Visualization of Fuel Cell Water Transport and Performance Characterization Under Freezing Conditions

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Project ID #: fc_37_kandlikar

Overview

Timeline

- Start date: 03/01/2007
- End date: 02/28/2010
- 70% complete

Barriers

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

Budget

- Total project funding
  - DOE: $ 2.68M
  - Contractor: $ 0.8M
- FY08: $ 0.9M
- FY09: $ 0.9M

Partners

- Interactions/ collaborations
  - Rochester Institute of Technology
  - General Motors Corporation
  - Michigan Technological University
- Project lead:
  Rochester Institute of Technology

Objectives - Relevance

Overall: • Improve fundamental understanding of the water transport processes in the PEMFC stack components under freezing and non-freezing conditions.

• To minimize fuel cell water accumulation while suppressing regions of dehumidification by an optimized combination of new gas diffusion layer (GDL) material and design, new bipolar plate (BPP) design and surface treatment and anode/cathode flow conditions.

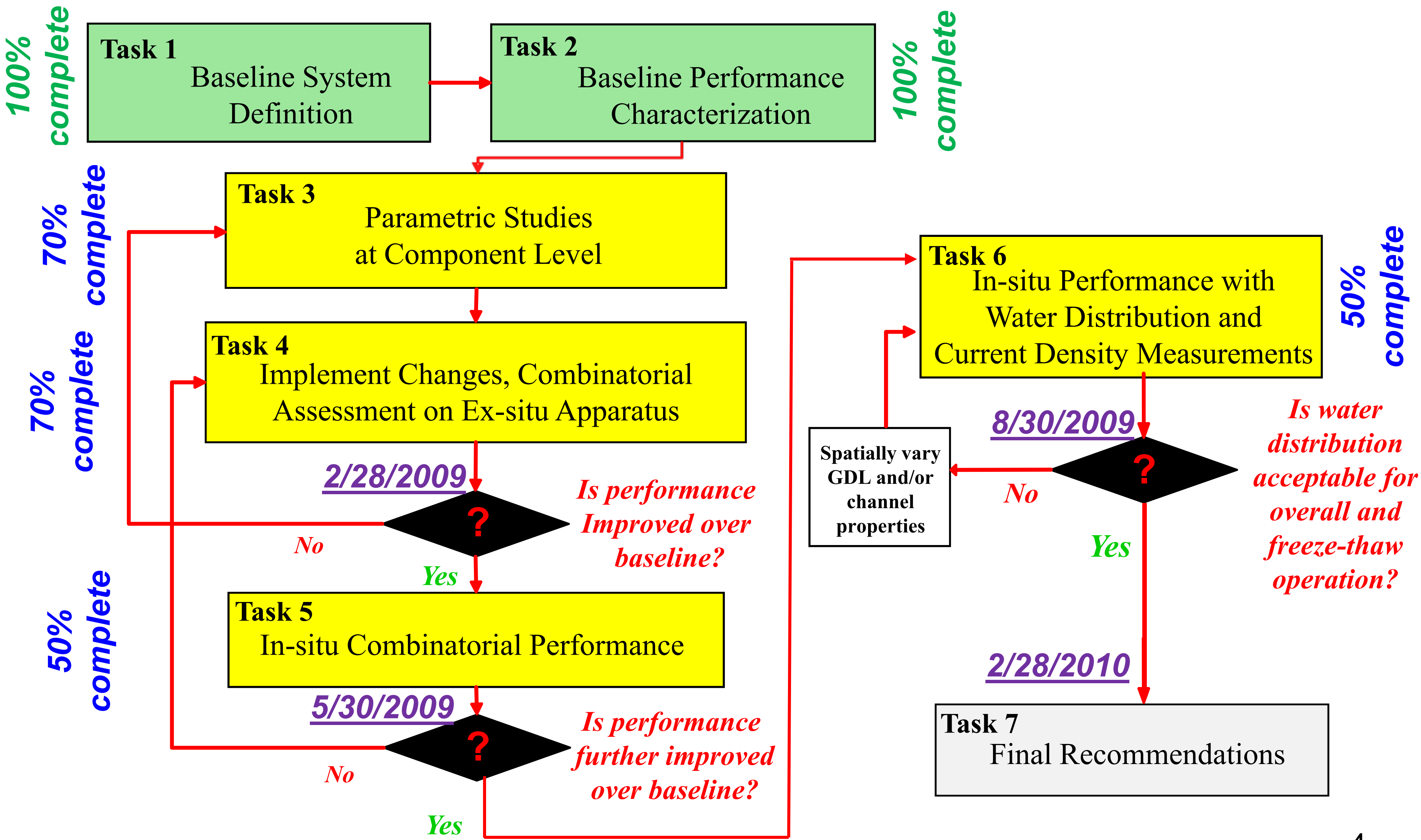
• To meet DOE 2010 targets for 80 kWe transportation stacks:

Start up and shut down energy from -20°C ambient	Unassisted start temperature	Cold start-up time to 50% of rated power @ –20ºC ambient
5 MJ	- 40 °C	30 s

FY08: • Implement changes to baseline system and assess the performance:

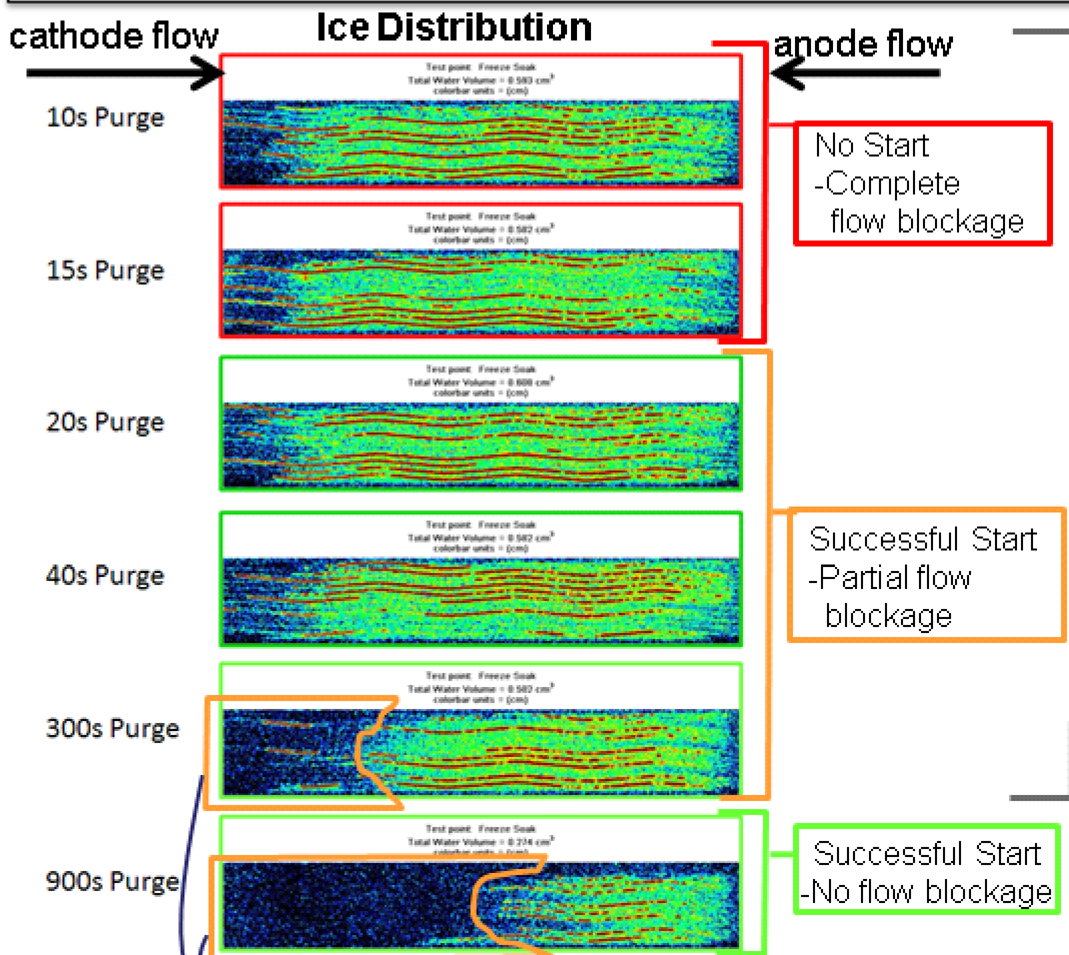
- Ex-situ combinatorial performance
- In-situ combinatorial performance
- Water distribution and current density distribution
- Microscopic study and models for water transport in GDL and parallel channels; Component characterization techniques and methods

Plan & Approach



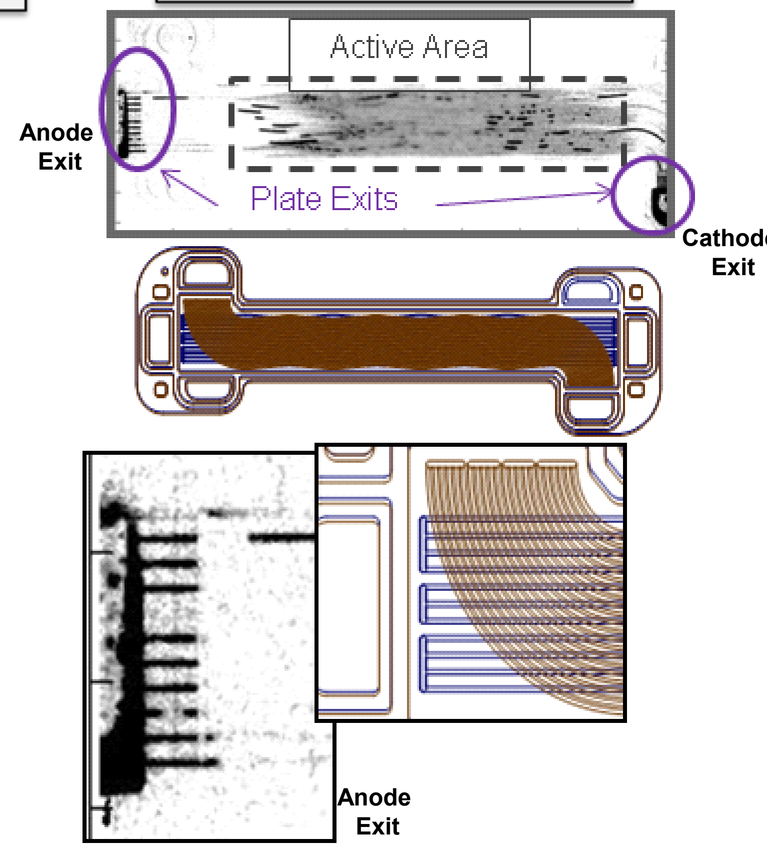
Water Accumulation Correlated to Freeze Failure

