Accelerated Stress Tests in PEM Fuel Cells: *What can we learn from it?*

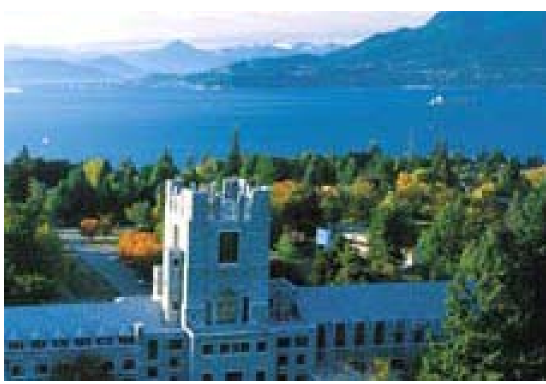
D.P. Wilkinson [1,3], W. Merida [2,3]

1st Workshop : Durability and Degradation Issues in PEM Electrolysis Cells and its Components

Fraunhofer ISE, Freiburg, Germany

(March 12th- 13th , 2013)

1. Department of Chemical and Biological Engineering, UBC
2. Department of Mechanical Engineering, UBC
3. Clean Energy Research Centre (CERC), UBC



CERC
Clean Energy Research Centre

UBC

Presentation Overview

- Introduction
- Examples of PEMFC durability and degradation issues
- In-situ diagnostic techniques
- Spatial diagnostics
- Accelerated stress tests
- Closing remarks / summary

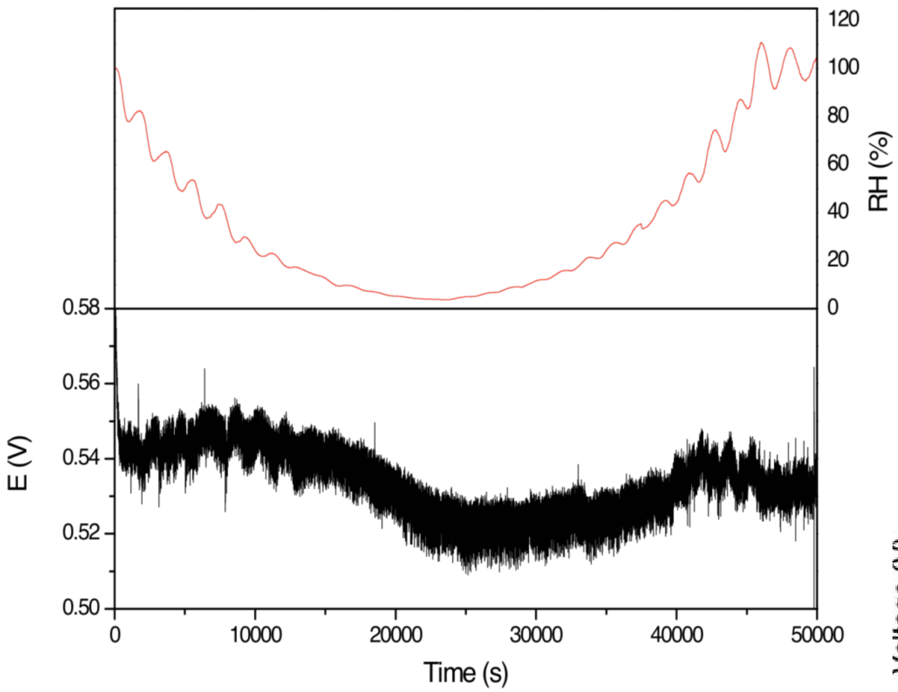
PEM Fuel Cell Research Closely Related to PEM Electrolysis

- Many PEM fuel cell advances applicable to PEM electrolysis
- Some related areas between the PEM fuel cell and PEM electrolysis:
  - Electrolysis anode has similar requirements to PEMFC anode in cell reversal (fuel starvation)
  - More durable and less expensive PEM membranes required
  - 2 –phase PEMFC cathode/flow field similar to 2-phase PEM electrolysis anode/flow field
  - PEMFC anode/ flow field similar to PEM electrolysis cathode/flow field
  - Bipolar stacked flat plate approach similar in both cases
  - Air bleed on PEMFC anode for reformate compared with O_2 cross-over to PEM electrolysis cathode
  - **Diagnostics and failure / durability testing similar for the PEM fuel cell and PEM electrolysis**
  - Etc, etc

Lifetime Issues

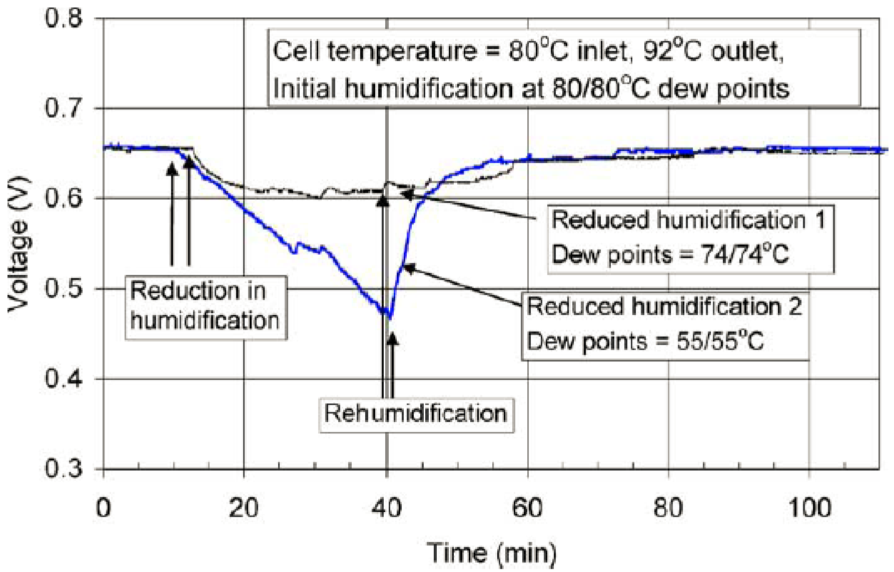
- Operational conditions, materials and design affect fuel cell lifetime
- Some key operational areas include:
  - Low humidification
  - High/excess humidification
  - Low reactant flows
  - High temperature
  - Low temperature
  - Fuel composition
  - Current density
  - etc

Failure Modes (Low Humidity)



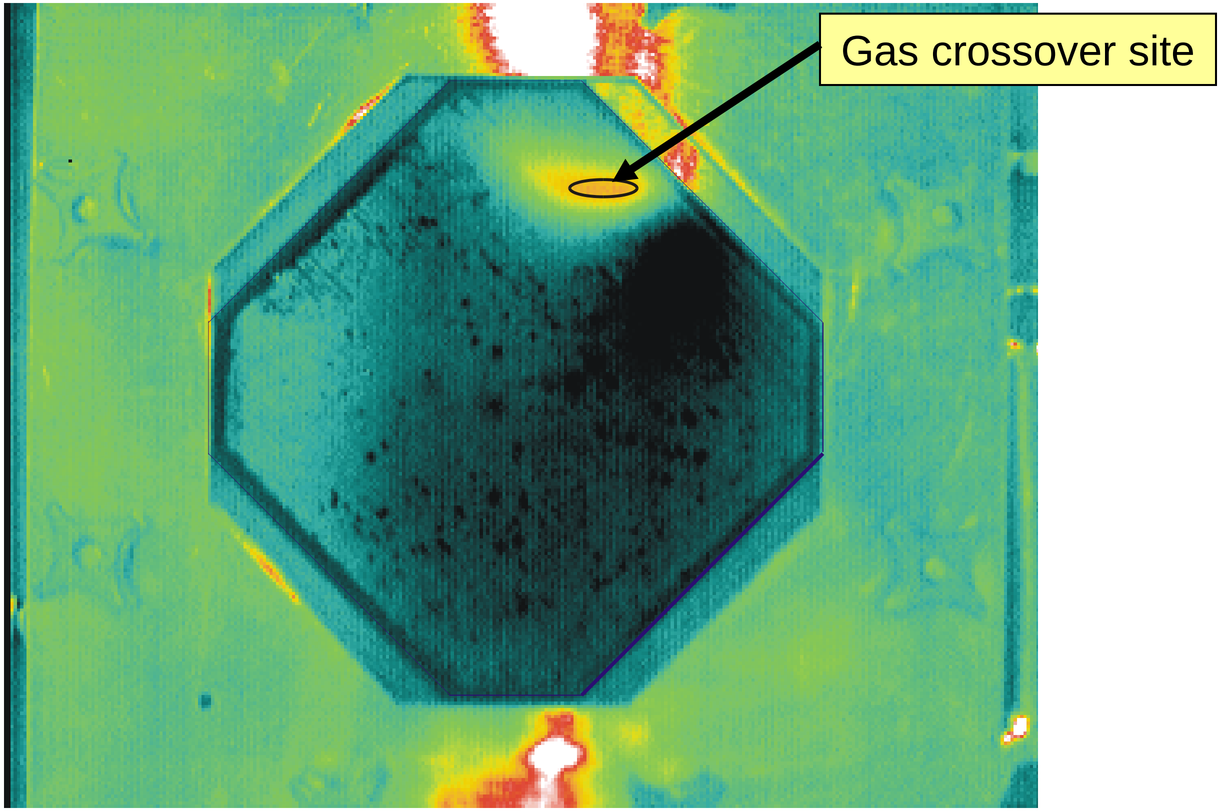
Low humidity

- Dehydration
- Resistance increase
- Increases cross-over
- Membrane pinhole development



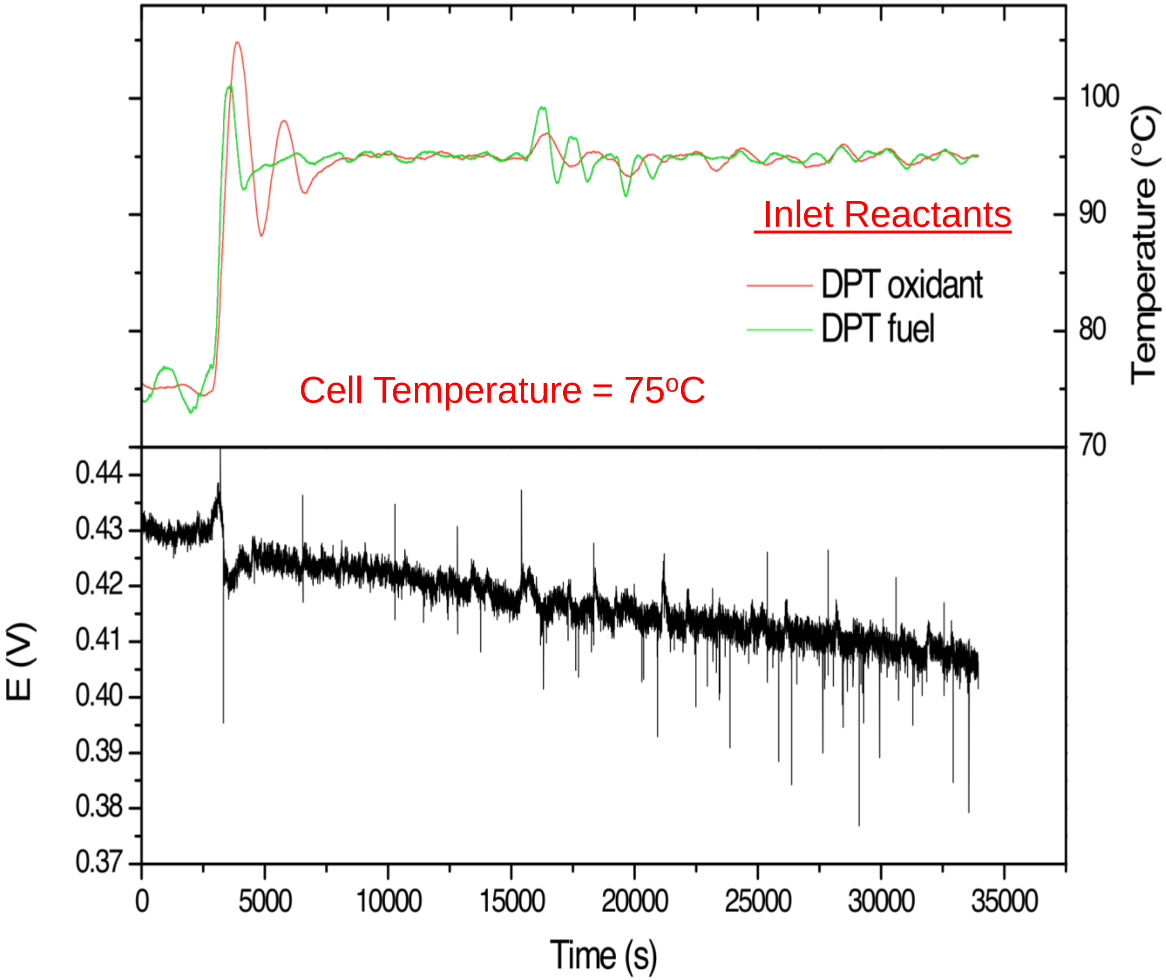
Knights, Wilkinson et al, J. Power Sources, 127, pp 127-134 (2004)

Low humidity and hot spots can lead to failures such as shorting and membrane holes (gas crossover detection by IR)



Wilkinson, Lamont : US patent 5,763, 765 (1998)

