PEM Fuel Cell Material Research

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Areas of Interest

- **Michael Fowler – Assistant Profession in Chemical Engineering at University of Waterloo (since 2004)**
- **Currently supervising (or co-supervising) 7 Graduate students**
- **Principal Areas of Interest**
  - **Reliability of Fuel Cell Materials (MEAs), Stacks and Systems**
  - **Membrane Electrode Accessibly Degradation Studies**
  - **Conductive Polymers for Bi-polar Plates**
  - **Hydrogen Energy System Design and Modeling**

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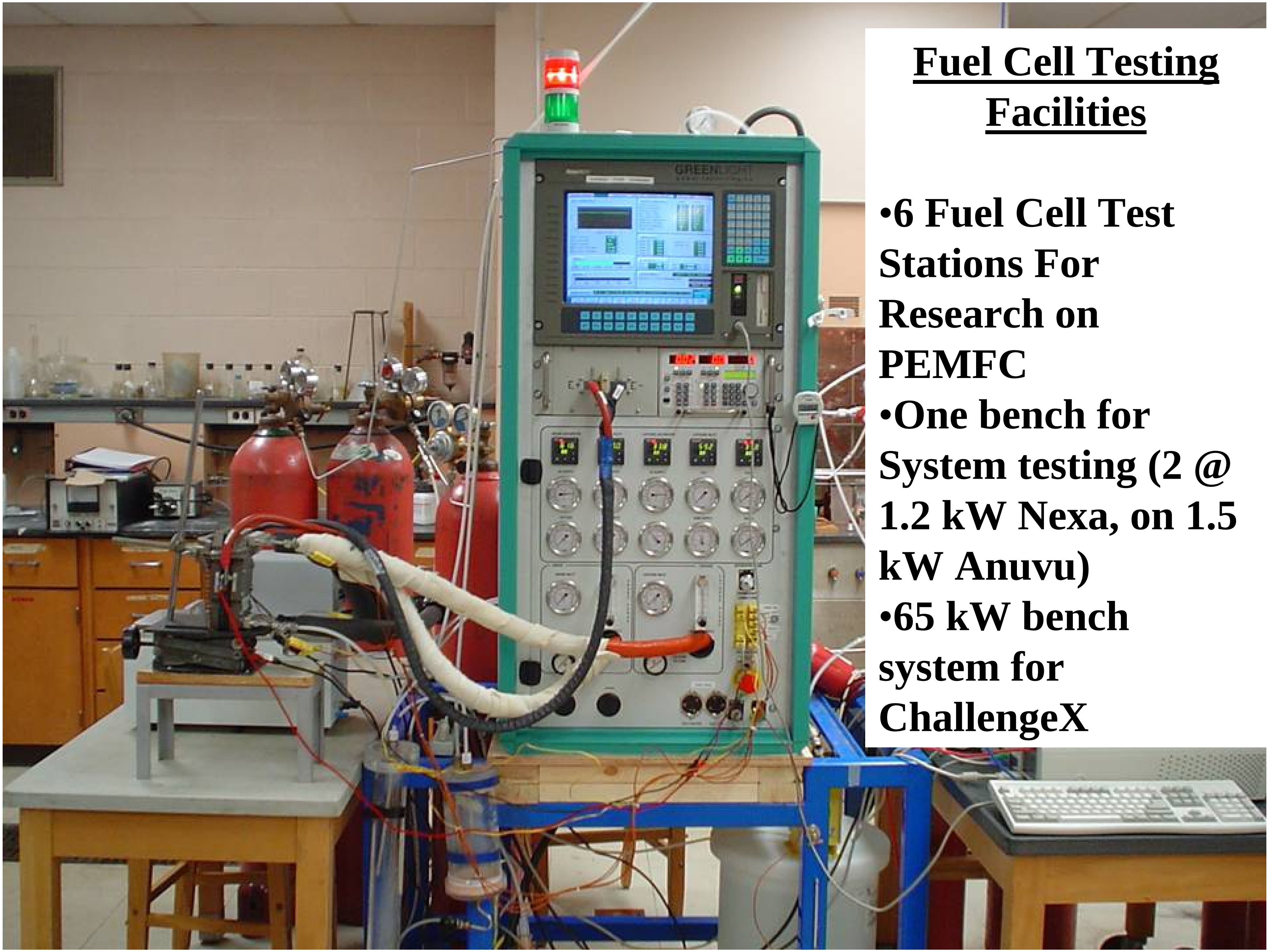
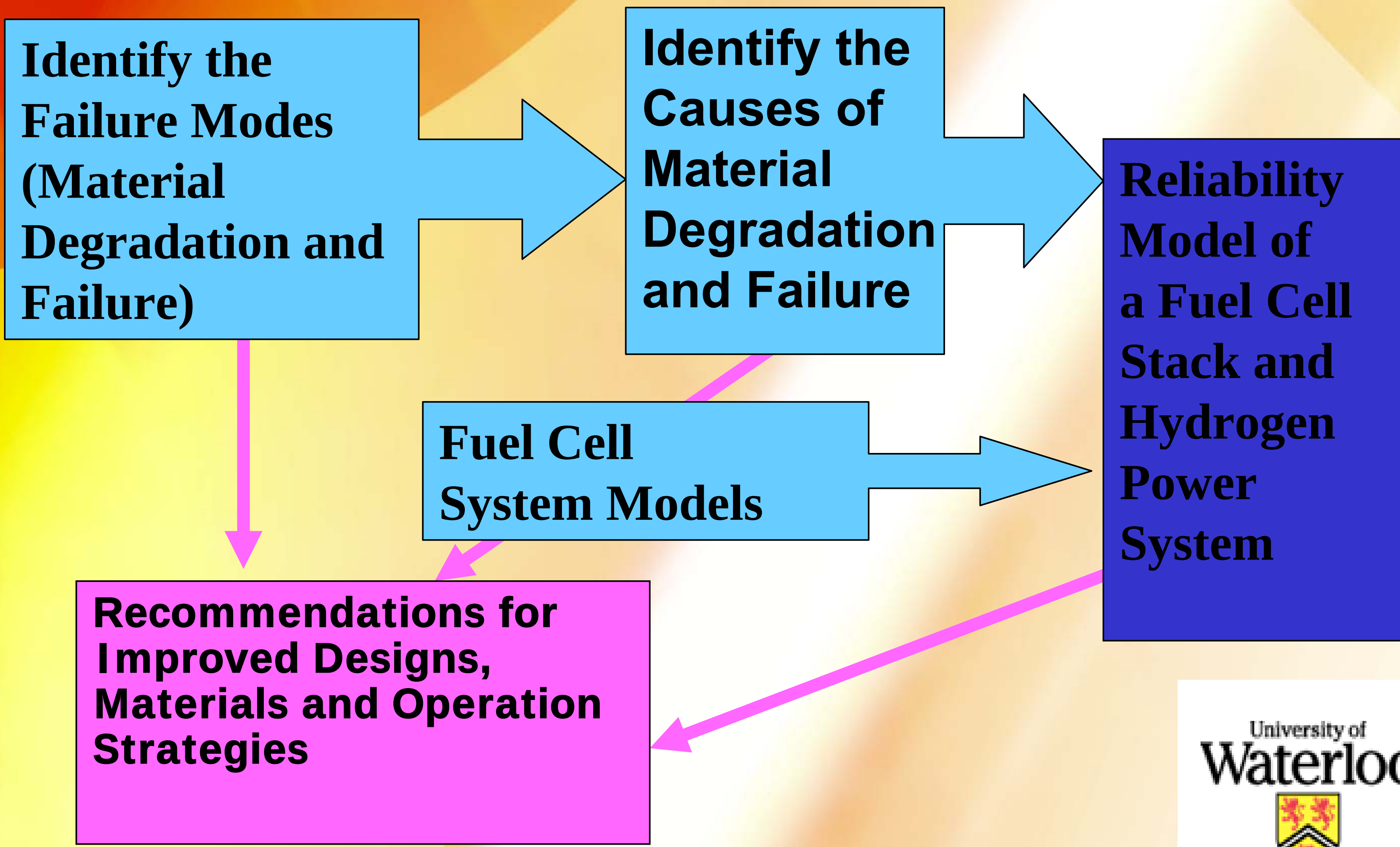


Fuel Cell Testing Facilities

- •6 Fuel Cell Test Stations For Research on PEMFC
- •One bench for System testing (2 @ 1.2 kW Nexa, on 1.5 kW Anuvu)
- •65 kW bench system for ChallengeX

Reliability Modeling



Membrane Electrode Degradation (MEA)

- **To understand the degradation of fuel cell materials**
- **To understand how operational conditions impact the mechanism and rate of degradation**
- **To understand the 2-D distribution of the above over the active area of the MEA**
- **What is done in the Lab:**
  - **Performance Assessment**
  - **Diagnostics**
  - **Forensics**

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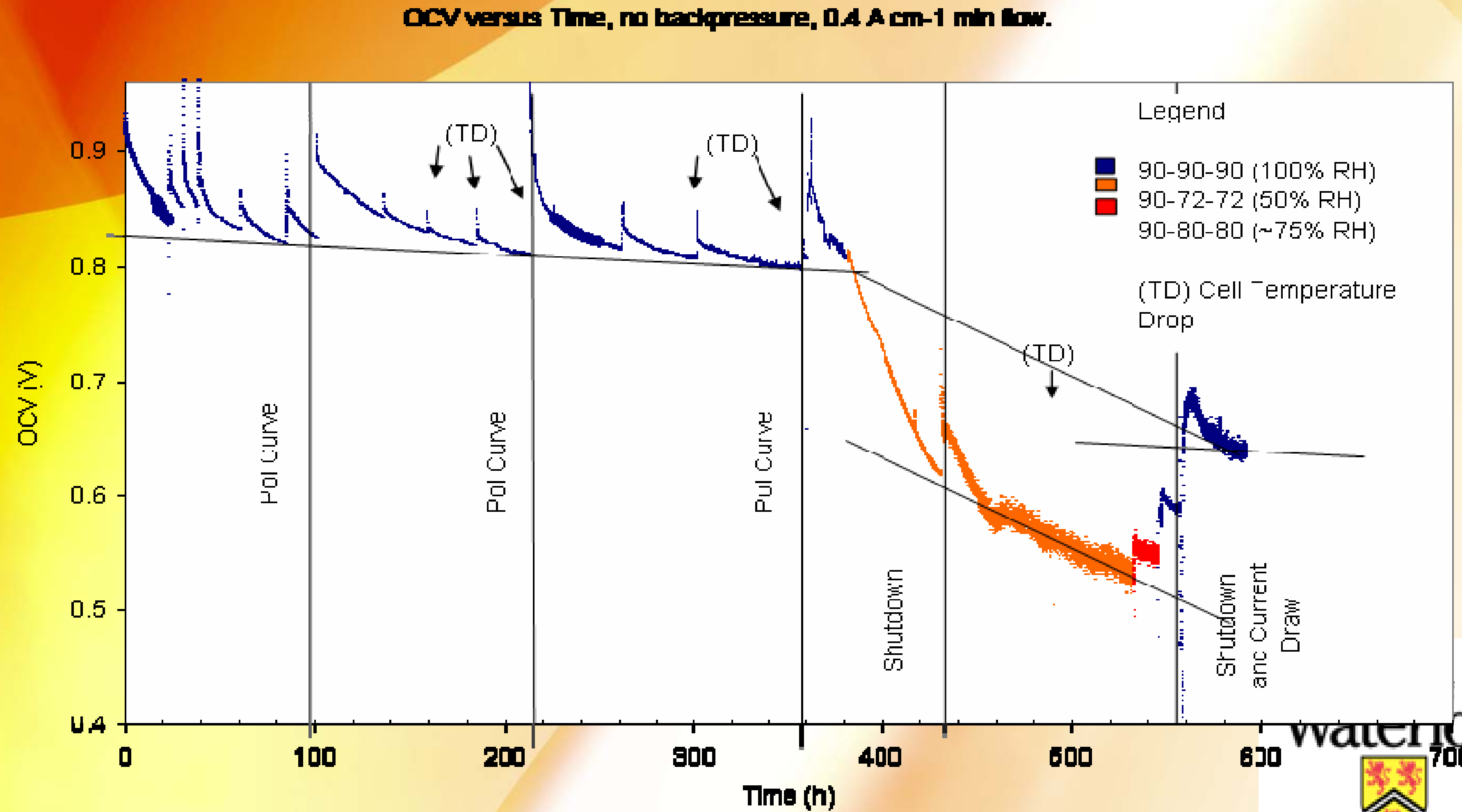
Current Work – Performance Assessment

- In-situ
  - Durability, OCV Testing, Hydration Cycling



Current Work – Performance Assessment

- Ex-Situ
  - Fenton's/Perox 80 Tests
  - Hydration cycling
  - Creep

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Current Work - Diagnostics

- The main cell diagnostics are
  - CV, Crossover current, AC impedance, Fluoride release rate,
- Ex-situ testing also includes
  - Mass, FTIR, DMTA, Tensile testing

Current Work - Forensics

- Forensic work is necessary when trying to understand the impact of degradation
  – e.g. SEM, Cryo-microtome, Crossover mapping, Catalyst removal

Modeling

- FEM stress modeling
- 2-D degradation model with OH radical and mechanical degradation.

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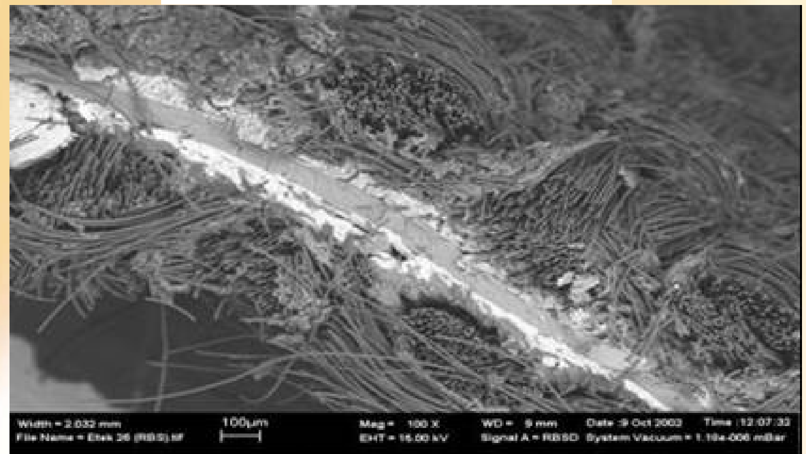
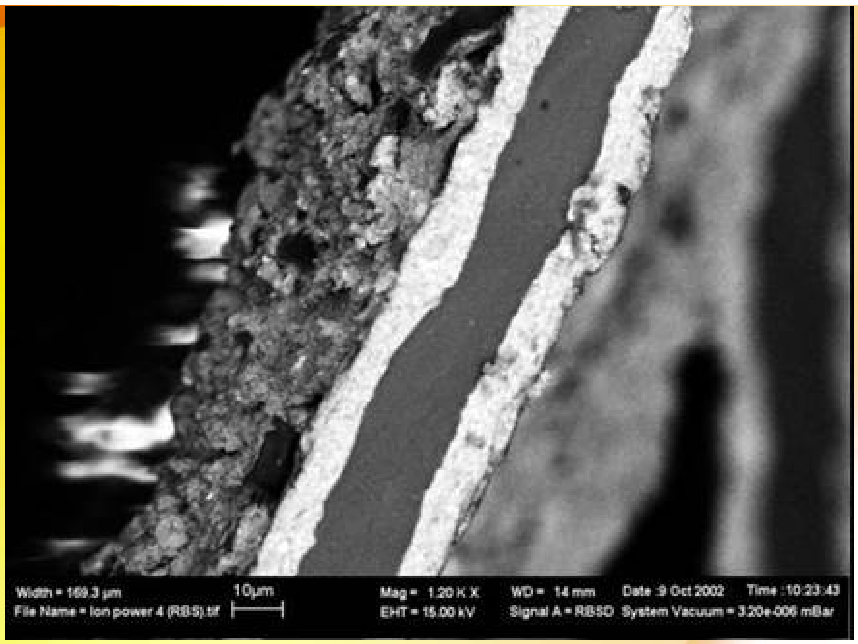
Forensics:
- Membrane Electrode Assembly

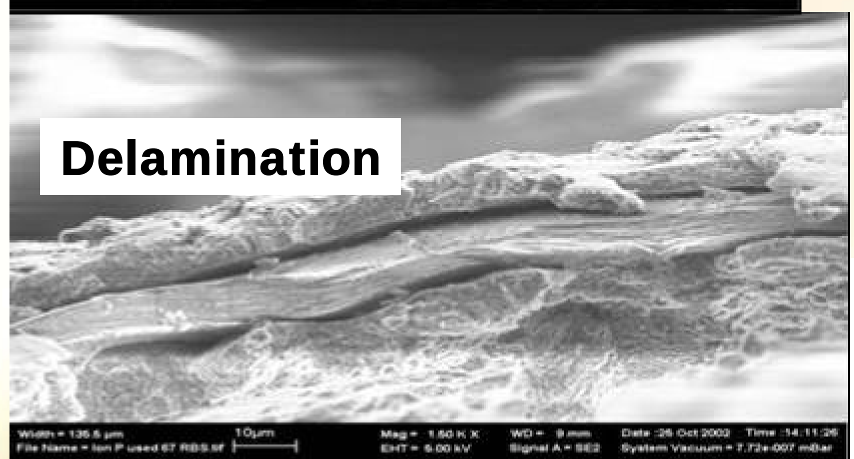
Pinholes and GDL Degradation



Contamination, Polymer degradation And Erosion

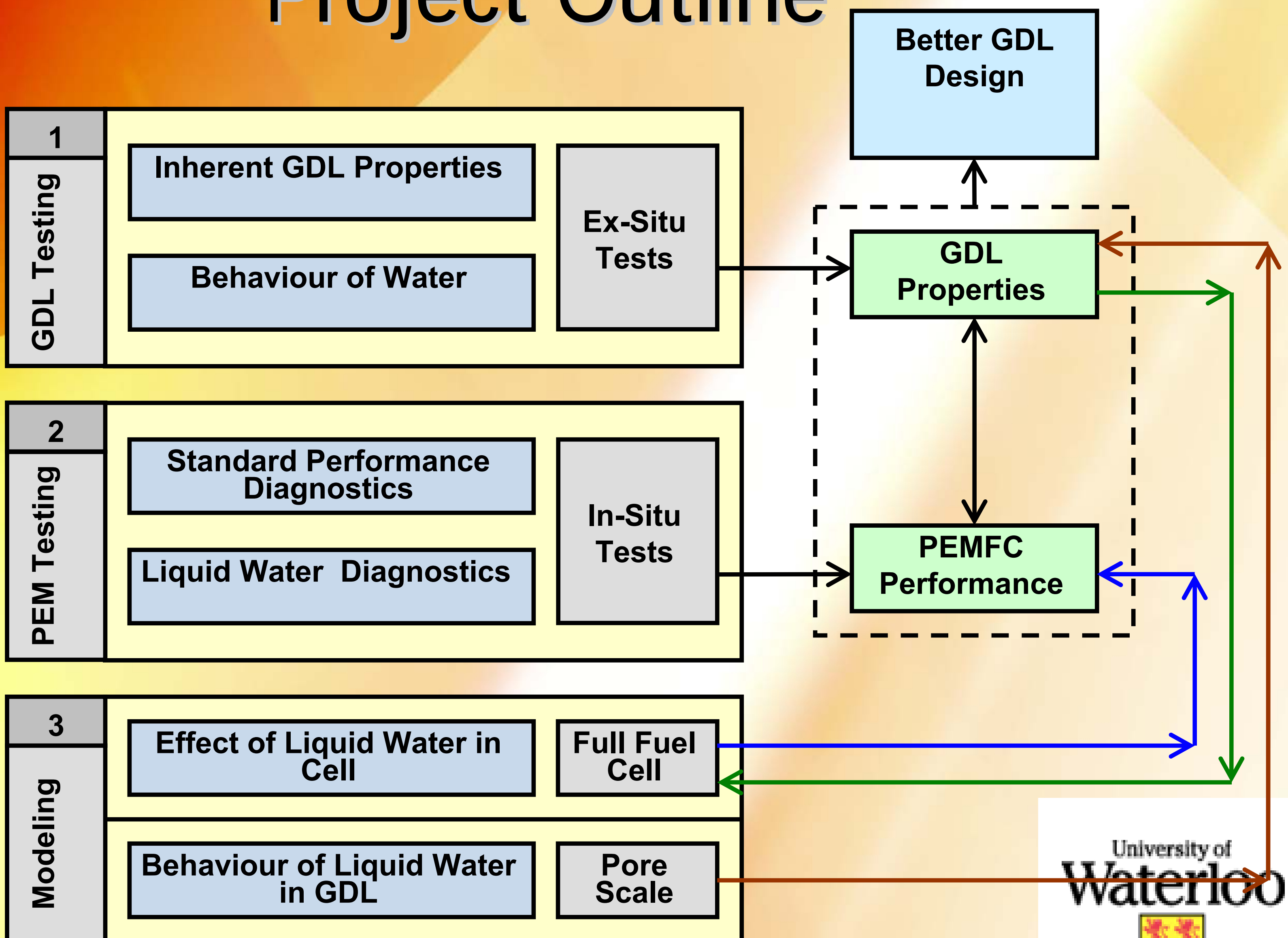


Delamination



Gas Diffusion Layer (GDL)

