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)
• 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.)

---
cathode GDL

---
membrane

---
anode GDL

---
anode channel
(H₂, N₂, O₂ conc.)

---
cathode catalyst

---
anode catalyst

---
Diffusion

---

\[ + \]

---

\[ - \]

---

\[ + \]

---

\[ - \]
Polarization Curve (normal operation)

At each electrode, all three reactions could occur:

\[ E_c = E_{0,z} + N_z(C^{ccat}) + \eta_z(i^{ccat}_z) \]

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

\[ N_o = \frac{RT}{4F} \ln \left\{ \frac{C_o}{C_{o,ref}} \right\} \]

(for example) and

\[ i_z = i_{z,ref} \left\{ \exp \left( \frac{\alpha_z F \eta_z}{RT} \right) - \exp \left( -\frac{(1 - \alpha_z) F \eta_z}{RT} \right) \right\} \]
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.
• 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 ($s_a=1.2$, $s_c=1.8$, $1\text{A/cm}^2$)
- The local model provides changes to these flows down channel
- It is a DAE system to solve in channel flows to outlet
Cathode Starvation: \( V = -0.045 \)

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

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)
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

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

\[
E_{c,t} = \frac{1}{C} \left( U_*^{-1}(E_c) - i \right), \quad E_{a,t} = \frac{1}{C} \left( i - U_*^{-1}(E_a) \right)
\]
Discretization (equivalent circuit)

grid point $j$

$U_a$

$R_m$

$U_h$

$E_a$ at $j=1$

$E_c$ at $j=1$

$Rp$

$Hydrogen Front \ x=f(t)$

$cathode plate$

$anode plate$

$U_a$
Results
Cathode Carbon Loss

![Graph showing Cathode Carbon Loss over position cm]
Stack Carbon Loss at Outlet

Chang, Kim, Promislow, Wetton, JCP 2007
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