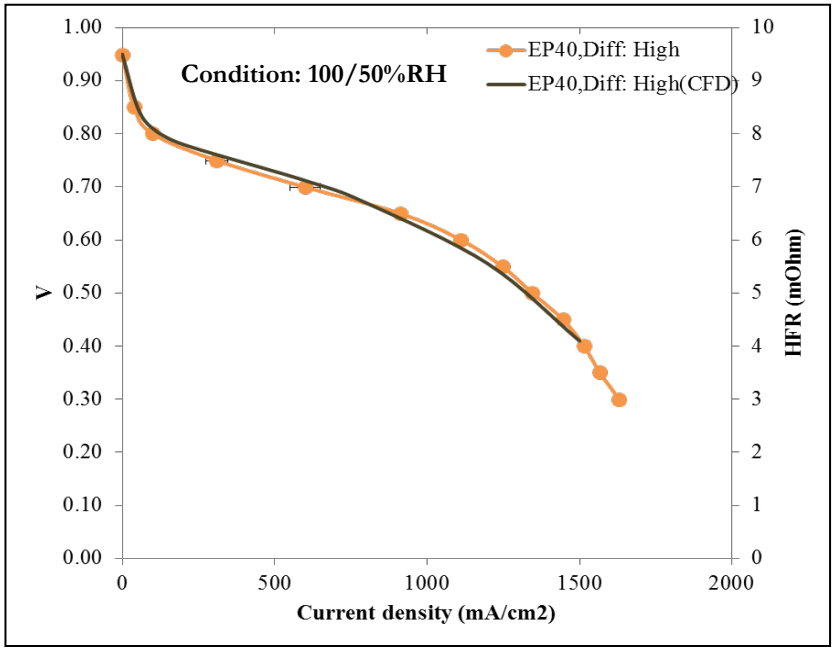
Using data of pore size distribution information and McMullin Number from GDL characterization, CFD predictions are able to compare well with experimental data.

