Argonne NATIONAL LABORATORY

Sub-freezing Start-up of a Fuel Cell

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THE UNIVERSITY OF CHICAGO

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Work sponsored by U.S. Department of Energy,
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Overview

Timeline

- Project start: October, 2006
- Project end: Open

Barriers addressed

- **A** : Durability
- **D** : Thermal, Air and Water Management
- **J** : Start-up Time / Transient Operation

Budget

- DOE share: 100%
- FY06 funding: $225K

Technical Targets

Characteristics	2010	2015
Start-up time to 90% rated power		
@ -20°C *ambient* T	30 s	30 s
@ +20°C *ambient* T	15 s	15 s
Survivability	-40°C	-40°C

Objectives

- To understand fundamental aspects of the start-up process at sub-freezing conditions and to identify the key mechanisms that
  - Limit rapid start-up
  - Lead to failure
- To study the effect of different start-up and shutdown protocols on fuel cell durability and performance

Approach

- Develop transient models for the fuel cell to
  - Quantify the interactions and contributions of multiple processes during start-up (mass transfer, kinetics, phase change, etc.)
  - Guide experimental characterization

- Conduct start-up experiments on a fuel cell (single cell initially)
  - At -40°C to +80°C
  - Investigate the effect of prior shutdown protocols
  - Validate model predictions

Published literature on experimental and theoretical work on fuel cell operation below freezing is limited

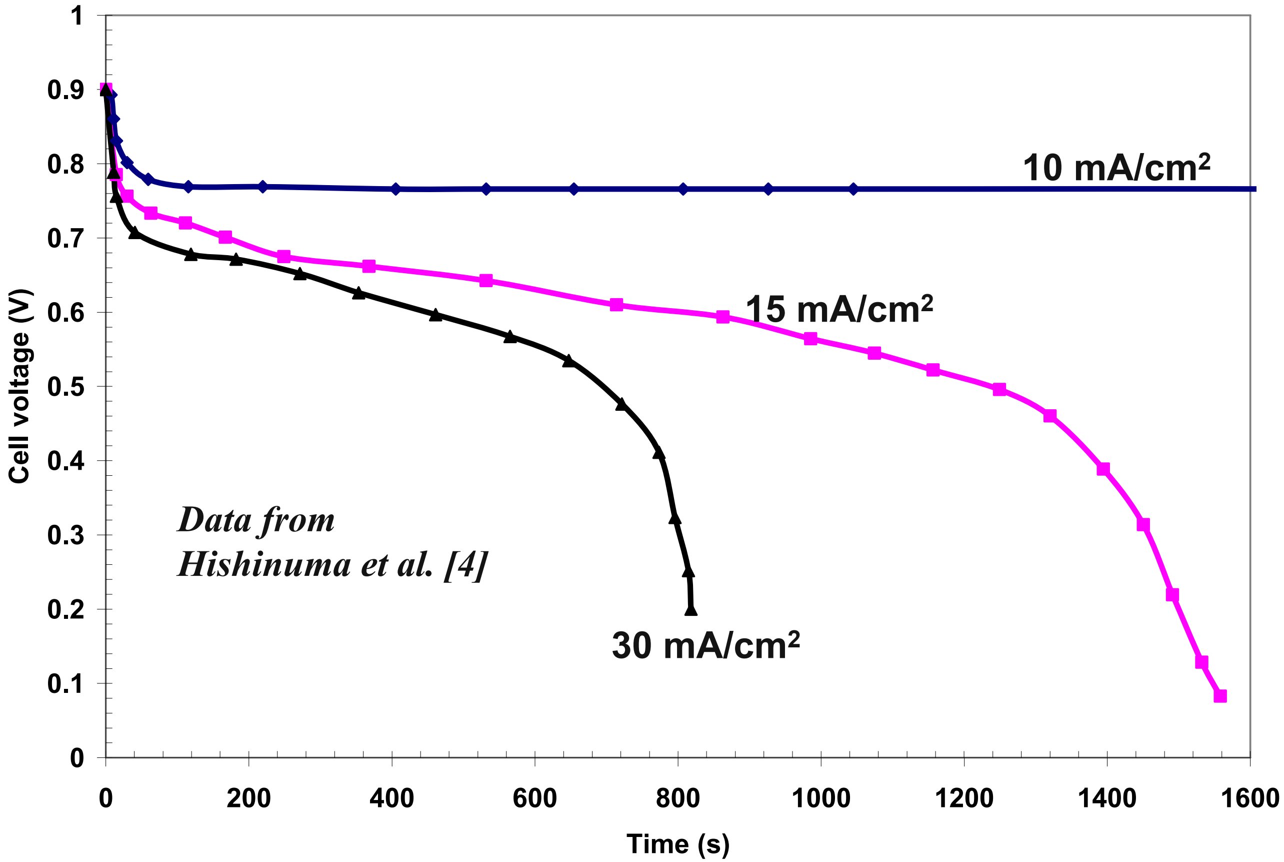
- **State of water**
  - Phase change in membrane affects transport properties [1,2]

- **Freeze/thaw cycling leads to**
  - Increased polarization resistance (2.8% loss per cycle [3])
  - Increased contact resistance between electrodes and PEM

- **Maintenance and prevention methods**
  - Dry gas purging before shutdown
  - Purge with antifreeze
  - Maintain temperatures above 0 °C (e.g., by electric heating)

- **Start-up at sub-freezing conditions**
  - Too much current draw may result in ice formation which can cover the electrochemically active surface area
  - High air flow-rates are needed to remove water
    - *Slows down the cell temperature rise*

Performance of PEFC decreases at low cell temperatures as ice formation reduces electrochemically active surface area

