Simulating Transport Processes in PEM Fuel Cells

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Joint work with:

- **Keith Promislow** (Michigan State University)
- **Akeel Shah** (Simon Fraser University)
- **Brian Wetton** (University of British Columbia)

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Background: Fuel cells

What is a PEM fuel cell?

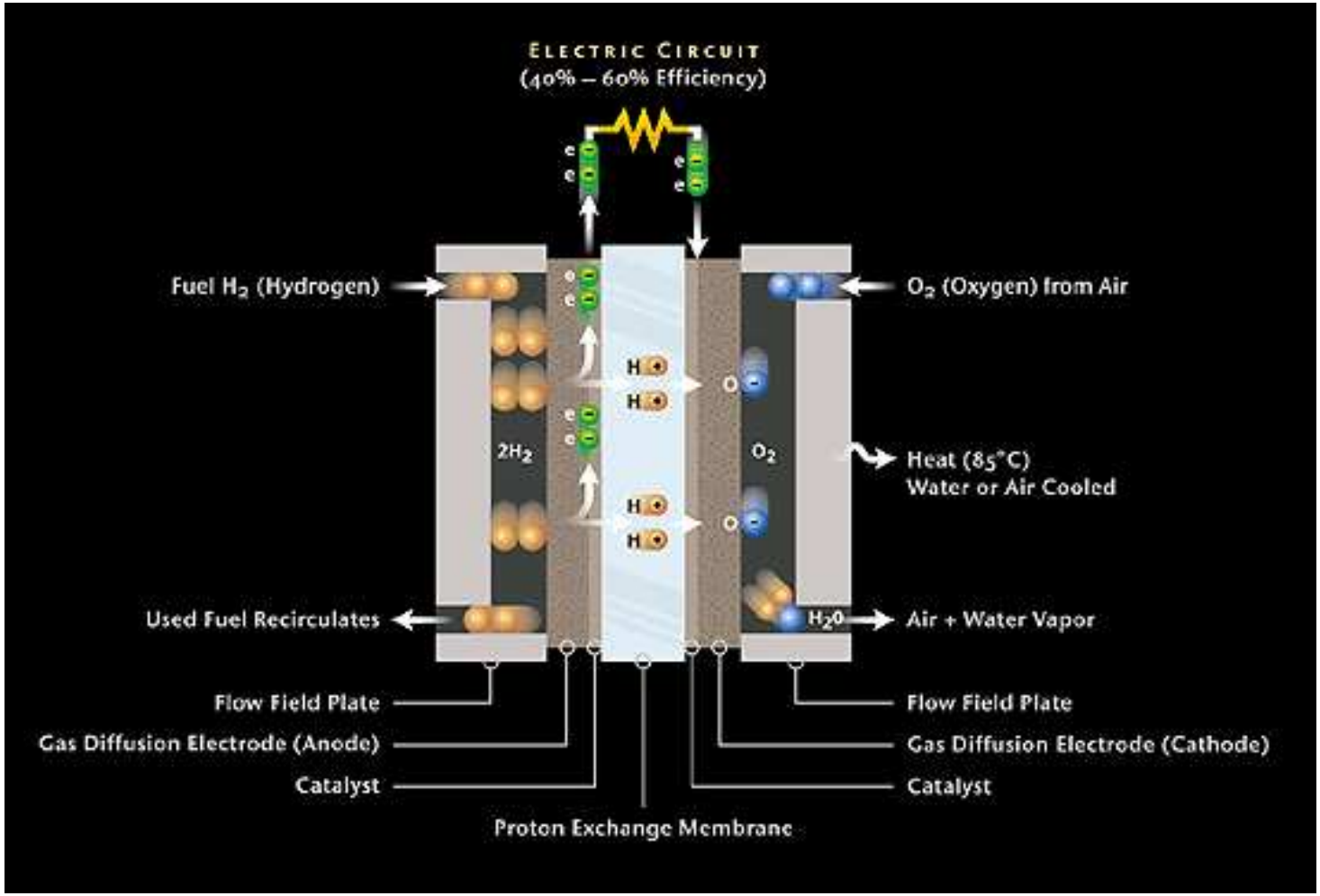
- Converts chemical energy of fuel (hydrogen and oxygen) directly into electricity
- Governing reaction is “reverse electrolysis”:

$$\text{Anode } (-): \qquad 2H_2 \xrightarrow{Pt} 4H^+ + 4e^-$$

$$\text{Cathode } (+): \qquad O_2 + 4H^+ + 4e^- \xrightarrow{Pt} 2H_2O$$

- The **proton exchange membrane (PEM)** lies at the “heart” of the fuell cell:
  - consists of a thin (50–200 μm) polymer sheet – Nafion®
  - permits only protons and water to pass through
  - prevents reactants combining (potentially explosively) in gaseous form
- No pollution, produces only water as a by-product
- Efficiency $\approx 50\%$: much higher than other energy sources

What is a PEM fuel cell? (2)



Source: Ballard Power Systems

A “multi-physics” problem

Fuel cells are incredibly complicated devices, involving:

- transport of mass, momentum and heat
- multiphase (gas / liquid) flow in porous media
- phase change (condensation / evaporation)
- conductive charge transport (electrons)
- membranes transport (protons and water)
- catalyzed reaction chemistry
- interfacial phenomena
- “nonstandard” materials (graphite, polymer membranes, Platinum, Teflon, etc.) with **composite, anisotropic, multiscale** structure

Fuel cell modelling

This talk is a survey of modelling and computational issues arising in two components of the PEM fuel cell:

1. transport and reaction in **catalyst** layers
2. multiphase transport in porous **electrodes**

Previous work

The vast majority of previous work on simulating fuel cells:

- uses “standard” fluid solvers (often commercial CFD codes)
  – **Sivertsen & Djilali (2004)**, **Hu et al. (2004)**, **Femlab**
- 2D/3D geometry, restricted to very small regions of the cell
- makes major, and sometimes questionable, simplifying assumptions (isothermal, multiphase “mist”)
  – **Um & Wang (2004)**, **Van Zee et al. (2001)**
- no in-depth analysis of the underlying equations, few analytical solutions
- little attention paid to fast, robust numerical solvers, that are tailored specifically to fuel cells
- unsuitable for stack level simulations

Our approach

As mathematicians and numerical analysts in this field, we’re breaking new ground by focusing on:

- deriving simpler models which take advantage of scale separation and dimensional reduction
- using analytical solutions to justify simplifications and validate results
- developing fast and robust solvers for component parts, and then coupling them together in sensible ways