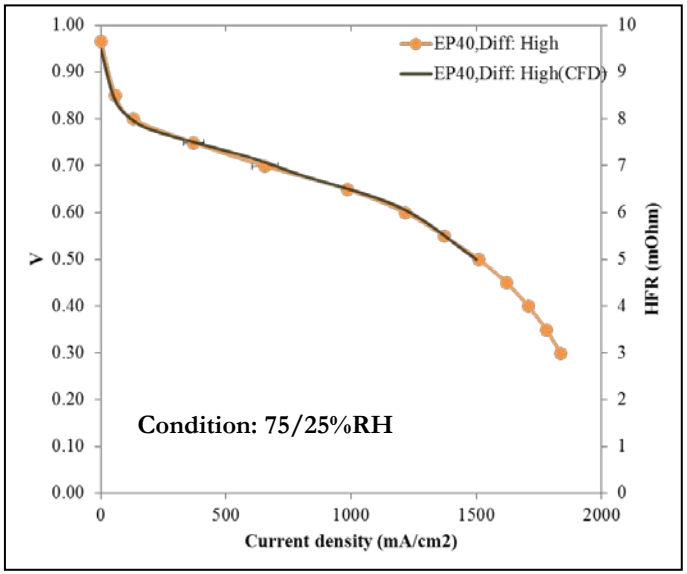
AvCarb GDLs Status

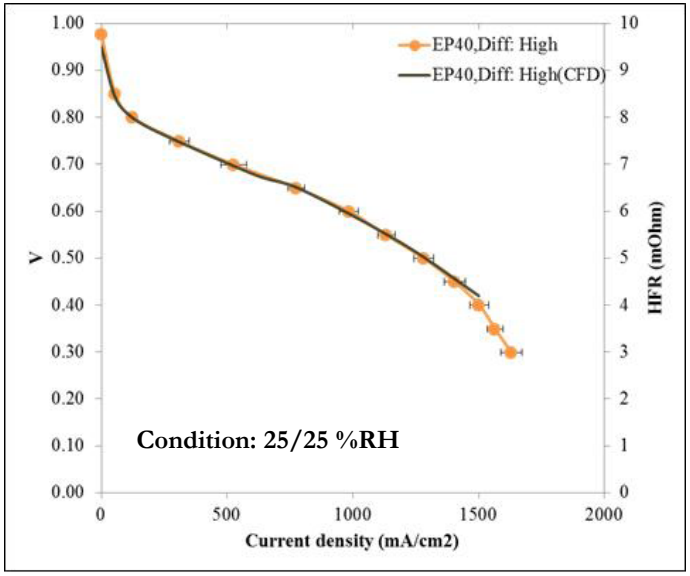
CFD comparison at Tcell = 80°C

MEA = Gore™ 57; Serpentine cell

GDL: EP40 Diffusivity High



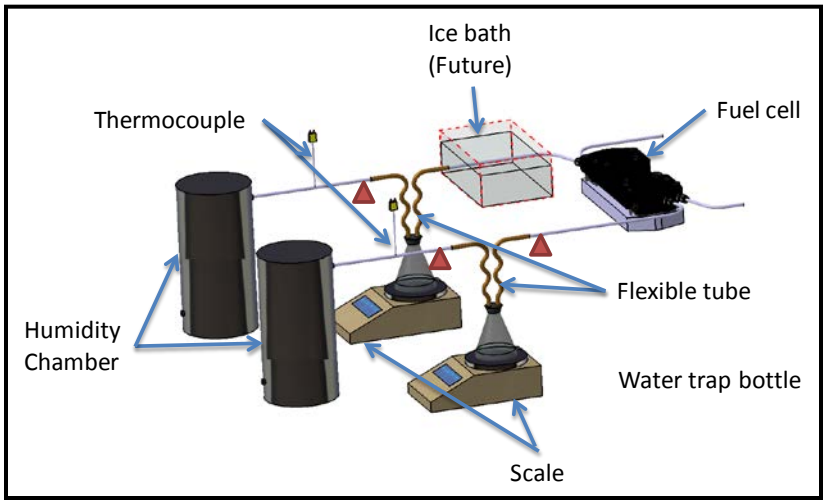




Using data of pore size distribution information and McMullin Number from GDL characterization, CFD predictions are able to compare well with experimental data.

Water balance measurement under different conditions

Experimental vs. CFD (Nafion® membrane)



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

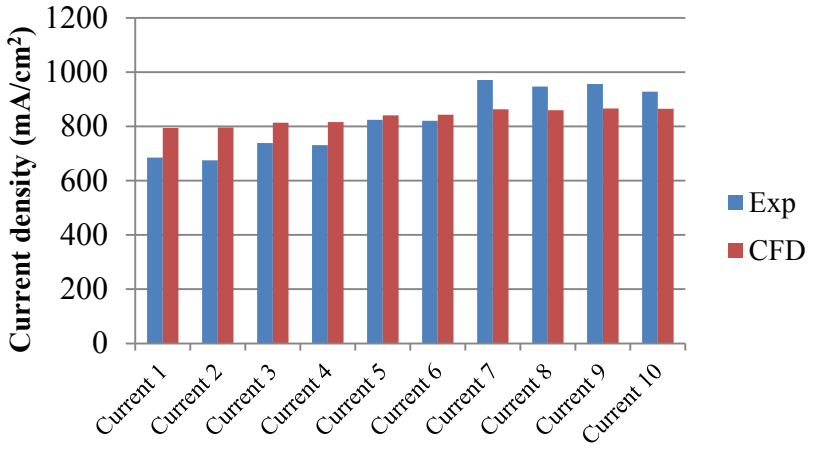
(80°C, 1.5/2.0 stoich H_2/Air)

Water balance shows the transport of water inside fuel cell. For different operating condition the water transport inside fuel cell will be different.

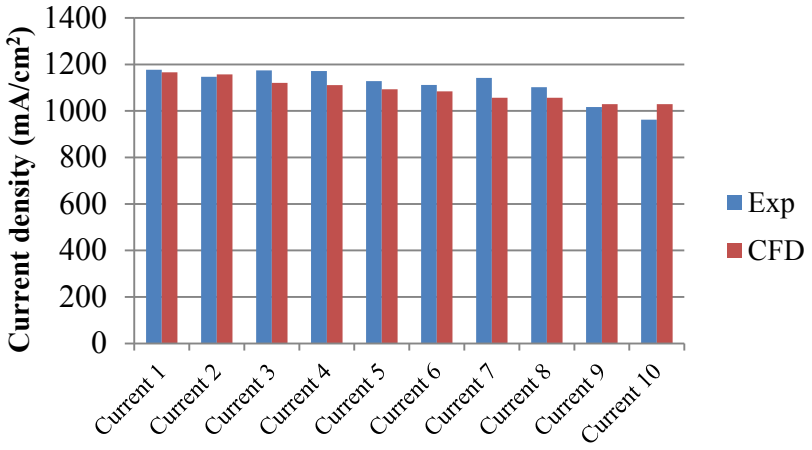
	i A/cm^2	RH	Anode Water Balance (mg/sec)			Cathode Water Balance (mg/sec)				error (%)
			Water in	Water out	Cross to Cathode	Water in	Gen.	Water out	Cross from Anode	
EXP	**0.4**	25/25	0.37	0.42	-0.20	1.15	1.87	2.81	-0.21	4.6
CFD	**0.4**	25/25	0.37	0.52	-0.15	1.15	1.87	2.85	-0.17	10
EXP	**0.4**	75/25	1.50	0.55	0.94	1.15	1.87	3.79	0.91	3.8
CFD	**0.4**	75/25	1.50	0.53	0.97	1.15	1.87	4.00	0.98	1
EXP	**0.6**	75/25	2.25	0.87	1.38	1.70	2.80	5.80	1.30	5.9
CFD	**0.6**	75/25	2.25	0.81	1.44	1.70	2.80	6.00	1.50	4

