#### Water Transport Exploratory Studies



#### **2007 DOE Hydrogen Program Review**

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#### **Project Lead: Los Alamos National Lab**

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Project ID # FCP24



### Overview

#### <u>Timeline</u>

- New Project for FY07
- 4 year Project Duration

#### Budget

- Total project funding
  - DOE Cost: \$6,550,000 (4 yrs)
  - Cost Share: \$290,811
- Funding for FY07
   LANL \$1000k
   Industrial Partners \$300k
   Other National Labs \$350k
   FY07 Total 1650

#### **Barriers**

Water management is critical to optimal operation of PEM Fuel Cells

- Energy efficiency
- Power density
- Specific power
- Cost
- Start up and shut down energy
- Freeze Start Operation
   Partners
- Direct collaboration with Industry, Universities and other National Labs (see list)
- Interactions with other interested developers
- Project lead: Los Alamos National Lab



### **Organizations / Partners**

- Los Alamos National Lab

   (Lead: experimental measurements, modeling)
- Sandia National Laboratory (modeling)
- Case Western Reserve University (characterization, modeling)
- W. L. Gore and Associates, Inc. (MEAs)
- SGL Carbon Group (GDLs, MPLs)
- Oak Ridge National Lab (characterization)
- National Institute of Standards and Technology (neutron imaging)





## **Objectives**

- Develop understanding of water transport in PEM Fuel Cells (non-design-specific)
- Evaluate structural and surface properties of materials affecting water transport and performance
- Develop (enable) new components and operating methods
- Accurately model water transport within the fuel cell
- Develop a better understanding of the effects of freeze/thaw cycles and operation
- Present and publish results





## Approach

#### Develop understanding of water transport

- Experimental measurement and testing
- Characterization
- Modeling
- Evaluate structural and surface properties of materials affecting water transport and performance
  - Measure/model structural and surface properties of material components
  - Determine how material properties of GDL, MPL, catalyst layers & interfaces affect water transport (and performance)
  - Determine properties change during operation (degradation effects)
- Develop (enable) new components and operating methods
  - Prevent flooding (high power operation)
  - Prevent dehumidification (low RH operation transportation)
- Develop a better understanding of the effects of freeze/thaw cycles and operation
  - Help guide mitigation strategies.





#### **Technical Accomplishments**

- Direct water imaging at NIST by Neutrons
  - High resolution (15  $\mu$ m) cross-section cell design
    - Cross Section view
    - High resolution
  - Low resolution (150  $\mu m$ ) imaging
    - Imaging of entire 50 cm<sup>2</sup> flowfield area
- GDL Characterization
  - Hydrophobicity characterization
  - Microscopic characterization of hydrophobic coating
  - Elemental compositional characterization
- Modeling of mass transport losses
  - Delineation of mass transport loss from IR, kinetics, etc.
  - Modeling of water-droplet detachment from the GDL/channel interface.





### **GDL Material Characterization**

- GDL Characterization
  - Hydrophobicity characterization
    - Contact angle and surface energy measurements
  - Microscopic characterization of hydrophobic coating
    - SEM, TEM
  - Elemental compositional characterization
    - XPS
  - Pore size distribution measurements
    - Water and mercury porosimetry
  - Humidity Fingerprint





## **Relative Humidity "Fingerprint"**



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The Matufunction of relative humidity

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## **GDL Fiber Chemistry and Contact Angle**



- Fiber graphitization can increase single-fiber contact angle ~ 10°
- Both graphitization T and PTFE loading can change the liquidwater wetting regime of the GDL substrate.





#### **Teflon Distribution on GDLs**



### **MPL Characterization**

#### **Fresh Material**



#### **After Drive Cycle Testing**



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- Fresh Materials
  - Gaps/openings on surface of MPL where Teflon appears to have been non-homogeneously dispersed within the MPL
- After testing:

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- MPL Layer shows higher degree of porosity
- Surface includes higher degree oflong fibers (of Teflon)

## **Elemental Compositional Changes of GDL Material**



Anode GDL composition shows little change

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Cathode GDL composition is enriched in fluorine on electrode side

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Cathode GDL composition is depleted in fluorine flowfield side

## **GDL Porosimetry**



- Decrease in large-pore volume (~ 30 to 60  $\mu$ m)
- Increase in overall small-pore volume
- Decrease in hydrophobic small-pore volume

