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

Department of Energy Annual Merit Review

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General Motors
Electrochemical Energy Research Lab

May 12, 2011

Project ID # FC092

Overview

Timeline

- Project start date: June 2010
- Project end date: May 2013
- Percent complete: 20%

Budget

- Total project funding
  - DOE share: $4.391M
  - Contractor share: $1.098M
- Funding received in FY10: $1.15M
- Funding for FY11: $1.15M

Barriers

- Barriers addressed
  - C. Performance
  - D. Water Transport within the Stack
  - E. System Thermal and Water Management
  - G. Start-up and Shut-down Time and Energy/Transient Operation

Partners

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

Collaboration

- **GM Electrochemical Energy Research Lab:** Jon Owejan, Jeffrey Gagliardo, Wenbin Gu, Anu Kongkanand, Paul Nicotera
- **Penn State University:** Michael Hickner, Jack Brenizer
- **Rochester Institute of Tech:** Satish Kandlikar, Thomas Trabold
- **University Of Tennessee:** Matthew Mench
- **DOE Transport Working Group**
- **National Institute of Standards and Technology (no-cost):** David Jacobson, Daniel Hussey, Muhammad Arif
- **W.L. Gore and Associates, Inc. (PR basis):** Simon Cleghorn
- **Freudenberg (PR basis):** Christian Quick

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.

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

Consider if a 1+1-D 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 a comprehensive macro-scale validation data sets. Identify shortcomings of 1-D approximations.

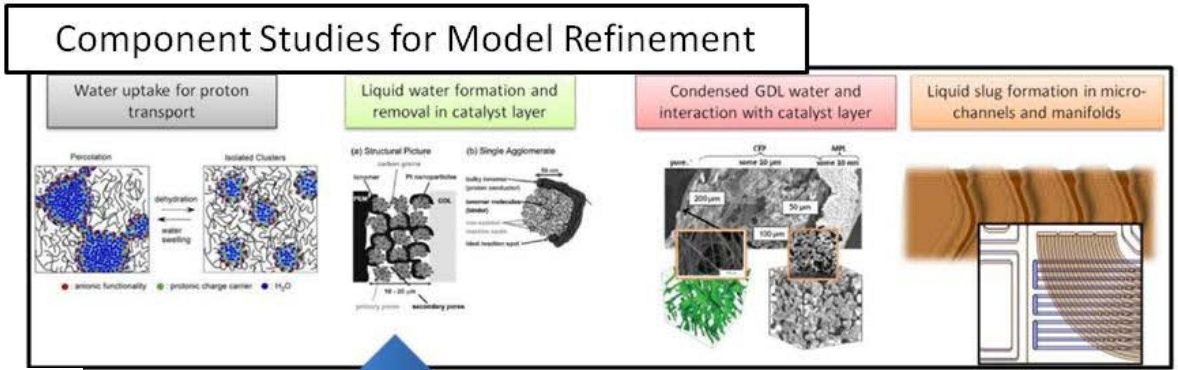
Identify critical parameters for low-cost material development

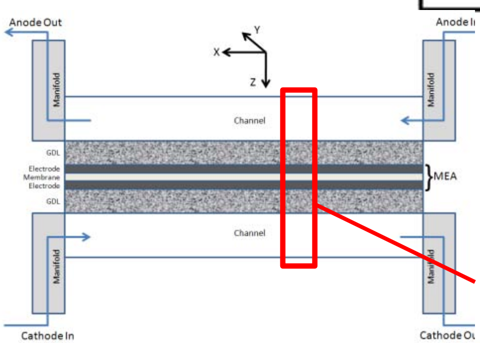
Execute combinatorial studies using the validated model to identify optimal material properties and trade-offs for low-cost component development in various operating spaces.

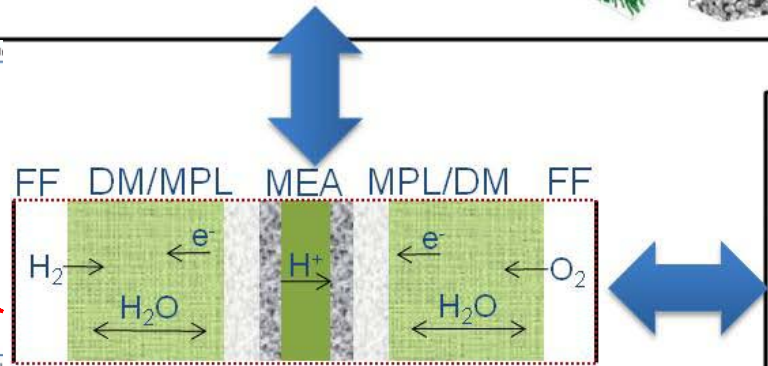
Approach-

Connecting Characterization with Validation

Material property characterization and micro-scale component models are combined to output interfacial and bulk transport resistances into a simplified 1+1-D down-the-channel model. In separate experiments, a comprehensive macro-scale validation database is generated with fully integrated material sets and local down-the-channel resolution.

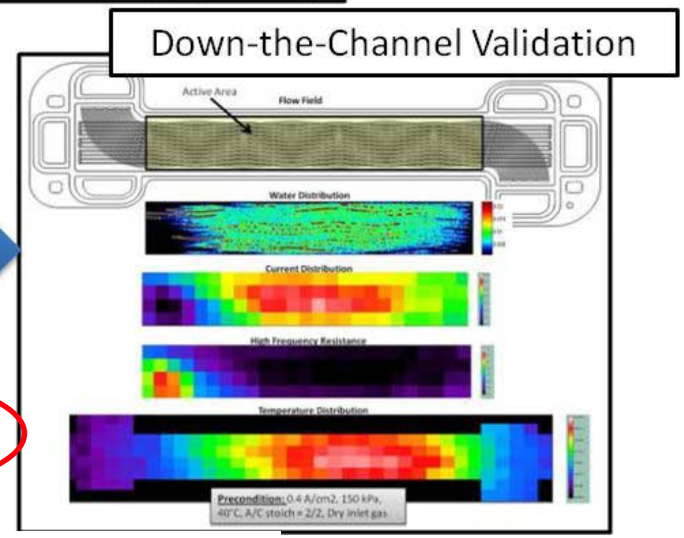






1D Model Including Interfacial Transport

$$E_{cell} = E_{rev} - i \cdot R_{\Omega} - \eta_{HOR} - \eta_{ORR} - i\left(R^{'}_{H^+,cath} + R^{'}_{H^+,an}\right) - \eta_{tx}$$



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).

Approach-

FY10-11 Deliverables: Measurement Focus

Baseline material set focused work:

- Task 1 – Down-the-channel validation data
  - Current and temperature distributions for standard protocol
  - Water distributions and balance for standard protocol
  - Upload data to project database
  - Define auto-competitive material set
- Task 2 – Ionomer characterization and initiate component modeling
  - Membrane water uptake, water diffusivity and hydraulic permeability*
  - Oxygen and water transport as a function of ionomer layer thickness
  - Evidence of nanophase/water morphological changes vs. film thickness
- Task 3 – Diffusion layer characterization and initiate component modeling
  - MPL thermal conductivity and D/D_{eff} *
  - Catalyst layer liquid water pressure as a function of saturation, pore size, and hydrophobicity*
  - Substrate thermal conductivity (wet and dry) and D/D_{eff} as a function of saturation*
  - Through-plane saturation and wet region boundary as a function of dT and operating temp.
- Task 4 – Channel characterization and initiate component modeling
  - CFP to channel interfacial transport resistance as a function of channel saturation
  - Channel dP as a function of saturation, temperature, flow, and current density
  - Manifold dP as a function of saturation, temperature, flow, and current density
- Task 5 – Component model integration into 1+1D down-the-channel wet model

*work underway but not included in this presentation

FY11-12: Repeat characterization and validation work with auto-competitive material set and complete component models.

FY12-13: Complete model integration into down-the-channel architecture, complete validation and make recommendations with combinatorial studies.

Link to these deliverables shown in this location on technical accomplishments slides.

Approach-

Project Standardization

Baseline Material Set

- Membrane
  – Gore 18 mm
- 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 0.96
- Microporous layer
  – 8:1:1 carbon-to-PTFE-to-FEP ratio, 30 mm thick
- Gas diffusion substrate
  – MRC 105 w/ 5% wt. PTFE, 230 mm thick
- Flow field
  – 0.7 mm wide by 0.4 mm deep channels with stamped metal plate cross-sectional geometry
  – 18.3 mm 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 mm
- 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 0.1 mg Pt/cm*2
  – 50% Pt/V made with 750EW ionomer I/C 0.7
- Microporous layer
  – 8:1:1 carbon-to-PTFE-to-FEP ratio, 30 mm thick*
  – *considering asymmetric MPL formulations
- Gas diffusion substrate
  – Non-conductive core / Metal shell 5% wt. PTFE, 130 mm thick *
  – *considering asymmetric carbon fiber substrates
- Flow field
  – 0.7 mm wide by 0.3 mm deep channels
  – 18.3 mm channel length
  – 0.25 mm cathode land width
  – 0.75 mm anode land width
  – Modified exit headers