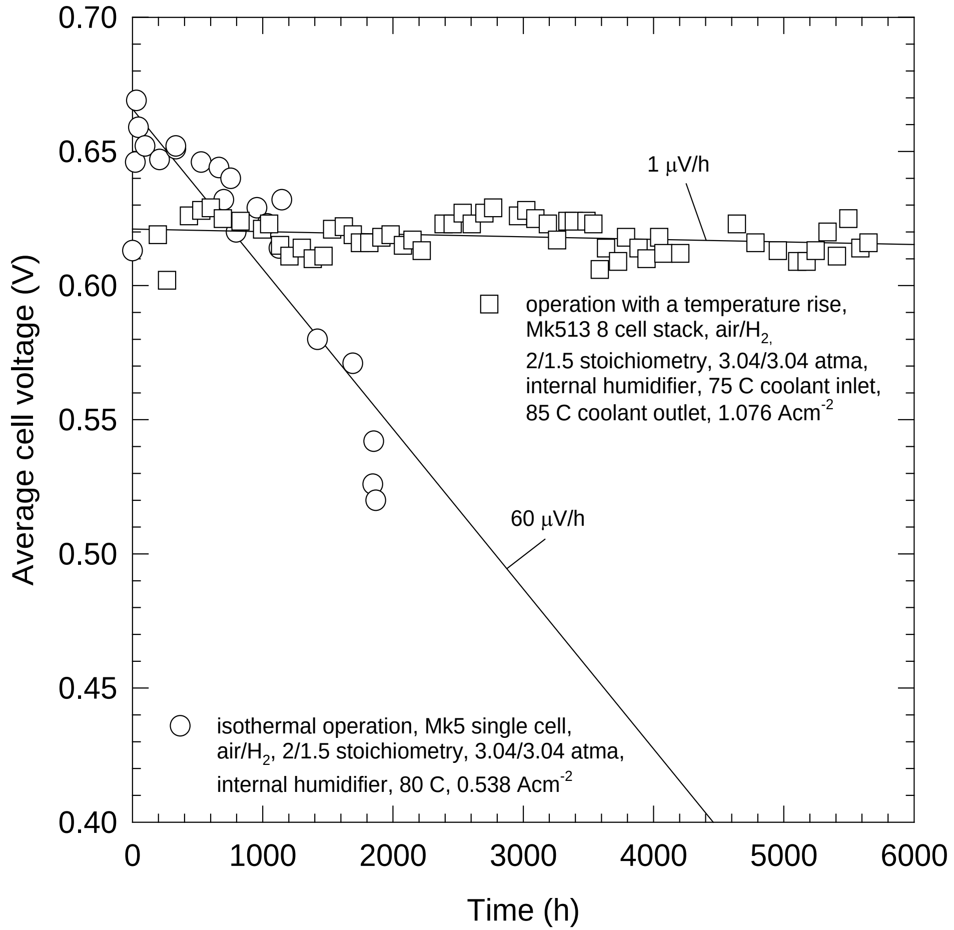
Failure Modes (Flooding)



Flooding

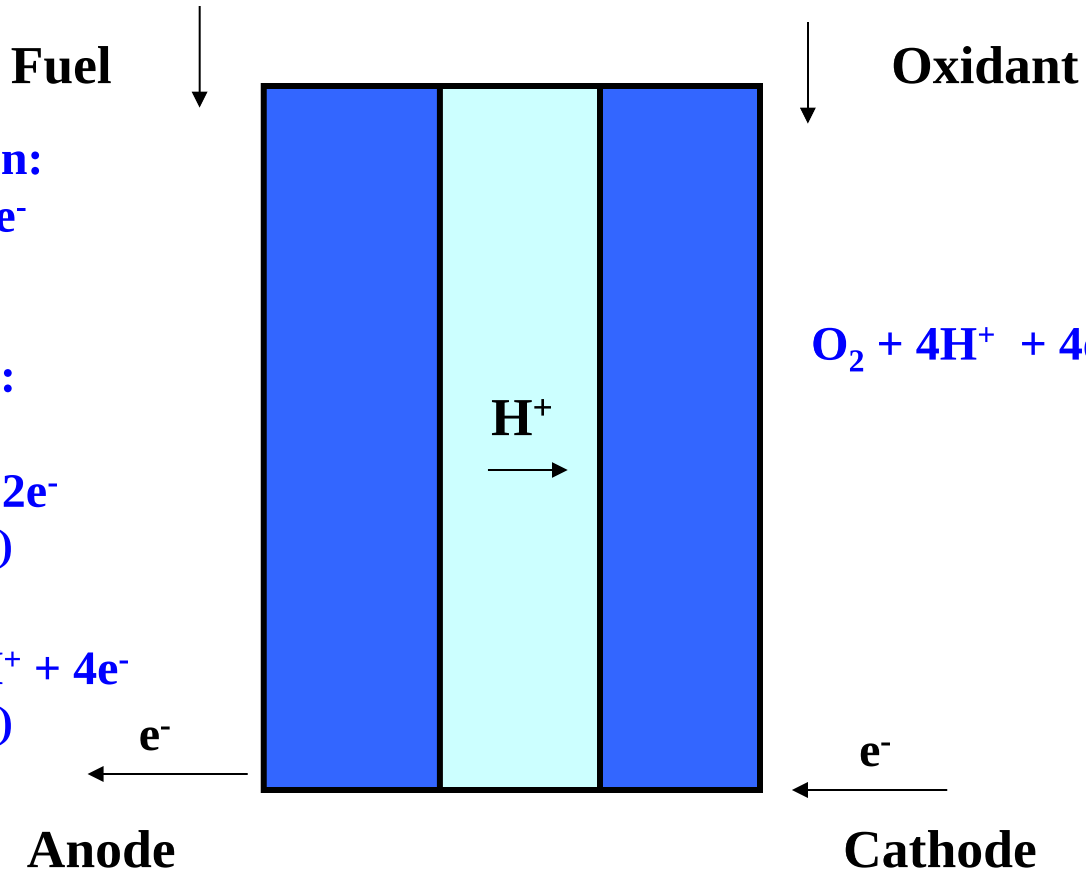
- High current issue
- Mass transport issues
- Purging required
- Cell design important

Effect of Cell Design for Water Management on Degradation



Pierre, Wilkinson et al J. New Materials for Electrochemical Systems,3, pp 99-106 (2000)

Failure Modes (Low Reactant Stoichiometry)



Normal reaction:

$2H_2 \rightarrow 4H^+ + 4e^-$

In absence of H_2 and depending on potential:

$H_2O \rightarrow 1/2\ O_2 + 2H^+ + 2e^-$

$(E^o_{25^oC} = -1.23\ V\ vs.\ NHE)$

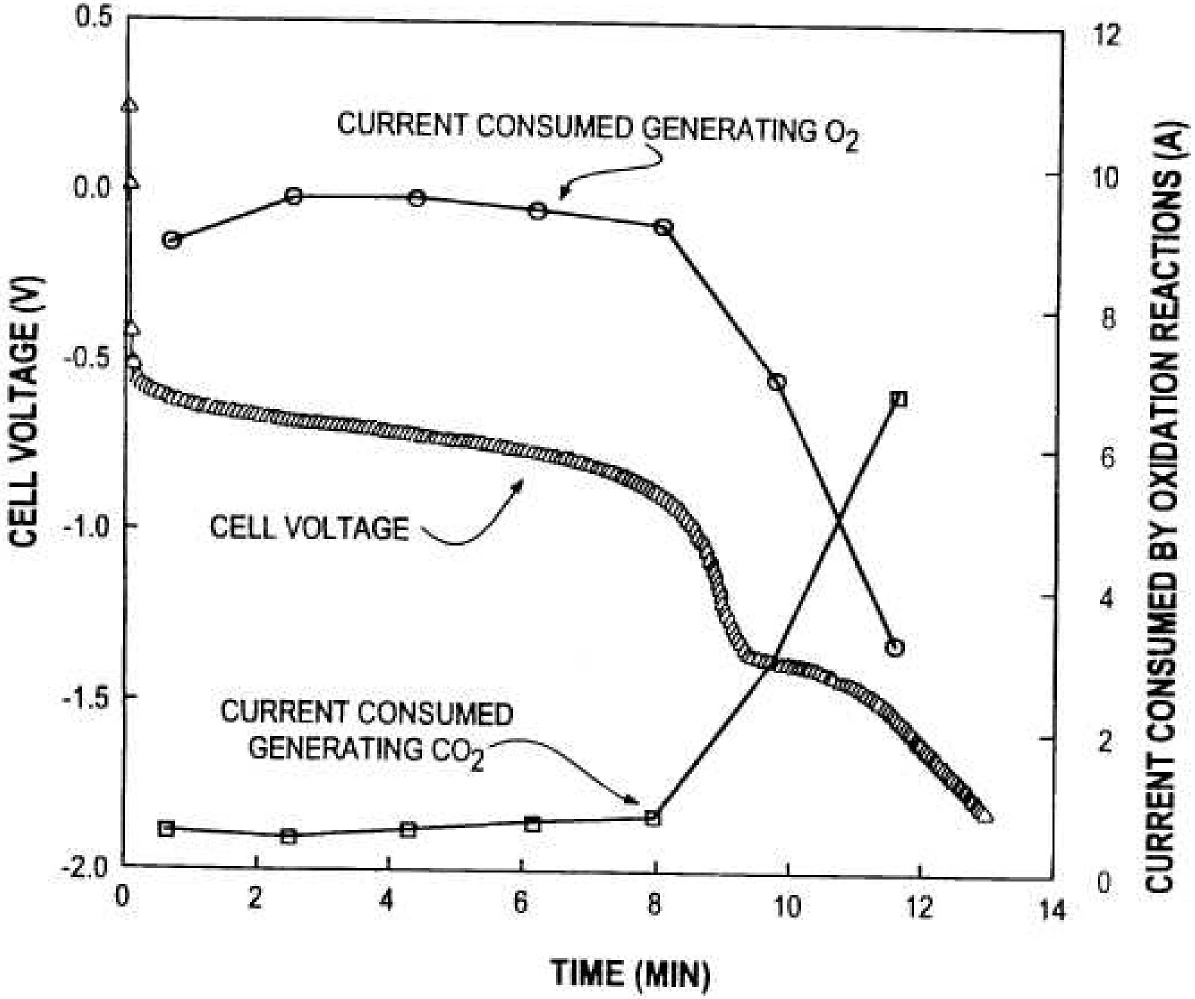
$C + 2H_2O \rightarrow CO_2 + 2H^+ + 4e^-$

$(E^o_{25^oC} = -0.21\ V\ vs.\ NHE)$

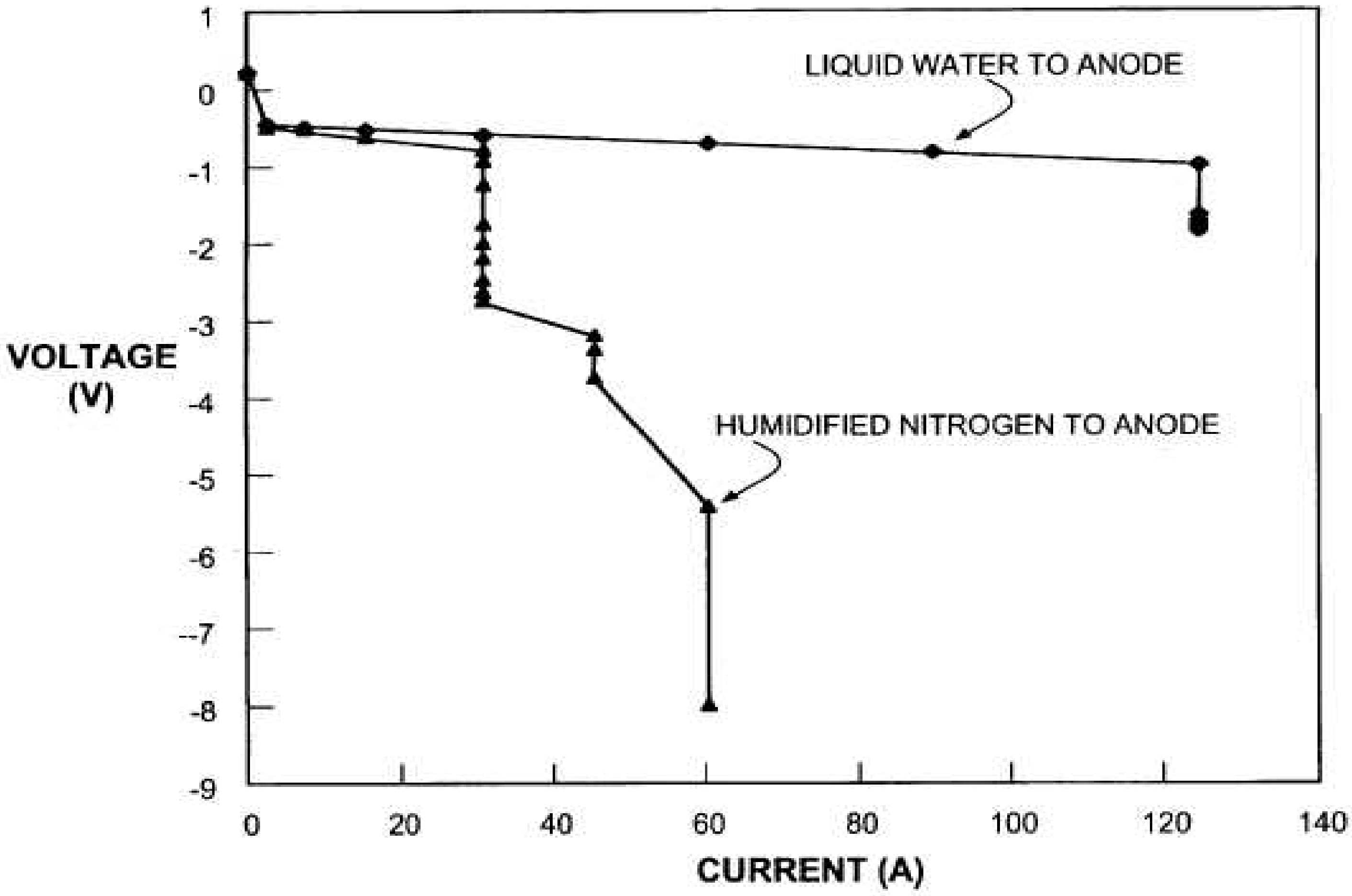
$O_2 + 4H^+ + 4e^- \rightarrow H_2O$

Thomas, Hudson, Wilkinson, Electrocatalyst Stability and the Role of Fuel Starvation and Cell Reversal Tolerant Anodes : ECS Transactions 1 (8) 67 (2006)

Currents consumed generating O_2 and CO_2 for fuel cell undergoing fuel starvation