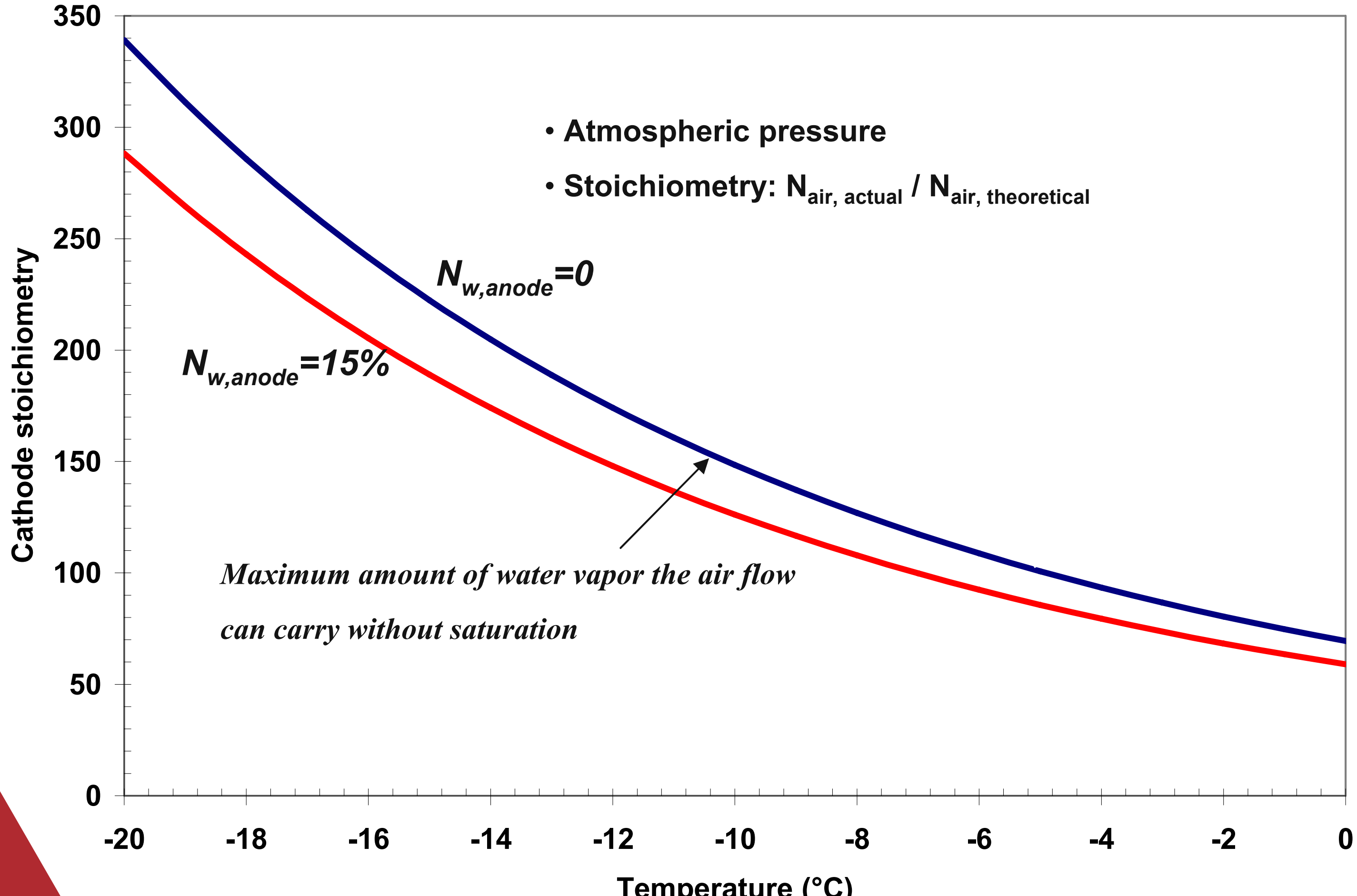


The case at 0.015 A/cm^2 represents a threshold value and has been used as a reference point in our modeling work

To maintain performance below freezing, water produced and removed must be in balance

High air flow rates would be needed to avoid water vapor saturation at low temperatures

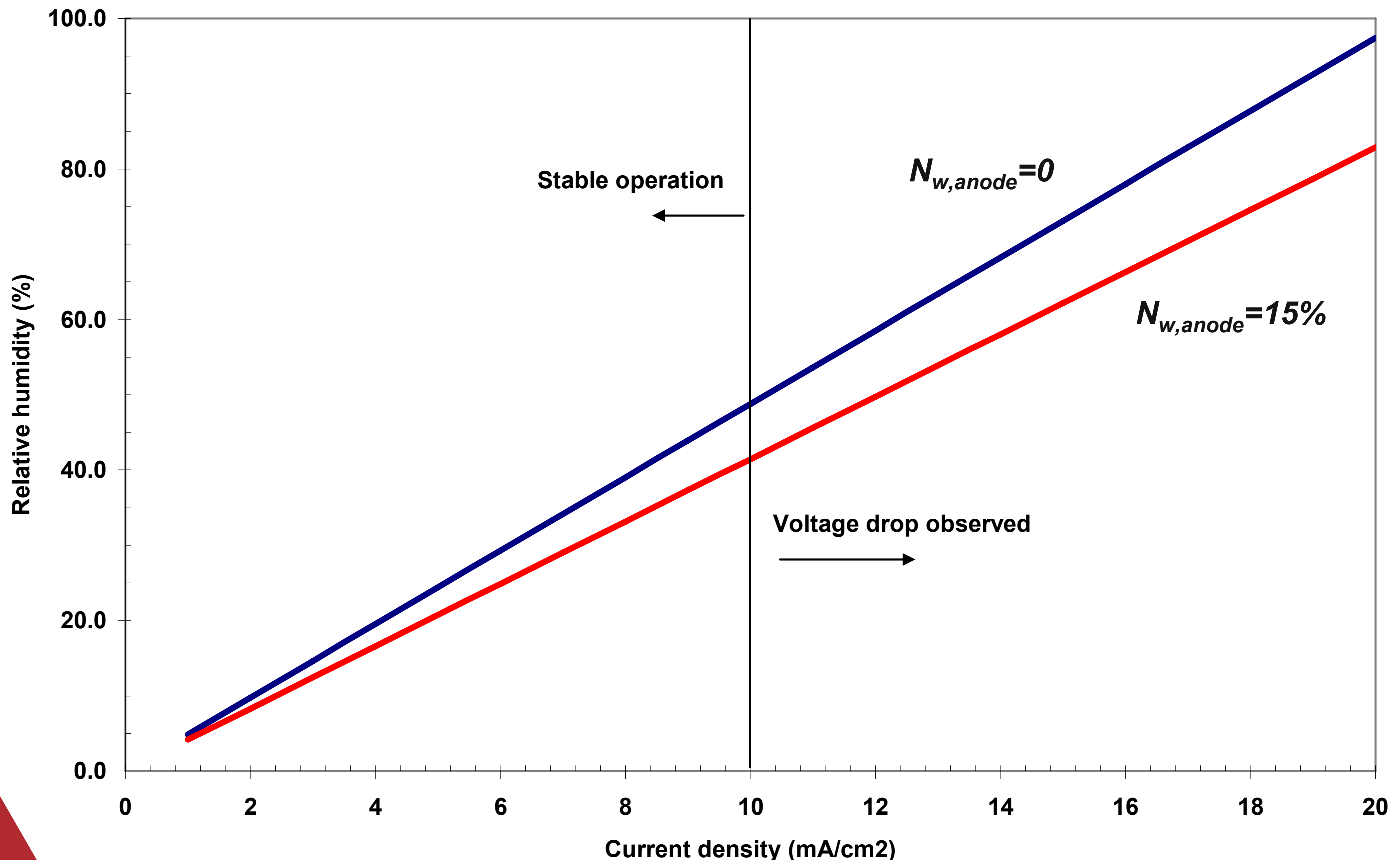
- For a cell with 100 cm^2 surface area at -10 °C, an air flow rate of 2.8 SLPM is needed to avoid saturation of water if the current density is only 10mA/cm^2. Calculations assume ideal conditions (no gradients).