Precondition: 0.4 A/cm2, 150 kPa, 35°C, A/C stoich = 2/2, Dry inlet gas
Purge condition: 0.1 A/cm2, 150 kPa, 35°C, A/C stoich = 2/12, Dry inlet gas



Evaporating water from porous layers extends run time while frozen, by providing space for additional ice formation and accumulation

Water Accumulation in the Exit Region and Headers

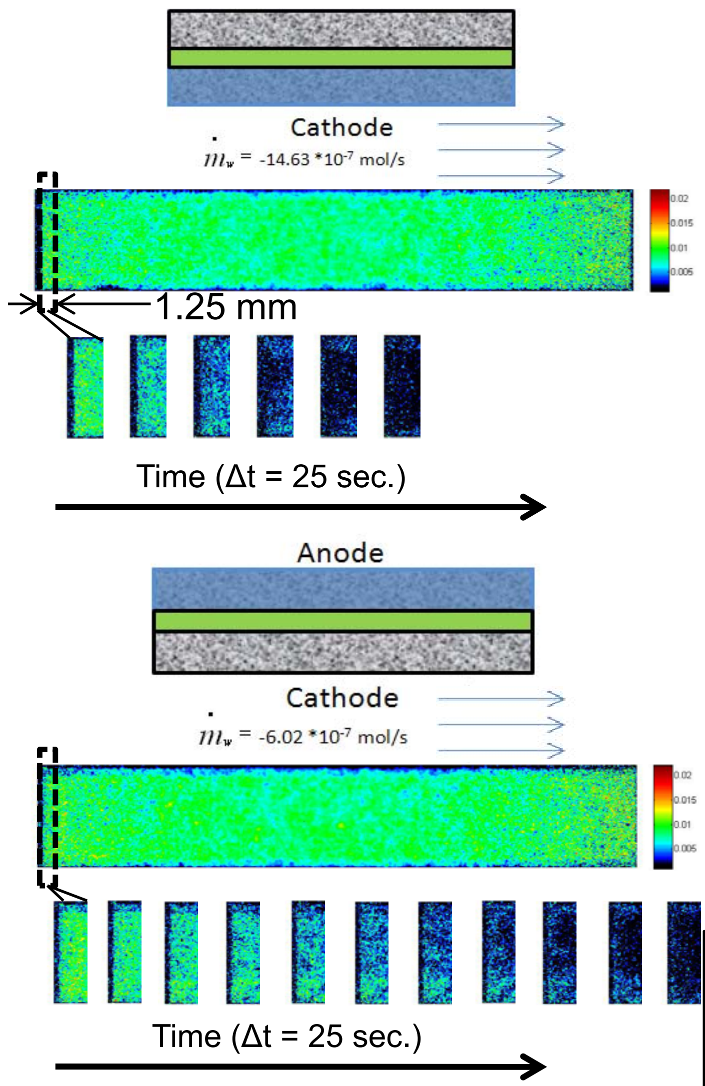


- Water at plate-to-header transition can contribute to flow blockage failure at short shutdown purge times

Technical Accomplishments–

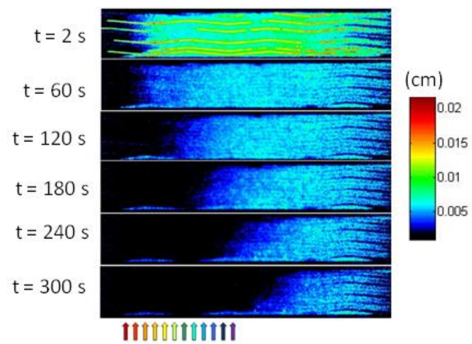
Purge Water Removal Rate Characterization

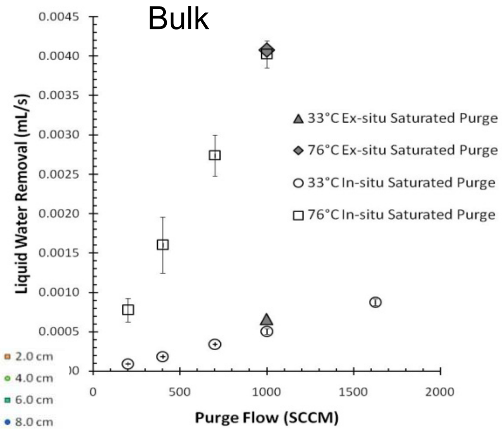
Ex-situ anode vs. cathode purge characterization

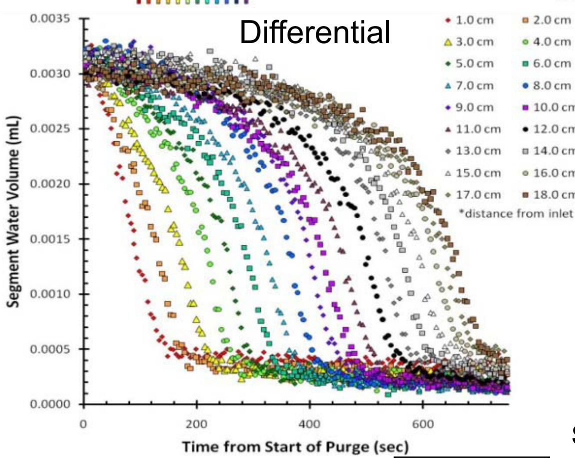


In-situ purge comparison

Precondition: 0.4 A/cm2, 150 kPa, 35°C, A/C stoich = 2/2, Dry inlet gas
Purge condition: 0.1 A/cm2, 150 kPa, 35°C, A/C stoich = 2/12, Dry inlet gas



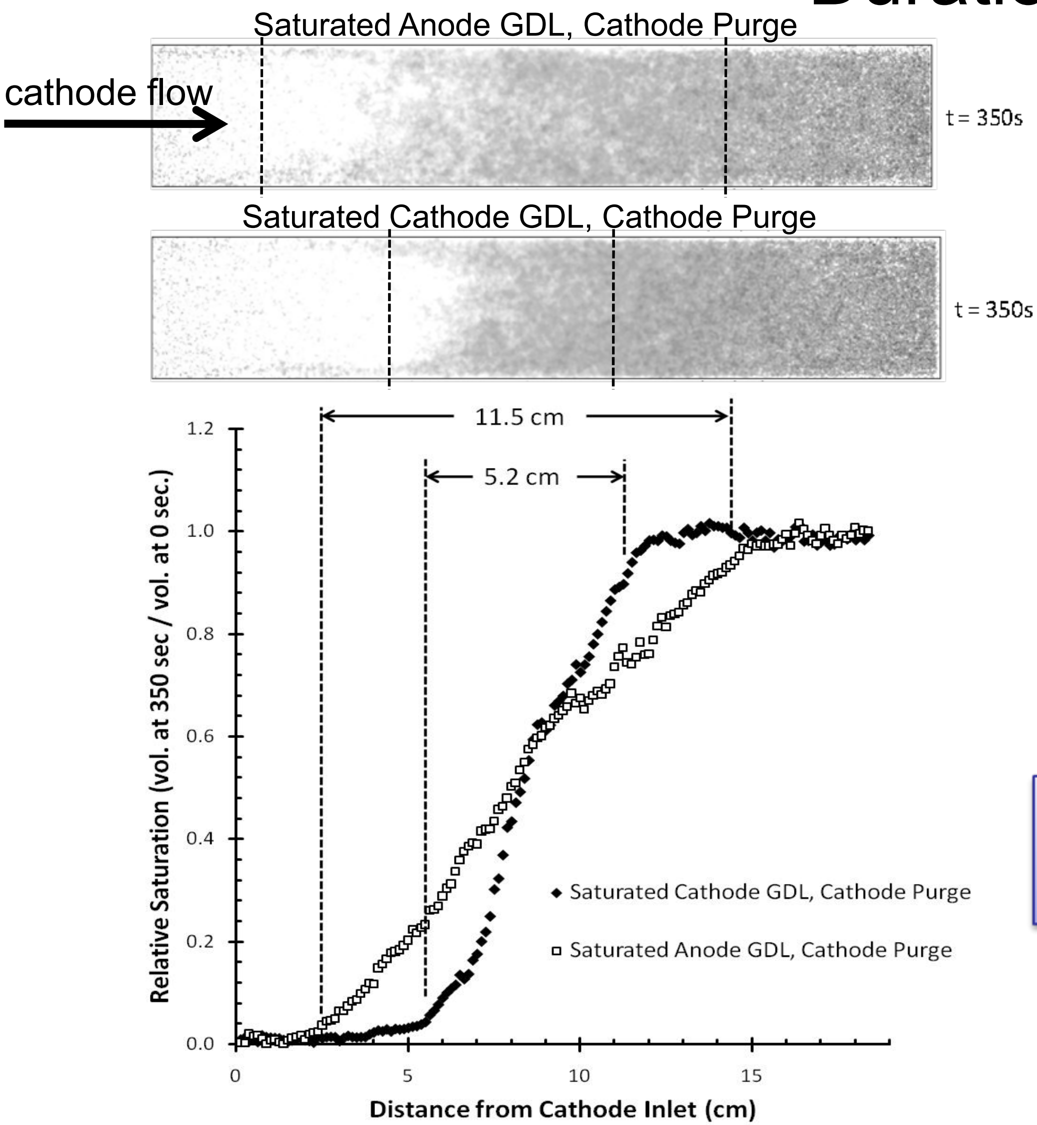




- Comparison of ex-situ and in-situ drying rates provide useful insight into the fuel cell drying performance.

e	Ex-Situ Saturated GDL	Differential Ex-Situ Removal Rate (μL/s)	Differential In-Situ Removal Rate (μL/s)
33°C	Cathode	0.020±0.002	0.010±0.001
33°C	Anode	0.009±0.001	
76°C	Cathode	0.076±0.008	0.028±0.003
76°C	Anode	0.028±0.002	

Water Location Impacts Purge Dynamics and Duration



Purge condition: 35°C, 1.0 slpm N_2 flow in cathode only

The length of the drying front can be predicted based on the parameters measured in the current work independent of flow.