Achievement: Model Verification: Serpentine

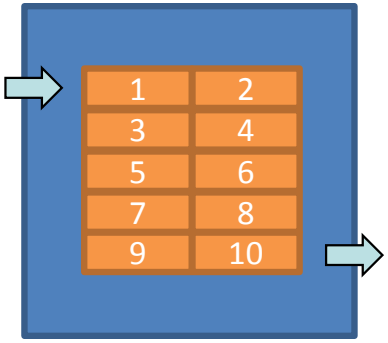
At potential=0.3V

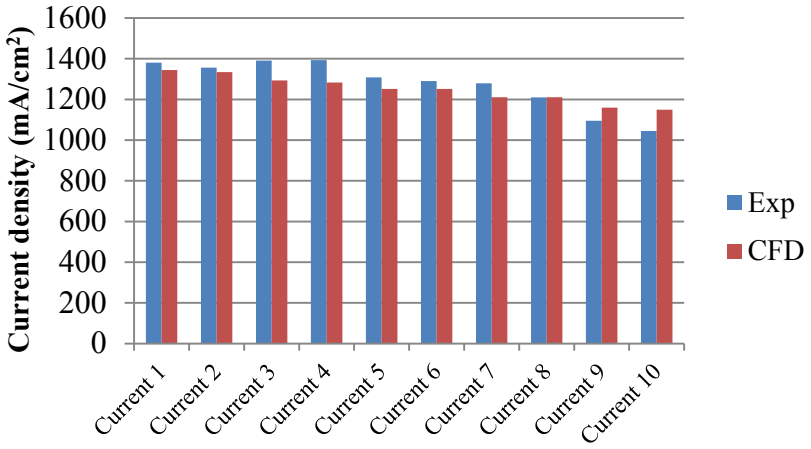


Anode 25%RH, Cathode 25%RH
Average current density = 809 mA/cm²



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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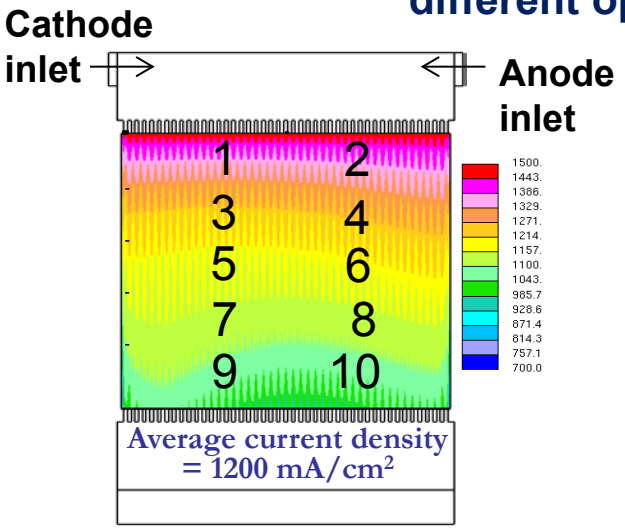
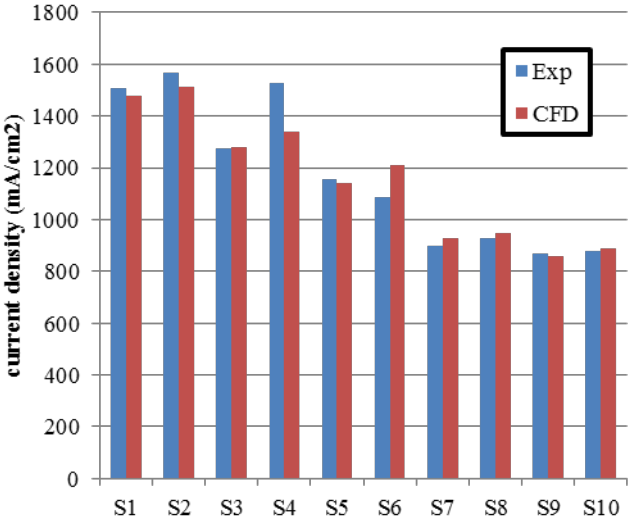
Numerical prediction and Experimental result of current density distributions for different operating condition (Nafion® membrane)

