

Mathematical Modeling of Fuel Cells

Mini-course.

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Goals: 1. Basic description of how fuel cells work.

Using
Fuel cells
as an example

- 2. Review modelling process
- 3. Numerical methods for nonlinear scalar and vector algebraic equations.
- 4. Finite difference methods for boundary value problems.

My experience:

- with an industrial collaboration with Ballard Power Systems, a fuel cell design company in Vancouver. Group project involving faculty, POFs, students and company scientists.
- Main contribution was computational modelling of fuel cell stacks based on experimentally-fit component models.
- Review article, "PEM Fuel cells: A Mathematical Overview" in SIAP v.70 (2009). I can send a pdf copy to you on request.

The big picture:

New Energy Economy:

- renewable sources (wind, solar, geo-thermal)
- reduce emissions (carbon light)

Energy from all sources can be stored in the form of Hydrogen gas.

Hydrogen can be converted to electrical power efficiently in fuel cells with no emissions.

Fuel cells are suitable for automotive, stationary and small scale portable power.

politically &
economically
motivated
↓

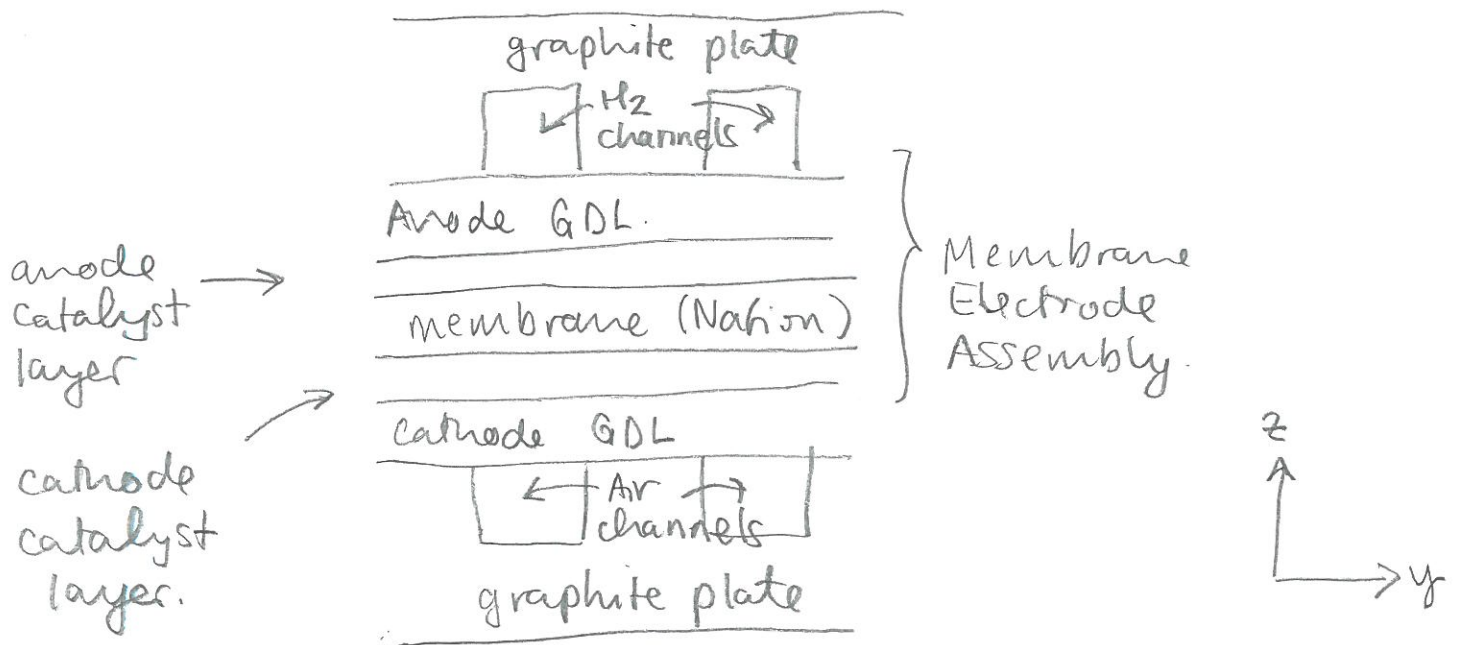
↑
environmentally
motivated.