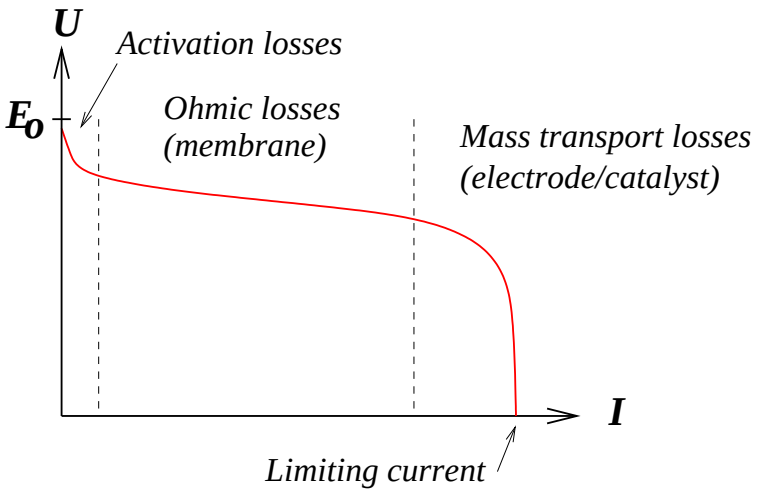
Our eventual aim is a comprehensive and efficient **stack-level** model

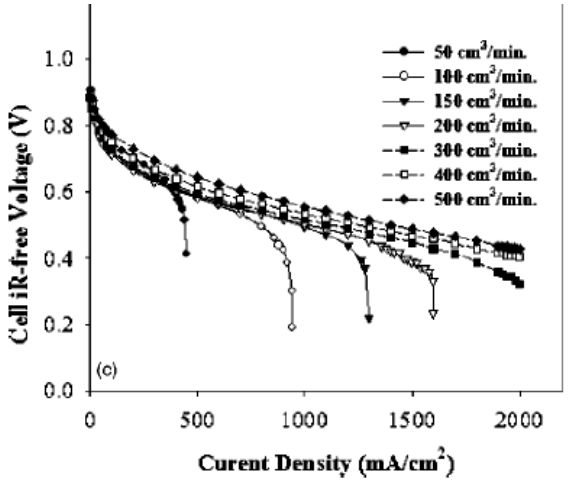
[See papers at `http://www.math.ubc.ca/~wetton/mmsc`]

Catalyst Layer Model

Limiting currents

- One indicator of PEMFC performance is the **polarization curve** – a plot of voltage (V) vs. current density (I)





Source: Williams et al. (2004)

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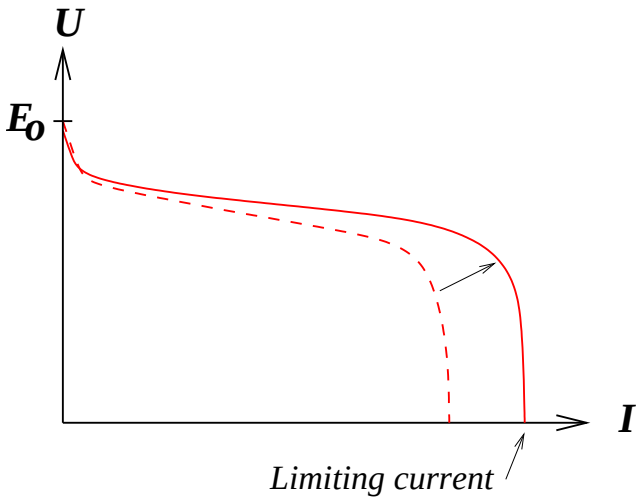
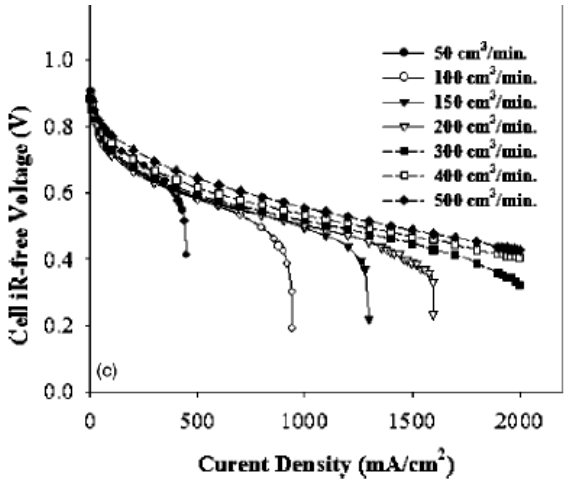




Source: Williams et al. (2004)

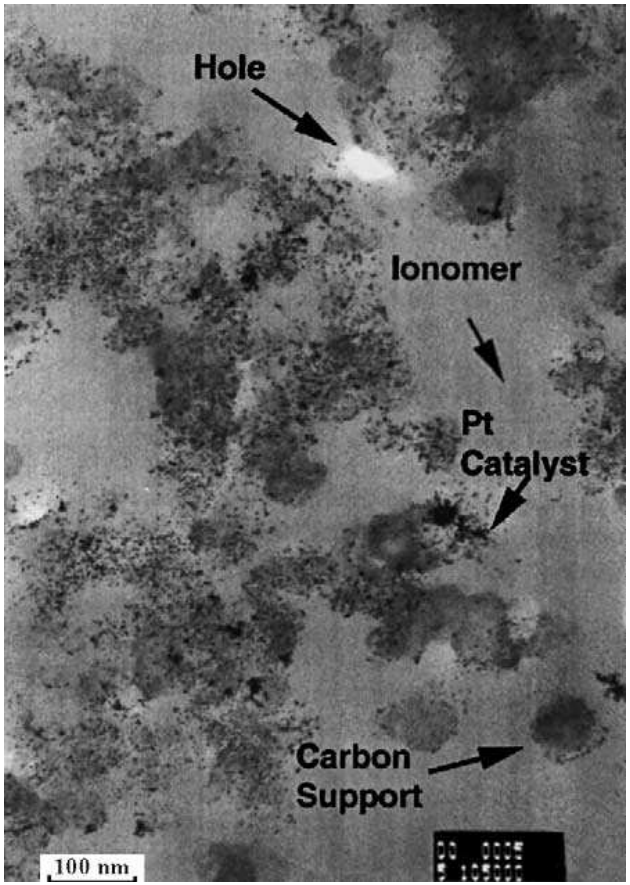
- Performance is improved by pushing the “knee” outwards
- **Limiting current** is attributed to a variety of sources in electrodes and catalyst – **Cutlip (1975)**, **Springer et al. (1993)**, **Kulikovsky (2004)**

Catalyst layer structure

Agglomerate structure:

Nafion (ionomer), Carbon, and Platinum

TEM (18,400 $\times$)