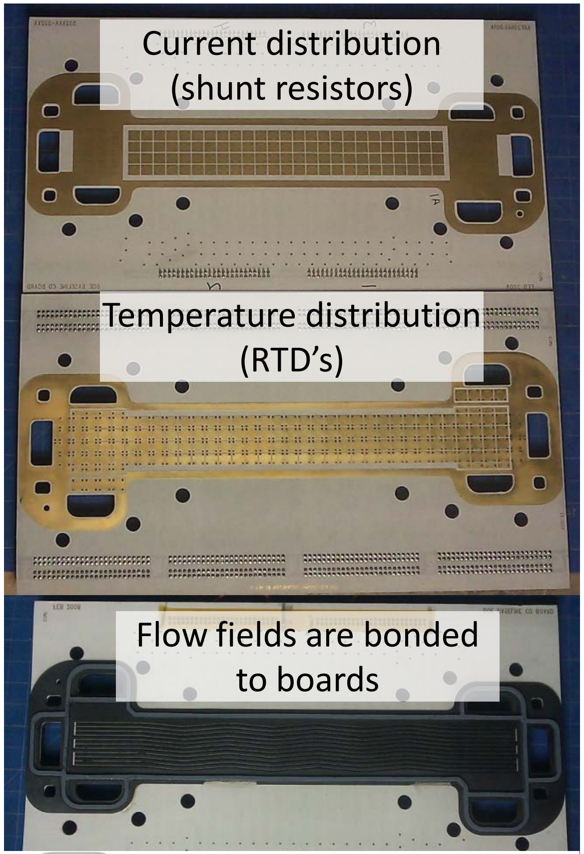
Standard Protocol

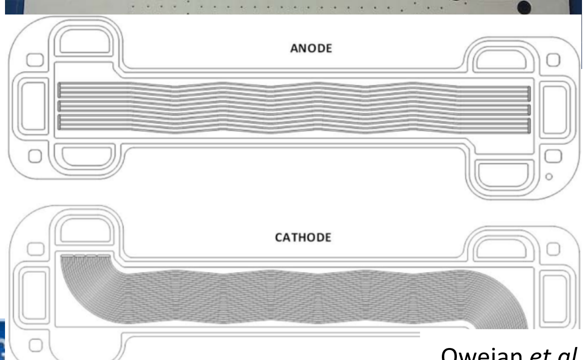
4 x 4 x 4 x 3 Factors

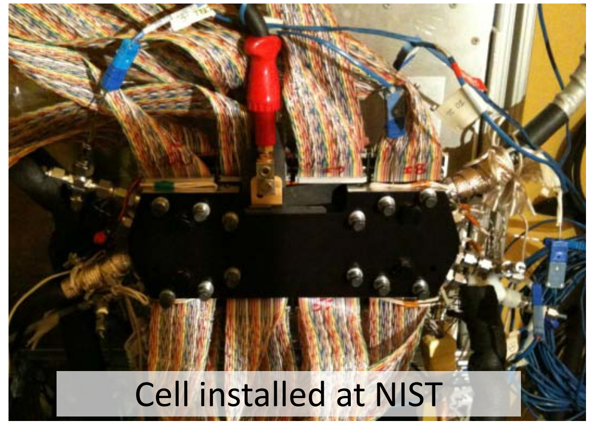
Temperature	Inlet RH (An/Ca)	Outlet Pressure (An/Ca)	Current Density
20, 40, 60, 80°C	95/95, 0/95, 95/0, 50/50%	150/150, 100/150, 150/100 kPa	0.1,0.4,1.5 A/cm^2

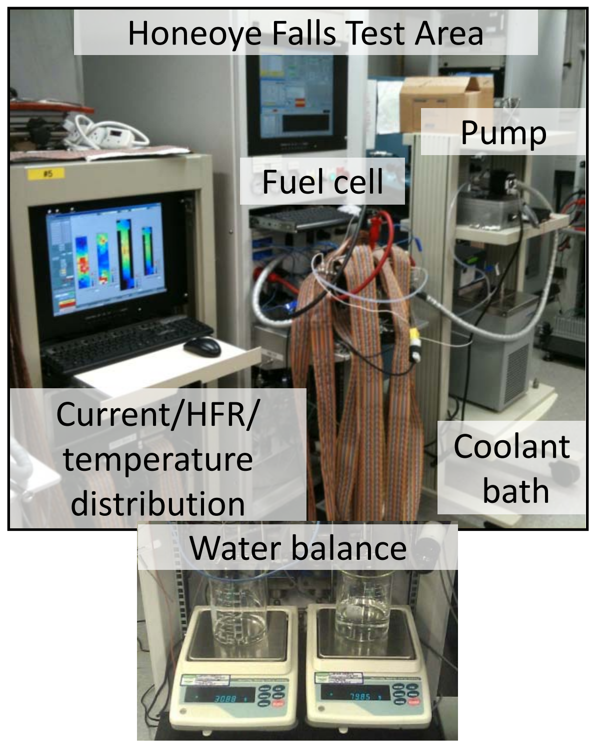
Technical Accomplishments-

Validation Experiments

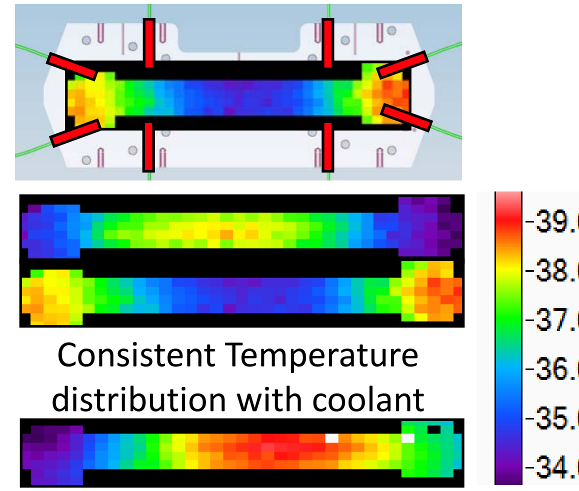


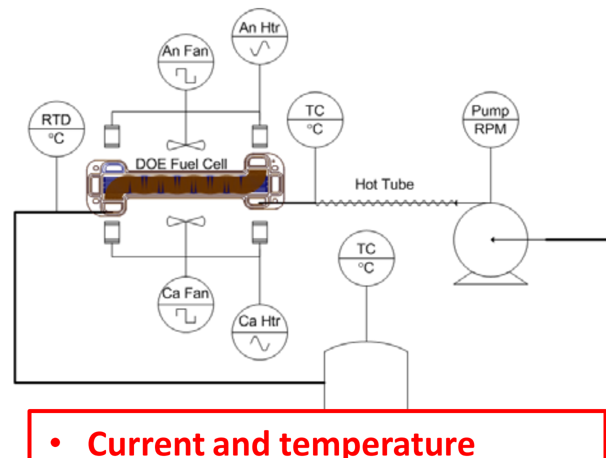






Heater Rod Temperature distribution transients

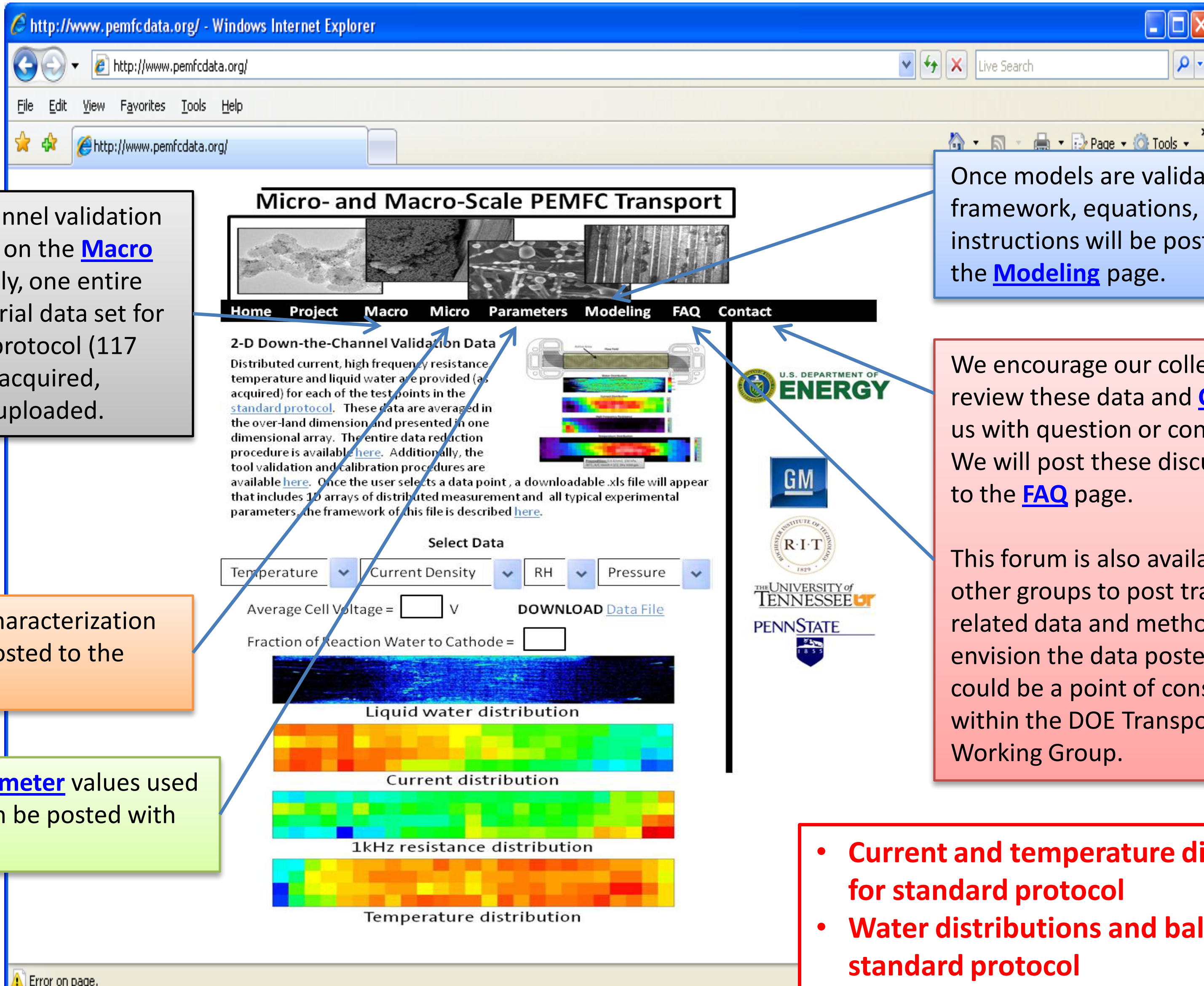




- **Current and temperature distributions for standard protocol**
- **Water distributions and balance for standard protocol**

Owejan *et al.,* International Journal of Hydrogen Energy, Volume 34, Issue 8, May 2009, Pages 3436-3444, Technical Accomplishments and Collaboration-

Database: www.PEMFCdata.org



Down-the-channel validation data is posted on the **Macro** page. Currently, one entire baseline material data set for the standard protocol (117 test points) is acquired, analyzed and uploaded.