Many energy systems have common needs for ^{1/2} nano-scale materials that allow multi-component (multi-phase) transport in components that are built into larger scale devices.

[possible last lecture on abstract materials science models].

Introduction to PEM Fuel Cells

Polymer Electrolyte Membrane



- Channel flow is into the page (x).
- Channels repeated in the spanwise direction y . channels can be straight or serpentine.
- Large aspect ratio ($\sim 2\text{mm}$ in z , $\sim 1\text{m}$ in x). We'll take advantage of that in the modelling.
- This is a unit cell. These are stacked in electrical series into a fuel cell stack. The cathode plate of one cell is against the anode plate of the next - the combination is a bipolar plate.
- Current moves in the z direction through the cell. As electronic current in plates and the GDL (gas diffusion layer). As protonic current in the membrane. Copper end plates collect the current into cables to the external circuit.
- Not shown are coolant channels

- Typical numbers for a unit cell (Ballard Mk 9) 3
 area 300 cm^2 , 1 A/cm^2 current, 0.7 V
 Can be stacked with ~ 100 unit cells.

H_2 diffuses in the y-z plane (cross-plane) to the anode catalyst layer.

H_2 oxidation ($\text{H}_2 \rightarrow 2\text{p}^+ + 2\text{e}^-$) occurs at low electrical potential.

Protonic current through the membrane, which has high protonic conductivity if it is wet (hydrated). The membrane has low electronic conductivity.

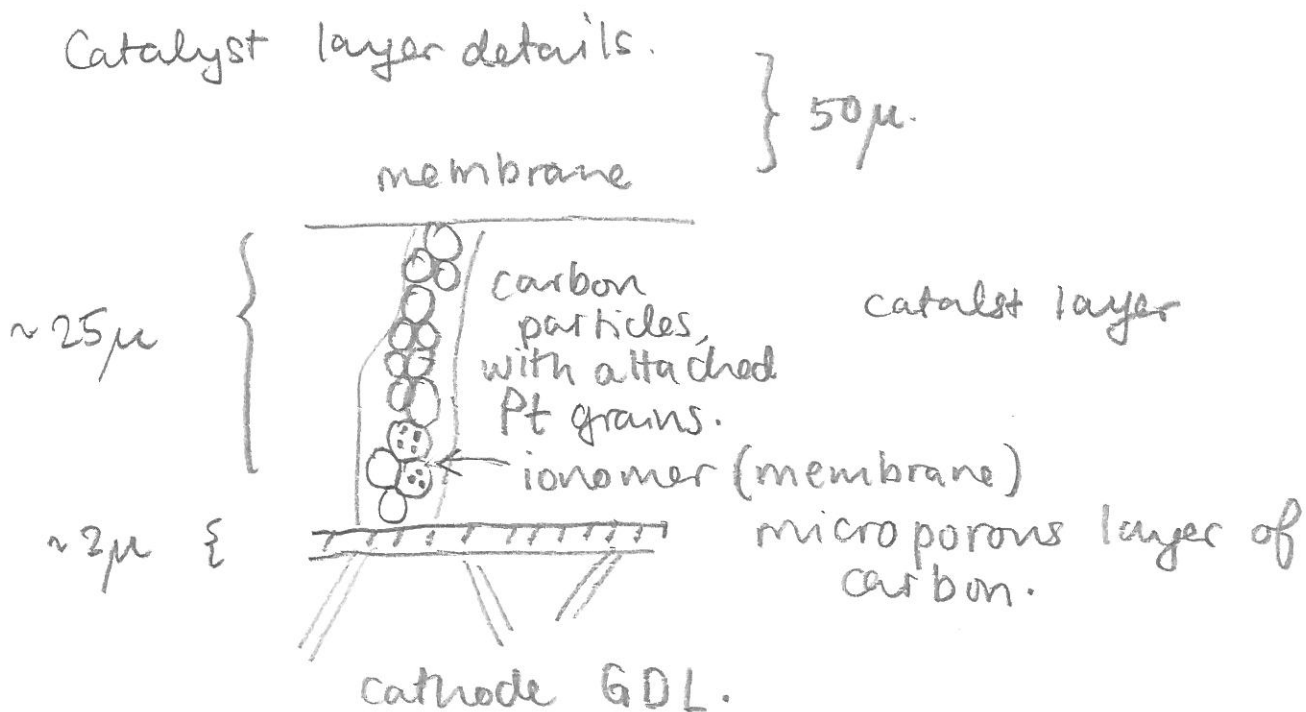
Protons combine with O_2 on the cathode side.