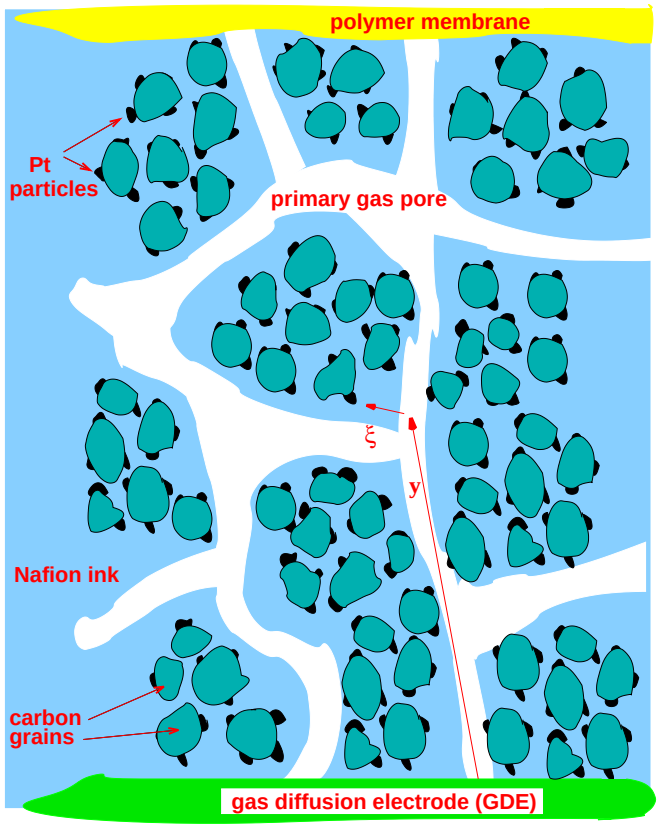
Source: von Spakovsky (2003)

Catalyst layer structure

Agglomerate structure:

Nafion (ionomer), Carbon, and Platinum

Idealized view



Catalyst layer structure

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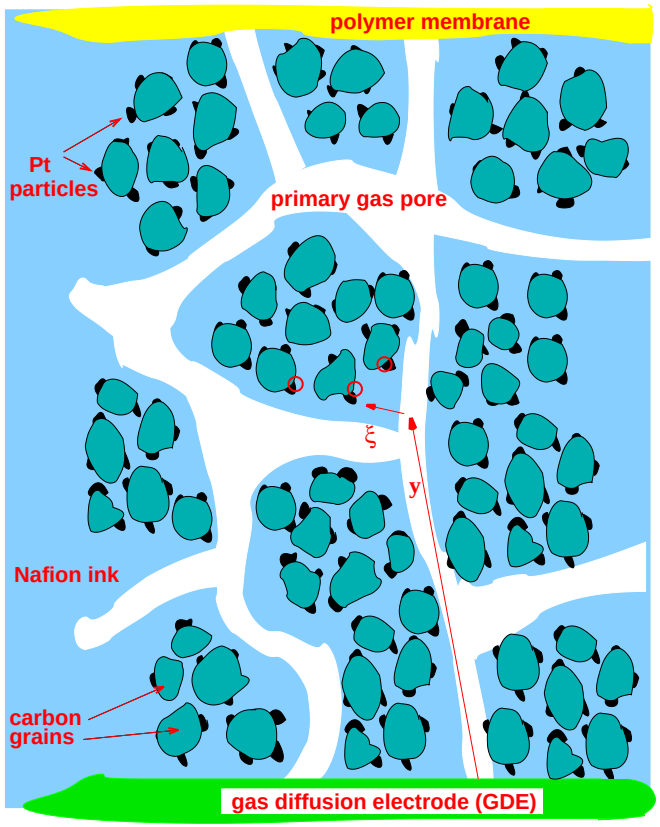
Reaction occurs only at locations where the three meet (a materials science challenge!)

Idealized view



Catalyst layer structure

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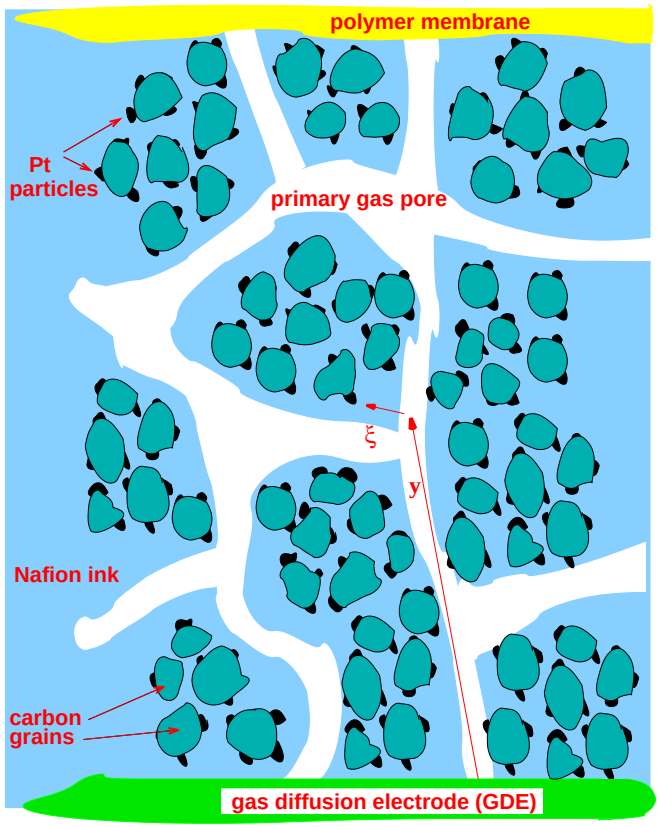
Possible limiting mechanisms in the cathode catalyst layer:

- ✔ diffusion in membrane phase
- ✔ diffusion in macro-pores
- ✘ diffusion in nano-pores (not shown)
- ✘ water flooding the catalyst

Idealized view



Model assumptions

Mechanism: O_2 diffuses through gas pores, dissolves in Nafion phase, and diffuses to active catalyst sites

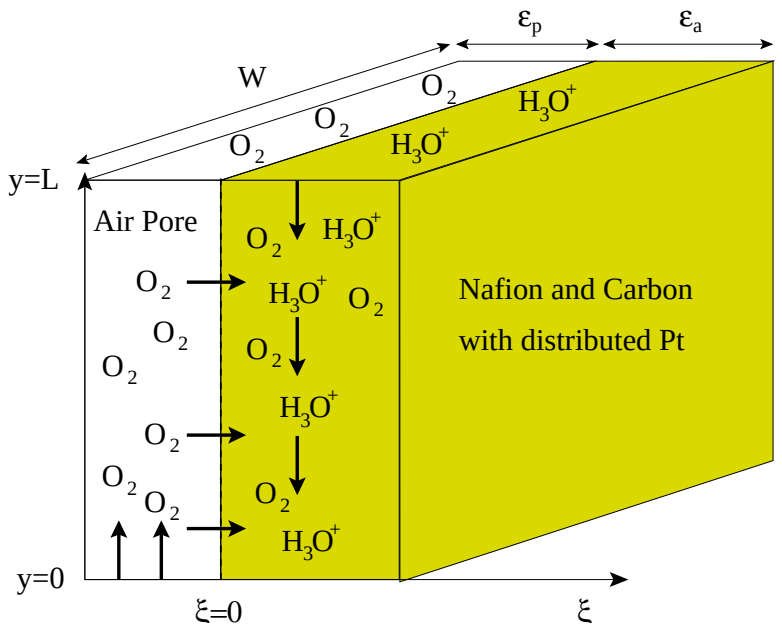
Primary assumption: The reaction is locally self-limiting due to O_2 adsorption kinetics