$N_{w,anode}$ denotes water flux from cathode to anode (Drag-Diffusion)

$N_{w,anode}$=15% means that 15% of the generated water diffuses to the anode and only 85% is removed by the cathode air flow

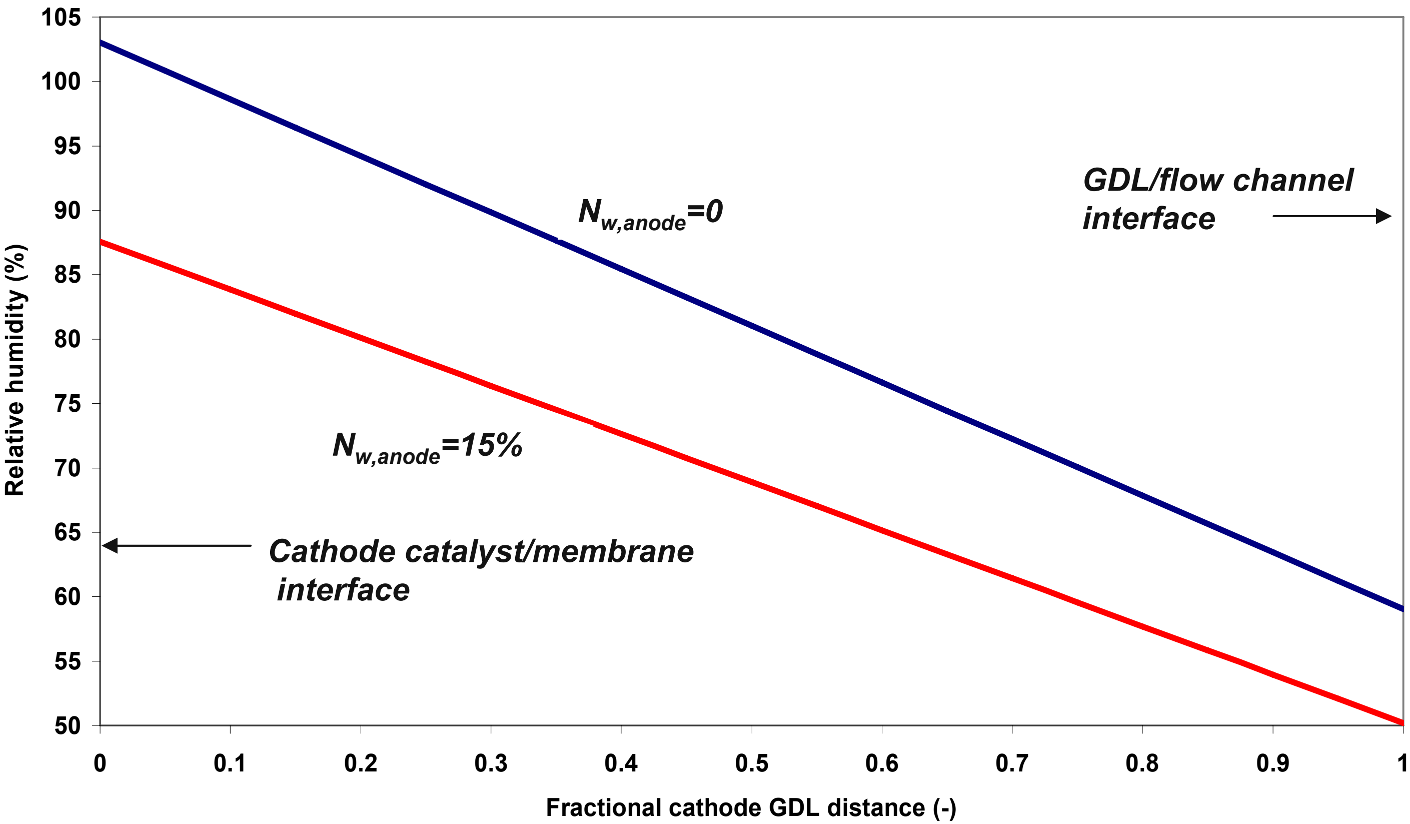
Using an idealized model, air in cathode channel is found to have a relative humidity less than 100% in the domain where voltage drop was observed



- Temperature: –10 °C
- Flow-rate: 6.33 L/min
- Membrane active area: 100 cm^2
- 100% relative humidity equals to 0.0028 bar of water vapor
- Air stoichiometry (6.33 L/min):
  380 at 10 mA/cm^2
  255 at 15 mA/cm^2

Hishinuma et al. concluded that ice formation caused voltage drop at current densities $\geq$ 10 mA/cm^2

Diffusion resistance in gas diffusion layer increases water concentration near the catalyst layer

