Mathematical Modelling of Electrochemical Systems

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Outline

UBC Institute of Applied Mathematics

Polymer Electrolyte Membrane Fuel Cell Modelling

- Industrial Collaboration
- Basic Stack Model
- Stack model

New Mathematics

- Artificial velocities in generalized Stefan problems at steady state

More Recent Work

- Direct Methanol Fuel Cell
- Generalized Dialysis System

Institute of Applied Mathematics

University of British Columbia

- Faculty participation from many departments.
- Interdisciplinary graduate programme.

Polymer Electrolyte Membrane Fuel Cell Modelling

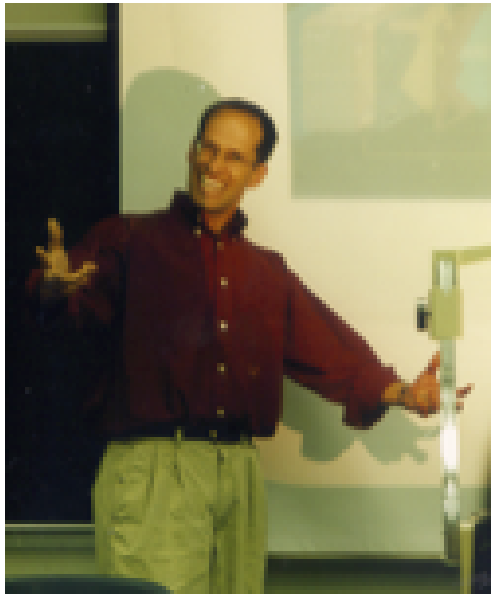
Overview

- 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," JCP **223** (2007).
  - "PEM Fuel Cells: A Mathematical Overview," SIAP **70** (2009).
- Our project involved multi-scale modelling of stack level fuel cell performance, based on experimentally-fit component models.

Industrial Collaboration

- MMSC group formed under MITACS
- Financially supported by Ballard and MITACS
- Academic collaboration with professors Keith Promislow, John Stockie, Ned Djilali, Huaxiong Huang, Brian Seymour, Anthony Peirce, Ray Spiteri
- From Ballard: John Kenna, Jean St Pierre, Juergen Stumper, Herwig Haas, Gwang-Soo Kim
- Students and PDFs: Radu Bradean, Arian Novruzi, Peter Berg, Atife Caglar, Paul Chang, Roger Donaldson, Leslie Fairbairne, Lloyd Bridge, Michael Lindstrom, Jason Boisvert

Some of the MMSC group


Keep the models as simple as possible

Jean St-Pierre, Hawaii Natural Energy Institute

Industrial Mathematics

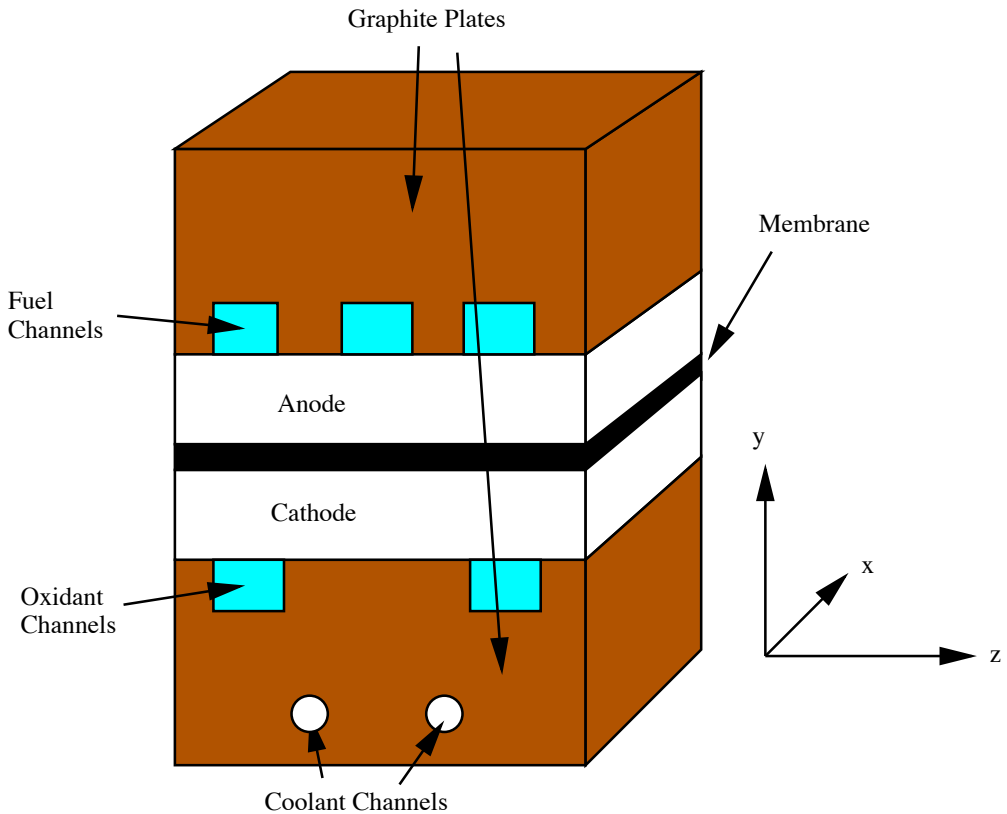
(According to Brian Wetton)

- Solving Industrial problems raises the profile of our discipline:
  - Recognition from the Community
  - Employment opportunities for our students
- It is enjoyable to use mathematical techniques that are not necessarily part of your research skill set to solve concrete problems.
- If you are lucky, some new and "interesting" mathematics will come your way.
- The research of Industrial Mathematics is not necessarily Mathematics Research.
- Industrial Mathematics is not a subset of traditional Applied Mathematics.

Basic Stack Model

Unit Cells

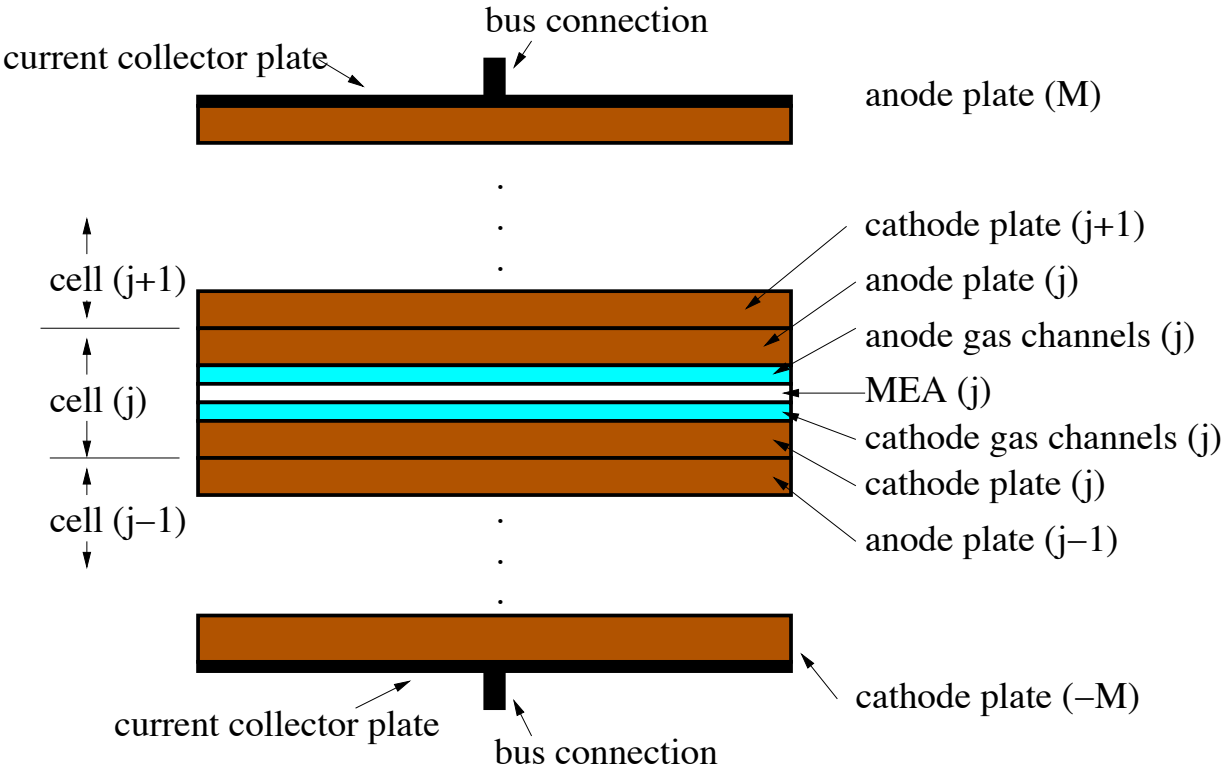
- Membrane Electrode Assembly (MEA):
  1. Electrodes
  2. Catalyst Layers
  3. Membrane
- Plates, Gas Channels, Coolant
- Large Aspect Ratio