- No electron transport limitations or membrane potential losses
- No convective gas transport (Fickian diffusion only)
- Membrane phase water content is constant
- All Pt surface area is available to react
- Steady state

Geometry

A simplified, rectangular geometry:

- y is the distance along a pore ($y \sim 10^{-5}\ m$)
- ξ is "burial depth" of reaction sites ($\xi \sim 10^{-8}\ m$)
- **Scale separation** with $\xi \ll y$ $\Longrightarrow$ **a 1+1D model**



Governing equations

The primary unknowns are:

$C_{o,p}(y)$ pore O_2 concentration (mol/m^3)

$C_{o,a}(y,\xi)$ dissolved O_2 concentration in agglomerate (mol/m^3)

($\mathcal{H}$ = Henry's constant)

$\eta(y)$ cathode overpotential (V)

$\phi(y)$ membrane phase electric potential (V),

$$U - \phi(y) = E_o - \eta(y)$$

(potentials taken independent of ξ since $\xi \ll y$)

$i(y,\xi)$ local (volumetric) current density (A/m^3)

$I_{avg}(y)$ average current density (A/m^2),

$$I_{avg}(y) = \int_0^{\varepsilon_a} i(y,\xi)\, d\xi$$

Governing equations (2)

Three nonlinear DE's in $C_{o,p}(y)$, $C_{o,a}(y,\xi)$ and $\eta(y)$:

$$-\frac{\partial}{\partial \xi}\left(\mathcal{H} D_m \frac{\partial C_{o,a}}{\partial \xi}\right) = -\frac{i}{4F} \qquad (O_2 \text{ in agglomerate})$$

$$-\varepsilon_p \frac{d}{dy}\left(D \frac{dC_{o,p}}{dy}\right) = -\frac{I_{avg}}{4F} \qquad (O_2 \text{ in pore})$$

$$-\frac{\varepsilon_a a F}{RT}\frac{d}{dy}\left(D_+ C_+ \frac{d\phi}{dy}\right) = -\frac{I_{avg}}{F} \qquad \text{(electric potential)}$$

Governing equations (2)

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$$-\frac{\varepsilon_a aF}{RT}\frac{d}{dy}\left(D_+C_+\frac{d\phi}{dy}\right)=-\frac{I_{avg}}{F} \qquad (\text{electric potential})$$

Using relationships for $\phi(y)$ and $I_{avg}(y)$:

$$\phi(y)=\eta(y)+U-E_o$$

$$I_{avg}(y)=\int_0^{\varepsilon_a} i(y,\xi)\,d\xi=\cdots=-4F\mathcal{H}D_m\frac{\partial C_{o,a}(y,0)}{\partial\xi}$$

the last two equations reduce to

$$\frac{d^2C_{o,p}}{dy^2}=-\sigma_1\frac{\partial C_{o,a}(y,0)}{\partial\xi} \qquad \text{and} \qquad \frac{d^2\eta}{dy^2}=-\sigma_2\frac{\partial C_{o,a}(y,0)}{\partial\xi}$$

Adsorption kinetics

Local current density i is determined by reaction kinetics ...

Let $\theta(x,t)$ denote the local fraction of Pt surface covered by O_2:

$$\mathcal{C}_{Pt}\frac{d\theta}{dt} = \underbrace{k_+\mathcal{H}C_{o,a}(1-\theta)}_{\text{adsorption}} - \underbrace{k_-\mathcal{C}_{Pt}\theta}_{\text{desorption}} - \underbrace{\frac{i}{4F}}_{\text{reaction}}$$

Set $\frac{d\theta}{dt} = 0$ (steady state) and $i = r_o\theta e^{-\alpha_c\eta}$ (Butler-Volmer):

$$\Longrightarrow \quad i = \frac{k_+\mathcal{H}C_{o,a}r_o e^{-\alpha_c\eta}}{k_+\mathcal{H}C_{o,a} + k_-\mathcal{C}_{Pt} + (r_o/4F)e^{-\alpha_c\eta}} \qquad (*)$$

So the limiting current density is $i_{lim} = \lim_{\eta\to-\infty} i = 4Fk_+\mathcal{H}C_{o,a}$

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So the limiting current density is $i_{lim} = \lim_{\eta\to-\infty} i = 4Fk_+\mathcal{H}C_{o,a}$

Note: With Butler-Volmer alone, $i_{lim} = \infty$

Solution algorithm

1. Given a target current density I^*, guess the cell voltage U.
2. Iterate on U:
   (a) Solve the following 1D BVP's $C_{o,p}(y)$ and $\eta(y)$:

$$\frac{d^2 C_{o,p}}{dy^2} = -\sigma_1 \frac{\partial C_{o,a}(y,0)}{\partial \xi} \quad \text{and} \quad \frac{d^2 \eta}{dy^2} = -\sigma_2 \frac{\partial C_{o,a}(y,0)}{\partial \xi}$$

   (b) Determine the agglomerate concentration $C_{o,a}(y,\xi)$:
   - Solve a 1D BVP in ξ at each y-location:

$$\frac{\partial^2 C_{o,a}}{\partial \xi^2} = \frac{i}{4F\mathcal{H}D_m}$$

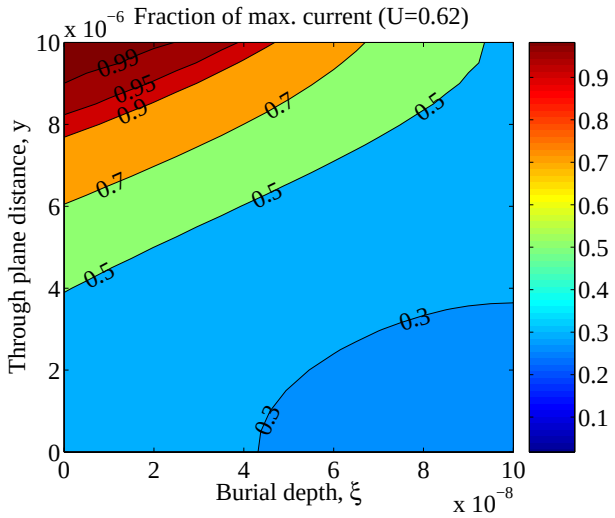
   - Use the current iterate for $C_{o,p}(y)$ as the boundary condition for $C_{o,a}(y,0)$.

   (c) Update i and I_{avg}.
   (d) If $|I_{avg} - I^*| > TOL$, then update U & return to step 2a.