Oxygen reduction ($\text{O}_2 + 4\text{p}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$) occurs at high electrochemical potential.

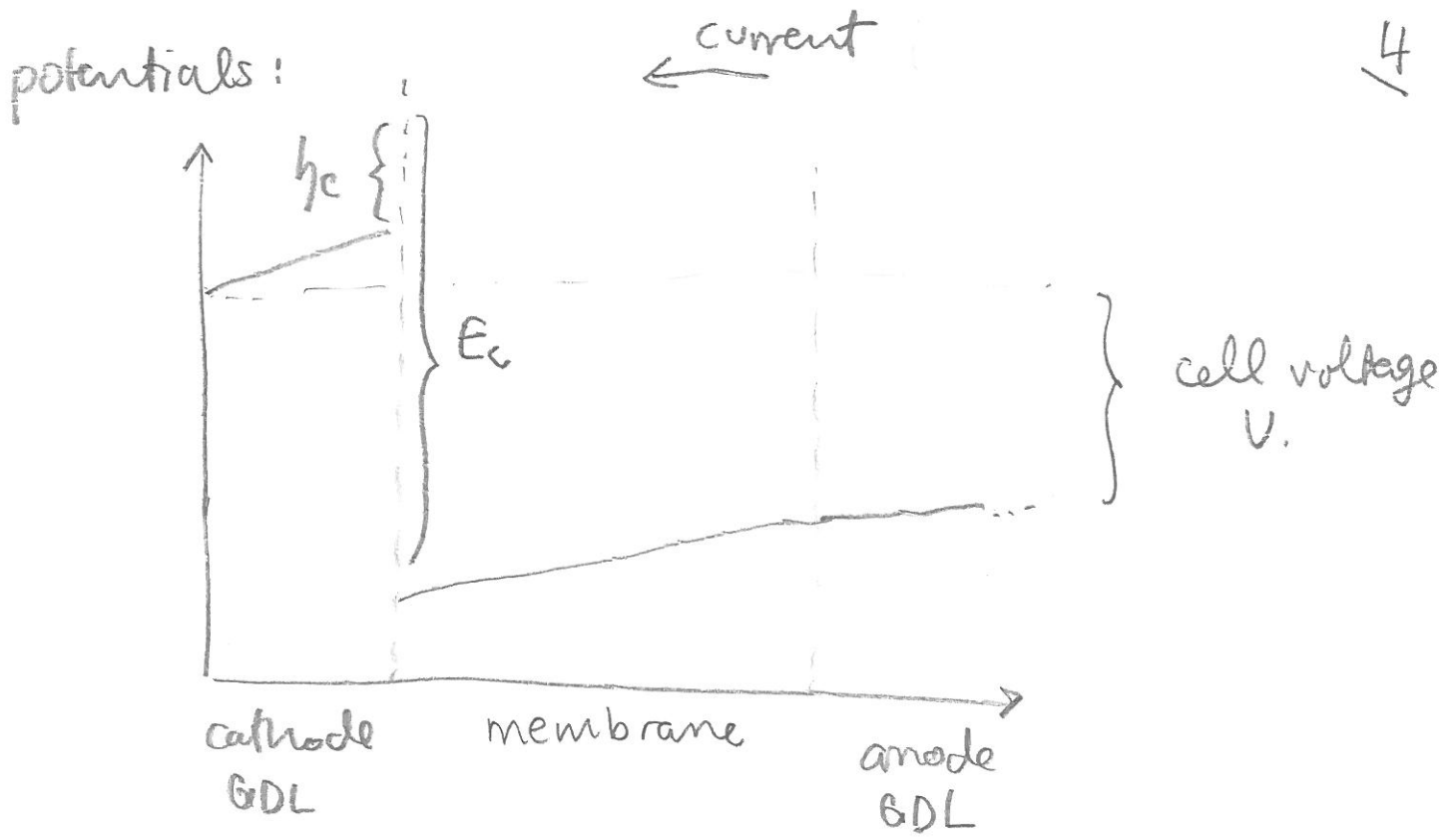
Other, unwanted reactions can also occur that degrade the device and limit its lifetime.