Introduction to PEM Fuel Cells

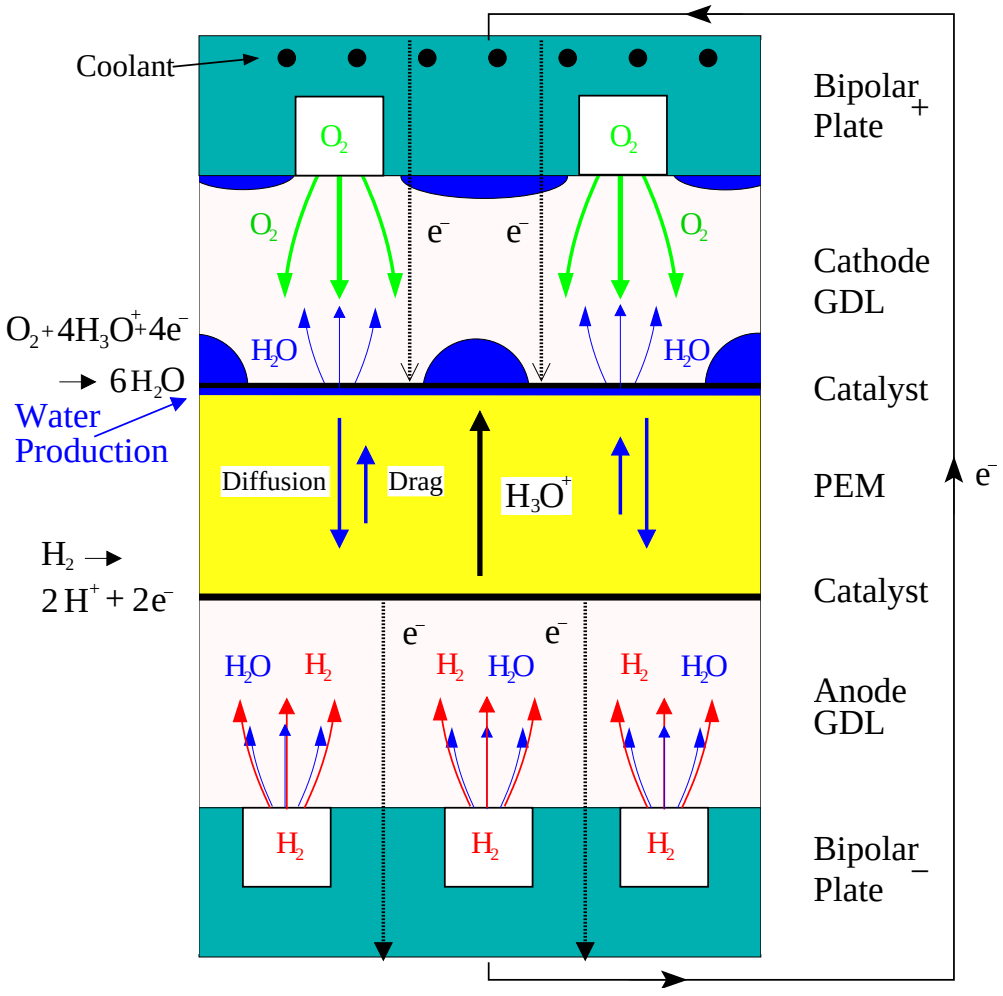
Fuel Cell Stacks

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



Introduction to PEM Fuel Cells

Water Management (cont.)



Introduction to PEM Fuel Cells

Electrochemical Reactions

Main reactions under normal conditions:

- Hydrogen oxidation at the anode (Platinum catalyst):

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

  occurs at low electrochemical potential.

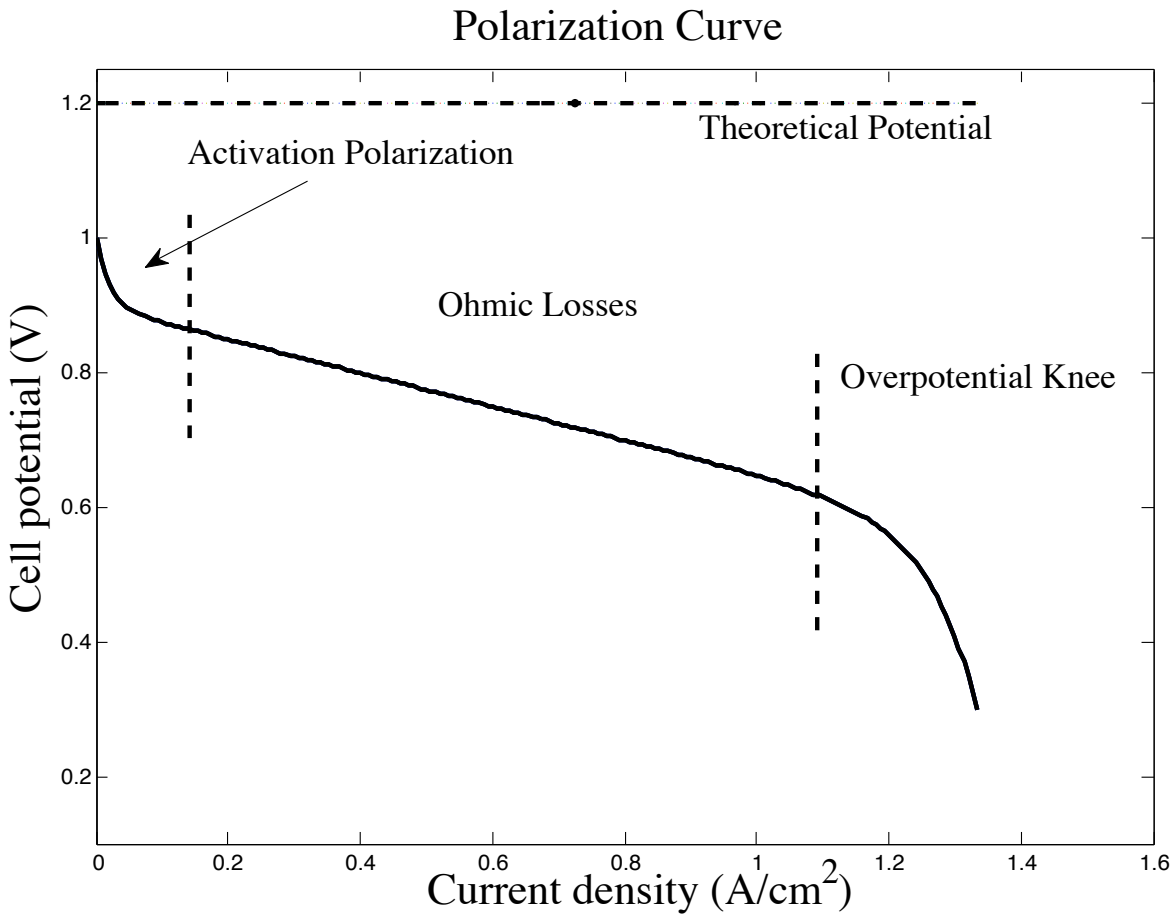
- Oxygen reduction at the cathode (Platinum):