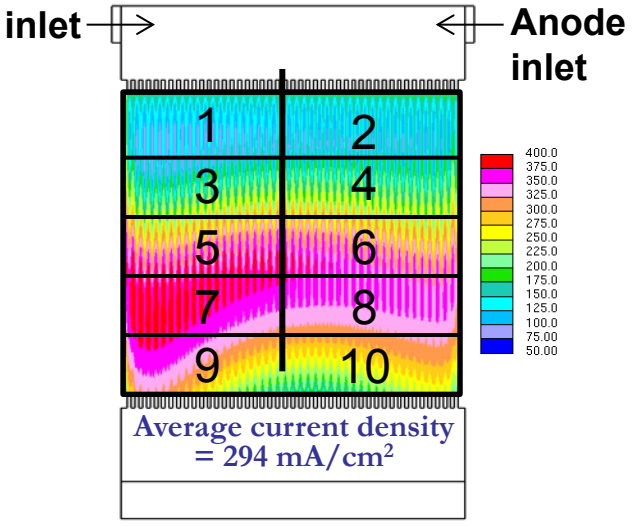


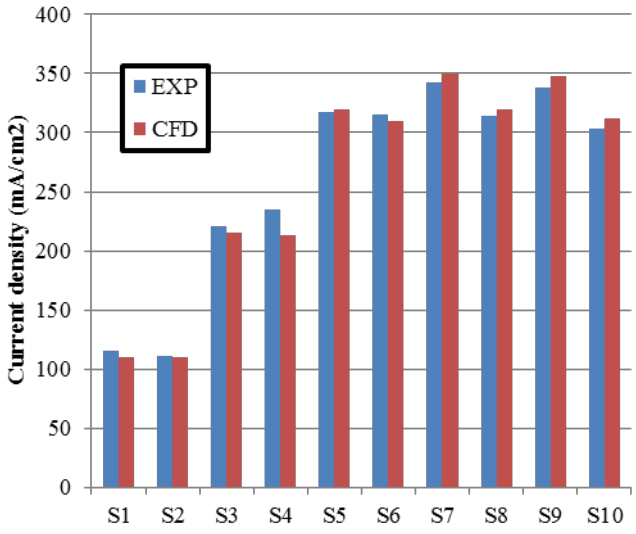


Operating condition:
Anode Stoich. = 1.5
Anode RH = 100%
Cathode Stoich. = 2.0
Cathode RH = 50%
Tcell = 80°C
System pressure = 136kPa

High Current Wet

Model Predicts Equally Well





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

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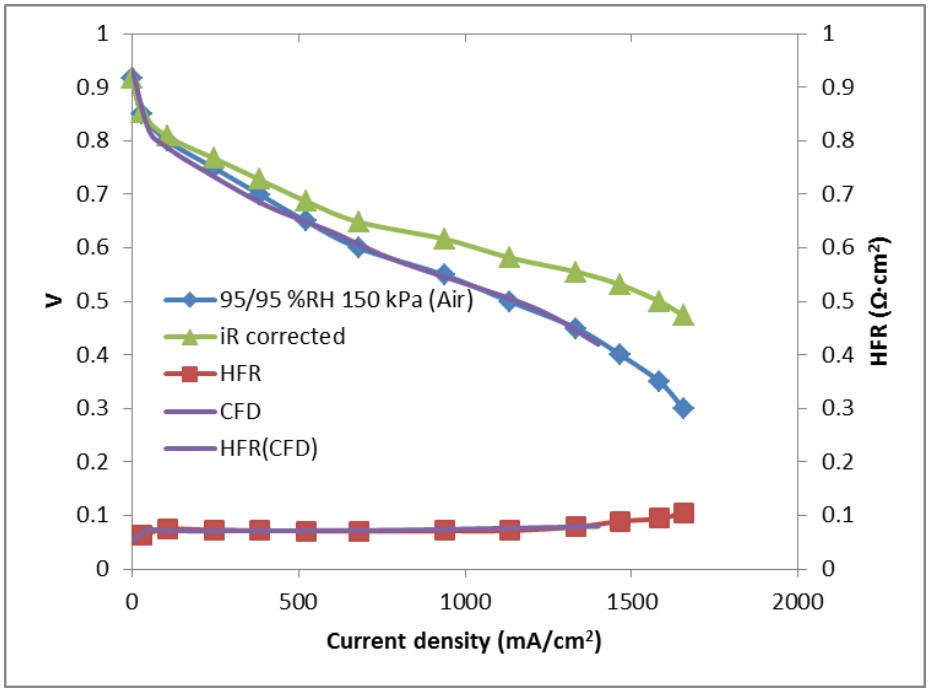
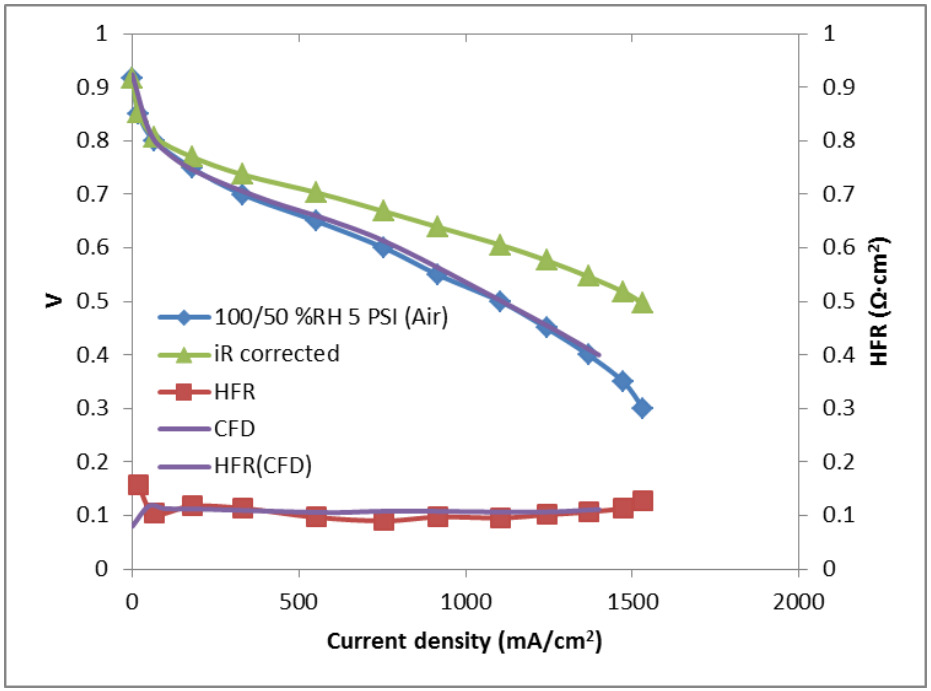
Polarization curves of VT MEA (update 01/14/2013)