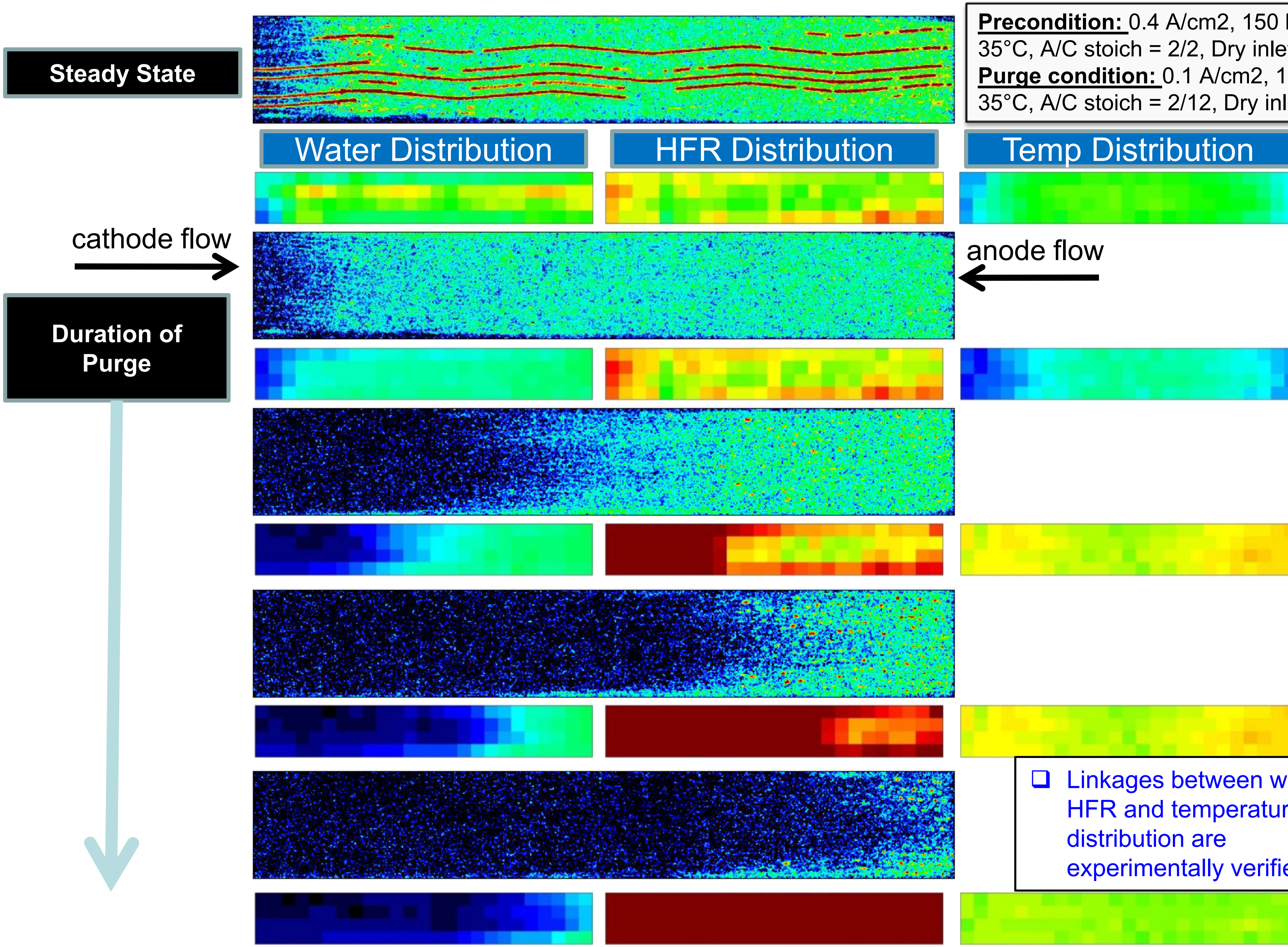
$$q = \left[\frac{\dot{m}_{air} c_{p_{air}} T_{in} \left(PR_{air}^{\frac{\gamma-1}{\gamma}} - 1 \right)}{\eta_{tot}} \right] t$$

Optimization:
Shutdown Energy - 2010 DOE target of 5 MJ
Start-up characteristics

- Drying rate information is used with purge energy consumption in meeting DOE targets.

Technical Accomplishments–

Ionomer Drying and Temperature Effects During Purge



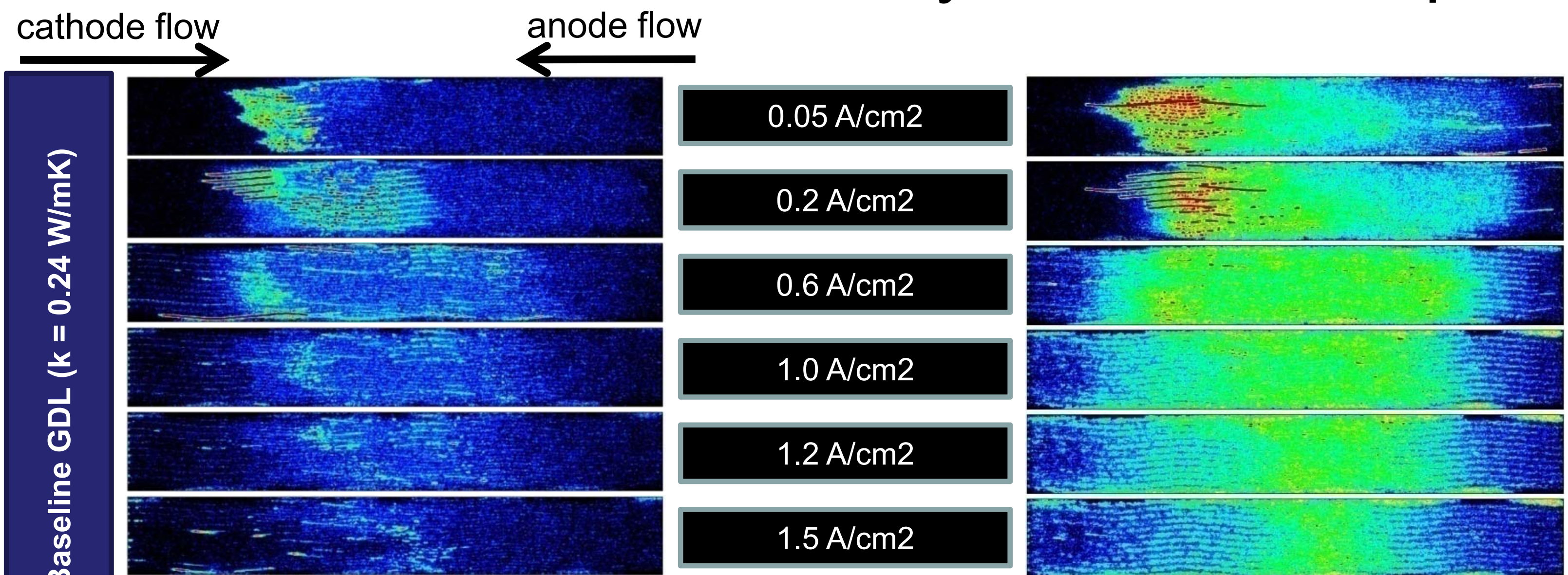
Precondition: 0.4 A/cm2, 150 kPa, 35°C, A/C stoich = 2/2, Dry inlet gas
Purge condition: 0.1 A/cm2, 150 kPa, 35°C, A/C stoich = 2/12, Dry inlet gas

- Linkages between water, HFR and temperature distribution are experimentally verified.

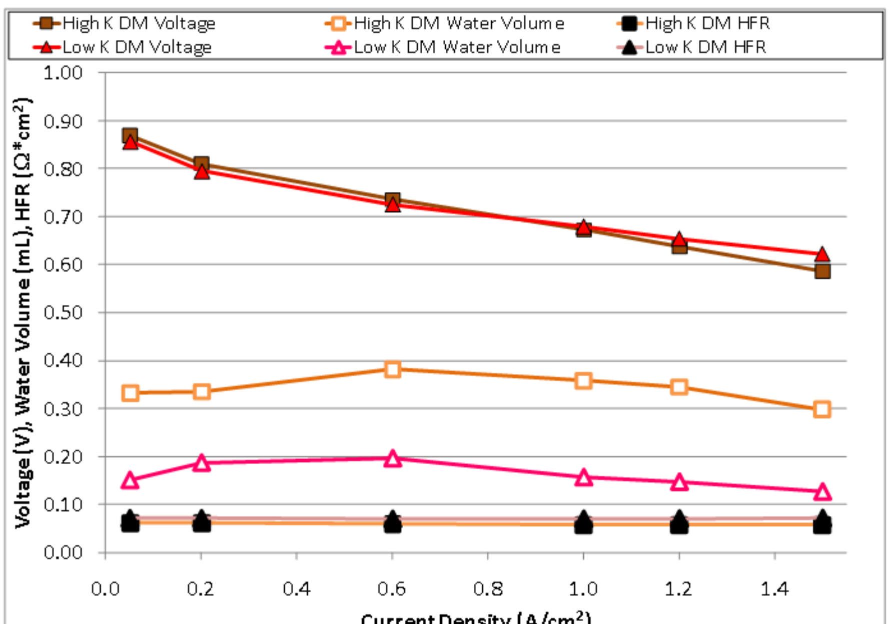
Technical Accomplishments–

GDL Thermal Conductivity Saturation Impact

Baseline GDL (k = 0.24 W/mK)



Increased Conductivity GDL (k = 0.49 W/mK)

