Mathematical Modelling of Fuel Cells
Mini-course, part II.

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More description:

There are other types of fuel cell: direct methanol, solid oxide (high temperature), molten carbonate (large scale), ...

There are external systems:

- Fuel production & storage
- Reformers
- Humidifiers
- Oxygen enrichment
- compressors
- power conditioning
- system control.

In the model we developed last time, there are a number of things missing:

+ Transients.
+ Concentration dependence of reference potential (Nernst term).
+ Condensation / evaporation. Our model implicitly assumed saturated conditions in the cathode, ignoring liquid water transport. "Water management" is a key issue in PEMFC operation:
    - too little water leads to membrane dehydration and increased membrane resistance
    - too much water leads to flooding in the MEA and/or channels.

At a minimum, to address water management you must include:

numerically, onset of liquid water corresponds to a lack of smoothness in the model

- temperature (saturation pressure depends strongly on T).
- membrane hydration and anode channel (water transport through the membrane is significant).

+ Stack level effects (today).
+ Additional reactions (carbon corrosion, Pt migration, ...)

In addition, we have avoided materials science models of the MEA structure. Models predicting performance from fabrication process for catalyst layers would be extremely useful.

Our model can give insight to <u>system</u> <u>performance</u> based on local, MEA <u>empirical</u> fit.

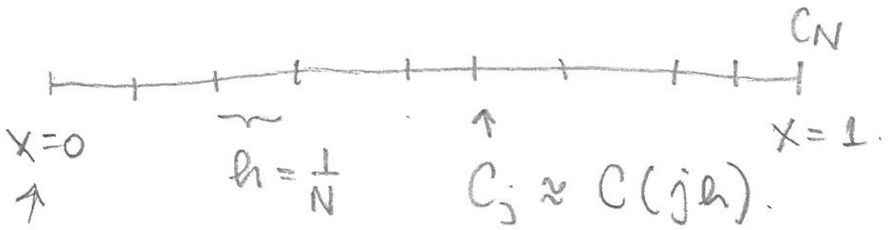
<u>Computational model</u> ★, from part I, p. 10.

Implementation will be posted online.

I reduced the model to the unknowns

V cell voltage, scalar

$\underline{C}$ vector of channel oxygen concentrations at subinterval ends.



C_0 known.

$C_0 = 0.21\ C_{tot}$

Consider $I_j := i((j-\frac{1}{2})h)$ $j=1, \cdots N$, the current density at cell centers.

$$\underbrace{U(I_j, \tfrac{1}{2}(C_j + C_{j-1}))}_{\text{Eqn (4) part I notes, } U(i,c)} = \mathcal{U} \qquad (1)$$

implicitly defines I_j in terms of $\mathcal{U}$ & $\underline{C}$.

Also, $\frac{\partial I_j}{\partial \mathcal{U}}$ and $\frac{\partial I_j}{\partial C_j}$, $\frac{\partial I_j}{\partial C_{j-1}}$ can be determined.

The desired solution satisfies

$$h \sum_{j=1}^{N} I_j = i_{ave} \qquad (2).$$

(midpoint rule approximation of $\int_0^1 i(x)dx = i_{ave}$)

Now consider the elimination of $Q(x)$ from ⊛:

$$C(x) = C_{tot} \frac{Q}{Q+Q_N} \Rightarrow Q = Q_N\left(\frac{C_{tot}}{C_{tot}-C} - 1\right)$$

$$\frac{dQ}{dx} = -\frac{i}{4F} \Rightarrow \frac{Q_N C_{tot}}{(C_{tot}-C)^2}\frac{dC}{dx} = -i/4F \Rightarrow$$

$$\frac{dC}{dx} = -(C_{tot}-C)^2 \frac{i}{4FQ_N C_{tot}} \qquad (3)$$

We approximate (3) with

$$\frac{C_j - C_{j-1}}{h} = -\left(C_{tot} - \tfrac{1}{2}(C_j + C_{j-1})\right)^2 \frac{I_{j-1/2}}{4FQ_N C_{tot}} \qquad (4)$$

$j=1, \cdots N.$

Structure of our discrete problem:

N+1 unknowns, $\mathcal{U}$ and $\underline{C}$.