6FPAEB-BPSH

(co-current flow: 80°C, 1.5/2.0 stoich, H_2/Air)



95/95 %RH 150 kPa (Air)

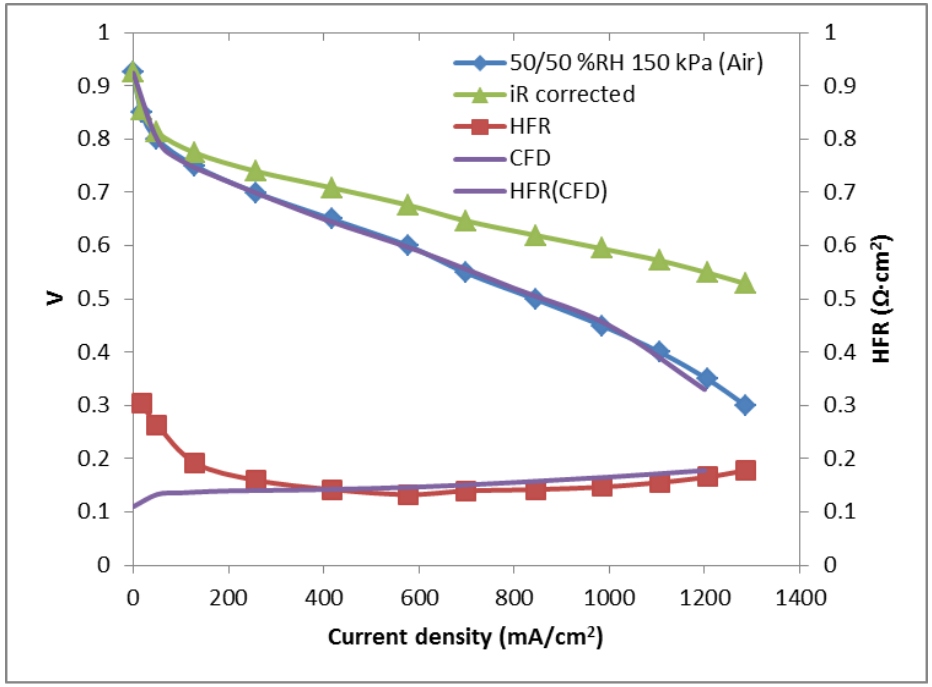


100/50 %RH 5 PSI (Air)

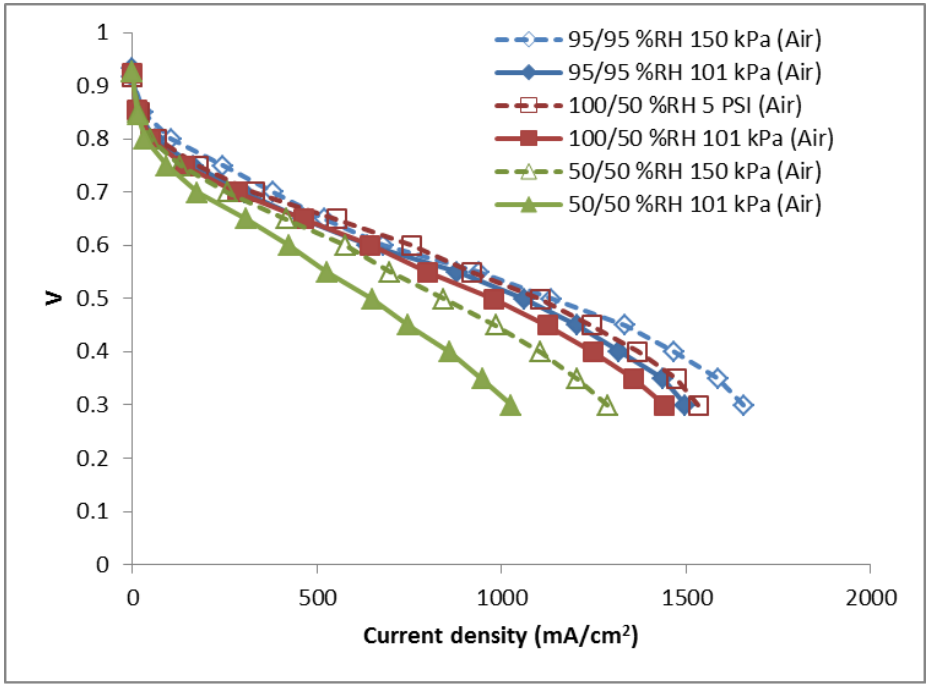
Polarization curves of VT MEA (update 01/14/2013)