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

  occurs at high electrochemical potential.

Introduction to PEM Fuel Cells

Polarization Curve



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 $Q(x)$:

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

- Channel concentration $C(x)$:

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

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.

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

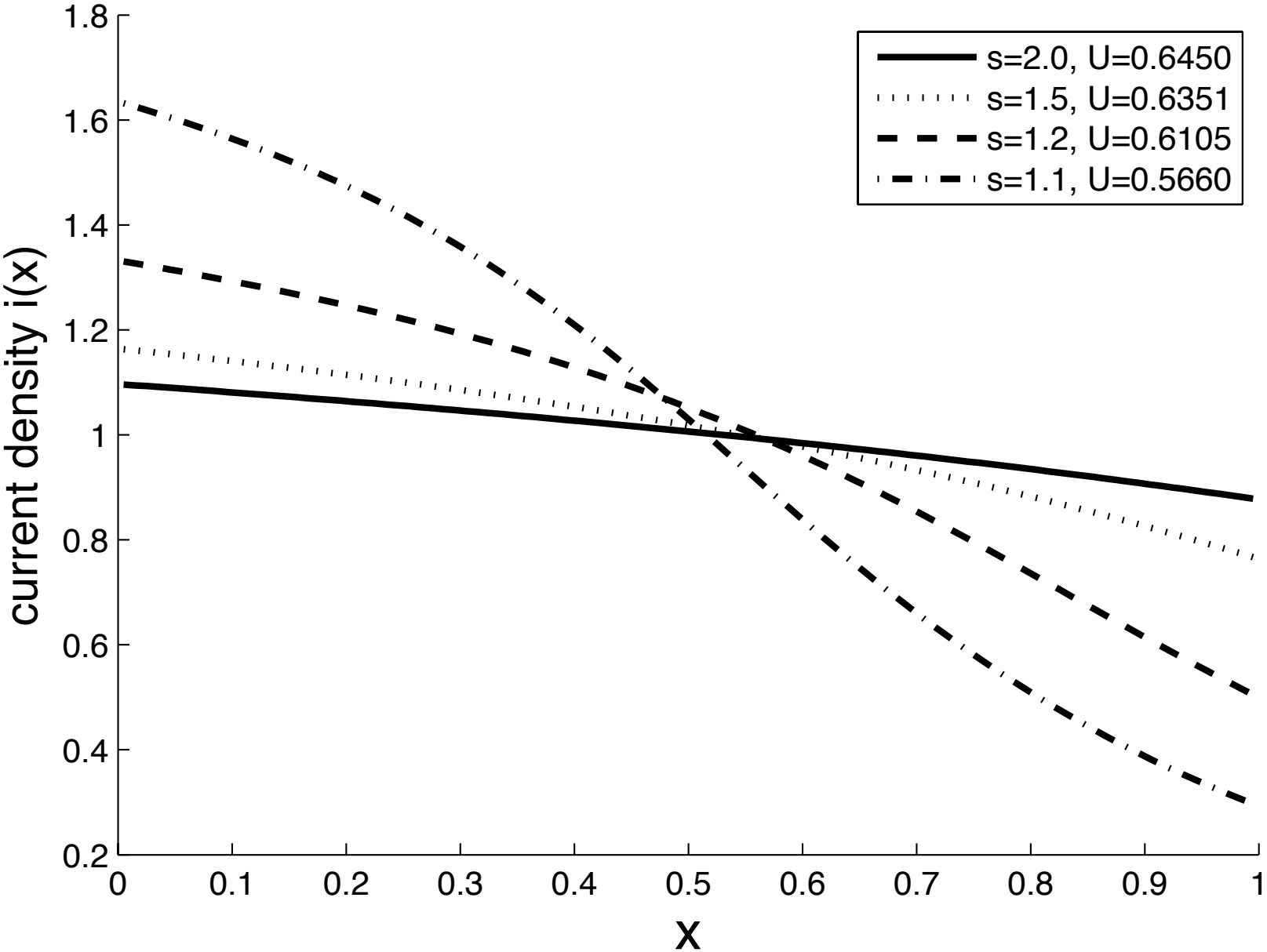
$$\frac{d^2 U_m}{dx^2} - \lambda(i_{m+1} - 2i_m + i_{m-1}) = 0$$

  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.