Project Outline



Degradation of Gas Diffusion Layer

GDL Properties

- Capillary Pressure Curves
- Hydrophilic Pore Fraction
- Distribution of PTFE
- Gas and Liquid Permeability
  - Thru Plane
  - In Plane
- Relative Permeability
- Compression Effects
  - Young's Modulus
  - Permeability
  - Porosity

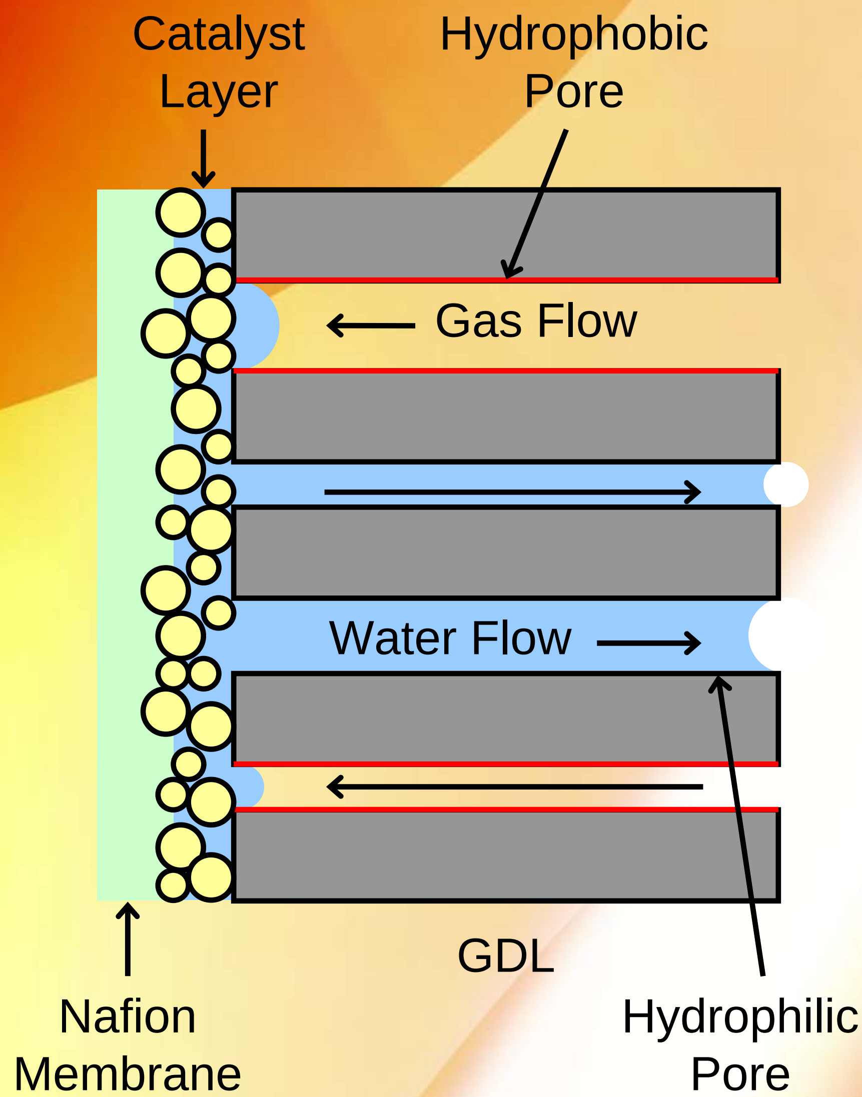
GDL Performance

- In Situ Saturation Tests
  - Current Interrupt, Water Collection, etc.
- Mass Transfer Tests
  - Limiting Current, AC Impedance.

PEMFC Model

- Model water transport at the cell scale
- Use *appropriate* models and well known parameters

Hydrophobic GDL



Conventional Wisdom:

PTFE treatment confines water to a subset of pores, assuring open pores for gas transport

Hydrophilic Pores:

Pores into which water spontaneously imbibes.

Saturation:

Fraction of pores filled by water

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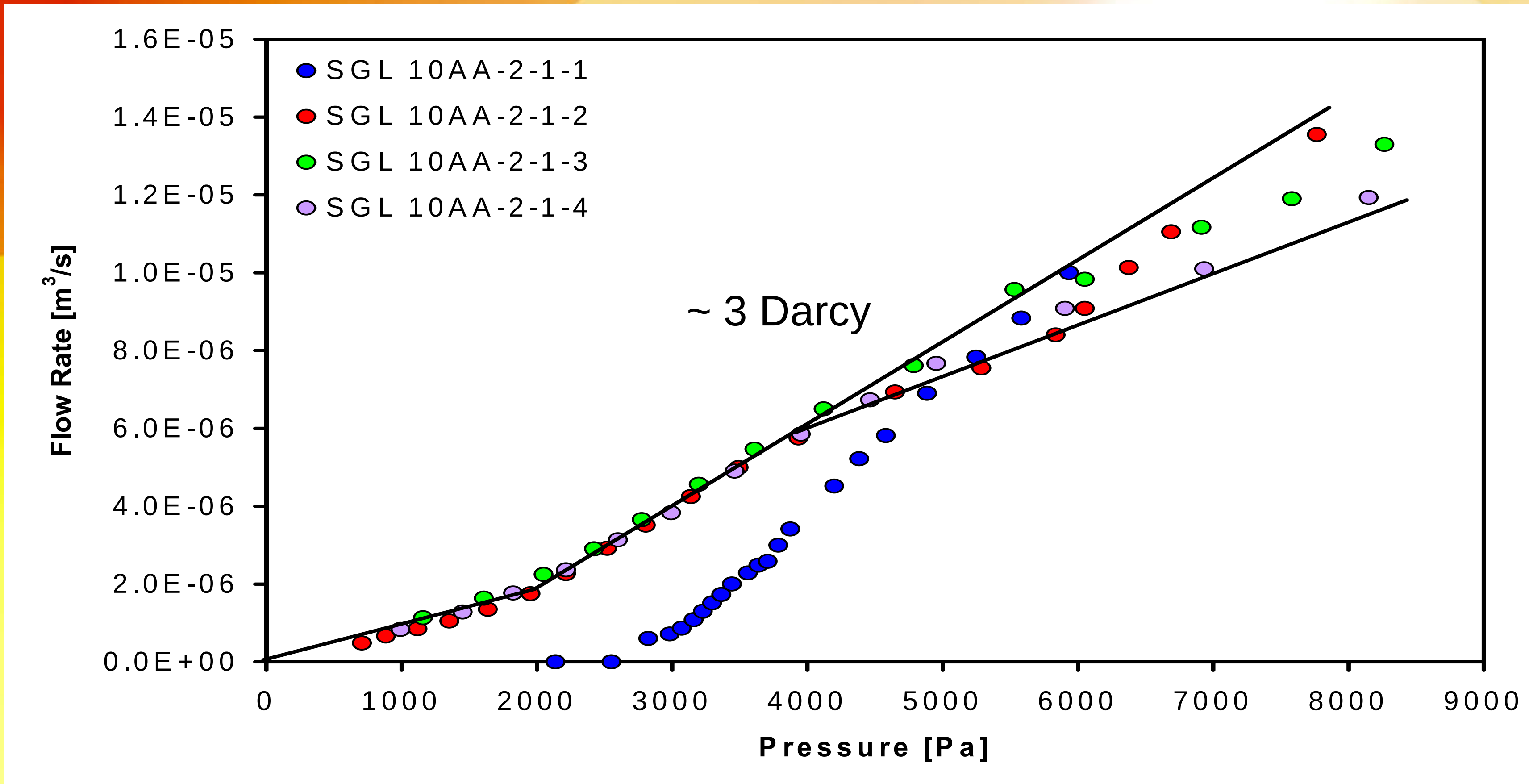
Liquid Permeability – Thru Plane



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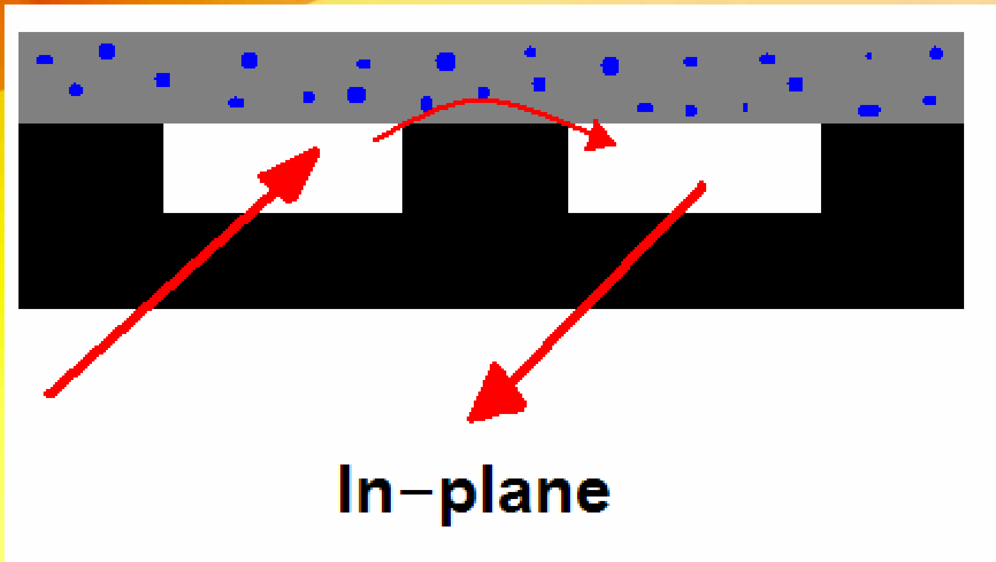
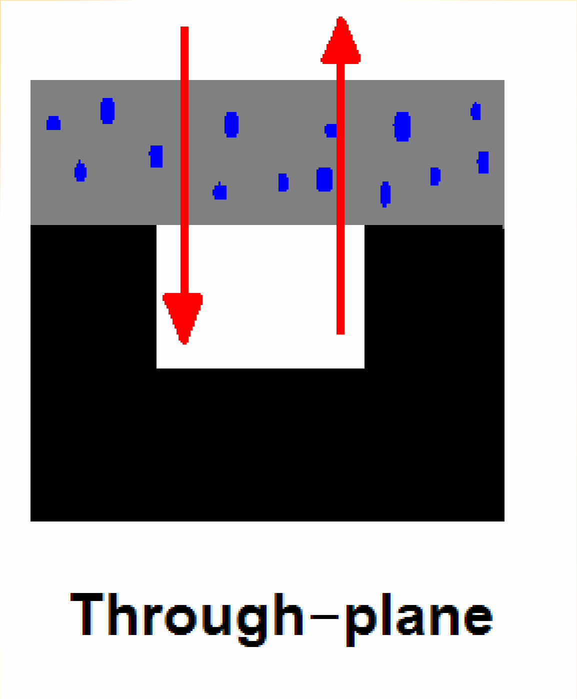
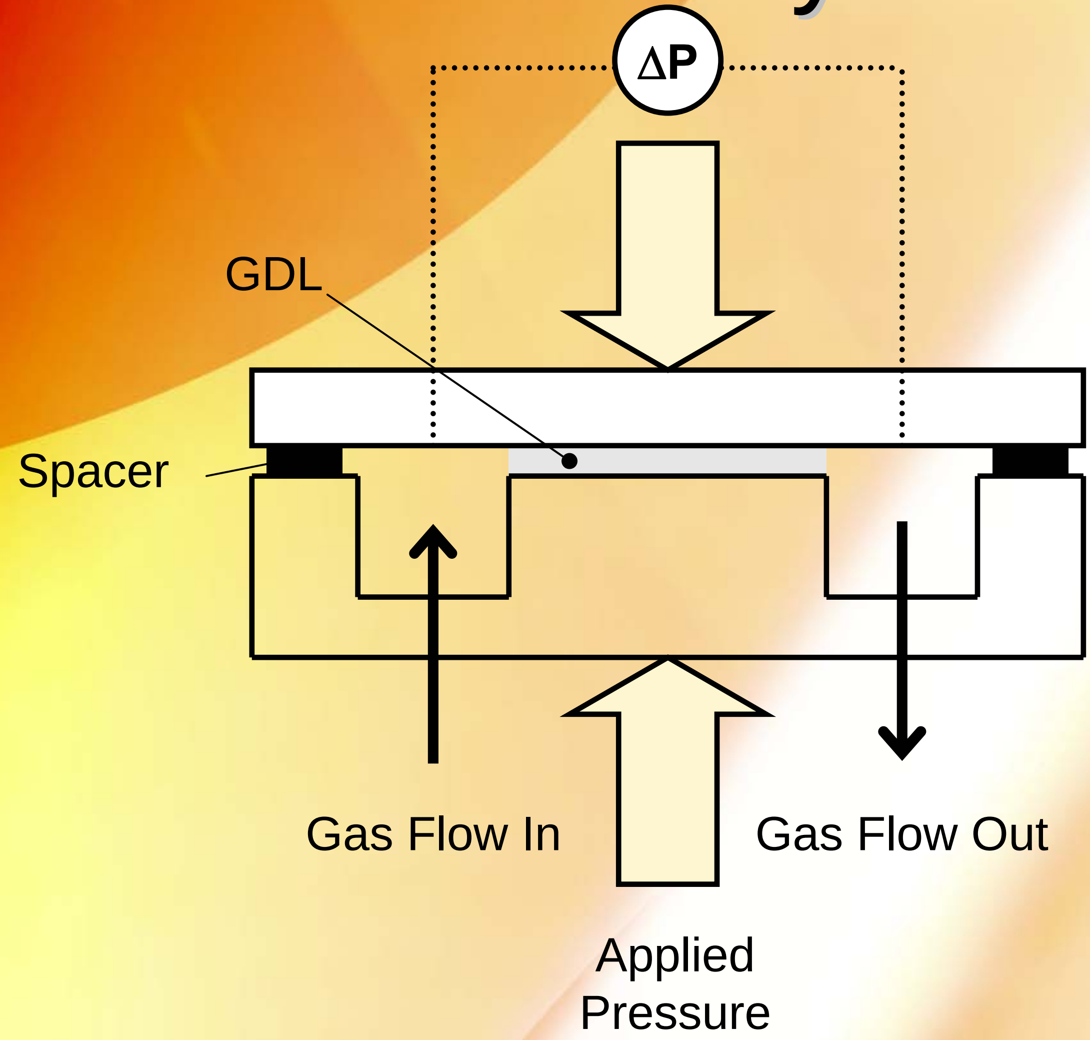
Mass transfer in-plane and through-plane in GDL

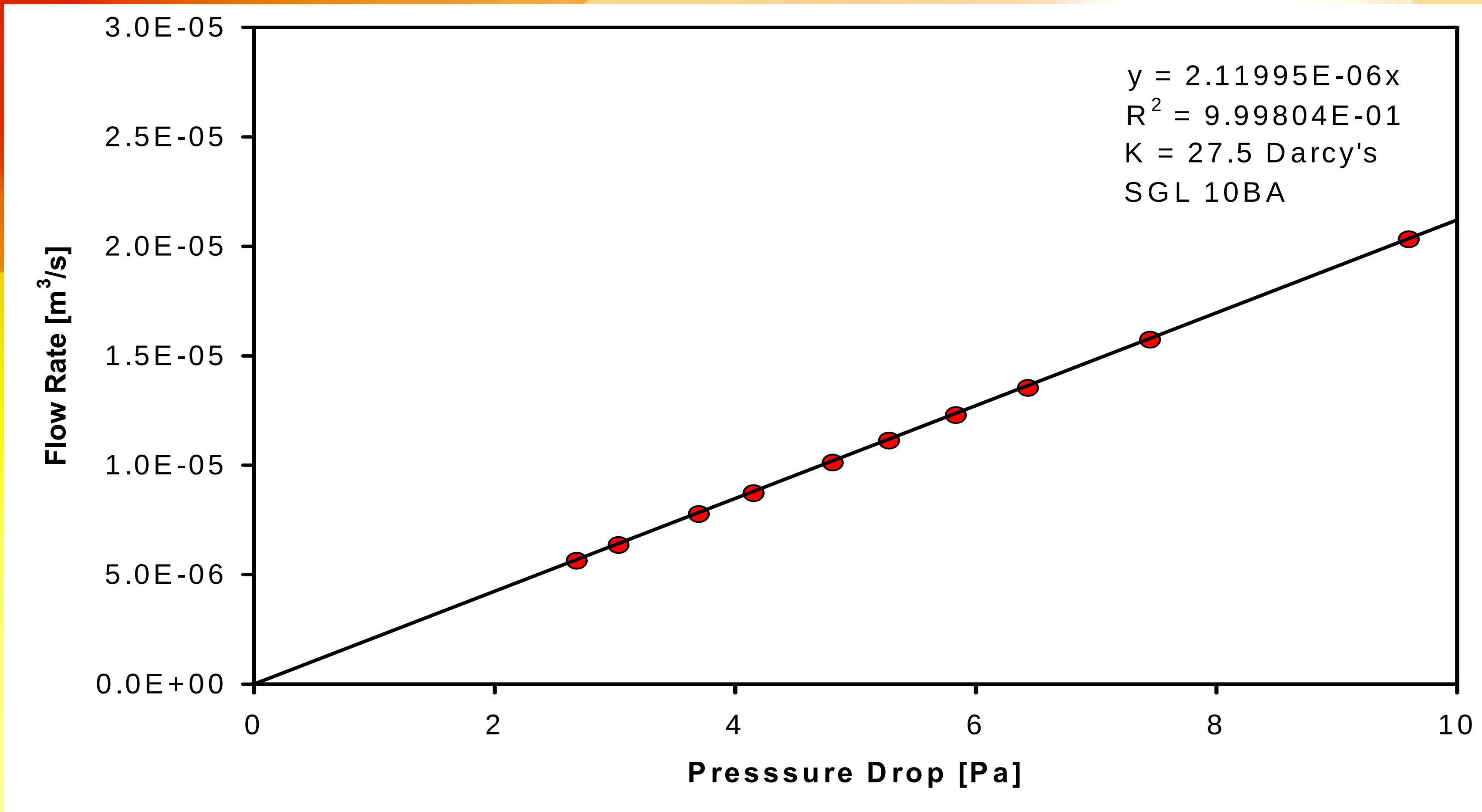




Gas Permeability – In Plane

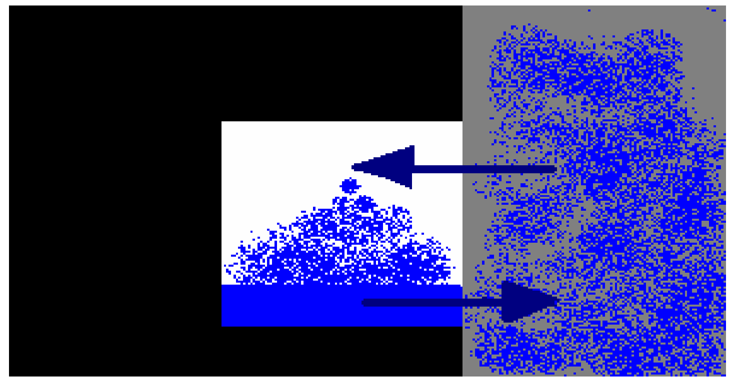


Gas Permeability – Thru Plane

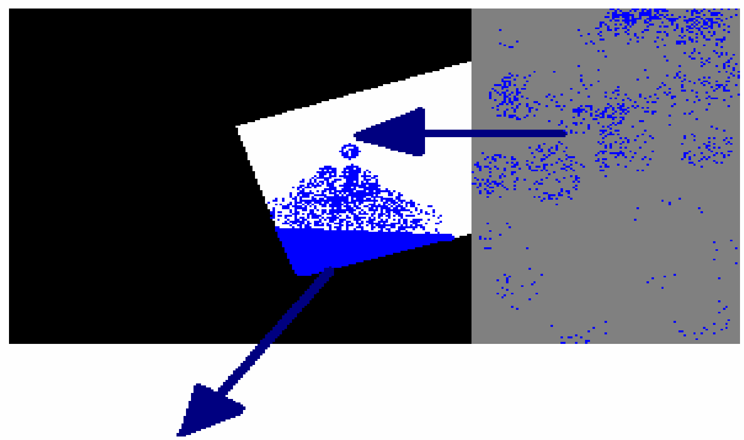


Characteristic of the channels

Traditional channel



Modified channel



Other MEA Initiatives

- Innovative Catalysis Distribution in the Electrode
- Low Cost Conductive Polymers