Component characterization data will be posted to the **Micro** page.

All single **Parameter** values used in models with be posted with uncertainty.

Once models are validated, the framework, equations, code and instructions will be posted on the **Modeling** page.

We encourage our colleagues to review these data and **Contact** us with question or concerns. We will post these discussions to the **FAQ** page.

This forum is also available for other groups to post transport related data and methods. We envision the data posted here could be a point of consensus within the DOE Transport Working Group.

- **Current and temperature distributions for standard protocol**
- **Water distributions and balance for standard protocol**
- **Upload data to project database**

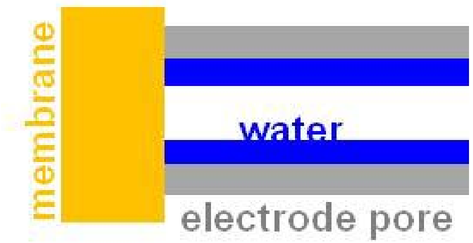
Technical Progress-

Electrode Model Framework

Pore-Scale Water Morphology (1+1D DTC)

Water film on surface

- Low water saturation



Capillary tube adjacent to membrane

- Water saturation exceeds threshold value

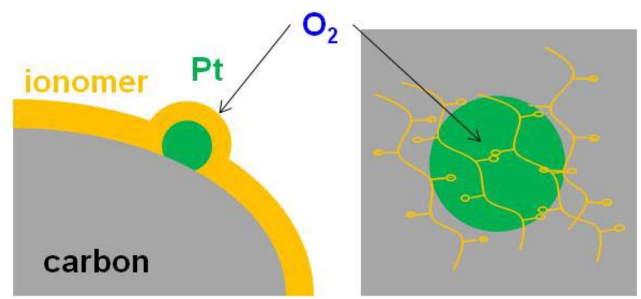
Transition from water film to capillary tube

- Pore size
- Surface energy of ionomer/catalyst

Nano-Scale Morphology (Component)

Local oxygen transport resistance

- Measure oxygen transport resistance (lumped) at a given RH as a function of film thickness
- Develop microscopic transport model based on the morphology of thin ionomer film on Pt/C catalyst

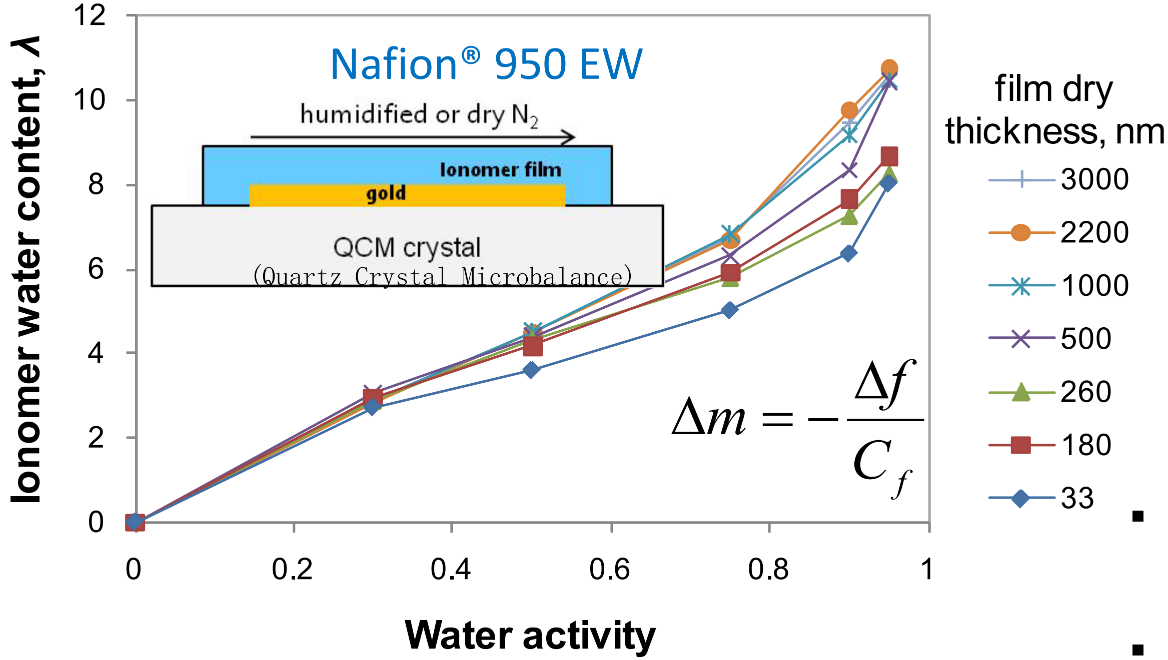


Use the model to de-convolute the measured resistance

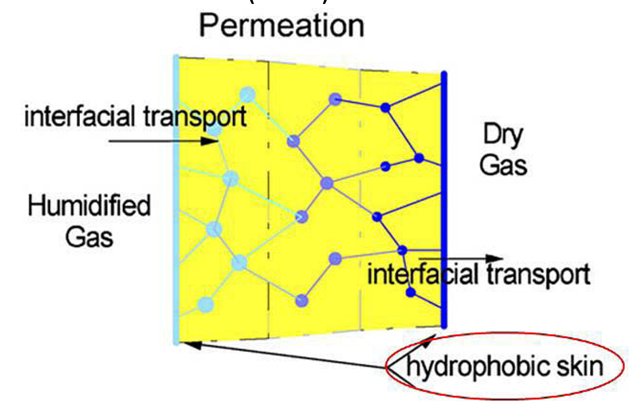
- Bulk resistance
- Interfacial resistance

Component model integration into 1+1D down-the-channel wet model

Water Content (λ) at Different Film Thicknesses (80°C)



From P.W. Majsztrik et al., *Journal of Membrane Science* 301 (2007) 93–106



Hypothetical Origin of R_{int}

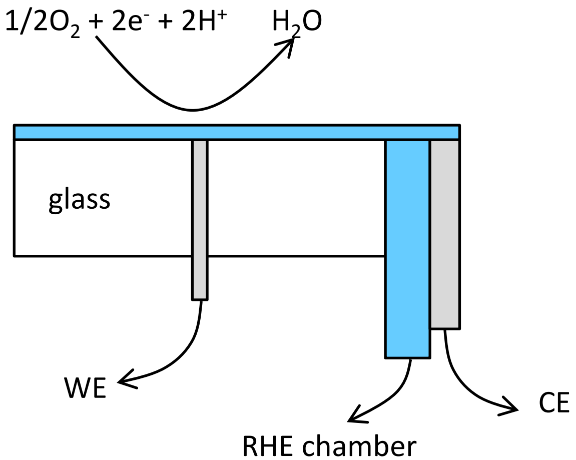
- Structural change in the water network at the gas/membrane interface. Formation of *less-permeable layers*.
- Evaporation/condensation processes.

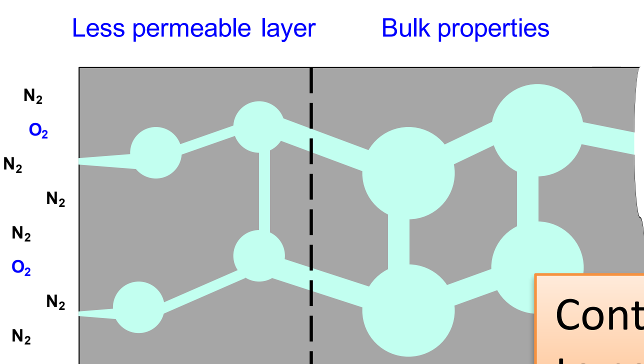
- Water contents (λ) at a given RH are comparable to bulk membranes for film thickness > 0.5 µm.
- Substantial decrease in ionomer water content observed in very thin ionomer.
  - Are we detecting the impermeable layer?
  - This may be due to surface confinement, interaction with substrate, change in ionomer structure.

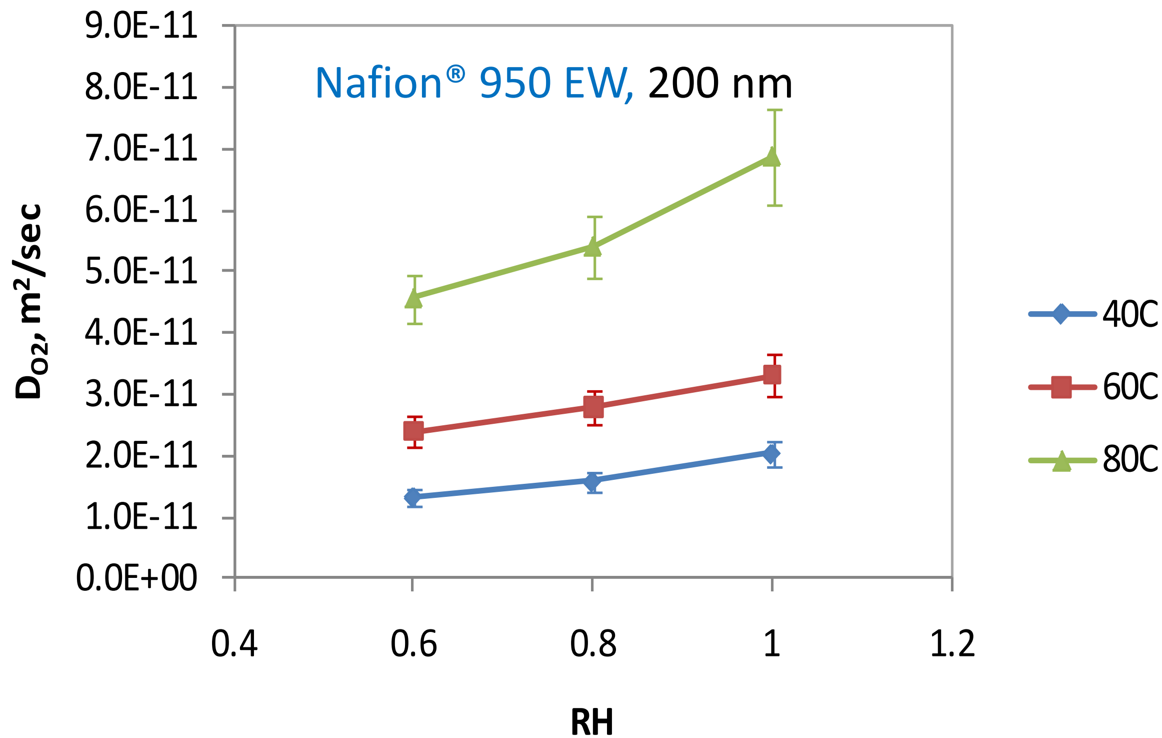
Oxygen and water transport as a function of ionomer layer thickness