6FPAEB-BPSH

(co-current flow: 80°C, 1.5/2.0 stoich, H_2/Air)



50/50 %RH 150 kPa (Air)

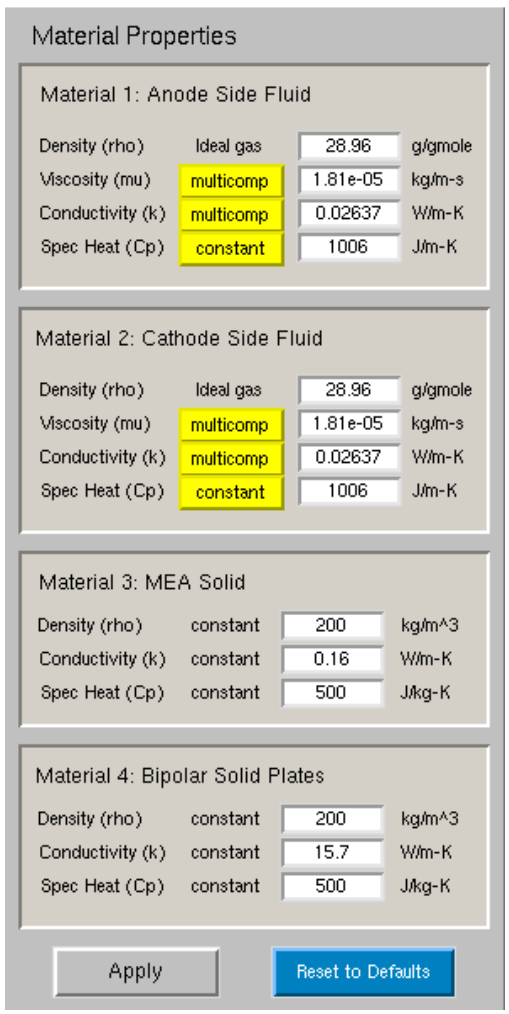


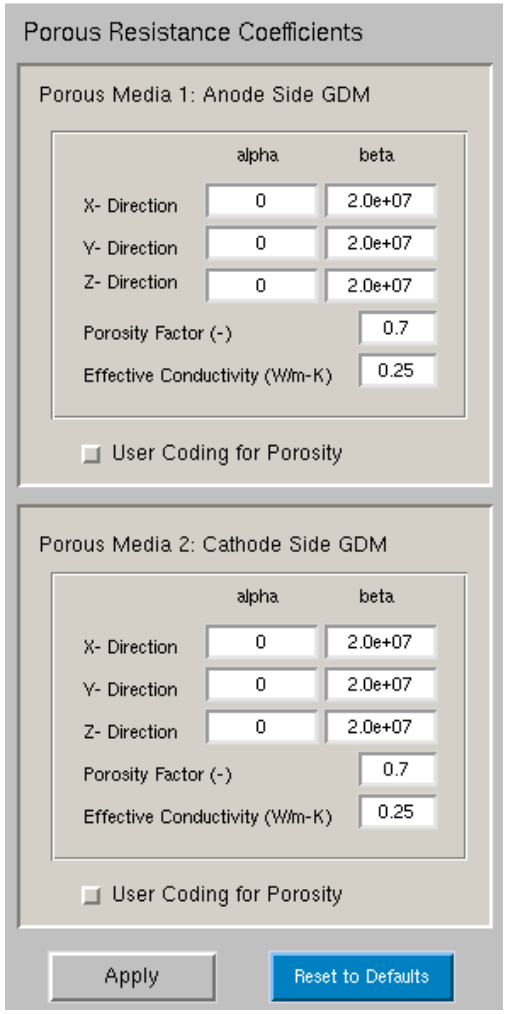
i-V polarization curve

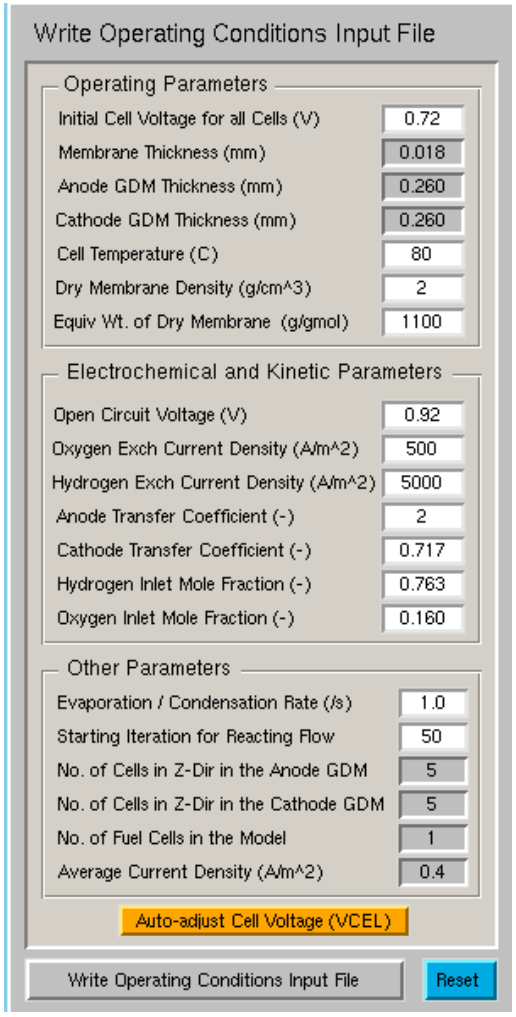
Backup Slides for Model's Input Parameters and Output Variables

