Investigation of Micro- and Macro-Scale Transport Processes for Improved Fuel Cell Performance

Department of Energy 2014 Annual Merit Review

Wenbin Gu

General Motors

Electrochemical Energy Research Lab

June 18, 2014

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

Project ID # FC092

Overview

Timeline

- Project Start Date: June 2010
- Project End Date: May 2013 (extended to May 2014 at no cost)
- Percent Complete: 95%

Barriers

- Barriers Addressed
  - C. Performance
  - D. Water Transport within the Stack
  - E. System Thermal and Water Management

Budget

- Total Funding Spent*: $5,306K
- Total Project Value: $5,489K
- Cost Share Percentage: 20%

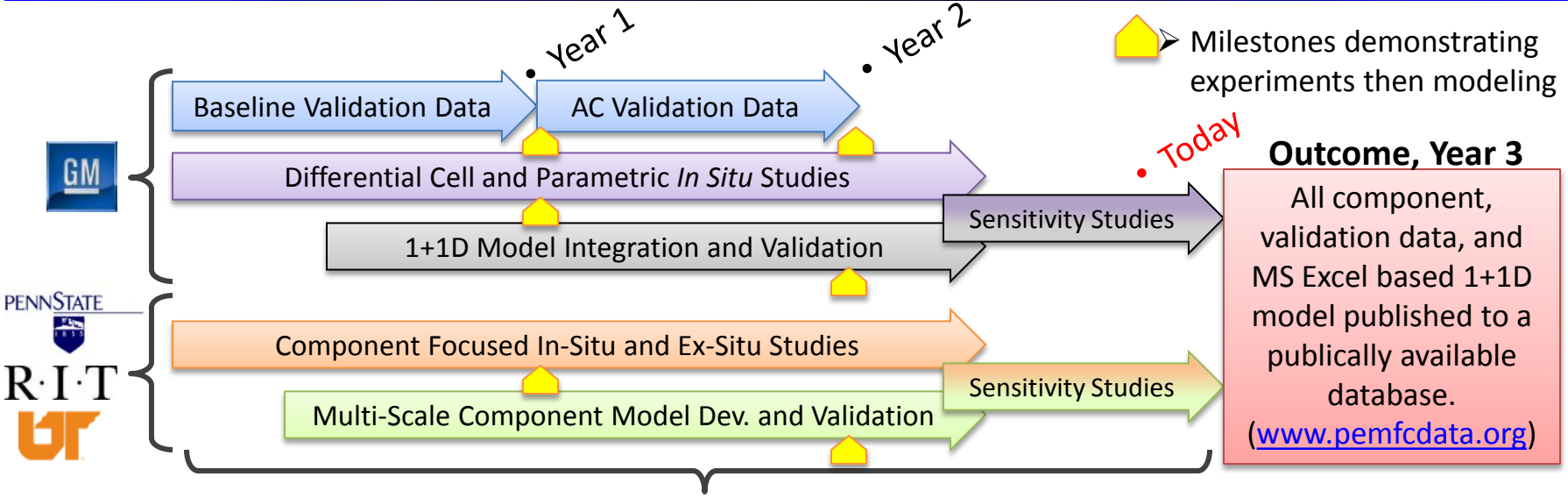
*as of 3/31/14

Partners

- Project Lead: General Motors
- Subcontract Partners:
  - Rochester Inst. of Technology
  - Univ. of Tenn. Knoxville
  - Penn State University
- Other collaborations with material suppliers

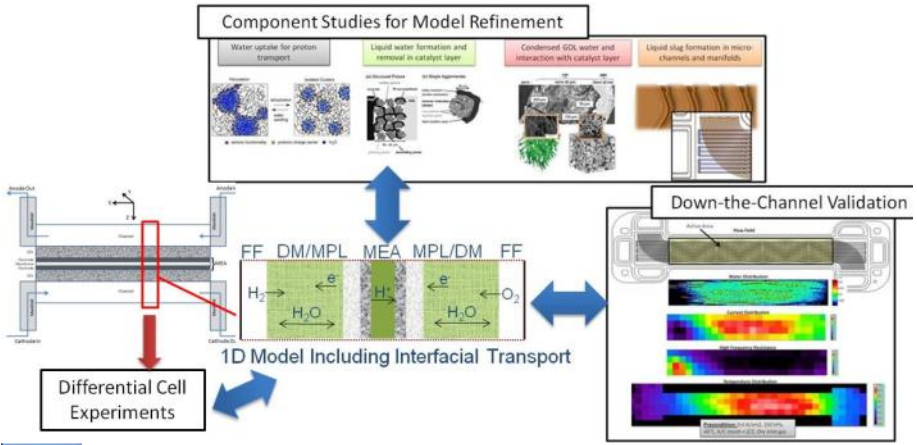
Approach-

Connecting Characterization Techniques with a Validated 1+1D Model



All work streams connected by the transport resistance associated with a component of:

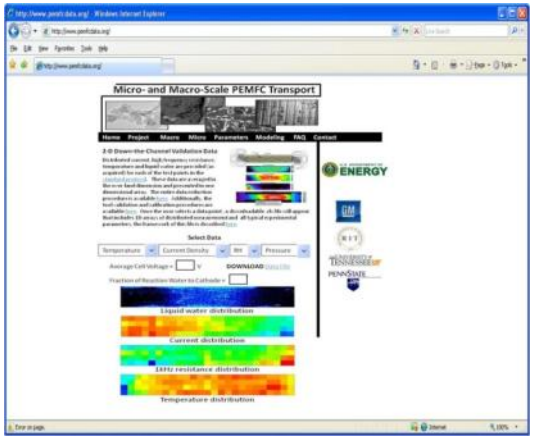
$$E_{cell} = E_{rev} - \eta_{HOR} - |\eta_{ORR}| - i \cdot R_{tx,e^-} - i \cdot R_{tx,Mem.} - i \cdot R_{tx,H^+} - \eta_{tx,O_2(Ch)} - \eta_{tx,O_2\,(GDL)} - \eta_{tx,O_2\,(electrode)}$$



Dry Model Starting Point:

W. Gu *et al.*, "Proton exchange membrane fuel cell (PEMFC) down-the-channel performance model," *Handbook of Fuel Cells* - Volume 5, Prof. Dr. W. Vielstich *et al.* (Eds.), John Wiley & Sons Ltd., (2008).

Database: www.PEMFCdata.org



Collaboration

- **GM Electrochemical Energy Research Lab (prime):** Jeffrey Gagliardo, Wenbin Gu, Ruichun Jiang, Anu Kongkanand, Vinod Kumar, Swami Kumaraguru
- **Penn State University (sub):** Michael Hickner
- **Rochester Institute of Tech (sub):** Satish Kandlikar, Thomas Trabold
- **University of Tennessee (sub):** Matthew Mench
- **University of Rochester (sub):** Jacob Jorne
- **DOE Transport Working Group**
- **National Institute of Standards and Technology (no cost):** David Jacobson, Daniel Hussey, Muhammad Arif
- **W.L. Gore and Associates, Inc. (material cost):** Simon Cleghorn
- **Freudenberg (material cost):** Christian Quick
- **Engineered Fiber Technologies (material cost):** Robert Evans
- **Queens University (no cost):** Kunal Karan
- **Carnegie Mellon University (no cost):** Shawn Litster
- **SUNY Alfred State (no cost)**: Jon Owejan

Relevance-

Core Objectives Addressing DOE Expectations

Topic 4a - Expected Outcomes:

- Validated transport model including all component physical and chemical properties
  - Down-the-channel pseudo-2D model will be refined and validated with data generated in the project
- Public dissemination of the model and instructions for exercise of the model
  - Project website to include all data, statistics, observation, model code and detailed instructions
- Compilation of the data generated in the course of model development and validation
  - Reduced data used to guide model physics to be published and described on project website
- Identification of rate-limiting steps and recommendations for improvements to the plate-to-plate fuel cell package
  - Model validation with baseline and auto-competitive material sets will provide key performance limiting parameters

Characterization and validation data

Employing new and existing characterization techniques to measure transport phenomena and fundamentally understand physics at the micro-scale is the foundation of this project. Additionally, a comprehensive down-the-channel validation data set is being populated to evaluate the integrated transport resistances. This work will consider a baseline and next generation material set.

Multi-Scale component-level models

Models that consider bulk and interfacial transport processes are being developed for each transport domain in the fuel cell material sandwich. These models will be validated with a variety of *in situ* and *ex situ* characterization techniques. One dimensional transport resistance expressions will be derived from these models. This work will consider a baseline and next generation material set.

1+1D fuel cell model solved along a straight gas flow path

Consider if a 1+1D simplified model can predict the saturation state along the channel, performance and the overall water balance for both wet and dry operating conditions within the experimental uncertainty of the comprehensive macro-scale validation data sets. Identify shortcomings of 1D approximations.

Identify critical parameters for low-cost material development

Execute combinatorial studies using the validated model to identify optimal material properties and trade-offs for low-cost component development in various operating spaces.

Approach, Progress-

Project Standardization

Baseline Material Set

- Membrane
  - Gore 18 µm
- Anode catalyst layer
  - target loading 0.05 mg_{Pt} cm^{-2}
  - 20% Pt/V made with 950EW ionomer I/C 0.6
- Cathode catalyst layer
  - target loading 0.3 mg_{Pt} cm^{-2}
  - 50% Pt/V made with 950EW ionomer I/C 0.95
- Microporous layer
  - 8:1:1 carbon-to-PTFE-to-FEP ratio, 30 µm thick
- Gas diffusion substrate
  - MRC 105 w/ 5% wt. PTFE, 230 µm thick w/MPL
- Flow field
  - 0.7 mm wide by 0.4 mm deep channels with stamped metal plate cross-sectional geometry
  - 18.3 cm channel length
  - 0.5 mm cathode land width
  - 1.5 mm anode land width
  - Exit headers typical to a fuel cell stack

Auto-Competitive Material Set

- Membrane
  - Gore 12 µm
- Anode catalyst layer
  - target loading 0.05 mg_{Pt} cm^{-2}
  - 20% Pt/V with 950EW ionomer I/C 0.6
- Cathode catalyst layer
  - target loading 0.1 mg_{Pt} cm^{-2}
  - 15% Pt/V with 950EW ionomer I/C 0.7
- Microporous layer
  - 8:1:1 carbon-to-PTFE-to-FEP ratio, 30 µm thick
- Gas diffusion substrate
  - Anode – prototype high diffusion res, w/ 5% wt. PTFE, 210 µm thick w/MPL
  - Cathode - MRC 105 w/ 5% wt. PTFE, 230 µm thick w/MPL
- Flow field
  - 0.7 mm wide by 0.3 mm deep channels with stamped metal plate cross-sectional geometry
  - 18.3 cm channel length
  - 0.25 mm cathode land width
  - 0.75 mm anode land width
  - Modified exit headers