Technical Progress-

O_2 Transport in Nafion® Thin Film Using 100 mm Pt Microelectrode







Contribution from less permeable layer → need thinner layer to confirm QCM results

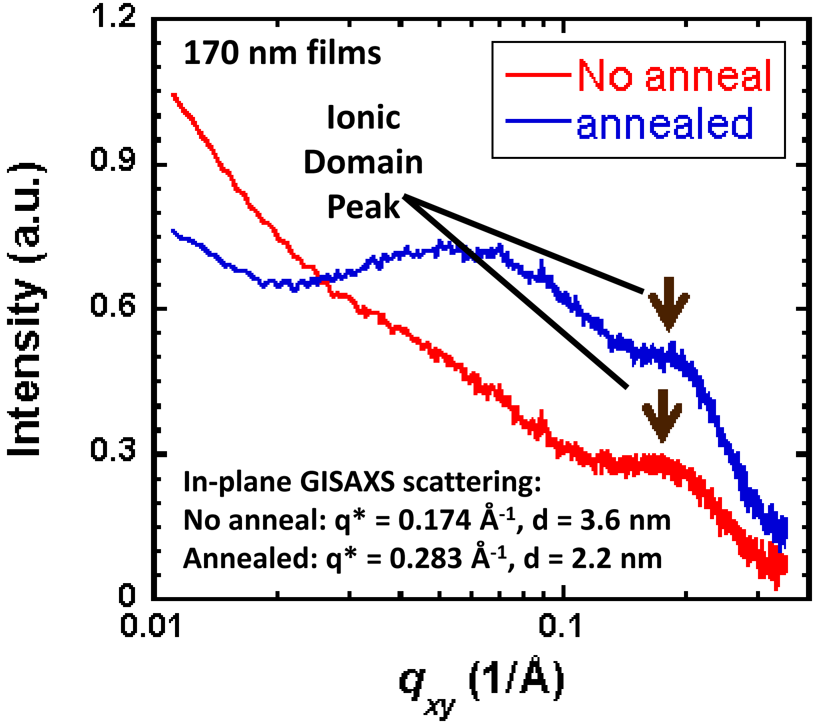
- D_{O2} in Nafion® thin films are similar to those measured on thick membrane for film thickness down to 200 nm.
- D_{O2} in thinner film will be determined in the future.

Oxygen and water transport as a function of ionomer layer thickness

Physical Measurement of Thin Ionomer Film Structure

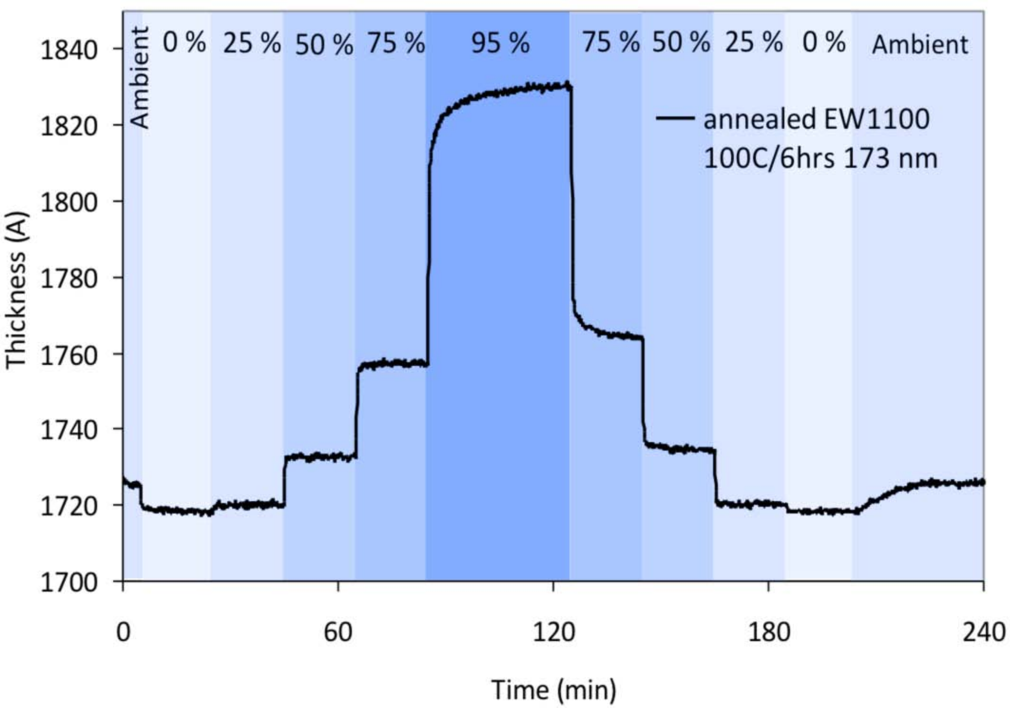
PENNSTATE 1855

Measuring Ionic Domain with GISAXS



Structural analysis as a function of thickness, substrate and RH is currently underway using GISAXS.

Dynamic Water Uptake with Ellipsometry



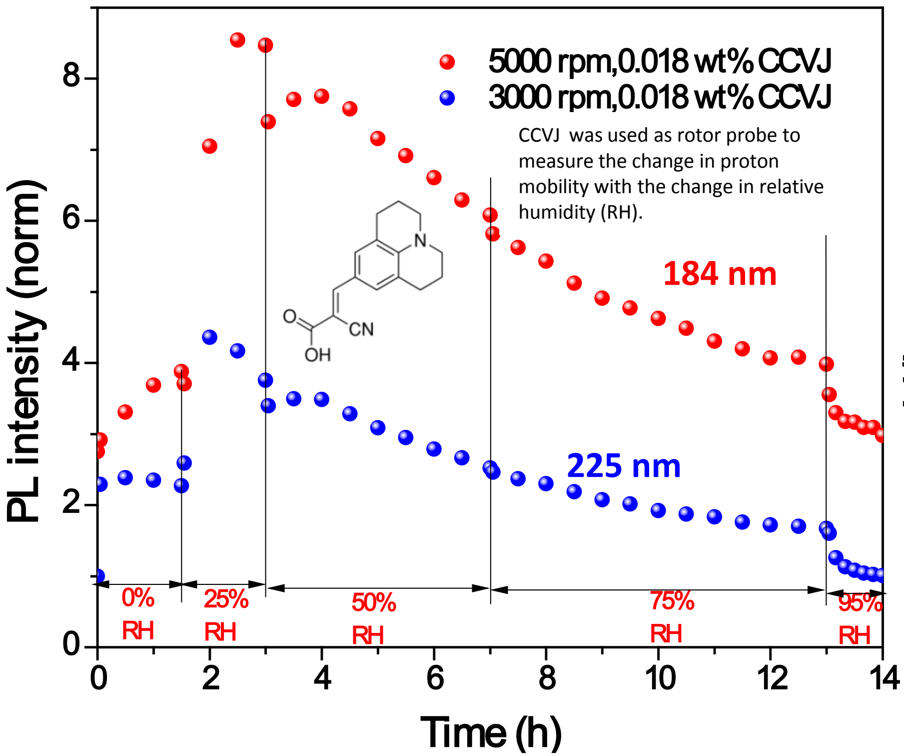
Dynamic uptake experiments show a significant contribution from polymer relaxation. Working on modeling methodology to recover diffusion contribution and account for relaxation effects in component models.

Evidence of nanophase/water morphological changes vs. film thickness

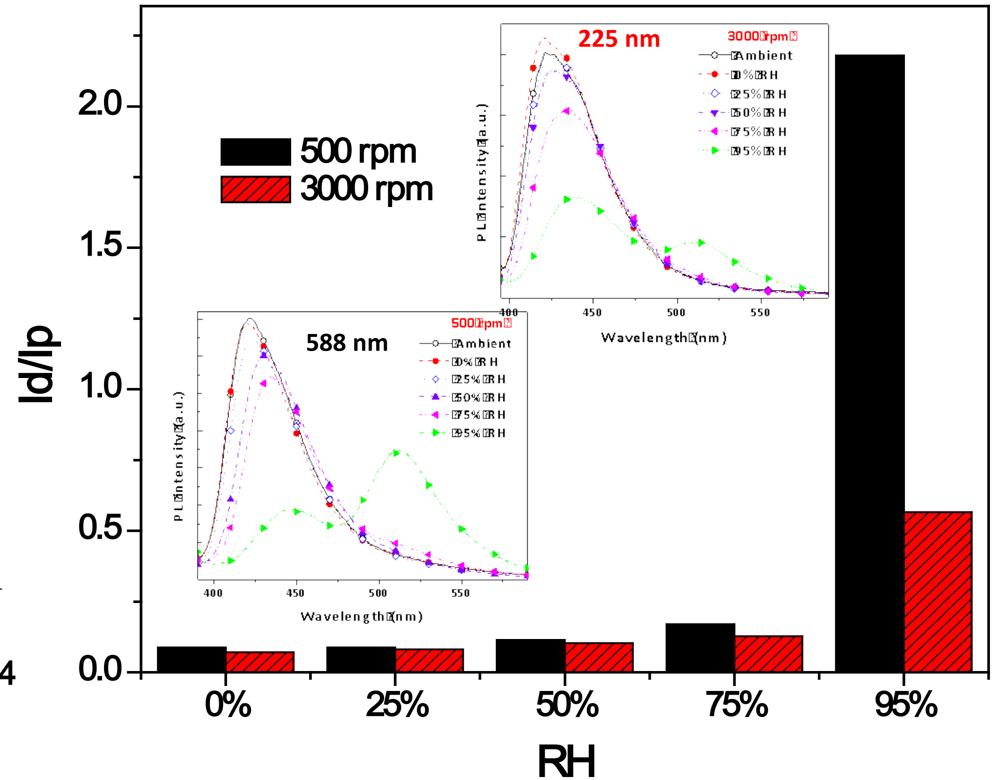
Technical Progress-

Probing Thin Ionomer Films

Measuring Change in Rotor Probe Mobility



Photoacid Dye Contrasts Proton Transfer Dynamics



Thin ionomer films have different mobility behaviors than thick films.