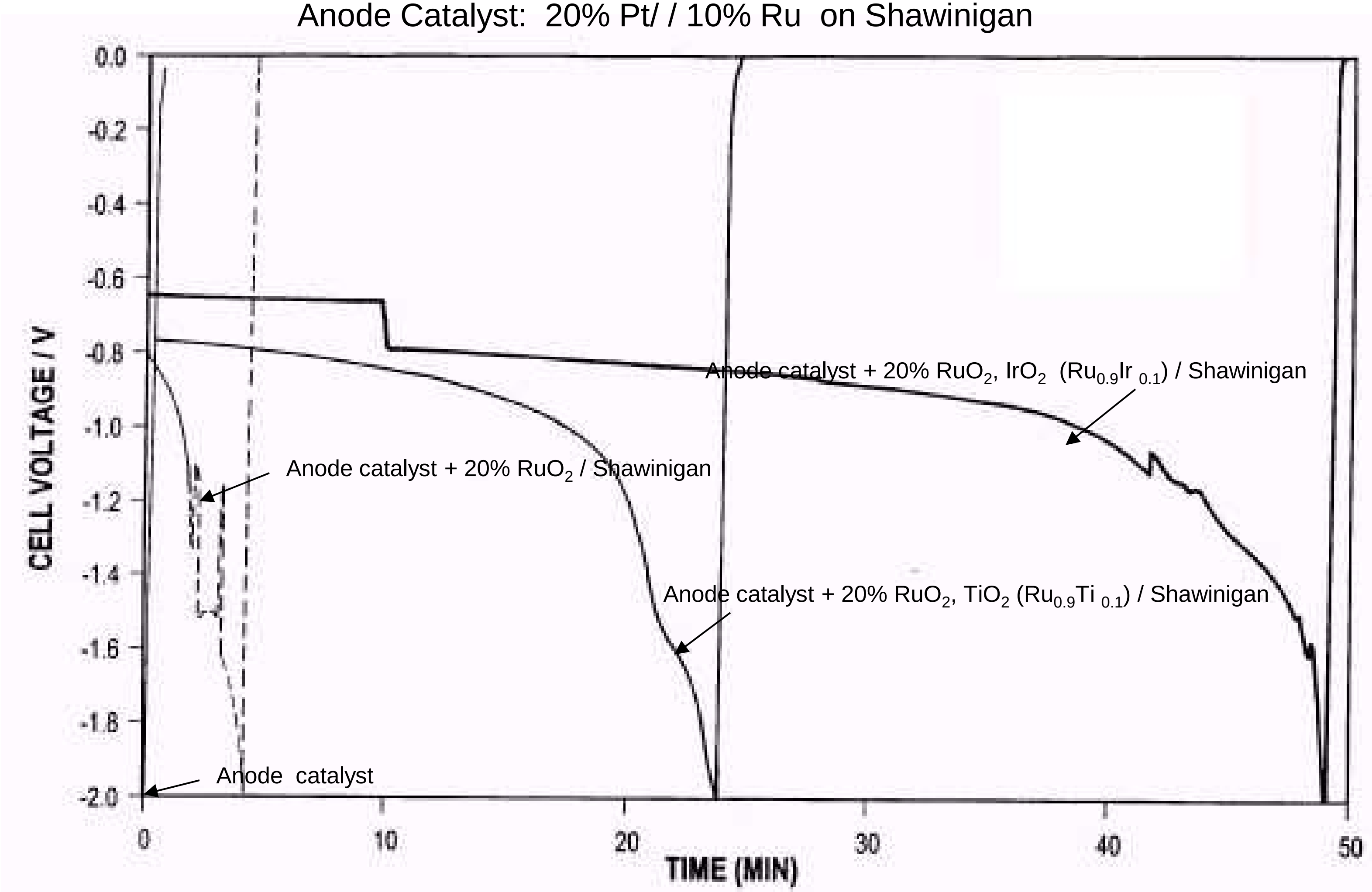


Enhanced water supply at anode sustains water electrolysis during fuel starvation reversal



Extended fuel starvation reversal at 200 mA / cm^2 with different catalyst compositions and structures

Anode Catalyst: 20% Pt/ / 10% Ru on Shawinigan

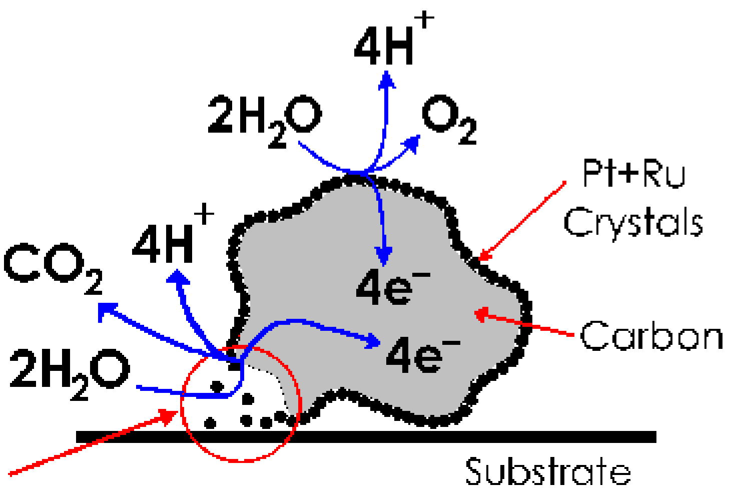


Wilkinson, Knights et al, US Patents: 6,527,943 (2003) ; 6,936,370 (2005), etc

Degradation of carbon catalyst support and other carbon components during fuel starvation

- When Pt anode catalyst is supported on carbon, degradation can occur due to loss of catalyst support.
- In addition to the O_2 evolution reaction, C oxidation can occur:

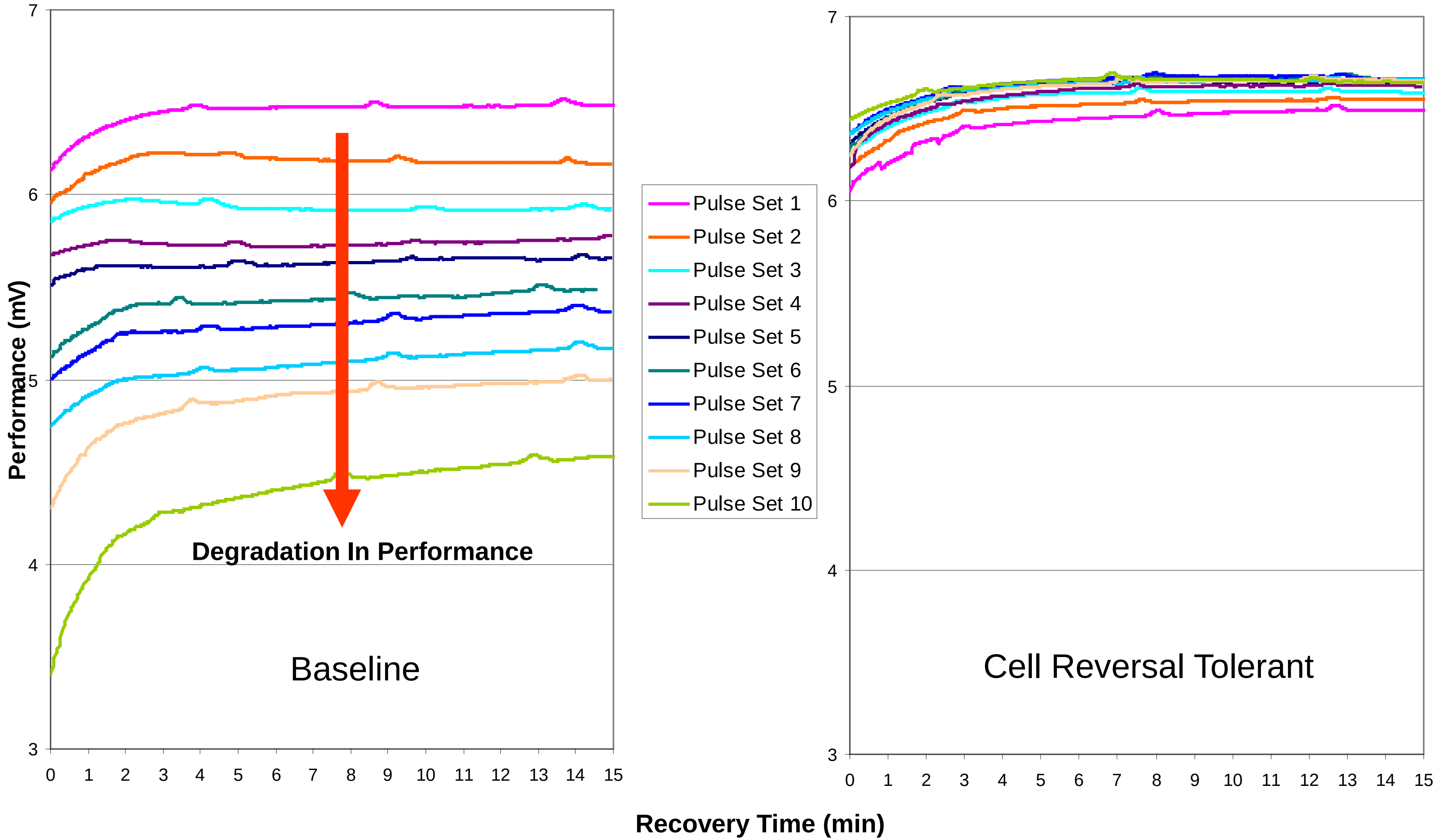
$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$



Degradation of carbon
Loss of Pt/Ru

Knights, Wilkinson et al, J. Power Sources, 127, pp 127-134 (2004)

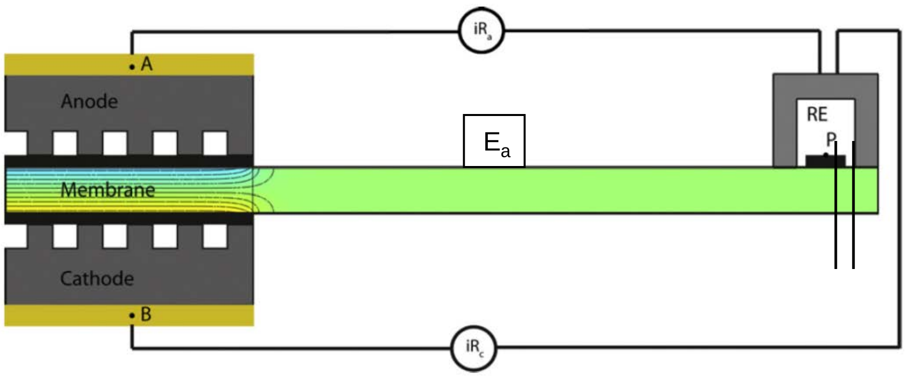
Average stack performance recovery vs time spent in fuel starvation reversal

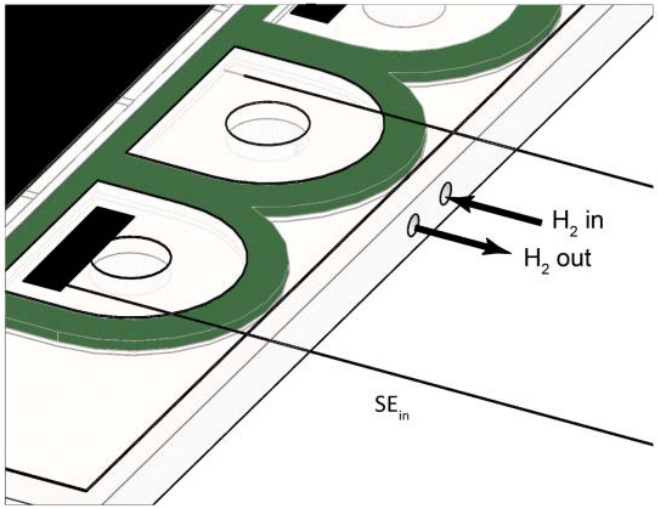


In-Situ PEM Cell Diagnostics for Durability and Degradation

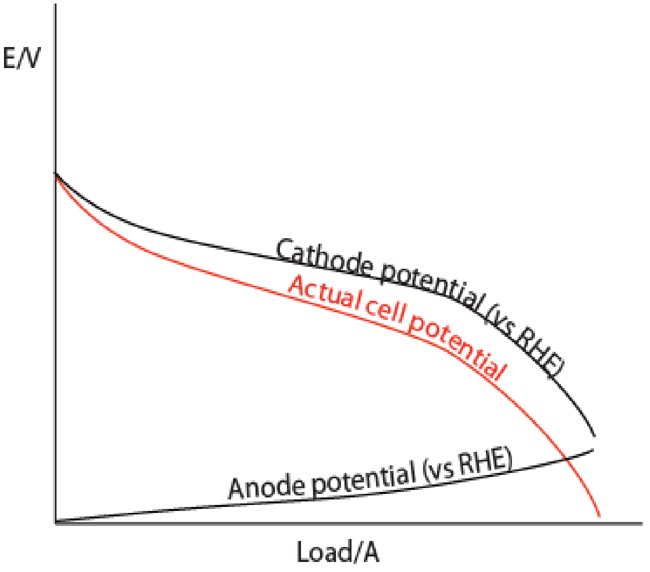
- Ideal approach should target:
  - As many failure modes as possible
  - Be specific to as many components as possible
    - Flow field
    - Membrane
    - Electrodes
    - Etc
  - Very low invasiveness
  - Low cost
  - Provide accelerated insight into mechanism(s), i.e., predict longer term issues