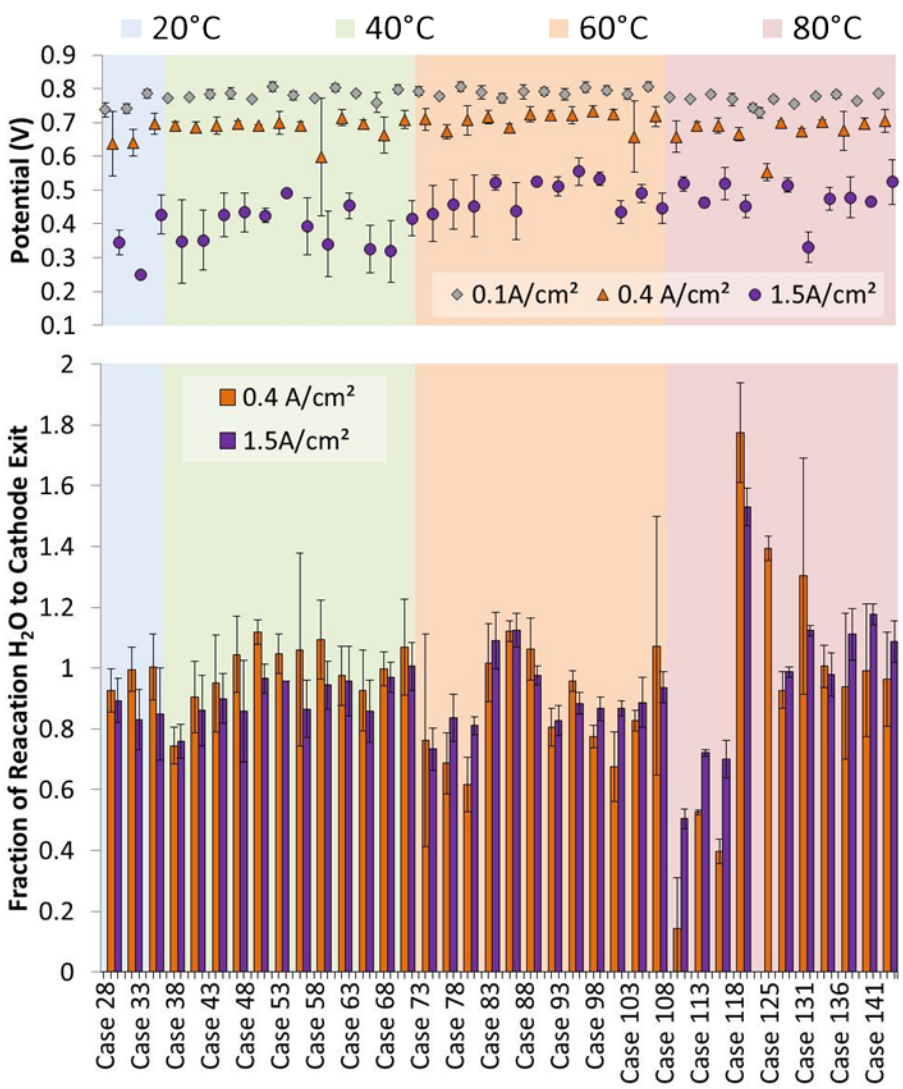
Standard Protocol

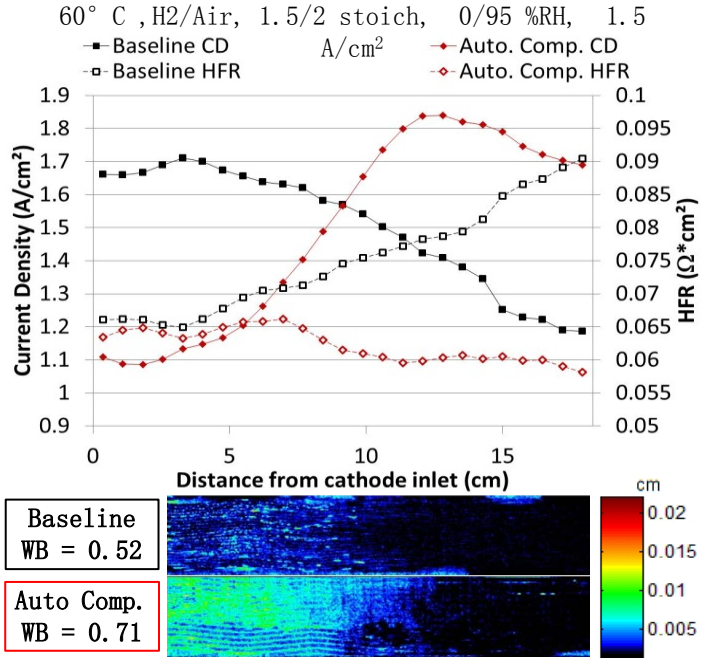
4 x 4 x 3 x 3 Factors

Temperature	Inlet RH (An/Ca)	Outlet Pressure (An/Ca)	Current Density
20, 40, 60, 80°C	95/95, 0/95, 95/0, 50/50%	150/150, 100/150, 150/100 kPa	0.1, 0.4, 1.5 A/cm^2

H_2/Air Stoichiometric Ratios = 1.5 / 2.0 for all experiments

Completion of Auto-Competitive Validation Dataset





Versus Standard Material Set

- Lower performance
- Higher level of uncertainty
- On average 16% more of the reaction water staying on the cathode
- Opposite trend in down-the-channel current distribution at a lower T

Detailed Test Conditions: http://www.pemfcdata.org/data/Standard_Protocol.xls

Simplify Material Changes

Baseline Material Set

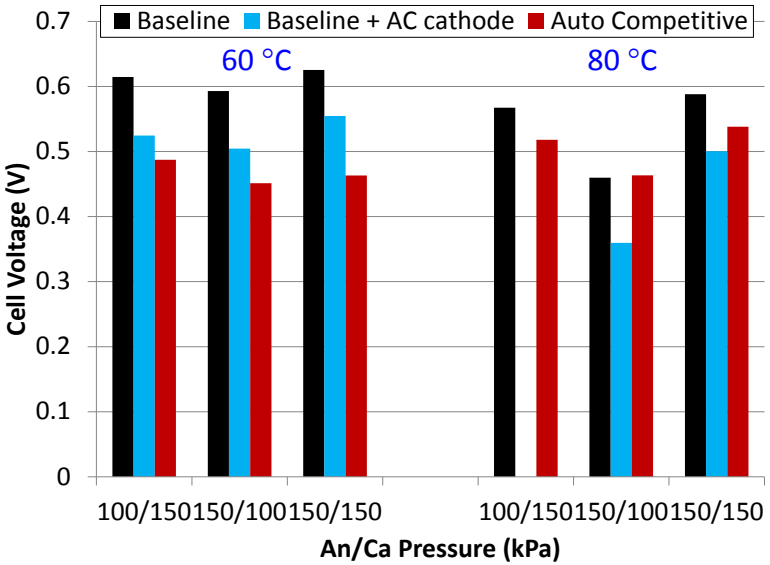
- Membrane
  - Gore 18 μm
- Anode catalyst layer
  - target loading 0.05 mg_{Pt} cm^{-2}
  - 20% Pt/V made with 950EW ionomer I/C 0.6
- Cathode catalyst layer
  - target loading 0.3 mg_{Pt} cm^{-2}
  - 50% Pt/V made with 950EW ionomer I/C 0.95
- Microporous layer
  - 8:1:1 carbon-to-PTFE-to-FEP ratio, 30 μm thick
- Gas diffusion substrate
  - MRC 105 w/ 5% wt. PTFE, 230 μm thick w/MPL
- Flow field
  - 0.7 mm wide by 0.4 mm deep channels with stamped metal plate cross-sectional geometry
  - 18.3 cm channel length
  - 0.5 mm cathode land width
  - 1.5 mm anode land width
  - Exit headers typical to a fuel cell stack

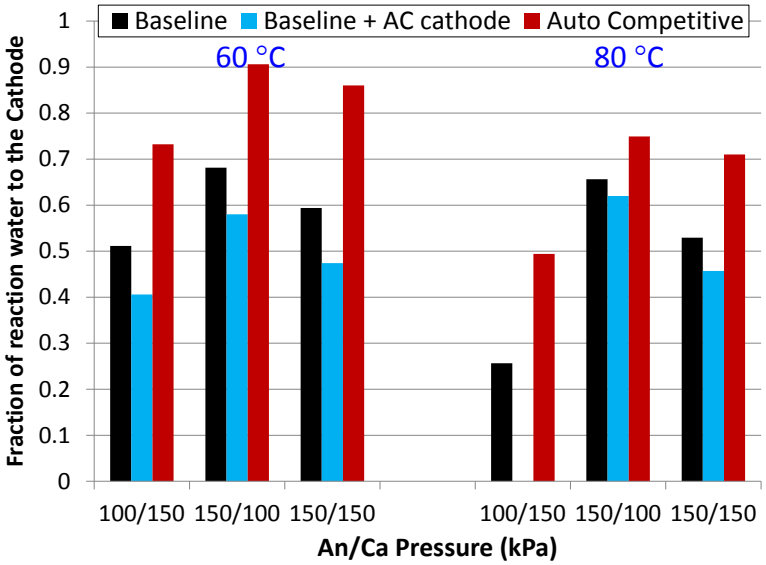
Low Loaded Cathode Material Set

- Membrane
  - Gore 18 μm
- Anode catalyst layer
  - target loading 0.05 mg_{Pt} cm^{-2}
  - 20% Pt/V with 950EW ionomer I/C 0.6
- Cathode catalyst layer
  - target loading 0.1 mg_{Pt} cm^{-2}
  - 15% Pt/V with 950EW ionomer I/C 0.95
- Microporous layer
  - 8:1:1 carbon-to-PTFE-to-FEP ratio, 30 μm thick
- Gas diffusion substrate
  - MRC 105 w/ 5% wt. PTFE, 230 μm thick w/MPL
- Flow field
  - 0.7 mm wide by 0.4 mm deep channels with stamped metal plate cross-sectional geometry
  - 18.3 cm channel length
  - 0.5 mm cathode land width
  - 1.5 mm anode land width
  - Exit headers typical to a fuel cell stack

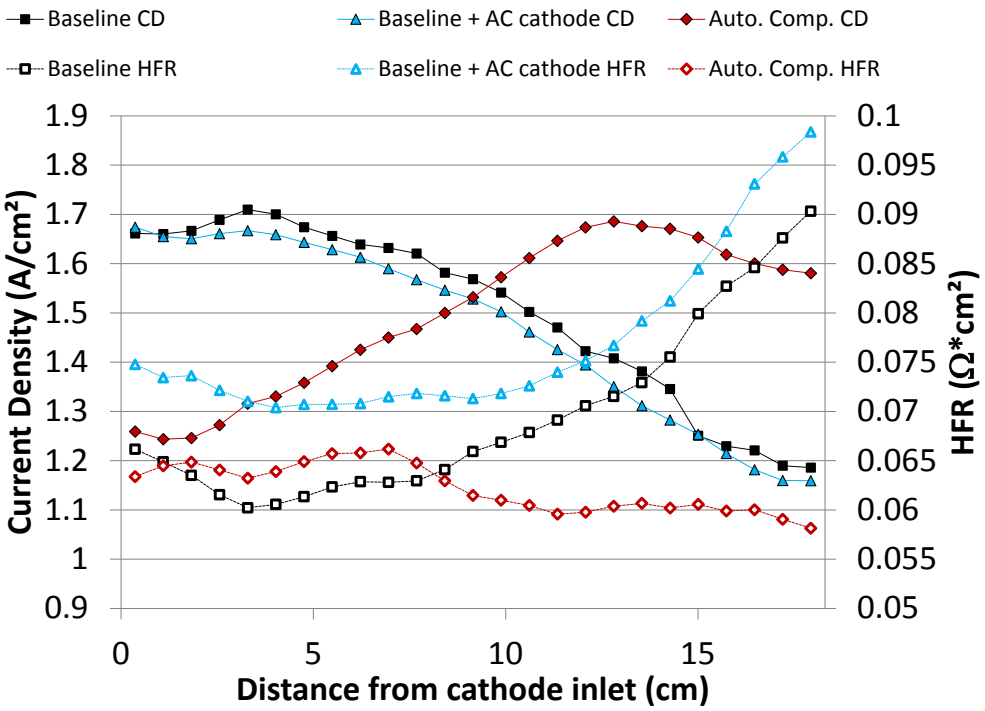
- Deconvolute the effects of high resistance anode diffusion and cell design differences used in DoE automotive competitive builds from low Pt-loaded cathode effects.

Effects of Low Pt-loaded Cathode and AC Anode DM





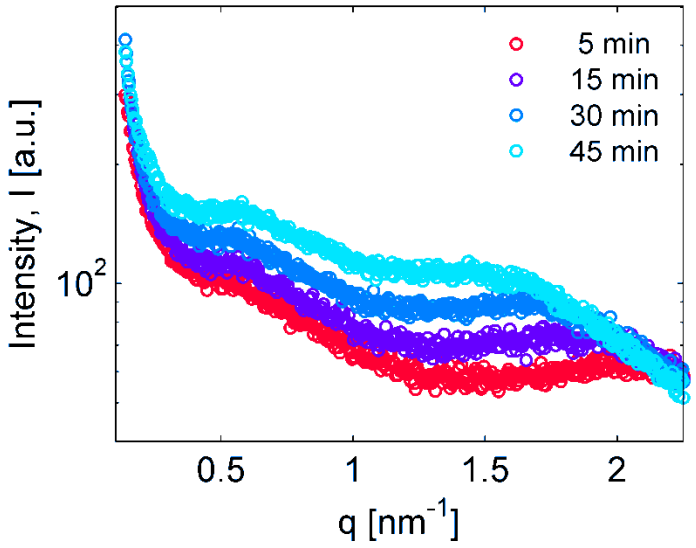
60 °C ,H2/Air, 1.5/2 stoich, 100/150 kPa, 0/95 %RH, 1.5 A/cm²



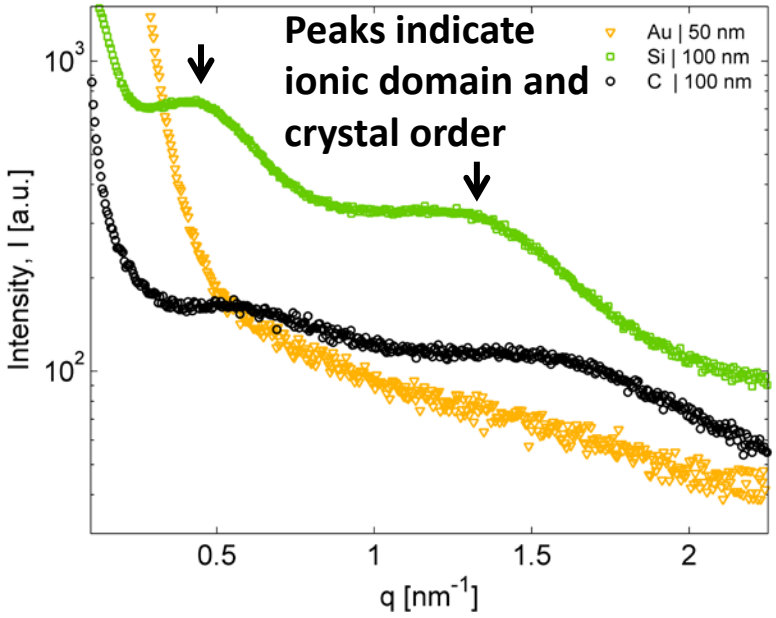
- Lower cell voltage results from lower Pt-loaded cathode.
- Less product water to the cathode flow-field is consistent with higher T-gradient due to lower voltage.
- Lower Pt-loaded cathode is not responsible for the opposite trend in current distribution; The highly tortuous anode DM is.

