Mathematical Modelling of Electrochemical Systems (Polymer Electrolyte Fuel Cell Example)

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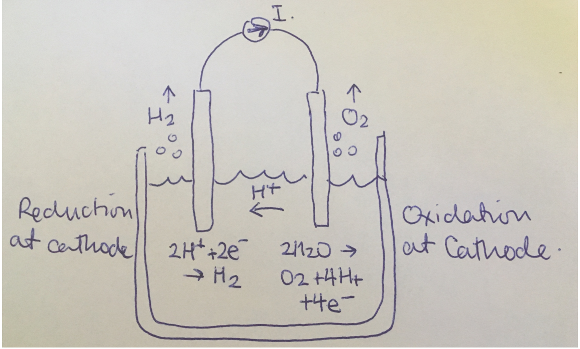
Electrochemistry

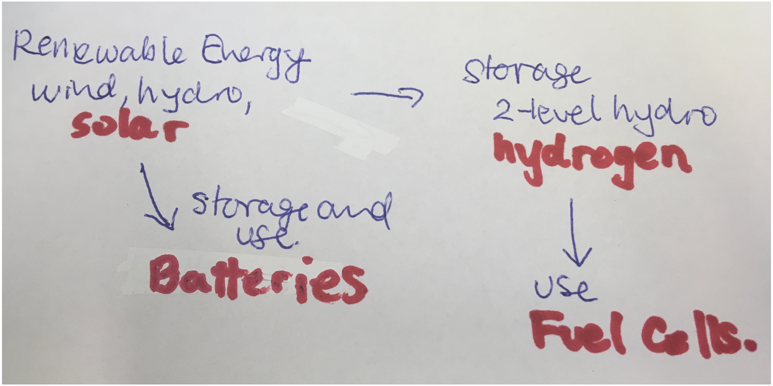
An electrochemical reaction is a chemical reaction that generates or is driven by an electric current. Electrolysis of water:



Newman and Thomas-Alyea: *Electrochemical Systems*

Electrochemistry in Energy Systems

Electrochemical systems play a role in power generation, storage and use:



Polymer Electrolyte Fuel Cells

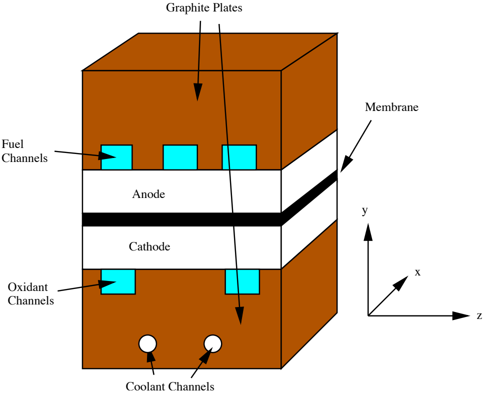
My background

- MITACS project with Ballard Power Systems 1998-2010, developing computational simulation tools to aid design.
- Review articles:
  - "Reduced Dimensional Computational Models of Polymer Electrolyte Membrane Fuel Cell Stacks," Journal of Computational Physics **223** (2007).
  - "PEM Fuel Cells: A Mathematical Overview" SIAM Journal of Applied Mathematics **70** (2009).
- Our project involved multi-scale modelling of stack level fuel cell performance, based on experimentally-fit component models.

FC Basics

PEMFC Unit Cells

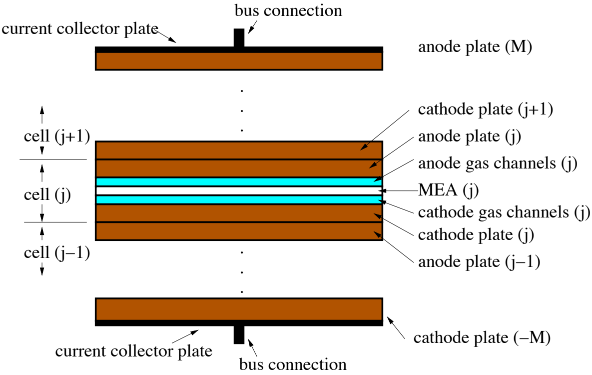
- Membrane Electrode Assembly (MEA):
  1. Electrodes
  2. Catalyst Layers
  3. Membrane
- Plates, Gas Channels, Coolant
- Large Aspect Ratio



