Modelling fuel cells in start-up and reactant starvation conditions

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Overview

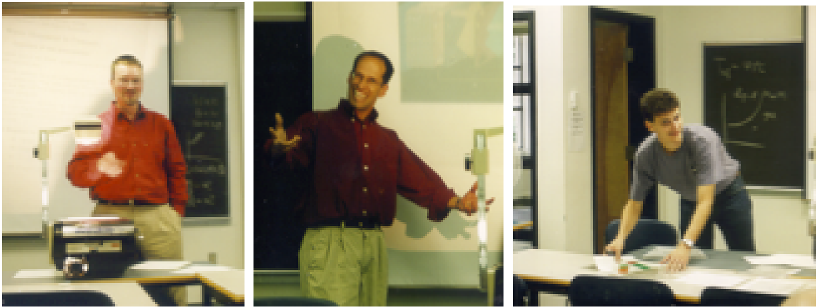
- Some history
- Introduction to Polymer Electrolyte Fuel Cells
- Reactions and Local Model
- Steady State Reactant Starvation
- Start-Up Scenarios

Collaboration with Ballard Power Systems 1998-2010

Industrial Mathematics

- MMSC group formed under MITACS
- Developed and validated computational simulation tools for Hydrogen Fuel Cells ("water management" Webber)
- Multi-scale modelling of stack level fuel cell performance, based on experimentally-fit component models Kreuer
- Reduced dimensional (lumped parameter) models rather than 3D CFD-based computations
- Materials limitations offset by engineering

Some of the MMSC group

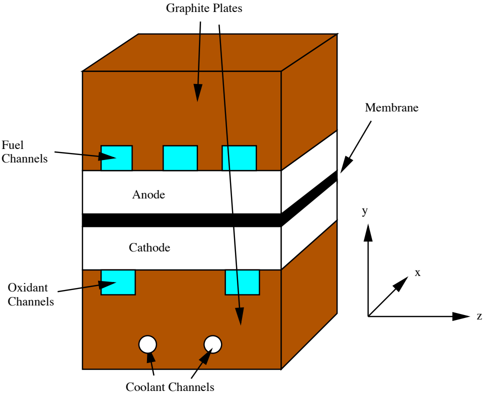


Summary Articles:

- Chang, Kim, Promislow, Wetton, JCP 2007
- Promislow & Wetton, SIAP 2009

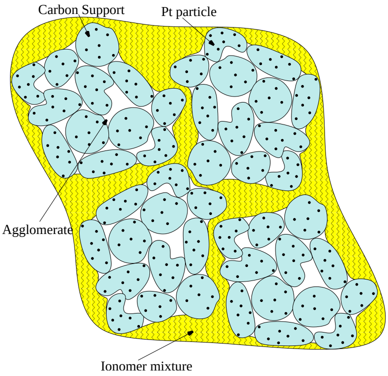
Introduction to PEM Fuel Cells (there are other types)

- Membrane Electrode Assembly (MEA):
  1. Electrodes
  2. Catalyst Layers
  3. Membrane
- Plates, Gas Channels, Coolant
- Large Aspect Ratio
- 2+1D models Secanell
- Cross-plane average (1+1D)



Detail of Catalyst Layer

- Composite Material: Pores, carbon particles, Pt particles, and ionomer.
- Located between the gas diffusion layer and the membrane
- Complicated multi-phase transport.
- At high electrochemical potentials, carbon corrosion of the catalyst support and other degradation mechanisms can occur.
- Fuel cell durability is a key current issue Borup et al, Chemical Reviews (2007)



Electrochemical Reactions

- Hydrogen oxidation at the anode (h):

$$H_2 \rightarrow 2p^+ + 2e^-$$

- Oxygen reduction at the cathode (o):

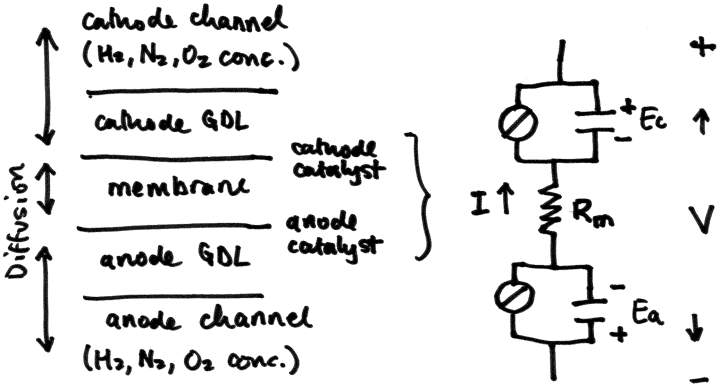
$$O_2 + 4e^- + 4p^+ \rightarrow 2H_2O$$

- Carbon Oxidation (c)