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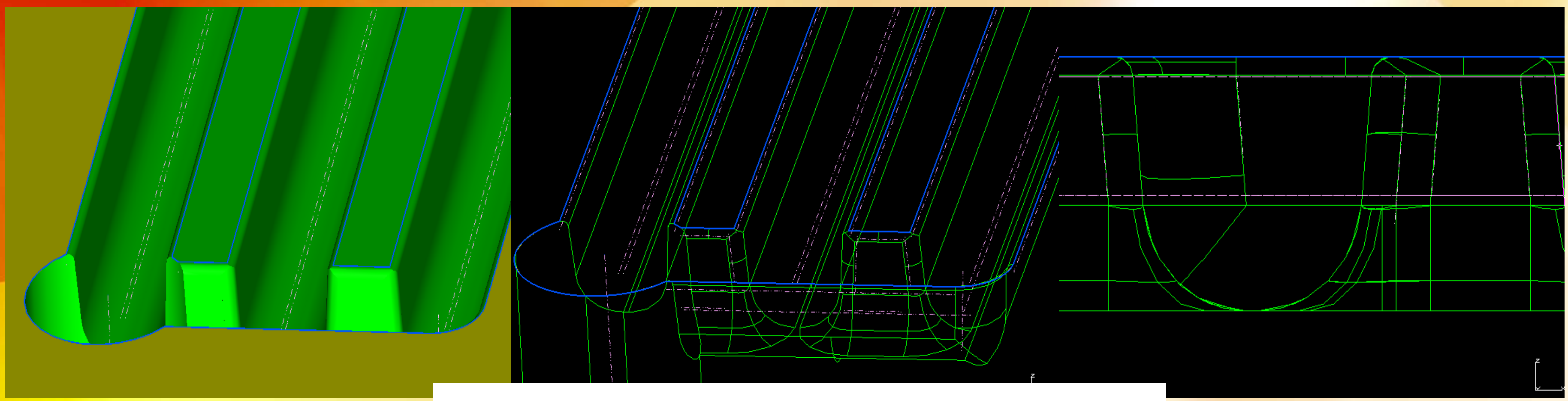
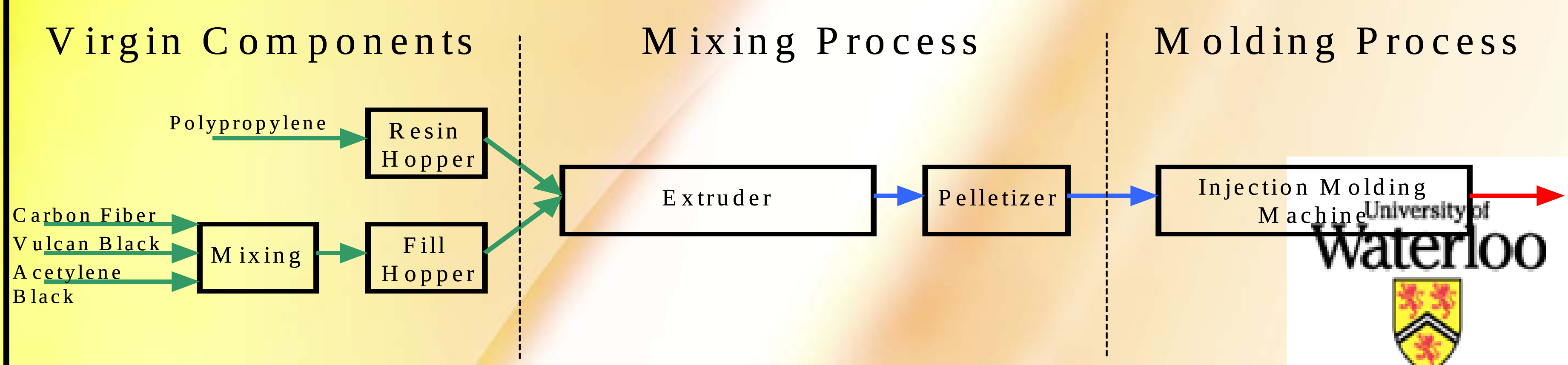
Conductive Polymers
Bi-Polar Plate Development



Solid Modeling of a Fuel Cell Plate

Injection Moldable Bi-Polar Plate



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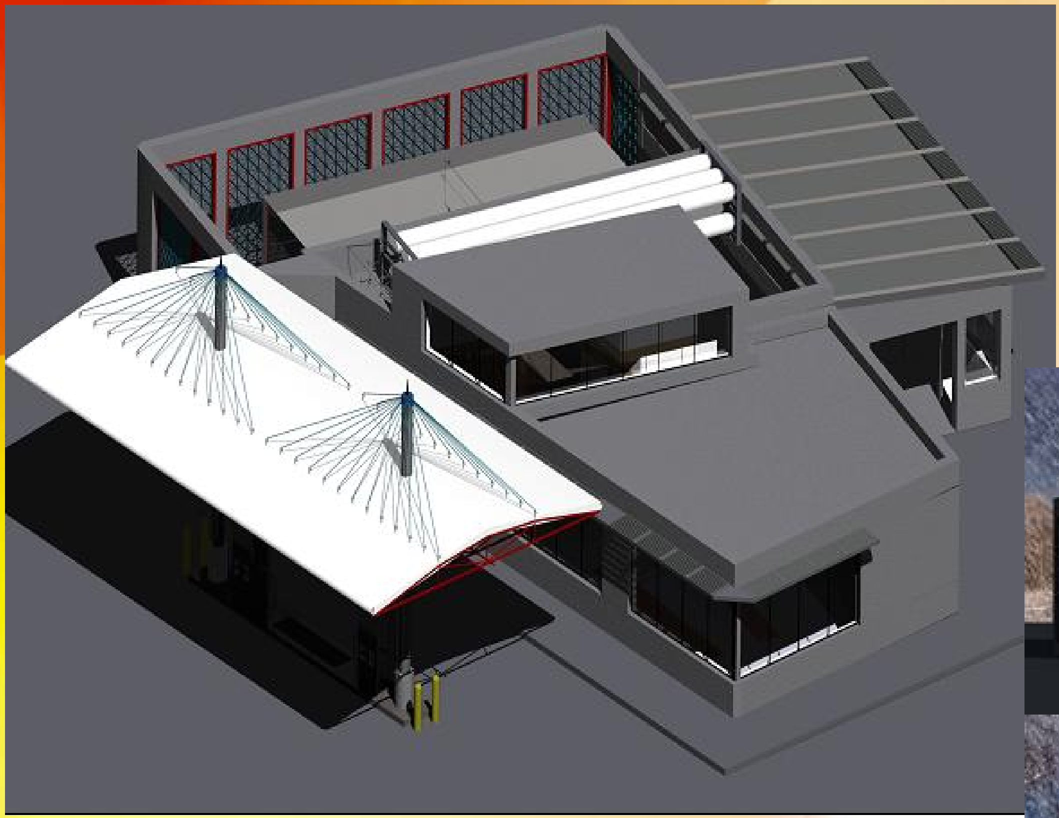
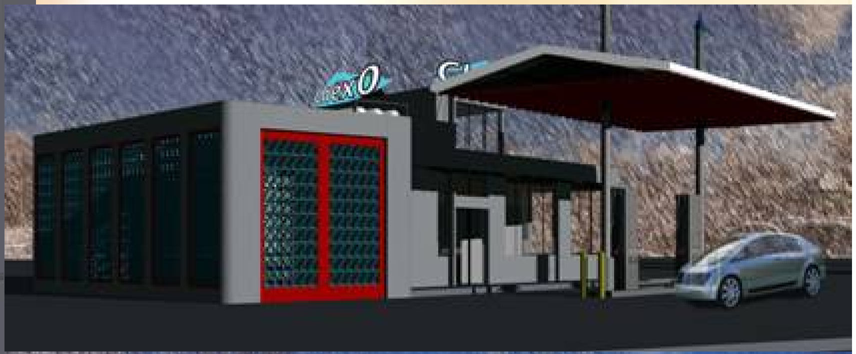
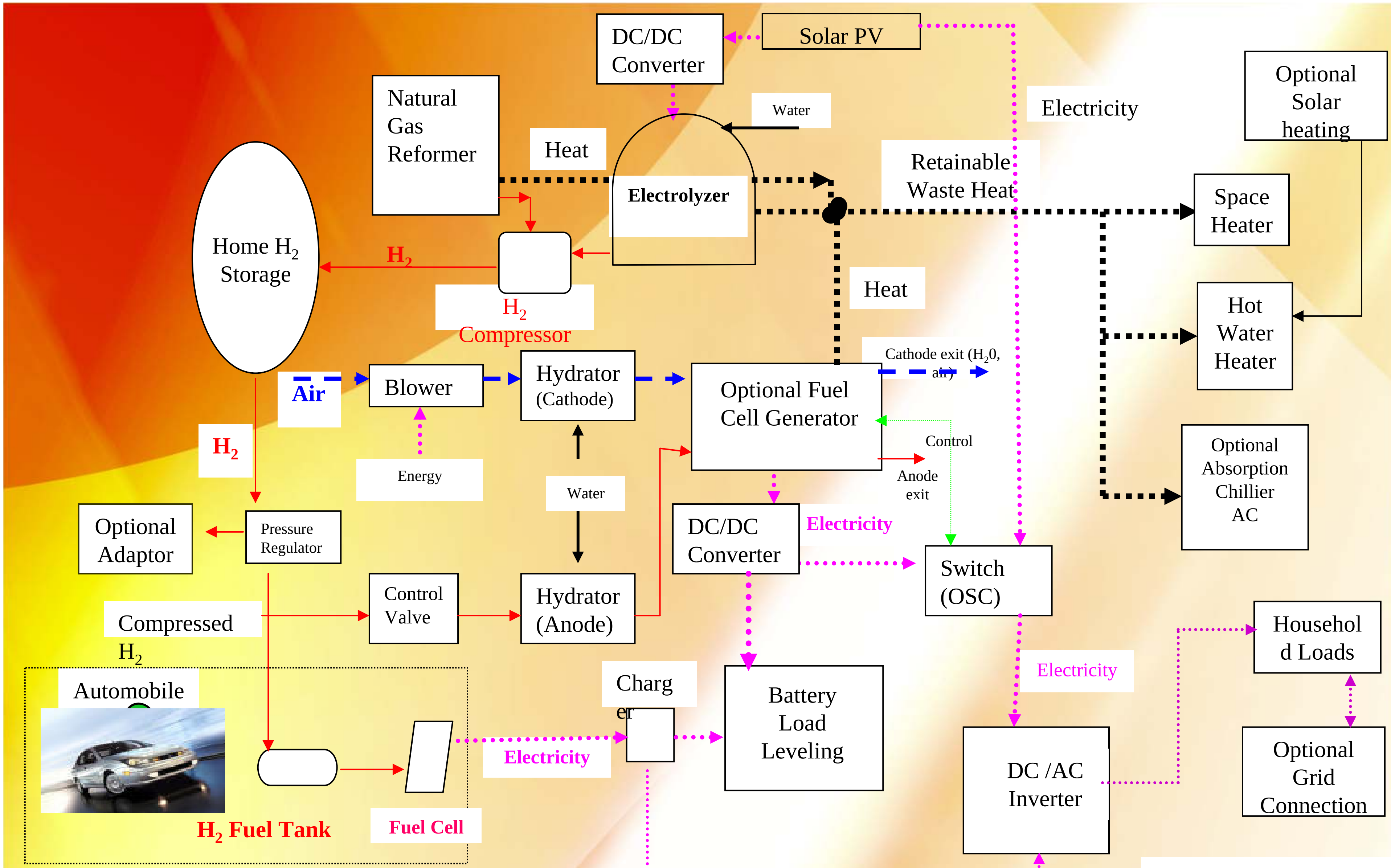
Design of a Hydrogen Retail Station

Waterloo was the Honourable Mention winner in the National Hydrogen Association 2005 H2U Competition







Home Based Distributed Energy System – Fowler-Waterloo

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University of Waterloo Alternative Fuel Team

UWAFT is one of the 17 teams that have been accepted to compete in ChallengeX. Waterloo Finished First in the first year (2005) of this 3 year competition.

Currently, UWAFT will install 65 kWatt Hydrogenics fuel cell technology into the Chevy Equinox drive train.

UWAFT would like to thank GM and the US DOE for sponsoring this competition.

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Questions

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GDL Research

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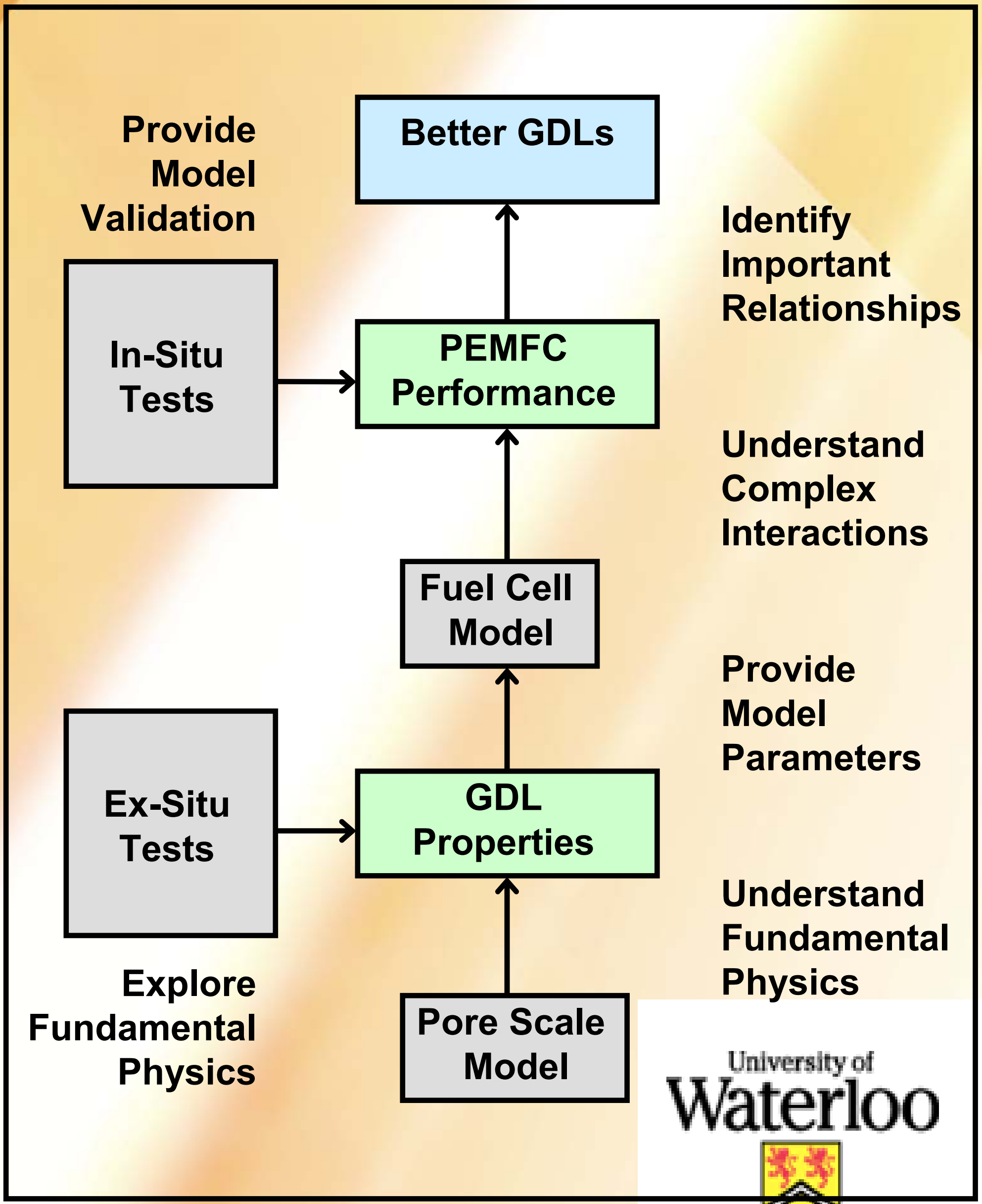
Objectives

Improve PEM fuel cell performance through focused study of the Gas Diffusion Layer

1. **Understand the behaviour of liquid water in the GDL**
2. **Elucidate the effects of liquid water in the GDL on fundamental mass transport properties**
3. **Develop a PEMFC model to effectively account for liquid water effects**
4. **Relate the performance of PEMFCs to fundamental GDL properties**



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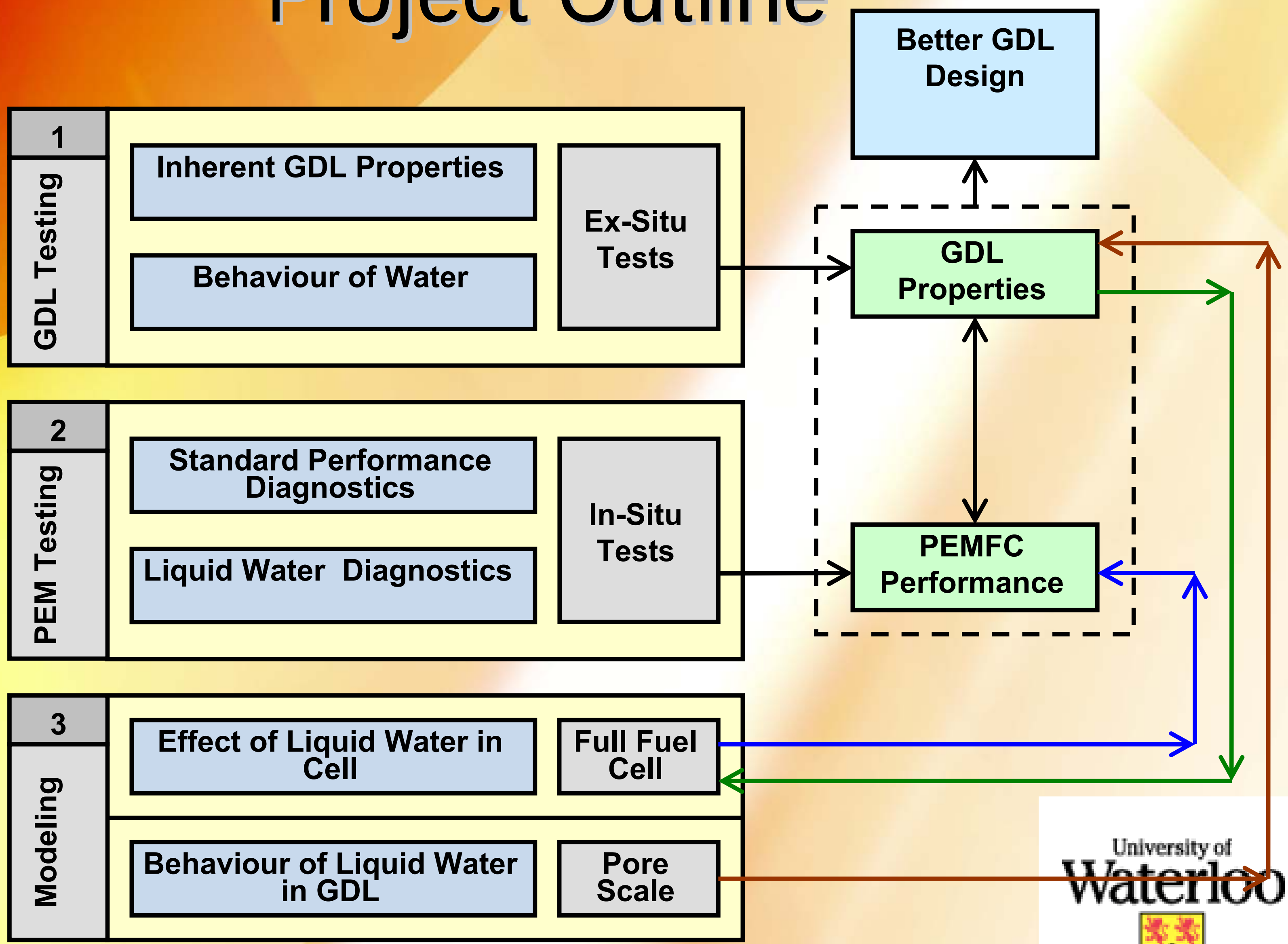
Project Outline



