Overview of PEM Fuel Cells

Computational Fuel Cell Dynamics

Banff International Research Center

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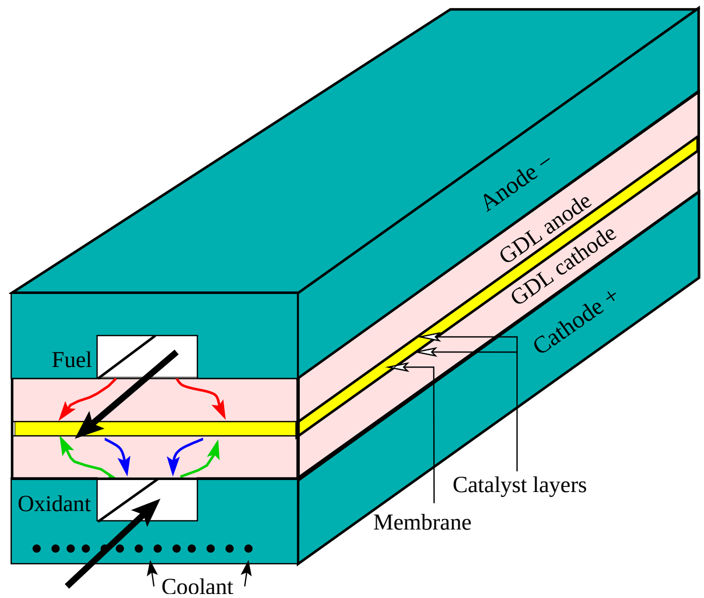
The PEM Unit Cell

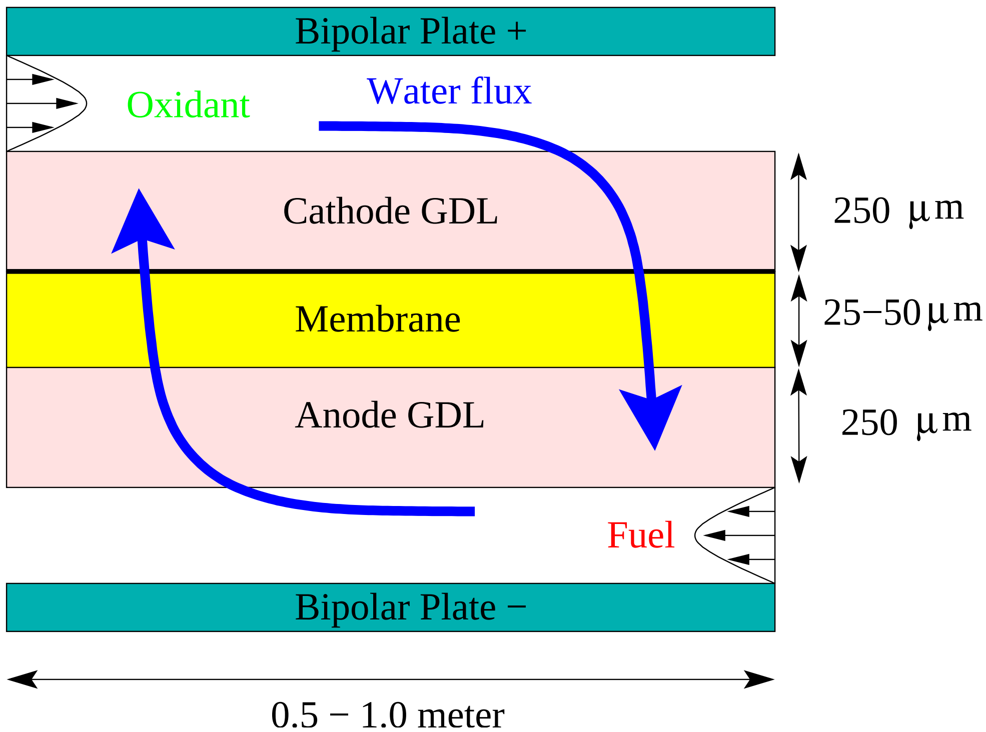
3D View



Principal Processes

Consumption of O_2 and fuel along channels
Gas diffusion in GDL
Production of H_2O and heat at cathode catalyst layers
Build-up of double-layer charge at catalyst interface
Ion and water motion in membrane
    Forms barrier for fuel, oxidant, e^-
    Conducts protons as H_3O^+
Condensation/Evaporation of water
Heat removal by coolant