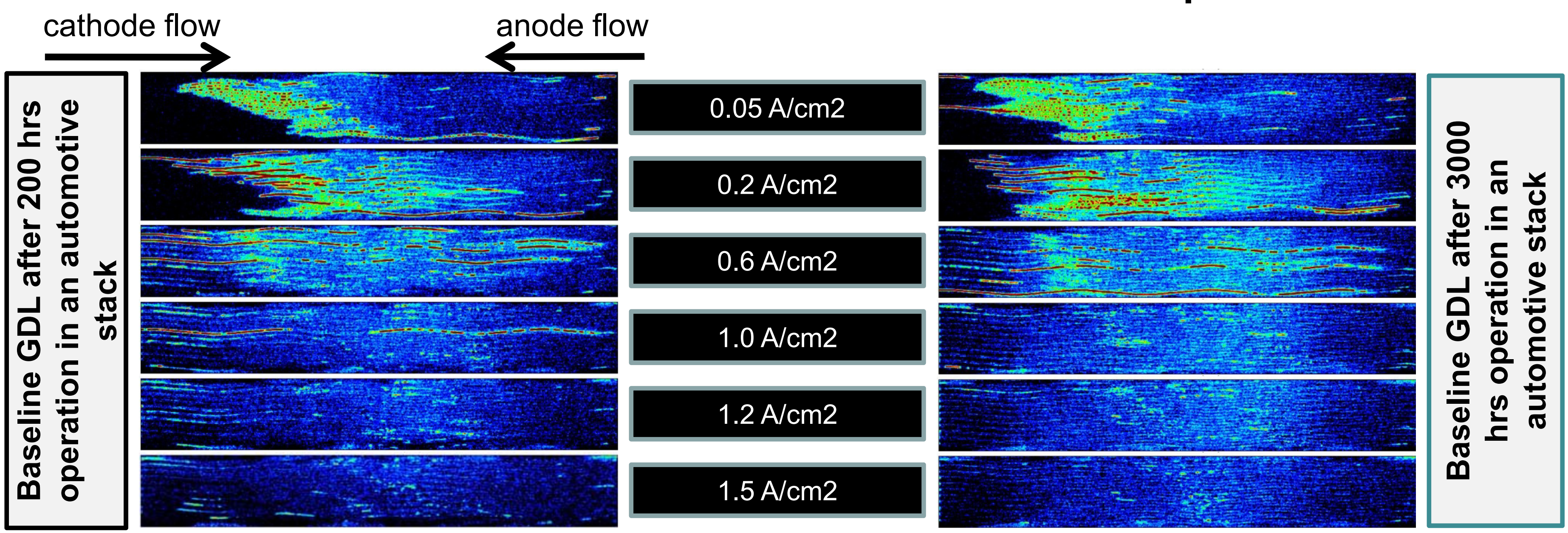


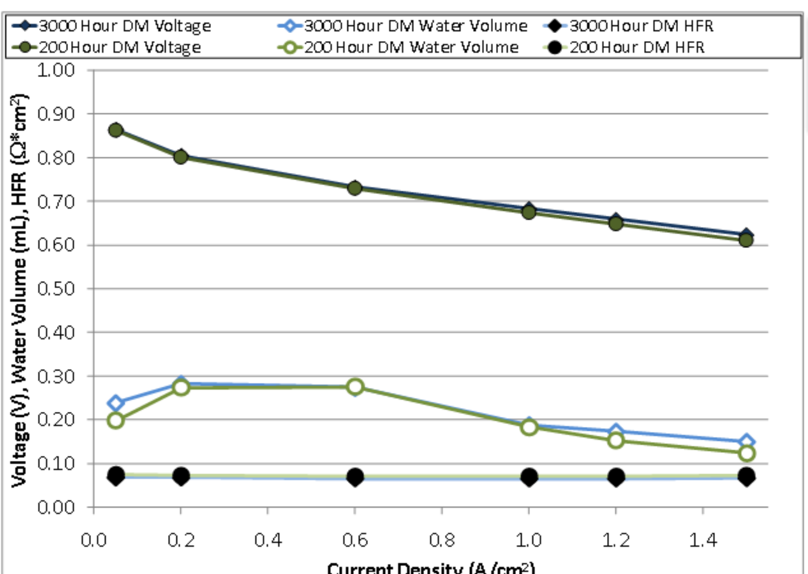
Pol Curve Condition:
200 kPa
80°C
A/C stoich = 1.5/2 100% RH inlet gas

- Lower thermal conductivity GDL leads to reduced water volume .

Technical Accomplishments–

GDL Saturation After 3000 Hours of Operation





Pol Curve Condition:
200 kPa, 80°C
A/C stoich = 1.5/2 100% RH

- ❑ Fuel cell performance (as see from the plot) remains essentially the same after 3000 hours of operation.

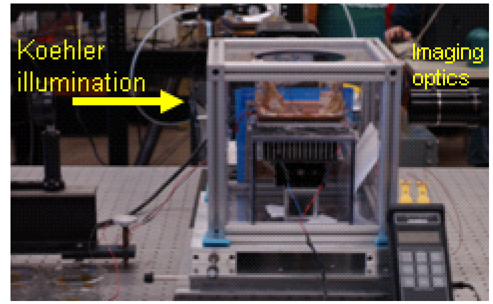
Fundamental Research Objectives

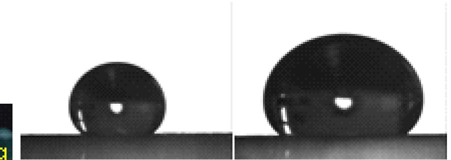
- ❑ In-situ studies indicate that the GDL properties and channel/header configuration affect water saturation.
- ❑ To reduce purge energy requirement, water accumulation in the fuel cell should be reduced.
- ❑ GDL morphological and channel two-phase flow studies are conducted by MTU and RIT to understand the fundamentals of water transport and accumulation in fuel cell.

Technical Accomplishments (MTU)–
GDL Wettability and Structure

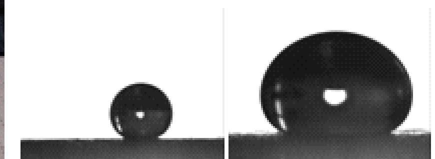
Wettability
- method developed for accurate measure of contact angle, θ, on rough surfaces (GDL)
- temperature control (up to 100°C)
- humidity control
- as temperature increases, θ decreases

Environmental chamber



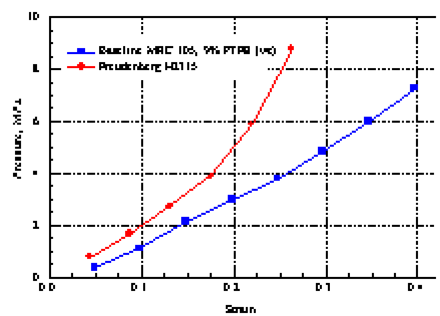


Baseline MRC 105, 9% PTFE (wt), $\theta \sim 140°$, 20°C

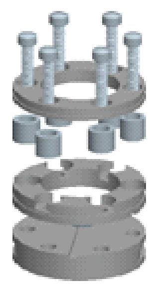


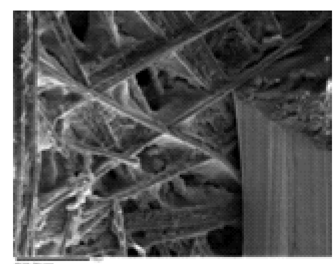
Toray T060, 7% PTFE (mass), $\theta \sim 155°$, 20°C

Structure
- developed calibrated SEM compression fixture
- GDL imaging under incremental compression
- stress-strain relationship for GDLs compressed beneath a channel
  - similar to that found in bipolar plates
- compression range:
  - up to 1600 psi, based on area of four (4) ½ standard samples
  - displacement resolution: +/- 6.5 μm

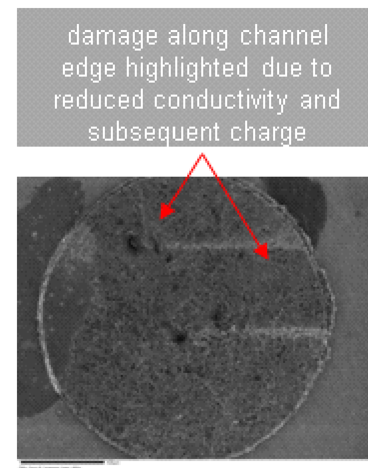


Sample holder





Baseline GDL under compression imaged at edge of channel



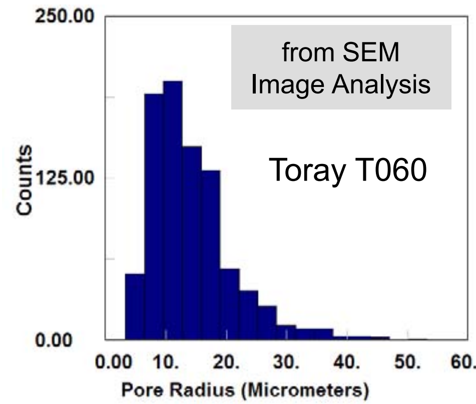
Baseline GDL post-compression showing damage

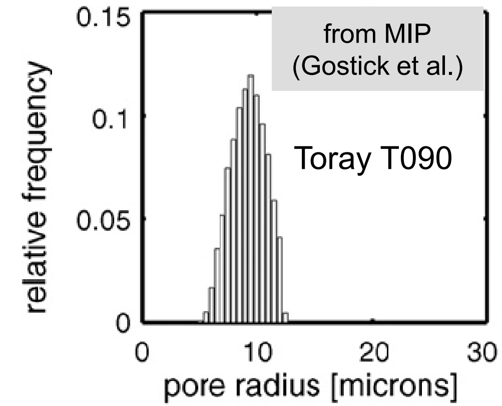
- ❑ Contact angle dependence on temperature and drop size being studied.
- ❑ GDL-bipolar plate interface studied for damage to GDL due to compression.