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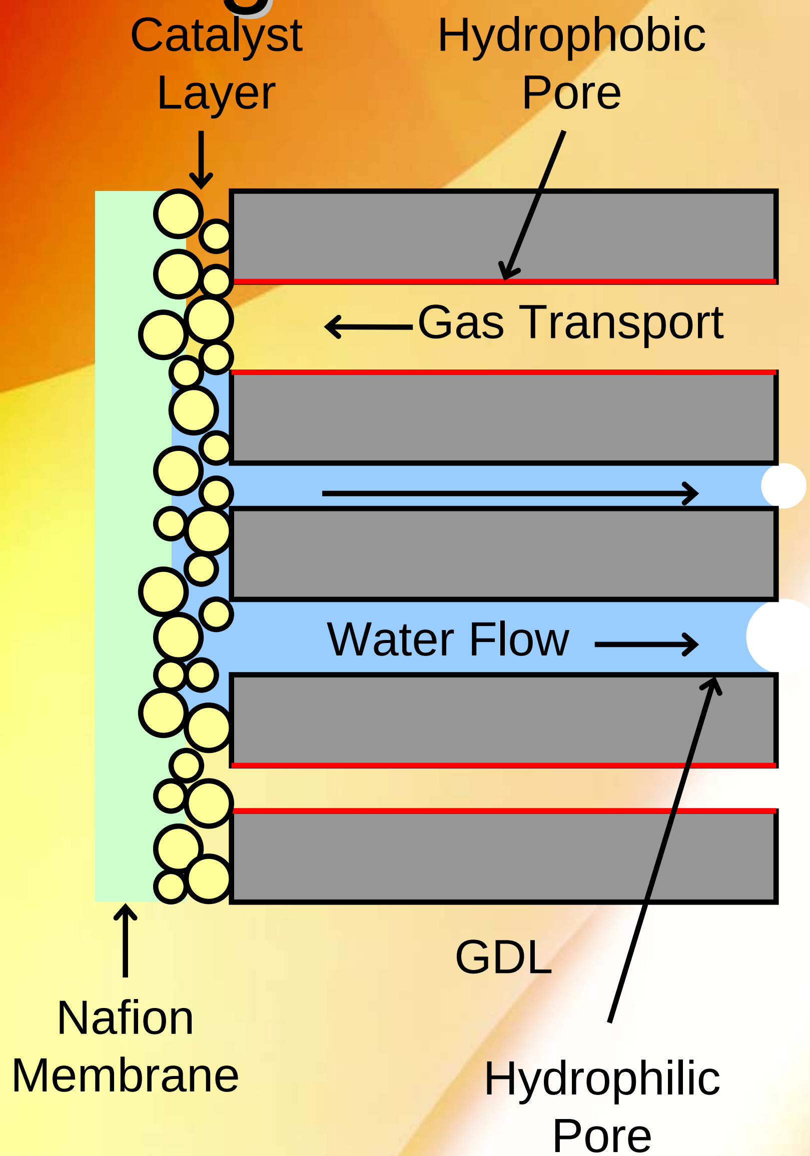
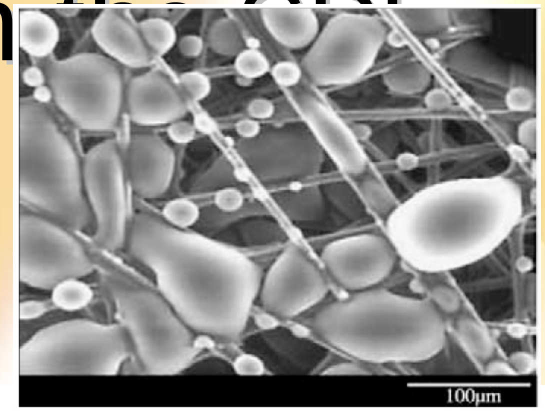
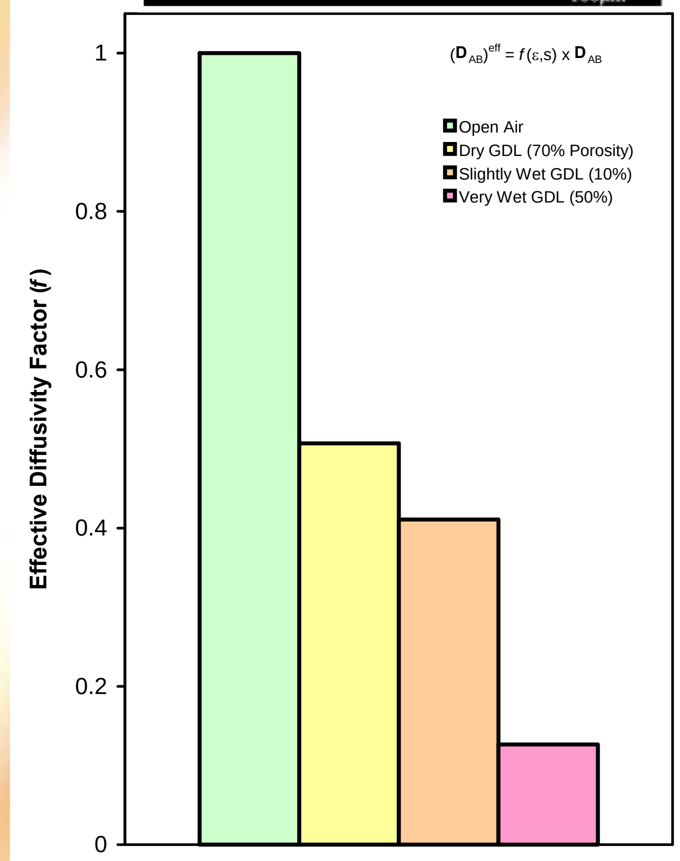
Background: Water in







Hydrophilic-hydrophobic Duality

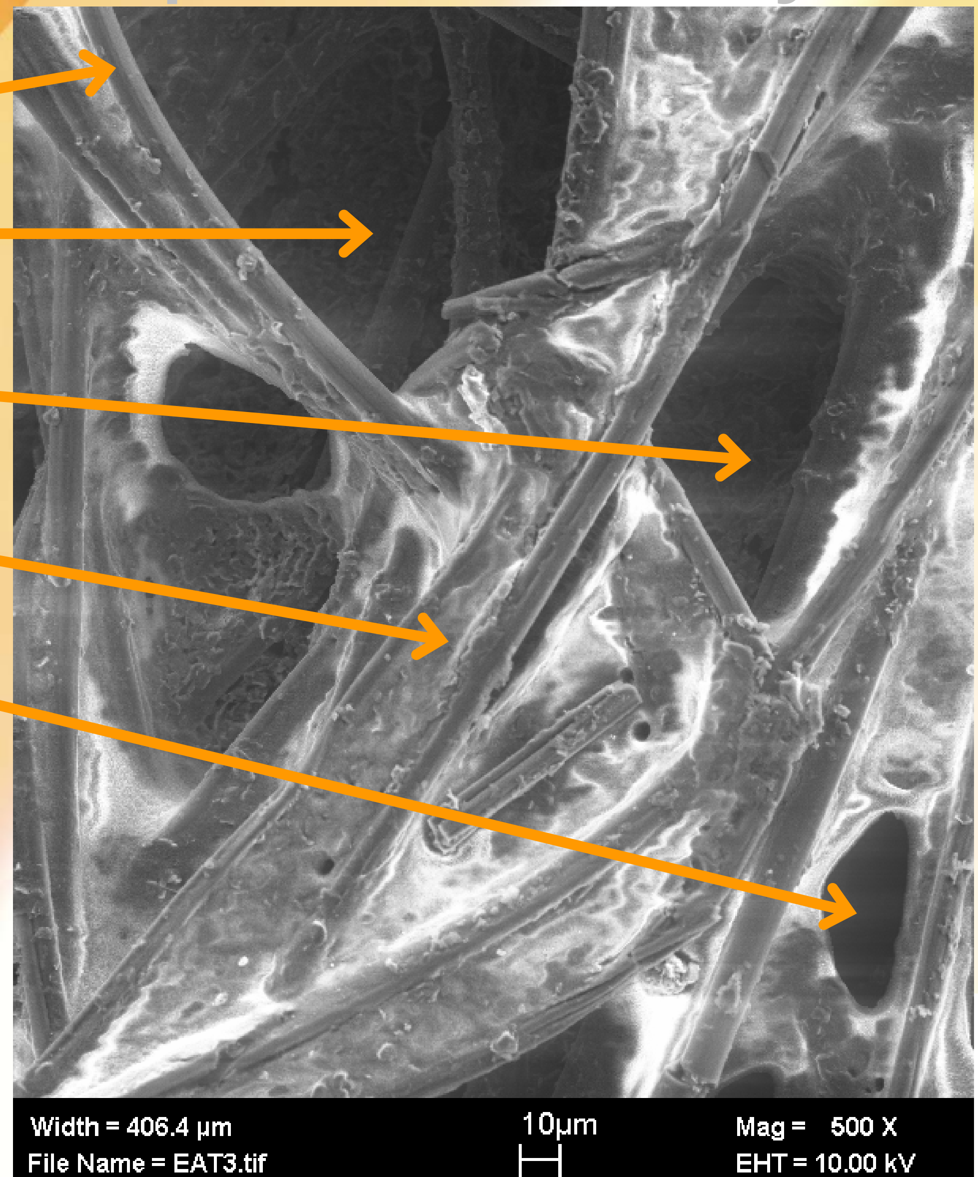
Carbon Fibre

Hydrophilic Pore

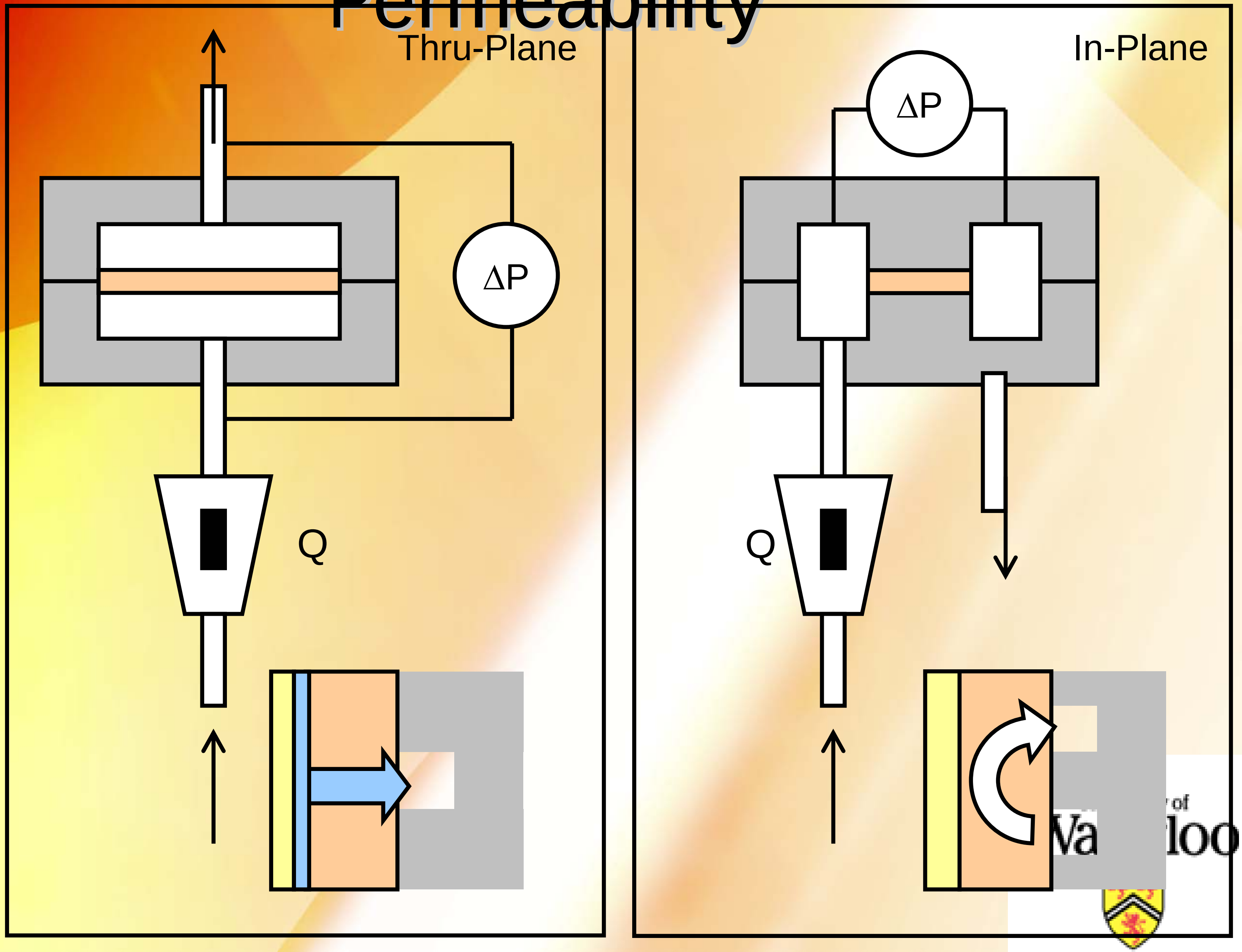
Dual Wettability Pore

PTFE Coating

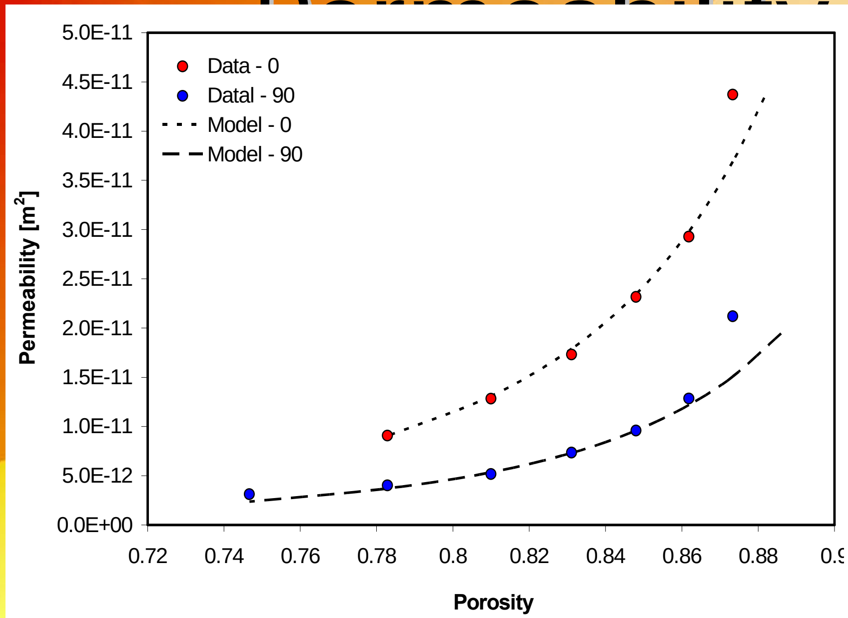
Hydrophobic Pore



Permeability

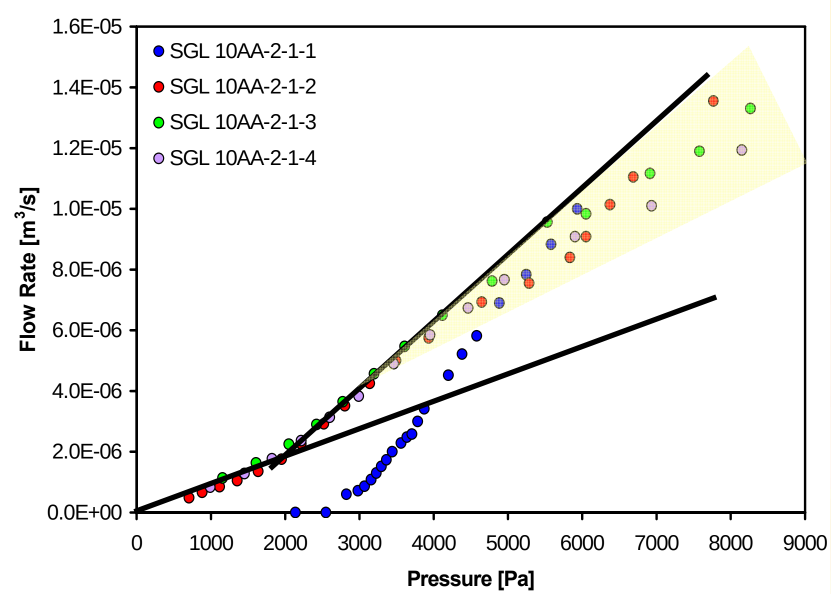


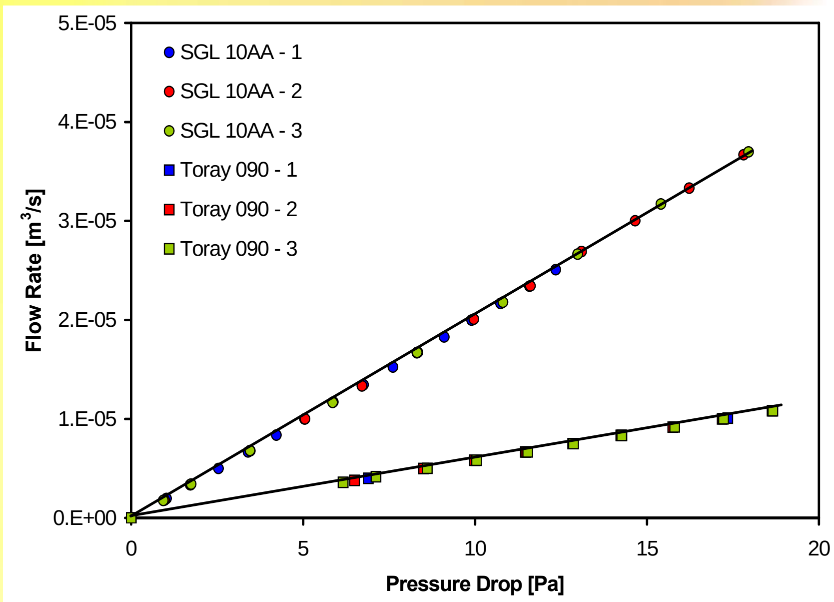
Permeability Results



← **In-plane with different compressions, simulating cell assembly conditions.**

↓ **Thru-plane with water, elucidating the effect of GDL hydrophobicity.**





← **Thru-plane with gas, characterizing absolute permeability.**

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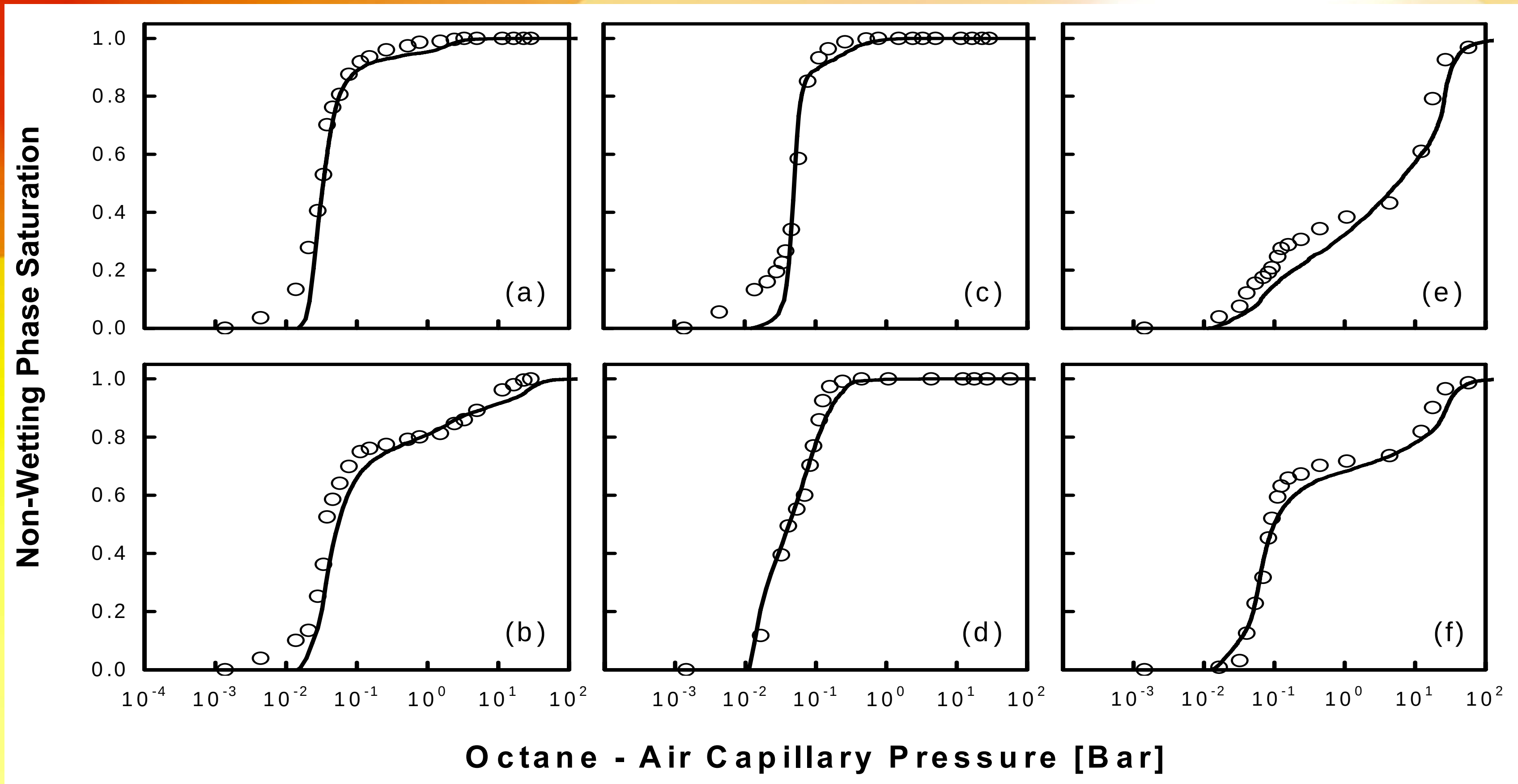
Capillary Pressure: MIP vs. MSP_O