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

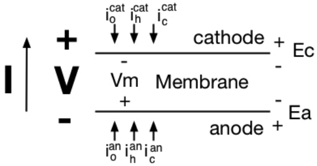
The first two reactions are reversible. Reaction rates can be expressed as currents. Positive currents are oxidation reactions.

Schematic of Local Model



Polarization Curve (normal operation)

At each electrode, all three reactions could occur:



Reaction rates must all match the electrode potential

$$E_c = E_{0,z} + \mathcal{N}_z(\mathbf{C}^{ccat}) + \eta_z(i_z^{ccat})$$

where $E_{0,o} = 1.19$, $E_{0,h} = 0$, $E_{0,c} = 0.207$ and

$$\mathcal{N}_o = \frac{\mathcal{R}T}{4\mathcal{F}} \ln\left\{\frac{C_o}{C_{o,ref}}\right\}$$

(for example) and

$$i_z = i_{z,ref}\left\{\exp\left(\frac{\alpha_z \mathcal{F}\eta_z}{\mathcal{R}T}\right) - \exp\left(-\frac{(1-\alpha_z)\mathcal{F}\eta_z}{\mathcal{R}T}\right)\right\}$$

Equation Counter

Electrochemical parameters, capacitance, and mass transport coefficients are found in the literature and from experiments done at Ballard.

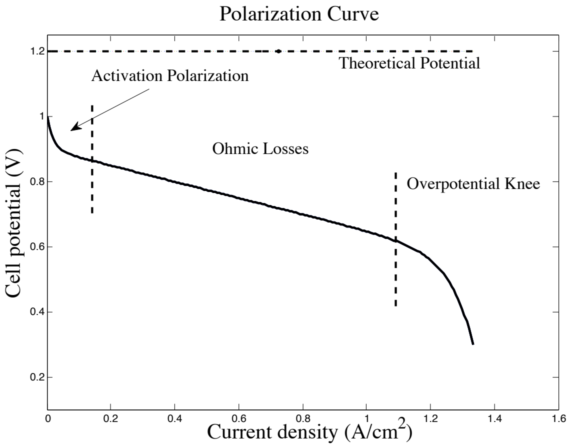
Two local problems. In both cases, channel concentrations and voltage V are given.

1. $E_a(t)$ and $E_c(t)$ are given. All reaction currents, I and catalyst concentrations can be determined and then

   $$\mathcal{C}\frac{dE_a}{dt} = I - i_o^{an} - i_h^{an} - i_c^{an}$$

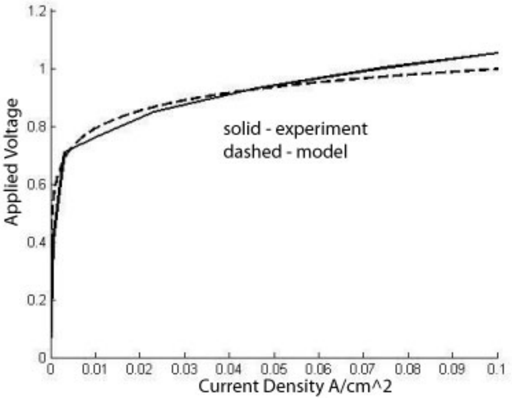
   Problem has a DAE structure.
2. At steady state, E_a and E_c are also determined algebraically.

Polarization Curve (normal operation)



- Open circuit voltage drop from E_0 explained by H_2 crossover from anode Vilekar & Datta JPS 2010

Polarization Curve (applied *V* air-air operation)

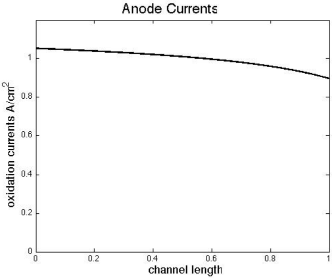


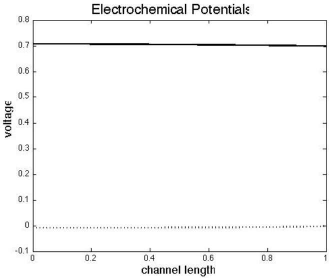
- Oxygen reduction at the anode and reverse Oxygen reduction (and Carbon corrosion) at the cathode (high potential).