Proton transfer dynamics were suppressed in thinner ionomer film.

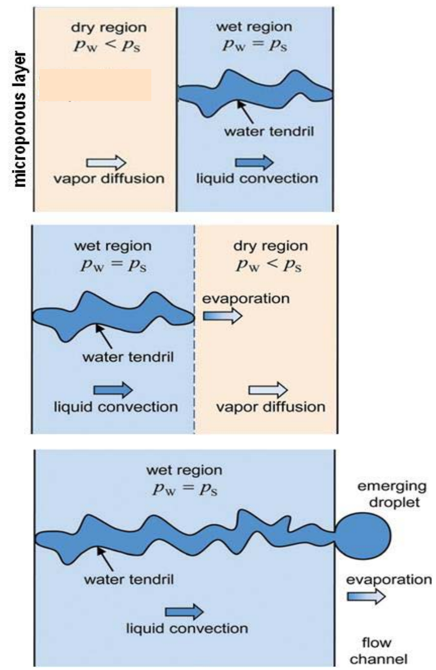
Evidence of nanophase/water morphological changes vs. film thickness

Diffusion Layer Model Framework

Two-phase transport and liquid/ vapor front (1+1D DTC)

1-D water tendril model – Ref. Caulk and Baker, *J. Electrochem. Soc.* 158 (4) B384-B393 (2011)

Condition depends on op. cond., diffusion and thermal properties

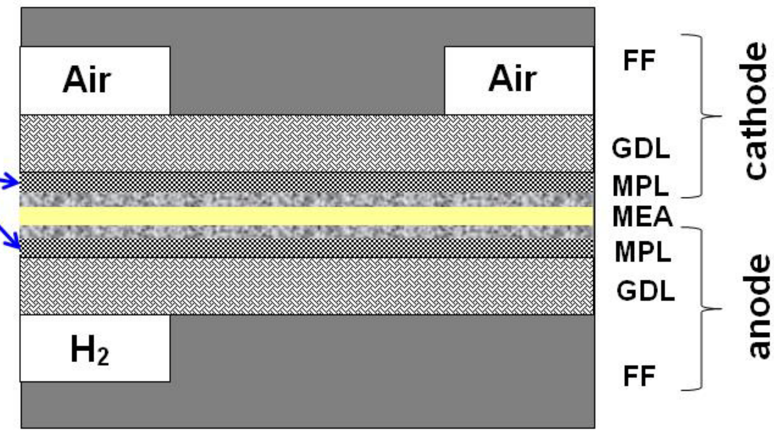


- Water saturation in wet region correlates to the measured D/Deff (= tortuosity/porosity)

Capturing land/channel effect in 1-D formulation (Component)

2-D, non-isothermal, two-phase transport model of GDL

Need to specify BC at MPL/CL interface

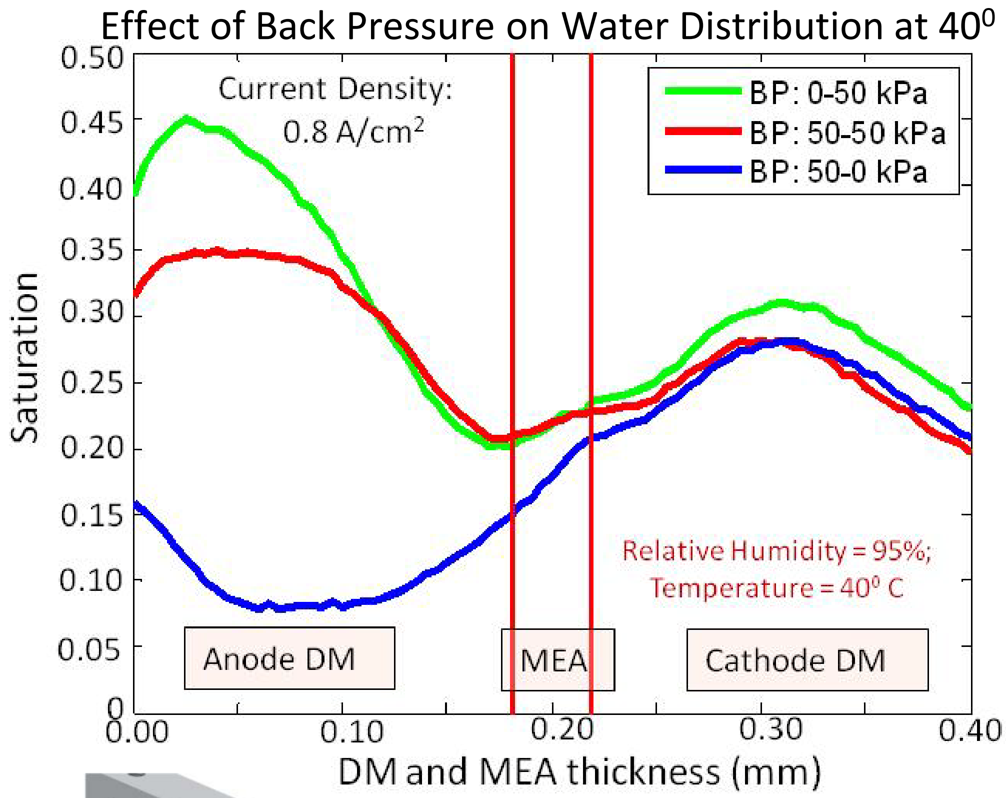


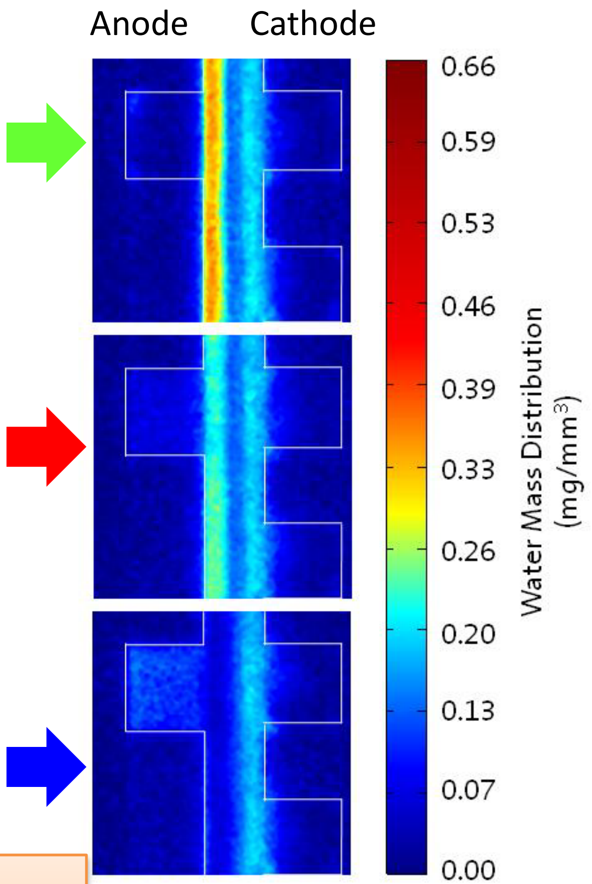
Liquid-water distribution over land and channel

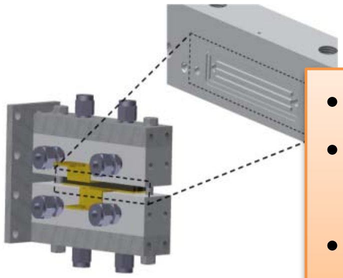
- Use maximum local water saturation (GDL material dependent)
- Obtain an average value for use in 1-D model