Gostick et al. (In Press)

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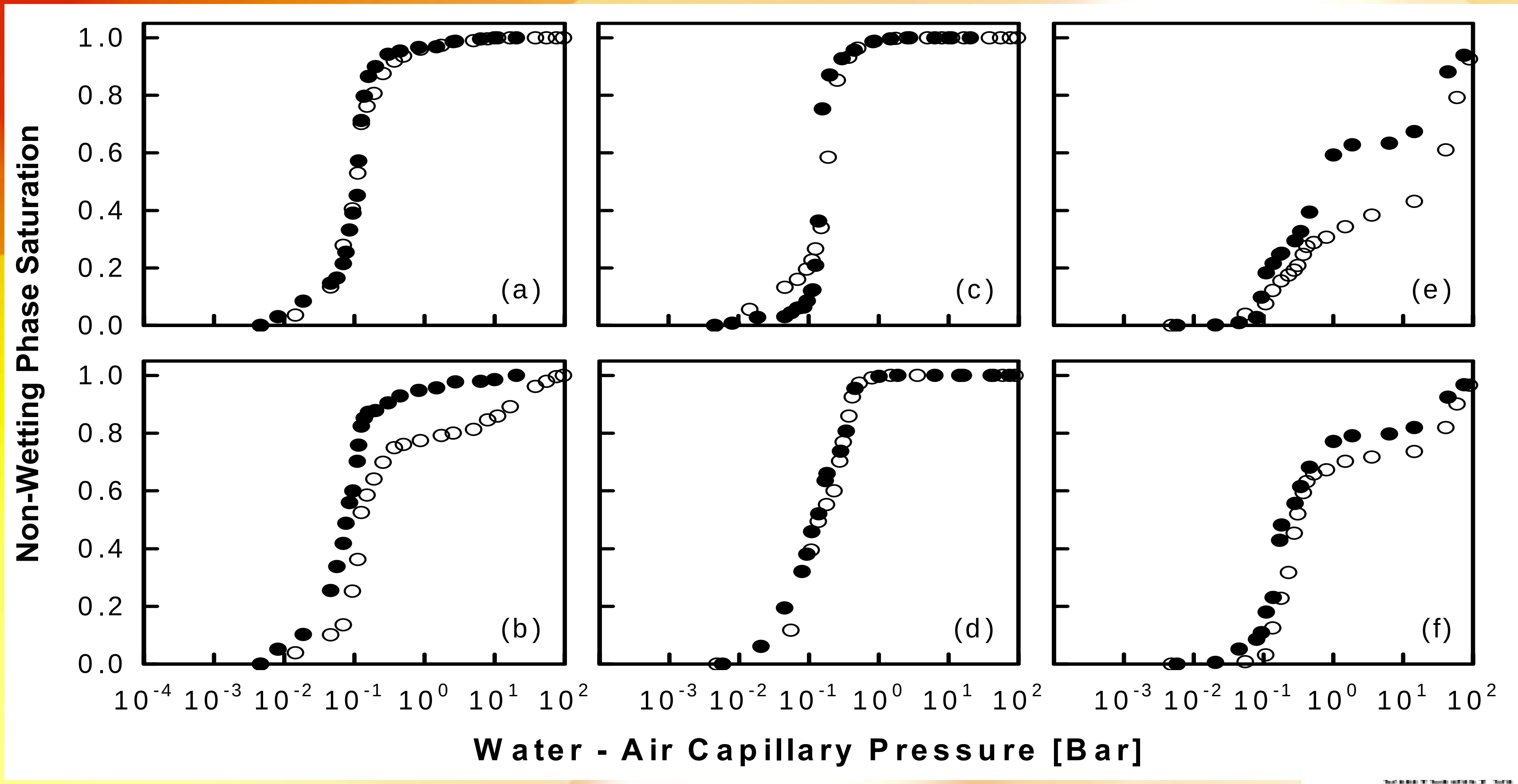
Capillary Pressure: MSP_W vs. MSP_O



Gostick et al. (In Press)

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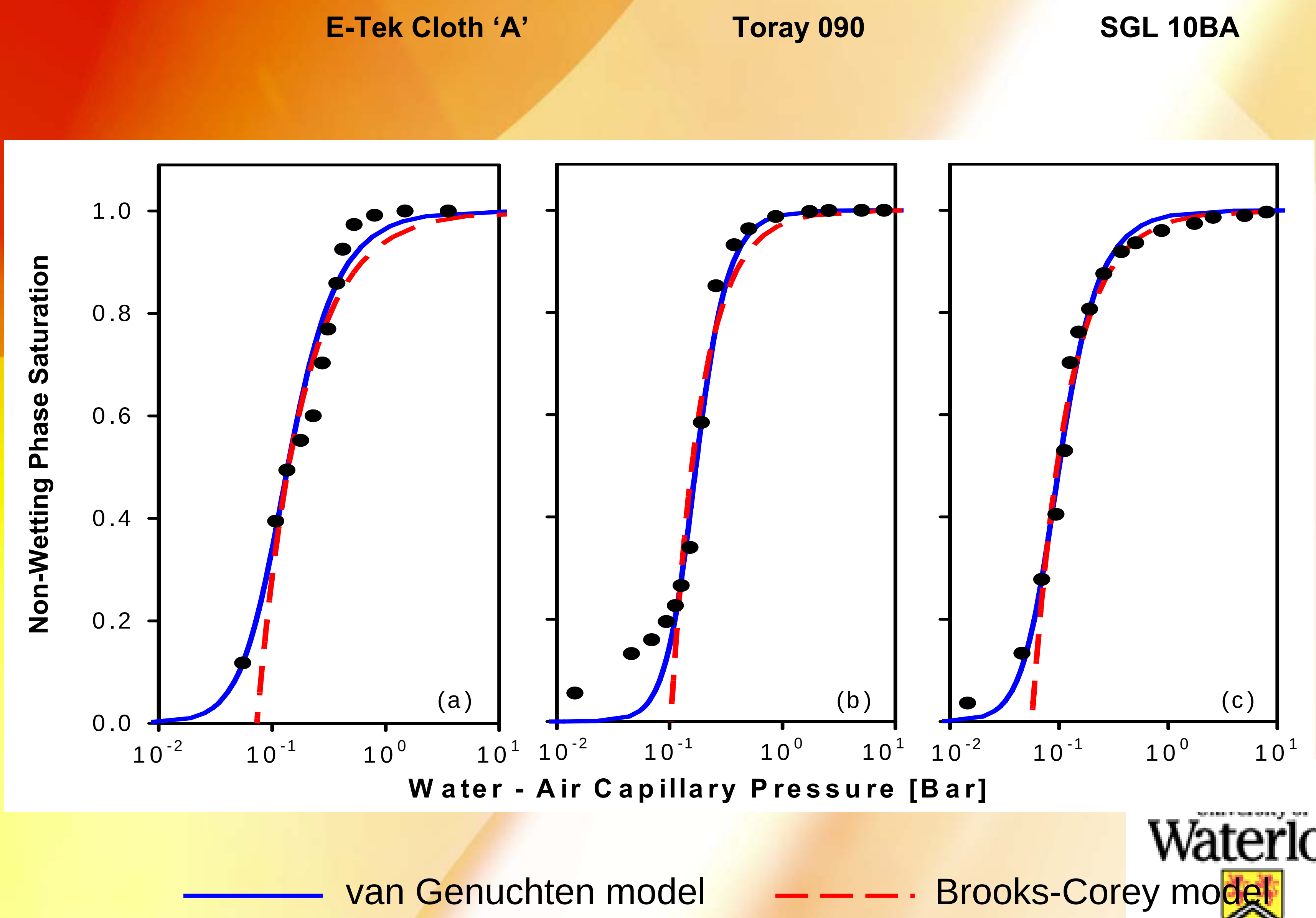
Capillary Pressure: Model Fits



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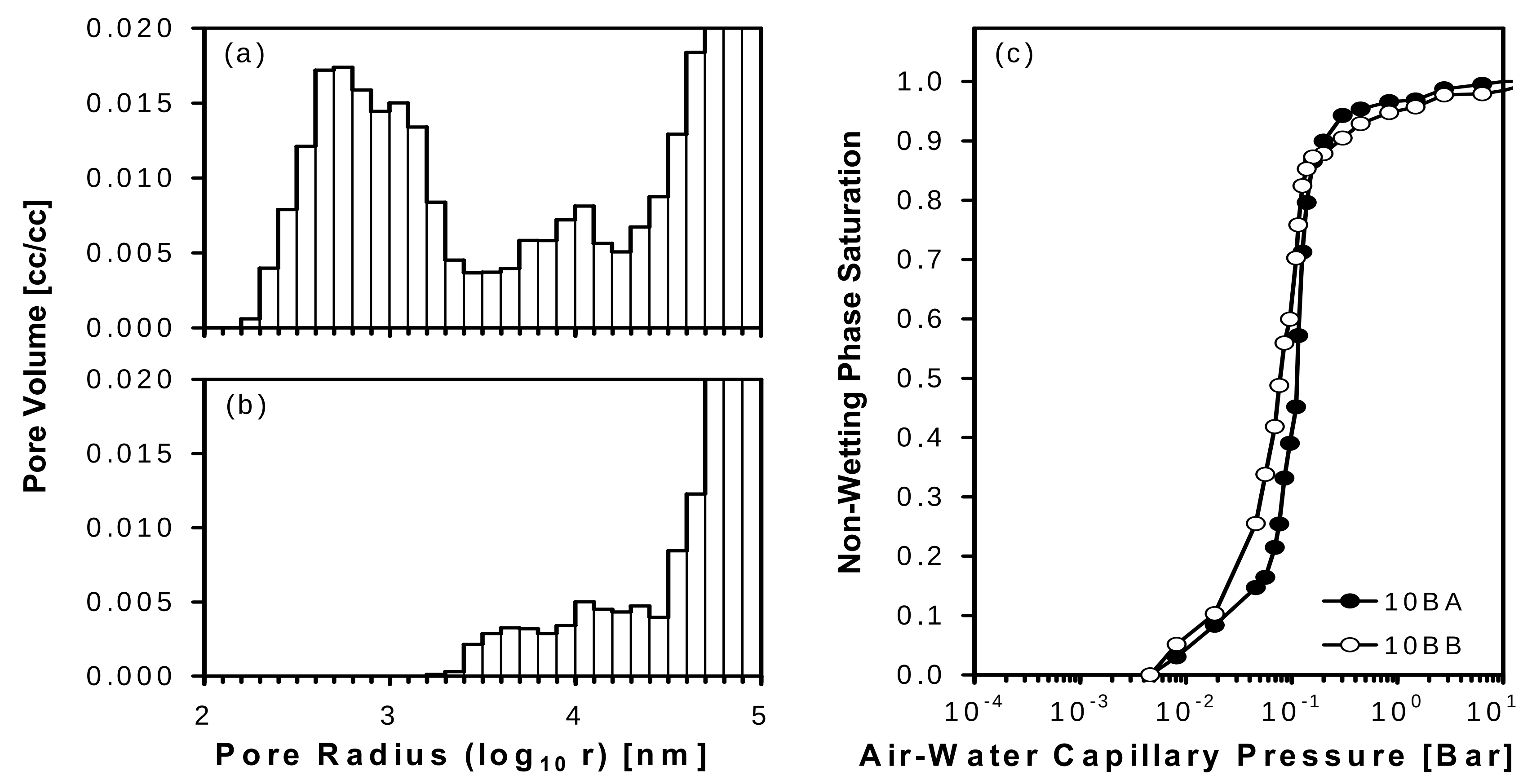
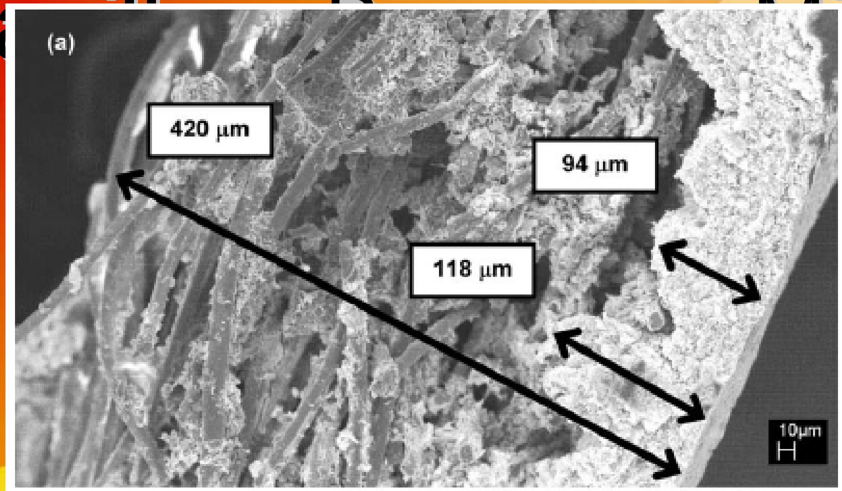
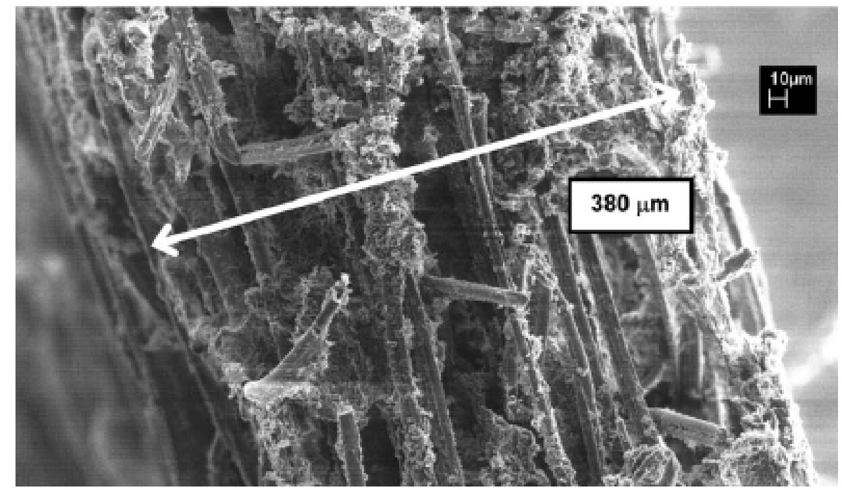
Gostick et al. (In Press)

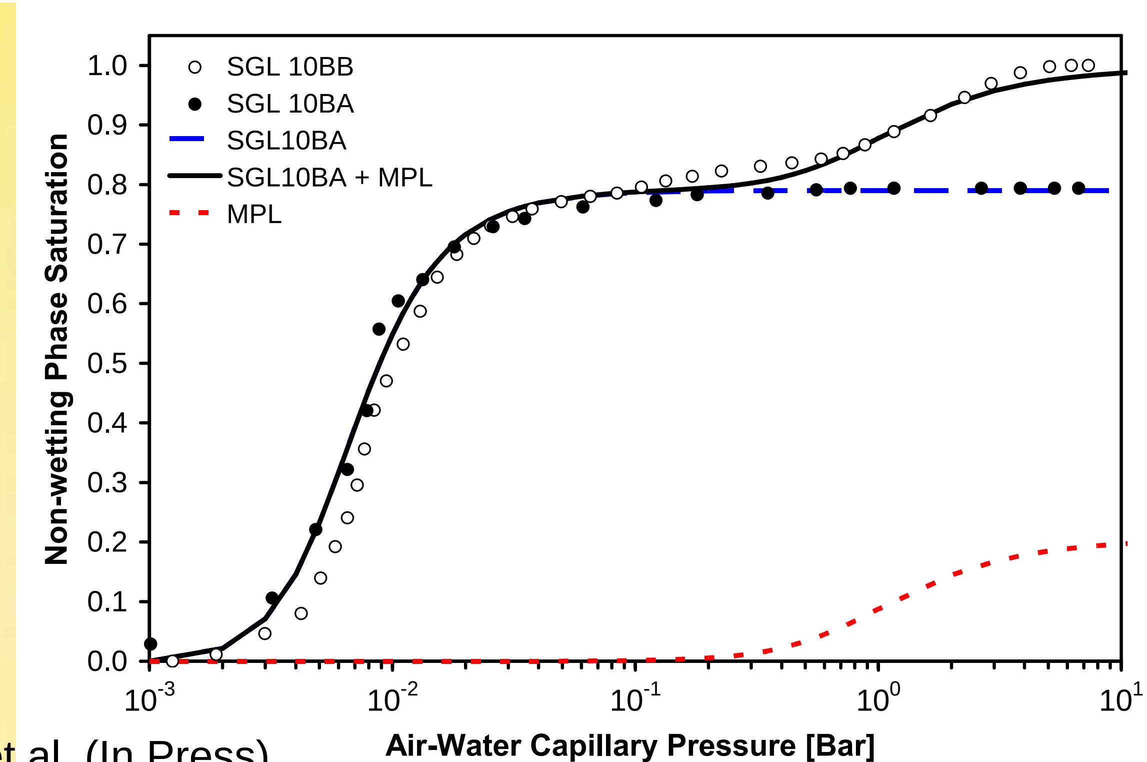
Capillary Pressure: Microporous Layer



Gostick et al. (In Press)