#### Hypothesis

- Large pore volume loss due to irreversible compression
- Small pore volume increase due to loss of carbon from MPL

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Fresh, ~1000 hr Aging and ~650 Fuel Cell Testing

0.4 mg-Pt/cm2 and SGL SIGRACET® GDL 24BC



## **Modeling of Mass Transport Losses**

$$\eta_{tx,elec} = (b^* - b_{ideal}) \cdot \log i_{eff} + \log \left[ \frac{(10L_{cath}A_{Pt,elec}i_{0,ideal})^{b_{ideal}}}{(10L_{cath}A_{Pt,elec}i_0^*)^{b^*}} \right]$$

$$\eta_{tx,GDL} = E_{eq}(T, p_{H_2}, p_{O_2}) - V_{iR-free} - \eta_{ORR}^*$$

- Difference in Tafel slope between dry air cathode and humidified O<sub>2</sub> cathode is basis for calculating mass-transport overpotential of electrode.
- After all other overpotentials have been calculated, balance is assigned to cathode GDL.

D. Wood, J. Davey, P. Atanassov, and R. Borup, Electrochemical Society Transactions, 3 (1), 753-763 (2006).

H.A. Gasteiger *et. al.*, Handbook of Fuel Cells, Vol. 3, Part 1, Chapter 46, pp. 593-610, John Wiley & Sons, New York (2003).

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M.V. Williams et. al., J. Electrochem. Soc., 152, A635 (2005).



## **Durability Performance Modeling Durability of iR-Corrected Overpotentials**



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• Modeling of masstransport losses extrapolated to 'overpotential'

• Definition of components leading to performance degradation

• Method for analyzing performance losses (iR, ORR, MT)

• Better understanding of long-term fuel cell test data



## Varying GDL Effect (50 cm<sup>2</sup>)

PROPERTY	UNITS	GDL A	GDL B	GDL C
Name		GDL 24 BC	GDL 24 BC	GDL 24 DC
Thickness	μm	237	231	239
Substrate Loading	% PTFE	5%	5%	20%
MPL Loading	% PTFE	23%	10%	10%
Aerial weight	$g/m^2$	101.1	105.8	117
Air Permeability	$cm^3/cm^2.s$	0.3	0.3	0.7
Specific Resistivity	mΩcm <sup>2</sup>	8.4	10.3	11.9

- GDL was varied with identical MEAs to evaluate water transport
- Standard Operating Conditions: 20 psia, 1.1/2.0 stoichs, 80 °C cell temp, 50% anode inlet RH
  - Vary GDL/MPL Teflon loading, cathode inlet RH, current density





## **Varying GDL Effect**





Low MPL teflon loading shows improved fuel cell performance

Cell Temperature =  $80 \,^{\circ}$ C Constant Stoich = 1.1 / 2.0Pressure =  $25 \,$  psia  $50 \,$  cm<sup>2</sup> active area Anode:  $0.2 \,$  mg/cm2 Pt Cathode:  $0.4 \,$  mg/cm2 Pt Anode RH: 50%Cathode RH: 50, 75, 100%

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#### **Cathode Inlet RH Effect**





 Inlet Cathode RH down to 50% does not affect performance

> Cell Temperature =  $80 \, ^{\circ}$ C Constant Stoich = 1.1 / 2.0Pressure = 25 psia  $50 \, \text{cm}^2$  active area Anode:  $0.2 \, \text{mg/cm} 2 \, \text{Pt}$ Cathode:  $0.4 \, \text{mg/cm} 2 \, \text{Pt}$ Anode RH: 50%Cathode RH: 50, 75, 100%





and Fuel Cell

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## **Comparison of Different Active Area Cells**



#### 2.25 vs. 50 cm<sup>2</sup> Performance

for Hydrogen and Fuel Cell

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- Performance of low area cells can be lower than the 50cm2 cells.
- The Institute Little pressure drop in these cells, cells may be drier at the current densities.