Unit Cell Model

Normal Operation: V=0.61

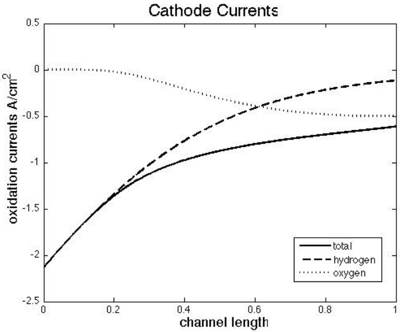
- Gas flow rates and composition are specified at inlet (s_a=1.2, s_c=1.8, 1A/cm^2)
- The local model provides changes to these flows down channel
- It is a DAE system to solve in channel flows to outlet

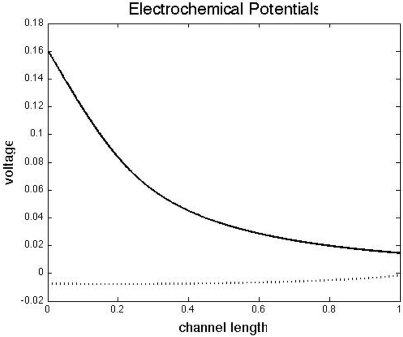




Cathode Starvation: V = -0.045

s_a=1.2, s_c=0.8, 1A/cm^2

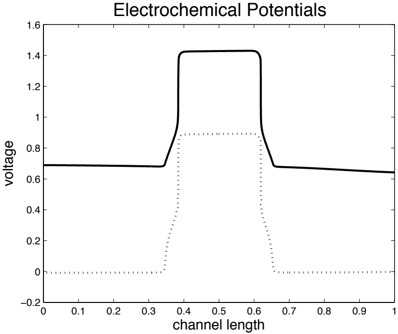




At cathode outlet, the current has a component made by hydrogen evolution.

Anode GDL blockage: $V = 0.525$

s_a=1.2, s_c=1.8, 1A/cm^2

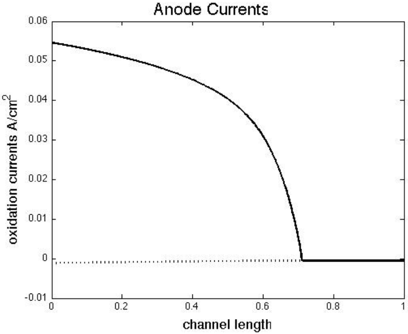


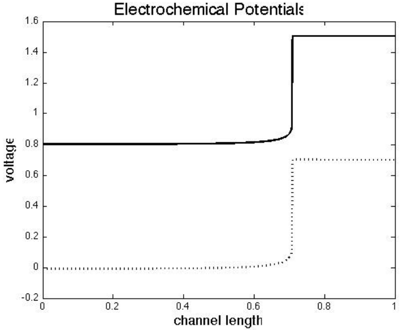
In the anomalous region, there is a reverse current, reverse ORR on the cathode, ORR on the anode (Oxygen from cathode crossing through the membrane to the anode).

Patterson & Darling E&S-S Letters 2006

Partial Anode Starvation (low current), V = 0.71

s_a=1.2, s_c=1.8, 0.03 A/cm^2

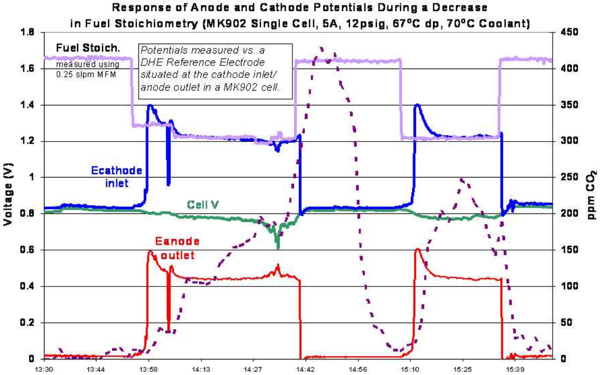




In the outlet region, there is a reverse current, reverse ORR on the cathode, ORR on the anode (Oxygen from cathode crossing through the membrane to the anode).