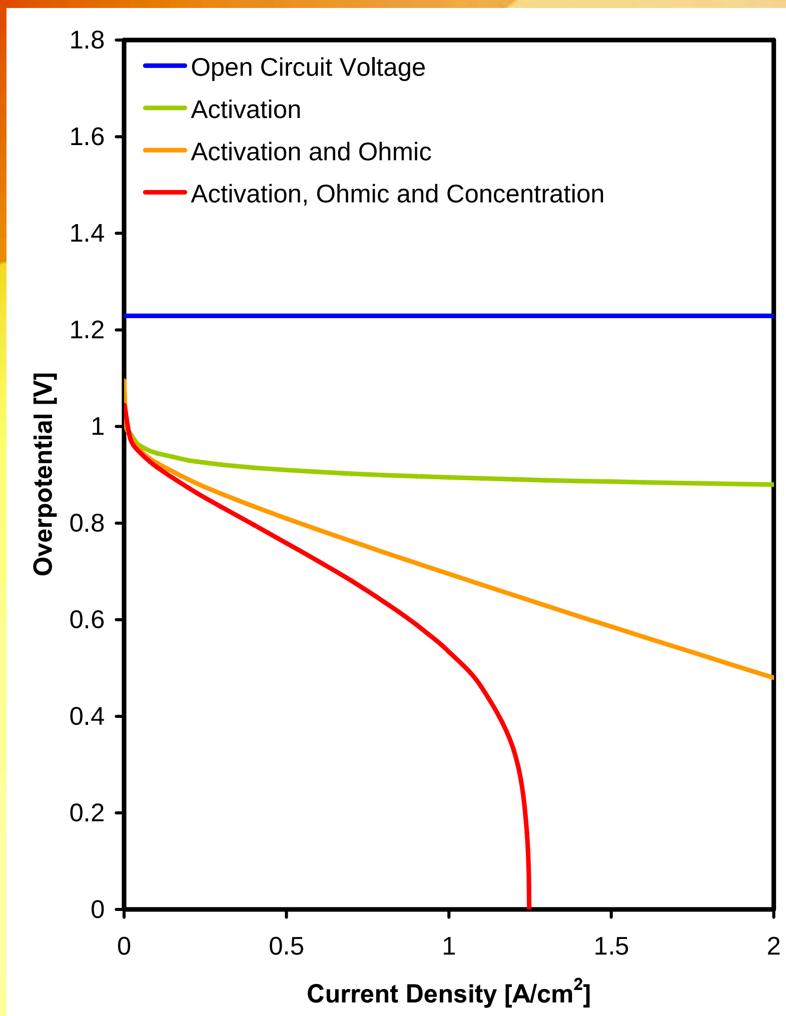


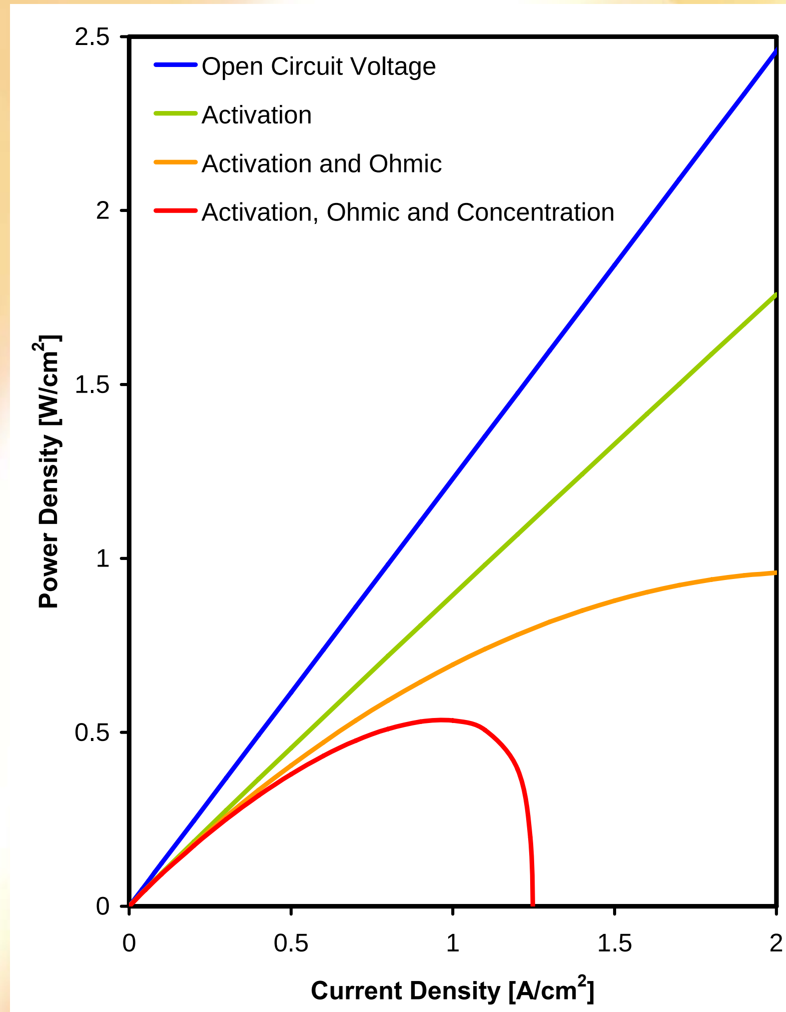


Gostick et al. (In Press)

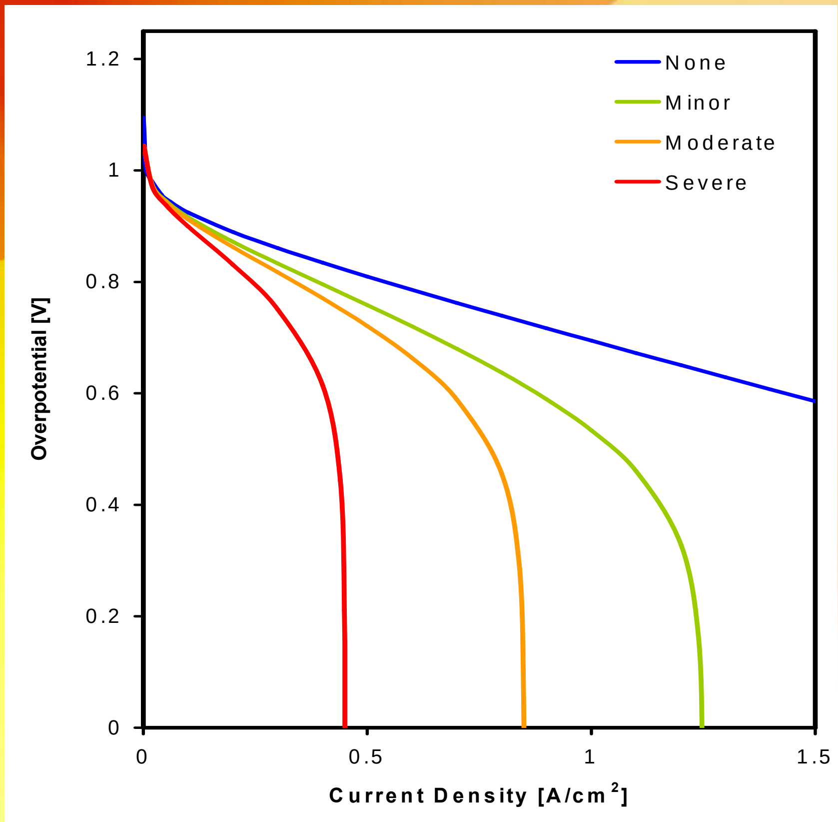
Polarization Losses: Contributions

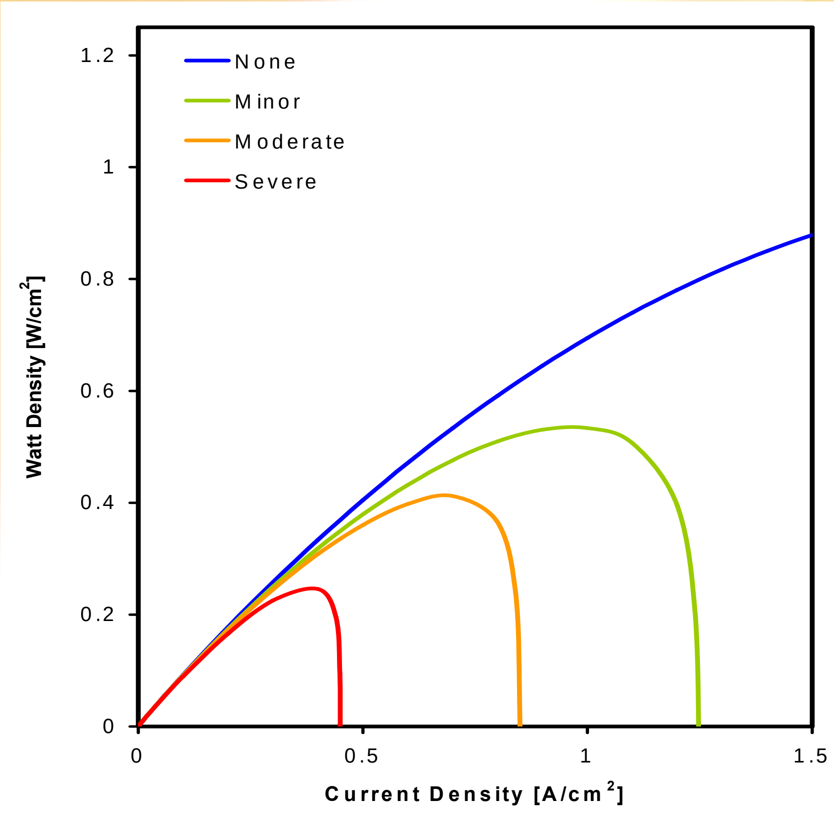
$$V_{CELL} = E_R - V_{ACT} - V_{iR} - V_{CONC}$$





Polarization Losses: Mass Transfer





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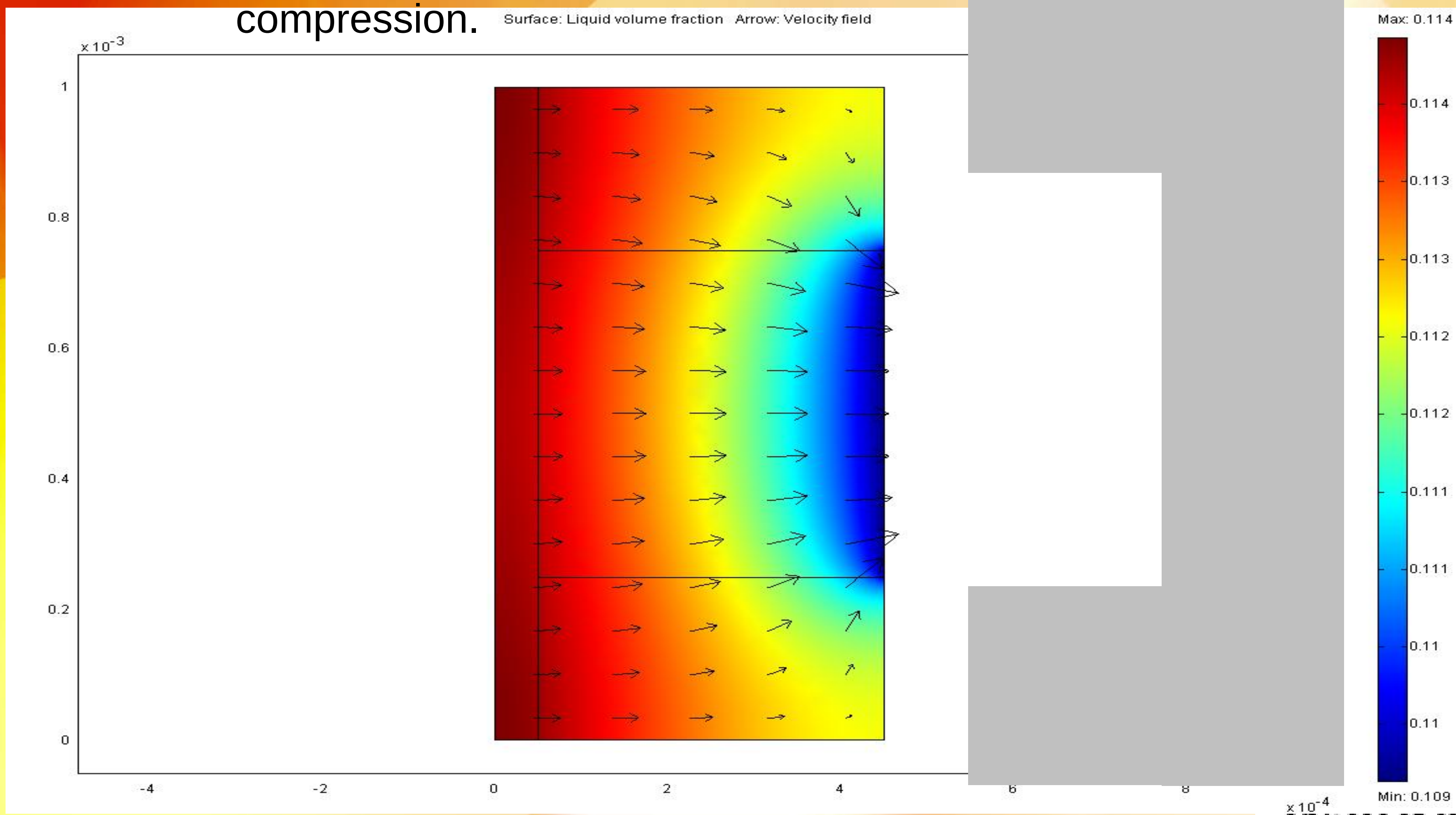
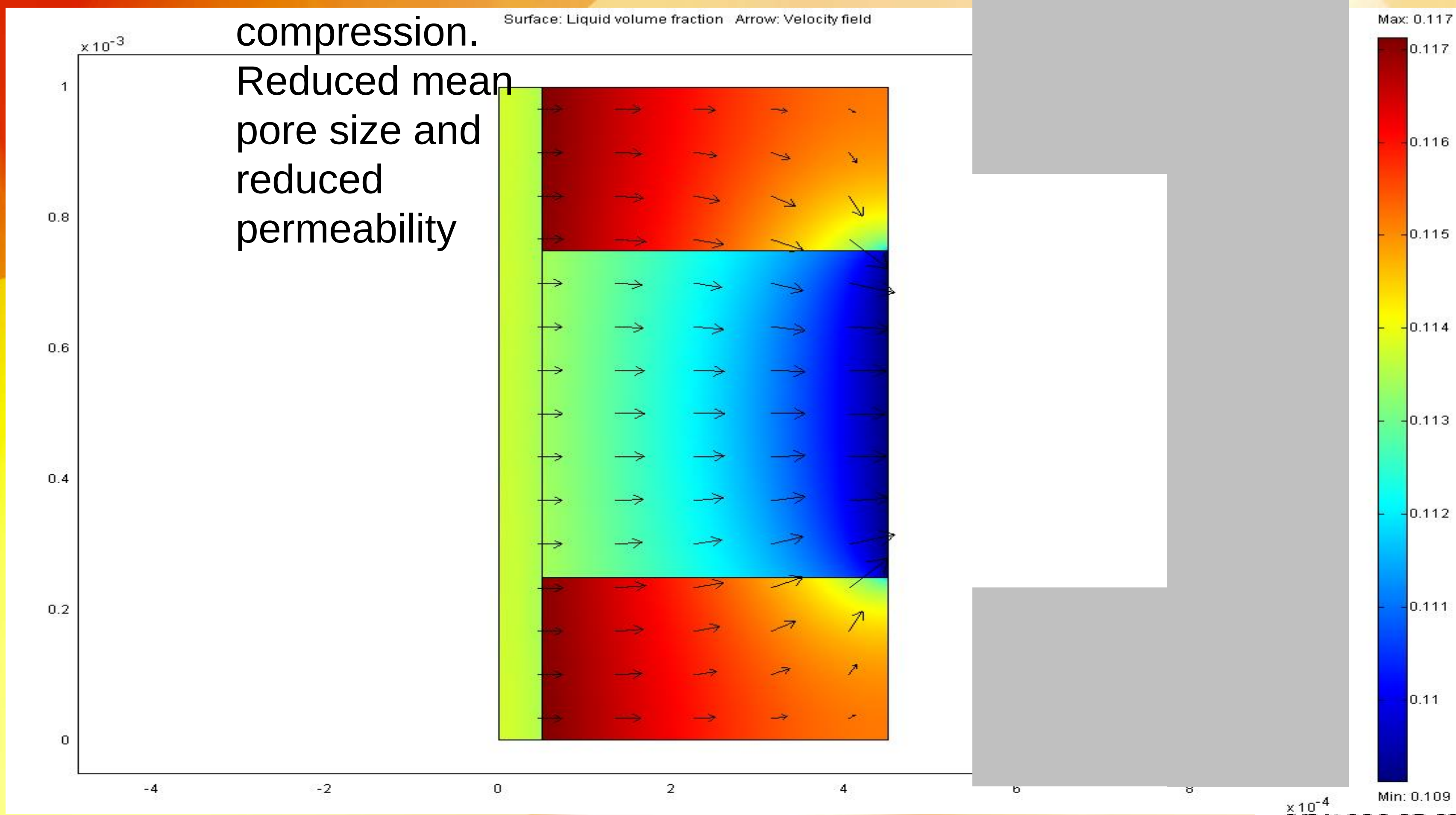
FEM Lab Model: 2D UFT

No under-land compression.



FEM Lab Model: 2D UFT

With under-land compression. Reduced mean pore size and reduced permeability



MEA Degradation Research

DEGRADATION FAILURE MODES

(leading to degradation of performance or *durability*)

- **Kinetic or activation loss in the anode or cathode catalyst –**

  Loss of Apparent Catalytic Activity
- **Ohmic or resistive increases in the membrane or other components –**

  Loss of Conductivity
- **Decrease in the mass transfer rate of in the reactants flow channel or electrode –**

  Loss of Mass Transfer Rate of Reactants

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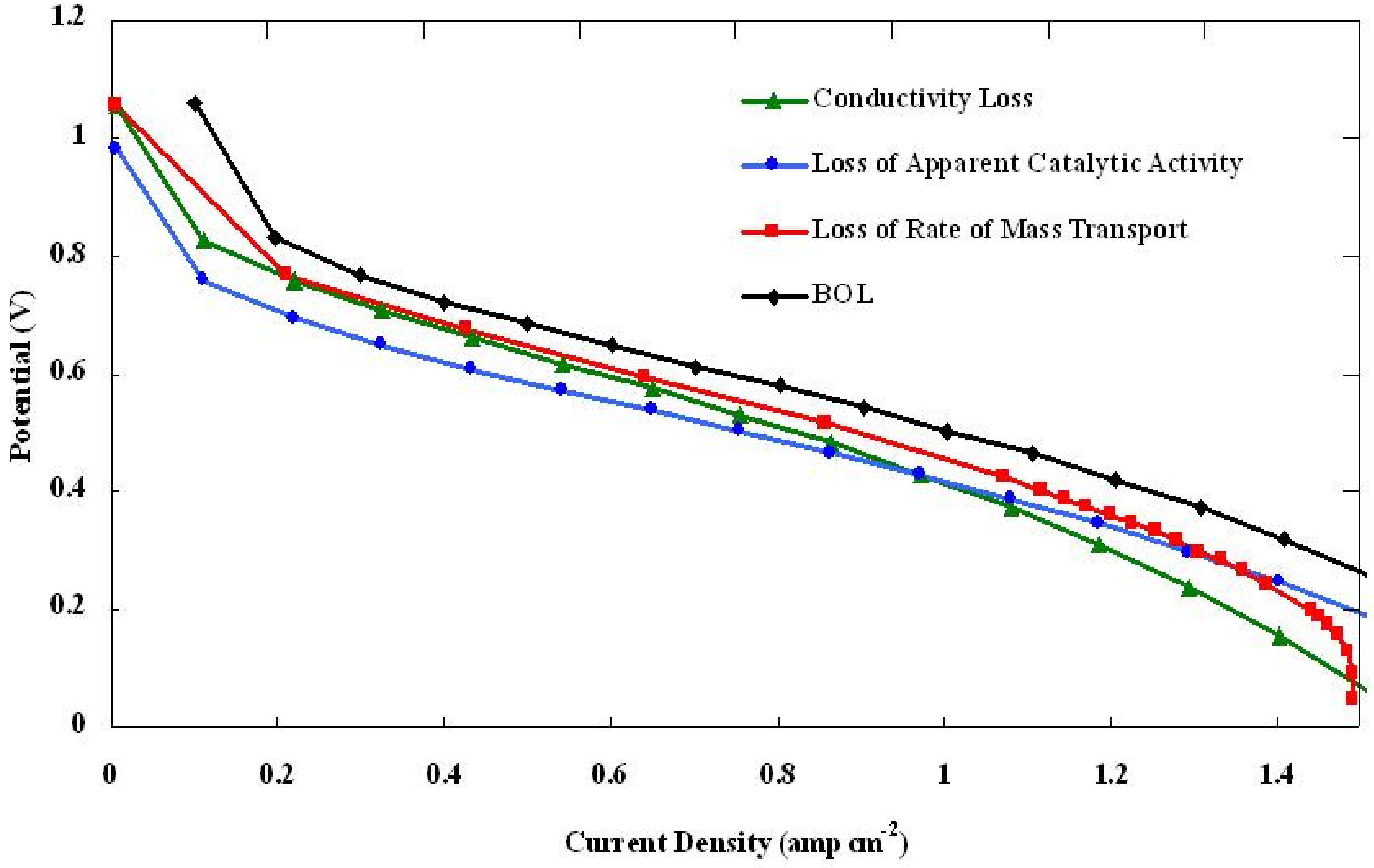
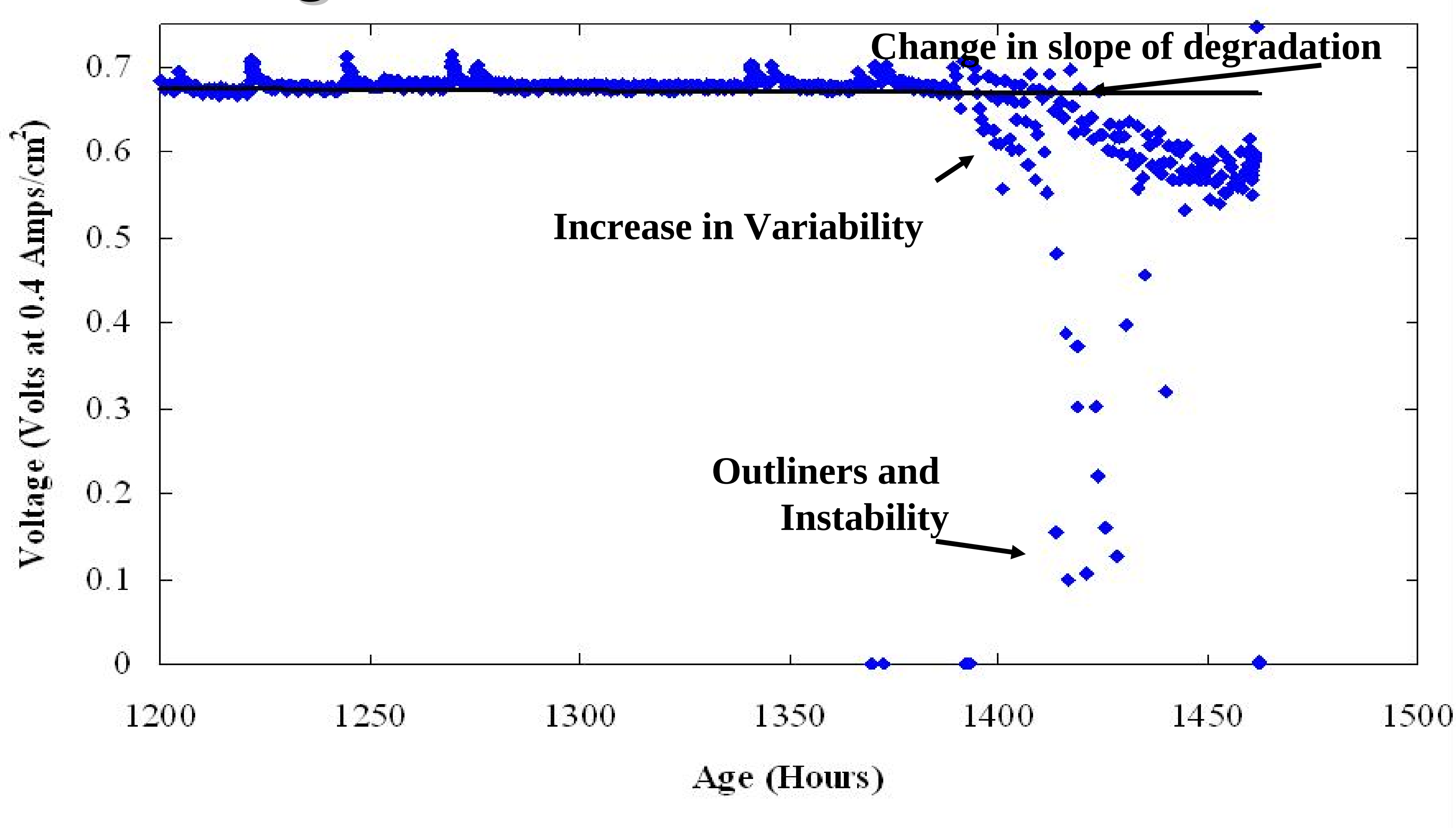
Performance Assessment
VOLTAGE DEGRADATION MODES