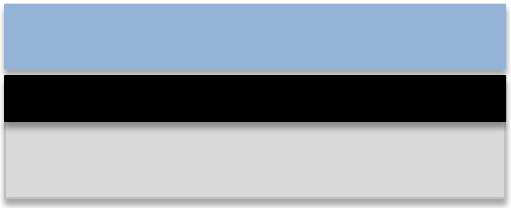
Thin Polymer Films on Gold and Carbon Surfaces

Swelling of 100 nm Nafion® thin film on carbon



Different ionic domain features on Au, C, and Si





Nafion®

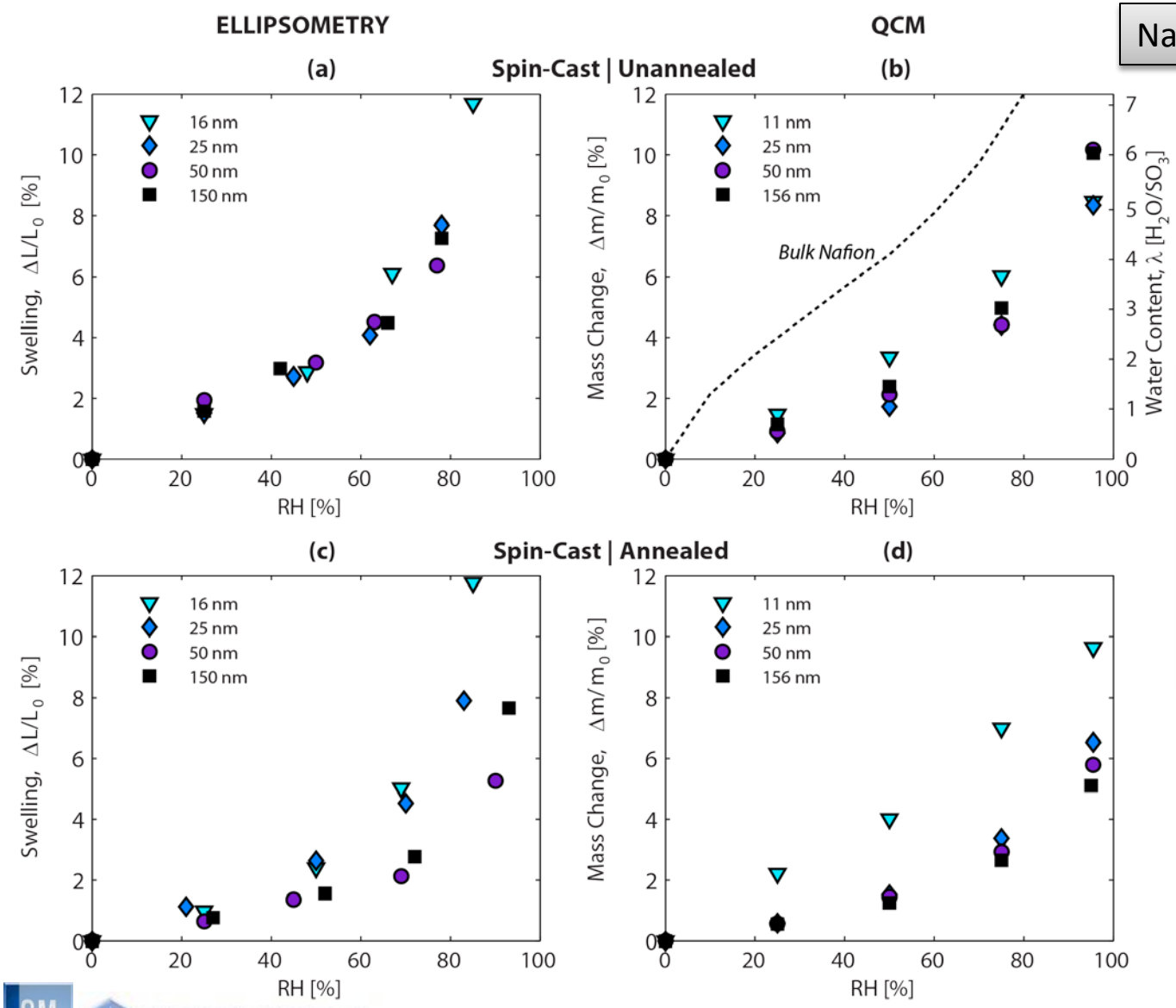
Pyrolized carbon

Si substrate

- Polyfurfuryl alcohol (PFA) is spun-cast onto a Si wafer and pyrolized.
- Resulting surfaces characterized by Raman and ellipsometry.

- Ionic domain and crystal ordering observed on Si and carbon substrates for 100 nm film.
  - Indicates that Nafion molecules can rearrange during the spin coating process.
- No ordering of 50 nm films on Au substrates indicates strong Nafion-metal interaction.

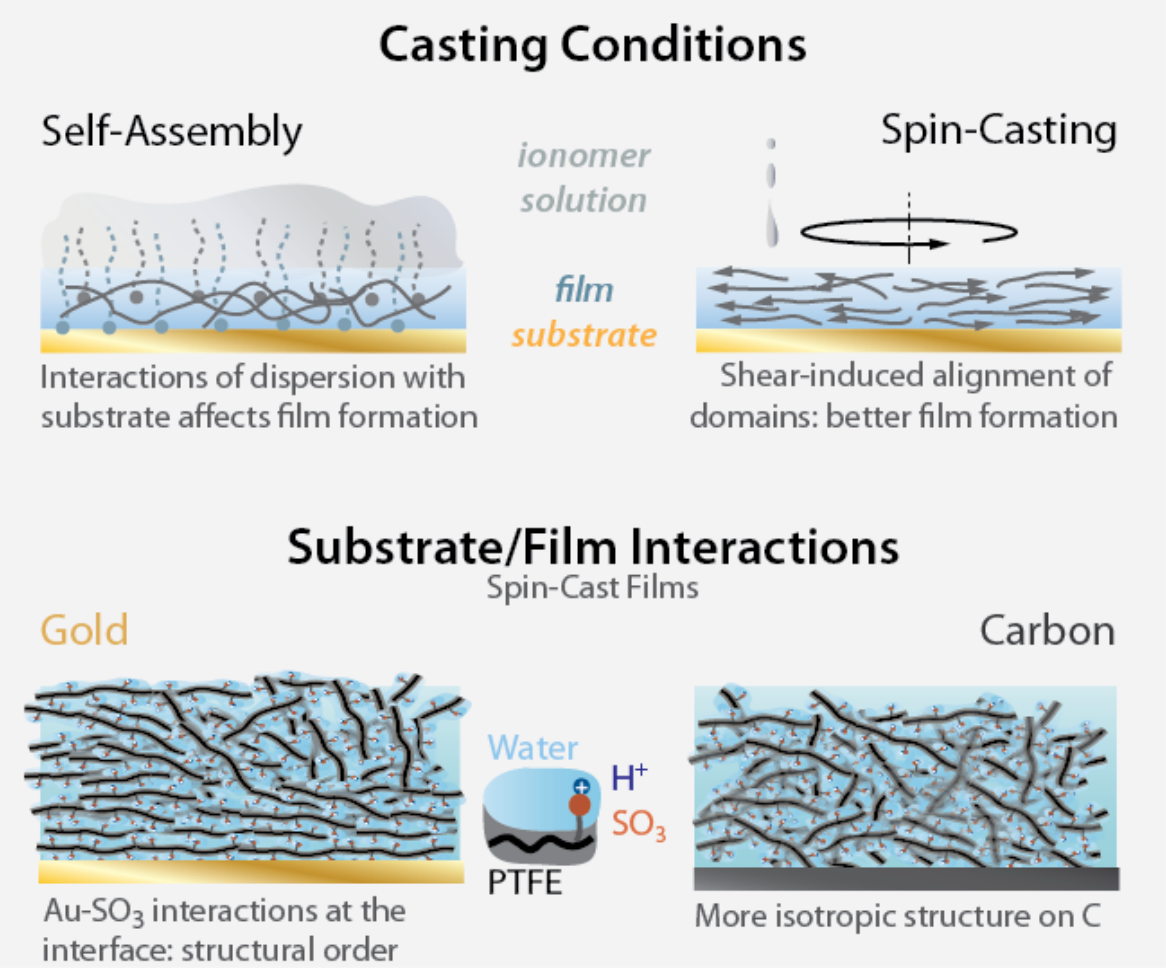
Changes in Films from Thickness Change and Mass



Nafion films on Au substrates

Both thickness swelling from ellipsometry and mass uptake from QCM show similar trends in terms of changes in the film with processing and thickness.

Effect of Processing and Substrate on Film Order



Physical models developed from small-angle scattering of ionic and crystal domain structures and swelling data.

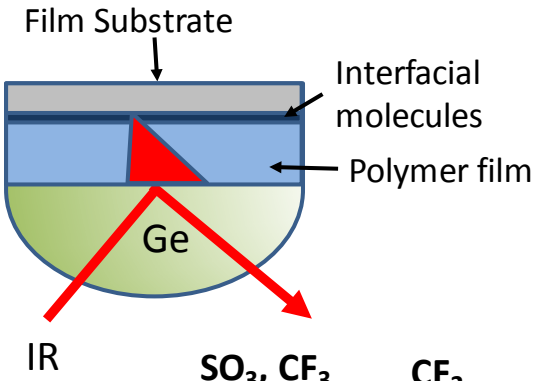
Need to confirm molecular alignment and surface associations with another technique.

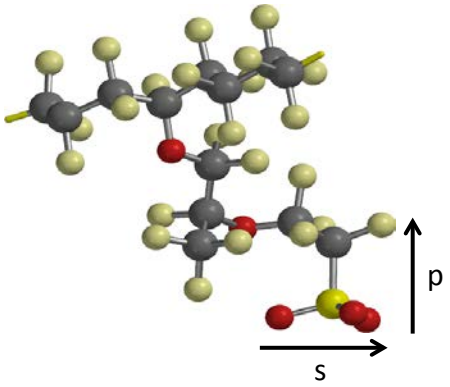
Move towards FTIR spectroelectrochemistry to measure films under potential control.

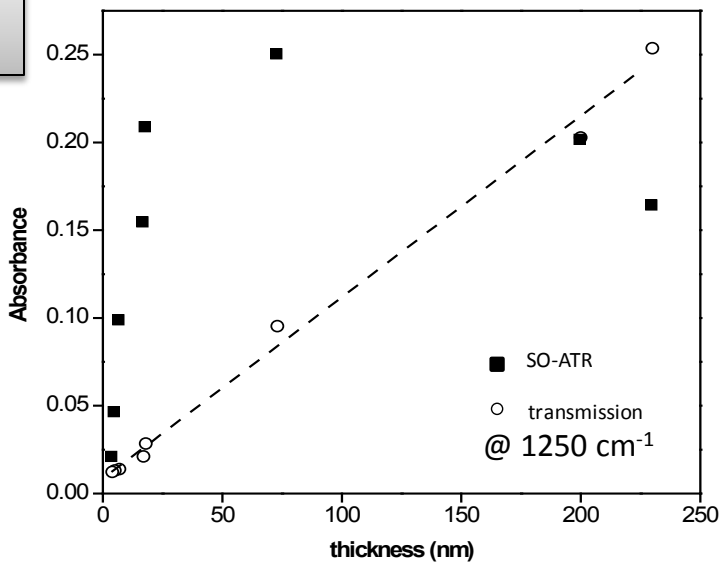
Impact of Substrate and Processing on Confinement of Nafion Thin Films
Kusoglu, Kushner, Paul, Karan, Hickner, Weber, *Adv. Func. Mater*. **2014**.

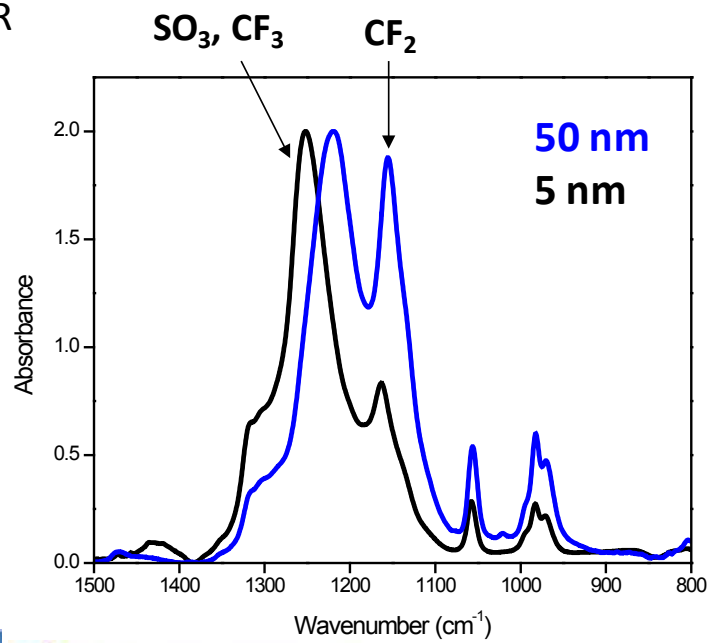
Molecular Surface Alignment from SO-ATR

Surface-overlayer enhanced FTIR increases signal strength of interfacial molecules at substrate.









- 50 nm film geometry shows CF_2, SO_3H, and CF_3 peaks near their wavenumber positions and intensities observed in bulk films.
- 5 nm film geometry has strong p-polarization due to substrate overlayer effect. Can observe SO_3 and CF_3 near the interface with a blueshift which might indicate surface binding.

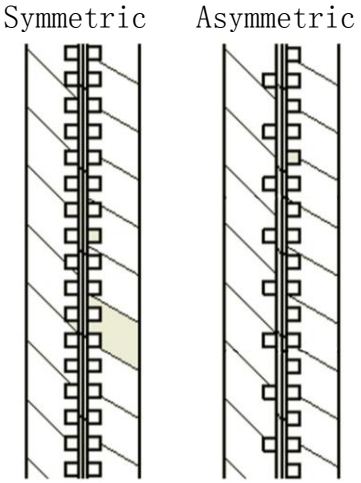
Will extend these studies to potential-dependent FTIR to measure how sulfonates adsorb and order on the surface.