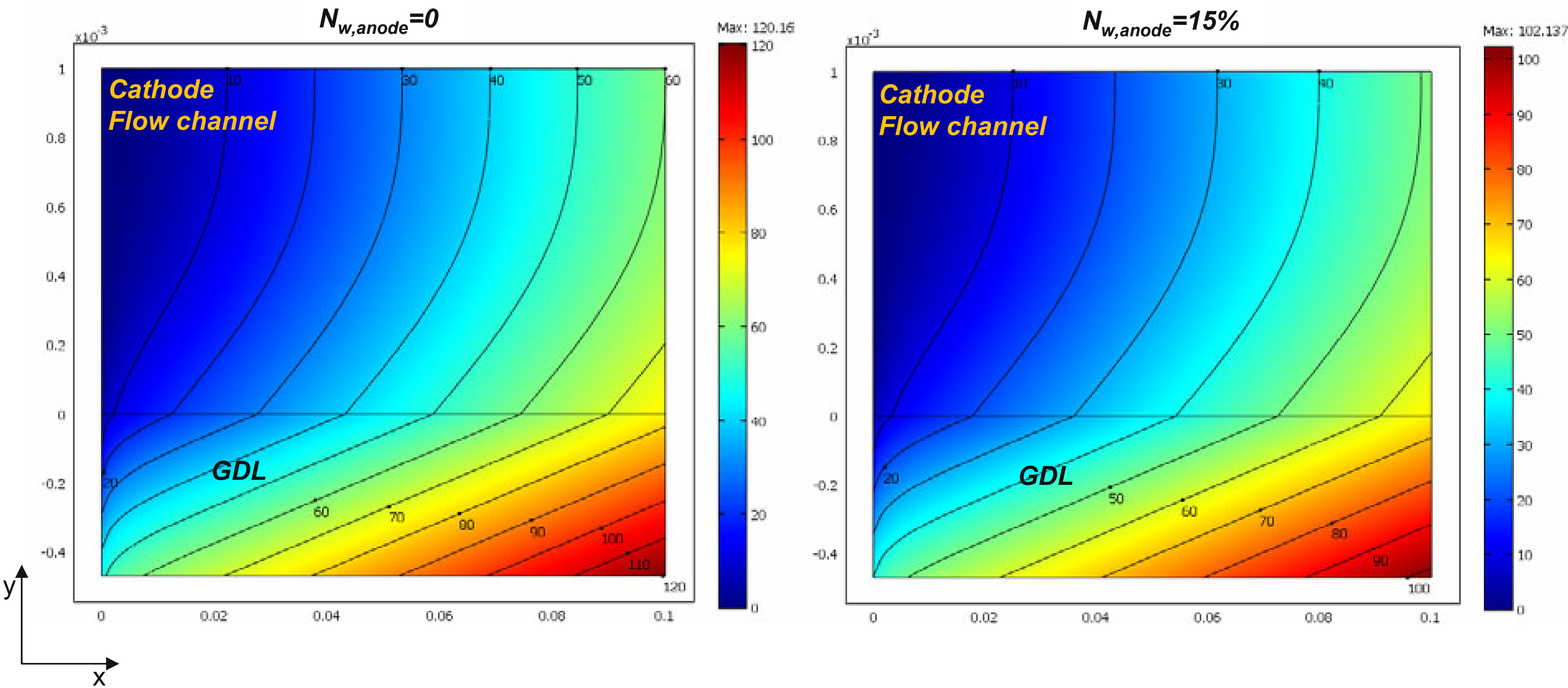


- Temperature: –10 °C
- Flow-rate: 6.33 L/min
- Membrane active area: 100 cm^2
- Current density: 15 mA/cm^2
- GDL thickness: 0.47 mm

With no water transport back to anode, water concentration barely exceeds saturation at 15 mA/cm^2

Water concentration increases towards the exit of the fuel cell

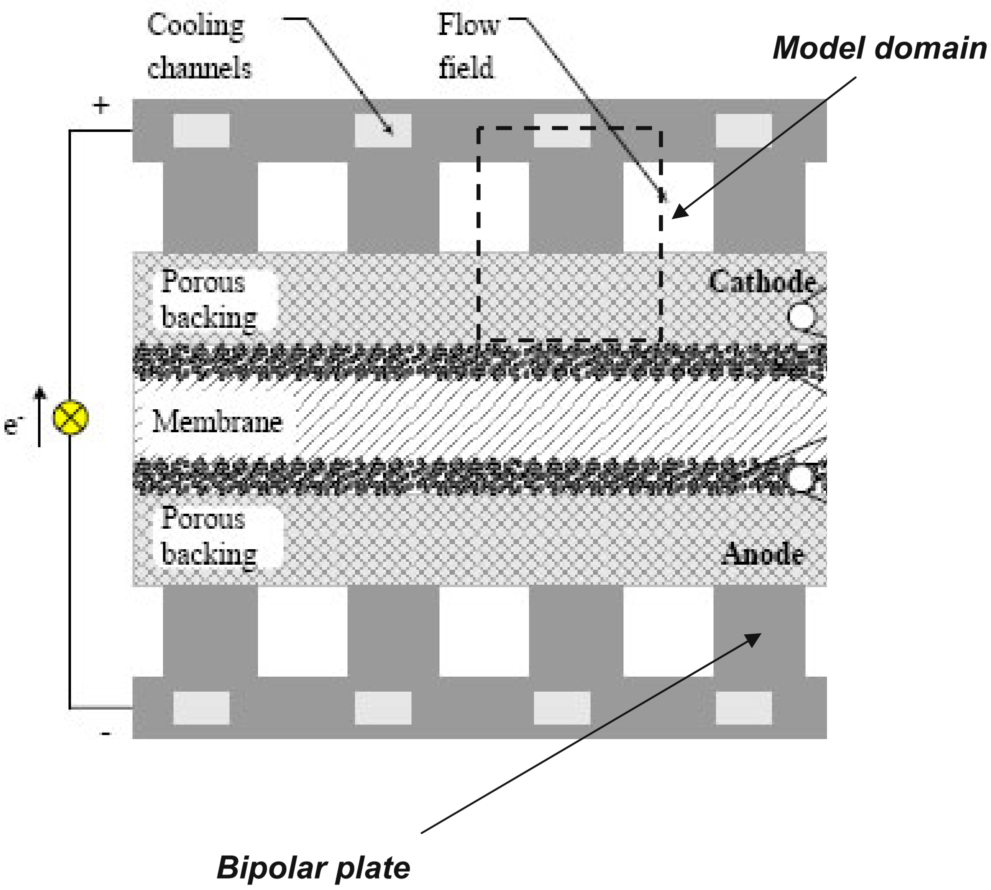
Color and contour lines denote relative humidity



Concentration of water predicted with a 2D model: T=–10 °C, Flow=6.33 L/min, Current density=15 mA/cm²