Component model integration into 1+1D down-the-channel wet model

GDL Water Saturation and Through-Plane Distribution





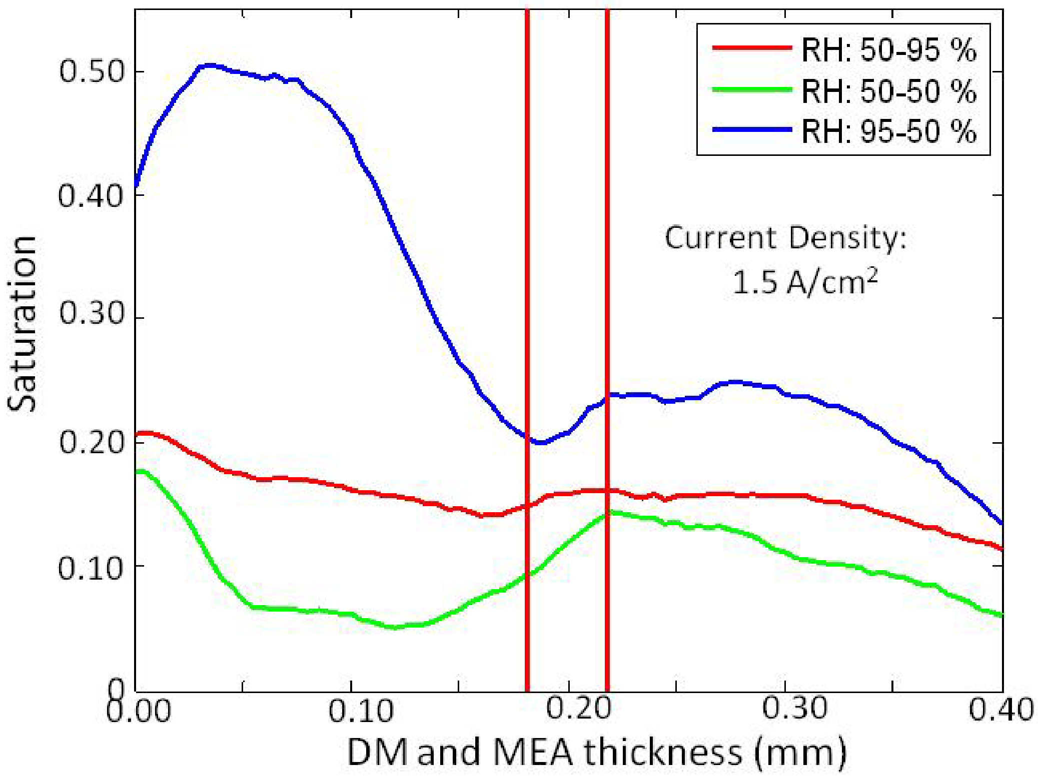


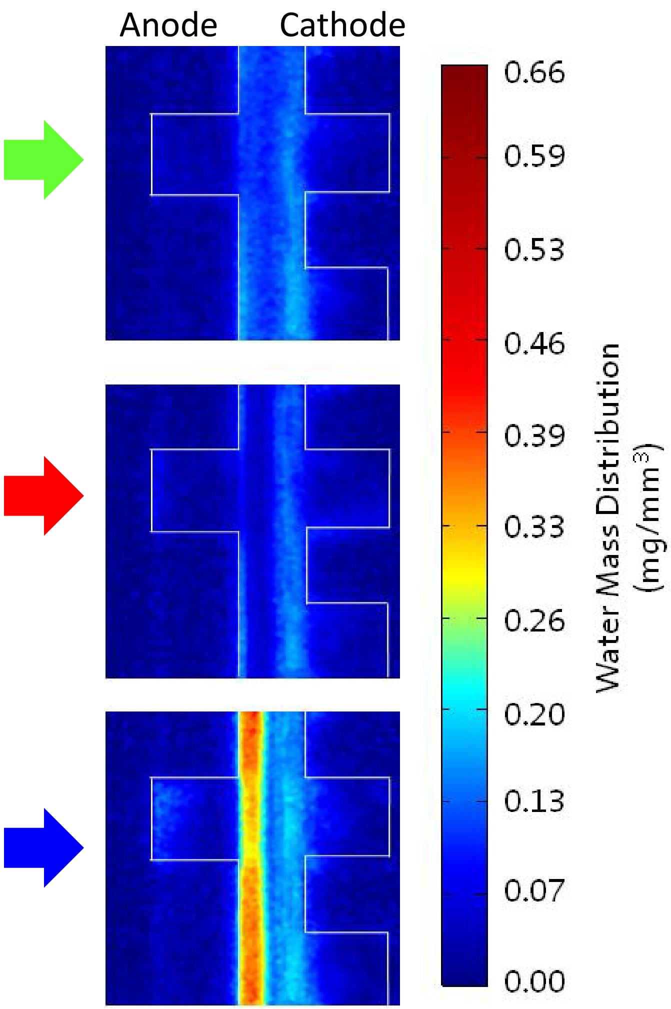
- Liquid cooled for stable temperature control.
- Asymmetric back pressure primarily impacts anode saturation.
- Data set extends through entire standard protocol, f(T, dP, RH, dT, flowrate, etc.) will be online.

Through-plane saturation and wet region boundary as a function of dT and operating temp.

GDL Water Saturation and Through-Plane Distribution

Effect of Relative Humidity on Water Distribution at 60^0 C





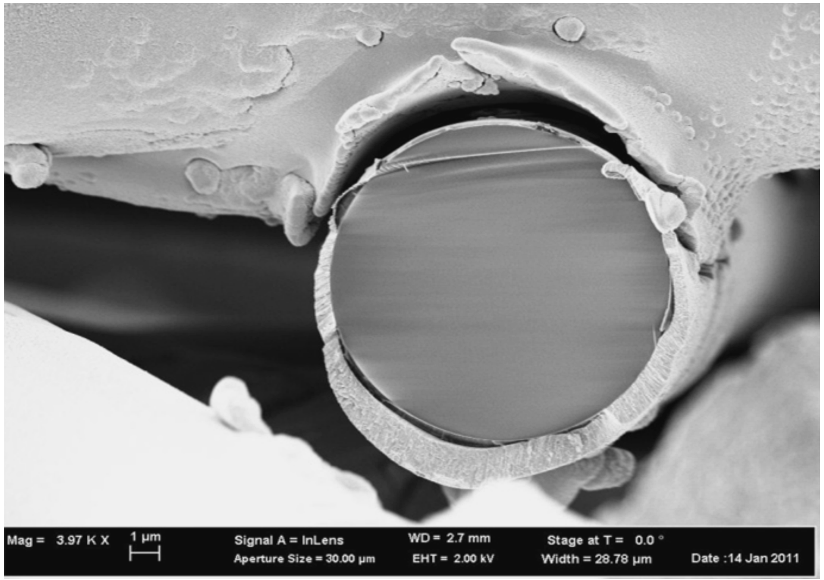
Anode GDL saturation is most sensitive to asymmetric operating conditions. These data provide insight into the complex water balance we intend to model.

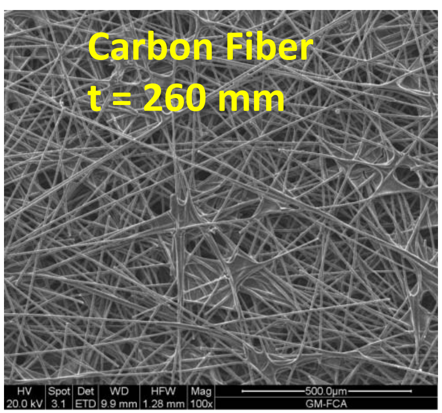
Through-plane saturation and wet region boundary as a function of dT and operating temp.

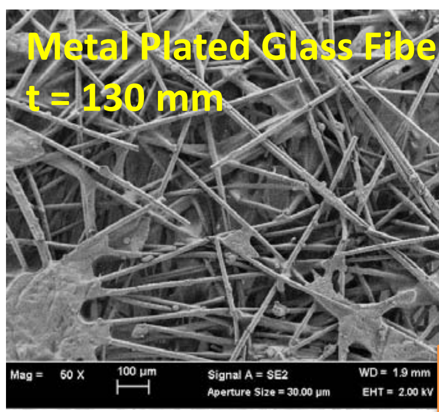
Technical Progress-

Evaluation of Auto-Competitive GDL Candidate

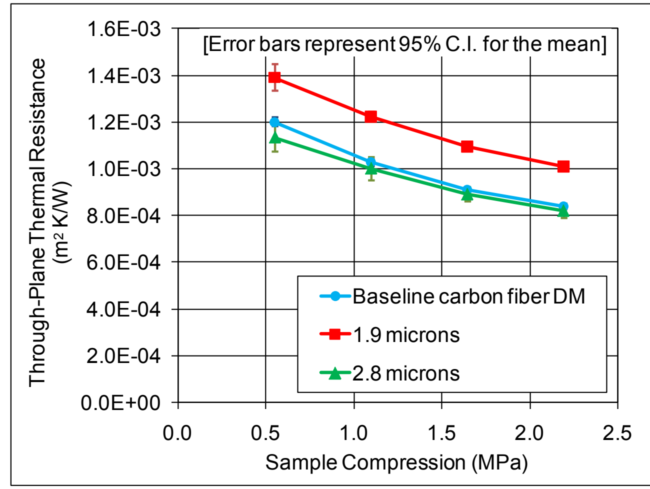
Metal Shell / Glass Core Diffusion Media