Matrix of Available Neutron Data

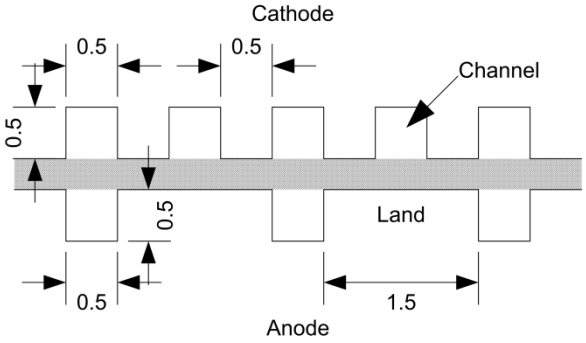
		40°C		60°C		80°C	
	Flowfield	Pressure	Relative humidity	Pressure	Relative humidity	Pressure	Relative humidity
Baseline Materials	Asymmetric	X		X	X	X	X
	Symmetric	X		X	X	X	X
Autocompetitive materials	Asymmetric	X		X	X	X	X
	Symmetric	X		X	X	X	X

At each condition:

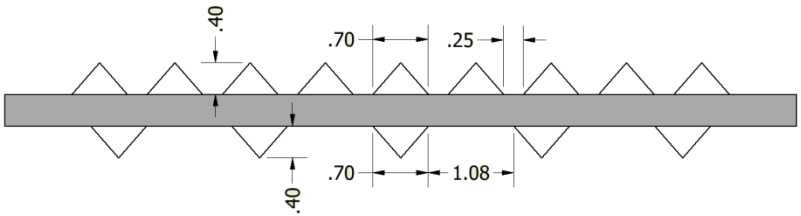
- **Constant flow rate of 84 sccm anode and 200 sccm cathode**
- **Current Densities tested: 0.1, 0.4, 0.8, 1.2, and 1.5 A/cm²**
- **Inlet relative humidity held at 95|95 %RH for exhaust pressure testing**
- **Exhaust pressure held at 150|150 kPa for relative humidity testing**



(a) Baseline Flowfield

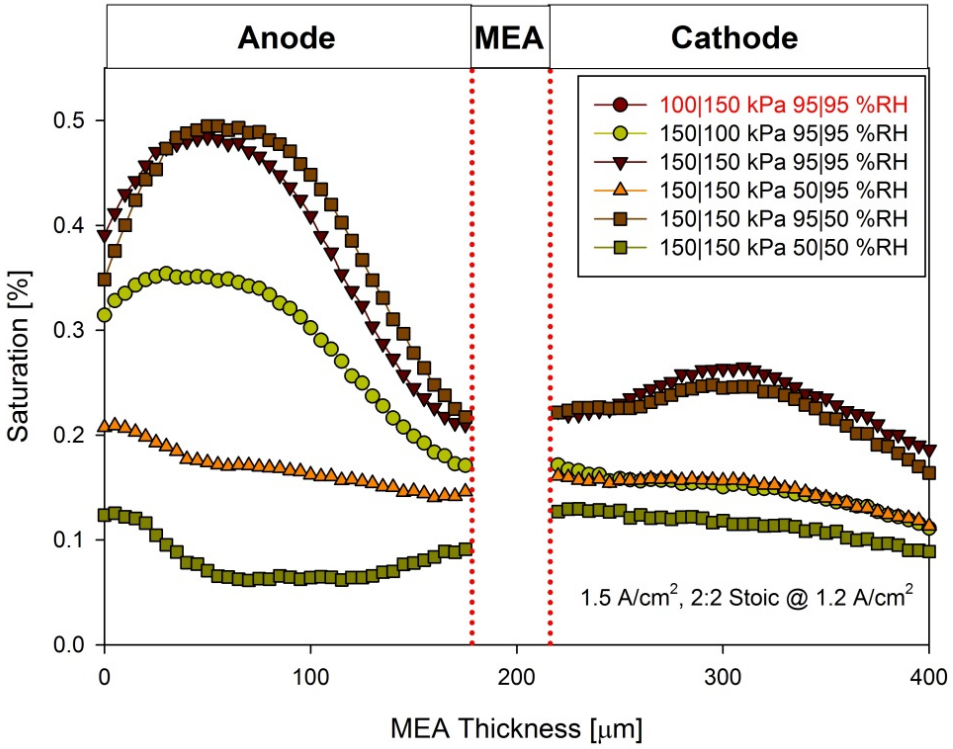


(b) Auto-Competitive Flowfield

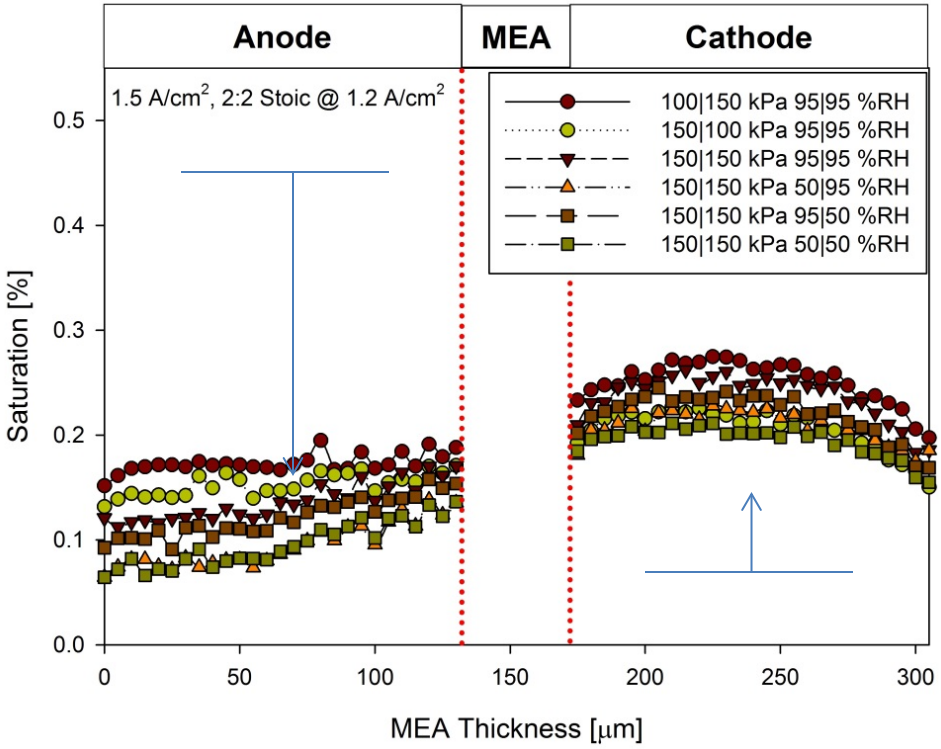


GDL Water Saturation at 60°C

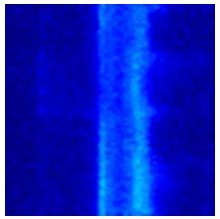
Baseline



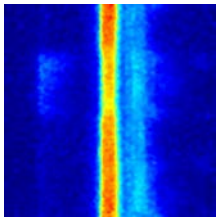
Auto Competitive



50|95%



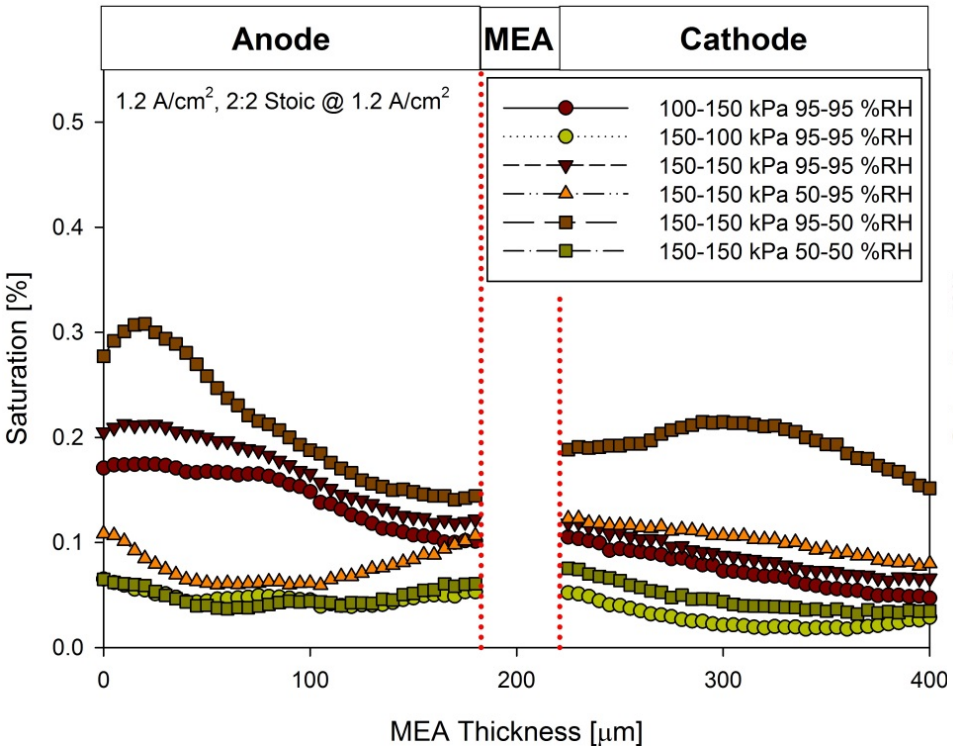
95|50%



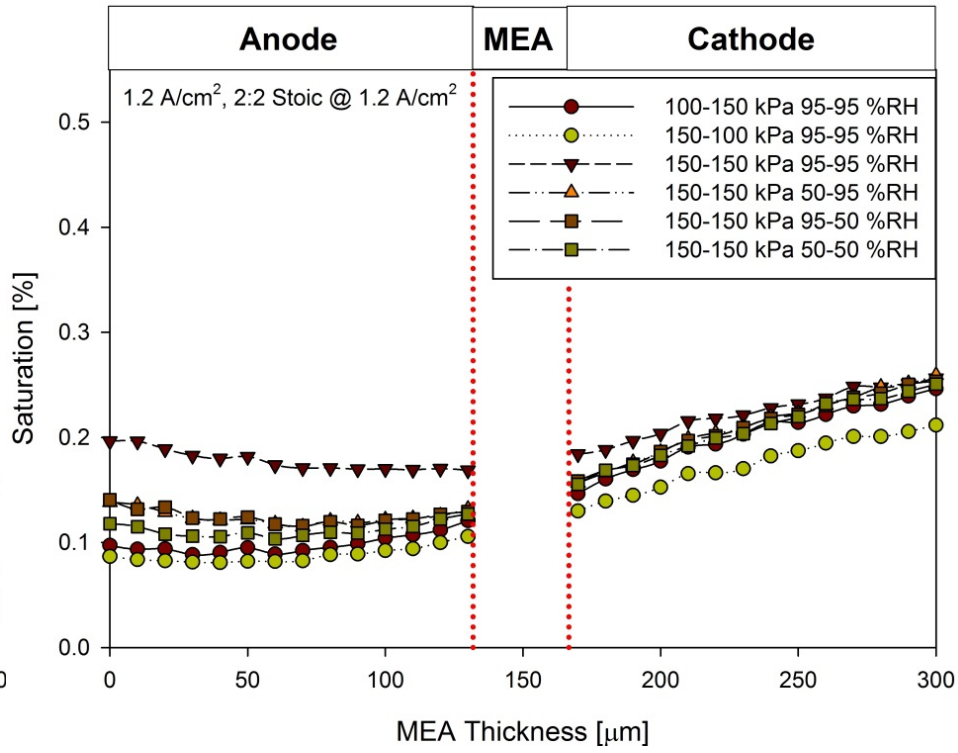
- Auto Competitive material set yields reduced anode water content (and increased cathode water content for most cases) due to high tortuosity DM and finer pitch, triangular channels and higher velocity.
- Tighter variation in water saturation expected from thermal effect

Strong Land/HT Impact on Water Storage

Baseline



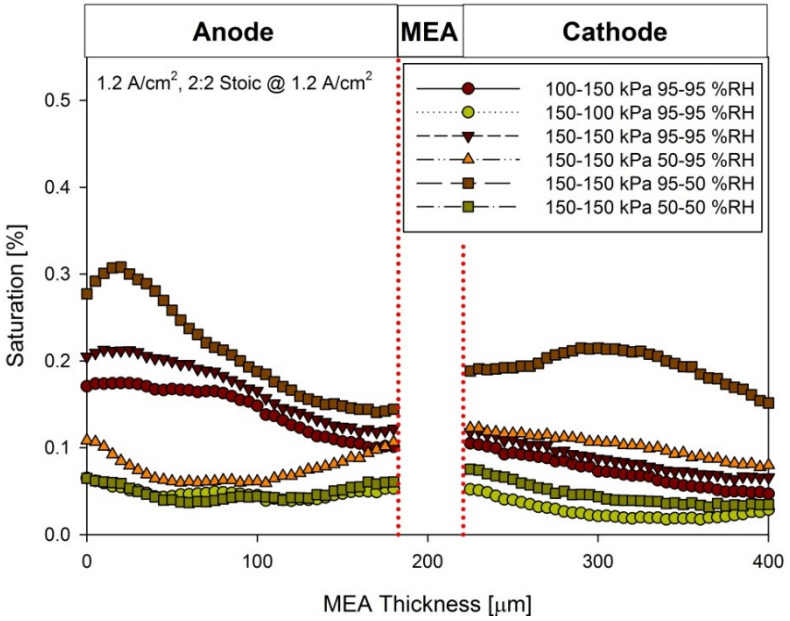
Symmetric Baseline



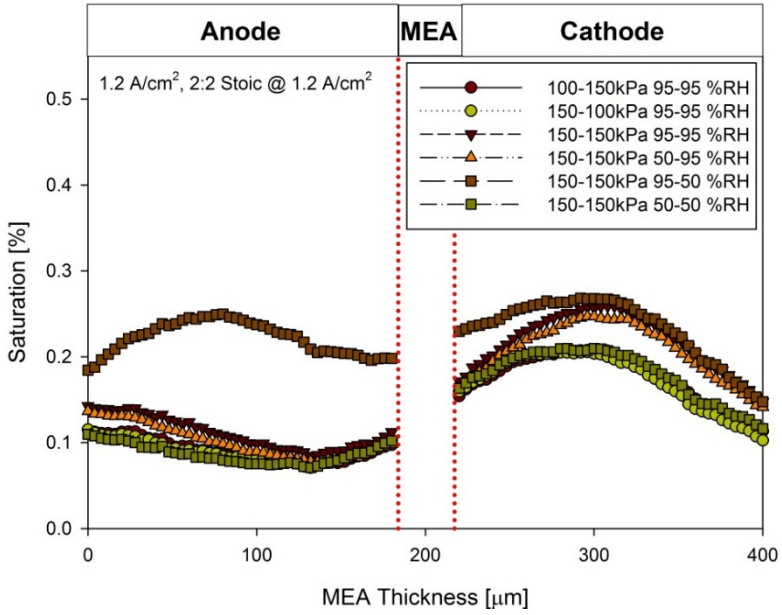
- Symmetric case does not show variation in water content that asymmetric flow field showed at 60 C
- Indicates a possible thermal effect (PCI flow) due to cooling area of anode lands or gas/liquid removal restriction due to low anode channel ratio