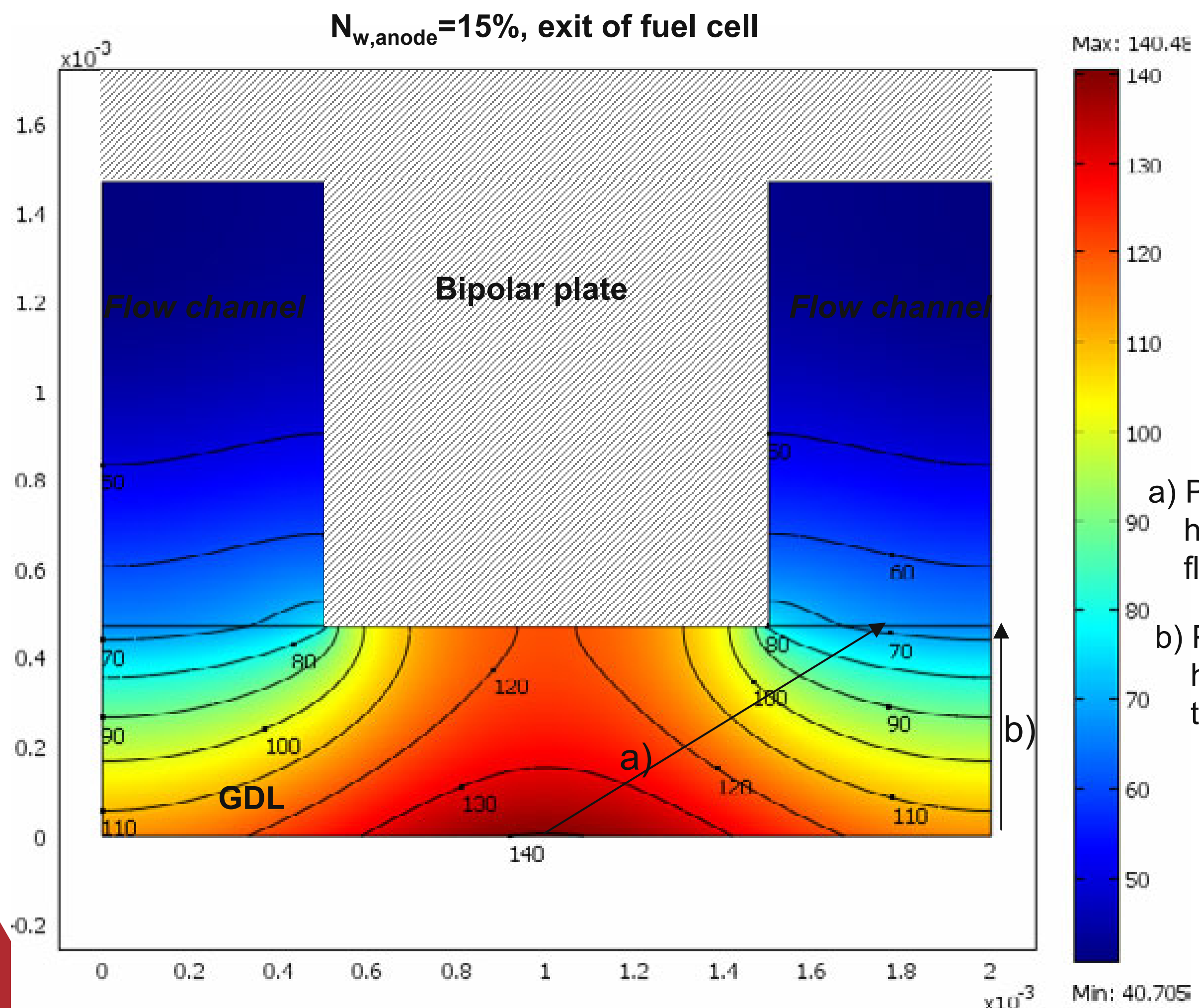
Water may reach saturation at the exit of the fuel cell if the water flux to the anode side is low

A 3D model of the fuel cell is being developed to understand the dimensional and geometric effects



The flow channels cover half the area of the porous backing (GDL)

The 3D model predicts formation of liquid water which can freeze. The ice may begin to form under the current collector and spread out towards the flow channel

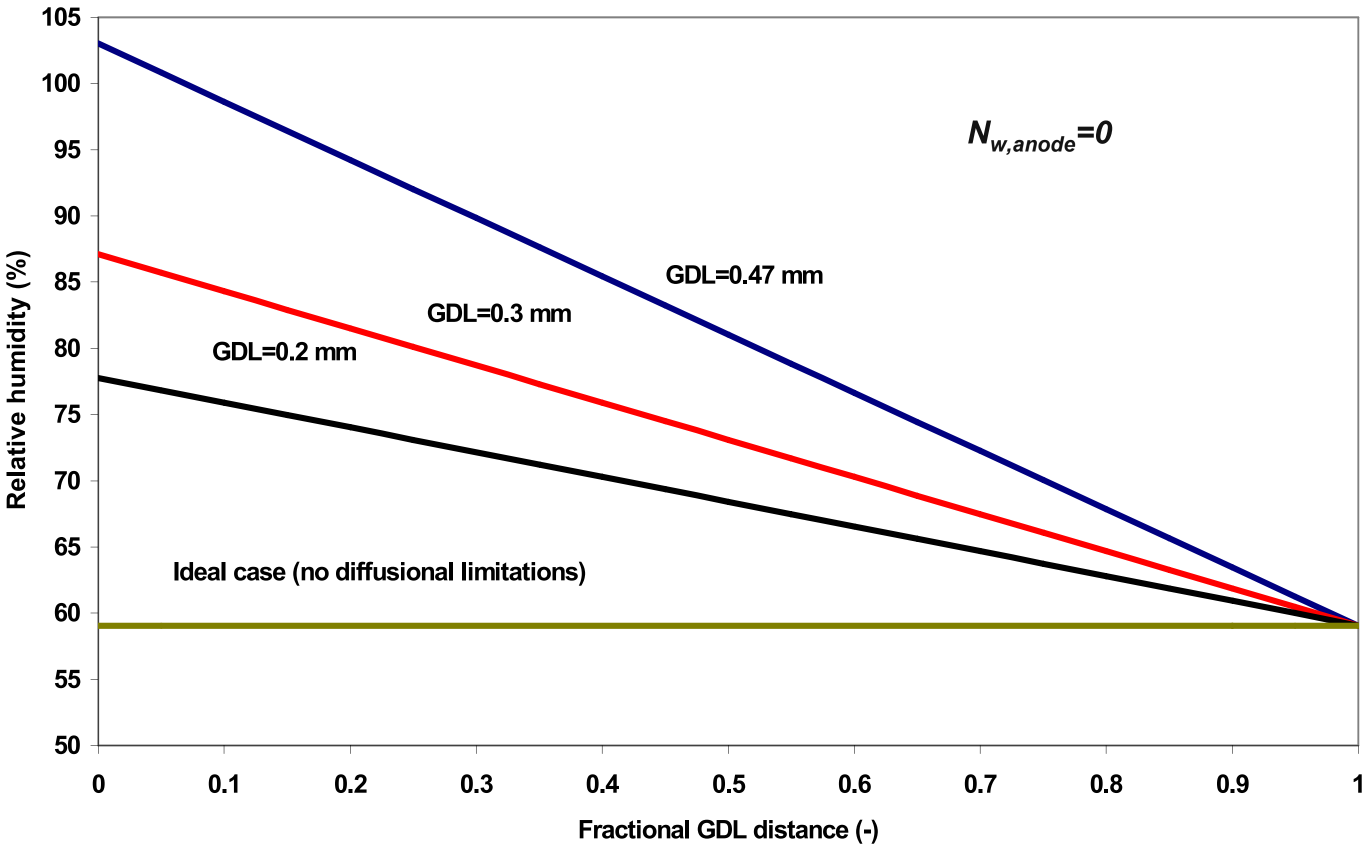


- Temperature: –10 °C
- Flow-rate: 6.33 L/min
- Membrane active area: 100 cm^2
- Current density: 15 mA/cm^2
- GDL thickness: 0.47 mm

a) Product water formed under the current collector has longer distance to be transported out to the flow channel