Along-the-Channel Slice



The anode reaction

$$\mathbf{H_2 \rightleftharpoons 2H^+ + 2e^-}$$

The cathode reaction

$$\mathbf{O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O.}$$

Dimensionless Quantities

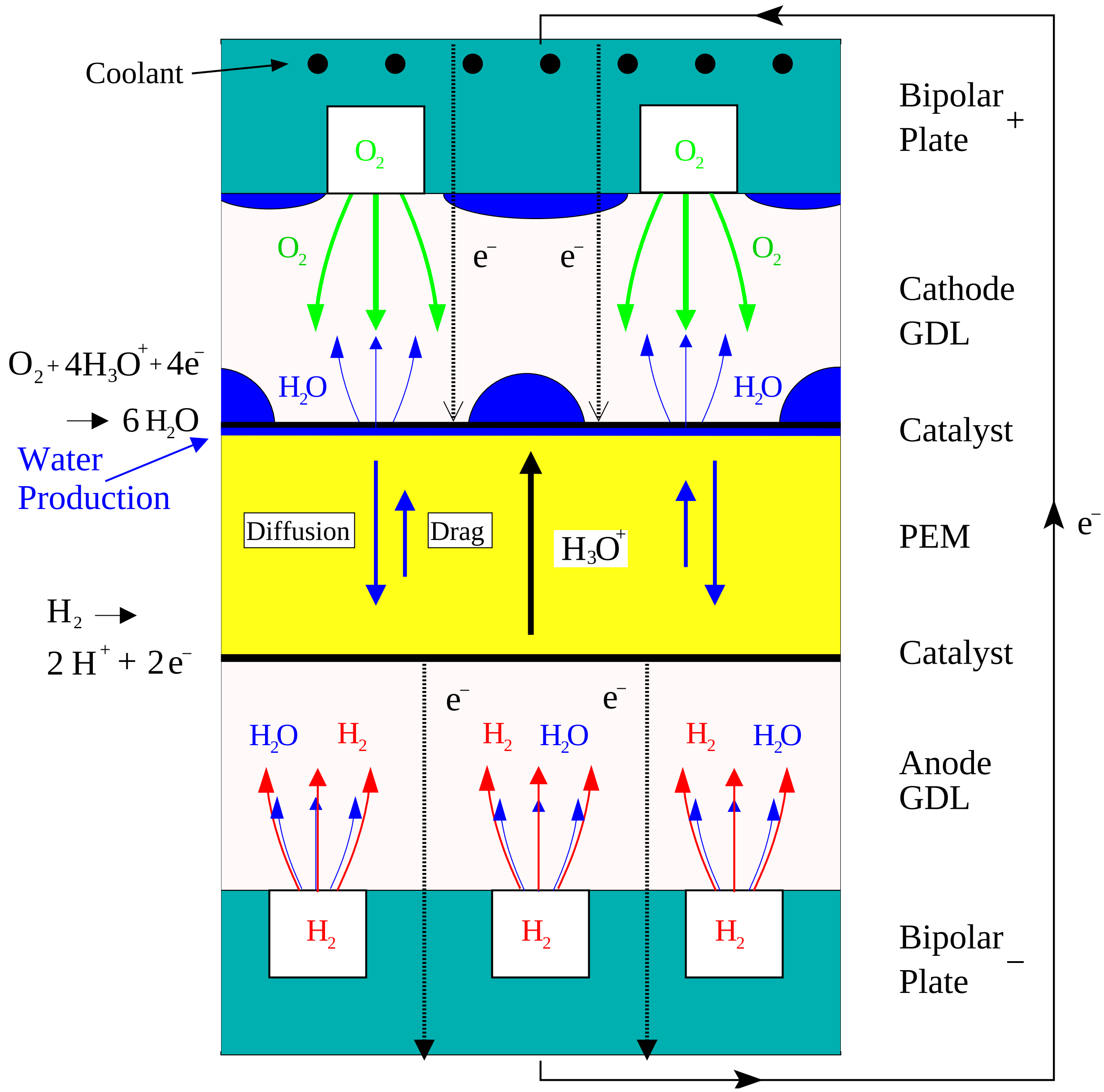
Cathode (Air) Stoich $\quad S_c = \dfrac{Q_{O_2}}{I_T/(4F)}$