Reference Electrodes



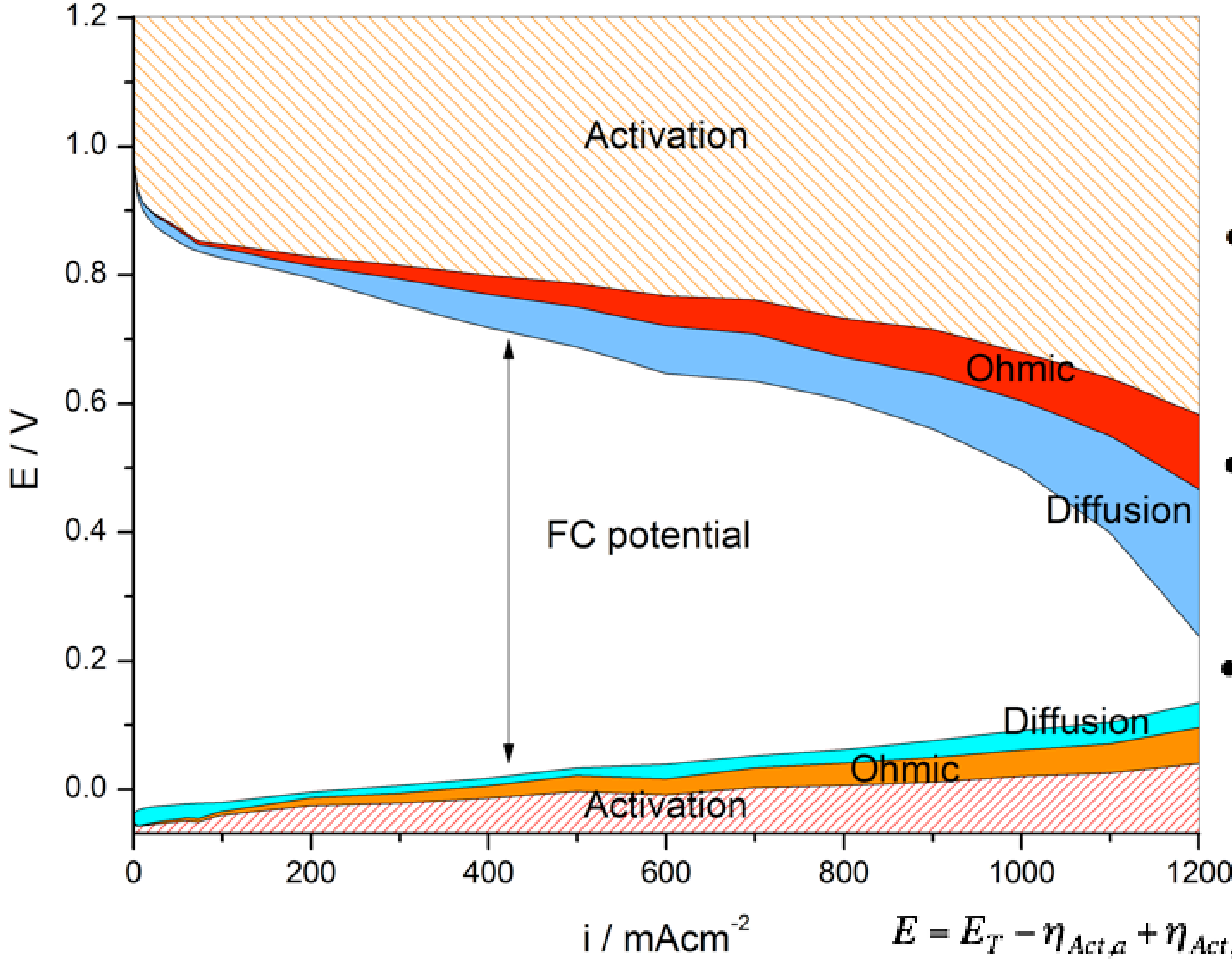


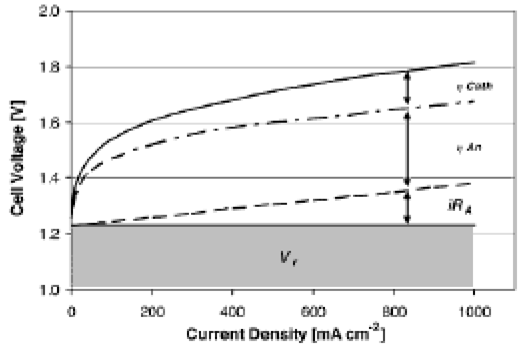
Fully hydrated hydrogen at constant conditions



1. O.E. Herrera, W. Mérida, and D.P. Wilkinson. "Sensing Electrodes for Failure Diagnostics in Fuel Cells." Journal of Power Sources 190, 103-109 (2009).
2. O.E. Herrera, W. Mérida, and D.P. Wilkinson. "New reference approach for fuel cell performance evaluation." Transactions of the Electrochemical Society 16(2), 1915-1926 (2008).

Anodic and Cathodic Component Overpotentials





- **Kinetics**

$$\eta_{Act,a/c} = b_{a/c} \ln \frac{i}{i_{0,a/c}}$$

- **Ohmic**

$$E_{\Omega} = i(R_a + \alpha R_m) + i(R_c + \beta R_m)$$

- **Diffusion**

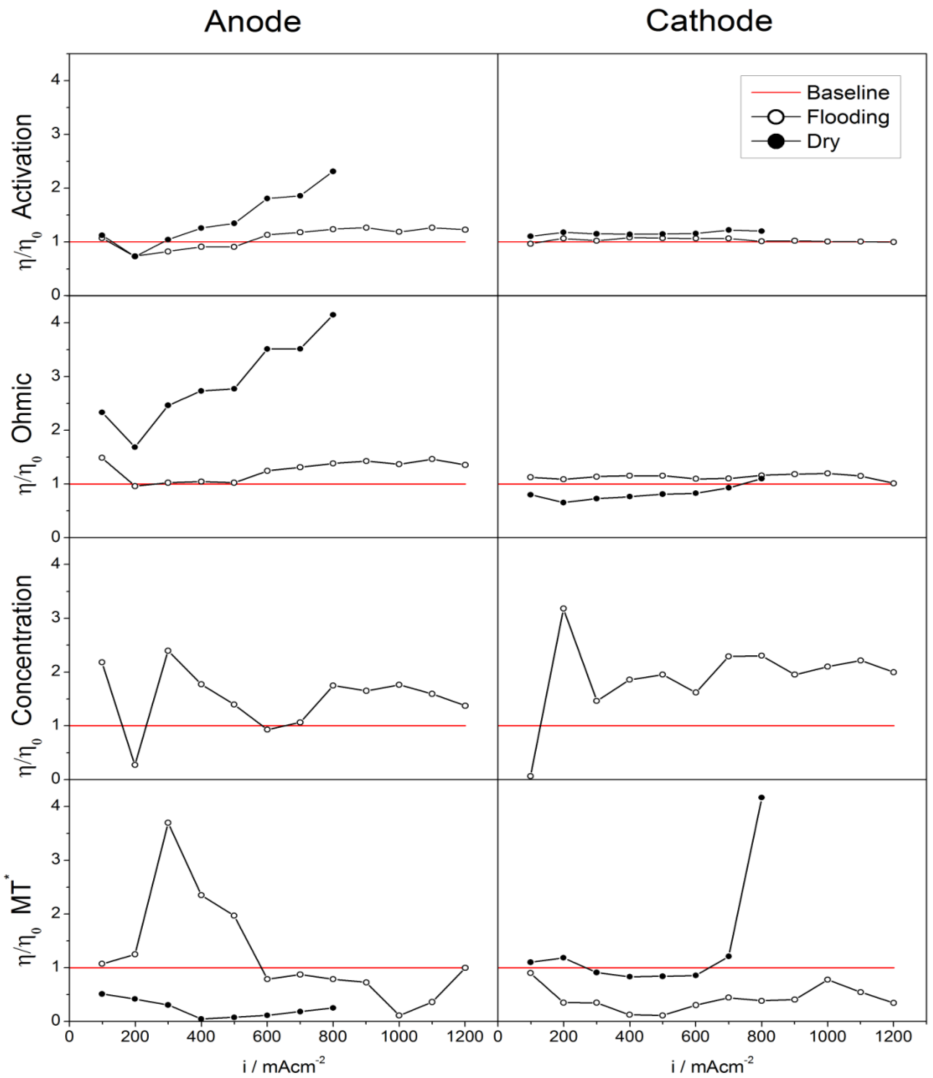
$$\eta_{d,a/c} = \frac{RT}{nF} \ln\left(1 - \frac{i}{i_{L,a/c}}\right)$$

$$E = E_T - \eta_{Act,a} + \eta_{Act,c} - \eta_{ohm,a} + \eta_{ohm,a} - \eta_{d,a} + \eta_{d,a}$$

O. Herrera, D. Wilkinson, W. Mérida. *"Electrode overpotentials and temperature profiles in a PEMFC."* Journal of Power Sources. **198**, 132-142 (2011).

Anodic and Cathodic Overpotential Ratios (effect of different operating conditions)

η / η0



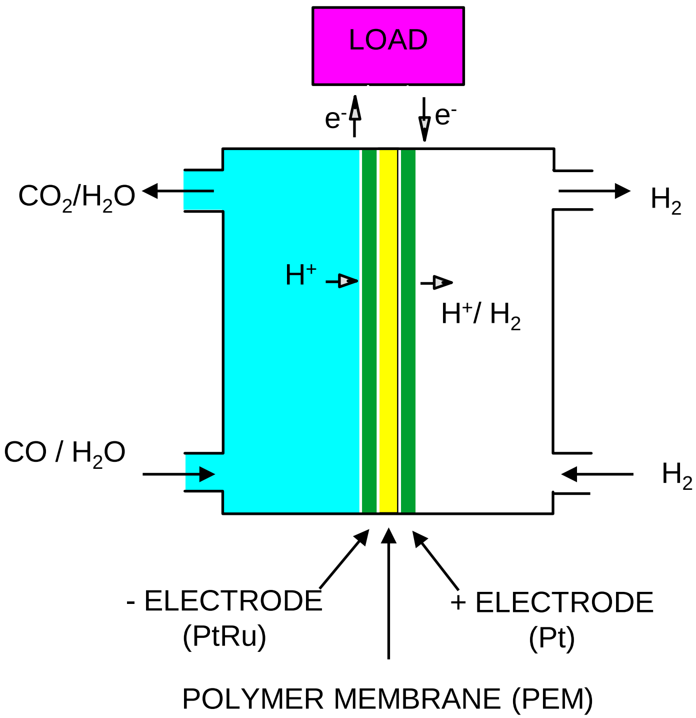
Activation

Ohmic

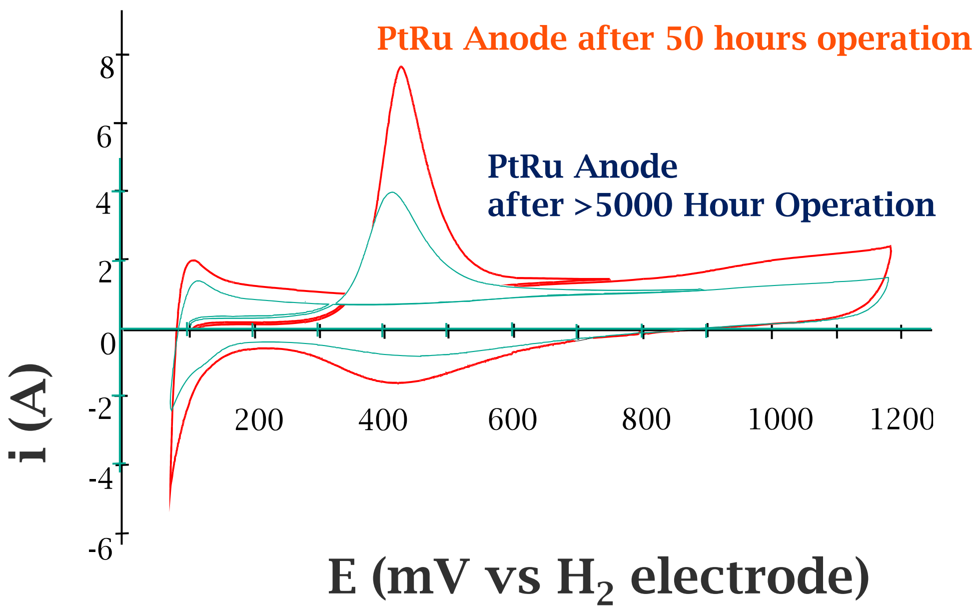
Concentration

Mass Transport

In-Situ Half Cell Electrochemistry for Electrode/Catalyst Evaluation



Example CVs after Lifetime Testing

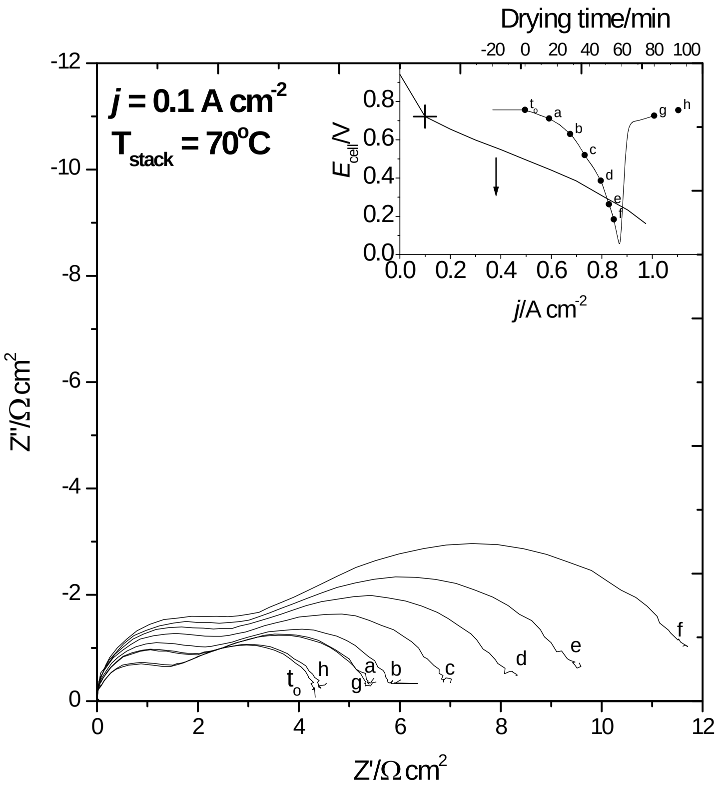


CO Stripping Voltammetry for Catalyst Surface Area

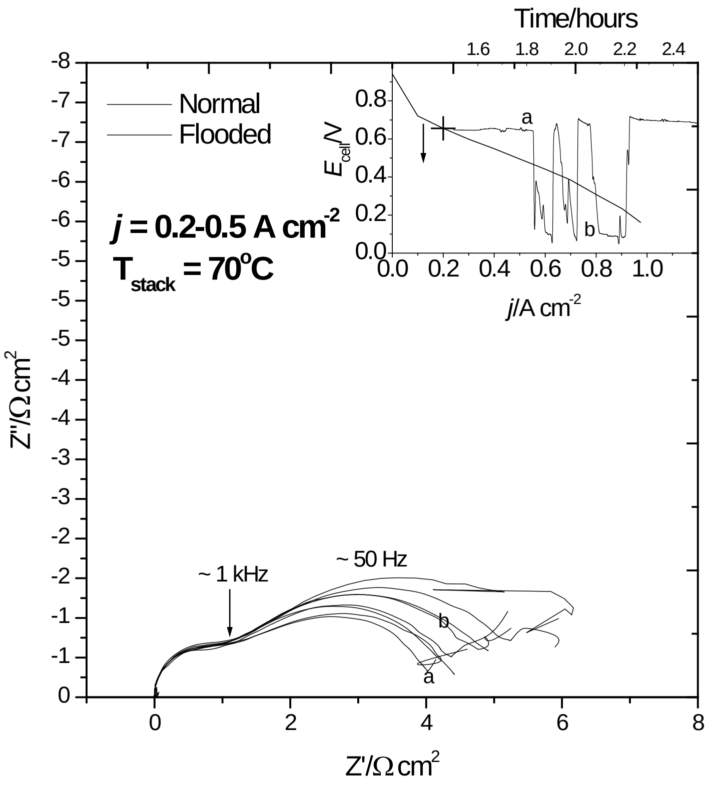
$(CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-)$