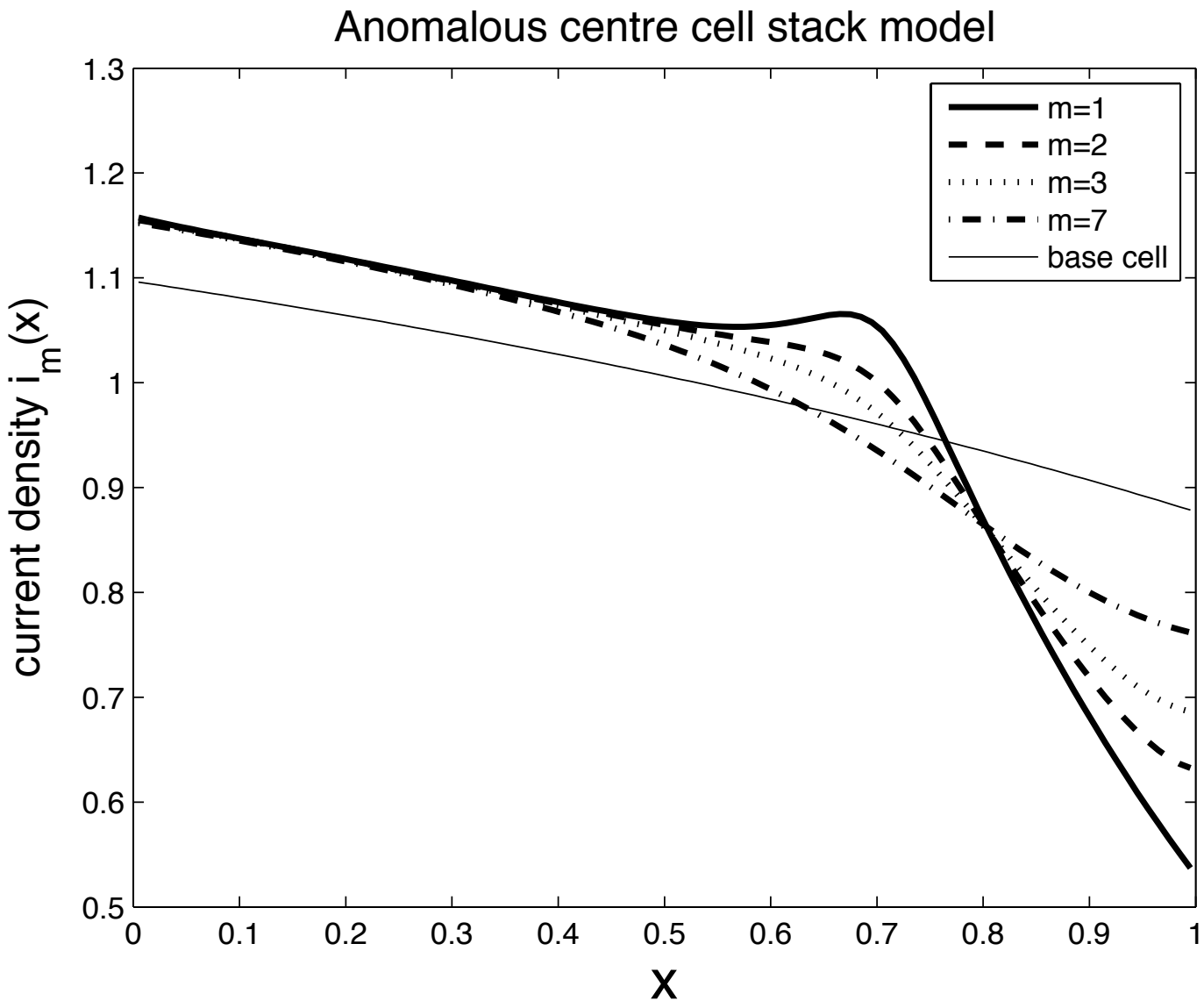
Stack level model

- 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.

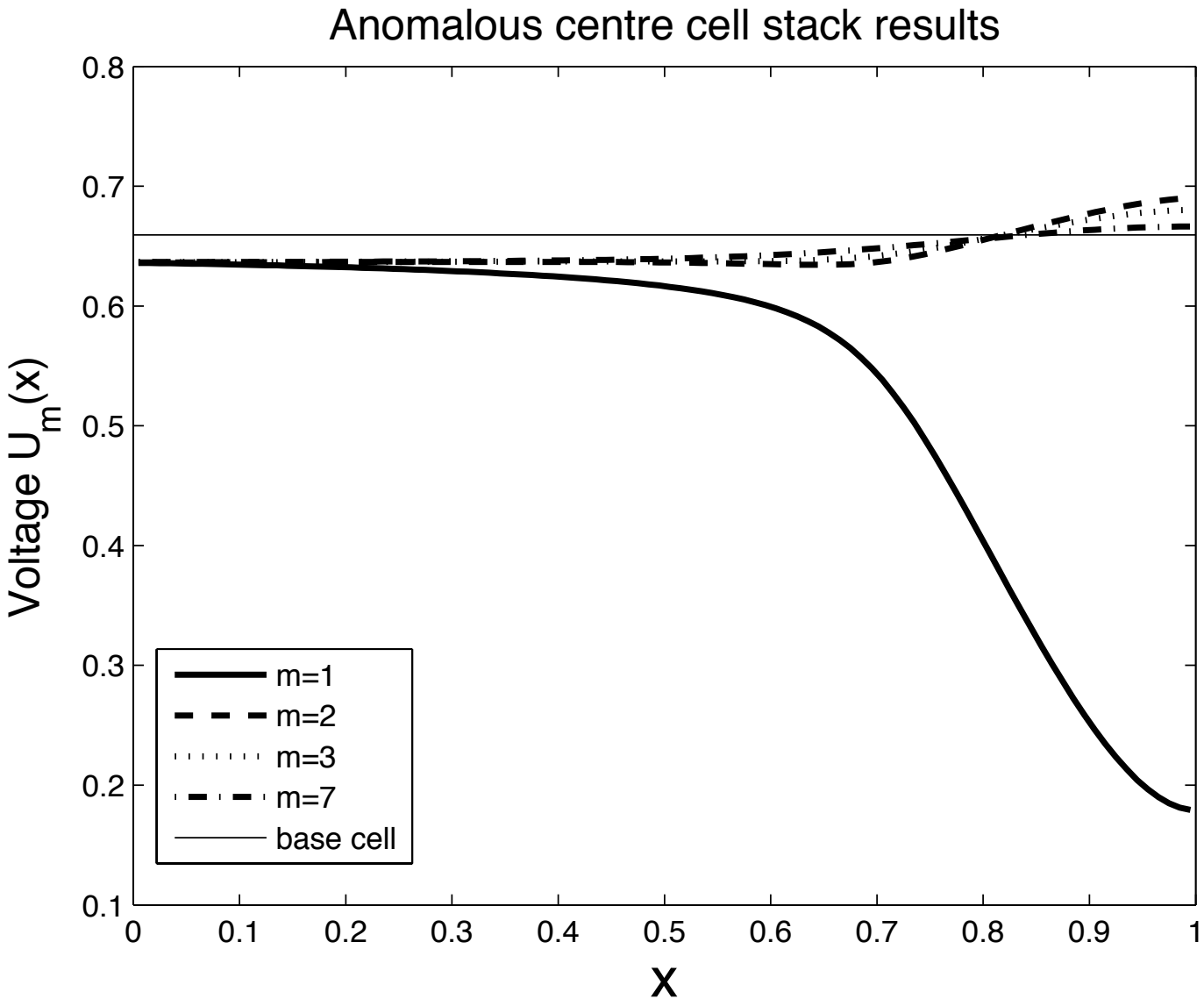
Unit Cell Results



Stack Results I - current densities



Stack Results II - voltages



Additions to the model

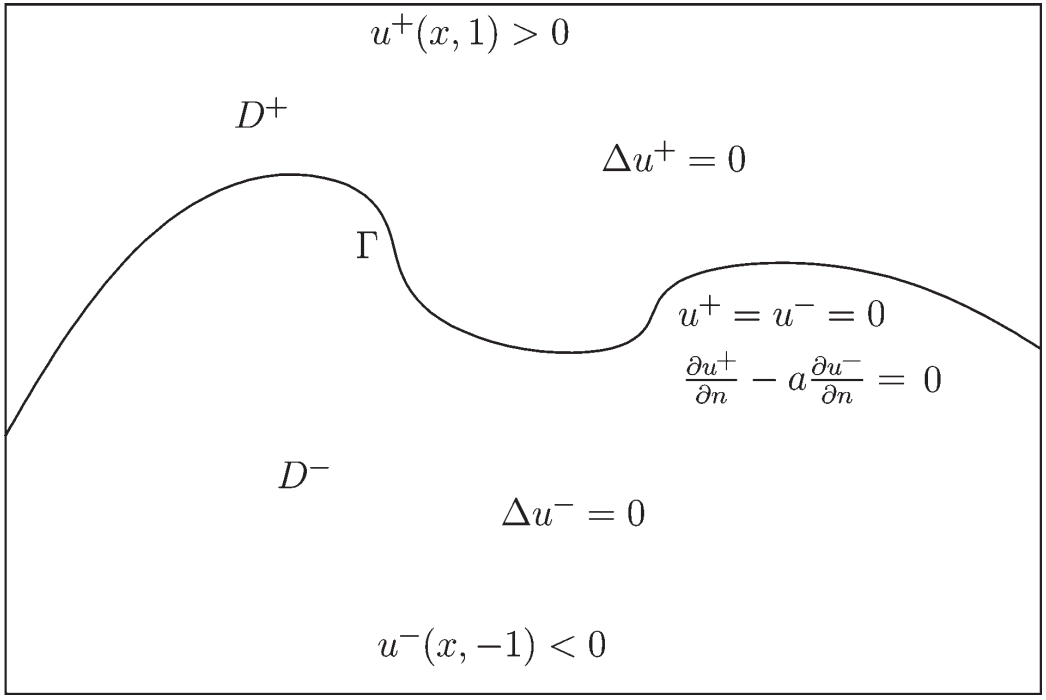
- Water management (strong coupling to thermal effects)
- Stack level coupling through inlet and outlet headers
- Additional electrochemistry - reverse reactions and carbon corrosion
- Transient effects during start-up
- Hydrogen recirculation operation