FC Basics

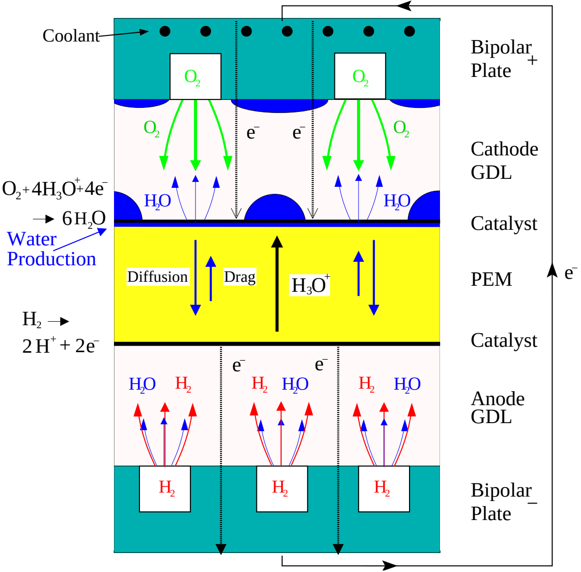
Fuel Cell Stacks

- Bipolar Plates
- Same Total Current Through Each Cell
- Electrical Coupling
- Thermal Coupling
- End Cell Effects



FC Basics

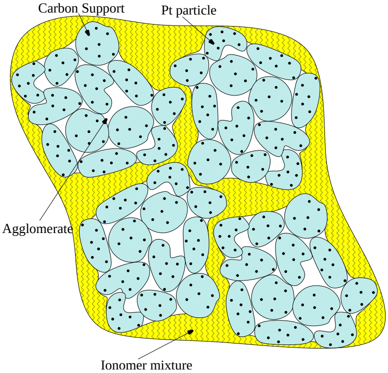
Cross Plane Transport



FC Basics

Detail of Catalyst Layer

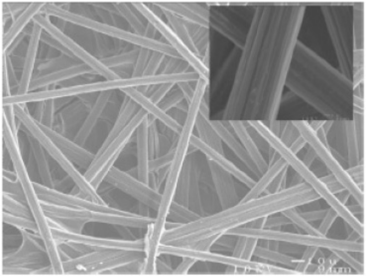
- Composite Material: Pores, carbon particles, Pt particles, and ionomer.
- Located between the gas diffusion layer and the membrane
- Complicated multi-phase transport.



FC Basics

Gas Diffusion Layer

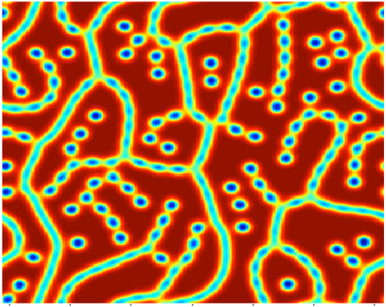
- Gas Diffusion Layer: teflonated carbon fibre paper
- Microporous layer



FC Basics

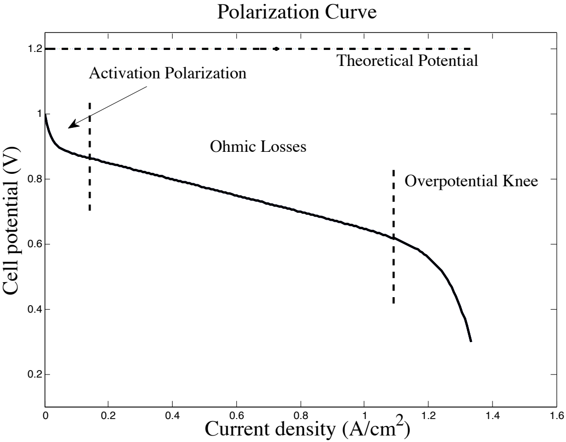
Membrane

- Nafion (acid groups on a teflon backbone)
- Proton conducting pores
- Mechanical properties