GDL details: teflonated carbon fibre paper, can be thought of as a porous media with low permeability.

Catalyst layer details.



Complicated multi-phase transport.



h_c overpotential losses due to drawing current.
 E_c Electrochemical potential.

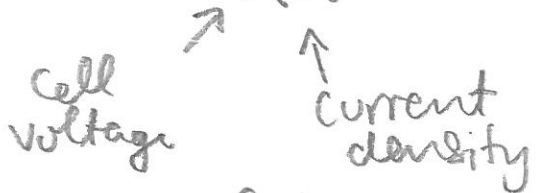
Note: $E_a = 0$ by definition, $h_a \approx 0$ can be neglected

Summary: complicated physics in MEA. outside the MEA it is straightforward mass, heat and current transport.

Exception: two phase flow in channels.

Empirical Fit of MEA response to experiments:

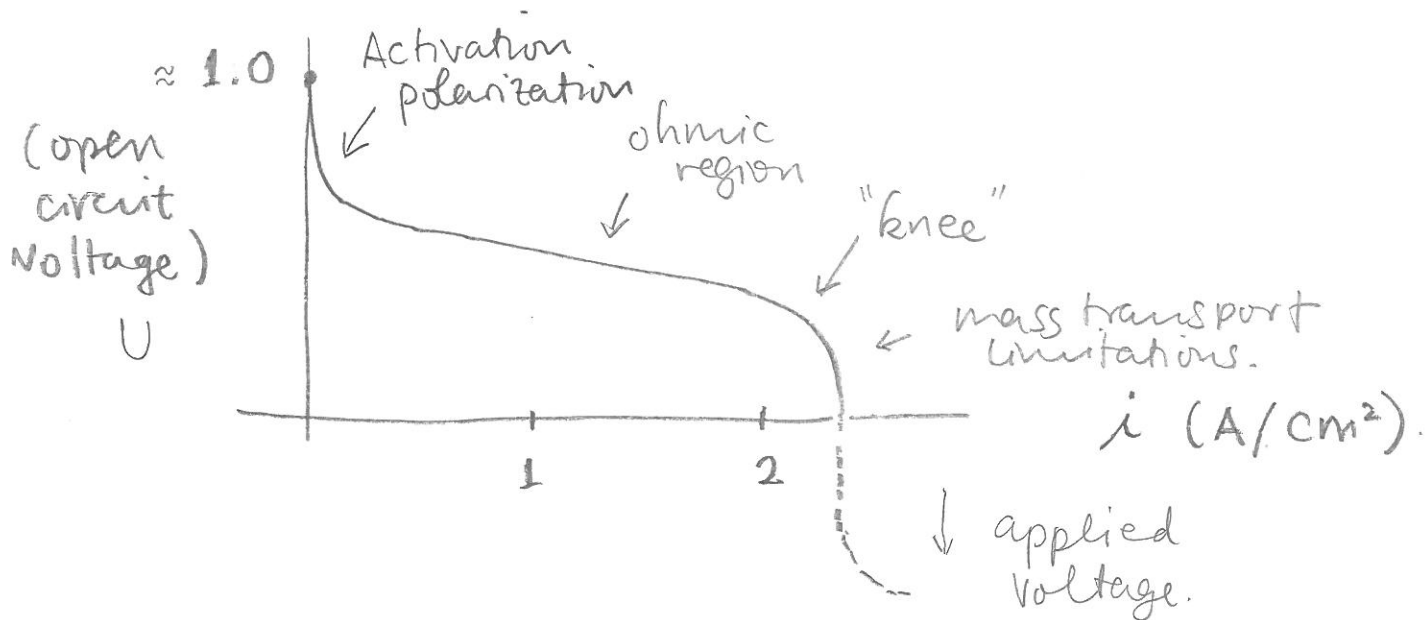
Imagine you could get the following experimental data $U(i)$