Additional Notes

- Full anode starvation leads to *severe* anode degradation. Mechanisms here fall outside the assumptions of this model.
- Results for partial anode starvation match experiments qualitatively (weak Carter criteria)

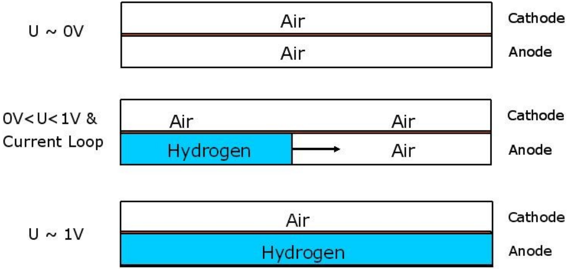


Response of Anode and Cathode Potentials During a Decrease in Fuel Stoichiometry (MK902 Single Cell, 5A, 12psig, 67°C dp, 70°C Coolant)

Potentials measured vs. a DHE Reference Electrode situated at the cathode inlet/ anode outlet in a MK902 cell.

PEMFC start-up

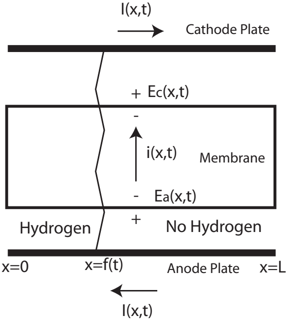
In the open circuit start-up transient, a fuel-rich area at inlet raises the cell voltage and drives a positive current, matched by a reverse current (including carbon oxidation at the cathode) at outlet.



Myers et al, JES v. 153, A1432-1442 (2006)

PEMFC start-up

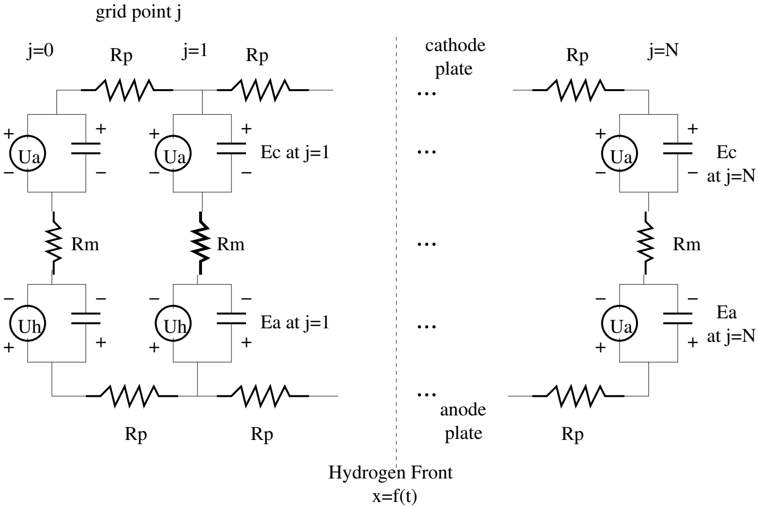
- Consider transient $E_a(x,t)$ and $E_c(x,t)$ in a unit cell setting
- Channel conditions taken to be (piecewise) constant



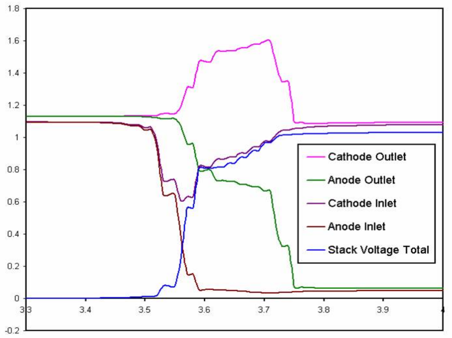
$$V_{xx} = -\frac{\lambda}{R_m}(E_c - E_a - V) \quad \text{Neumann conditions at x=0,1}$$