Impedance Analysis for Failure / Degradation Analysis

Low Humidity Failure Mode



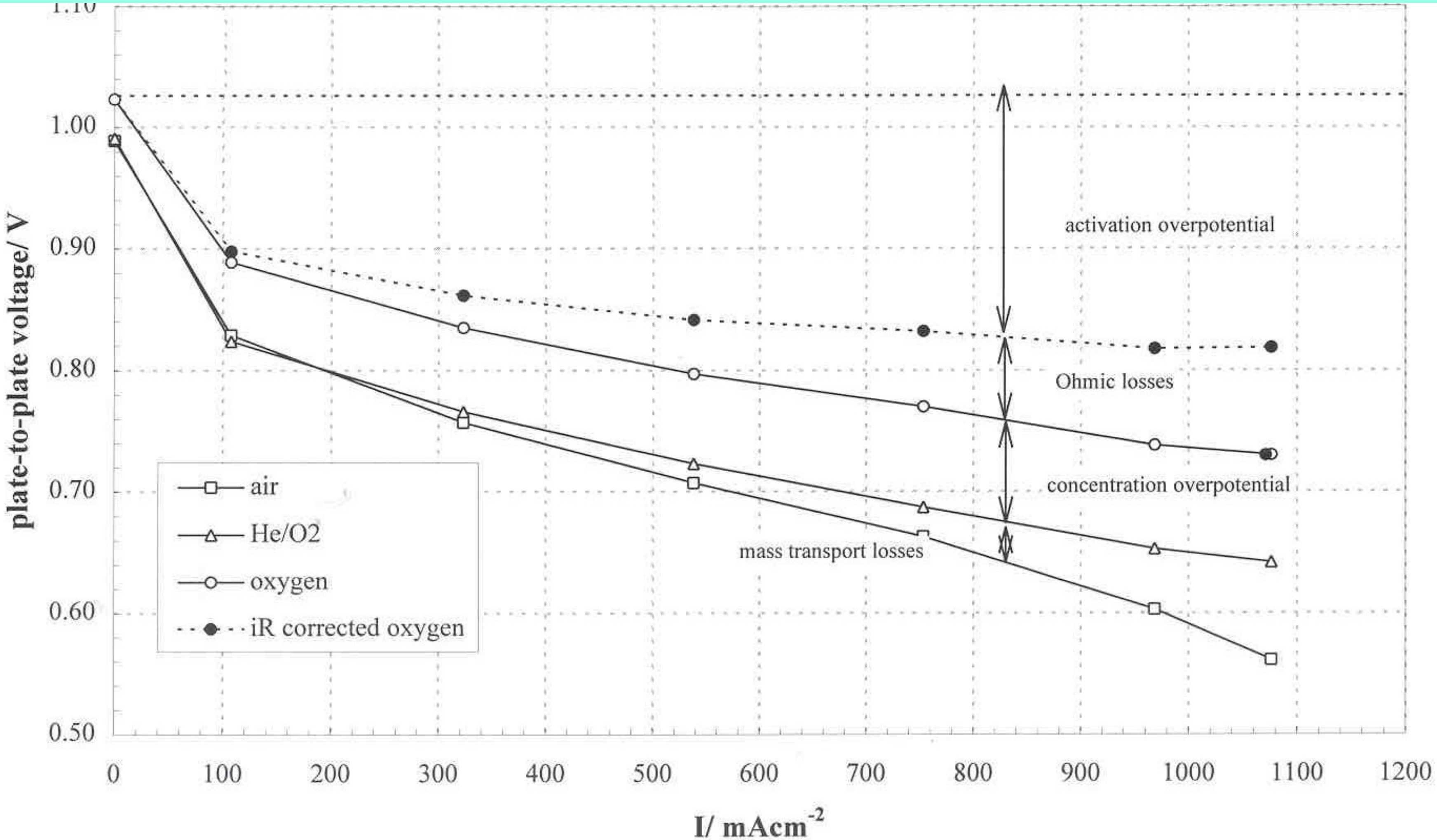
Flooding Failure Mode



W. Mérida, "*An Empirical Model for Proton Exchange Membrane Fuel Cell Diagnostics*", Electrochemical Society Transactions **5**(1), 229-239 (2007).

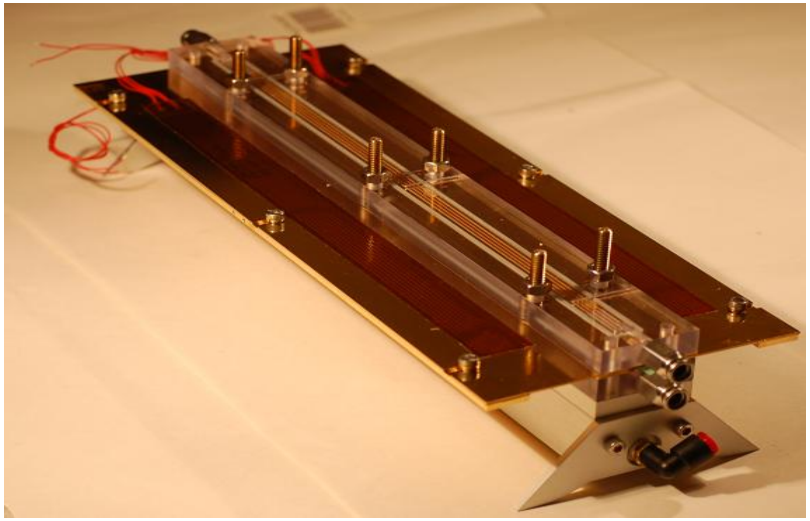
Performance Losses from Tri-Oxidant Polarization

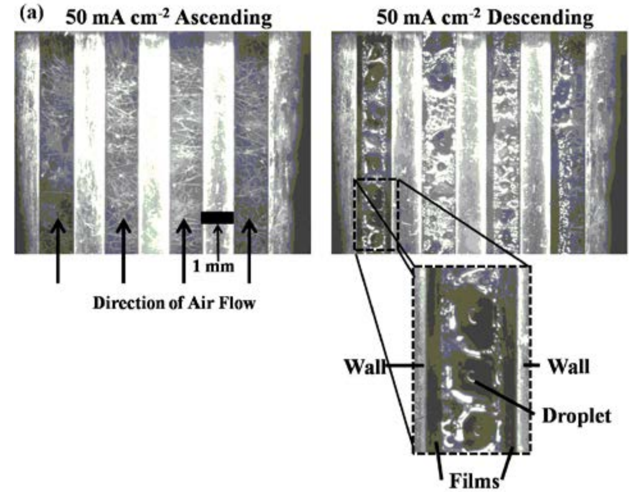
(O_2 (21%)/N_2, O_2 (21%)/He, O_2(100%)) : D (O_2/He) / D(O_2/N_2) ~ 3; D(O_2)D(O_2/N_2)~ 7

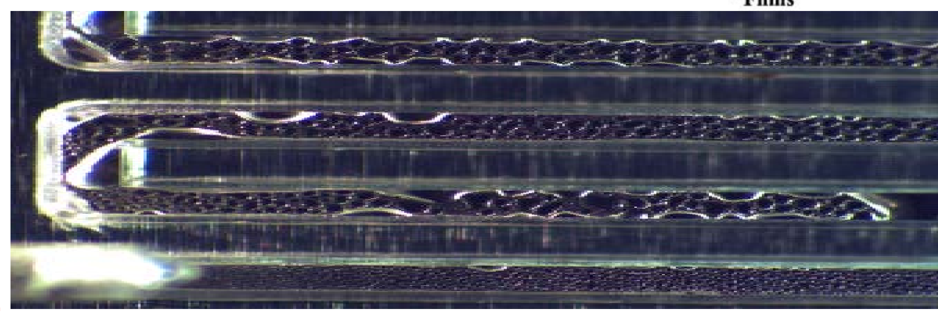


Multi-component gas analysis (experimental and theoretical analysis)
(J. Electrochem. Soc., Vol. 141, No.8, August 1994, pp 2084-2088 ; ibid., pp 2089 – 2090)

2-Phase Flow Analysis in PEM Based Cells





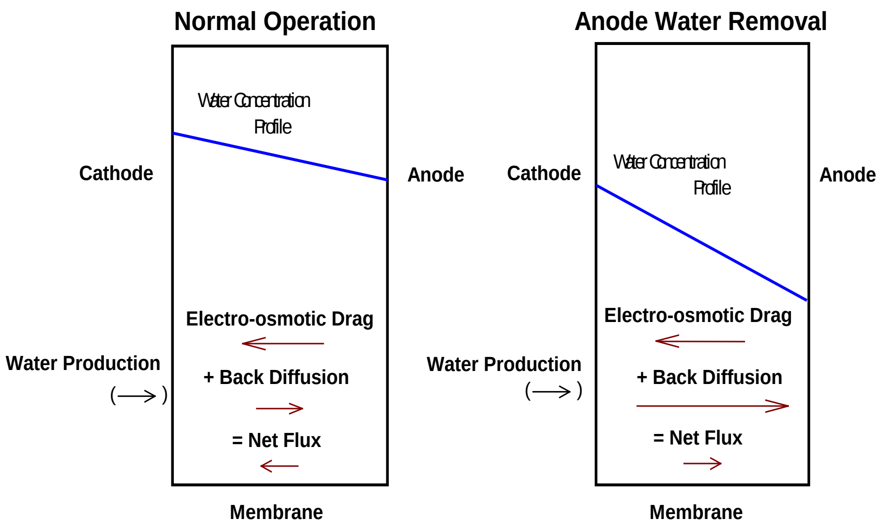


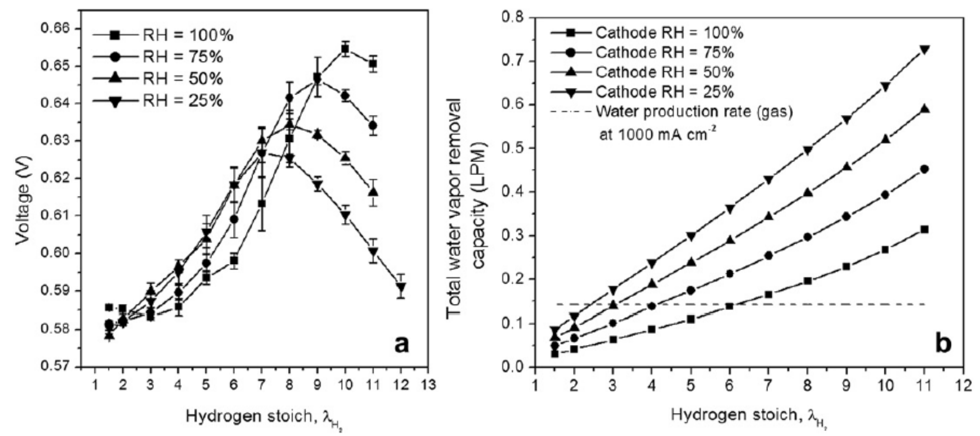
- Diagnostic tools to understand two-phase flow and flow distributions in PEMFC flow fields
- Provides better solutions for water management in PEMFCs
- This approach can be applied to PEM electrolysis

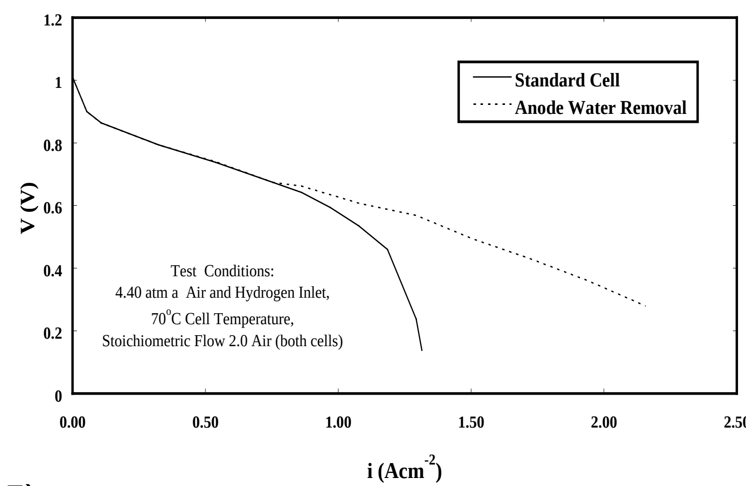
$$H_2O\ (l) = 1/2O_2 + 2H^+ + 2e^-$$

1. R. Anderson, D.P. Wilkinson et al, A critical review of two-phase flow in gas flow channels of proton exchange membrane fuel cells, J. Power Sources 195 (2010) 4531-4553
2. R. Anderson, D.P. Wilkinson et al, Two-phase flow pressure drop hysteresis in parallel channels of a proton exchange membrane fuel cell, J. Power Sources 195 (2010) 4168-4176
3. L.Zhang, D.P. Wilkinson et al, Gas-liquid two-phase flow behavior in minichannels bounded with permeable walls, Chem. Eng. Sci., 3377-3385 (2011)