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#### **AC Impedance Evaluation**

#### AC Impedance Model Circuit



Anode	Cathode
GDL A	GDL C
50%RH	100%RH
25 psia	25 psia
1.1 stoich	2.0 stoich
	Anode GDL A 50%RH 25 psia 1.1 stoich





### **AC Impedance Evaluation**



- High Frequency Resistance (HFR)
  - Decreases with increasing RH
- Charge transfer resistance
  - Decreases with increasing RH
- Mass transfer resistance
  - Increases with increasing RH





### **AC Impedance Comparison**



- High Frequency Resistance (HFR)
  - Decreases with increasing current
  - Greater for GDL with 23% PTFE in MPL



- Charge transfer resistance
  - Decreases with increasing current
  - Greater for GDL with 23% PTFE in MPL
- Mass transfer resistance
  - · Increases with increasing current
  - Greater for GDL with 23% PTFE in MPL





#### **Neutron Imaging Cross-Section Design for High Resolution Imaging**

### High resolution (15 μm) cross-section cell



#### **Design Considerations:**

- Maximum field of view is 2 cm X 2 cm for the high resolution neutron detector.
  - Limits X dimension to 2 cm.
- Outermost edge to image = 3 cm from the detector for good focus.
  - Detector is 0.5 cm inset of the face plate, → 2.5 cm available
- Active area < 1 cm in length
  - Entire cell is < 3 cm from detector

#### **Design:**

- 2.25 cm<sup>2</sup> active area
- No hydrocarbon materials
- Metal hardware
  - No plate porosity of hardware for water hold-up
- 1 cm linear water imaging length
- Shallow single serpentine flowfield
  - Attempt to simulate pressure drop of real flowfields





### **Cross-Section Design for Neutron Imaging**





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#### High Resolution (15 μm) Cross-Section Water Imaging of Operating Fuel Cells

- See water in the outer walls of the serpentine flow fields
  - The flow filed near the MEA is mostly clear
- Cathode GDL contains more water than anode GDL with more water accumulating toward the outlets
  - Steeper drop in the line profile intensity (darker areas)
- More water in the GDLs above the land than the GDLs above the channel
  - Water created at catalyst layer over land needs to diffuse laterally through GDL and get to the channels before being taken away into the flow fields
- MEA (3 pixels) contains the most water





## Water Image of MEA Cross-Section GLD A

#### • More water in:

 $0.2A/cm^2$ 

Cathode 50%RH 2.0 Stoich

Anode

50%RH 1.1 Stoich

- Cathode GDL vs the Anode GDL
- Outlets vs the Inlets
- GDL above the land vs the GDL above the channel



- Less water in the flow channels at high current densities
  - Higher flow of gases keeps the channels clear of water
- Significant water content in the anode GDL near outlets
  - Back diffusion of water from cathode to anode is significant (Driven by water concentration gradient)



## Water Image of MEA Cross-Section **GLD B**

- Less water in GDL B when compared to GDL A
  - Explains better performance of GDL B esp. at higher current densities
  - Teflon content in the microporous layer (10wt% vs 23wt%) has a major influence on water transport
  - Higher teflon content in the MPL leads to flooding



High water density at the cathode GDL • More near the outlet and over the land area

 $0.2A/cm^2$ Cathode 50%RH

Anode 50%RH

Anode

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Higher water content everywhere when compared to the • low RH/low current density operation



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## Water Image of MEA Cross-Section GLD C

- Similar water in GDL C when compared to GDL B
  - Explains the better performance when compared to GDL A
  - Explains the similar performance of this GDL to GDL B
  - Teflon content in the substrate (5 wt% vs 20 wt%) does not have a major role in determining water content



## Water Image of Flowfield (50 cm2 **MEA) GLD A**

- More water accumulation near the inlet at higher cathode inlet RHs/high current density
- Water accumulates at the turns of the serpentine flow channels

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• Low gas flow rate leads to more water in the channels especially near the outlet



## Water Image of Flowfield (50 cm2 MEA) GLD B

- More water accumulation near the inlet at higher cathode inlet RHs high current density
- Water accumulates at the turns of the serpentine flow channels
- Low gas flow rate leads to more water in the channels especially near the outlet



#### Water Image of Flowfield (50 cm<sup>2</sup> MEA) GLD C

- More water accumulation near the inlet at higher cathode inlet RHs high current density
- Water accumulates at the turns of the serpentine flow channels
- Low gas flow rate leads to more water in the channels especially near the outlet



## **Durability of Cloth and Paper GDLs Slow Freeze/Thaw Cycles**



Fully humidified cells: T<sub>room</sub> to -40°C in 3 hours No change for cloth backing MEA; Significant degradation for paper backing MEA after -40-80°C FT cycling