GDL Morphology

Morphology

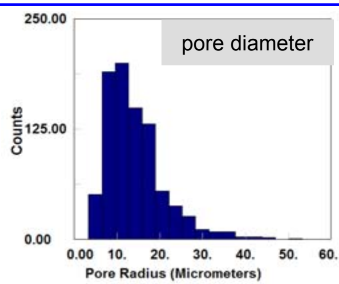
- statistical analysis from single SEM image of GDL
  - ➢ **pore size distribution**
    - ▪ Weibull distribution to characterize distribution
    - ▪ Weibull coefficients used to generate network for capillary flow model
  - ➢ pore depth distribution (stereo SEM imaging)
  - ➢ pore roundness distribution
  - ➢ pore orientation distribution (Rose plot)
  - ➢ nearest neighbor distribution (randomness of pore size distribution)
  - ➢ chemistry (x-ray spectrometry)
- assessing relative importance of each parameter

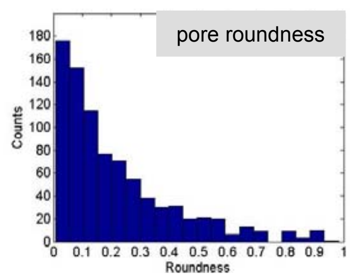


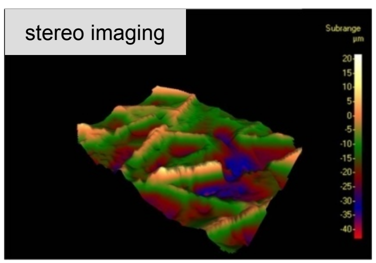


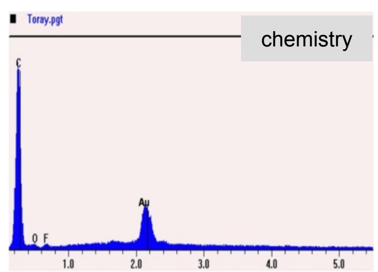
GDL sample	Weibull distribution coefficients		
	k	λ	r_{min}
MRC 105, 9%(wt)	1.3	2	6.7
E-Tek LT1200-N	1.5	25.5	6.5
Toray T060, 7%(m)	1.65	12.16	3.35

Toray T060
9% PTFE (m)









- ❑ Rapid analysis of important GDL parameters using SEM images.
- ❑ Significant advantages over capillary-flow porosimetry and mercury-intrusion porosimetry (MIP).

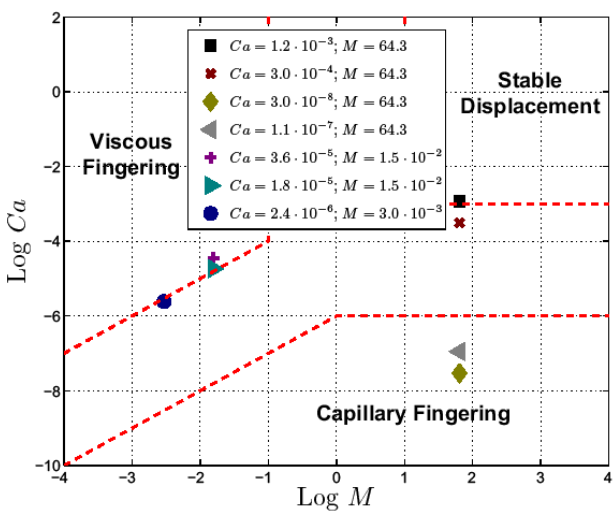
Technical Accomplishments–

GDL Transport Characterization

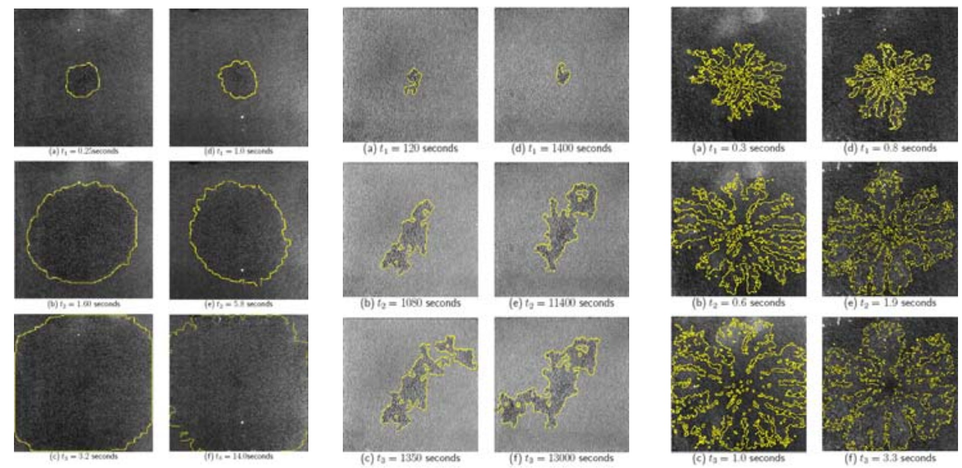
Drainage

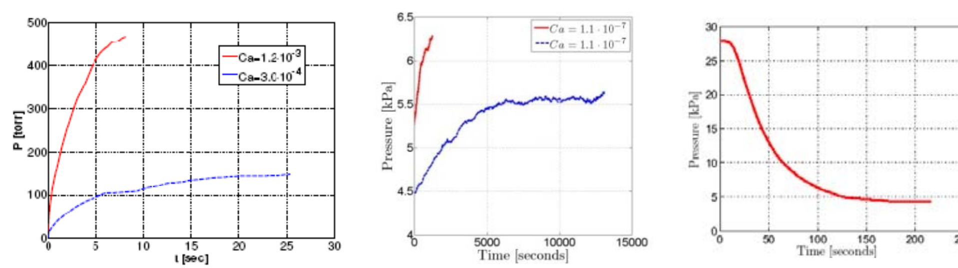
- pseudo-Hele-Shaw experiments
- phase drainage phase map for GDLs
- unique phase drainage diagram for each GDL
- unique capillary pressure curve for each type of displacement and GDL
- provides quantitative input for capillary flow model

Drainage Phase diagram: Toray T060



stable displacement | **capillary fingering** | **viscous fingering**





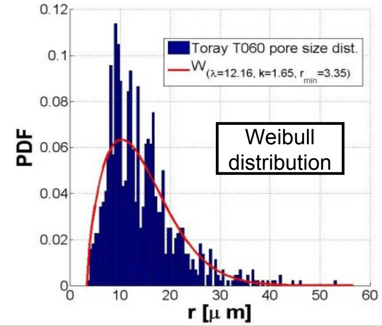
- ❑ A novel method developed to represent water transport in GDL
- ❑ Captures capillary effects
- ❑ Data used to “calibrate” capillary flow model for each GDL

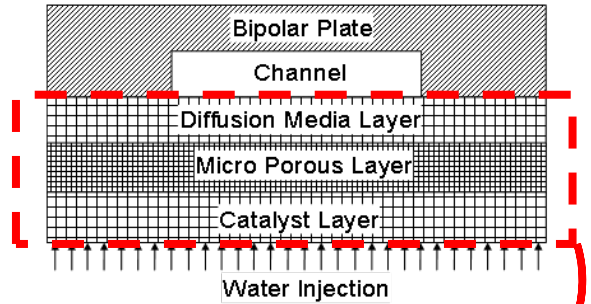
Technical Accomplishments–

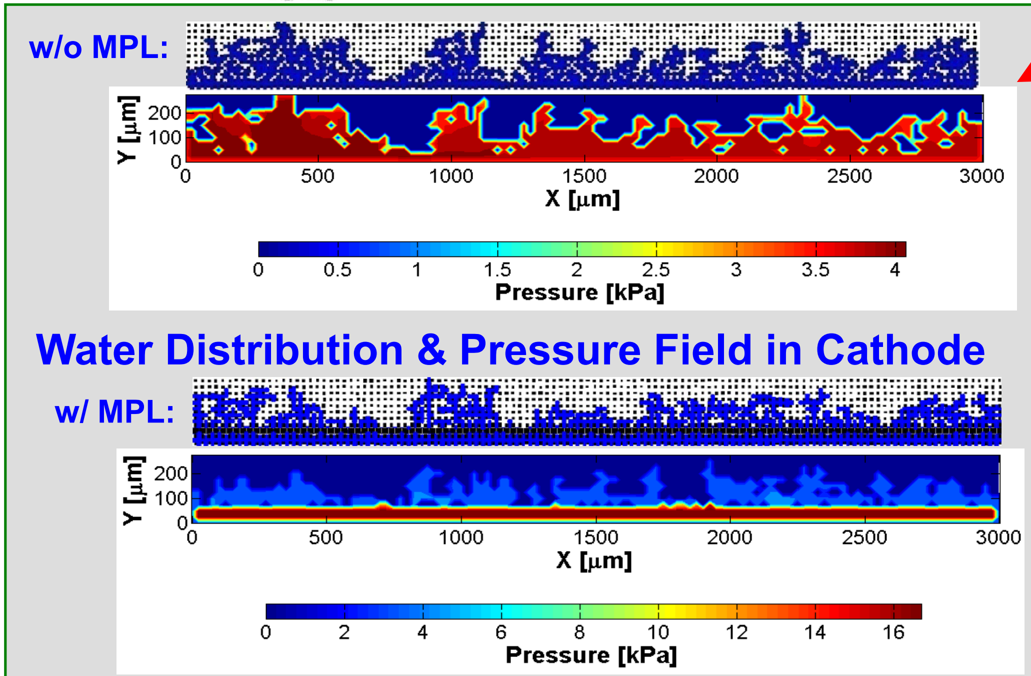
Capillary Flow Model

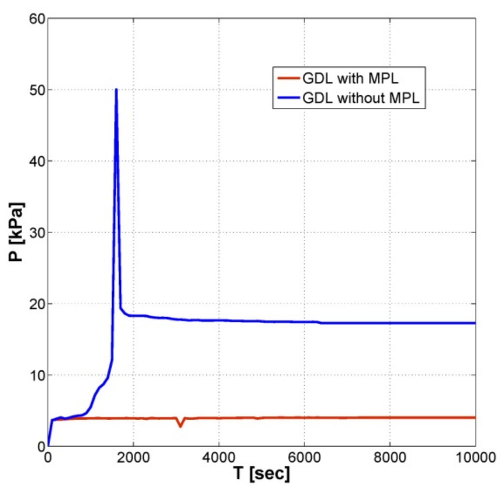
Network Model

- model details presented last year
- model inputs:
  - ➢ contact angle (from Wettability studies)
  - ➢ pore size distribution (from Morphology studies)
- unique phase drainage diagram for each GDL
- unique capillary pressure curve for each type of displacement and GDL







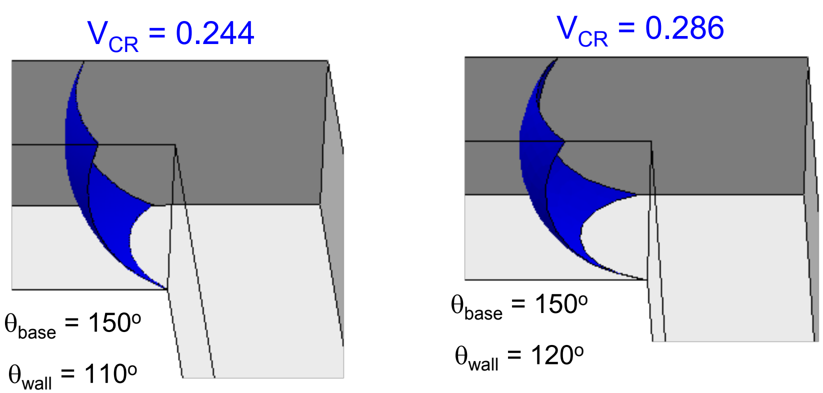


❑ Capillary Flow Model presents a simple methodology for characterizing capillary effects in GDLs.