Anode Purge Diagnostic based on Anode Water Removal





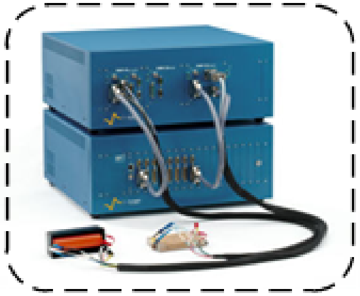


1. Wilkinson et al, Electrochimica Acta, 40, pp 321-328 (1995)
2. Blanco, Wilkinson et al, Int. J. of Hydrogen Energy, 3716093 (2012)

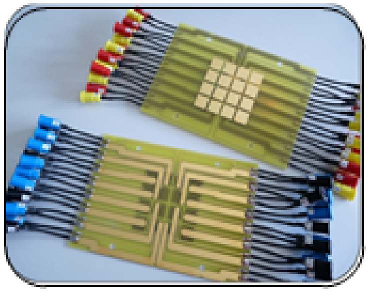
In-Situ Characterization and Diagnostics at UBC

– Challenges by regions or components

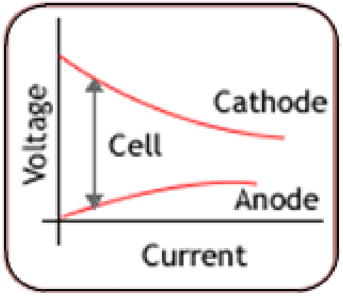
- Spatial resolution
- Concurrent techniques
  - impedance, electrochemical techniques
  - anode water removal, transient operating conditions, etc
- High throughput (combinatorial analysis)
  - Material performance and degradation



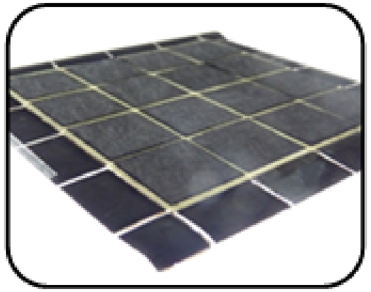
(a) Impedance



(b) Segmented hardware



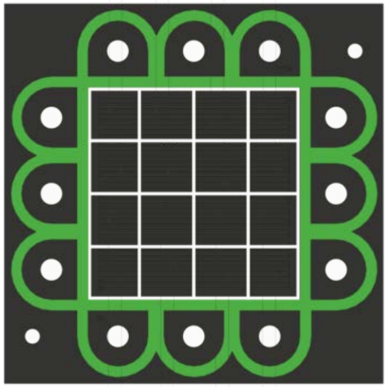
(c) Reference electrodes

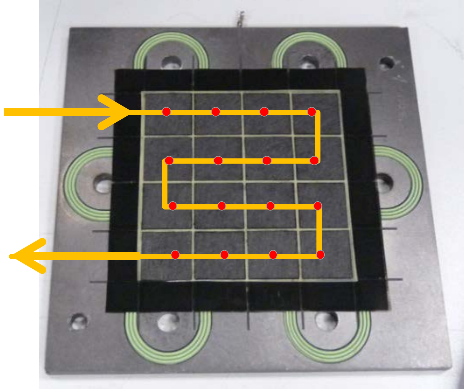


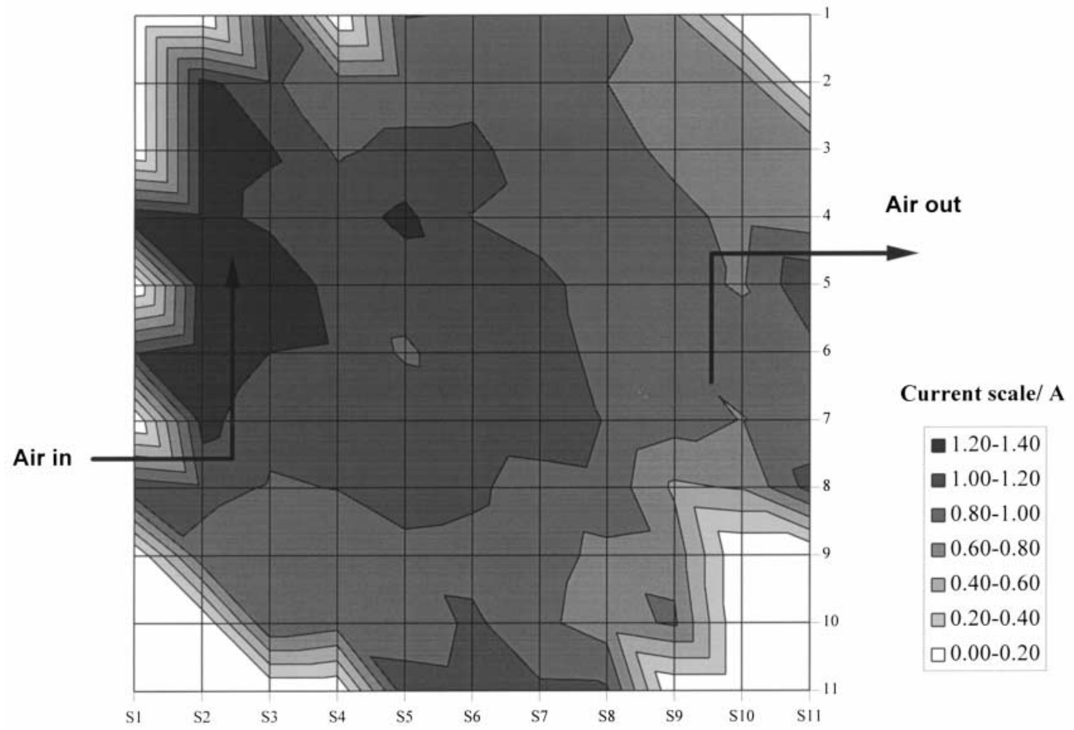
(d) Full cell segmentation

Spatially resolved current distribution mapping in an operating fuel cell using segmented cells

UBC Fuel Cell:
4 x 4 segmentation over 50 cm^2

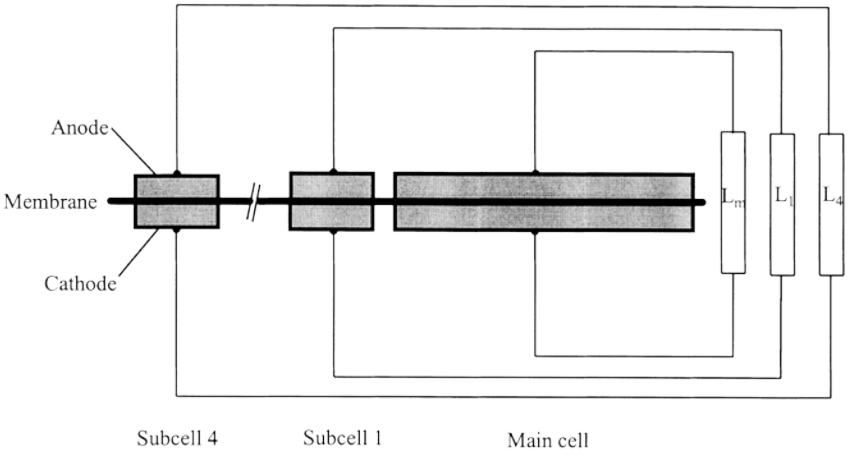


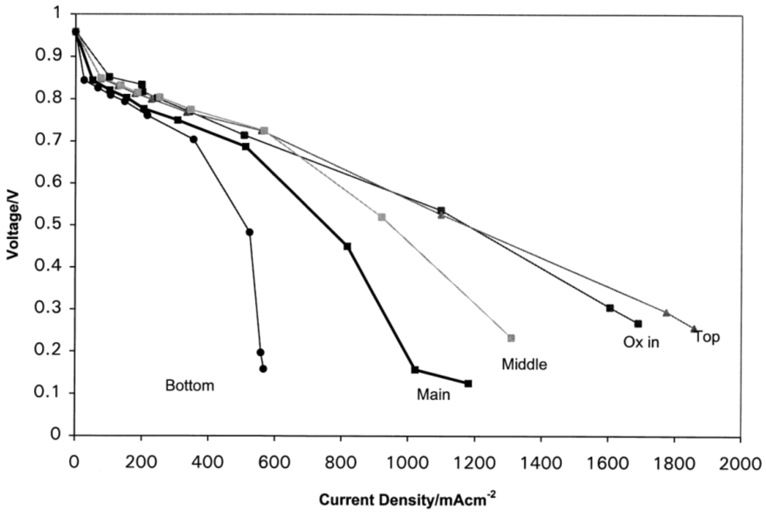


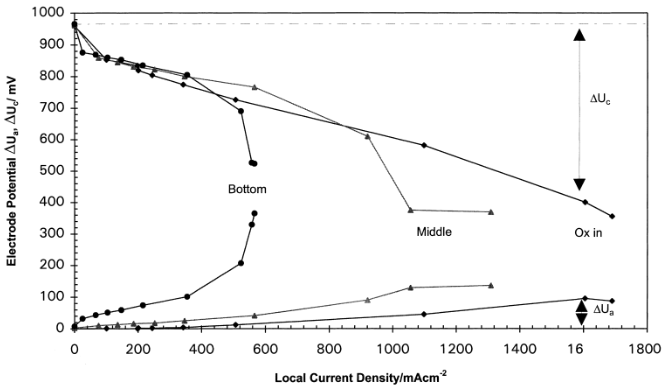


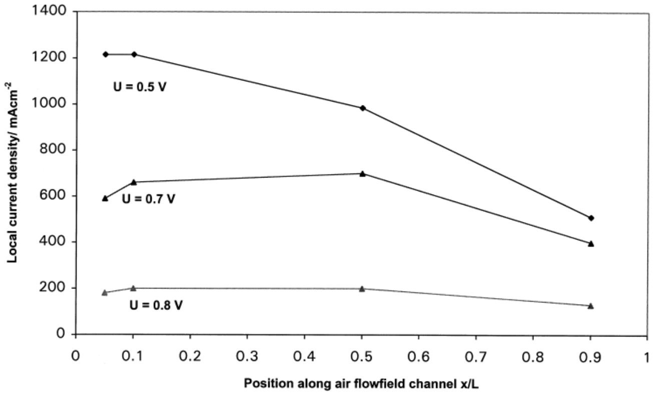
J. Stumper, D.P. Wilkinson et al, Electrochimica Acta, Vol. 43, No.24, 3373 (1998)

Spatially resolved current distribution mapping in an operating fuel cell using fully isolated subcells



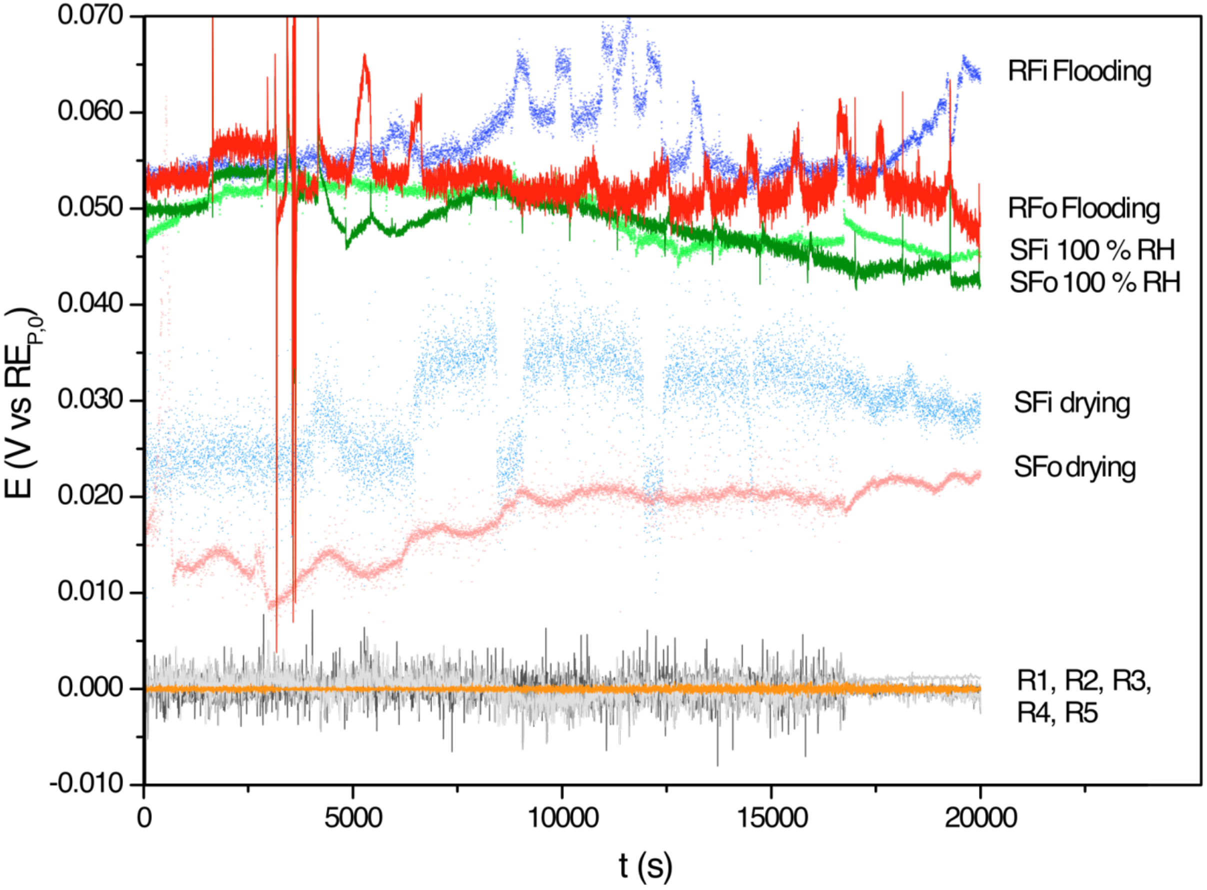


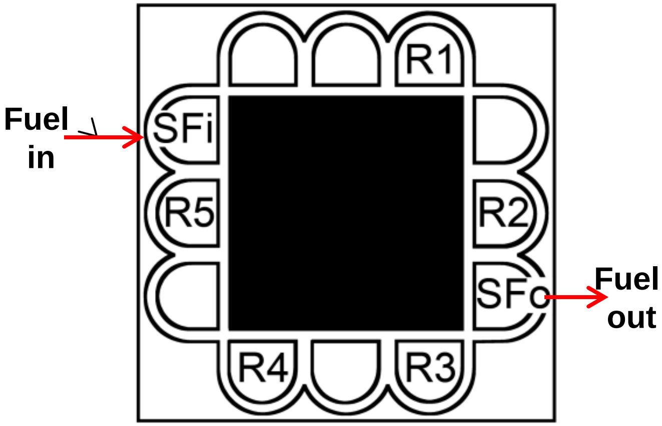




J. Stumper, D.P. Wilkinson et al, Electrochimica Acta, Vol. 43, No.24, 3373 (1998)

Effect of Failure Mode Conditions on Sensing Electrodes
(example for sensing external to active area)