## Durability of Paper GDLs fast Freeze/Thaw Cycles



#### Freeze Thaw Cycles (-40 to 80°C)

Significant mass transport problem after 80 FT cycles for paper GDL Accelerated testing Fully humidified cells Fast cooling rate (30 mins from 80°C to -40°C) Resistance increases more at lower potentials

Previous results (confocal microscopy) have shown problems with fiber breakage



#### **Predicting the Onset of Water-Droplet Detachment**

Motivation: droplet detachment from GDL/channel interface is a key mechanism for liquid-water removal in PEM fuel cells. Elucidating water-droplet detachment from GDL/channel interface and being able to predict the critical air-flow velocity required to detach droplets can provide useful design and operational guidelines.



Schematic of water-droplet growing and being deformed by flowing air drag at the GDL/flow-channel interface

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### **Simplified Model**

Force balance on water droplet at onset of detachment: (assumption: pressure drag due to inertial effect dominates)

Pressure drag exerted = Surface tension acting on droplet surface along contact lines

Solving for the critical air-flow velocity,  $V_c$ , yields<sup>\*</sup>:

$$V_{c} = \left[\frac{H_{c}}{\rho\mu}\right]^{1/3} \left[\frac{\pi\gamma\sin^{2}\theta_{s}\sin\frac{1}{2}(\theta_{a}-\theta_{r})}{5(\theta_{s}-\sin\theta_{s}\cos\theta_{s})d}\right]^{2/3}$$

#### Where:

- d = water droplet diameter,  $H_c$  = channel height,  $\rho$  = density,  $\mu$  = viscosity,  $\gamma$  = surface tension,  $\theta_s$  = static contact angle,  $\theta_a$  = advancing contact angle,  $\theta_r$  = receding contact angle.
- The critical air-flow velocity increases rapidly with decreasing droplet size  $(V_c \sim d^{-2/3})$ ;  $V_c$  also increases with raising channel height and decreasing  $\rho\mu$ .
- Making GDL surface more hydrophobic (i.e., increasing static contact angle,  $\theta_s$ ) and less rough (i.e., lowering contact-angle hysteresis) reduces critical velocity,  $V_c$ .

\*Reference: Chen, K. S., "A simplified model for predicting the critical air-flow velocity at the onset of water-droplet detachment in PEM fuel cells", manuscript in preparation.

Ken S. Chen (kschen@sandia.gov)



#### **Effects of GDL Properties on** Water-Droplet Detachment

#### Sample prediction and model validation



- Model yields good agreement with experimental data.
- More hydrophobic GDL reduces the critical velocity required to detach water droplets.
- Decreasing contact-angle hysteresis (e.g., reducing GDL surface roughness) enhances droplet removal.



#### Effect of contact-angle hysteresis





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## *Internal* contact angle to water and surface energy of the GDL matrix:

➤Technique developed at Case

Define properties which affect the capillary action in the <u>GDL</u> <u>pores</u>, rather than GDL surfaces.

Sample	<i>Ө</i> н20 [ <sup>0</sup> ]	$\gamma^d_{SV}$	Y SV	$\gamma_{sv}$
30% PTFE carbon type 1	89±3	13±1	8±2	21 ± 2
70% PTFE carbon type 1	101±3	$13.8 \pm 0.8$	3.1±0.8	17 ± 1
30% PTFE carbon type 2	88±7	14 ± 2	8±3	$22 \pm 4$
70% PTFE carbon type 2	96±7	14 ± 2	4±2	19±3



V. Gurau et al., Journal of Power Sources, 160, (2006), 1156-1162

#### CASE WESTERN RESERVE UNIVERSITY

## In plane, through-plane, viscous and inertia permeability for micro-porous layers and macro-porous substrates of GDLs

Developed apparatus and measurement techniques

Correlate GDL structure with transport properties



V. Gurau et al., Journal of Power Sources, 165, (2007), 793-802

#### CASE WESTERN RESERVE UNIVERSITY

P-P-P

# New method for capillary pressure measurements in GDLs:

Motivation:

Inherently, catalyst layers lack the flexibility to control the amount of water that resides in their pores during fuel cell operation;

SGDLs may be designed to promote or inhibit water flow out of the catalyst layer pores; to achieve this, one needs to be able to asses the capillary pressure as function of water saturation  $P_c(s)$  in the GDL;