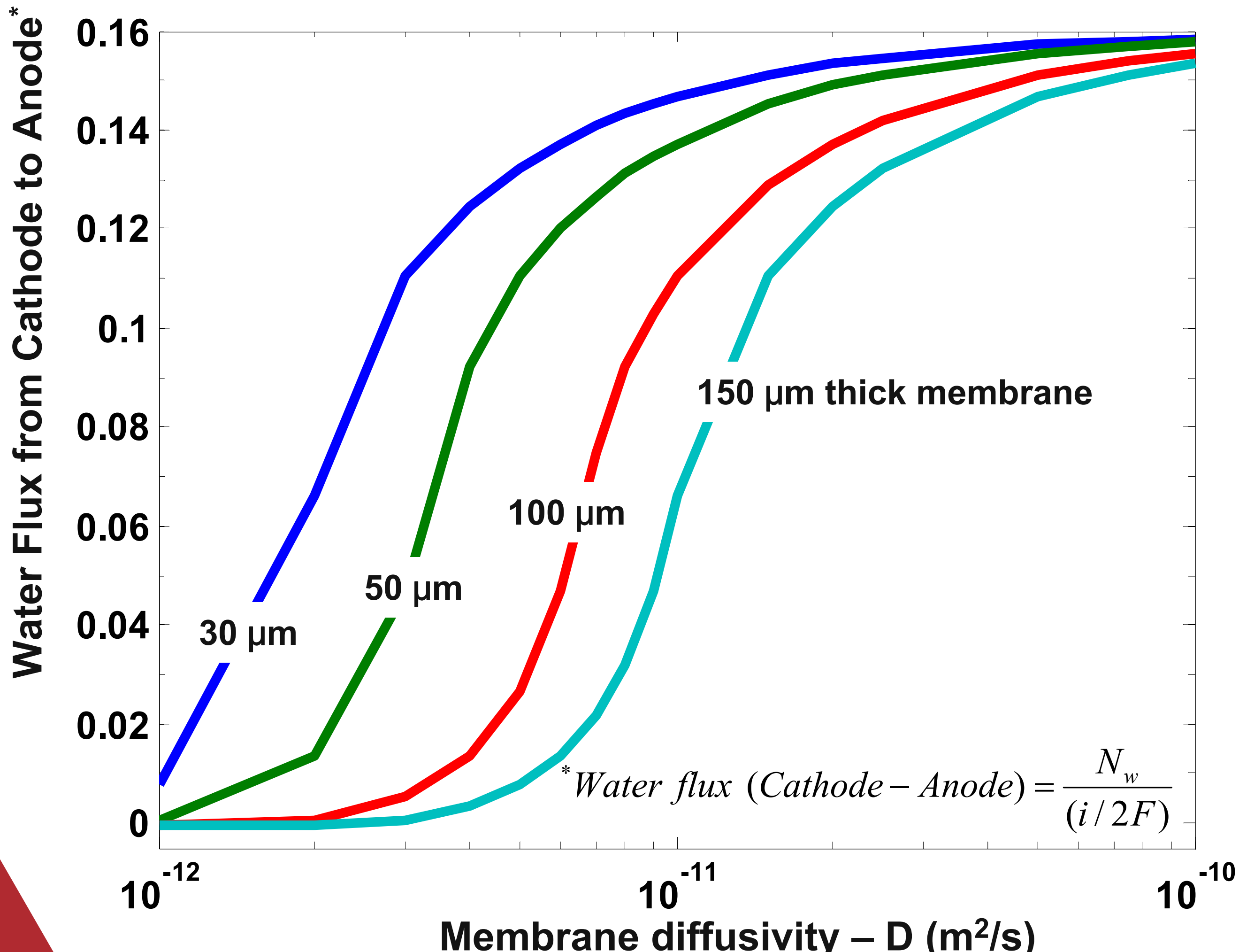
b) Product water formed under the flow channel has a short way to be transported out from the GDL

Thinner gas diffusion layers will lower the concentration gradients



- Temperature: –10 °C
- Flow-rate: 6.33 L/min
- Membrane active area: 100 cm^2
- Current density: 15 mA/cm^2

Thinner membrane layers lead to higher water flux from cathode to anode



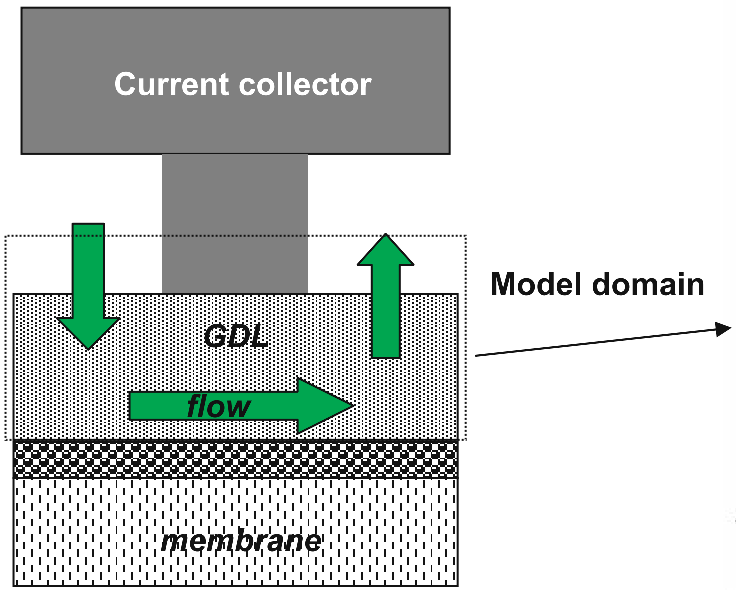
$$^{*}\text{Water flux (Cathode} - \text{Anode)} = \frac{N_w}{(i/2F)}$$

- Temperature: –10 °C
- Cathode flow-rate: 6.33 L/min
- Anode flow-rate: 0.8 L/min
- Membrane active area: 100 cm^2
- Current density: 15 mA/cm^2