Diagnostics:

Voltage Performance at End of Life



Objectives of the overall research

- To understand the mechanisms and factors leading to failure
- To understand how manufacturing and operational conditions influence the dominant degradation mode
- To design better membranes and control strategies to mitigate material limitations.

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Reliability Jargon

- **Durability** - ability to resist permanent change in performance over time, i.e. degradation or irreversible degradation. This phenomena is related to ageing.
- **Reliability** - The ability of an item to perform the required function, under stated conditions, for a period of time. Combination of degradation, and failure modes that lead to catastrophic failure.
- **Stability** - recoverable function of efficiency, voltage or current density decay or reversible degradation.

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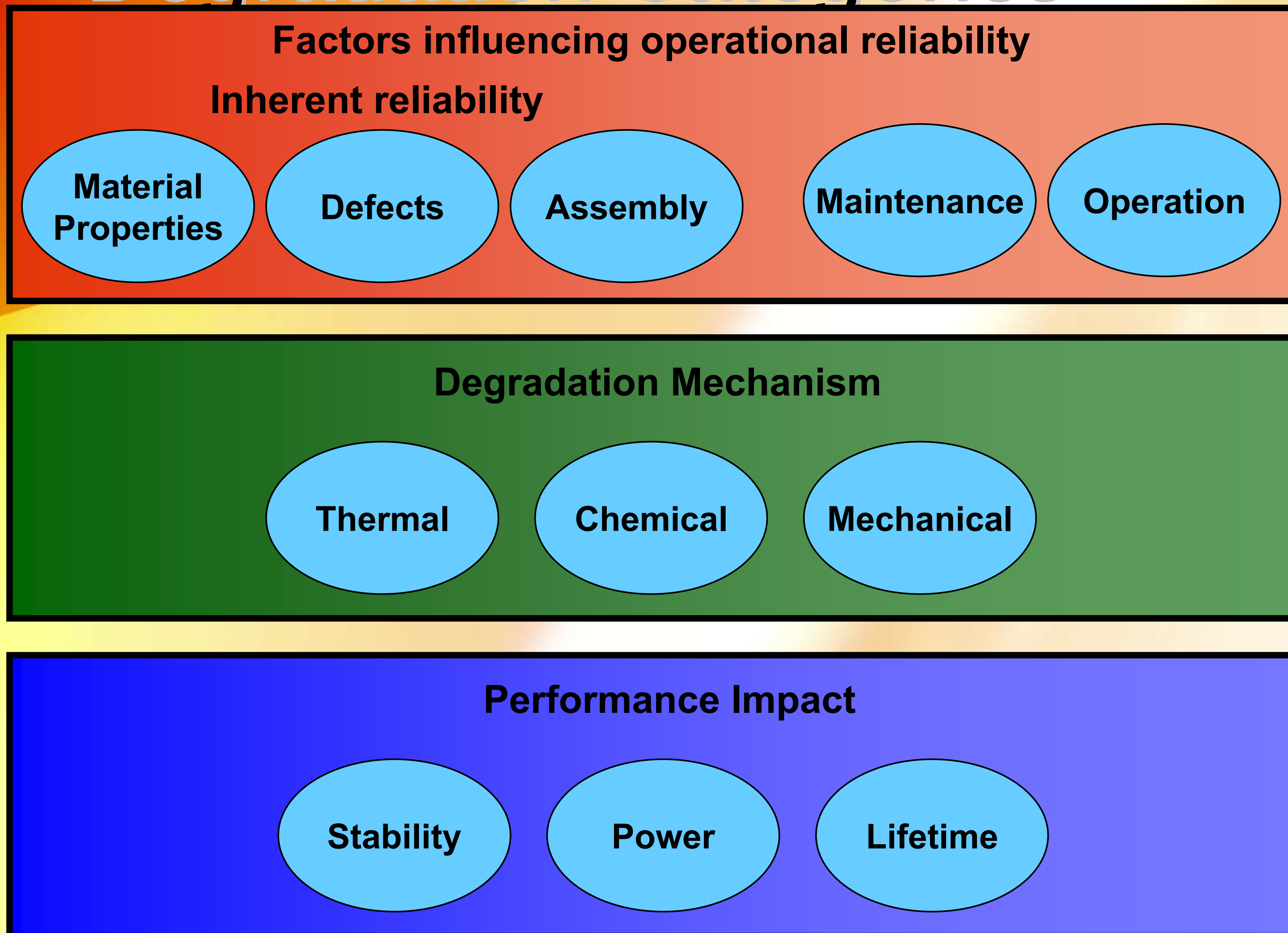
Degradation Categories



Factors Influencing Reliability

- These include:
- Inherent Reliability
  - component properties (conductivity, mechanical strength)
  - component defects (cracks, catalyst clusters)
  - Manufacturing (cell compression, MEA manufacturing)
- Other Influencing Factors
  - operational environment (humidity, start stop)
  - Maintenance (stack deconstruction)

- After these are specified the way in which the cell will degrade is determined.

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Degradation Mechanism

- Thermal Degradation
  - Thermal decomposition
- Chemical Degradation
  - Radical attack
  - Contamination
  - Catalytic area loss
  - Catalyst migration
- **Mechanical Degradation**
  - Pinching
  - Creep
  - Erosion
  - Delamination
  - GDL Compression

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Performance Impact

- Ultimately what we want out of a fuel cell is POWER!
- In general the impact of the degradation mechanism can be categorized into three impacts
  - Catalytic area loss
  - Conductivity loss
  - Mass transport ability loss
- The importance of one degradation mode over another is based on how much it impacts performance and lifetime
- Voltage, Current, power
- Stability, catastrophic failure
- Lifetime

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Reliability testing

- Durability testing at Waterloo consists of three main steps:
- **Performance Evaluation**
  - Polarization curves, voltage, current, power, efficiency (and degradation of these), lifetime
  - **Performance data is not enough**
- **Diagnostics**
  - Cyclic voltametry, crossover, impedance, fluoride release rate, HELIOX tests, current decay, current interrupt
- **Forensics**
  - Electron microscopy, pinhole mapping, infrared spectroscopy, mechanical property analysis, de-catalyzation

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MEA Features in New Membranes

- Manufacturing plays a crucial role in durability
- Inherent reliability
- Here is where defects and morphology can be controlled
    - Cracking
    - Delamination
    - Thickness variations
    - GDL MP layer morphology
    - Nafion clusters
    - Platinum clusters
    - Macroscopic orientation

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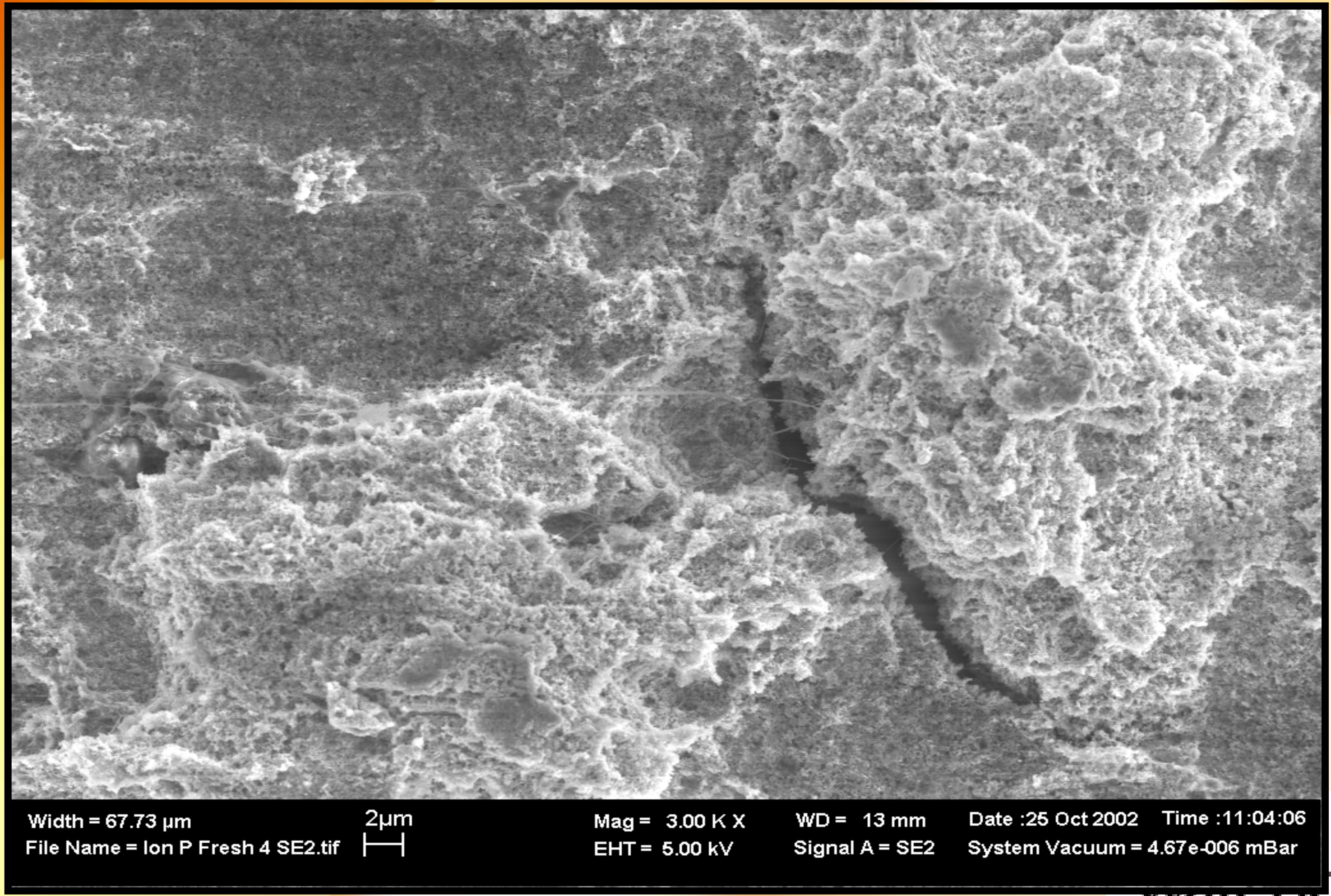
Cracking


Width = 67.73 µm
File Name = Ion P Fresh 4 SE2.tif
2µm
Mag = 3.00 K X
EHT = 5.00 kV
WD = 13 mm
Signal A = SE2
Date :25 Oct 2002
Time :11:04:06
System Vacuum = 4.67e-006 mBar

Causes and Impacts of Cracking

- Impacts
  - Location for defect propagation to a pinhole
  - Areas of catalytic inactivity
  - Increased resistance in the catalyst layer
  - Flooded areas
  - Areas for catalyst erosion

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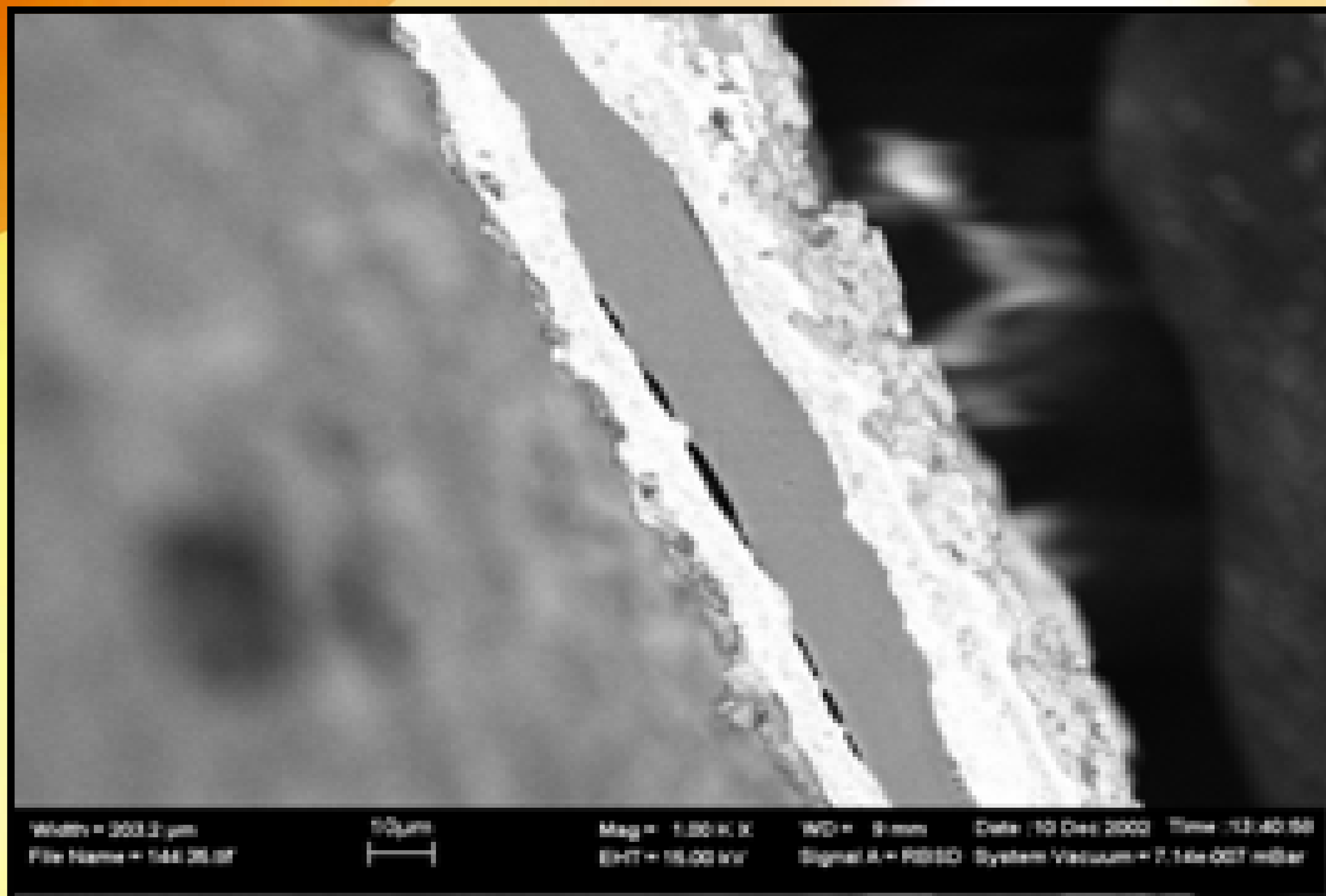
Delamination



Causes and Impacts of Delamination

- Impacts
  - Vulnerable location for further delamination
  - Increased resistance between the layers
  - Flooded areas
  - Imbalance in current and ion flow on the membrane