Perspective

- Used the results of simple experiments to fit heuristic, macroscopic models of the behaviour of complicated microstructure.
- Built multi-scale models using this locally fit behaviour and well understood physics at the macro-scale.
- Validated the resulting models against independent experiments.
- The models are then used by Engineers to gain insight into the phenomena and to aid in the design process.
- If new materials are used in the fuel cell design, their impact on stack performance can evaluated quickly using the same simple experiments
- Not clear how big our lasting impact in the company was

New Mathematics

Artificial velocities in generalized Stefan problems at steady state



- Transient problem physical $V = [\kappa \partial u/\partial n]$.
- Using boundary conditions $[\kappa \partial u/\partial n] = 0$, $[u] = 0$ and $V = u_{\pm}$ gives a better conditioned problem (no spatial grid related stability restriction on explicit time steps).

Generalized Steady State Stefan Problems

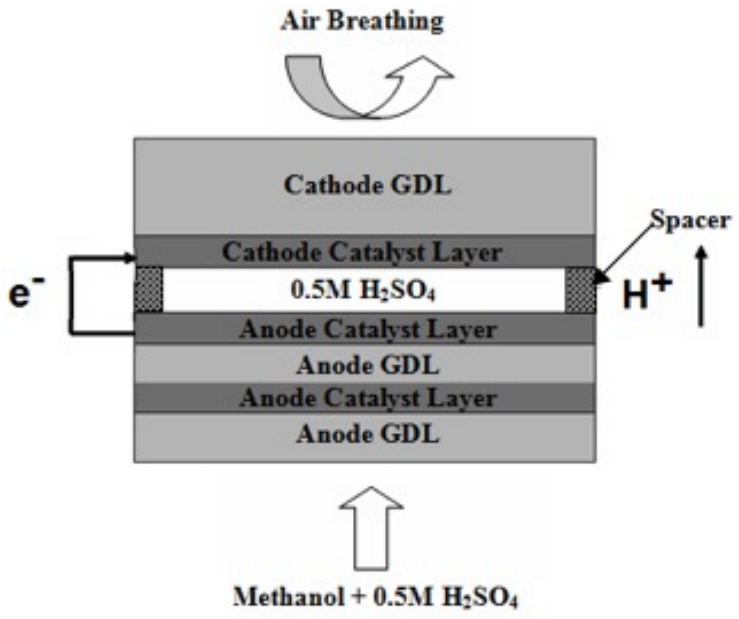
- Generalize to free boundary value problems with n components of second order elliptic problems on one side of the interface and m on the other with $n + m + 1$ mixed boundary conditions at the interface.
- Algebraic conditions for well posed-ness to perturbations of flat interfaces and given far field conditions.
- Algebraic conditions for "good" choices of normal velocities to compute steady interfaces.
- "Solving steady interface problems using residual velocities," IMAJAM **71**, 2006. [Roger Donaldson]
- "The residual velocity method applied to a steady free boundary-value problem of vector Laplacian type," IMAJAM **74**, 2009. [Wan Chen]

Other moving interface problems

- Capturing method for moving interfaces in two phase flow (water and vapour) with degenerate diffusion
- "A mixture formulation for numerical capturing of a two-phase/vapour interface in a porous medium," JCP **225**, 2007. [Lloyd Bridge]
- Ongoing interest - mathematical structure of an easier problem (from bread baking) and convergence analysis of the iterations in the numerical scheme.

Direct Methanol Fuel Cell

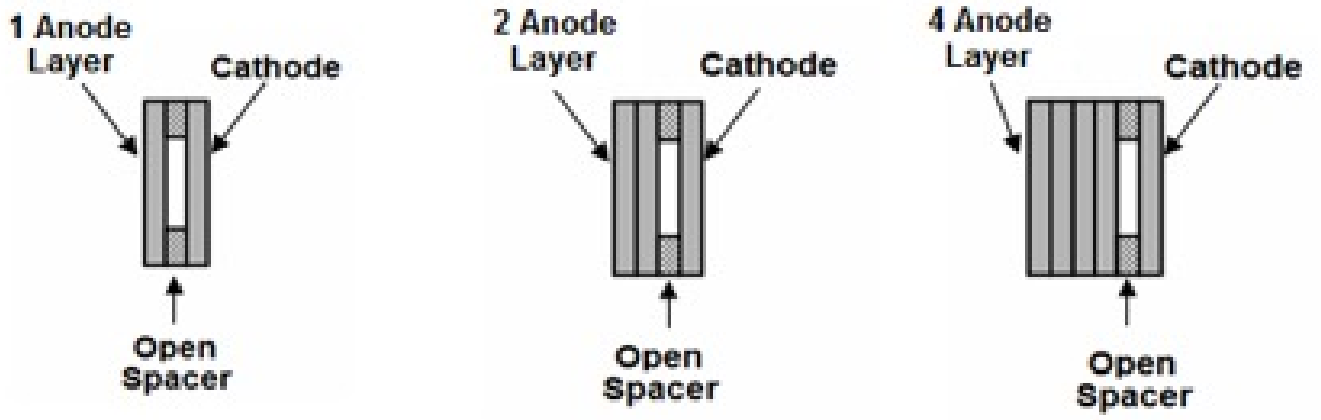
System Overview



- Small, direct methanol test system
- No membrane, multi-anode structure to reduce methanol crossover
- Alfred Lam, BW, David Wilkinson, JES 158, B29-B35 (2011).