FC Basics

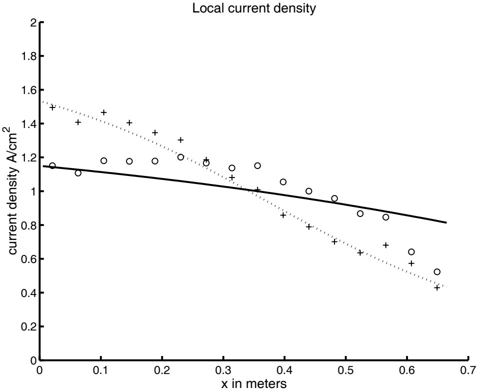
Polarization Curve



FC Basics

Performance along the channel

- Unit cells are operated at a given current.
- Inlet flow rates are given in terms of stoichiometric ratios to that current.



Polarization Curve

Semi-empirical fit

$$U(i, C) = E_c - \frac{RT}{\alpha F}\left\{\ln \frac{i}{i_0} - \ln \frac{C - \delta i}{C_{ref}}\right\} - R_m i$$

where $E_c = 1.28V$, $C_{ref} = 40.9\text{mol}/\text{m}^3$ and α, i_0, δ and R_m are fitted parameters.

- Fitted δ is larger than $L/(4DF)$ from GDL transport.
- R_m is slightly larger than the membrane resistance.
- U is used as a computational variable, not i.
- Local fit, how does this behaviour scale up to stack level, where i and C can vary within a cell and between cells?

Channel Concentrations

- Simplifications for the talk:
    - Constant T and P
    - Cathode channel gas is saturated and ideal
    - Quantities are averaged over the cross plane z
    - Channels are well mixed
- Channel oxygen flux $Q(x)$:

$$\frac{dQ}{dx} = -\frac{i}{4F} \text{ with } Q(0) = sLi_{ave}/(4F)$$

- Channel concentration $C(x)$:

$$C(x) = C_{tot}\frac{Q}{Q+Q_n} \text{ with } Q_n = (0.79/0.21)Q(0)$$

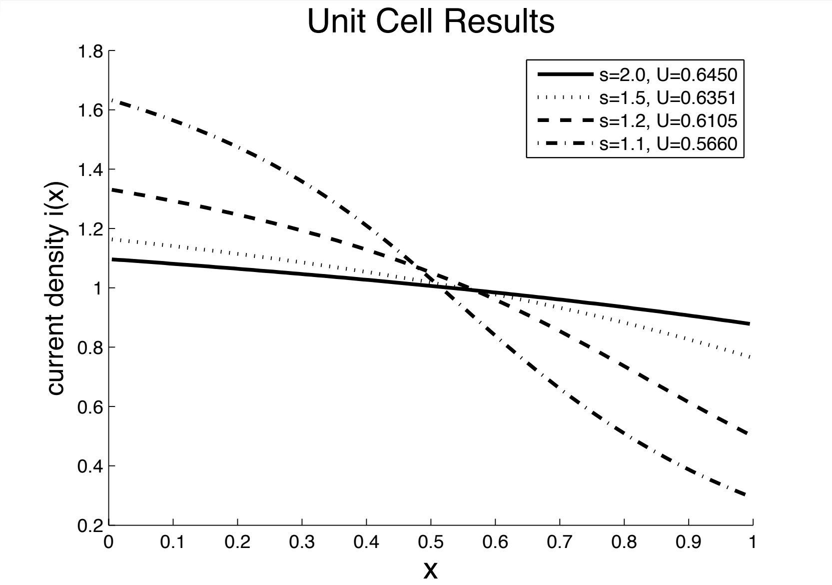
Unit Cell Problem

$$U(i(x), C(x)) \ , \quad \frac{dQ}{dx} = -\frac{i}{4F} \ , \quad C(x) = C_{tot}\frac{Q}{Q+Q_n}$$

Given: i_{ave}, s, T, C_{tot}, determine U constant, $i(x)$, $Q(x)$, and $C(x)$ that satisfy the relationships above and

$$\frac{1}{L}\int_0^1 i(x)dx = i_{ave}$$

Nonlinear, nonlocal problem, approximated with a suitable discretization and Newton iterations, with continuation if needed.