#### CASE WESTERN RESERVE UNIVERSITY

# New method for capillary pressure measurements in GDLs:

The new method consists in monitoring simultaneously

≻the liquid water pressure

➤ the water saturation in an REV of the GDL sample using neutron imaging (at NIST)

Advantage:

The method is dynamic; no need to wait until saturation equilibrium is achieved in the sample (usually needs more than 24 hours to reach equilibrium for a single point);

Status:

➢Apparatus was built at Case

➢April 28-29, prove of concept scheduled at NIST using 3M GDL samples (micro-porous layer applied on polyimide films)

- Developed two-phase model for PEMFC (flow field, GDL, catalyst layer and membrane)
- Capture two-phase transport and equilibrium:
  - *within* the fuel cell components (GDL, catalyst layer, membrane)
  - *between* the fuel cell components (droplet formation at channel-GDL interface and saturation equilibrium at GDL-catalyst layer interface)
- Capture competing mechanisms of water transfer between the catalyst layer pores and the ionomer distributed in the catalyst layer:
  - •Sorption/desorption
  - •Electro-osmotic drag of water out of the ionomer by the secondary current (dominant mechanism, not identified in the past)

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Study the effect of the GDL structural properties on the amount of water accumulated in the GDL and the catalyst layer during fuel cell operation



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Study the water dynamics in the fuel cell components



Dynamics of liquid water stream-lines in GDL and catalyst layer (play animation)

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CFX#

Study the electro-osmotic drag of water out of the ionomer by the secondary current:

•Phenomenon identified and quantified solely by means of mathematical analysis;

$$S_{\lambda(drag \text{ sec ondary current})} = -n_{drag} \frac{\left(a \cdot i_0\right)_{cathode}}{F}$$

•Is the dominant mechanism of water transfer between ionomer and catalyst layer pores (sorption/desorption is slow, being diffusion controlled)

•Water content in ionomer (●) may be lower than initially predicted when this phenomenon was ignored

•Additional experimental evidence needed to substantiate it; Demonstrate it with apparatus built at LANL

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Study two-phase equilibrium at channel-GDL interface

- •Equilibrium influences the amount of water contained in GDL
- •Currently the model incorporates Tate's law as condition for droplet detachment;
- •Needs to implement the more advance model developed at Sandia

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### **RH Transient Tracking Testing**

- Realistic drive cycle operation will include:
  - Relative humidity, Temperature, Pressure as a function of power level during drive cycle
  - Shut-down/Start-up





#### **RH Transient Tracking Testing**

#### FUEL CELL TEST STATION WITH GAS FLOW HUMIDIFICATION TRACKING AND STOP/START SIMULATION





LEGEND:

Use multiple MFCs for anode/cathode with/without humidification to enable fast inlet humidity transient response



### **Future Work**

- Water Balance Measurements
  - Transient inlet RH measurements
- NIST Neutron Imaging (May 19 23)
  - Hydrophillic catalysts
  - Freeze Operation
- Freeze Measurement
  - in situ monitoring of ice formation
- Two-phase model development
  - Analyzing flow mal-distribution among PEM fuel cell channels.
  - Sub-model of liquid-water removal due to evaporation at the liquid/gas interface.
  - Develop a multi-dimensional (quasi-3D) model of water transport and removal
    - incorporate sub-models of liquid-water removal via droplet detachment and evaporation





## **Summary**

- Changing mass transport properties during fuel cell operation lead to decreased performance
  - GDL material properties change during aging
  - Mass transport decay correlates to hydrophocity loss of GDL
  - Fluorine redistributes in GDL during start/stop operation
- Teflon loading in GDL and MPL affects water transport
  - Greater mass transfer resistance for GDL with 23% PTFE in MPL
  - Substrate Teflon content does not have major role in determining water content
- Neutron imaging shows water distribution of flowfield and of MEA crosssection
  - Water build-up in flowfield of both anode and cathode at constant stoichiometric operation
- Freeze/Thaw
  - Significant mass transport problem after 80 FT cycles for paper GDL
- Modeling predicts:
  - More hydrophobic GDL materials reduce the critical velocity required to detach water droplets.
  - Decreasing contact-angle hysteresis (e.g., by reducing GDL surface roughness) enhances droplet removal.