For a small piece of MEA, over which channel conditions (humidity, temperature, pressure, oxygen concentration) did not vary.

(local) polarization curve.

5.



Semi-empirical fit to this curve

Note: specific resistivity in $\Omega\text{-m}$

Theory:

$$U = E_c - h(i) - R_m i$$

← membrane resistivity.

$$R_m \approx 0.1 \Omega\text{-cm}^2 \quad (1)$$

for Nafion 112 well hydrated.

↑ varies with oxygen concentration, temperature

Neglecting ohmic losses in the GDL & plates & external circuit.

Already a mismatch between the theory and the experiment, since $U(i=0) = E_c$ which has a theoretical value of ≈ 1.28 at standard conditions.

Butler-Volmer equation

$$i = i_0 \left\{ \frac{C_o}{C_{o,ref}} \exp \left[\frac{\alpha F}{RT} h \right] - \exp \left[-\frac{\alpha R F}{RT} h \right] \right\} \quad (2)$$

i_0 : exchange current density. Literature values for smooth Pt surfaces.

C_o : oxygen concentration.

R : ideal gas constant

α : transfer factor

8.314 J/(mol K)

F : Faraday's constant 96,485 C/mol

T : Temperature in K, 350 K. ($\approx 80^\circ\text{C}$)

i_0 is small, so for any reasonable currents i , η is large and the second (reverse reaction) term can be neglected. 6

$$i \approx i_0 \frac{C_0}{C_{ref}} \exp \left[\frac{\alpha F}{RT} \eta \right].$$

$$\eta = \frac{RT}{\alpha F} \left\{ \ln \frac{i}{i_0} - \ln \frac{C_0}{C_{ref}} \right\} \quad \text{Tafel Approximation (3)}$$

$$\ln i - \ln i_0$$

Note that if you consider i_0 as a parameter to fit, looking at (1), there is a constant term $E_c - \ln i_0$.

↔ arbitrary allocation of constant term between E_c and i_0 .

Let's keep $E_c = 1.28$ (literature value) and fit i_0 .

So far, we can't explain the "knee" in the experimental curve with C_0 kept constant.

Oxygen diffuses from channel concentration C_{chan} to catalyst sites through the GDL, so it has a lower concentration at catalyst sites.

$$\text{Oxygen flux} \quad \frac{i}{4F} = \frac{D}{L} (C_0 - C_{chan}).$$

$$C_0 = C_{chan} - \frac{L}{4DF} i$$

fit parameter δ using limiting current

$$i_{lim} = \frac{C_{chan}}{\delta}$$

Note: δ is larger than that which you would get from GDL length and oxygen diffusivity in air.

channel concentration \bar{c}

Now fit

$$U(i) = E_c - \frac{RT}{2F} \left\{ \ln \frac{i}{i_0} - \ln \frac{c - \delta i}{c_{ref}} \right\} - R_m i \quad (4)$$

to experimental data, U in volts, i in A/cm^2 .

$$E_c = 1.28 \text{ V.}$$

$$c_{ref} = 40.9 \text{ mol/m}^3$$

$$\text{Fit: } \alpha = 1, i_0 = 10^{-7} \text{ A/cm}^2, \delta = 8 \frac{\text{moles/m}^3}{\text{A/cm}^2}$$

$$R_m = 0.1 \Omega\text{-cm}^2$$

Note: (4) is not defined for $i \leq 0$ or $i \geq \frac{c}{\delta}$. Thus i is a poor choice as a computational variable. We actually want $i(U)$ but can't invert (4) analytically. We will use Newton's method.