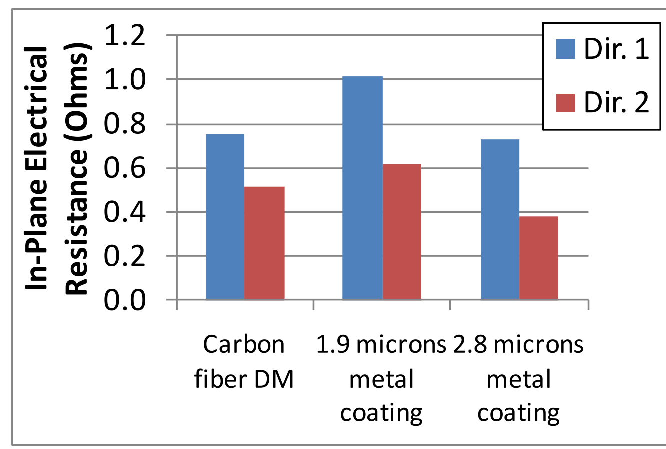






Ex-situ Characterization



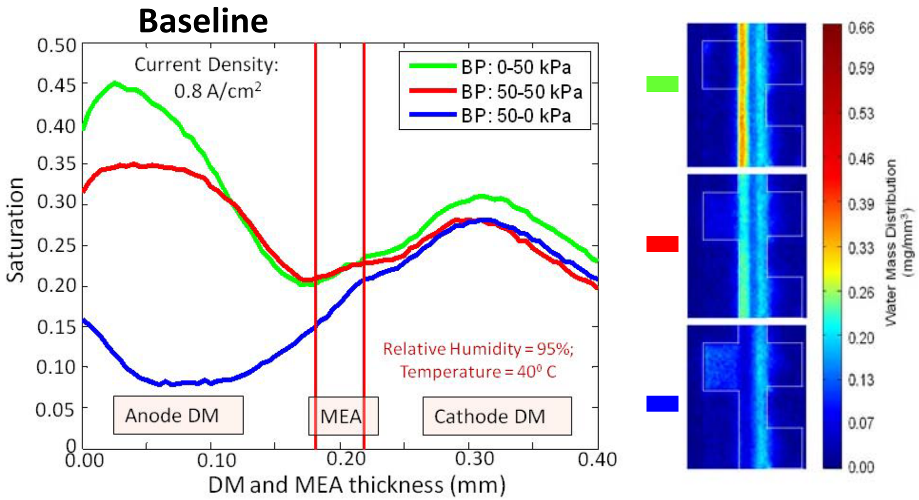


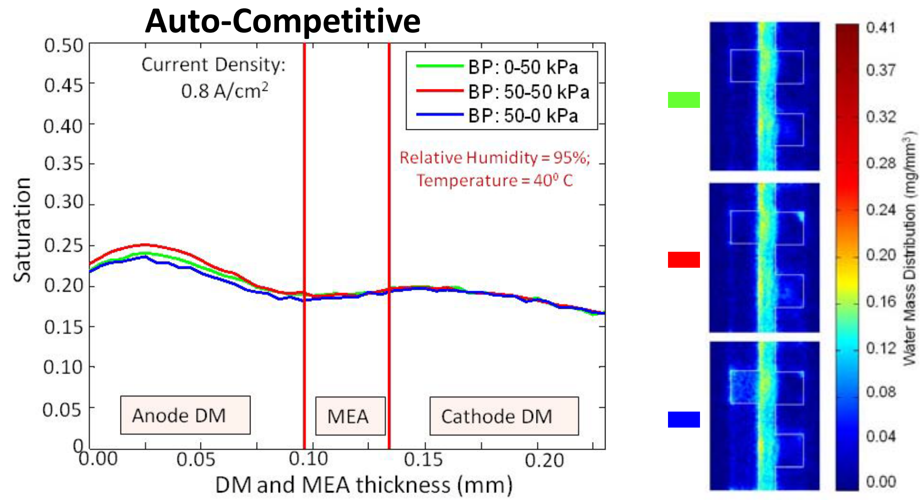
High through-plane electrical resistance relative to baseline GDL. Uneven through-plane plating and oxide layer are being investigated.

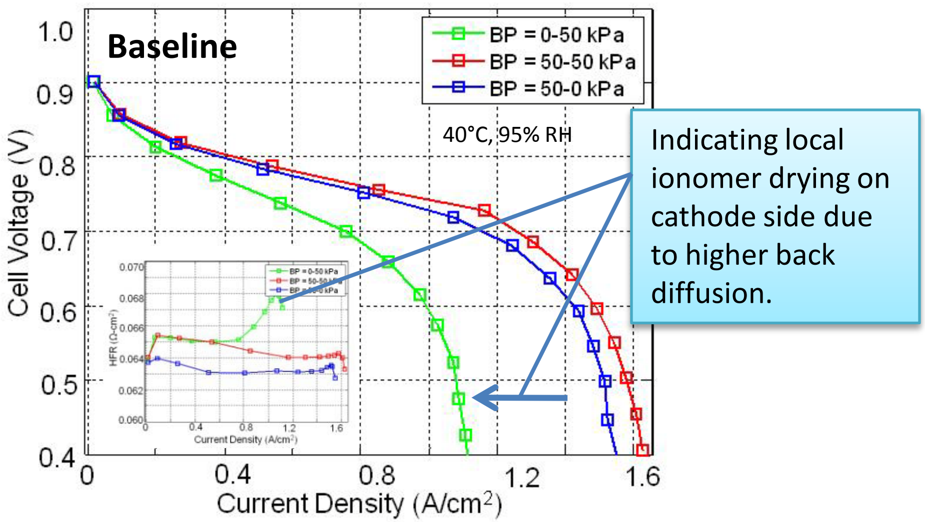
Define auto-competitive material set

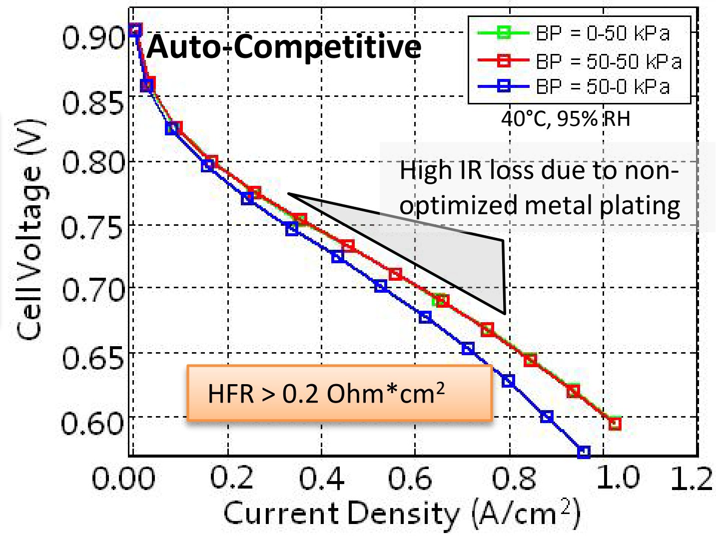
Technical Progress-

Evaluation of Auto-Competitive GDL Candidate









-A-C GDL has high ohmic resistance, plating needs optimization
-A-C material saturation is less sensitive to changes in operating conditions
-Additional evaluation of A-C GDL candidates are also underway

- **Define auto-competitive material set**
- **Through-plane saturation and wet region boundary as a function of dT and operating temp**

Flow Distributor Model Framework

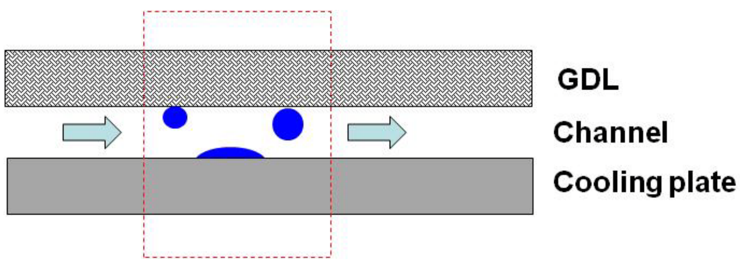
Two-phase transport and resulting resistance (1+1D DTC)

Pressure drop

- Over a 1-D segment, given upstream gas condition and water flow from GDL into channel → local water saturation & downstream gas condition

O2 transport resistance

- Normal to GDL interface, as a function of local water saturation



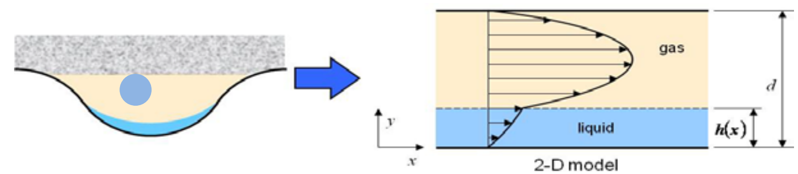
Express Sherwood number in terms of water saturation

- Sh = constant + f(channel water saturation)

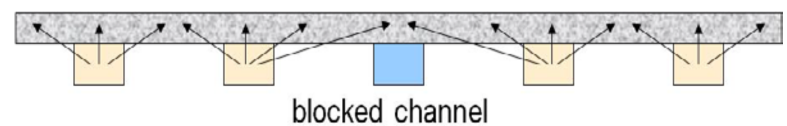
Transport around blocked channels (Component)

2-D, non-isothermal, two-phase transport model of flow network

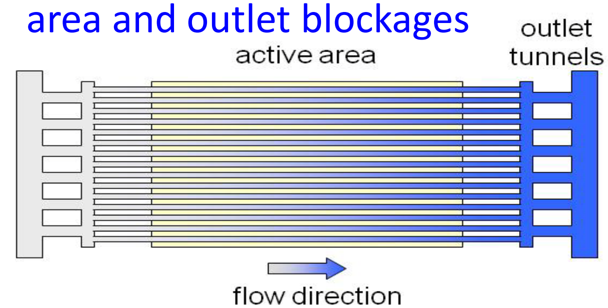
- Predict slug formation



- Transport related to unbalanced flow



- Overall flow distribution related to active area and outlet blockages



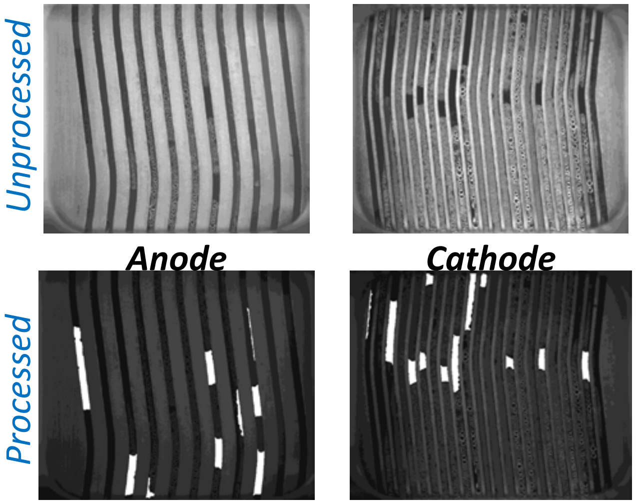
- Average surface coverage and hydraulic diameter