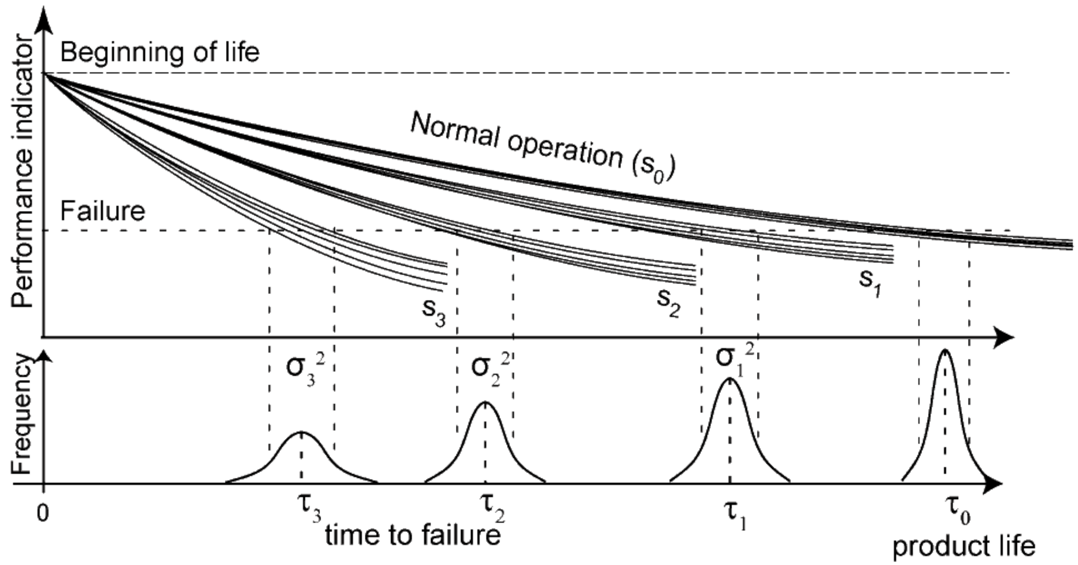


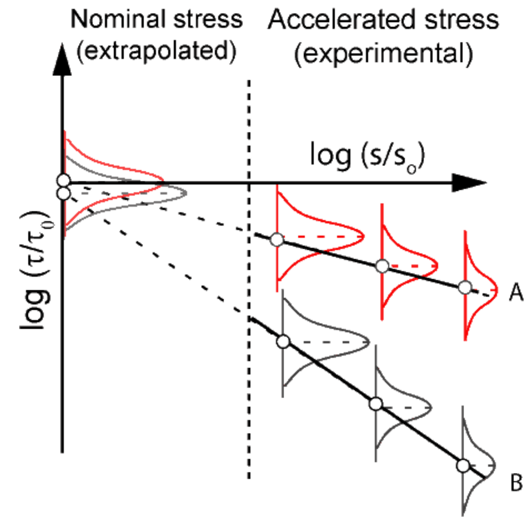


Differences of SEs at different conditions while REs remain constant

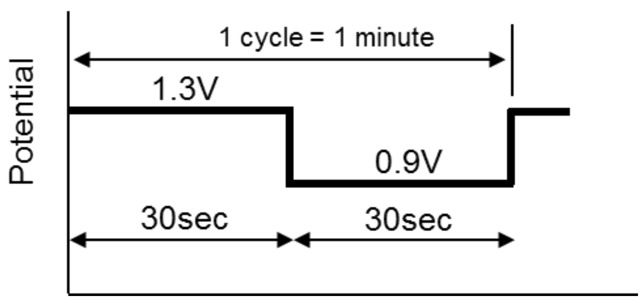
O.E. Herrera, W. Mérida, and D.P. Wilkinson. *"Sensing Electrodes for Failure Diagnostics in Fuel Cells."* Journal of Power Sources 190, 103-109 (2009).

Accelerated Fuel Cell Testing and Product Life





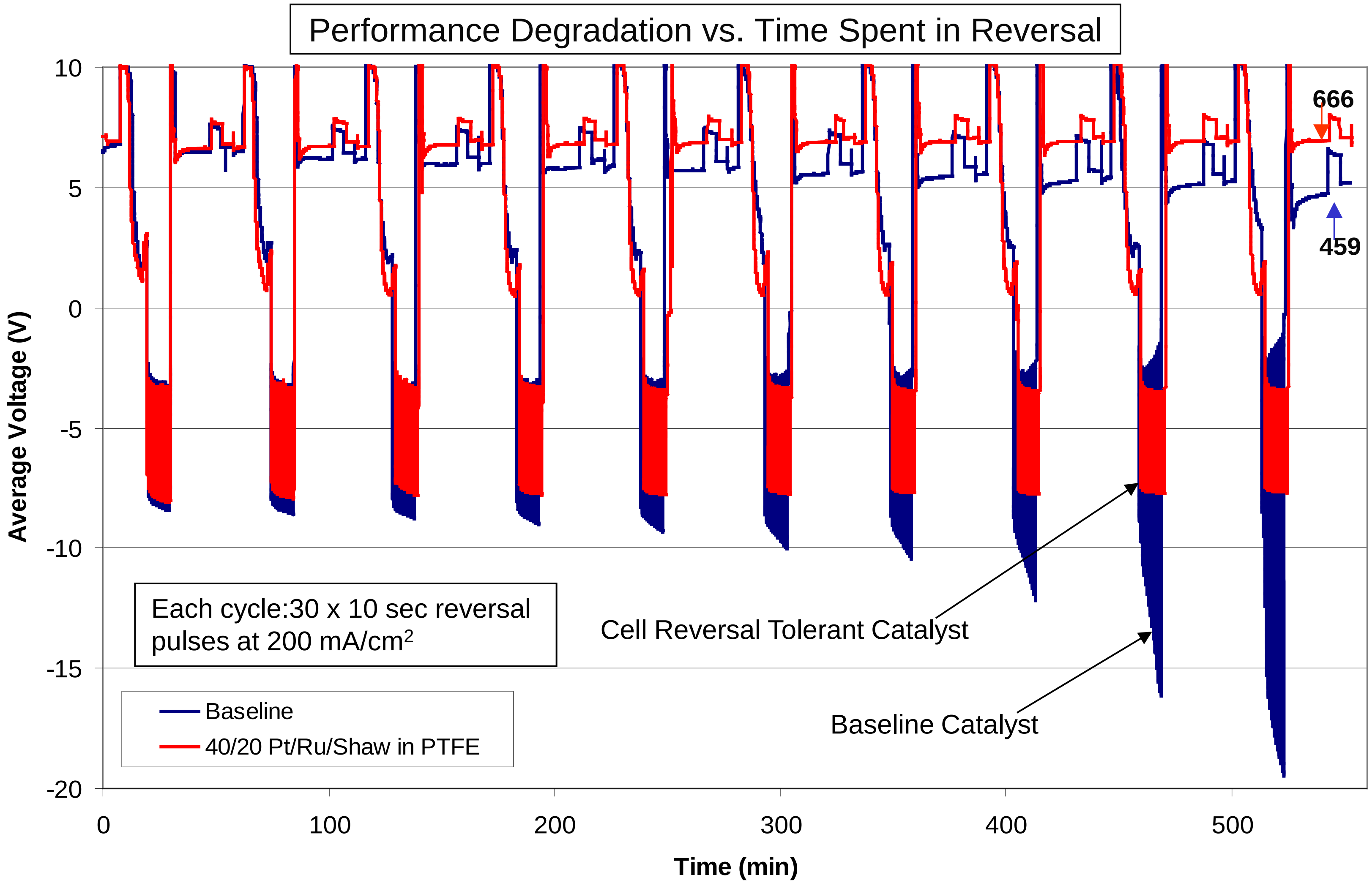
Voltage cycling



<u>Accelerated Stress Parameters</u>

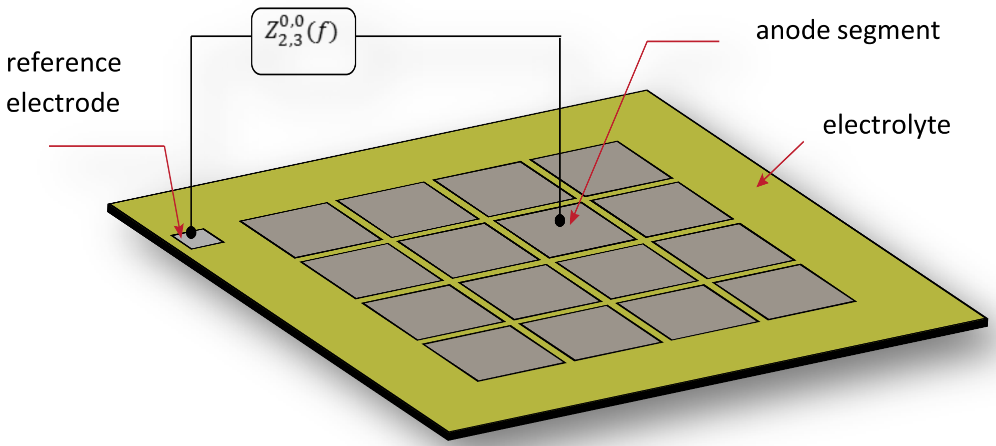
- voltage, current density
- temperature
- humidification
- reactant concentration
- catalyst loading
- Etc, etc

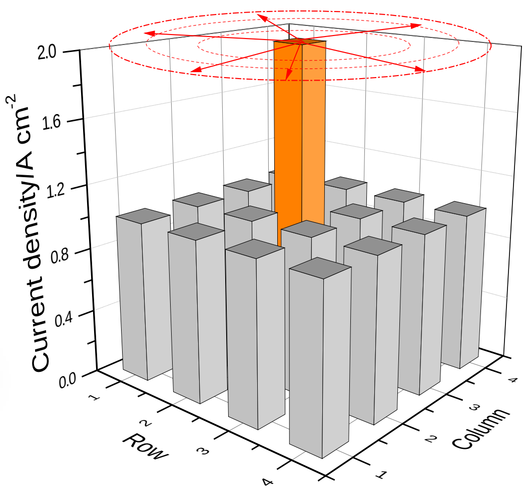
Transient Testing for Accelerated Performance Degradation (e.g., cell voltage reversal testing)



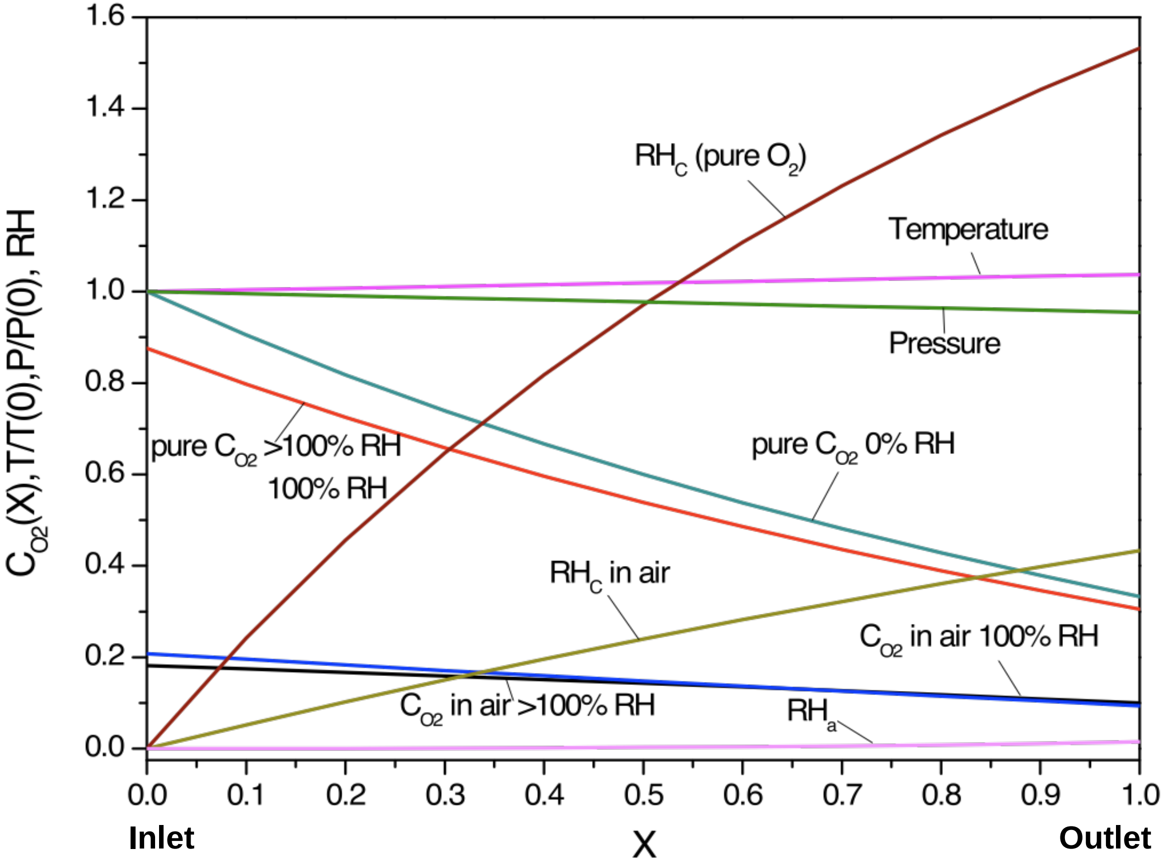
Accelerated Spatially Resolved Stress Testing