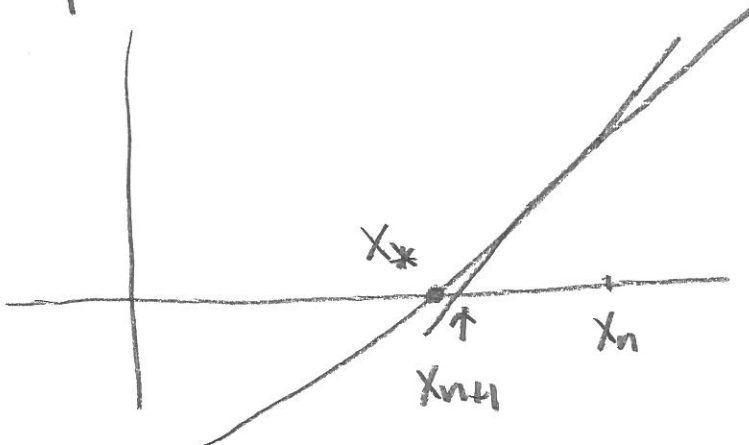
Review: Newton's method.

Iterative method for finding roots of nonlinear problems $f(x) = 0$.

Sequence $\{x_n\}$ of approximations

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$

Nice picture:



x_{n+1} is the root of the tangent line approximation to $f(x)$ at x_n .

Theory: $x_n \rightarrow x^*$ if $f'(x^*) \neq 0$ and x_0 is "sufficiently close" to x^* .

8.

$$x_{n+1} - x^* \approx C f''(x^*) (x_n - x^*)^2$$

quadratic (fast) convergence.

Practice: May need a good estimate for x^* .

For inverse function problems

$$f(x) = y \quad \text{given } y.$$

Consider $g(x) = f(x) - y$ use Newton's method to find $x = f^{-1}(y)$.

Note that $[f^{-1}]'(y) = \frac{1}{f'(x)}$ can be approximated using the converged value of x .

Exercise 1 with $C = 20 \text{ moles/m}^3$ plot $U(i)$ & $U'(i)$ from (4) with $i \in [0.01, 2.49] \text{ A/cm}^2$

\uparrow
 $i_{em} = 2.5$ in this case.

Write a code to compute $i(U)$ and $i'(U)$ using Newton's method for $U \in [0, 1.3]$. Make sure it agrees with your first plot. You may need to be careful with initial values for the iterations, especially for U near zero and above 1.

Unit cell model

Consider a unit cell operating with total current I , Area $A = LW$, straight channels.

We'll average performance in the cross plane $y-z$, (done in fitting) consider variations in $x \in [0, L]$ only.

Consider the oxygen flow (mol/s) needed to generate the current I :

$$\frac{I}{4F}$$

The actual oxygen flow input is.

$$Q_o(0) = \frac{s I}{4F} \quad Q_o(x) \text{ decreasing.} \quad (5)$$

$s > 1$ stoichiometric flow rate - operating condition (s given). Also have an unreactive Nitrogen flux

$$Q_N = \frac{0.79}{0.21} Q_o(0) = \frac{0.79}{0.21} \frac{s I}{4F} \quad \text{independent of } x. \quad (6)$$

Consider $i(x)$ and U constant.

$$w \int_0^L i(x) dx = I \quad (7)$$

to match the specified total current.