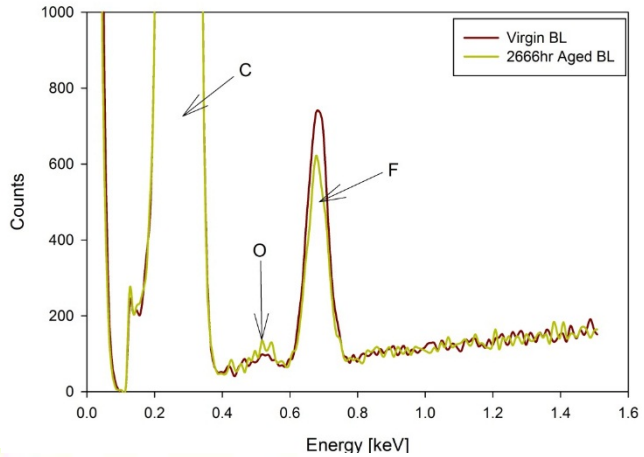
Water Content Increases for Aged Materials

Baseline



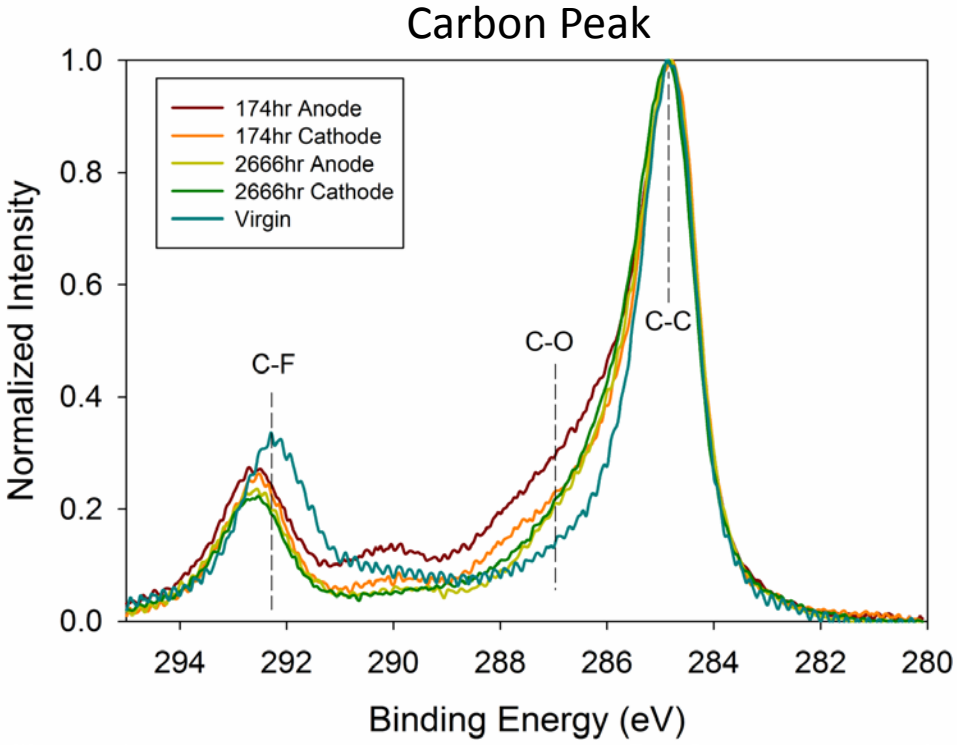
2666hr Aged

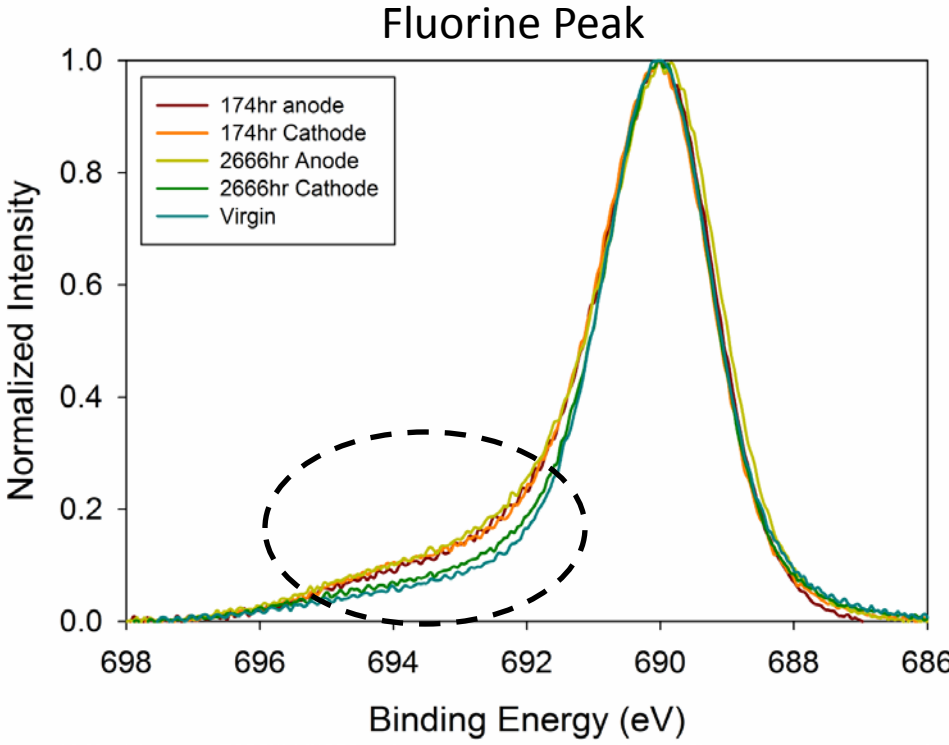




- Net increase in cathode while the anode water content decreased for most cases
- The degraded sample did not run any conditions at 1.5 A/cm^2
  - ✓ Initial Indication of PTFE Wash-Out with EDS
    - A reduction in fluorine peak for degraded sample indicates a loss of PTFE from the DM
    - Small increase in oxygen content on fibers
    - Additional testing such as XPS are being scheduled to expand EDS results

XPS Shows a Decrease in C-F Bonds and an Increase in C-O Bonds





- Increase in C-O bonding and decrease in C-F bonding indicates a shift from hydrophobic to hydrophilic
- Decrease in C-F occurs rapidly during initial operation <100 hours
- Increase in high binding energy region of fluorine peak (circled) due to charging indicating a breakdown in PTFE chain with increased chain isolation

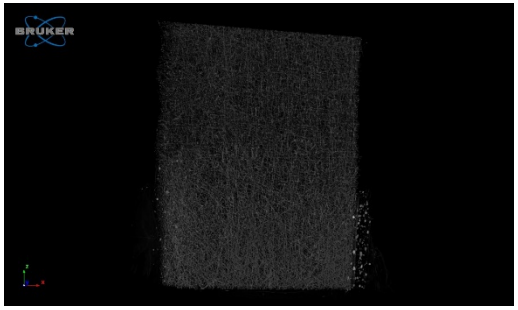
Component Level Modeling of GDL

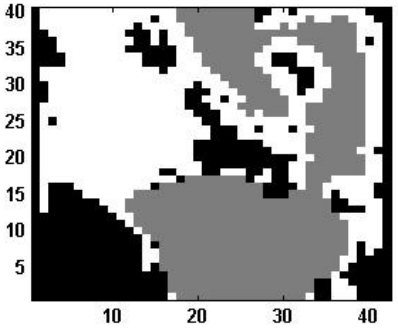
Progress (Real Geometries)

- **Multiphase flow in digitized micro-tomographies of baseline and auto-competitive GDL samples were investigated.**
- **The data was provided by the x-rays and representative areas were extracted for both samples. Single component multiphase LBM was applied.**

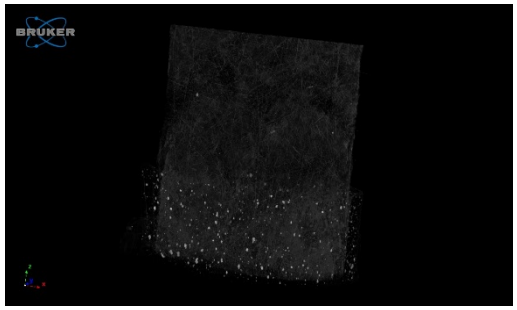
Learning to Date:

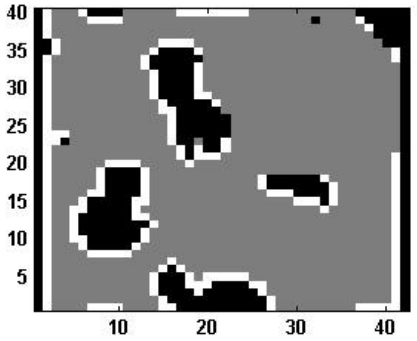
- **After the critical condensation points stated below, no further gas flow observed.**
- **Baseline: 0.46222**
- **Auto-competitive: 0.85827**





Baseline	Condensation	Effective Porosity	Tortuosity
Φ=0.79812	0.00000	0.77750	1.19829
	0.15193	0.62798	1.44443
	0.22910	0.57083	1.45745
	0.30868	0.51190	1.46880
	0.40756	0.43869	1.54081
	0.46222	0.00000	-

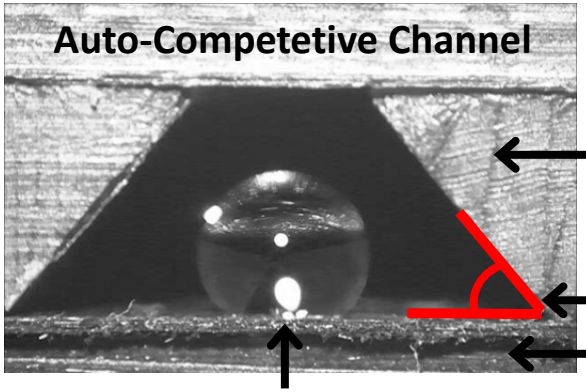




Auto-competitive	Condensation	Effective Porosity	Tortuosity
Φ=0.87000	0.00000	0.86875	1.07299
	0.20288	0.68812	1.18843
	0.39568	0.51250	1.12352
	0.50288	0.40500	1.13674
	0.69784	0.12625	1.08405
	0.85827	0.00000	-

Droplet – Channel Corner Interaction

Effect of Channel Wall Material

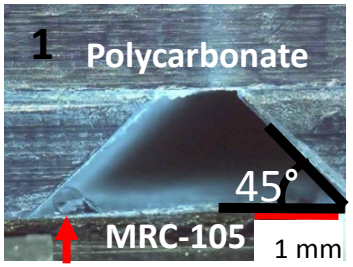


Higher contact angle hysteresis does not allow corner filling.

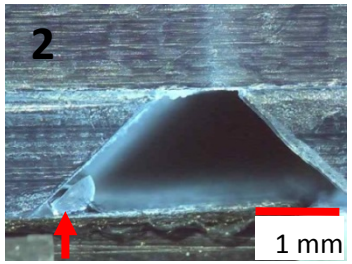
Channel Material	Polycarbonate	Copper (Cu-110)	Graphite	Stainless Steel (SS-2205)
Contact Angle Hysteresis [°]	25	27	50	19
Range of Air Velocity for Non-Filling [m s^{-1}]	0.4 - 2.4	0.4 - 2.4	0.2 - 2.4	0.4 - 2.4

Graphite provides a wider range of conditions for non-filling.