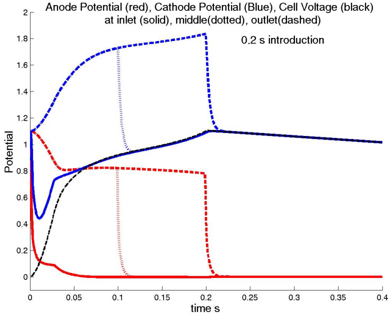
$$E_{c,t} = \frac{1}{C}(U_*^{-1}(E_c) - i)\ , \quad E_{a,t} = \frac{1}{C}(i - U_*^{-1}(E_a))$$

Discretization (equivalent circuit)

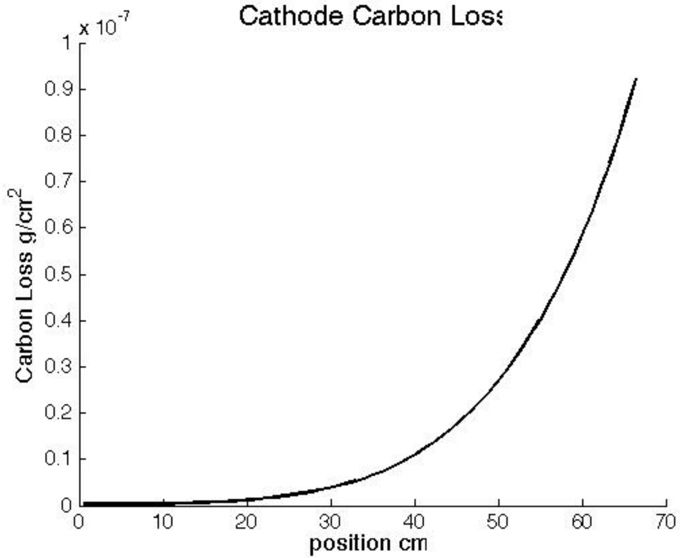


Results

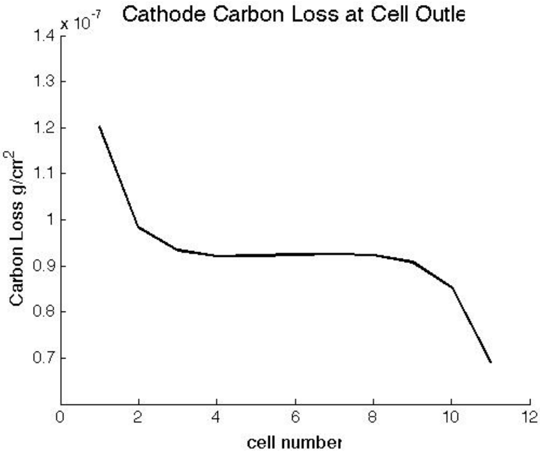

Cathode Outlet
Anode Outlet
Cathode Inlet
Anode Inlet
Stack Voltage Total
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4


Anode Potential (red), Cathode Potential (Blue), Cell Voltage (black)
at inlet (solid), middle(dotted), outlet(dashed)
0.2 s introduction
Potential
time s
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4

Cathode Carbon Loss



Stack Carbon Loss at Outlet

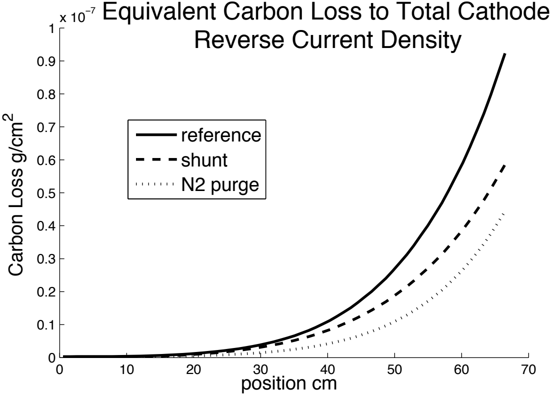


Chang, Kim, Promislow, Wetton, JCP 2007

Additional Notes

Can investigate mitigation strategies:

- Short circuit cell at startup
- Nitrogen purge anode



Summary

1. Introduction to PEM Fuel Cells
2. Simple, local empirical model of mass transfer and electrochemistry fitted to experiments
3. Unit cell and stack level multi-scale simulations
4. Insight gained into conditions that lead to high electrochemical potentials that lead to carbon corrosion of the catalyst and other degradation mechanisms