N+1 nonlinear equations (2) and (4)

1 equation   N equations

put the unknowns in a column vector

$$\underline{z} = \begin{bmatrix} U \\ c_1 \\ c_2 \\ \vdots \\ c_N \end{bmatrix}.$$

Our discrete problem is a system of nonlinear equations:

$$\underline{F}(\underline{z}) = \underline{0}.$$

Solve with Newton's method: " $\underline{\delta} = \mathbb{J}^{-1} \underline{F}$ "

$$\left.\begin{aligned} \underline{z}_{n+1} &= \underline{z}_n - \underline{\delta}_n \\ \text{where } \underline{\delta}_n \text{ solves } \quad \mathbb{J}(\underline{z}_n)\, \underline{\delta}_n &= \underline{F}(\underline{z}_n) \end{aligned}\right\} \quad (5).$$

and $\mathbb{J}$ is the $n \times n$ matrix with entries

$$\mathbb{J}_{ij} = \frac{\partial F_i}{\partial z_j} \quad \text{(Jacobian matrix)}.$$

This works if the initial guess $\underline{z}_0$ is close enough to the solution.

Exercise 5 $\mathbb{J}$ is a sparse matrix for our problem. Show the pattern of nonzero entries of $\mathbb{J}$ and show that Gaussian Elimination can be done to solve $\mathbb{J}\underline{\delta} = \underline{F}$ in $O(N)$ operations

Exercise 6* Continue Exercise 3. Consider $T = 350K$ fixed. For what combination of values of C_{tot}, i_{ave} and S does a solution to ⊛ in part I notes exist? Decide whether these solutions are unique - either prove they are or give an example of non-unique solutions. A resolved, computational example would be sufficient.

Exercise 7 The computational method is designed to be second order accurate (errors $O(h^2)$). Do a numerical convergence study to verify this property.

Exercise 8* Following Exercise 6. For cases where there is a unique solution, show that the corresponding discrete problem has a unique solution (for h sufficiently small) and that the discrete solutions converge to the continuous one.

Notes: In this problem, we could consider U given, do local marching for c and find U that matches the given i_{ave} using a simple bisection algorithm. This approach won't extend to the stack level model that we'll develop next.

Q: Should we have looked for a package to use to solve (*)? Slightly unusual structure to the problem... the question is about the time it takes to

find a code that can do your problem and figure out how to make it work

vs

write & debug your own code.

Some codes to be aware of:

MATLAB ode and bvp solvers.
DASSL for dae problems.
Comsol Multiphysics (commercial) - fem package
deal ii (freeware) - fem package

Q: What about initial estimates for U and $\underline{C}$ to start Newton iterations?

It may be very difficult to get initial guesses that will converge in all situations.

You may need to use a technique called Continuation, which I'll illustrate with an example below.