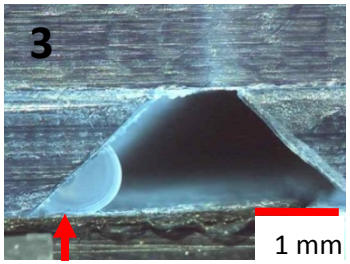
Effect of Water Injection Location



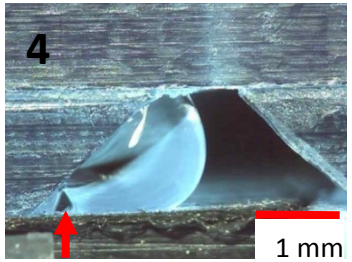
Droplet inlet at side



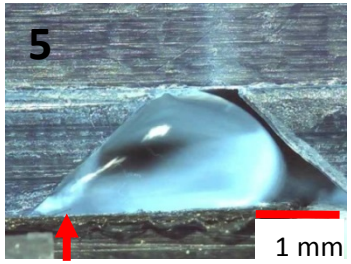
Touches sidewall



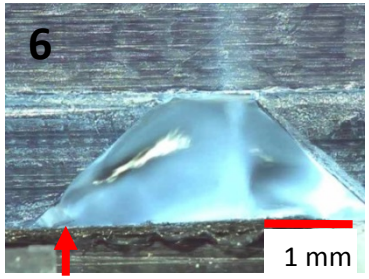
Corner filling



Touches top wall



Droplet grow

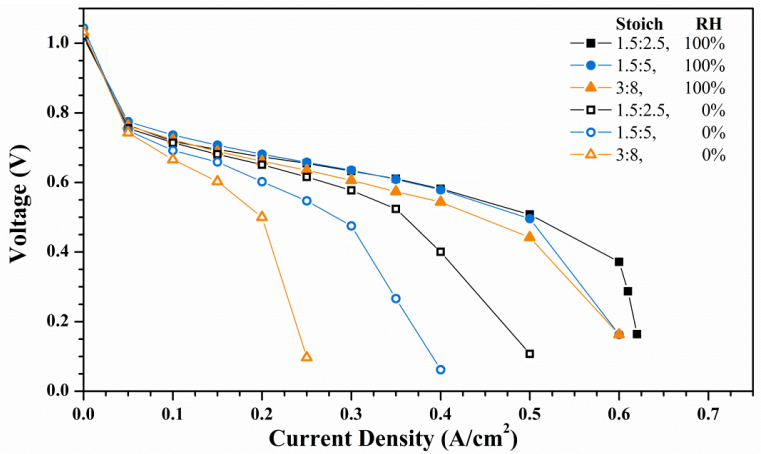


Channel filling

Corner filling is observed irrespective of air velocity.

Pressure Drop - Low Current Densities

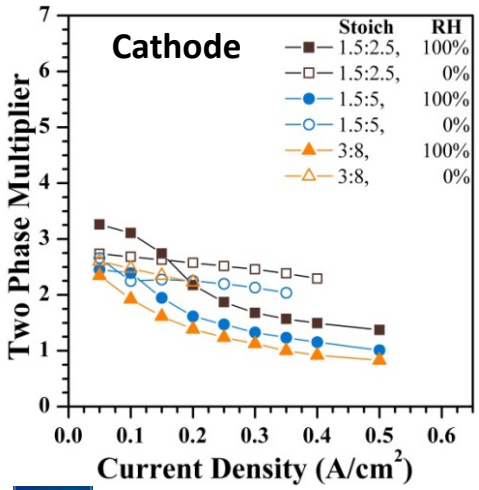
Visualization Cell Performance

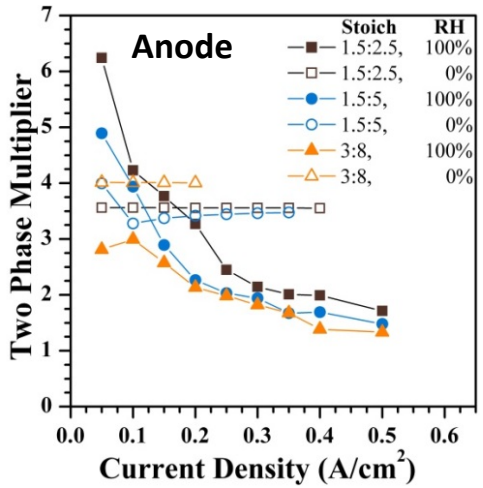


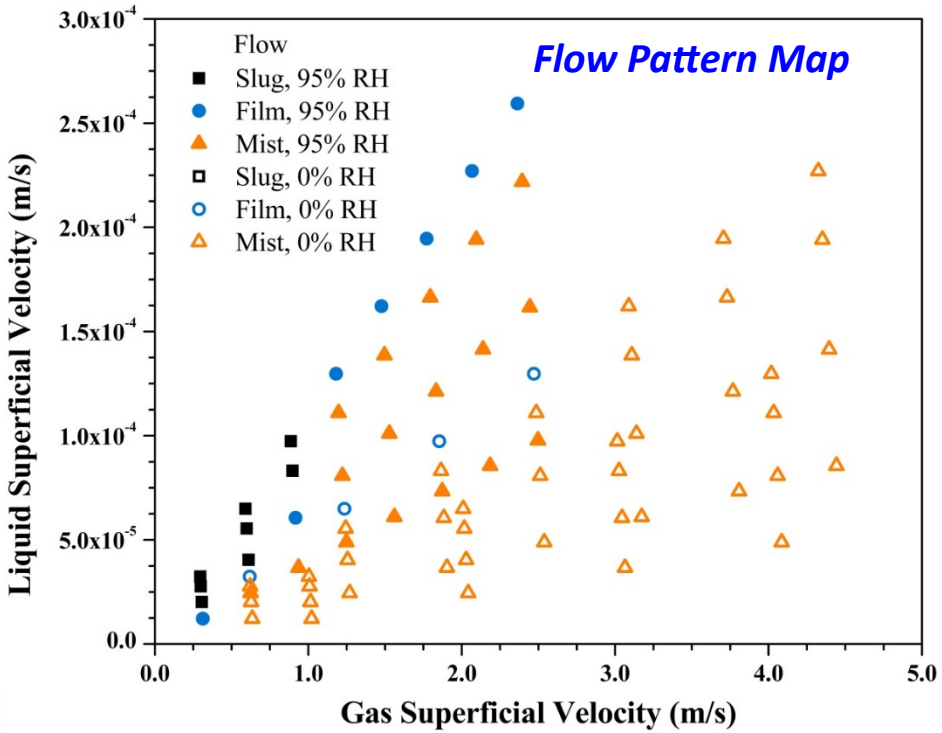
RH and Stoich changes cell performance

Two-Phase Multipliers at Low Current Densities

$$\text{Two} - \text{Phase Multiplier} = \frac{\text{Two–Phase Pressure Drop}}{\text{Single–Phase Gas Pressure Drop}}$$





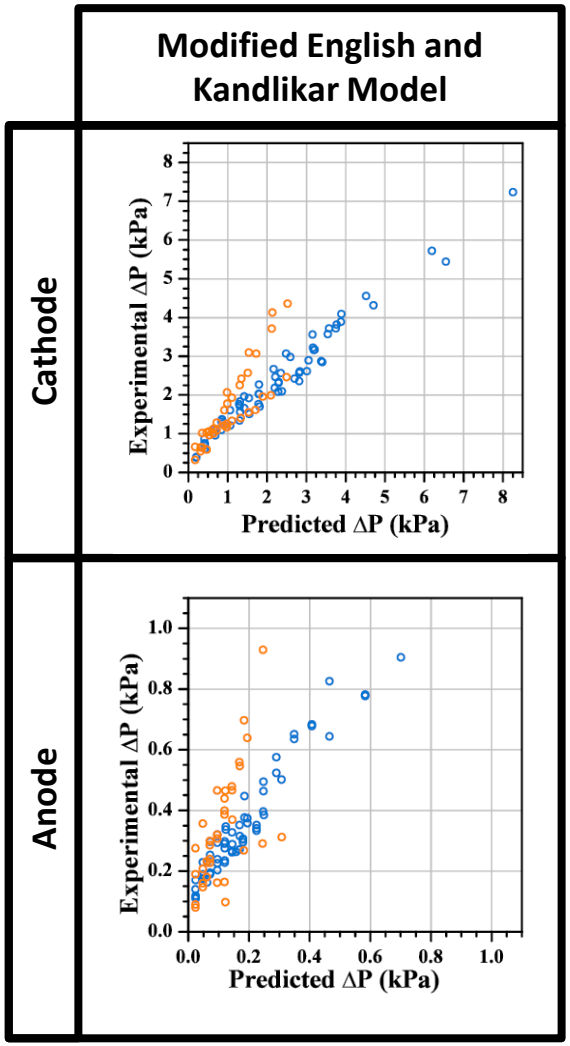


- Flow pattern map used for elemental ΔP modeling*
- Model segments compared against experimental observations from visualization windows
- 198 in situ tests used to validate model

Low current densities dominated by slug flow result in high two-phase flow multiplier

* See and Kandlikar, ECS Transactions, **50**(2), pp. 99-111 (2012)

Pressure Drop Model Validation

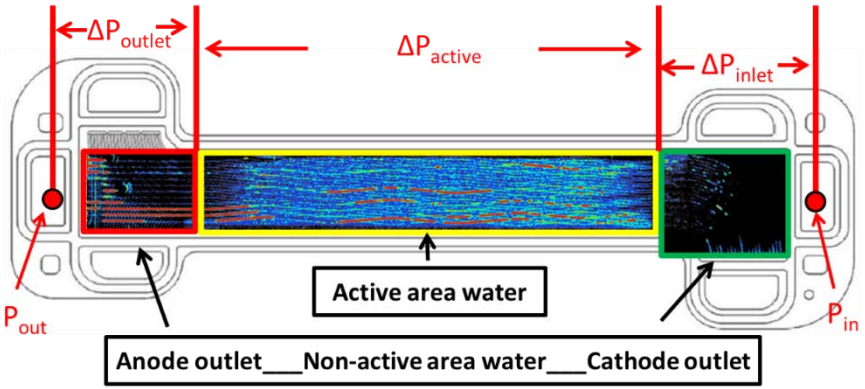


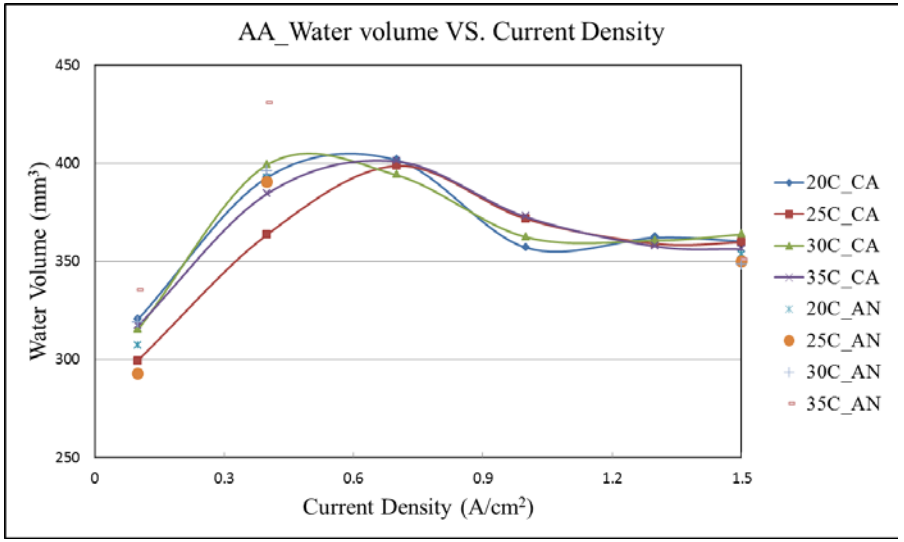
- Six different models have been evaluated in the proposed modeling scheme
- English and Kandlikar with modifications by Grimm et al. works best to predict ΔP in PEMFC reactant channels
- Modified English and Kandlikar model has a mean error of 5.2% with fully humidified cathode inlet

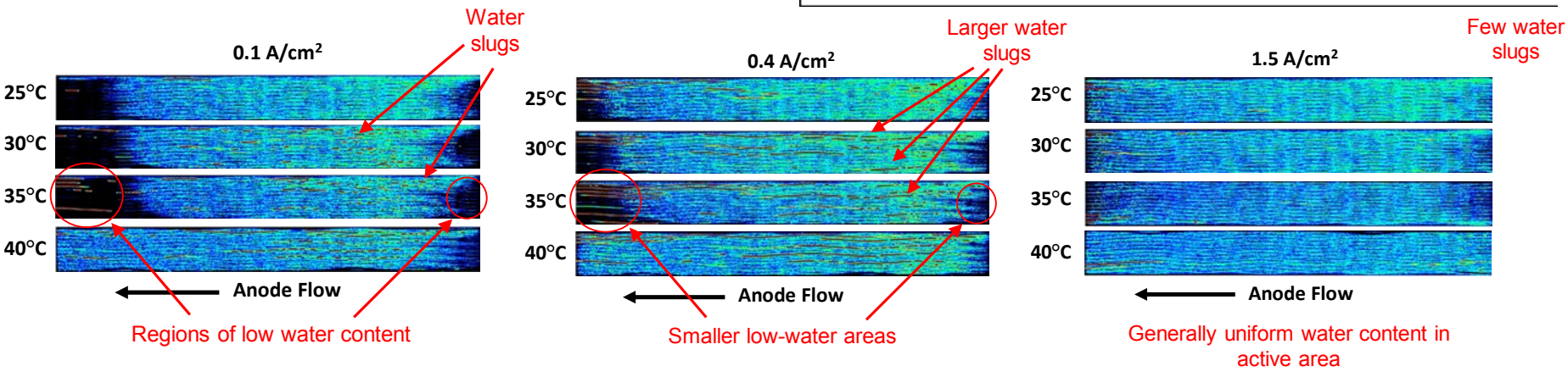
Correlation	Mean error (Cathode 100% RH)	Mean error (Cathode)	Mean error (Anode)
Mishima and Hibiki	13.0%	23.7%	56.1%
English and Kandlikar	5.4%	11.6%	48.7%
Lee and Lee	13.8%	24.3%	56.7%
Saisorn and Wongwises	18.5%	25.4%	55.7%
Modified English and Kandlikar	5.2%	11.6%	40.2%
Grimm et al. "Slug Correlation" (2012)	6.5% (3.2%)*	8.8%	106.0%
Grimm et al. "Film Correlation" (2012)	137.8%	70.8%	893.3%