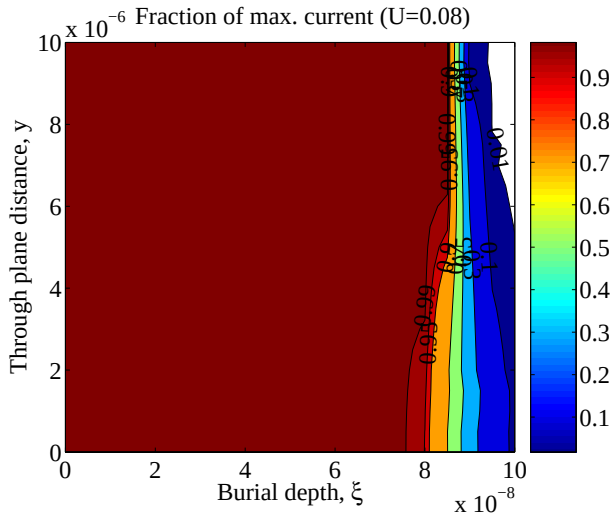
Results: Base case

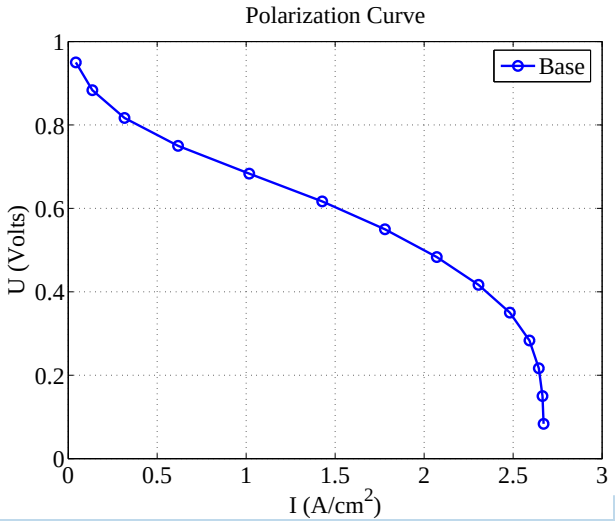
Computation time: $20\ s$ for a 20×20 grid

$U = 0.62\ V$



$U = 0.08\ V$

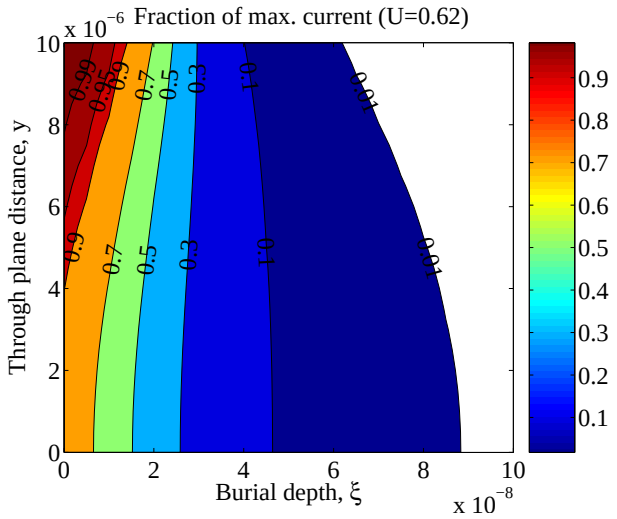




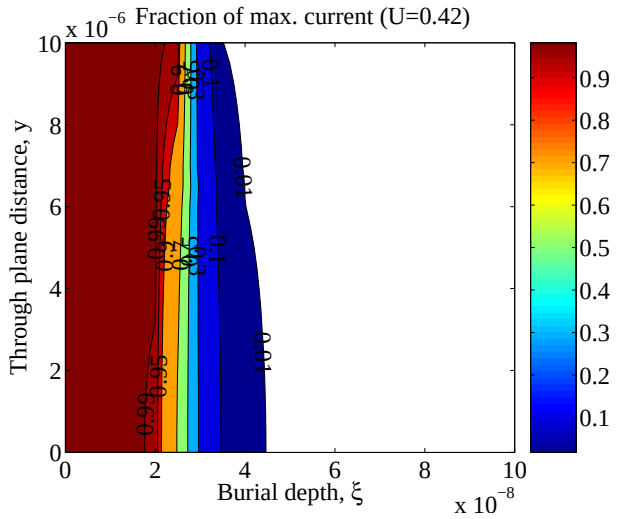
Results: Dry membrane

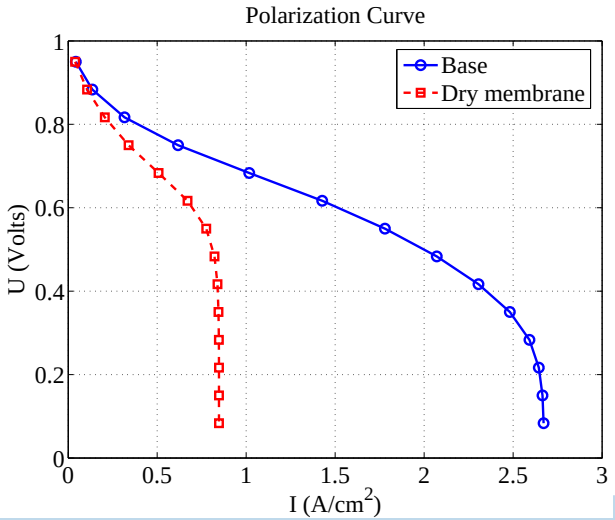
Reduce membrane diffusivity D_m by a factor of 10:

$U = 0.62\ V$



$U = 0.42\ V$

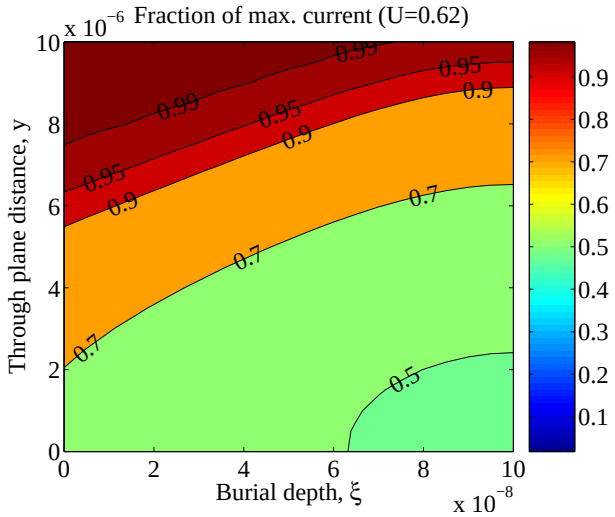




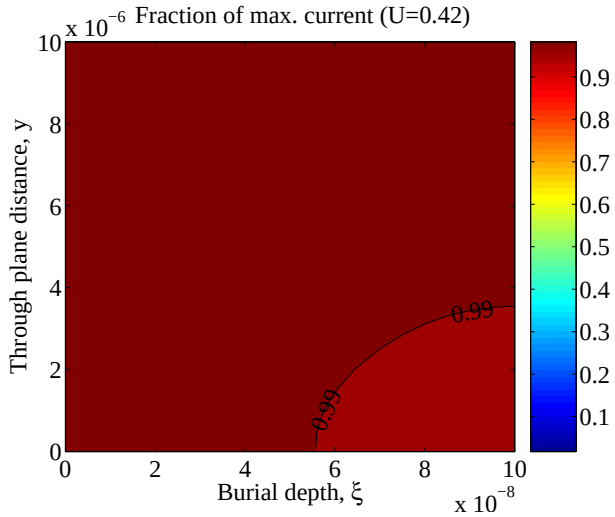
Results: Narrow pore

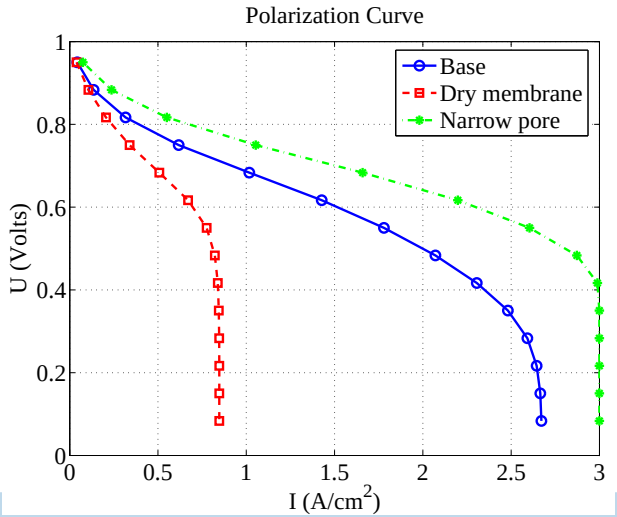
Reduce pore size ε_p by a factor of 2:

$U = 0.62\ V$



$U = 0.42\ V$





Summary

- Developed a 1+1D two-scale model for the cathode catalyst layer, incorporating a self-limiting reaction rate
- Dead core region observed under a variety of operating conditions
- Study catalyst utilization and optimize microstructural properties

Future work

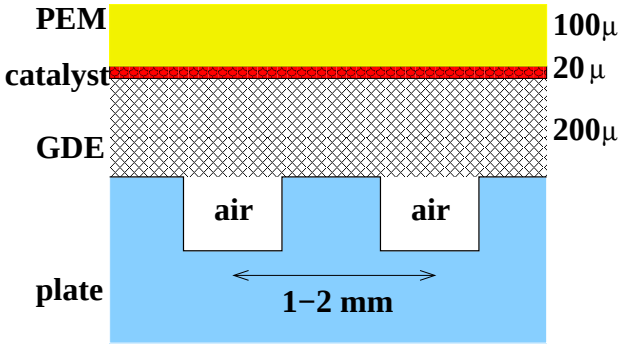
- Investigate other limiting mechanisms:
  - liquid water
  - diffusion in nanopores (multiscale pore structure)
- Develop a faster iterative algorithm
- Incorporate a detailed catalyst model into our unit cell model for use in stack simulations
- Include more aspects of microstructure into a continuum (macro-scale) model $\Longrightarrow$ **multiscale methods**

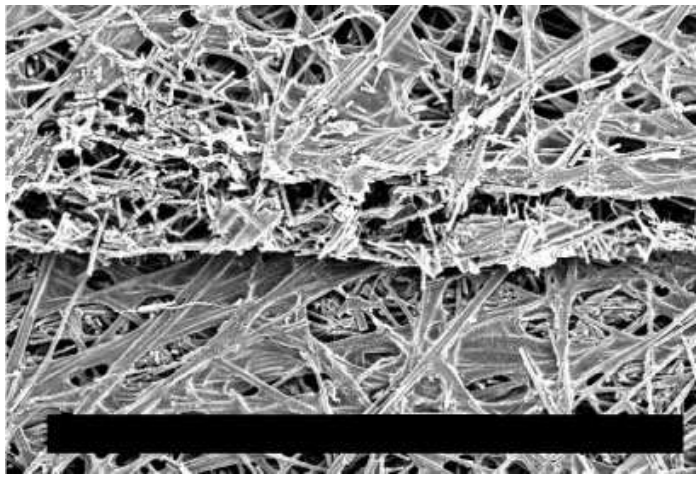
Electrode Model

Gas diffusion electrode

The gas diffusion electrode (GDE) consists of carbon fibre paper, sandwiched between catalyst / PEM and flow channels:

- anisotropic, fibrous porous medium
- approximately 200–300 μm thick
- treated with Teflon to improve water transport





Source: C. Y. Wang (2003)

Water management

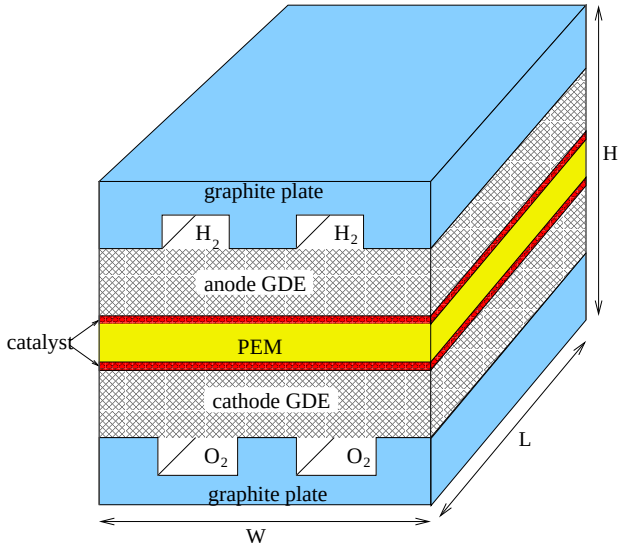
Water management is a key and complex issue, with direct impact on performance:

- membrane protonic conductivity is a strong function of water content
- liquid water in the flow channels or porous electrodes hinders reactant transport
- high temperature prevents water from condensing **BUT** damages certain components (e.g., PEM)
- “electro-osmotic drag”: water is dragged along with protons, from anode to cathode
- both inlet gas streams are humidified
- Teflon is applied in electrode and catalyst to improve wetting behaviour

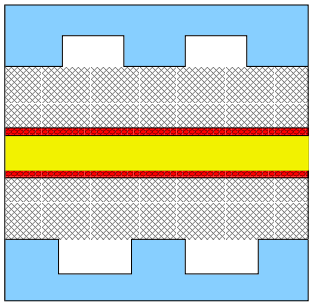
Geometry

Two 2D cross-sections

$H < W \ll L$

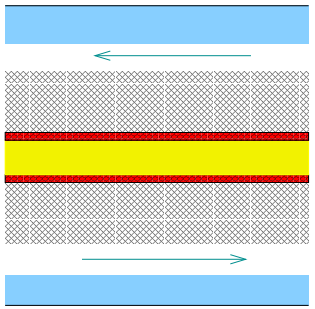


1) Cross-channel



Detailed local geometry for flow channel optimization

2) Down-the-channel



Averaged cross-channel, ideal for stack simulations (scale separation)