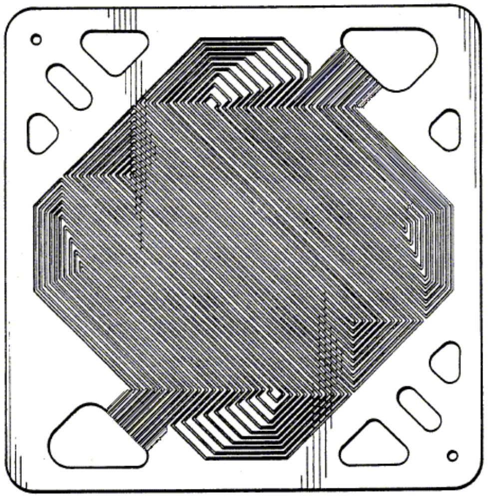
- Gradients in operating conditions allow accelerated testing because of enhanced sensitivity in some regions
- A variety of *in situ* characterization techniques can be applied and spatially determined
- Dynamic/transient spatially resolved measurements
  - Water transport
  - Current density, etc





Parameter Change as a Result of In-plane Gradients



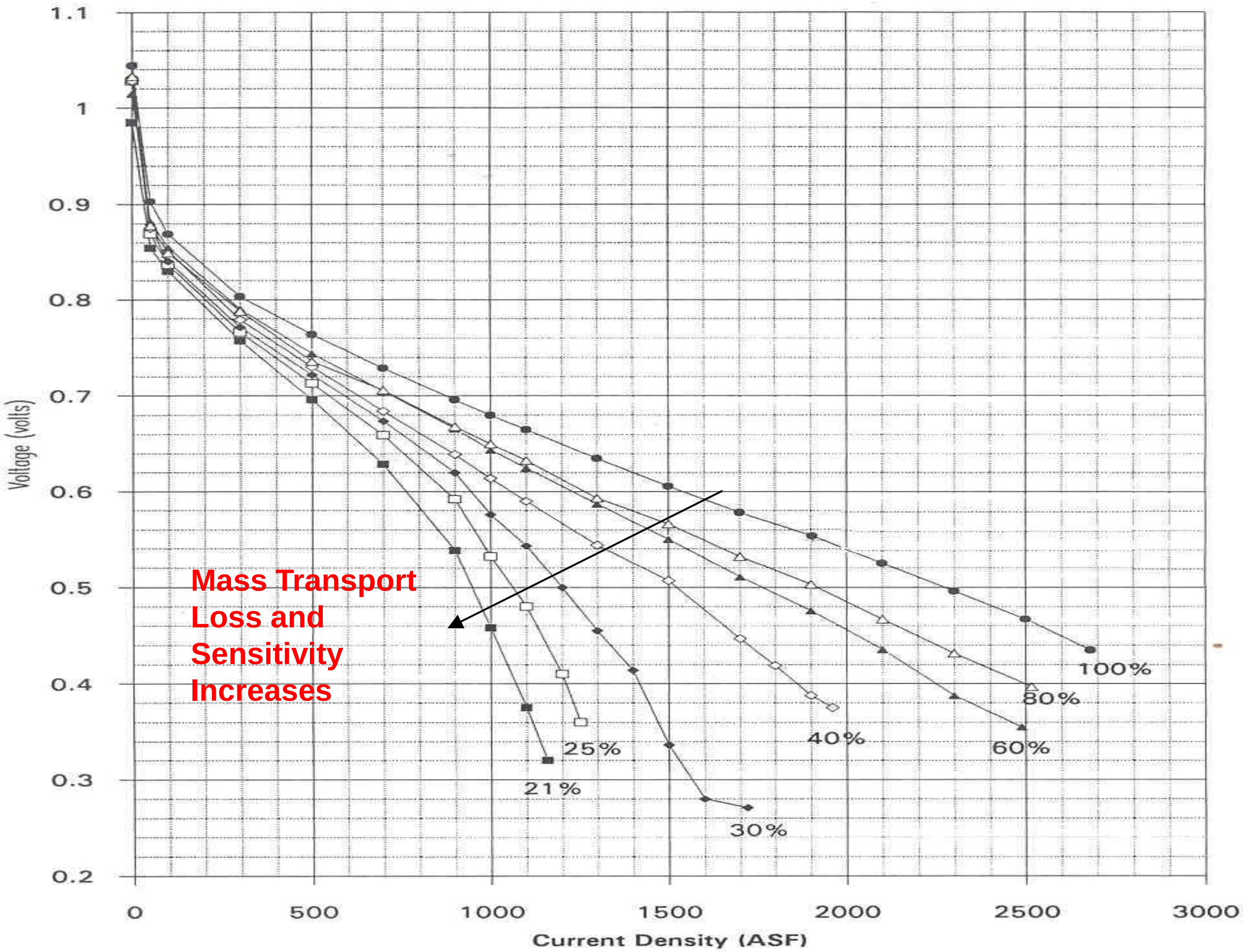


Dimensionless oxygen concentration, temperature, and relative humidity profiles across a PEMFC flow field, x = dimensionless distance

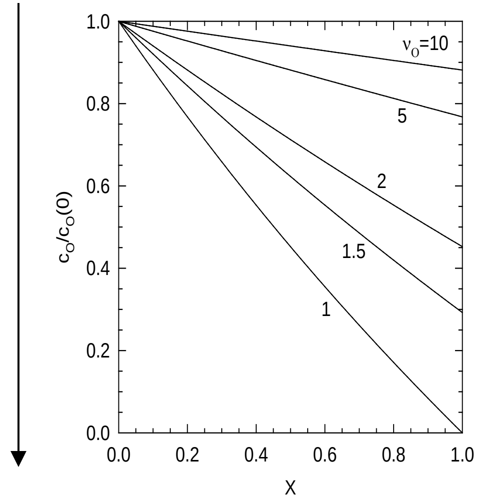
D.P. Wilkinson and J. St. Pierre, J. Power Sources, 113, pp 101-108 (2003)

Increased Sensitivity with Lower Reactant Concentration

Cell inlet reactant concentration decreased

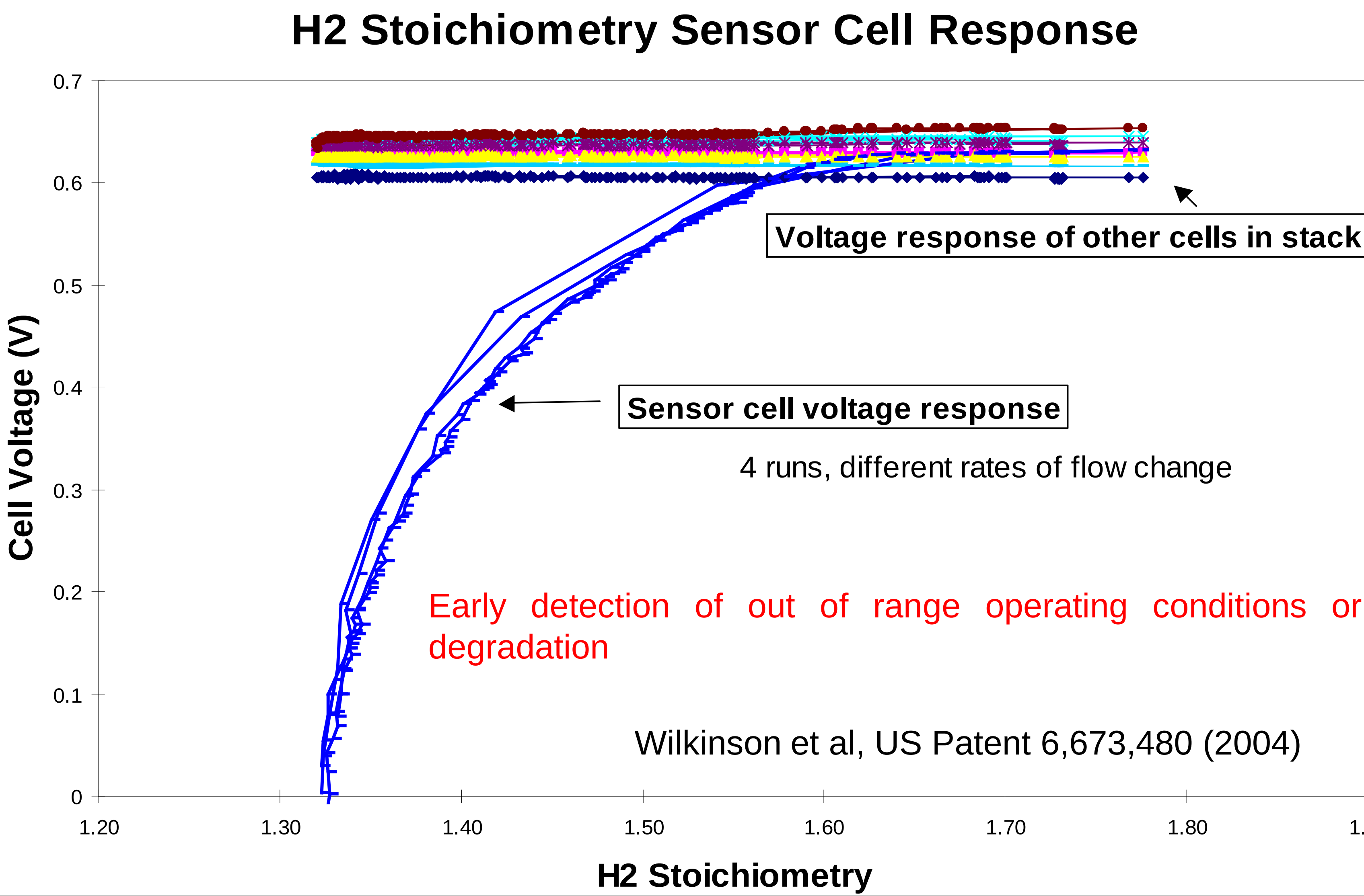


Effect of stoichiometry on concentration gradient



Sensitivity Increases

Increased sensitivity to operating parameters

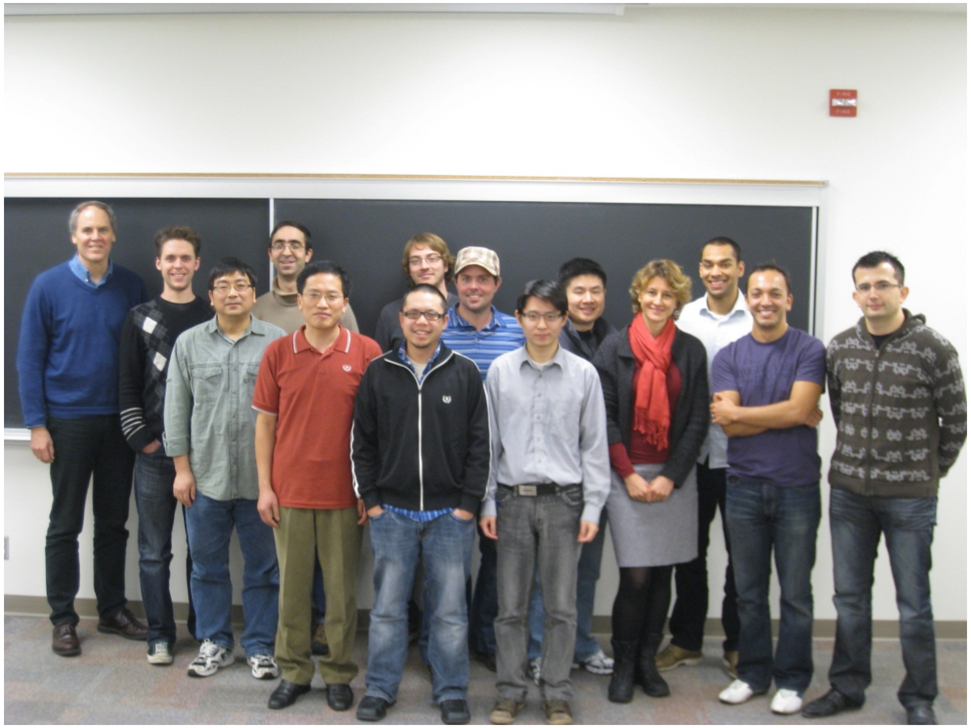


Summary

- Many diagnostics and failure/durability testing methods for the PEM fuel cell are applicable to PEM electrolysis
- In-situ PEM cell diagnostics can have low invasiveness and provide specific component and mechanistic information
- More sensitive operating conditions and transients can be used to provide accelerated test information
- Spatially resolved measurements can provide an important accelerated test platform for
  - operating conditions
  - component materials and designs

Wilkinson Electro/Photo-Chemical Research Group (since 2004)

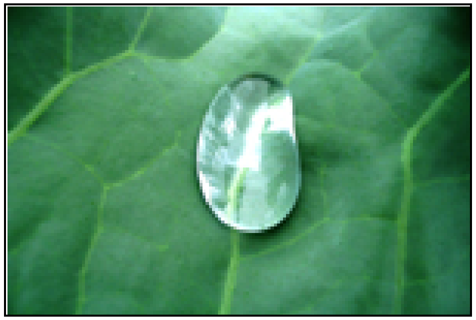
- Fuel Cell and Battery Research
  - New materials and new approaches
  - Technology simplification
  - New catalysis approaches
  - Failure modes, durability, and accelerated testing methods
- Clean Energy Research
  - Electrochemical approaches to clean energy and clean water
  - CO_2 reduction and solar fuels
  - Hydrogen production and storage
    - Photochemical & Photo-electrochemical hydrogen production
    - Advanced electrolysis
    - Metal and chemical hydrides
- Water treatment



Some Wilkinson Group Research Members

Sources of Funding:

- NSERC
- NRC
- CMC
- PICS
- CRC
- CFI
- WED
- Industry



Thank You!
Questions?

“We have not inherited this world from our parents, but we have it on loan from our children”

- Native British Columbia Haida Quote