Direct Methanol Fuel Cell

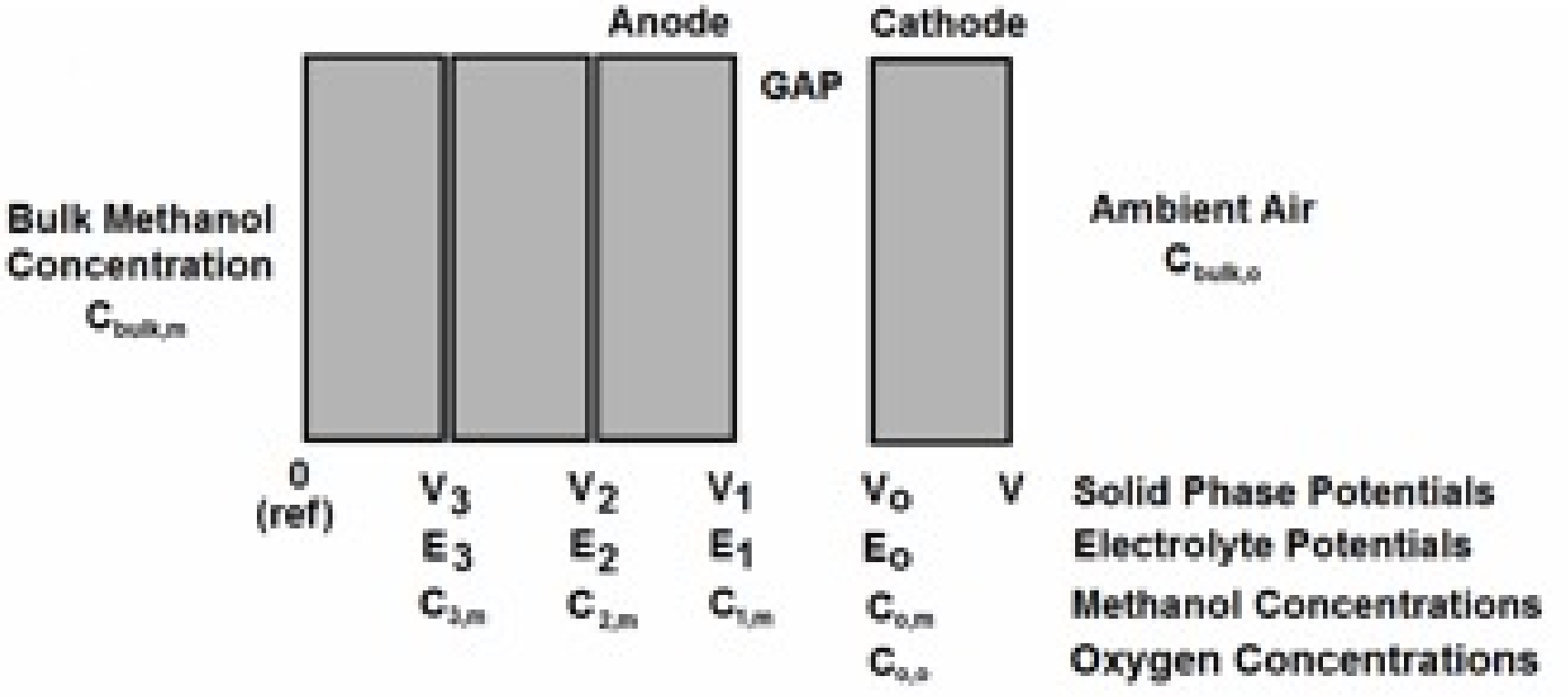
System Overview



- The engineers had intuition that adding more anode layers would reduce crossover losses.
- They had some experimental validation.
- A model would help optimize the design and get insight into the behaviour between the layers.

Direct Methanol Fuel Cell

Model unknowns

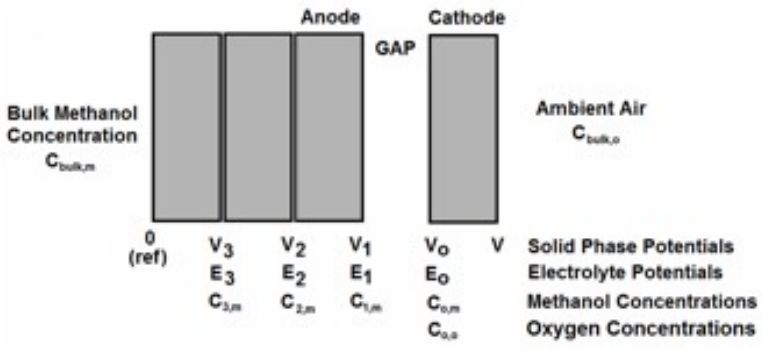


- Catalyst layers idealized as interfaces.
- Model is a nonlinear algebraic system with these unknowns, with total current I given, V to be determined.

Direct Methanol Fuel Cell

Equation Counter

- 14 unknowns
- V and E differences give electric and protonic currents, which must match I in each layer (5).
- Current differences must match diffusive fluxes (4).
- The difference between V and E must match Nernst plus overpotential terms (5*).



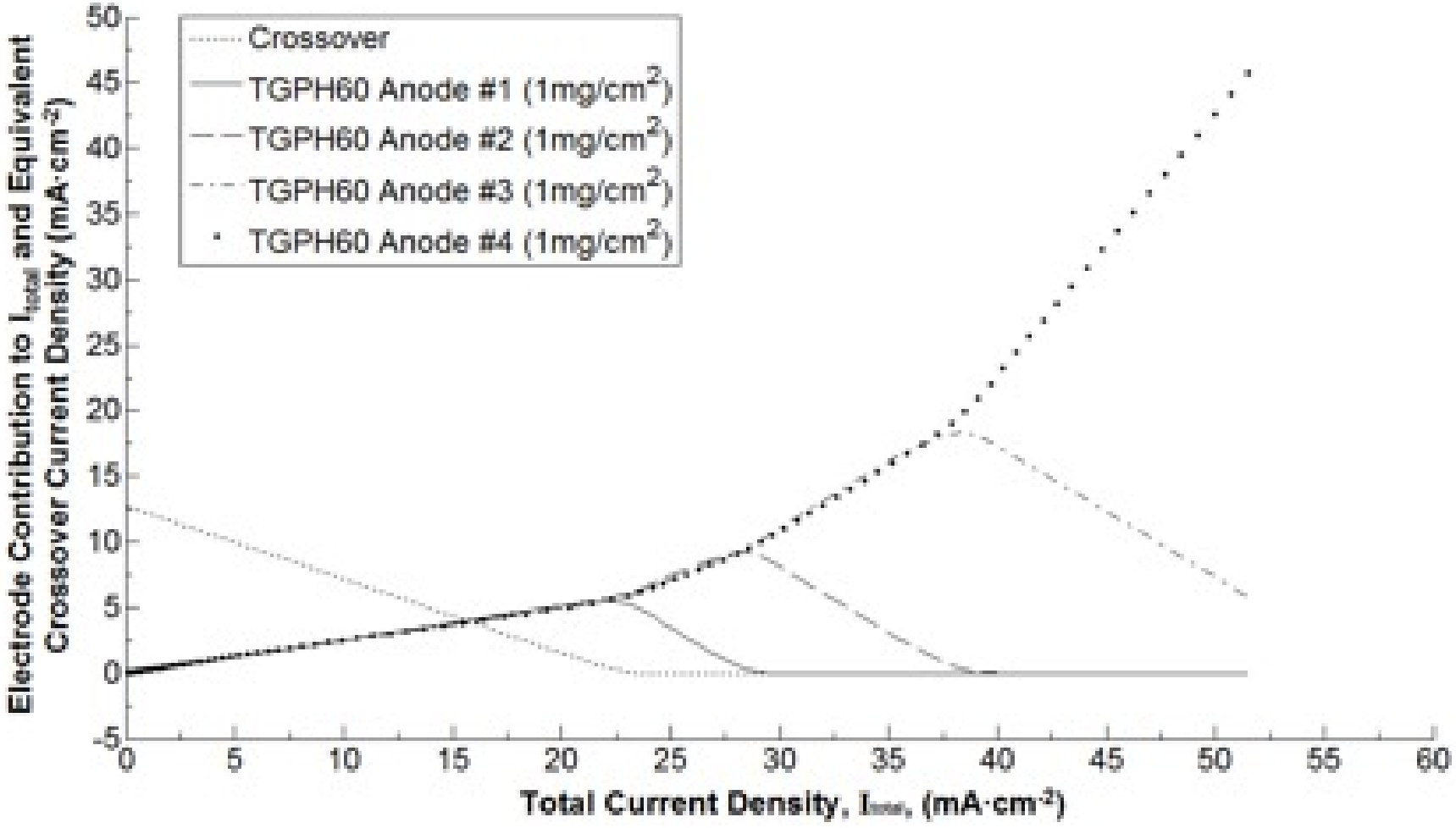
Direct Methanol Fuel Cell

Aside

- (Highly) Nonlinear system in 14 unknowns. Used logarithmic variables for concentrations to maintain positivity; Newton's method with continuation.
- Math and computations are "easy" but just beyond the reach of many research engineers (not all).
- I enjoy working in this gap, my department values it.
- For me, an important contribution was in the training of the CHBE graduate student/PDF, Alfred Lam.