Consider modifying (3) using a parameter $\theta \in [0,1]$ as follows

$$\frac{dC}{dx} = -\theta\,(C_{tot} - C)^2 \frac{i}{4FQ_N C_{tot}} \qquad (6).$$

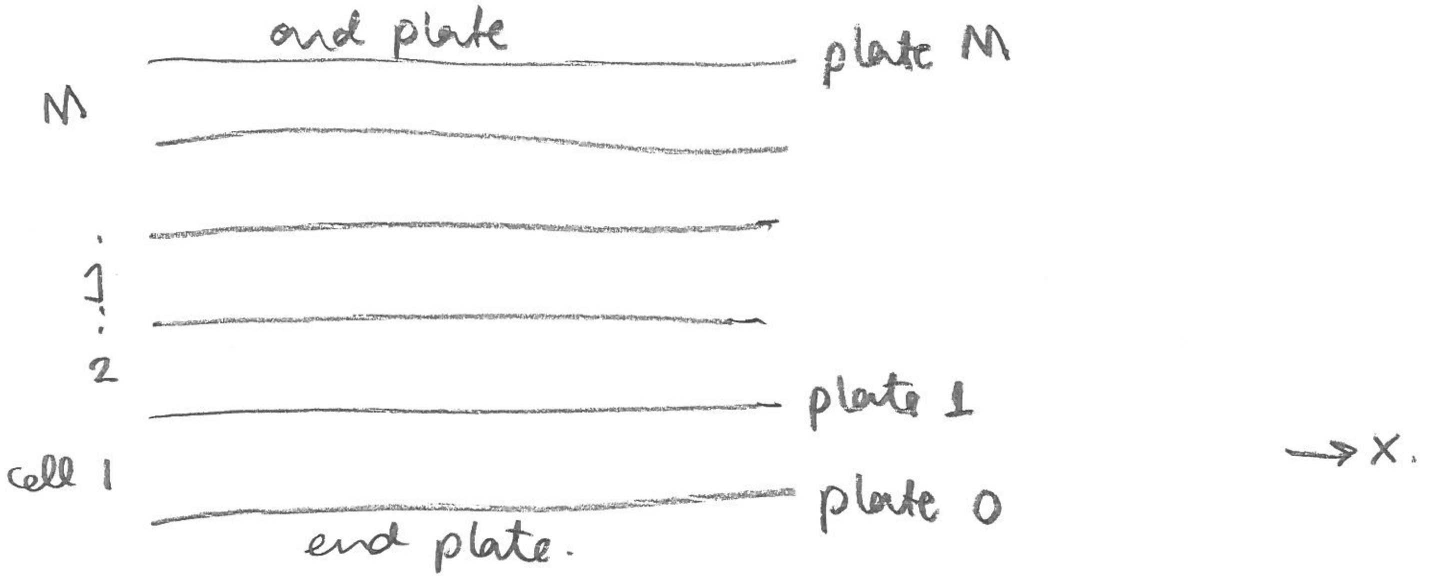
We want to solve our system with $\theta = 1$. but $\theta = 0$ is easy to solve because then

$C(x) = C(0)$ is constant

So $i(x) = i_{ave}$ is constant and the cell voltage $U = U(i_{ave}, C(0))$ can be determined explicitly. Consider using this $\theta = 0$ solution as an initial guess for the $\theta = 1$ problem. If this does not converge, search for a $\theta \in (0,1)$ for which the iterations do converge (guaranteed for θ sufficiently small) then repeat for θ increasing until you reach $\theta = 1$.

Exercise 4 (revised) Implement the computational framework (1), (2), (4) using continuation (6).

let's consider now a stack level model.



M cells, assume that each cell is at the same pressure (C_{tot}) and temperature T. However, we will allow the inlet flow rates $\{S_m\}$, $m = 1, \dots M$ to vary.

Notes: • If $S_m = S$ $\forall m$ do not vary, then $i_m(x) = i(x)$ will be common for each cell as will $U_m(x) = U$.

• If the resistance of the bipolar plates is negligible, then even if $\{S_m\}$ vary, $i_m(x)$ and U_m independent of x can be computed separately using our previous code.

• Consider the general case of $\{S_m\}$ not identical and plate currents with resistance.

Introduce plate currents $I_m(x)$ ← per unit width. and resistivity λ. Here $U_m(x)$ will be an unknown, no longer constant for the cell.

More modelling

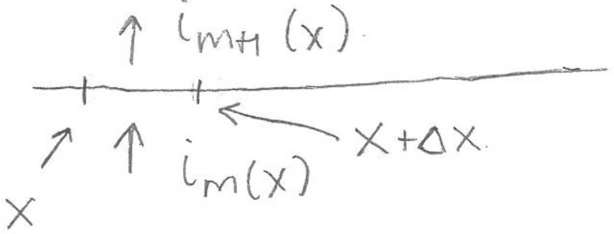


plate m.