This presentation does not contain any proprietary, confidential, or otherwise restricted information

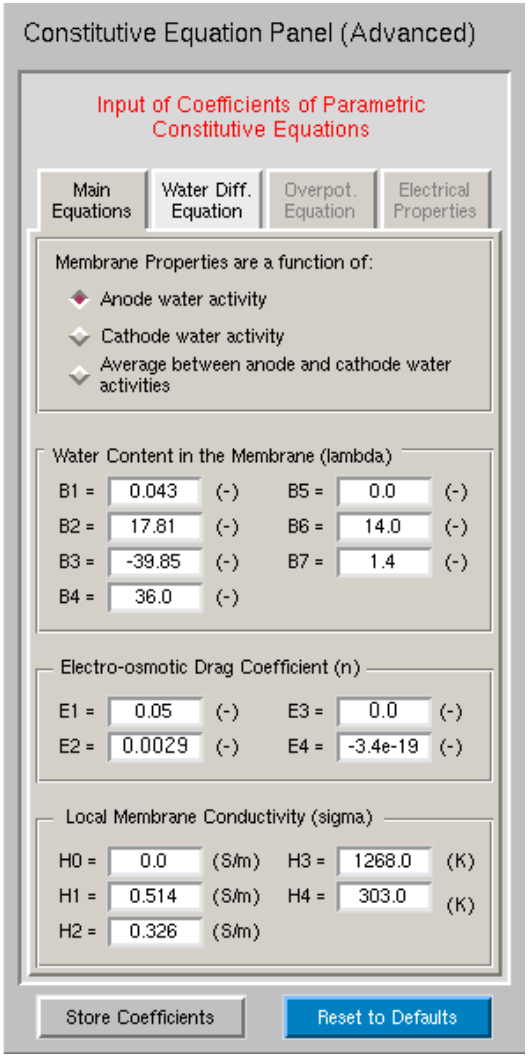
Modeling Input Parameters