Direct Methanol Fuel Cell

Model results: four anodes



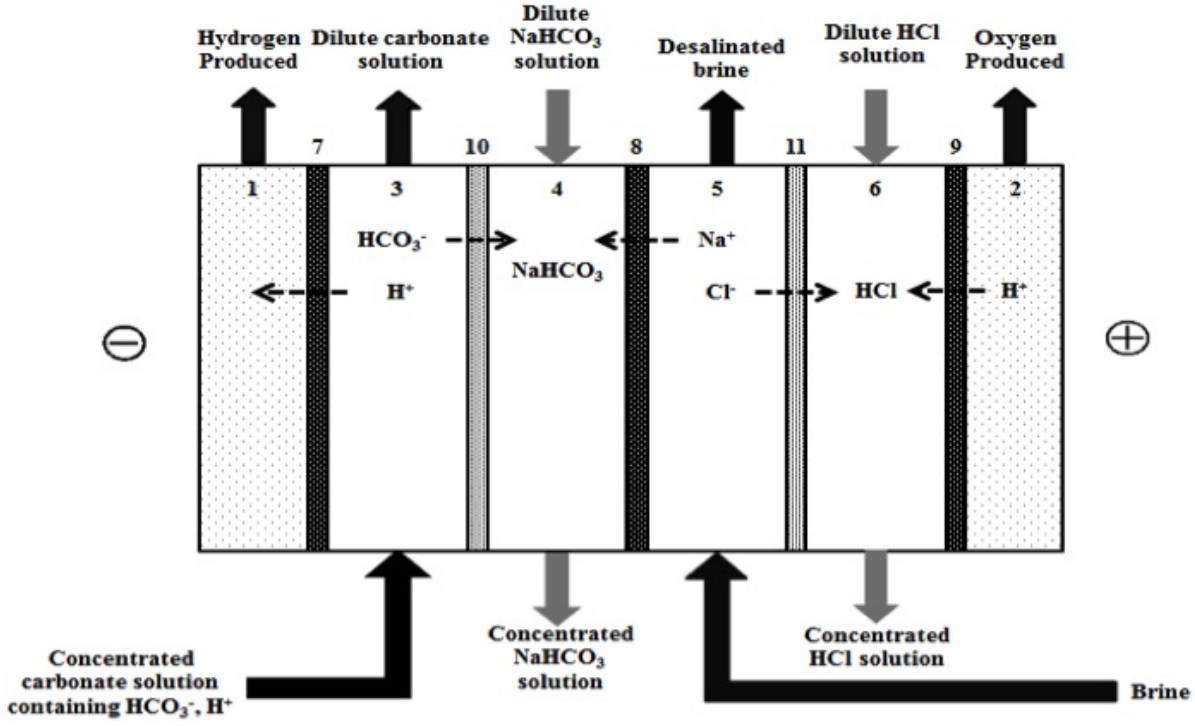
Direct Methanol Fuel Cell

The rest of the story

- Improved performance, reduced methanol crossover achieved.
- Model used to optimize the Pt loading on a four anode system. Model results matched later experiments.

General Dialysis System

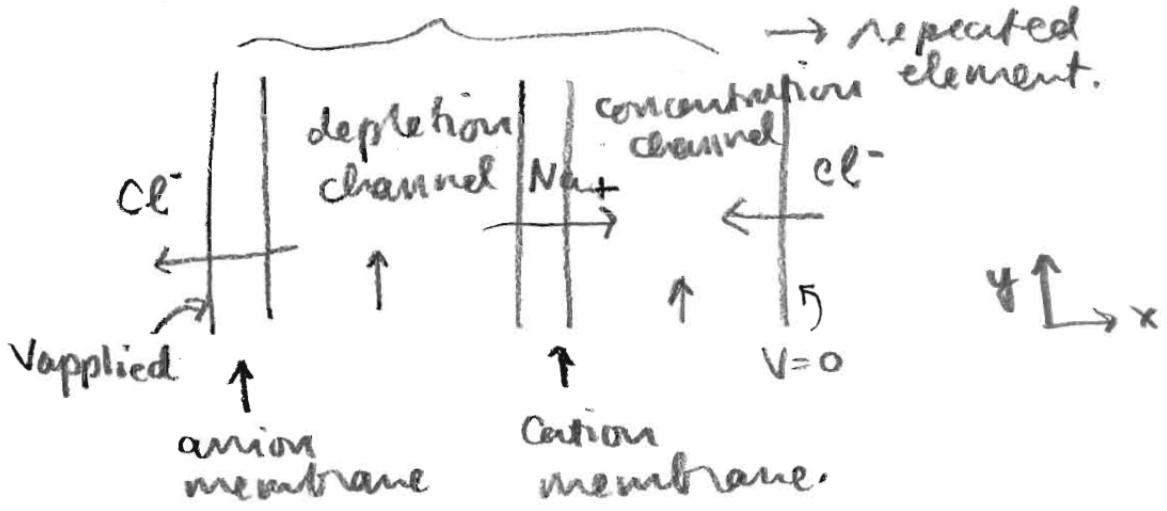
Preliminary Design



- Proposed system for purifying waste water from fracking, with production of useful chemicals as value added.
- Net current through device (power applied); cation and anion selective membranes.

General Dialysis System

Warm-up model: Brackish water desalination



- $c(x, y)$ concentration of both Na_+ and Cl_-
- $\phi(x, y)$ voltage
- After scaling with large aspect ratio, diffusive and voltage gradients in y can be neglected, convective terms remain.
- Turbulence "modelled" in a simple, mock worthy way.

General Dialysis System

Brackish water desalination equations (scaled)

- Ion conservation:

$$\begin{aligned} -(c\phi_x)_x - c_{xx} + sc_y &= 0 \\ \delta(c\phi_x)_x - \delta c_{xx} + sc_y &= 0 \end{aligned}$$

where δ is the ratio of ionic diffusivities, s is a combination of parameters including input flow rate.