Conservation of current

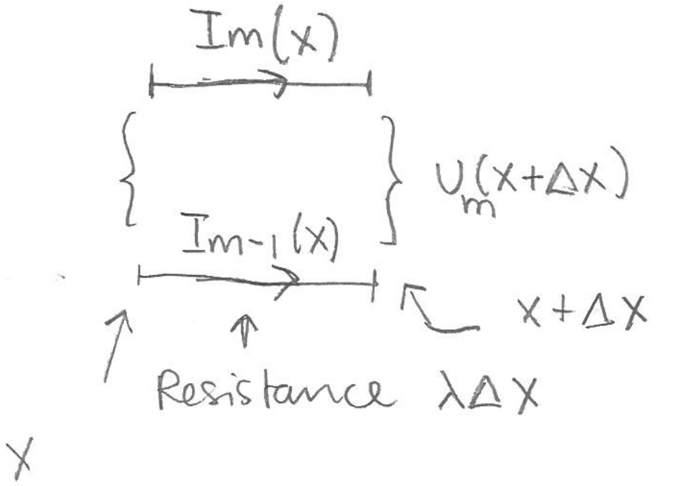
$$I_m(x+\Delta x) - I_m(x) = \int_x^{x+\Delta x} \left(i_m(x) - i_{m+1}(x)\right)dx$$

Taking the limit as $\Delta x \to 0$ gives

$$\frac{dI_m}{dx} = i_m(x) - i_{m+1}(x), \quad m=1,\ldots M-1. \qquad (7).$$

Note that $I_m(0) = I_m(1) = 0$, no currents at the end of the plates.

Now consider the voltage changes due to these plate currents, away from the end plates.



$$U_m(x+\Delta x) - U_m(x) \approx -\lambda \Delta x \left(I_m(x) - I_{m-1}(x)\right).$$

Taking the limit as $\Delta x \to 0$ gives.

$$\frac{dU_m}{dx} = -\lambda\left(I_m(x) - I_{m-1}(x)\right) \qquad m=2,\ldots M-1. \qquad (8).$$

Take $\frac{d}{dx}$ of (8) and use (7) to eliminate the plate currents, leading to

$$\frac{d^2U_m}{dx^2} - \lambda\left(i_{m+1} - 2i_m + i_{m-1}\right) = 0 \qquad (9).$$
$$m = 2, M-1.$$

Assuming the end plates have zero resistance, the voltages in the end cells are governed by

$$\left.\begin{aligned} &\frac{d^2U_1}{dx^2} - \lambda\left(i_2 - i_1\right) = 0. \\ &\frac{d^2U_M}{dx^2} - \lambda\left(i_{M-1} - i_M\right) = 0. \end{aligned}\right\} \qquad (9b)$$

$I_m(0) = I_m(1) = 0$ translates into boundary conditions for U_m:

$$\frac{dU_m}{dx}(0) = \frac{dU_m}{dx}(1) = 0. \qquad (9c).$$

In each cell, we also have (3):

$$\frac{dC_m}{dx} = -\left(C_{tot} - C\right)^2 \frac{i_m}{4F\underbrace{Q_{N,m}}_{Q_N \text{ depends on } S_m} C_{tot}} \qquad (10).$$

$$C_m(0) = 0.21\, C_{tot}.$$

Finally, the current through the stack is arbitrary in the model so far. We must add the condition

$$\int_0^1 i_1(x)\,dx = i_{ave} \qquad (11).$$

(9) - (11) with local $i(U,C)$ relationship define the stack level model.

Exercise 9 The average current is explicitly matched in cell #1 by (11). Show that the model implies that

$$\int_0^1 i_m(x) = i_{ave} \quad \text{for all } m = 1, \dots M.$$

Exercise 10 Show that the stack voltage is independent of x, ie. that

$$V = \sum_{m=1}^{M} U_m(x)$$

does not depend on x.

Exercise 11* Consider an "infinite" stack $m = -\infty, .. \infty$

Suppose $S_m = S$ for $m \neq 0$ and $S_0 = S - \varepsilon$. linearize around the stoich S solution and describe the effect of the anomalous cell $m=0$.

Exercise 12 * Approximate the stack model numerically, using continuation (6) in (10) as before. Investigate the question in Exercise 11 using $M = 13$ and varying the stoich S_7 of the centre cell.

Note: $\lambda = 0.01\ \Omega\text{-cm}^2$ is a reasonable value to start with.

Exercise 13 * How does the stack behave as $\lambda \to \infty$?

Exercise 14 Show that zero resistance in the end plates leads to (9b).