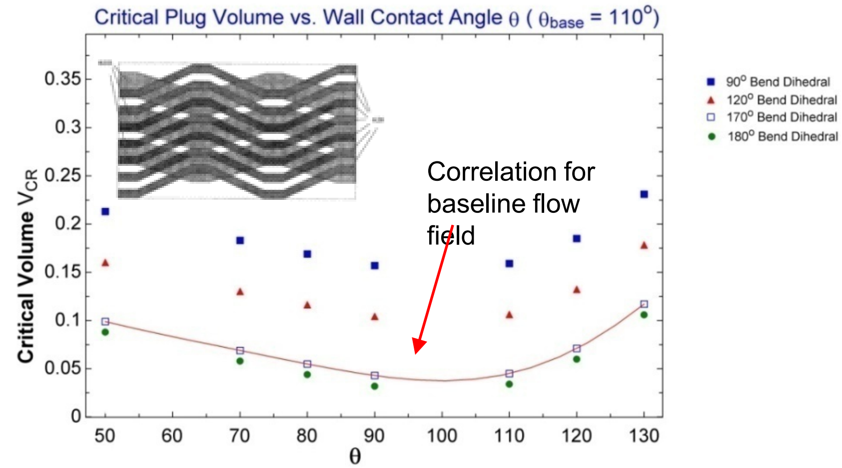
Channel Characterization

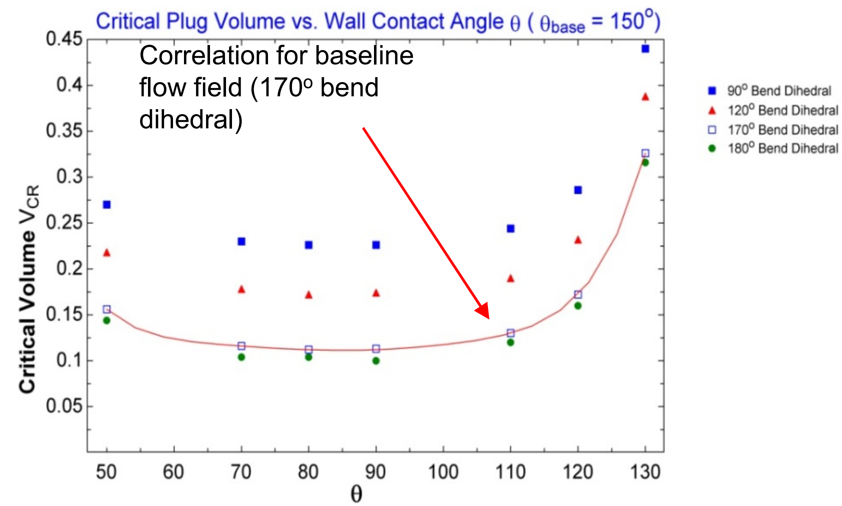
Single Channel Experiments

- effect of wettability on 2-phase flow transition presented.
- high speed microscopy shows extreme pressure spikes and density waves in channels at typical reactant purge velocities
- determined critical volume at which static liquid film or drop will spontaneously plug a channel:
  - function of channel and base (GDL) contact angles
  - solution generated via *Surface Evolver*
- use to predict location of channel plugging
- assist with developing channel purge strategies



symmetry plane on bend dihedral

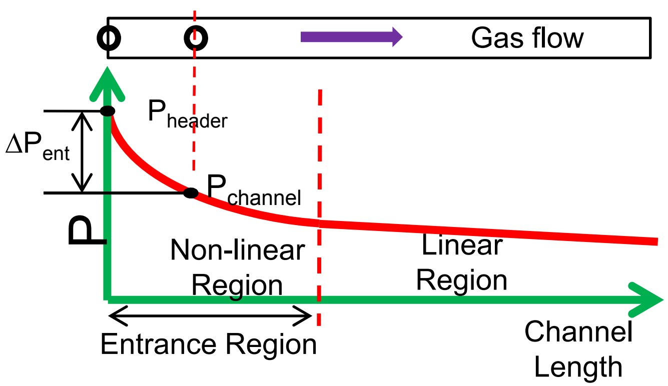




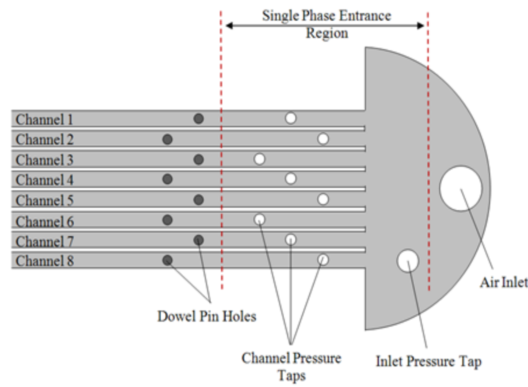
- Understanding critical volume for liquid plug formation can assist with flow field purge strategy.

Water Transport in Channels - Flow Maldistribution

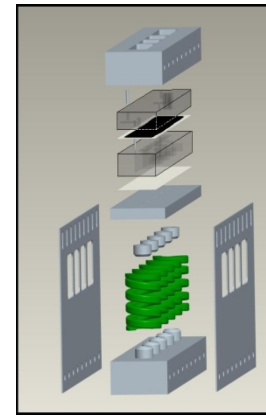
Entrance Region Pressure Drop Method:



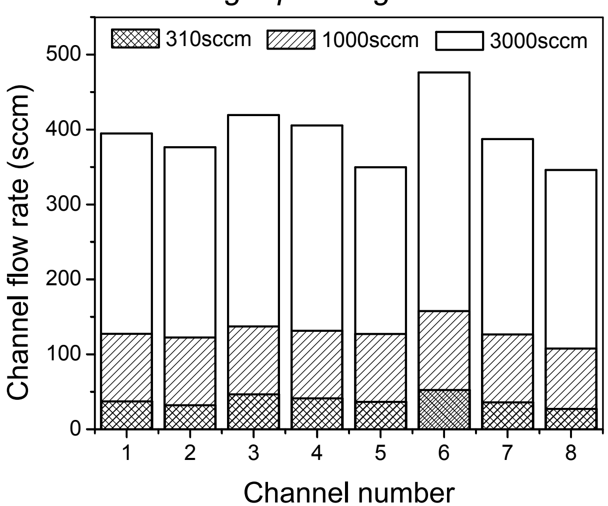
Individual pressure taps at the channel entrance



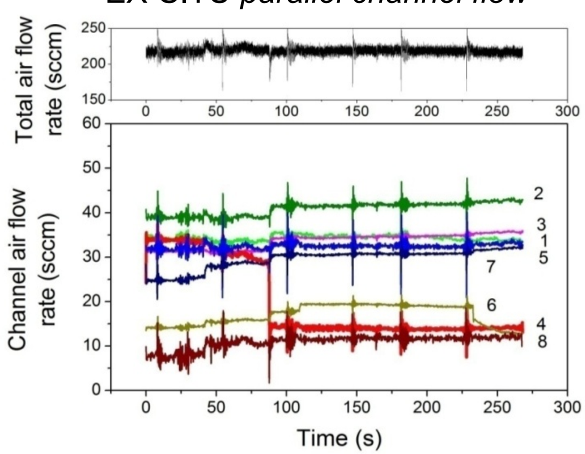
Test section with visual access



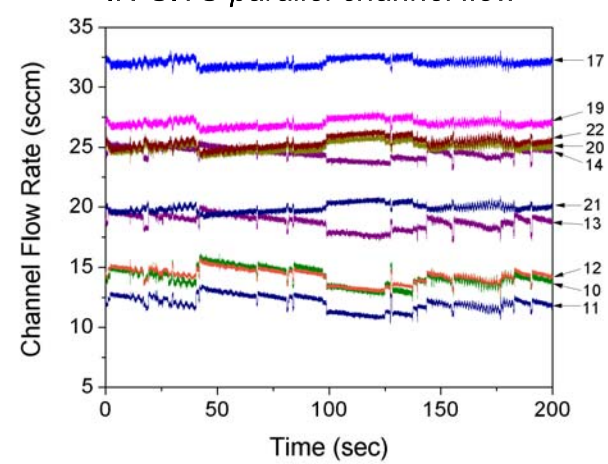
Channel maldistribution
Single-phase gas flow



EX-SITU *parallel channel flow*



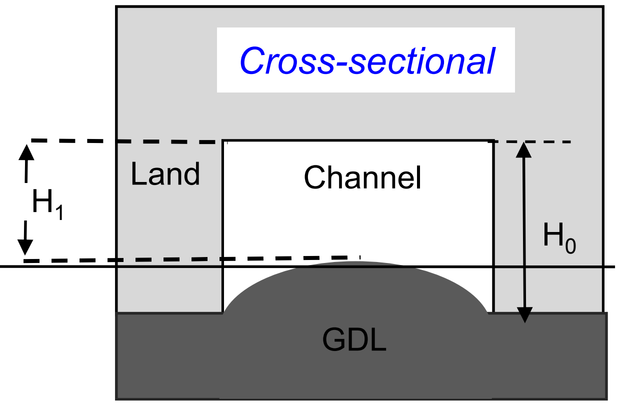
IN-SITU *parallel channel flow*

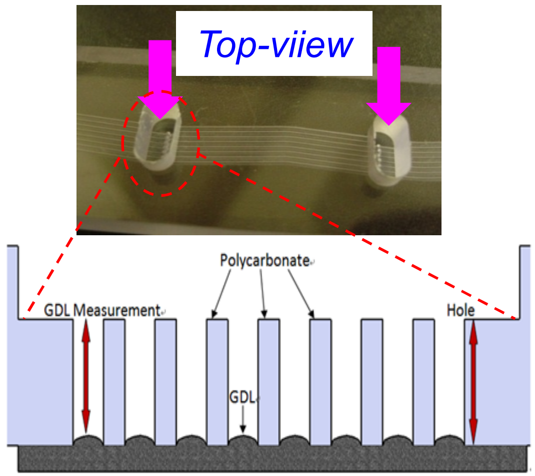


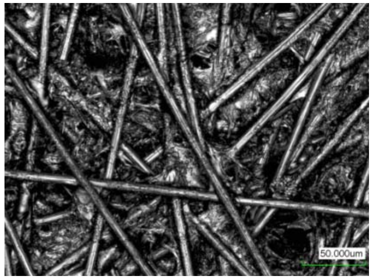
- ❑ Instantaneous flow distribution in individual channels measured.
- ❑ In-situ and ex-situ flow maldistribution and two-phase flow interactions in fuel cell gas channels characterized.