Two more things to close the model:

$$\text{Oxygen consumption: } \frac{dQ_o}{dx} = - \frac{w i}{4F} \quad (8)$$

Oxygen concentration:

Consider the channel gasses to be ideal at constant pressure P and temperature T . Therefore, the channel gas molar concentration is

$$C_{tot} = \frac{P}{RT} = \underset{\substack{\uparrow \\ \text{Oxygen} \\ \text{concentration}}}{C} + \underset{\substack{\uparrow \\ \text{Nitrogen concentration}}}{C_N} \quad (9)$$

The gas moves with total flow Q , so

$$Q_o = C / C_{tot} Q \quad Q_N = C_N / C_{tot} Q$$

Eliminating Q using (9) gives.

10.

$$C = \frac{P}{RT} \frac{Q_0}{Q_0 + N}. \quad (10).$$

C_{tot} , alternative operating parameter to P .

Do a partial scaling $x = \hat{x}L$, $\hat{Q}_0 = Q_0/A$,
 $\hat{Q}_N = Q_N/A$, introduce $i_{ave} = I/A$, write
 equations without the $\hat{}$'s:
← or C_{tot} .

Given: i_{ave} , s , P , T and electrochemical parameters
 for $U(i)$ in equation (4).

Determine: constant ψ , $i(x)$, and $C(x)$ for
 $x \in [0, 1]$ such that

$$U(i(x), C(x)) = \psi \quad \text{for all } x.$$

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

$$\frac{dQ}{dx} = -\frac{i}{4F}.$$

$$Q(0) = \frac{S i_{ave}}{4F}.$$

$$C(x) = C_{tot} \frac{Q}{Q + Q_N}$$

$$Q_N = \frac{0.79}{0.121} Q(0).$$

(★)

Exercise 2 Perform a full nondimensionalization
 of (★) including Eq (4). What dimensionless
 parameters are introduced?

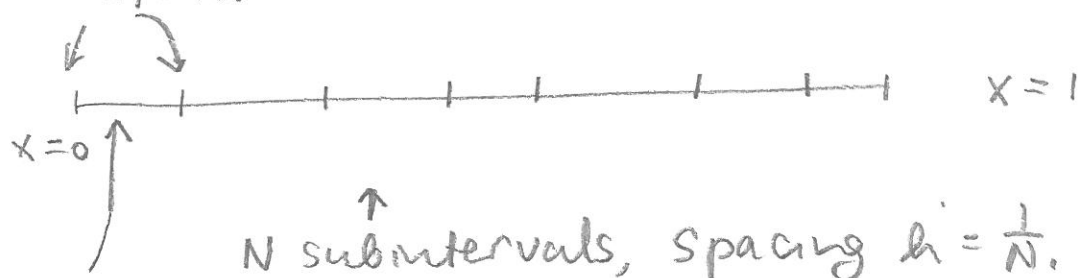
Exercise 3 With $C_{tot} = 100 \text{ mol/m}^3$, $T = 350 \text{ K}$,
 and $s = 2$, what is the maximum value of
 i_{ave} for which there is a solution to (★)?

Exercise 4 Develop a computational approximation to \star . Take $C_{tot} = 100 \text{ mol/m}^3$, $T = 350 \text{ K}$ and $i_{ave} = 1 \text{ A/cm}^2$. Plot $i(x)$ for the cases $S = 2, 1.5, 1.2$ (or 1.3 if the solution for 1.2 does not exist). How do the values of V change for these different S ?

There are many possibilities here to approach this computationally. I am going to try to implement the following:

V scalar unknown.

Q, C values are unknowns at subinterval ends



i values

unknowns

at subinterval centers.

or better $i(x) = i^c(V, C(x))$ using Exercise 1.

$V(i(x), C(x)) = V$ approximated at cell centers, using average C values.

$Q(0)$ initial value, $\frac{dQ}{dx} = -\frac{i}{4F}$ approximated using short differences at cell centers.

$\int_0^1 i(x) dx = i_{ave}$ approximated with midpoint rule.

$C(x) = C_{tot} \frac{Q}{Q + Q_{in}}$ at subinterval ends.

This gives a vector nonlinear problem $F(\underline{V}, \underline{C}, \underline{Q}, \underline{i}) = \underline{0}$ which I'll solve with vector Newton's method, using continuation.