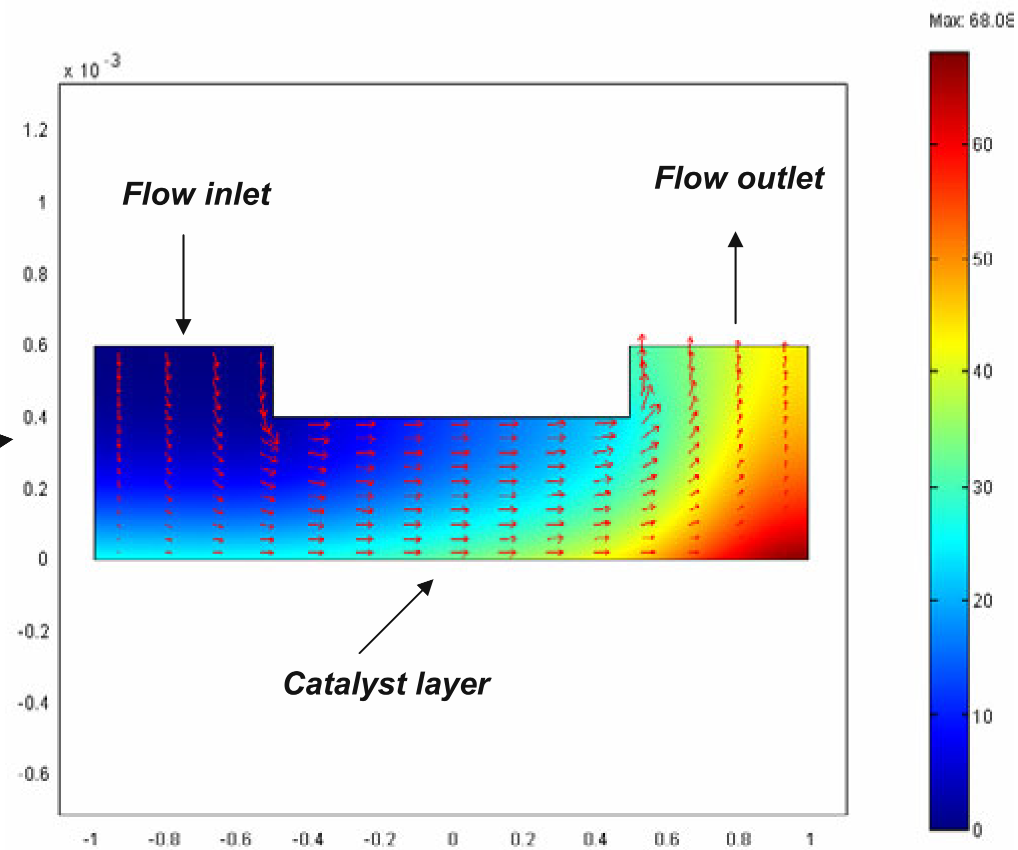
***D* (30 °C) ~ 4x10^{-10} m^2/s [5]**

***D* (-20°C) ~ 2x10^{-11} m^2/s [1]**

Interdigitated flow avoids water condensation and freezing.
Interdigitated flow causes higher pressure drop.



- Temperature: -10 °C
- Flow-rate: 6.33 L/min
- Membrane active area: 100 cm^2
- Current density: 15 mA/cm^2
- $N_{w,anode}=0$



Arrow = Flow field
Color = water concentration (Relative humidity)

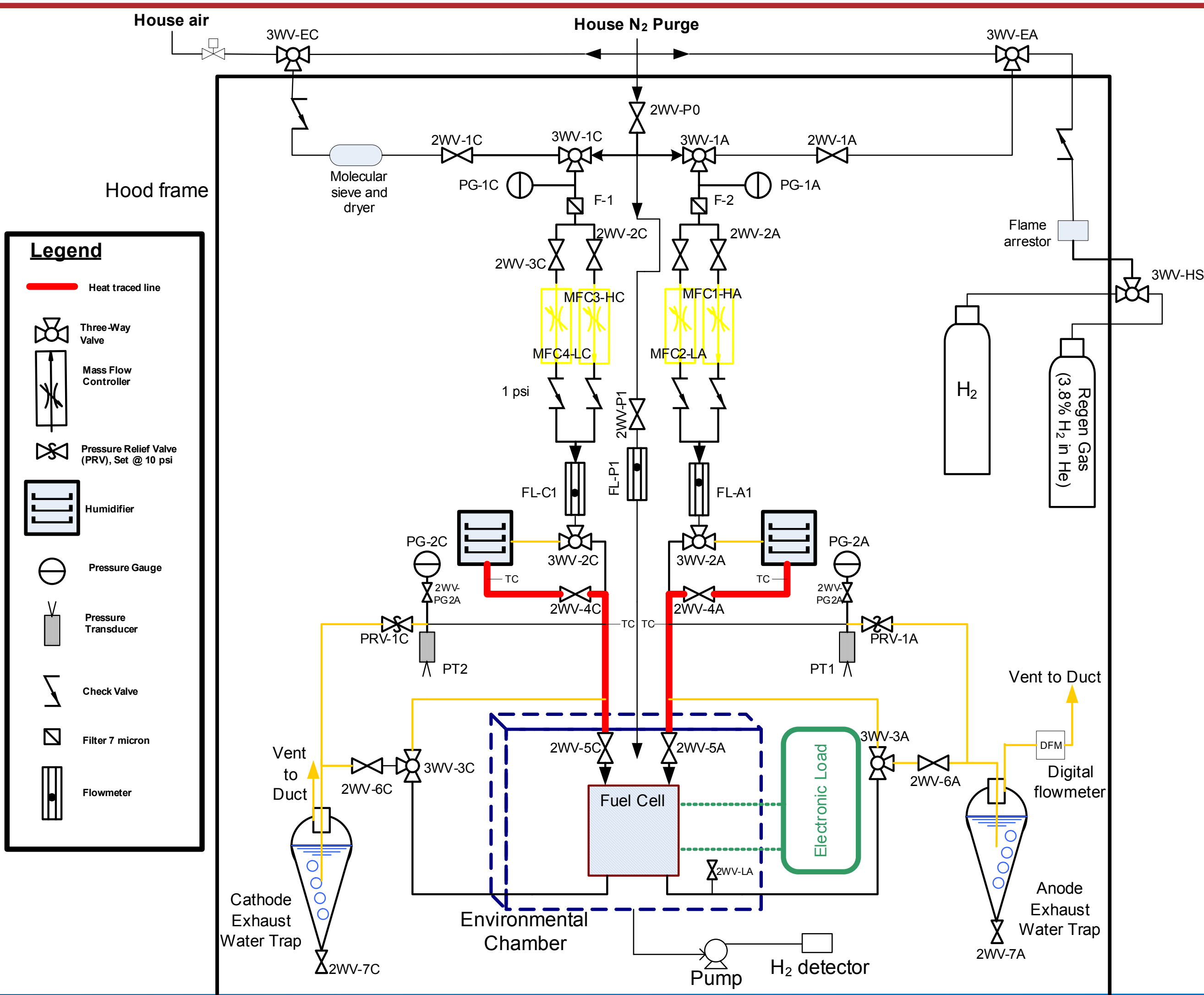
Accomplishment: Model was used to show alternative explanations of freezing mechanism

- A thick gas diffusion layer may induce a steep concentration gradient of product water. Water may condense and freeze at the electrochemically active surface area.

