Modelling fuel cells in start-up and reactant starvation conditions

Brian Wetton    Radu Bradean
Keith Promislow    Jean St Pierre

Mathematics Department
University of British Columbia
www.math.ubc.ca/~wetton

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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)
• 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

cathode channel
(H₂, N₂, O₂ conc.)

<table>
<thead>
<tr>
<th>Cathode GDL</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Anode GDL</td>
</tr>
<tr>
<td>Anode channel</td>
<td>Catalyst</td>
</tr>
</tbody>
</table>

(H₂, N₂, O₂ conc.)

Diagram:

\[ \text{I} \uparrow \quad R_m \quad \frac{\text{Ea}}{\text{Ea}} \downarrow \]

\[ \text{+} \quad \text{Ec} \quad \uparrow \quad \text{V} \quad \downarrow \quad \text{-} \]
Polarization Curve (normal operation)

At each electrode, all three reactions could occur:

\[ E_c = E_{0,z} + \mathcal{N}_z(C_{ccat}^{\text{cat}}) + \eta_z(i_{z}^{\text{cat}}) \]

where \( E_{0,o} = 1.19, \ E_{0,h} = 0, \ E_{0,c} = 0.207 \) and

\[ \mathcal{N}_o = \frac{RT}{4F} \ln \left\{ \frac{C_o}{C_{o,\text{ref}}} \right\} \]

(for example) and

\[ i_z = i_{z,\text{ref}} \left\{ \exp \left( \frac{\alpha_z F \eta_z}{RT} \right) - \exp \left( -\frac{(1 - \alpha_z) F \eta_z}{RT} \right) \right\} \]
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

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

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
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 \((s_a = 1.2, s_c = 1.8, \text{1A/cm}^2)\)
- The local model provides changes to these flows down channel
- It is a DAE system to solve in channel flows to outlet
Cathode Starvation: $V = -0.045$

$s_a=1.2, s_c=0.8, 1\text{A/cm}^2$

At cathode outlet, the current has a component made by hydrogen evolution.
Partial Anode Starvation, $V = 0.71$

$s_a = 1.2$, $s_c = 1.8$, $0.03 \, \text{A/cm}^2$

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).
• Full anode starvation and local anode blockage scenarios can also be investigated in this framework

• Results match experiments qualitatively (weak Carter criteria)
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.

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)

grid point $j$

$E_a$ at $j=1$

$R_m$

$U_a$

$U_h$

$R_p$

$E_c$ at $j=1$

Hydrogen Front $x=f(t)$

Cathode plate

Anode plate

$E_a$ at $j=N$

$E_c$ at $j=N$
Results

[Graph showing various potential and voltage values over time with legends for Cathode Outlet, Anode Outlet, Cathode Inlet, Anode Inlet, and Stack Voltage Total.]

[Graph showing Anode Potential (red), Cathode Potential (blue), and Cell Voltage (black) at inlet (solid), middle (dotted), and outlet (dashed) with a 0.2 s introduction time.]
Cathode Carbon Loss

Carbon Loss g/cm$^2$

position cm
Stack Carbon Loss at Outlet

Cathode Carbon Loss at Cell Outlet

Carbon Loss g/cm²

1.4 x 10⁻⁷

cell number
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