*Error when only averaged over conditions where slug flow was seen

In-situ Neutron Imaging – Active Area Water Volume





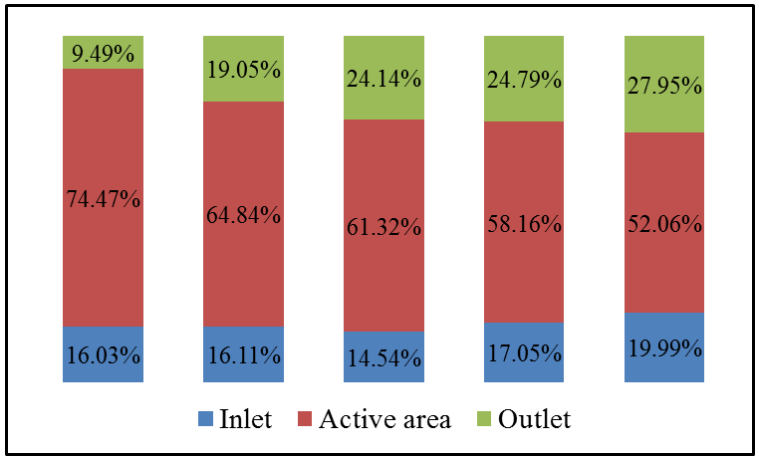


All temperatures show peak water volume in the range 0.4 - 0.7 A/cm²

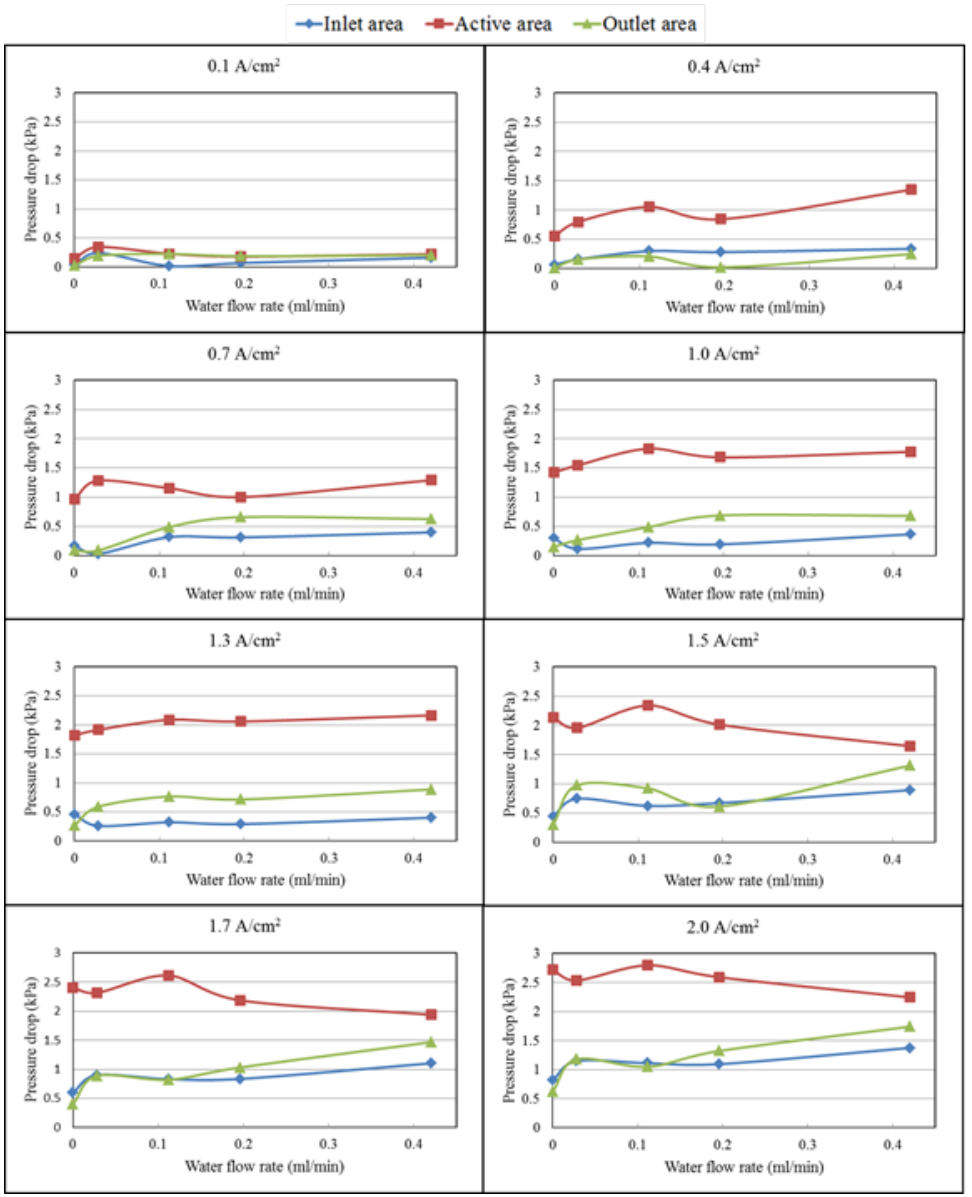
- Should be a relationship between gas momentum and hydraulic force to support accumulation. Water accumulation model under development.

Pressure Drop Contribution

On average, the outlet region contributes more to the total ΔP for higher water flow rates

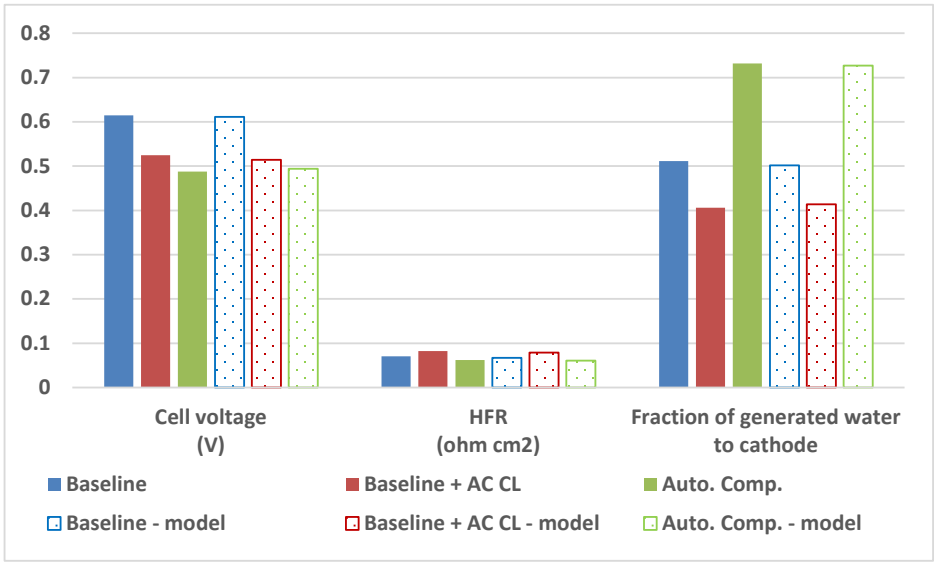


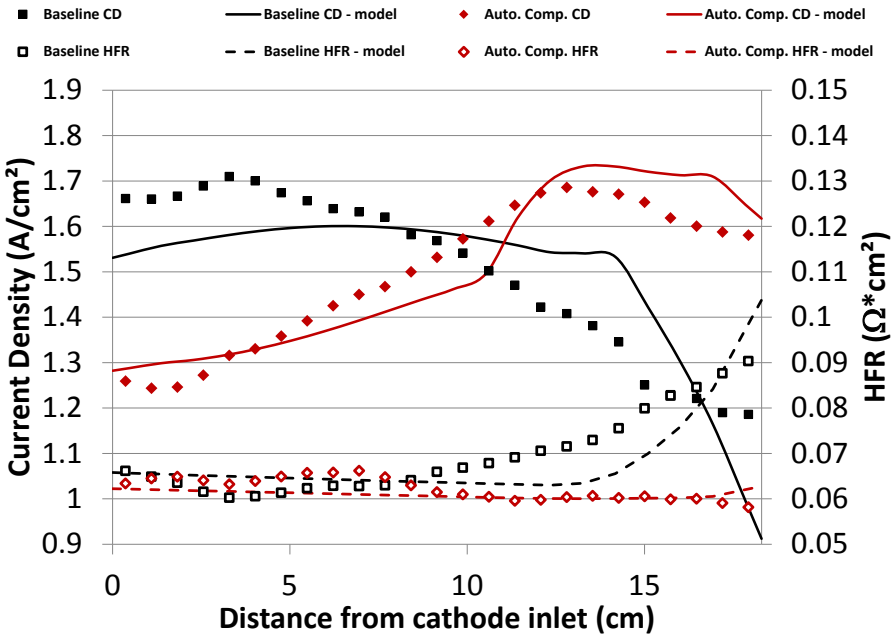
- Significant pressure drop over non-active area.
- Water mitigation strategies should focus on outlet non-active area as well as channel-to-manifold interface, especially on anode side.



Model-Data Comparisons

60 °C ,H2/Air, 1.5/2 stoich, 100/150 kPa, 0/95 %RH, 1.5 A/cm^2





- Model with single set of parameters fit to all three data sets
  - The model captures the trend change in down-the-channel current distribution with an empirical correlation of water saturation to local RH within cathode.
  - The discrepancy in current distribution for the baseline with low Pt-loaded cathode case reflects mismatch to water content distribution measured by neutron radiograph imaging which cannot quantify the degree of flooding in the electrode.

Responses to 2013 AMR Reviewers' Comments

- On the robustness of the model, need a sensitivity analysis to test how much the predictions of the model respond to changes in the parameters.
  - Focus on land/channel effect.
- Larger discrepancies between model and data at high current and low temperature indicate that there are issues dealing with liquid water or high water saturation.
  - Improve electrode liquid water model.
- As model input, it is not clear whether or how the two interfacial resistances at the Pt-ionomer and ionomer-gas interfaces would be varied for other materials sets.
  - Expected to be material specific; Need further research to understand their origins.
- More work needs to be done to convince the community that the model has predictive power.
  - In addition to voltages on a pol curve, use current, HFR and water distribution data for model validation.
- "Not a clear description of how the various components of the model may interfere with each other, thus difficulty in the interpretations."
  - A case study for voltage loss contributions under the influence of each component.
- "Developed model is somewhat specific to the architecture of the flow field studied with the specific transitional areas, which limits its industrial applicability."
  - Look for fundamental insights.
- "It would be interesting to see model predictions for the material sets developed with the gradient features both through and in-plane directions or produce narratives on model outcome if such material is developed."
  - Doable but challenging in timing.

Summary

- **Baseline with low Pt-loaded cathode experiments complement to the baseline and auto-competitive validation data set for model validation**
  - **Low Pt-loaded cathode yields lower performance with similar current distribution compared to the baseline case, confirming that the highly tortuous anode DM is responsible for the observed opposite trend in current distribution.**
- **Several 1-D relationship have been established and refined for use in the 1+1D model**
  - **Continued study on thin ionomer film – carbon substrate interaction leads to fundamental understanding of the local oxygen transport resistance in the electrode.**
  - **Neutron imaging data on liquid water saturation within GDL for the effects of GDL type, aging, and flowfield shows the impact of GDL surface properties and heat transfer.**
  - **Validated flowfield pressure drop model includes the effects of water droplet-channel corner interaction, liquid water flow pattern, and local operating condition.**
  - **Significant pressure drop occurs in the non-active, channel-to-manifold region due to liquid water accumulation therein; Peak active area water volume exists likely due to gas momentum and hydraulic force balance.**
- **Down-the-channel 1+1D model improved with new relationships integrated**
  - **Performance, water balance, and current distribution predictions agree to data with an improved electrode model assuming cathode flooding relationship with RH.**
- **Database updated**
  - **Visit www.PEMFCdata.org (development will continue throughout the project).**

Future Work

- **Finalize wet 1+1D model**
  - **Further improve the model via model-data comparisons.**
- **Wrap-up component characterization and modeling**
  - **Link findings from various ionomer studies and identify a critical path forward.**
  - **Document component models and provide a clear linkage to the 1-D resistance used in the finalized model.**
- **Reporting**
  - **Based on parametric studies using the finalized model, make recommendations for key focus areas to improve next generation PEMFC technology.**
  - **Publish data for public use through on-line database and peer-reviewed journals.**