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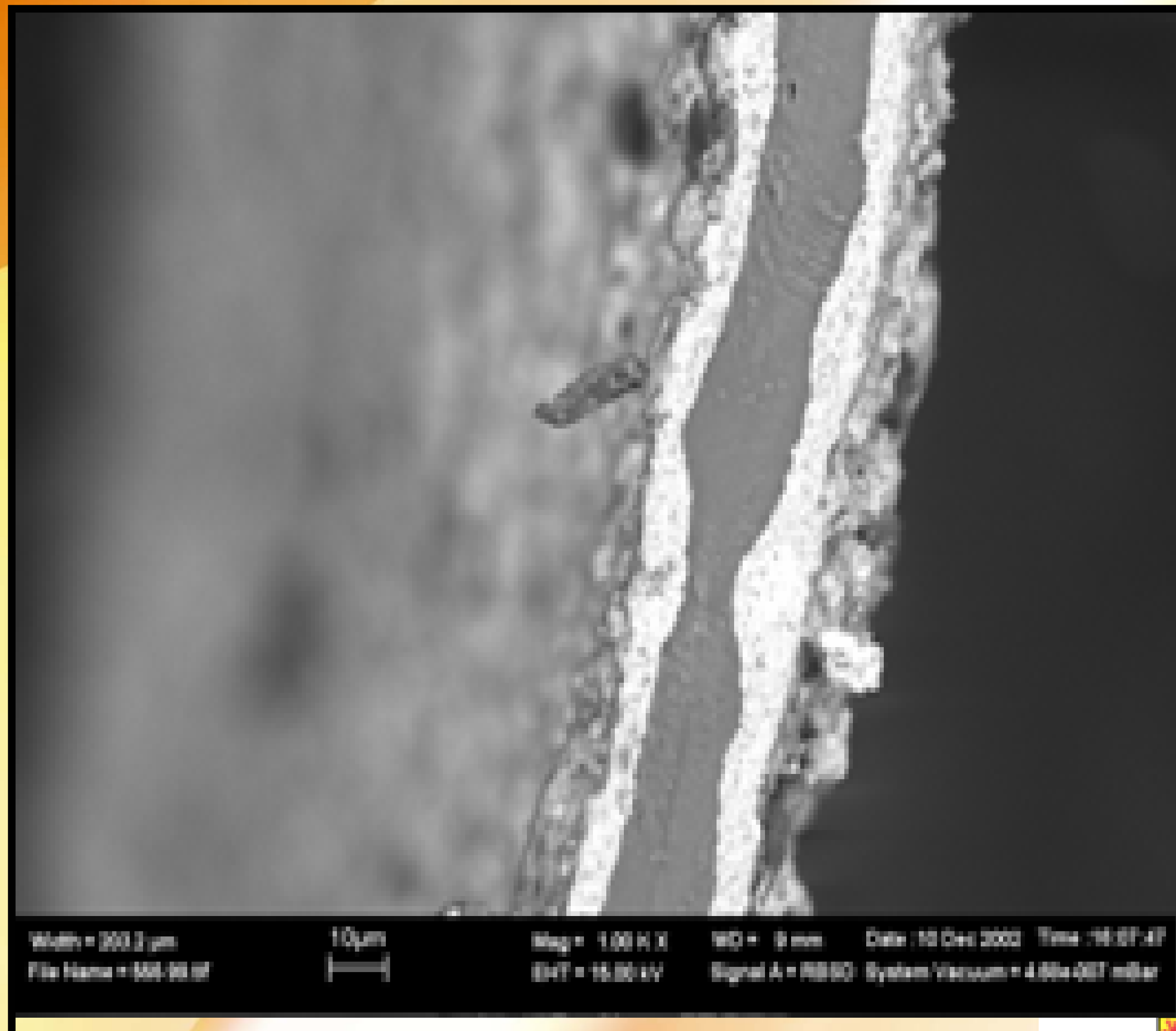
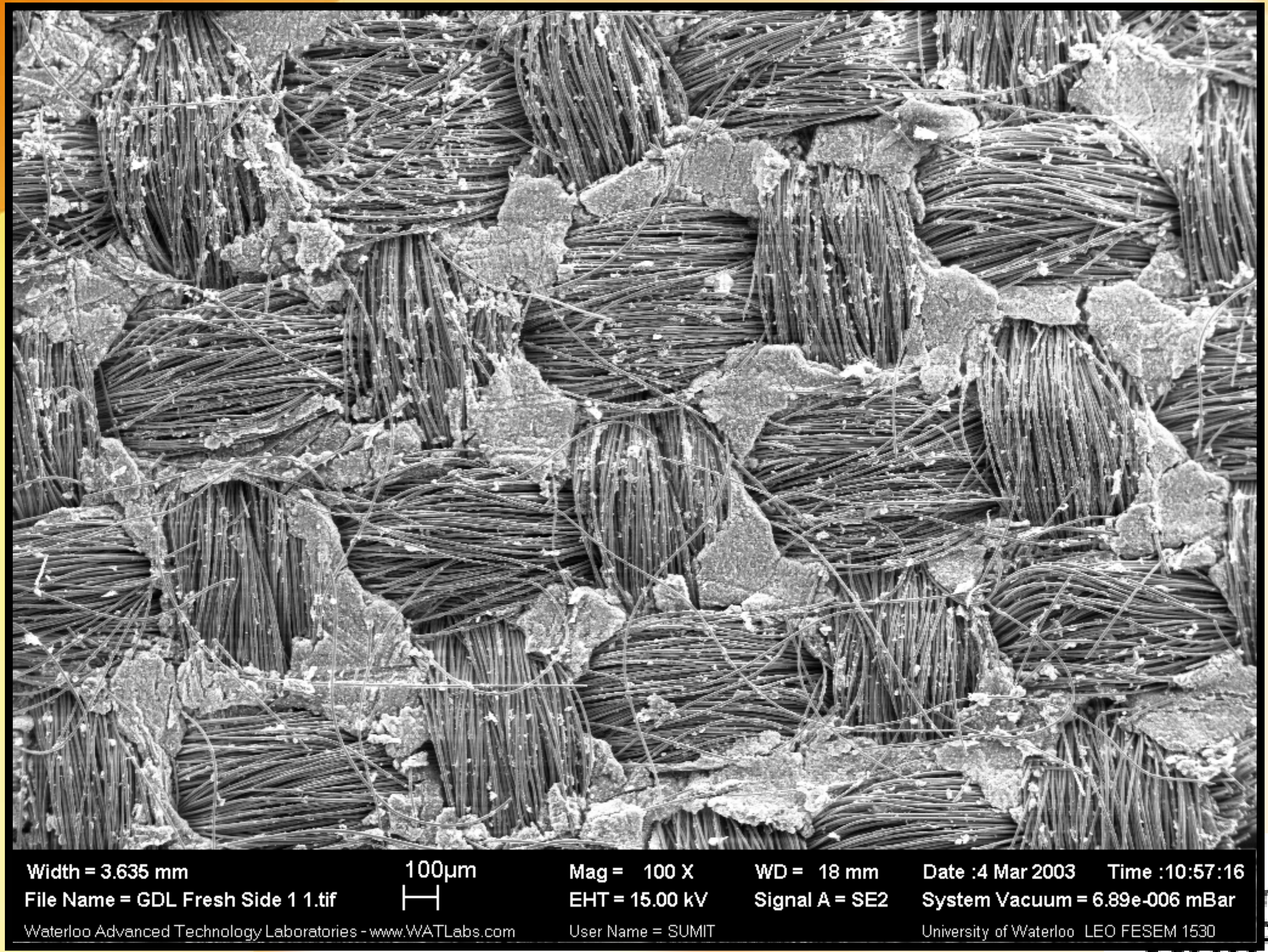
Thickness Variations



Causes and Impacts of Thickness Variations

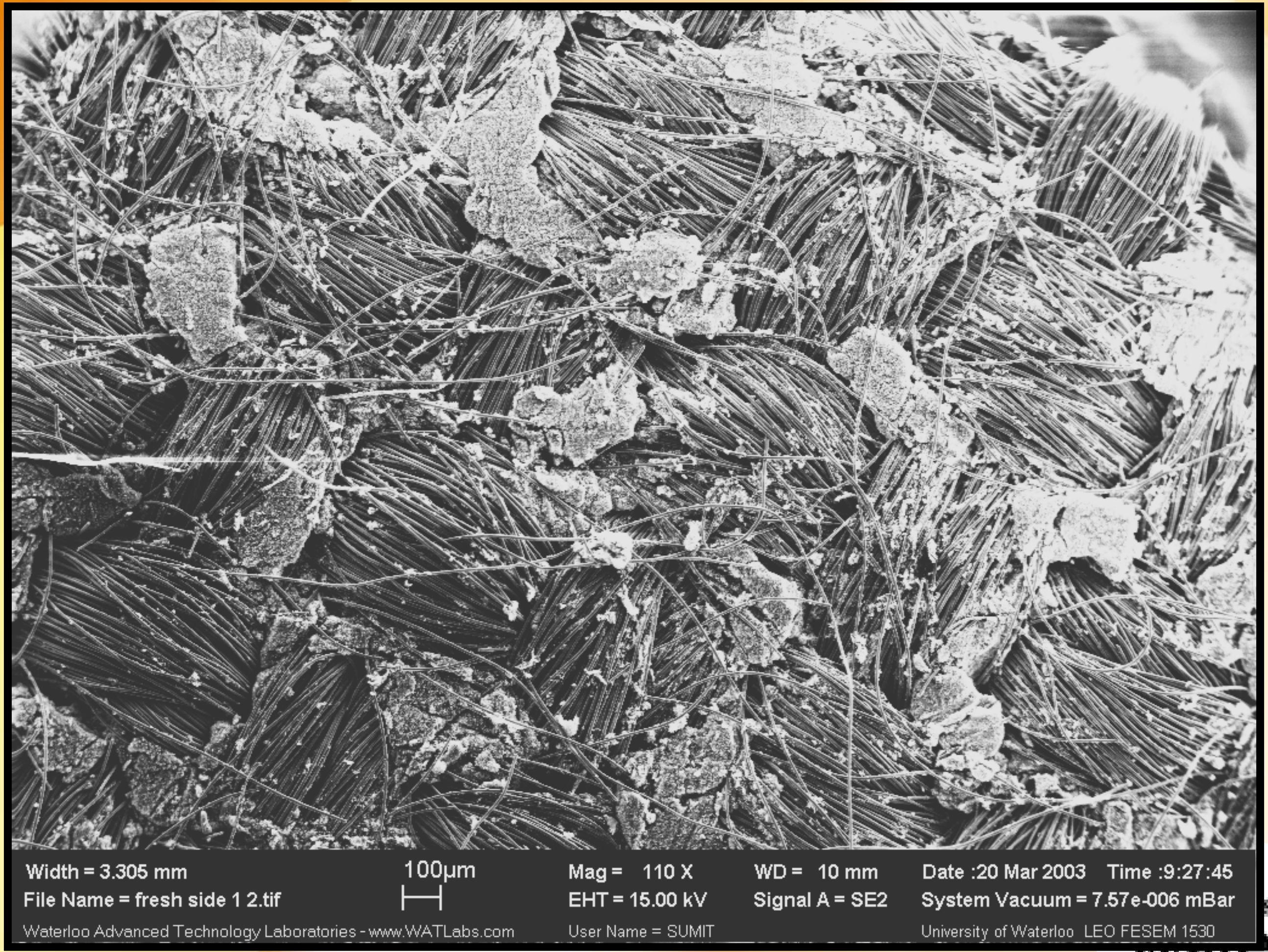
- Impacts
  - Crossover
  - Mechanical weak spot
  - Shorting
  - Pinholes

GDL Degradation



Fresh

GDL Degradation



2000 hours of external ageing

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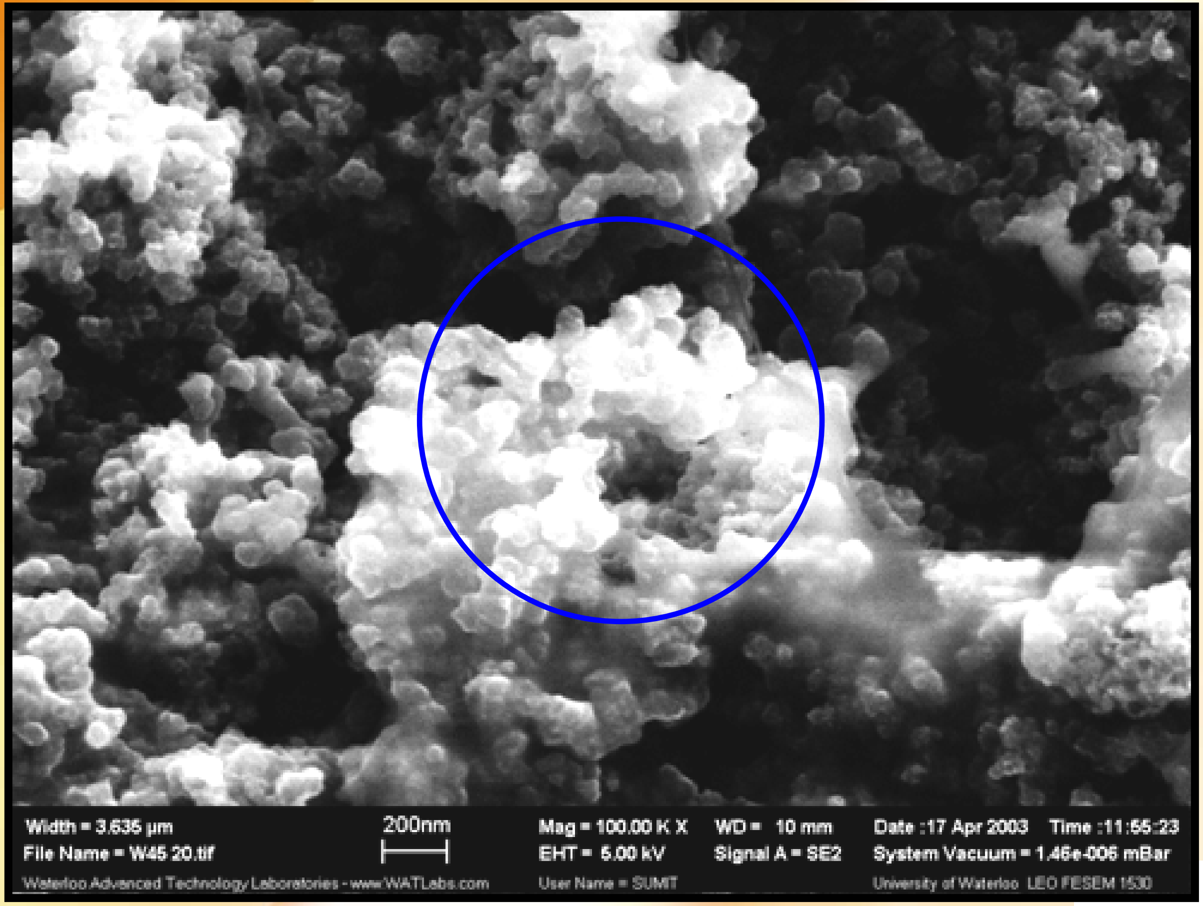
GDL Degradation

- Morphology impacts degradation
- The manufacturers have control over morphology
- Impacts
  - Loss of PTFE = more water accumulation
  - Increased flooding

Nafion Clusters



Nafion Clusters

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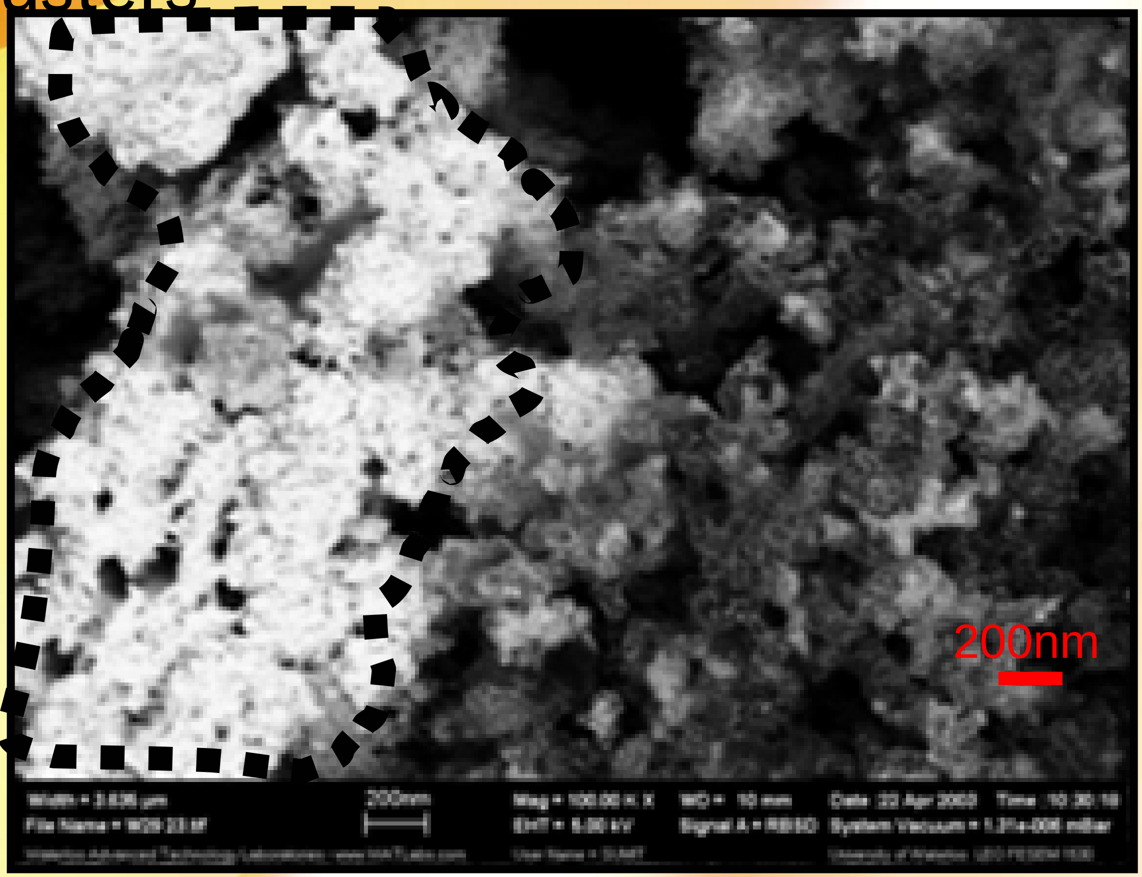
Cluster Identification

- Backscattered electron detector
- Bright spots were shown to be platinum clusters



Causes and Impacts of Clusters

- Impacts
  - Increased resistance to ion transport
  - Reduction of active catalyst area
  - Hot spots/cold spots

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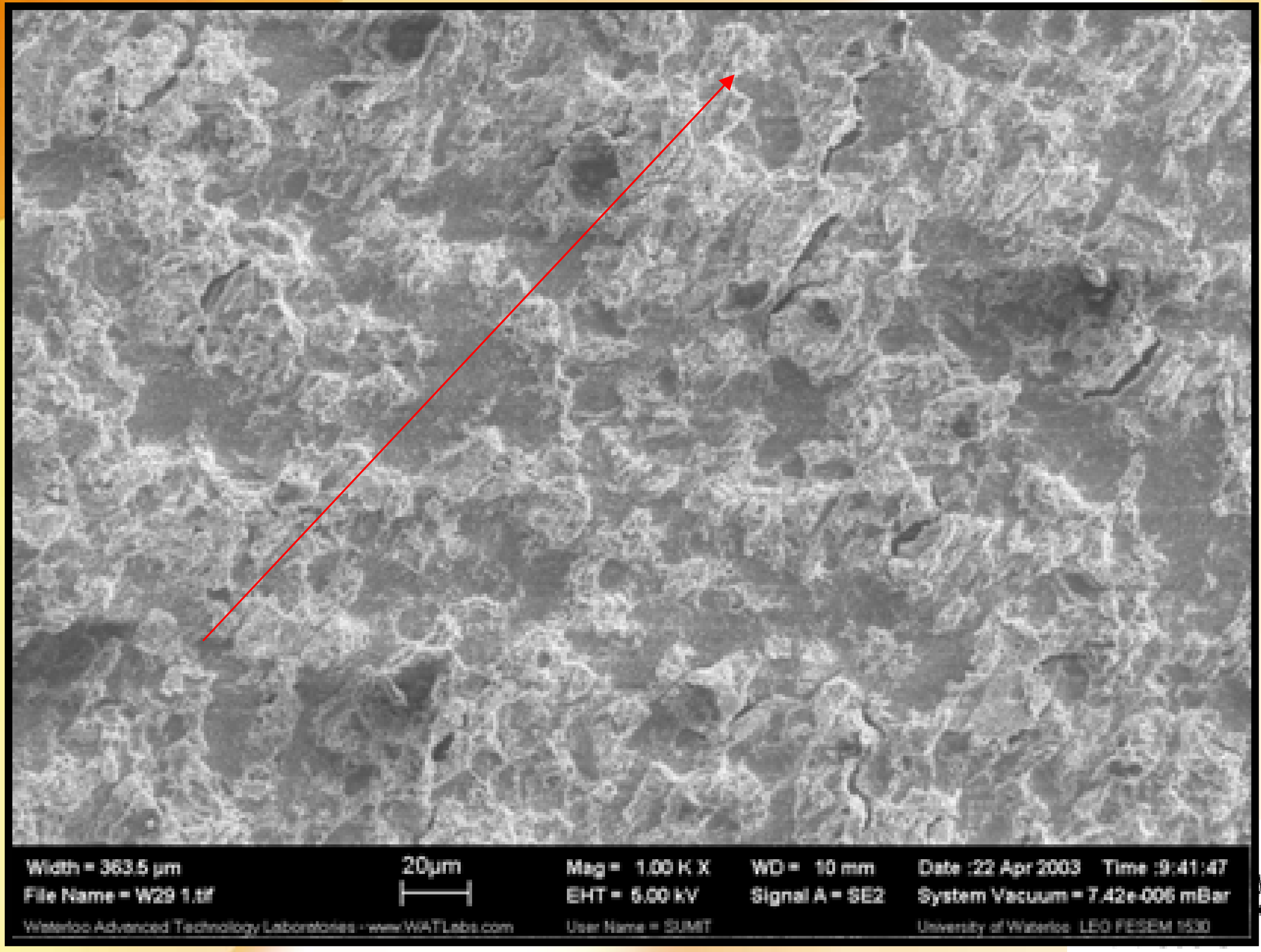
Macroscopic Orientation of Material



Causes and Impacts of Orientation

- Impacts
  - Contact resistance variation
  - Mechanical Stress variations
  - Less control over morphology

Conclusions

- There are many different morphological features in an MEA
- These are created largely during the manufacturing process
- Some of these features will have a clear impact on the performance and reliability of the fuel cell
- Since they are created at the manufacturing level, thus there is the potential to control them

Future Work

- Showing links between morphological features and degradation
- Examining pin hole formation and the role of mechanical stress
- Establishing links between operating conditions and the mechanism of degradation and failure
- Designing better membranes and control strategies

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