- Thick membranes limit transport of water from cathode to anode. Water may remain in cathode and freeze.

- Water may start to freeze under the current collector and spread out towards the flow channel.

Experimental: A fuel cell test apparatus has been setup for sub-freezing start-up experiments

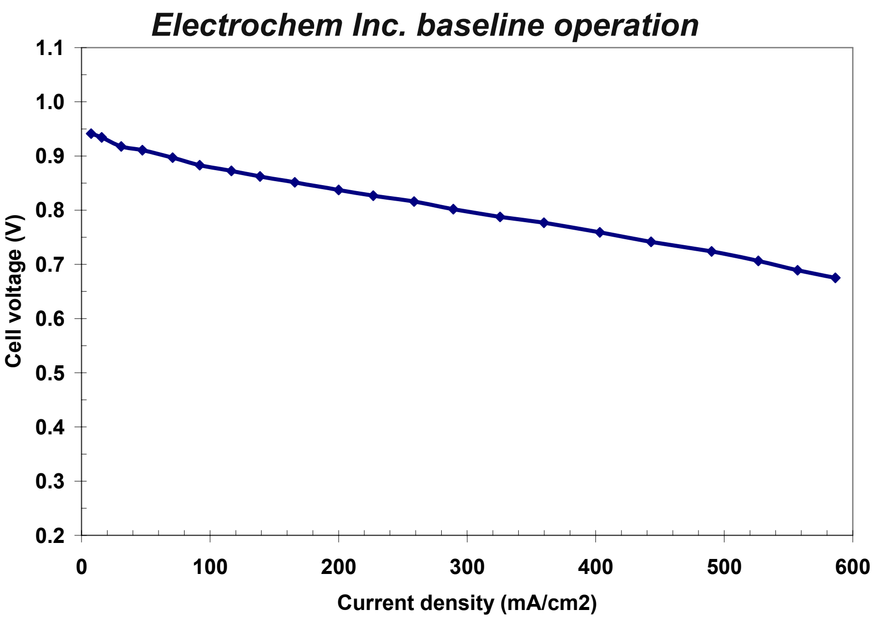


The environmental chamber allows operation from –40°C to 80°C

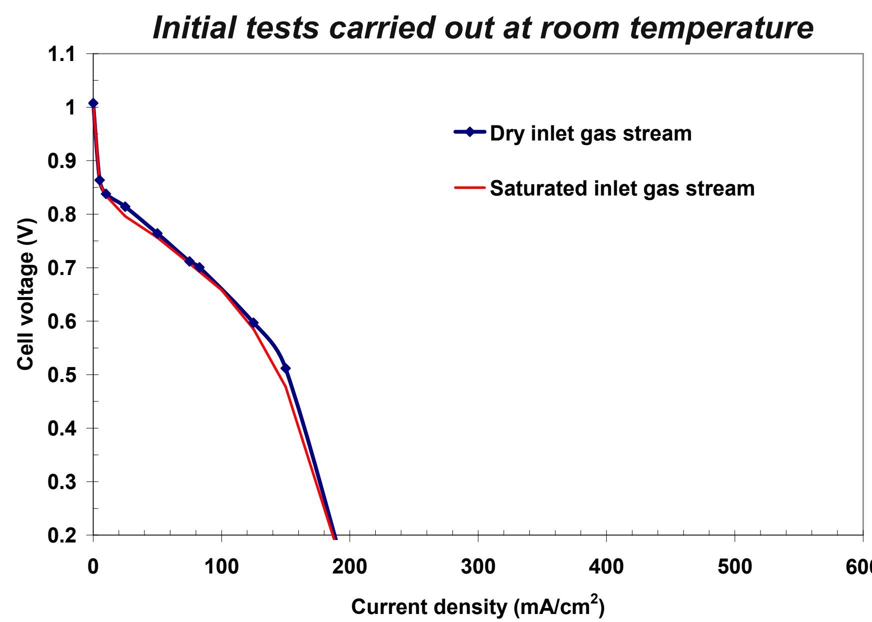
Fuel cell test apparatus. Walk-in hood, test stand, and chamber (from left to right)

Initial experiments are being conducted to establish baseline operation of the fuel cell

- Pressure: 3 atm
- Temperature: 75°C
- Reactants, H_2/O_2



- Pressure: 1 atm
- Temperature: 25°C
- Reactants, H_2/Air
- (H_2=190 cm^3/min, Air=500 cm^3/min)



- Active area: 50 cm^2
- Membrane: Nafion® 1135
- GDL: Toray paper 060
- Straight channel flow pattern

Summary

- Developed initial models (1D, 2D, 3D) to analyze water transport properties in GDL and flow channels
  - 3D models are necessary to understand geometrical effects
  - Water may start to freeze under the current collector and spread out to the flow channel
  - Thinner gas diffusion and membrane layer as well as optimized flow-field may lead to less ice formation

- Fuel cell test apparatus has been completed to evaluate cell performance from -40 °C
  - Baseline operation data is being generated

Future work and milestones

<u>Future Work</u>

- Continue model development and validate models with experimental data
  - Complete 3D model incorporating complete description of physico-chemical phenomena to confirm direction of freeze propagation
  - Use 3D model to refine transient 1D model including geometrical effects
  - Study the effect of prior shutdown scenarios and power draw as function of time and temperature

<u>Milestones</u>

Complete startup tests from 0ºC on one or more cells	05/2006	On-schedule
Complete initial startup tests of cells/stacks from –20ºC	09/2006	On-schedule

References

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2. Cappadonia, M., Erning, J.W. and Stimming, U. (1994). Proton conduction of Nafion® 117 membrane between 140 K and room temperature. *Journal of Electroanalytical Chemistry*, **376**, 189-193.
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5. Springer, T.E., Zawodzinski, T.A. and Gottesfield, S. (1991). Polymer electrolyte fuel cell. *Journal of the Electrochemical Society*, **138**, 2334-2342.