- Inflow conditions $c(x, 0) = 1$
- Boundary conditions at $x = 0$

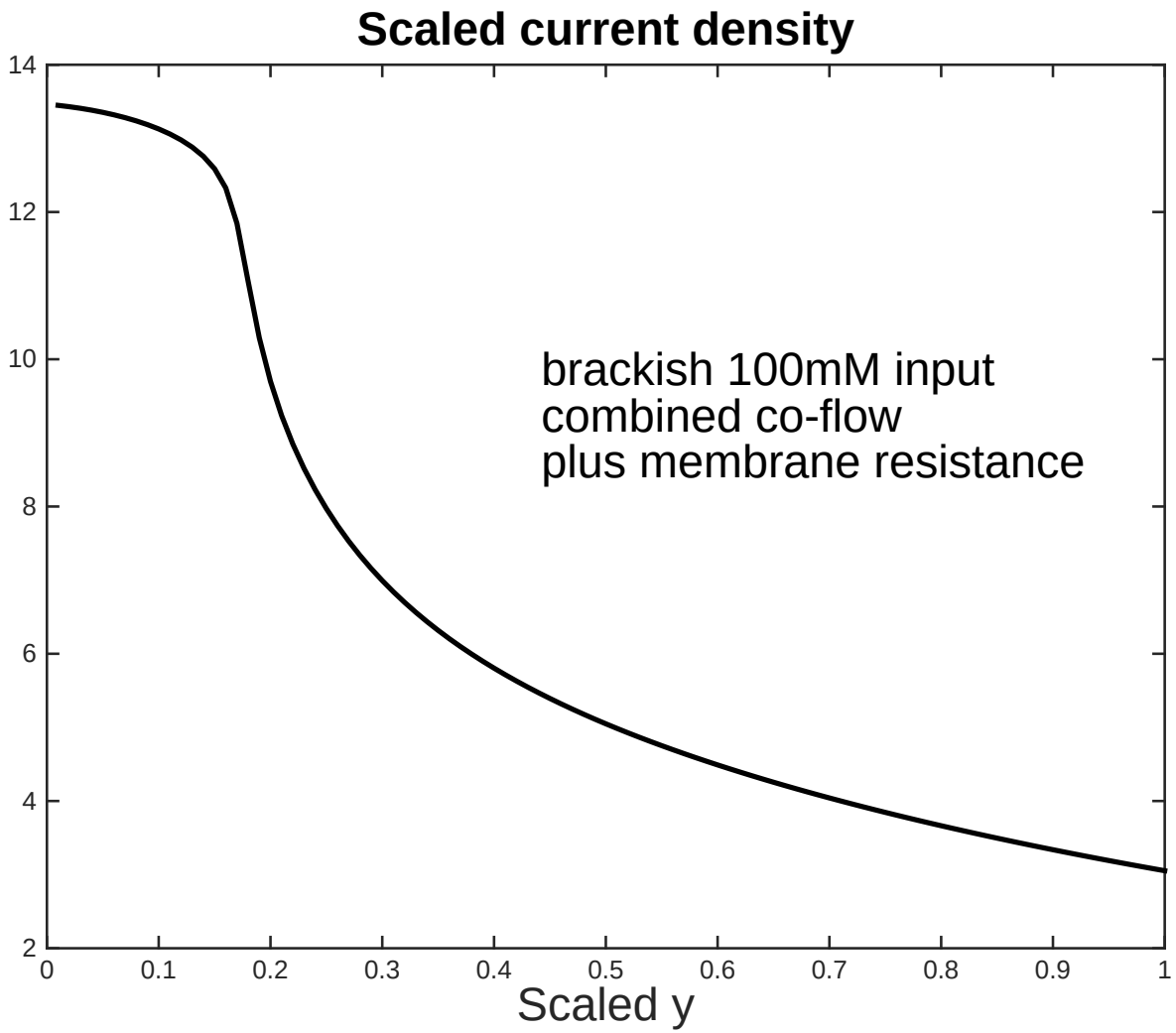
$$\begin{aligned} c\phi_x + c_x &= 0 \quad \text{(no cation current)} \\ \phi &= \beta - R(c\phi_x - c_x) \quad \text{(applied voltage)} \end{aligned}$$

At $x = 1$ we have no anion current and the cation current and voltage match those in the depletion region.

A mixed nonlinear system, solved using implicit steps in y

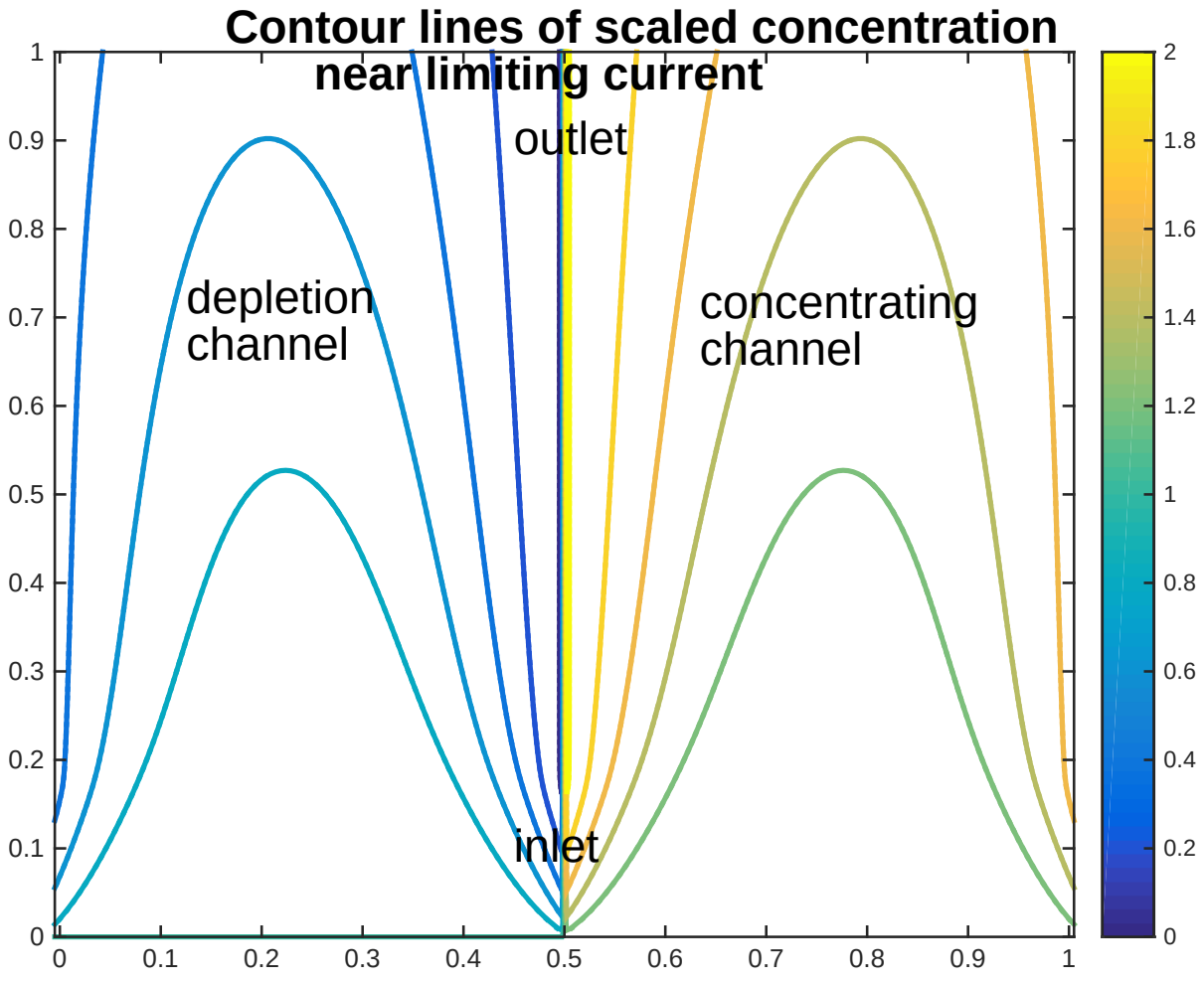
General Dialysis System

Brackish water desalination results-I



General Dialysis System

Brackish water desalination results-II



General Dialysis System

Ongoing work

- Carbonic acid channel severely limits the current in experiments: model validates this.
- Joint publication will appear shortly.