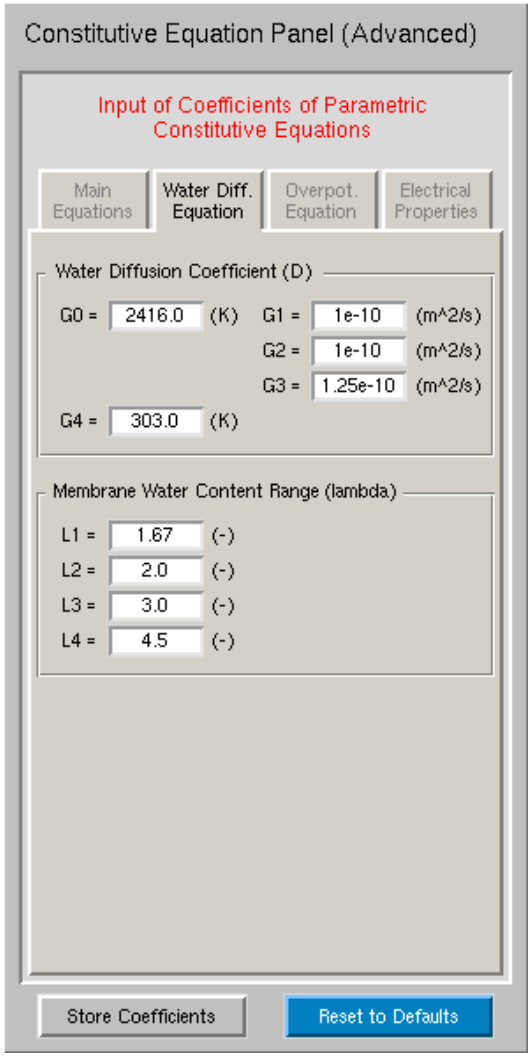


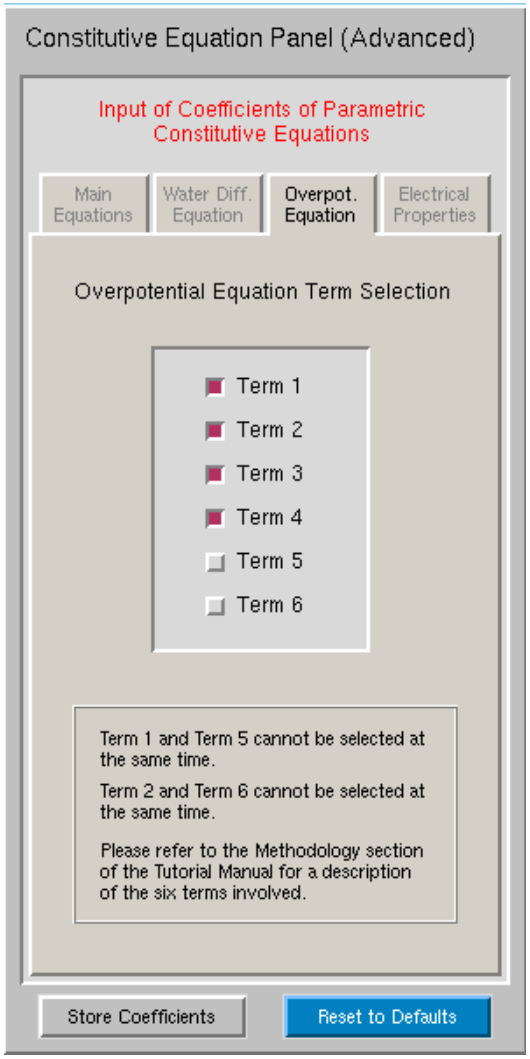
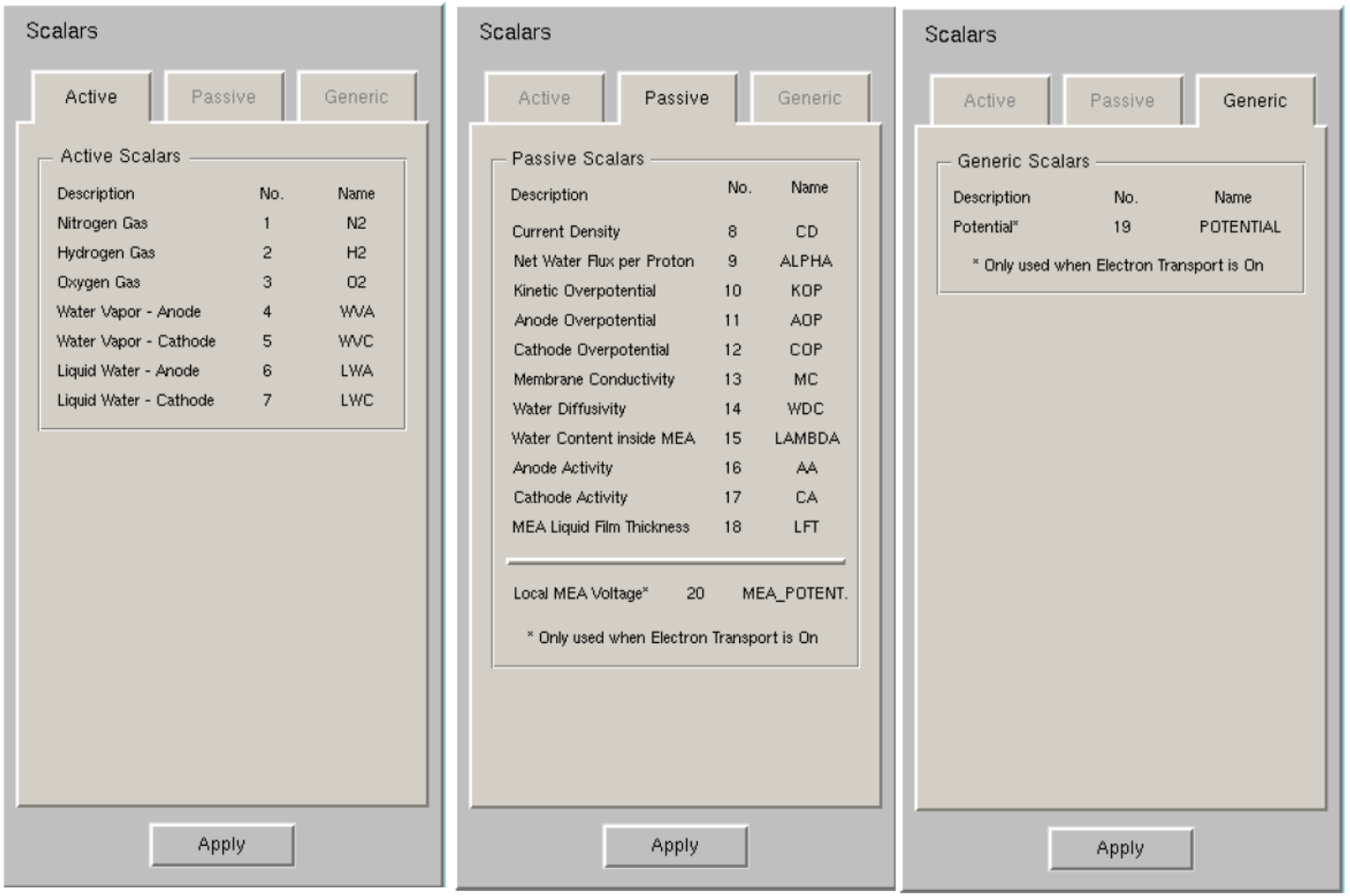




Modeling Input Parameters (Cont.)







Modeling Outputs