Component model integration into 1+1D down-the-channel wet model

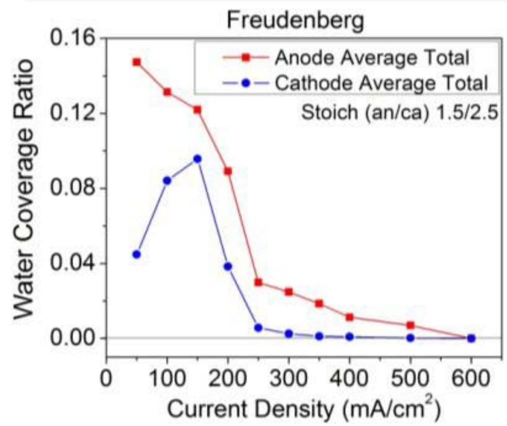
In-situ Characterization of GDL Surface Coverage

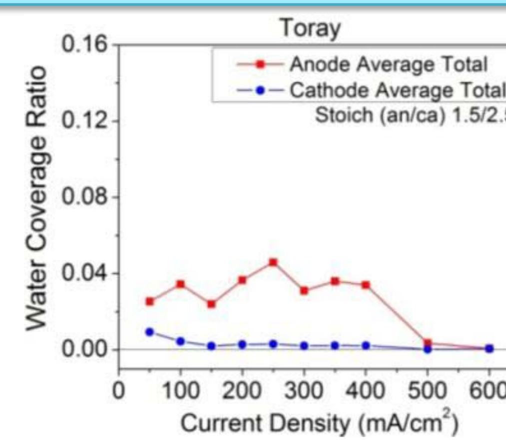
R·I·T

Statistical Analysis of GDL Diffusion Surface Area Loss Due to Liquid Water

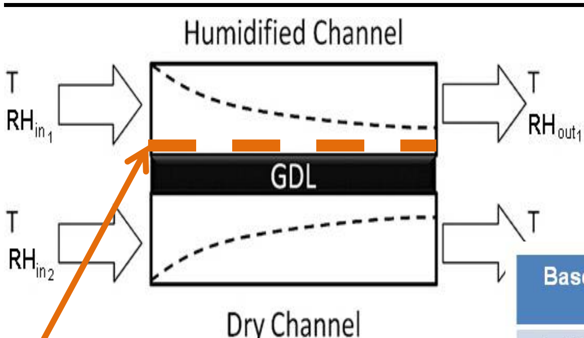


Water coverage ratio = total liquid water present in the flow field channels divided by the total channel area (time-averaged)





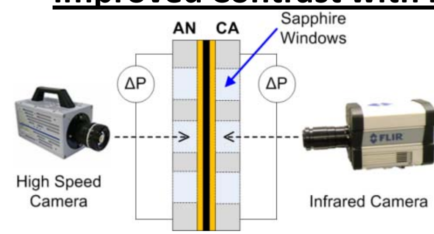
GDL to Channel Interfacial Resistance

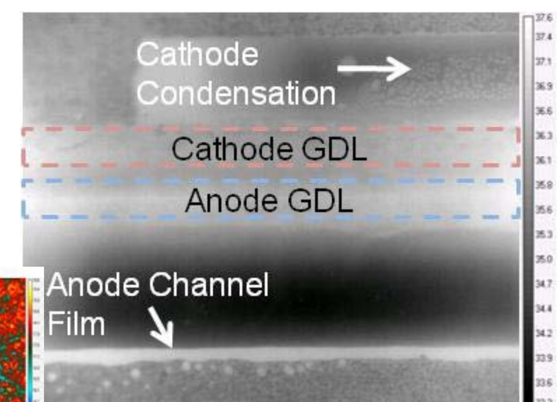


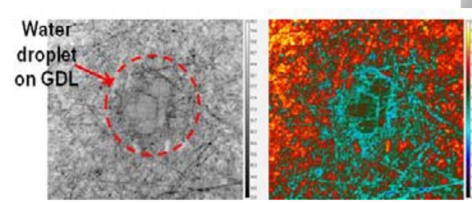
Baseline GDL Diffusion Values	
w/o MPL	0.095 cm^2/s
w/ MPL	0.070 cm^2/s

Artificial surface coverage layer to measure average change in diffusion due water coverage in the channel.

Improved Contrast with IR Imaging for Water Morphology





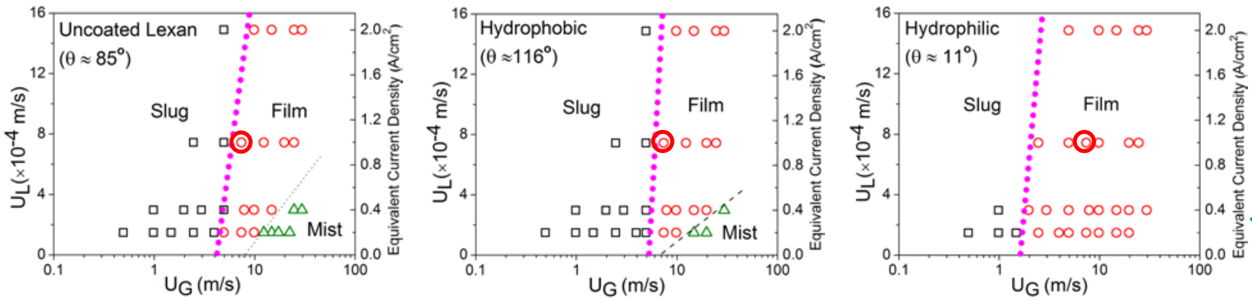


CFP to channel interfacial transport resistance as a function of channel saturation

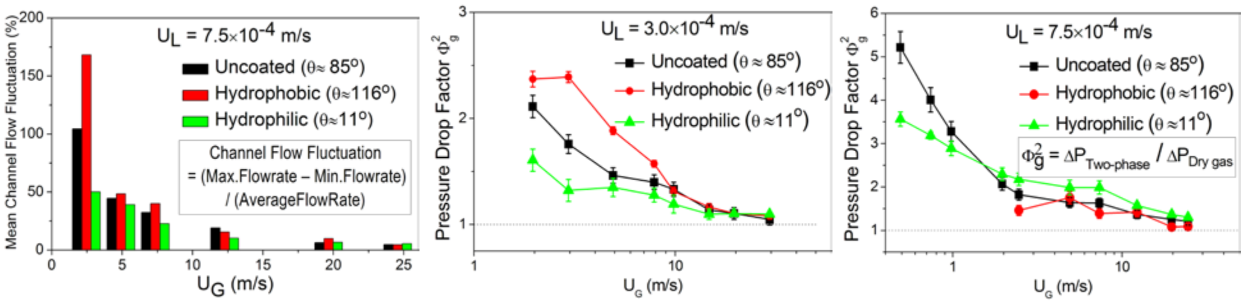
Technical Progress-
Characterization of Water Transport in Channels

R·I·T

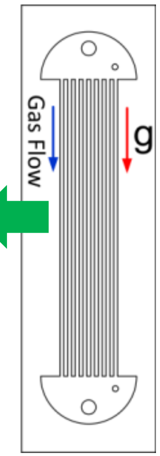
Effects of Channel Surface Wettability

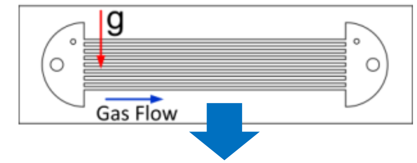


Flow regime specific modeling required to predict channel dP and flow variation



Effects of Orientation

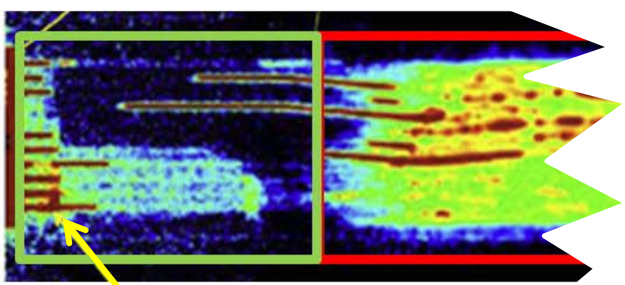




Horizontal Orientation
Longer water slugs observed, indicating gravitational effects as slug volume increases.

Hydrophilic channels:
- Larger film flow regime and more uniform water distribution
- Higher stability of individual channel gas flow rate
- **Pressure drop factor is lower in slug flow regime, but higher in film flow regime.**

Outlet Water Retention



Additional analysis of DTC validation data set beyond active area

Measure outlet liquid volume fraction vs. operating condition via in-situ neutron radiography

- **Channel dP as a function of saturation, temperature, flow, and current density**
- **Manifold dP as a function of saturation, temperature, flow, and current density**

GM FUEL CELL

Summary

- Project is standardized by materials and operating space
  - Baseline and auto-competitive material sets chosen based on parametric variations that consider degradation and cost vs. performance trade-offs.
- Key relationships required for a wet 1+1D model and characterization methods are defined
  - Subject matter experts are developing and executing characterization methods to generate physical understanding of fundamental processes.
  - Component models describing processes are being generated and will be used to output bulk and interfacial transport resistances.
  - Modeling framework for 1+1D model is defined.
- Down-the-channel baseline material validation data set complete
  - Additional repeat experiments being executed to define uncertainty.
- Database on web for dissemination of data and modeling
  - Visit www.PEMFCdata.org (development will continue throughout the project)

Future Work

- Complete component characterization method development
  - Several characterization techniques are still under development. In FY11, ex-situ measurement methods of diffusion as a function of saturation will be finished (currently underway in all cases).
- Define remaining auto-competitive components
  - Gas diffusion substrate type and configuration will be finalized based on the state-of-the-art and ongoing characterization work.
- Apply characterization methods to auto-competitive components
  - Finish baseline material evaluation and apply same techniques to auto-competitive material set.
  - Conduct parametric studies to fill gaps between material sets if necessary.
- Complete down-the-channel validation
  - Populate database with full baseline and auto-competitive data sets (4 repeats of most measurements).
- Integrate component model transport resistances into 1+1D model
  - Indentify water balance and performance divergence from baseline and auto-competitive validation data
  - Isolate relationships with significant contribution to divergence through combinatorial studies and continue refinement.

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