Unit Cell Results
current density i(x)
x
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
s=2.0, U=0.6450
s=1.5, U=0.6351
s=1.2, U=0.6105
s=1.1, U=0.5660

Stack Level Electrical Coupling

- The bipolar plates have a non-negligible resistance. The voltage in cell m can vary $U_m(x)$.
- The Fundamental Voltage Equation

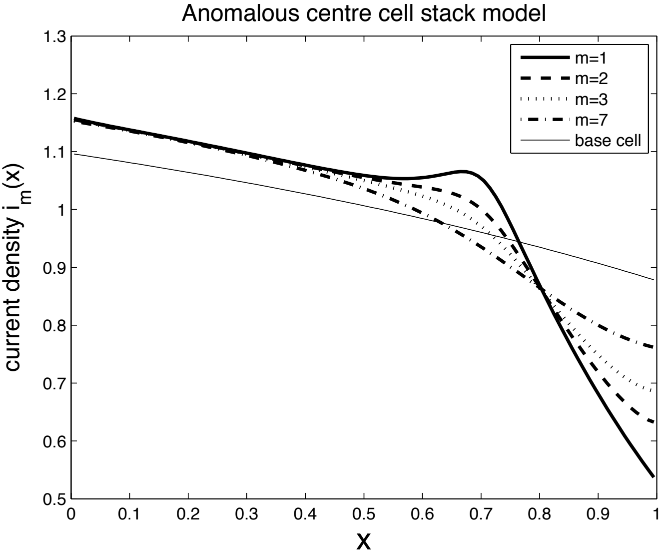
$$\frac{d^2 U_m}{dx^2} - \lambda(i_{m+1} - 2i_m + i_{m-1}) = 0$$

  with Neumann conditions in x and discrete Neumann conditions in m (rank deficient).
- Scaled λ is the Wagner number W.
- W is related to the number of cells affected by a cell with anomalous behaviour.

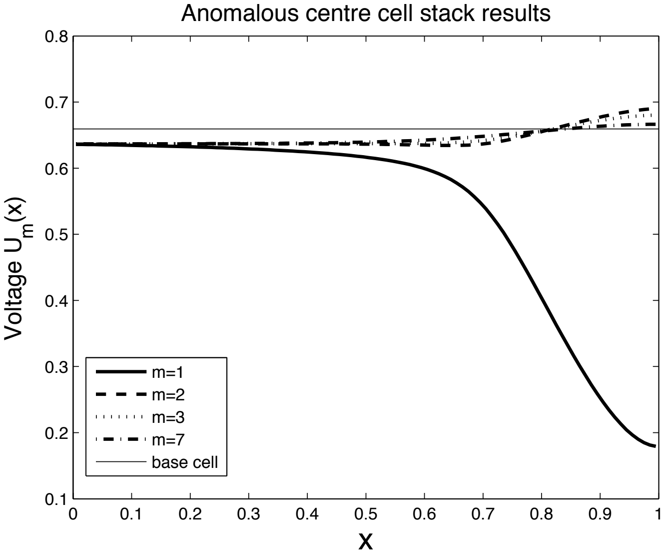
Stack level model

- Unit cells are in electrical series, i_{ave} is common to all cells.
- s, C_{tot}, and electrochemical parameters can vary between cells and in x.
- If all parameters are the same, each cell behaves identically.
- If $\lambda = 0$ all cells behave independently.
- Results for a stack with a single anomalous cell with a reduced s are shown on the next page.

Stack Results I - current densities



Stack Results II - voltages



Summary

1. Overview of PEM Fuel Cells
2. Mathematical Model
3. Mathematical Flavour:
    - Heavy modelling component
    - Multiscale models with unusual coupling (analysis and computational challenge)
    - Industry interest also in nanostructure materials modelling