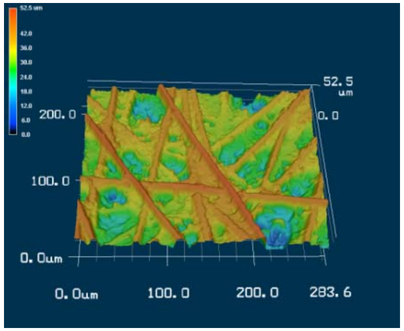
GDL Compression and Intrusion

Optical measurements:









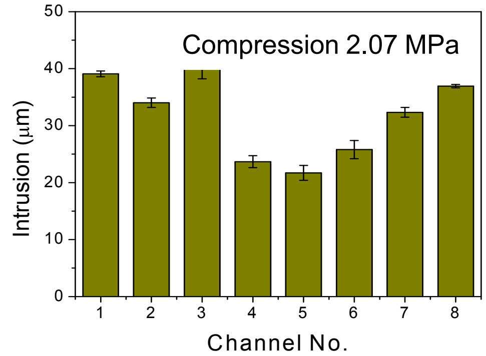
Entrance Region model:

$$\Delta p_{GDL,core} = \Delta p_{GDL,meas} - \Delta p_{minor}$$

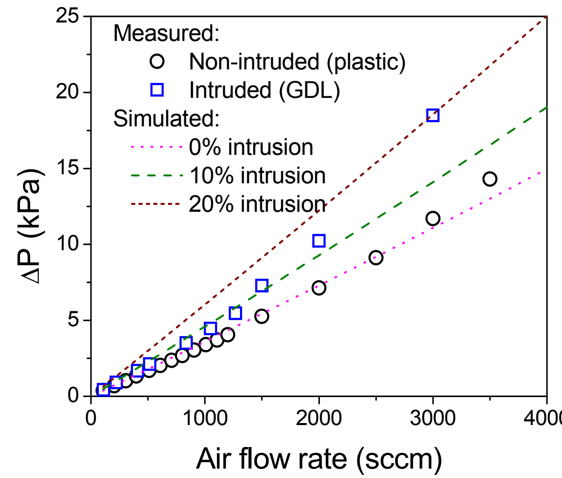
$$\Delta p_{core} = 2\frac{f_{app}\,\mathrm{Re}\,\mu x}{D_h^2}$$

$$H = \frac{W \cdot D_h}{2W - D_h}$$

Optical measurements of intrusion



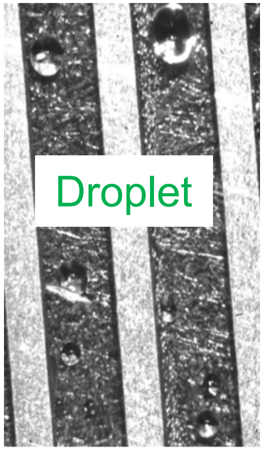
Intrusion effect on pressure drop

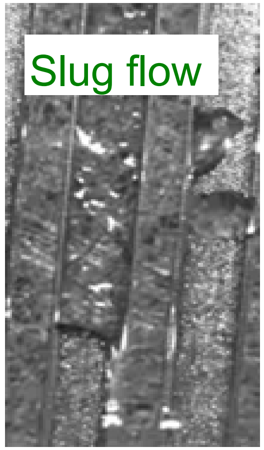


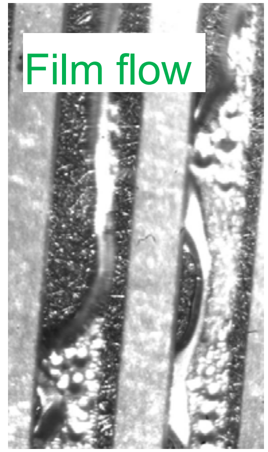
- Intrusion effects are seen as multiple orifices in series, rather than uniform reduction in channel flow area.
- Optical intrusion measurements correlate well with pressure drop predictions and experimental data.
- Instantaneous channel flow measurement in individual channels under in-situ and ex-situ conditions

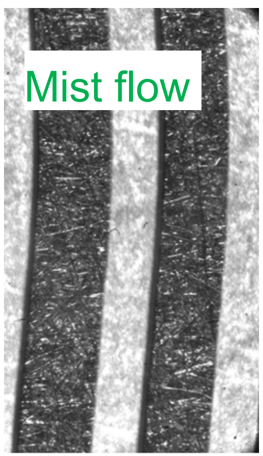
Technical Accomplishments–

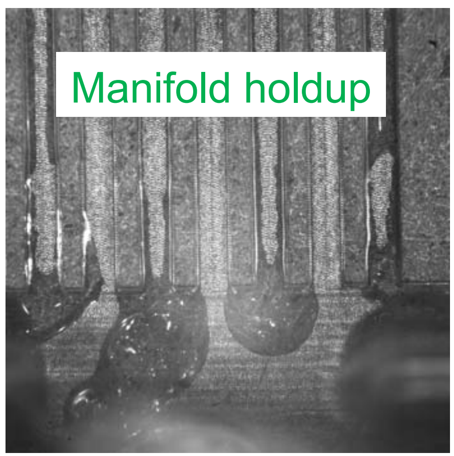
Two-Phase Flow Patterns



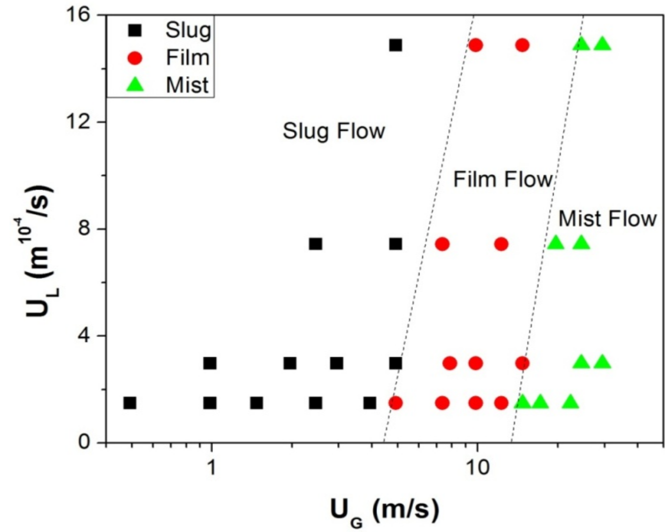




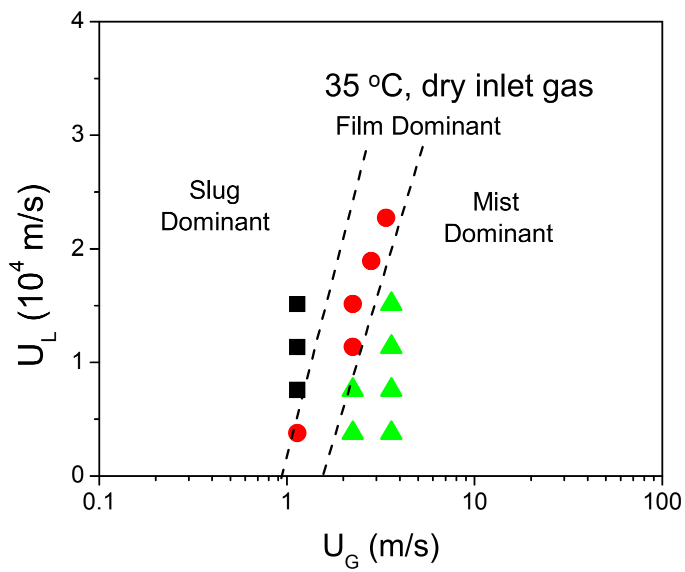




Ex-situ Flow Pattern Map



In-situ Flow Pattern Map

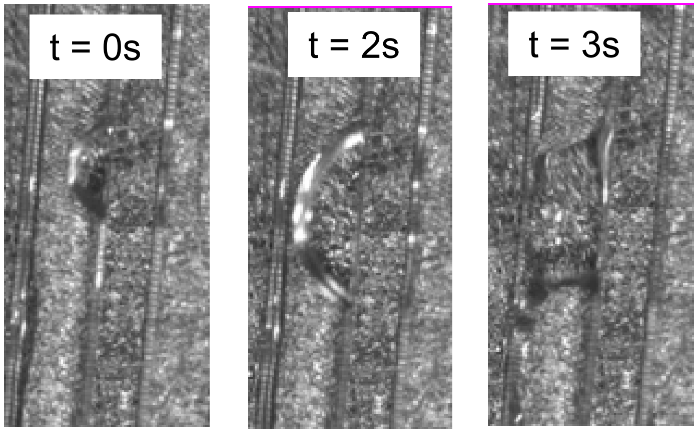


- Three basic flow patterns observed: Slug Flow, Film Flow and Mist Flow in both in-situ and ex-situ experiments.
- Slug flow is highly undesirable as it leads to severe flow maldistribution.
- Manifold water holdup adversely affects channel flow.