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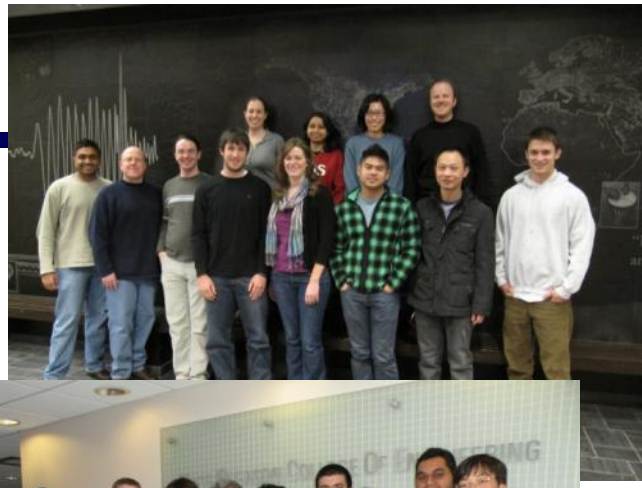
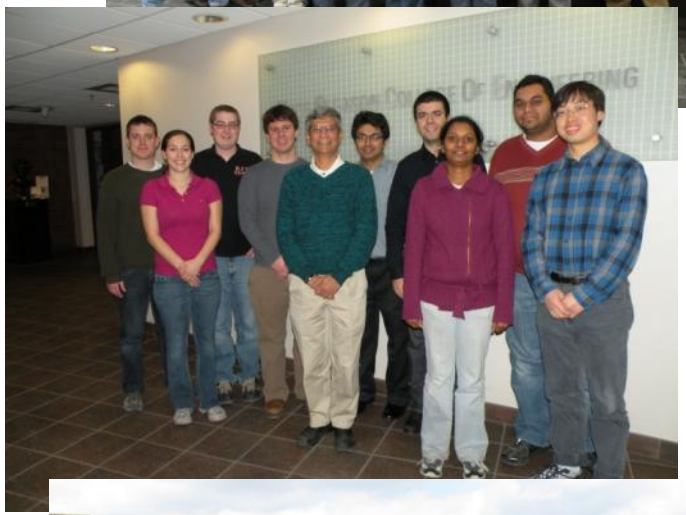
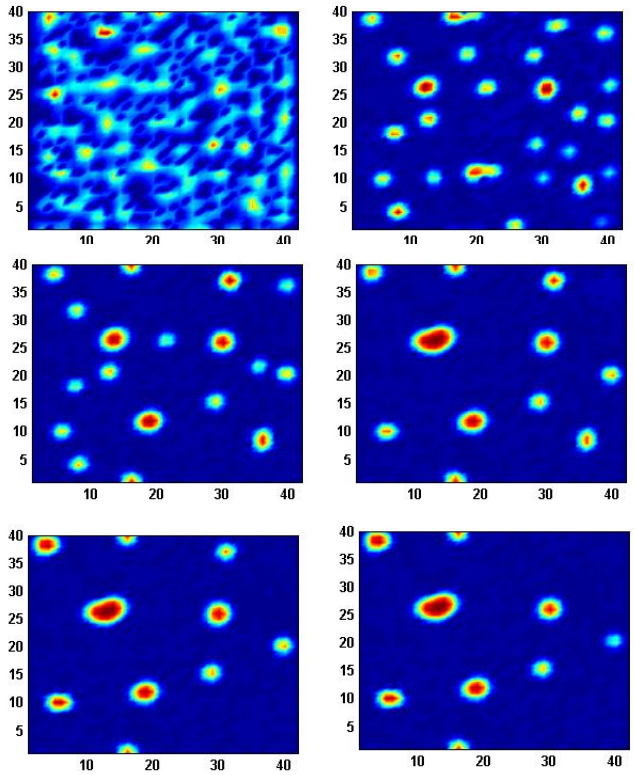


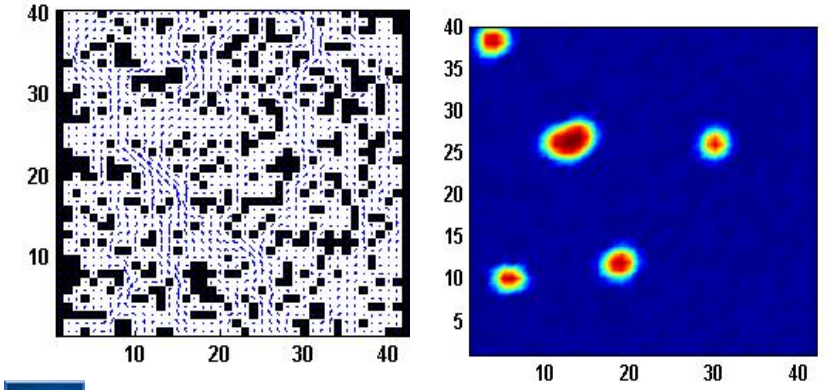


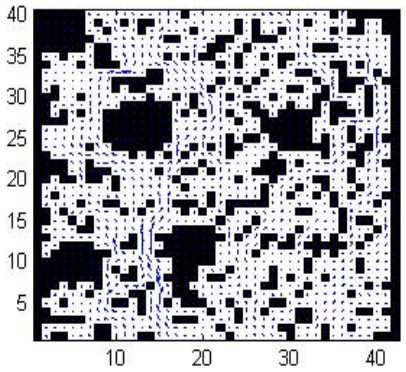
Component Level Modeling of GDL

Progress (Single Component Multiphase Model)

- **A non-ideal gas was assumed to flow in porous channels and van Der Waals equation of state was applied to determine the inter-particle attraction forces.**
- **Assumptions and Missing Physics:**
  - **Temperature is constant.**
  - **Hydrophilic and hydrophobic effects of the structure were not considered.**
  - **The gas is in non-ideal state.**
  - **Pressure is increased to observe condensation.**
- **Liquid particles were observed to form clusters in different sections of the GDL and they blocked the gas flow partially.**



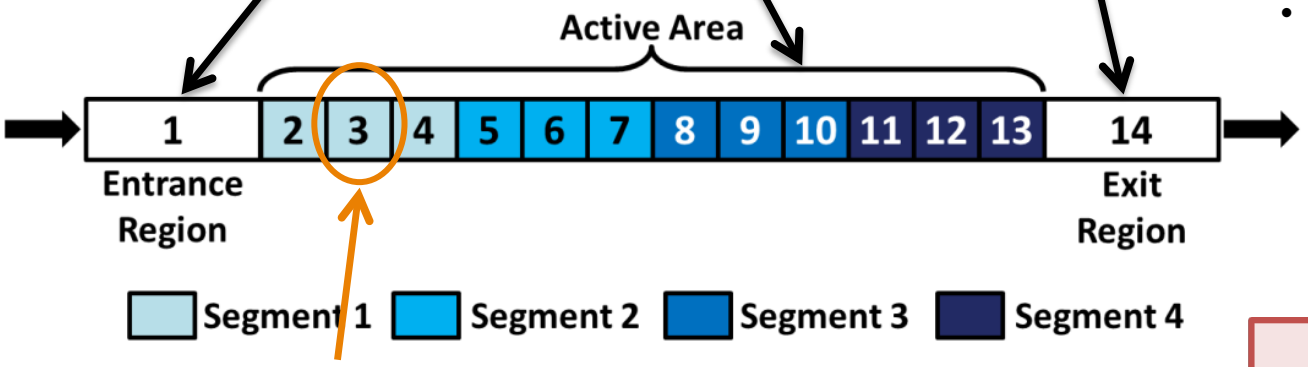




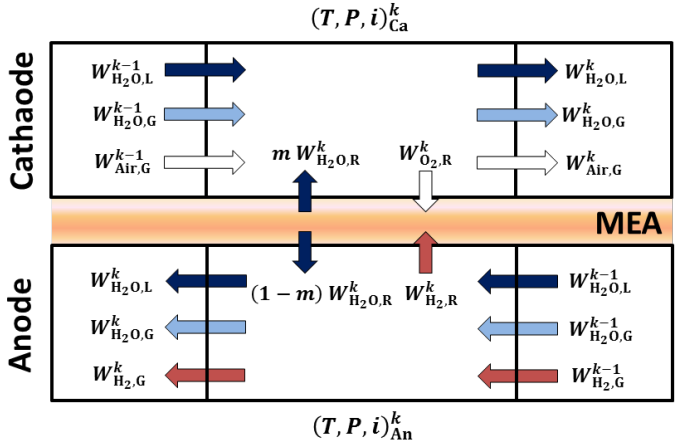
Pressure Drop Modeling Approach

Elemental Approach

$$\Delta P_{tot} = \Delta P_{in} + \Delta P_{cont} + \Delta P_{ent} + \sum_{k=a}^{b} [\mathrm{fRe}\frac{2L_e \mu_g W_{tot}}{\rho_g A_c D_h^2}]^k + \Delta P_{exit} + \Delta P_{expan}$$

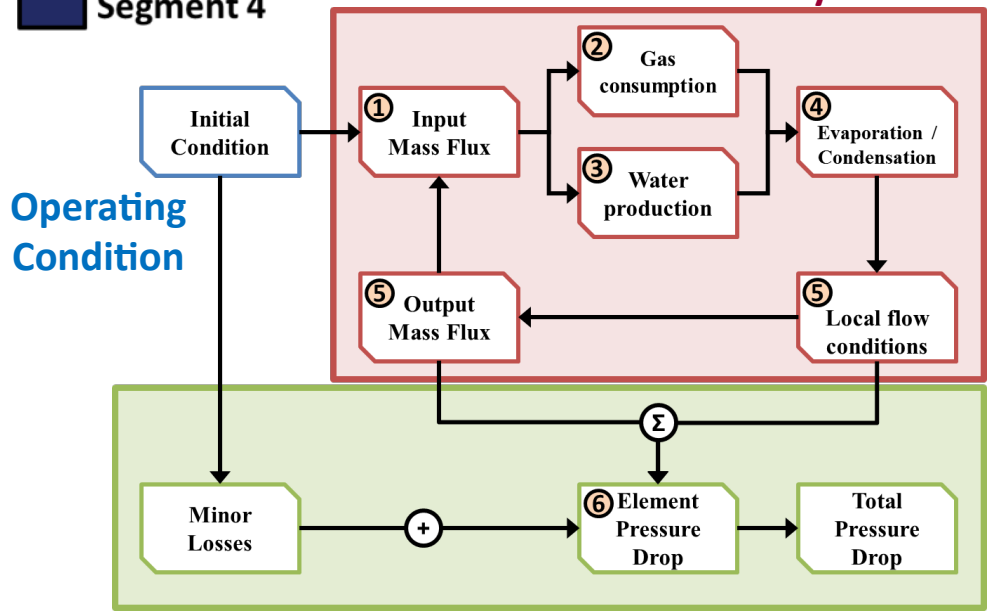


- Summation of elemental pressure drop for including local effects
- Entrance and exit constants found through correlations by Kays and London
- 'f' obtained through different existing correlations



Computational Flow

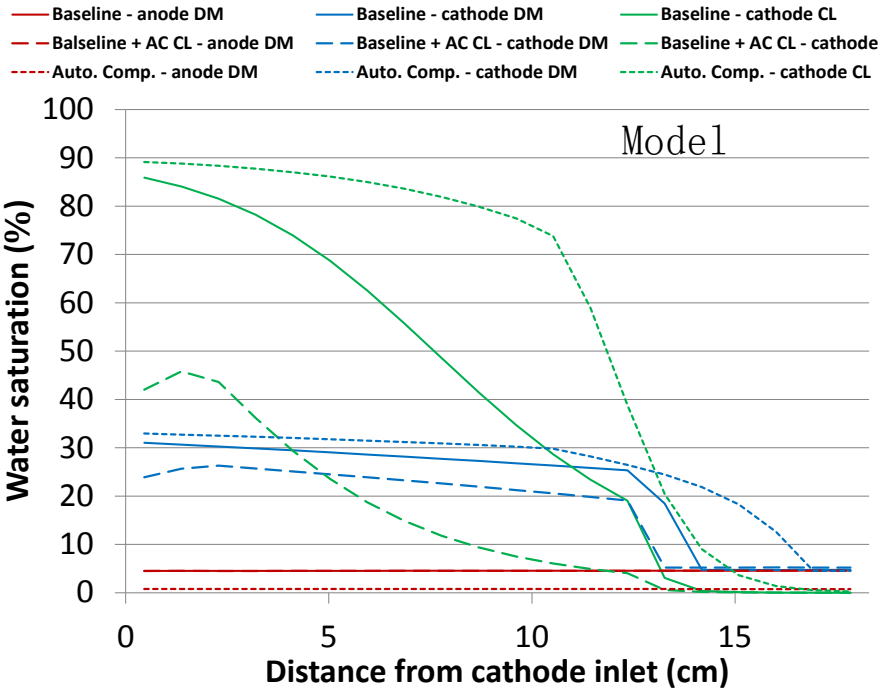
Control Volume Analysis

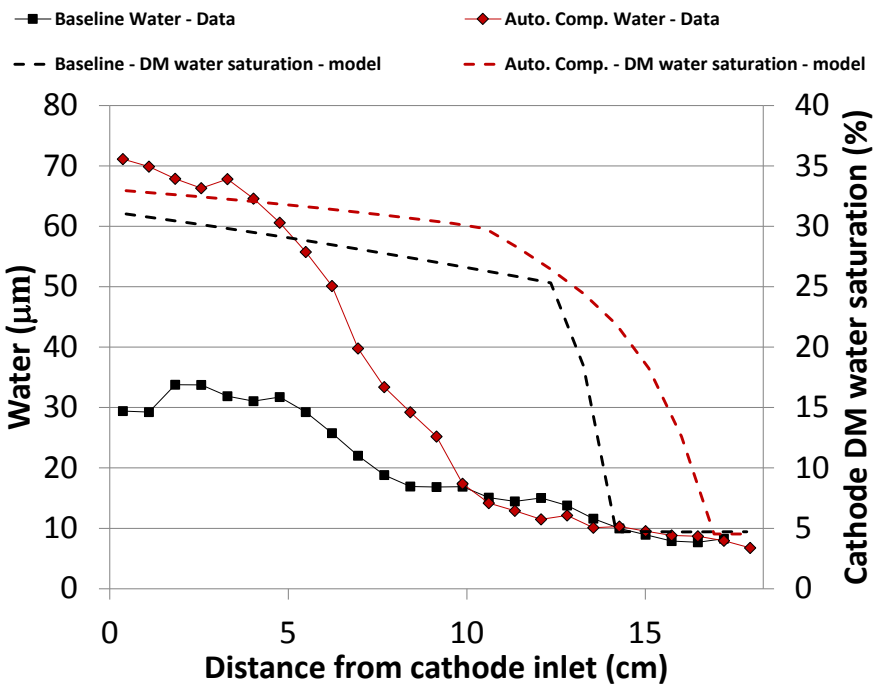


Elemental Pressure Drop Summation

Water Distribution – Model vs. Data

60 °C ,H2/Air, 1.5/2 stoich, 100/150 kPa, 0/95 %RH, 1.5 A/cm^2





- Qualitative agreement in water content distribution
  - The model shows more water near cathode inlet and dry-out near anode inlet, consistent with the neutron imaging data.
  - However, quantitative agreement is poor, indicating that there is room for model improvement → more work is required to account for the effect of land/channel dimensions on liquid water accumulation under the land.