Governing equations

The primary unknowns are:

C	gas mixture concentration ($\rho = MC$)
C_o, C_v	oxygen and vapour concentrations
T	phase-averaged temperature
s	liquid saturation

The following conservation laws govern multiphase flow in cathode GDE:

$$((1-s)\rho)_t + \nabla \cdot \left(\rho \vec{U}_g\right) = -M\Gamma \qquad \text{(gas mixture, } \rho = MC\text{)}$$

$$((1-s)C_o)_t + \nabla \cdot \left(C_o \vec{U}_g + \vec{J}_o\right) = 0 \qquad \text{(oxygen)}$$

$$((1-s)C_v)_t + \nabla \cdot \left(C_v \vec{U}_g + \vec{J}_v\right) = -\Gamma \qquad \text{(water vapour)}$$

$$(\overline{\rho c}T)_t + \nabla \cdot \left(\overline{\rho c U}T - \kappa \nabla T\right) = \frac{I^2}{\sigma} + h\Gamma \qquad \text{(energy)}$$

$$s_t + \nabla \cdot (s\vec{U}_\ell) = \Gamma / C_\ell \qquad \text{(liquid water)}$$

Governing equations (2)

Constitutive equations:

$$\vec{J}_i = -CD_i \nabla \left(\frac{C_i}{C} \right) \qquad \text{(Fick's law, } i = o, v\text{)}$$

$$\vec{U}_i = -\frac{K\ k_{rel,i}(s)}{\varepsilon \mu_i} \nabla P_i \qquad \text{(Darcy's law, } i = g, \ell\text{)}$$

$$P_g = CRT \qquad \text{(ideal gas law)}$$

$$P_\ell = P_g + P_c(s) \qquad \text{(capillary pressure)}$$

Condensation / evaporation rate:

$$\Gamma = \begin{cases} \gamma^+(1-s)(C_v - C_v^{sat}(T)), & \text{if } C_v \geq C_v^{sat}(T) \\ \gamma^- s(C_v - C_v^{sat}(T)), & \text{if } C_v < C_v^{sat}(T) \end{cases}$$

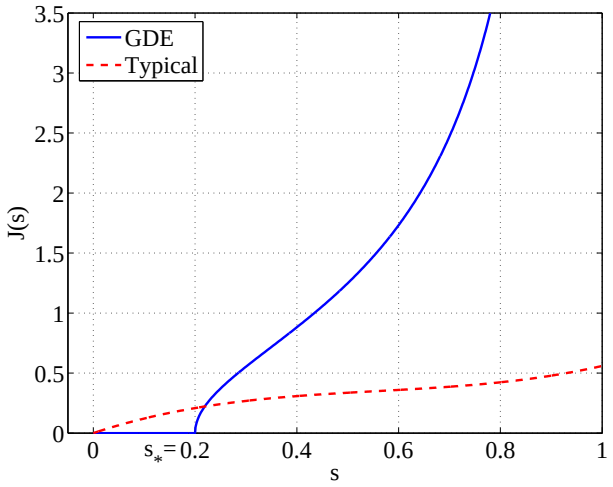
Boundary conditions.

Liquid transport

- Porous media exhibit an immobile saturation, s_*
- Define a reduced saturation, $\widetilde{s} = \frac{s - s_*}{1 - s_*}$
- Two key constitutive relations for GDE:

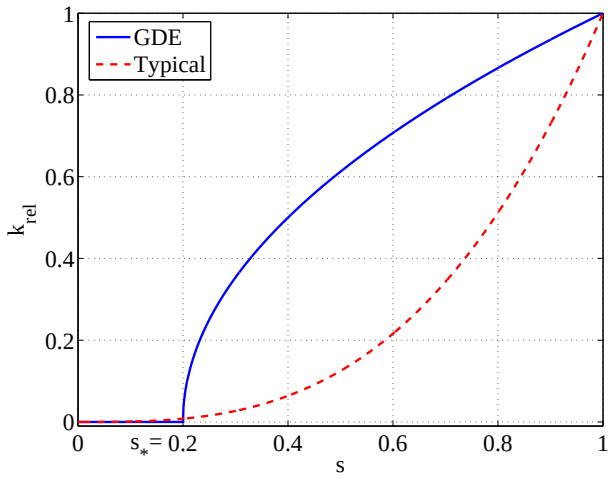
Capillary pressure (van Genuchten)

$$P_c(s) = A_c \, \mathcal{J}(s)$$
$$= A_c \left[(1 - \widetilde{s})^{-2} - 1 \right]^{1/2}$$



Relative permeability

$$k_{rel,\ell}(s) = \widetilde{s}^{1/2}$$



Comparison: Groundwater flow

- Advanced methods have been developed for multiphase transport in groundwater flow and oil reservoir simulation
- These methods are not generally applicable to fuel cells

	Groundwater	**Fuel cell GDE**
time scales:	hrs to yrs	μs to ms
length scales:	m to km	μm to mm
anisotropy:	low	high
wettability:	hydrophilic	hydrophobic
dominant mechanism:	convection	diffusion (and convection)

- Experiments are much harder to undertake on fuel cells, and so many material properties are not known

Numerical method

- Conservative finite volume discretization
- **Stiff system** with time scales ranging from $10^{-7}\ s$ to $10^{2}\ s$

  $\Longrightarrow$ use stiff solver `ode15s` in `Matlab`
- Saturation equation is a **degenerate** diffusion equation:

$$s_t + f(s)\nabla s + \nabla \cdot (g(s)\nabla s) = h(s) + \Gamma/C_\ell$$

with $g(s) = Ask_{rel,\ell}(s)\mathcal{J}'(s)$

$\Longrightarrow$ regularize $k_{rel,\ell}$ and $\mathcal{J}$ **KEY!**

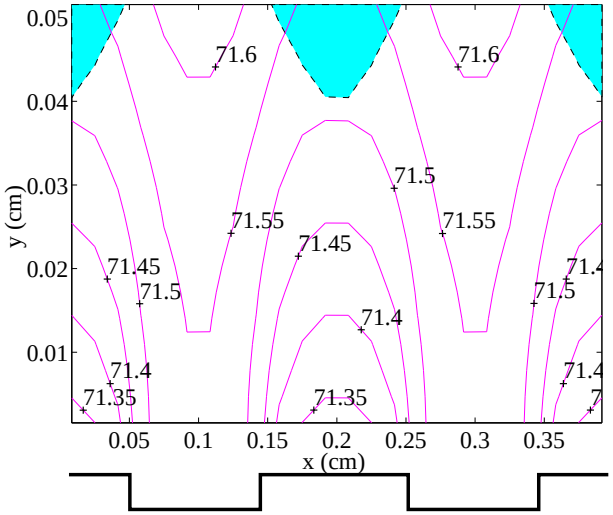
- Γ source terms are typically very large