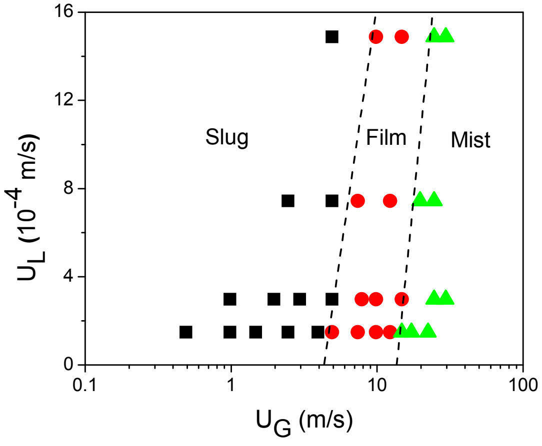
Technical Accomplishments–

Slug Formation and Droplets on Channel

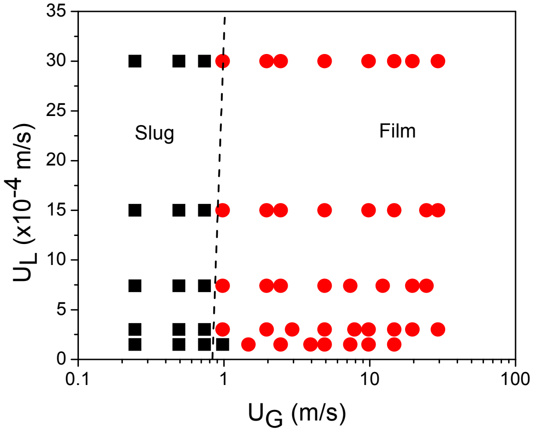
- ❑ An important trigger for the slug formation in channel is the large stationary droplets on the channel wall.
- ❑ The critical droplet size is a function of
  - ➢ channel contact angle
  - ➢ channel contact angle hysteresis.



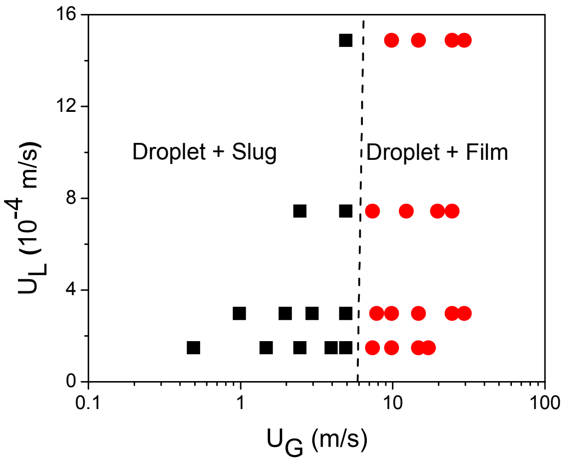
Non-treated channel
θ ~ 60º



Hydrophilic channel
θ ~ 15º



Hydrophobic channel
θ ~ 100º



- ❑ Hydrophilic channels are preferred as they promote film flow rather than slug flow.
- ❑ Large contact angle hysteresis is not desirable as it promotes slug formation.

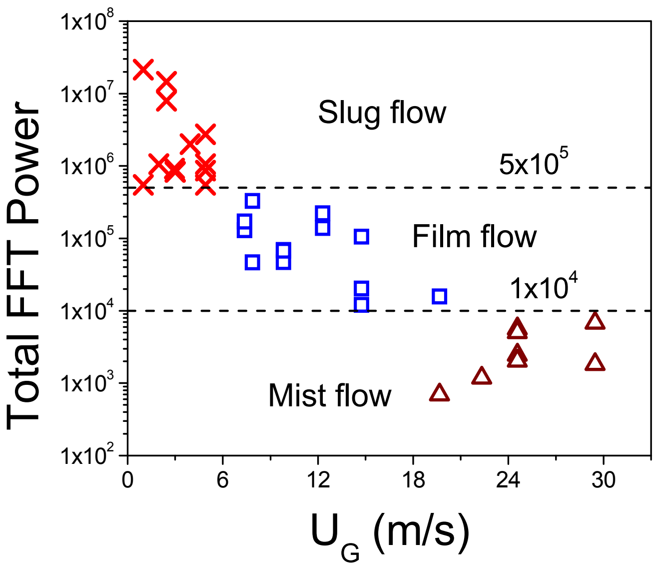
Pressure Drop Signature and Liquid Holdup

Fourier Transform Analysis:

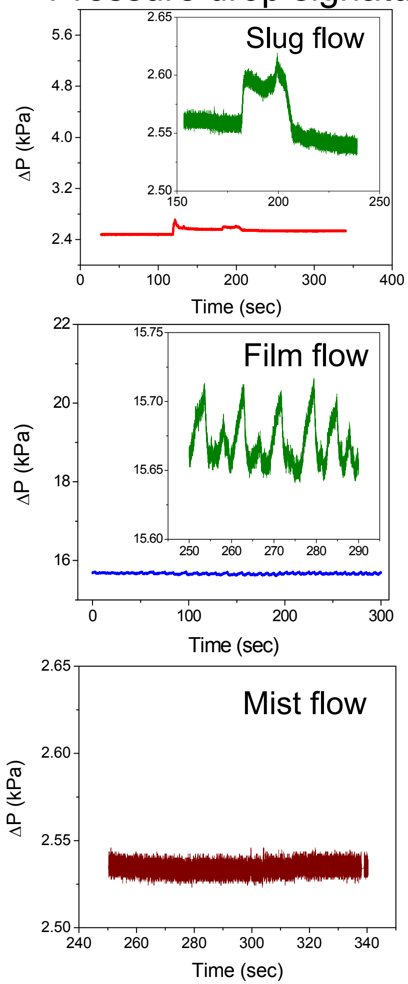
$$F\{x_i(t)\} = \sum_{i=0}^{n-1} x_i(t) e^{-j2\pi ik/n}$$

$$F(k) = Re + jIm$$

$$M = \sqrt{Re^2 + Im^2}$$

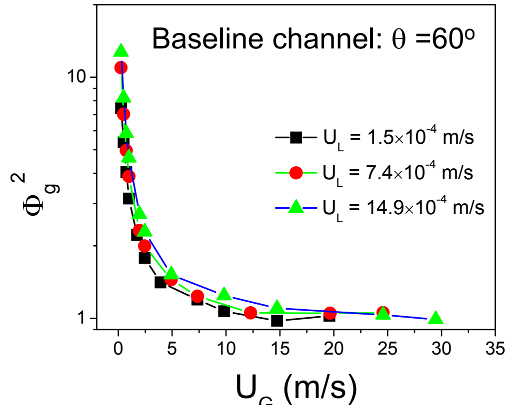


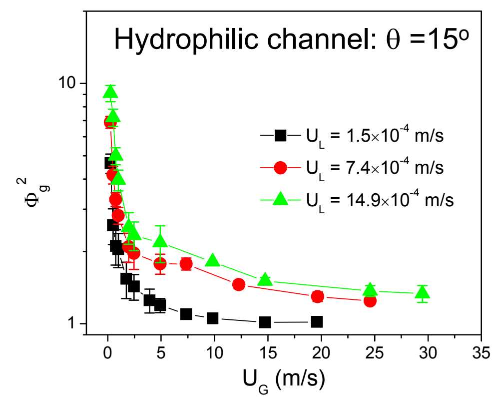
Pressure drop signature:



Flow pattern Identification

Two-phase friction multiplier : $\Phi_g^2 = \frac{\Delta P_{2\phi}}{\Delta P_g}$





- ❑ Two-phase multiplier is able to serve as the flow pattern indicator: High Φ_g^2 → slug flow; lower Φ_g^2 → film flow; Φ_g^2 =1 → mist flow.
- ❑ Hydrophilic channel has a lower water holdup in the low gas flow region, and a higher water holdup in the high gas flow region.

Collaborations

RIT:

- RIT, GM: Development and Integration of Novel Materials for Hydrogen Fuel Cells Applications: experimental study of water generation and transport in gas diffusion media, NYSERDA , February 2008 – May 2009

MTU:

- MTU: Hydrogen Education Curriculum Path at Michigan Technological University, DOE DE-FG36-08GO18108
- MTU, State of Michigan: Fuel Cell Water Control System Prototype – Alternative Energy, Michigan Universities Commercialization Initiative (MUCI)
- VirginiaTech, U. Louisiana-Lafayette, Purdue, MTU: Micro-Hydroforming Processes for Enhancement of PEM Fuel Cell Water Management and Component Manufacturing (NSF Proposal 0900435)
- MTU: Center for Fundamental and Applied Research in Nanostructured and Lightweight Materials (CNLM), DOE DE-FG36-08GO88104

GM:

- NIST: "Partnership for Neutron Imaging of Fuel Cells," December 2008 - December 2009.

Proposed Future Work for FY09

MATERIAL SET for Combinatorial Performance Evaluation

CHANNEL

- Implement changes to flow field channel to incorporate the channel geometries which are representative of high volume manufacturing processes (stamped metal and molded carbon composite):

  (i) sinusoidal, and (ii) trapezoidal cross-section (RIT, GM)
- Further adjust the channel surface treatment and assess its effects on the water transport and holdup in channels. (RIT, GM, MTU)
- Develop predictive tools for water hold-up and two-phase flow in channels. (RIT, MTU).

GDL

- Evaluate the effects of GDL thickness and thermal conductivity on water transport and assess the in-situ combinatorial performance. (RIT, GM, MTU)
- Incorporate GDL compression into network model. (MTU)
- Examine the formation of ice and freeze propagation in GDL. (GM, MTU)

PURGE PERFORMANCE

- Evaluate purge performance of the Phase 2 material set, involving GDL and channel materials which are known to accumulate less liquid water under steady-state conditions (GM).
- Evaluate purge performance of GDL and channel materials with spatially varying properties (GM).
- Combine neutron imaging with printed circuit board measurements of distributed current density, high-frequency resistance and temperature to support pseudo-2D ("down-the-channel") model representation of the shutdown purge process (GM).
- Evaluate freeze start performance of optimized material set, combined with optimized shutdown purge protocol (GM).

Summary – Water Management under Freezing Conditions

Drivers:

- Shutdown Energy: 2010 DOE target of 5 MJ.
- Start-up Time: 30 sec. to 50% of rated power at -20^{o}C.
- Material degradation and performance considerations.

Accomplishments:

- Start-up characteristics:
  - membrane dryout (ionic conductivity), performance
  - ice formation and deposition – amount and location
- Water Transport:
  - location and amount (cathode vs. anode, headers, drying front, purge energy requirements), GDL water holdup, two-phase flow patterns in channels, flow pattern maps, flow maldistribution, water transport models, effect of water holdup on performance
- Material Considerations:
  - Reduced water holdup in GDL
  - Flow pattern and pressure drop characteristics in gas channels
- Identified New material set:
  - GDL thickness
  - GDL thermal conductivity
  - GDL morphology
  - Channel geometry and surface treatment