Computation time: 15 mins for a 20×20 grid
(compare to **days** for a straightforward discretization)

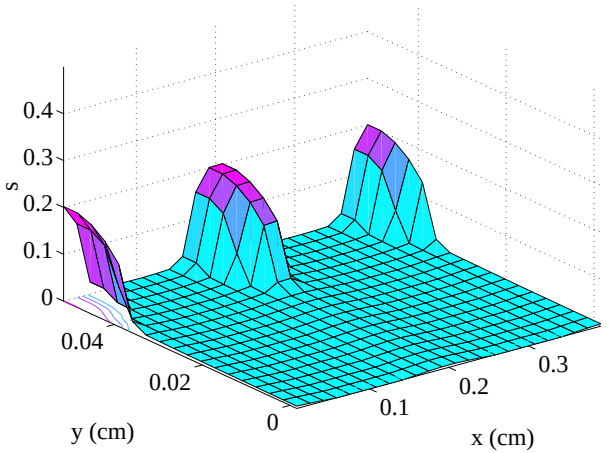
Results

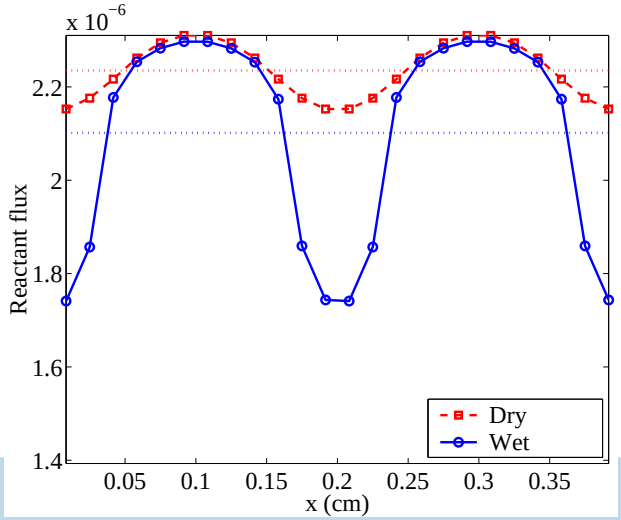
Cathode fed with humidified air at 70^oC:

Temperature contours



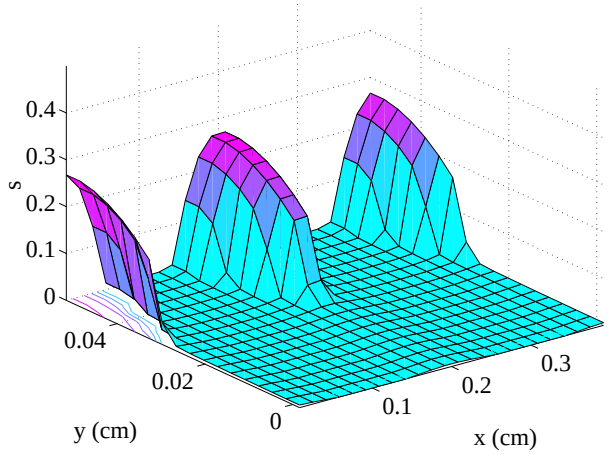
Saturation



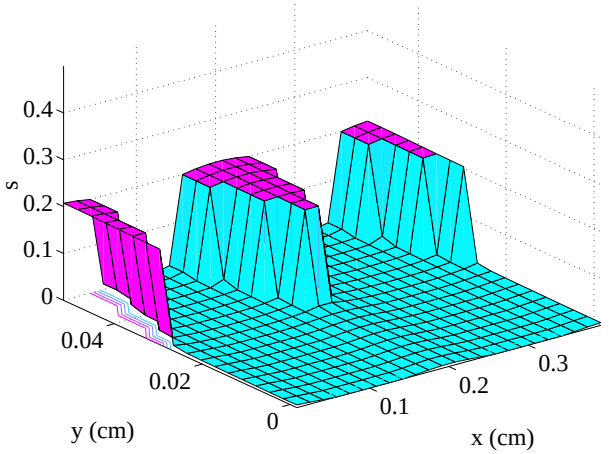


Results: Wettability comparison

Hydrophilic



Hydrophobic

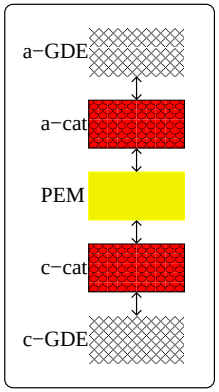


- Hydrophobic nature of GDE leads to sharp wetting fronts

Future work

- Explain severe stiffness observed in computations (also present in 1D through-plane GDE model)
- Develop more efficient methods based on **splitting** (liquid time scale is much slower)
- Investigate multi-scale approaches for catalyst and PEM.
- Derive reduced 1D (semi-analytical) models – ideal for **1+1D stack-level simulations**

1D MEA model



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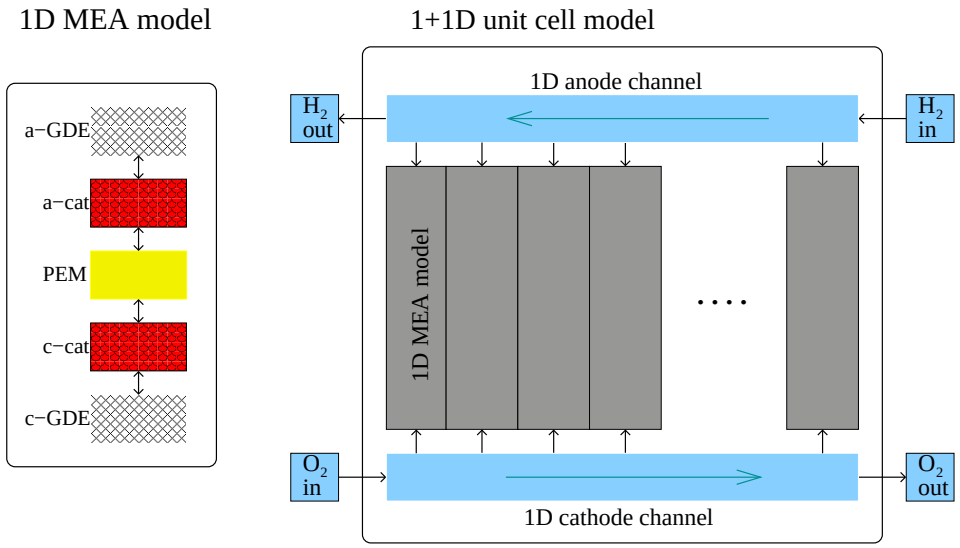

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