Anode (Fuel) Stoich $\quad S_a = \dfrac{Q_{H_2}}{I_T/(2F)}$

Local Water transfer $\quad \alpha = \dfrac{J_w}{I/(2F)}$

Aspect ratio $\quad \mathbf{2000 : 1}$

Cross-sectional Slice



Multiphase Flow

Phase change and two-phase flow in hydrophobic carbon fiber paper

Gas diffusion through the carbon fiber paper (GDL)

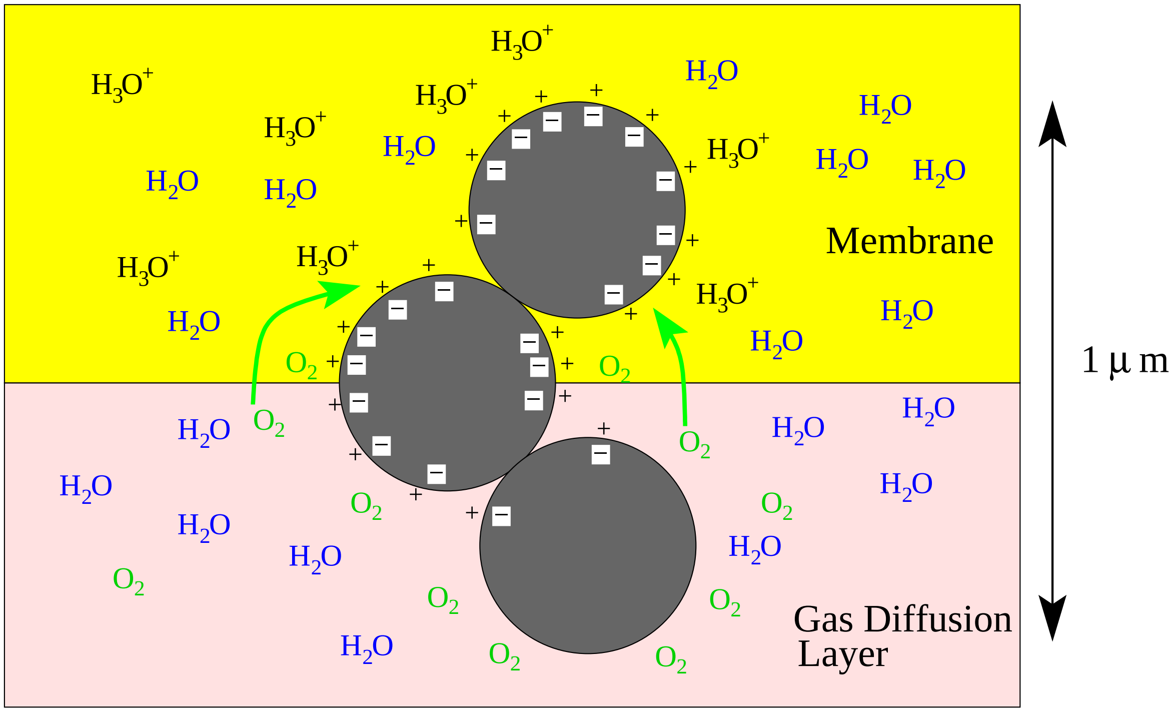
Liquid water exchange between:

membrane and GDL

GDL and Channel

Rivulet flow of water in channel

Polarization Curves

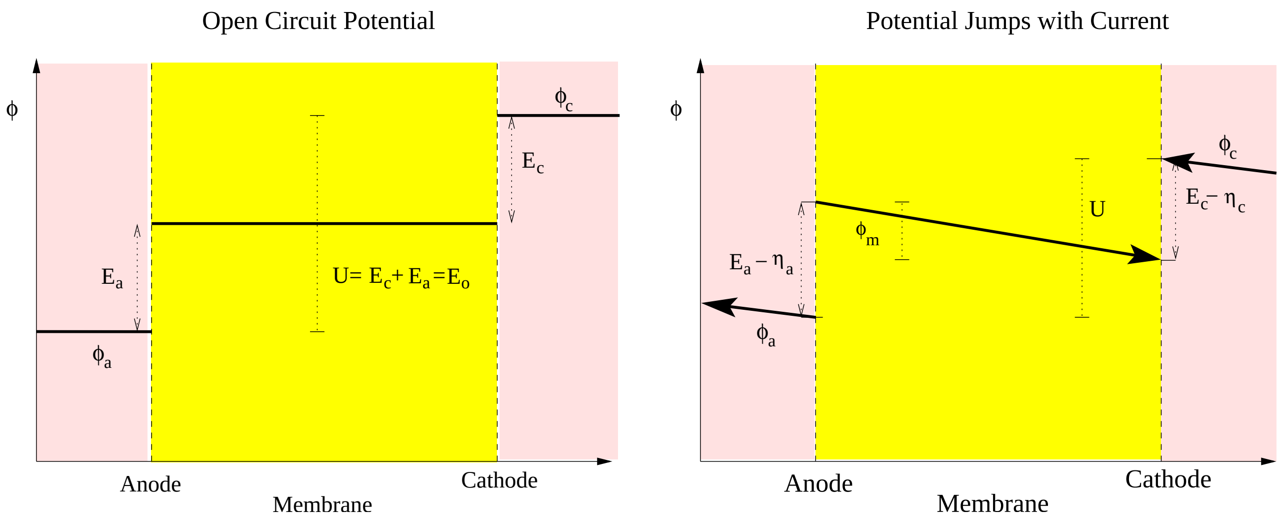


The catalyst/membrane/GDL triple junction points are the active catalyst sites

- O_2 diffusion from GDL and through membrane water
- H_3O^+ transport through membrane
- proton surface diffusion on Pt
- electrical conductivity of carbon support

The double layer at the catalyst surface acts as a *capacitor*

- Voltage jump proportional to charge $V = QC$
- Charge Q depends upon
  - supply of reactants
  - discharge rate (current)
  - reaction kinetics



The electric potential pushes electrons anode to cathode
protons cathode to anode

Butler-Volmer Equations

$$I_c = i_{o,c}\left(\frac{c_O}{c_{O,\text{ref}}}\right)^{e_c}\left[\exp\left(\frac{\alpha_c F}{RT}\eta_c\right) - \exp\left(-\frac{(1-\alpha_c)F}{RT}\eta_c\right)\right]$$
$$I_a = i_{o,a}\left(\frac{c_H}{c_{H,\text{ref}}}\right)^{e_a}\left[\exp\left(\frac{\alpha_a F}{RT}\eta_a\right) - \exp\left(-\frac{(1-\alpha_a)F}{RT}\eta_a\right)\right]$$

describe non-equilibrium kinetics of current generation

Local Potential balance

$$U = E_o - \eta_c(I) - \eta_a(I) - \phi_m(I)$$

Under the simple approximation

$$c_O = c_O(\,\text{channel}\,) - \delta I,$$

the cathode overpotential

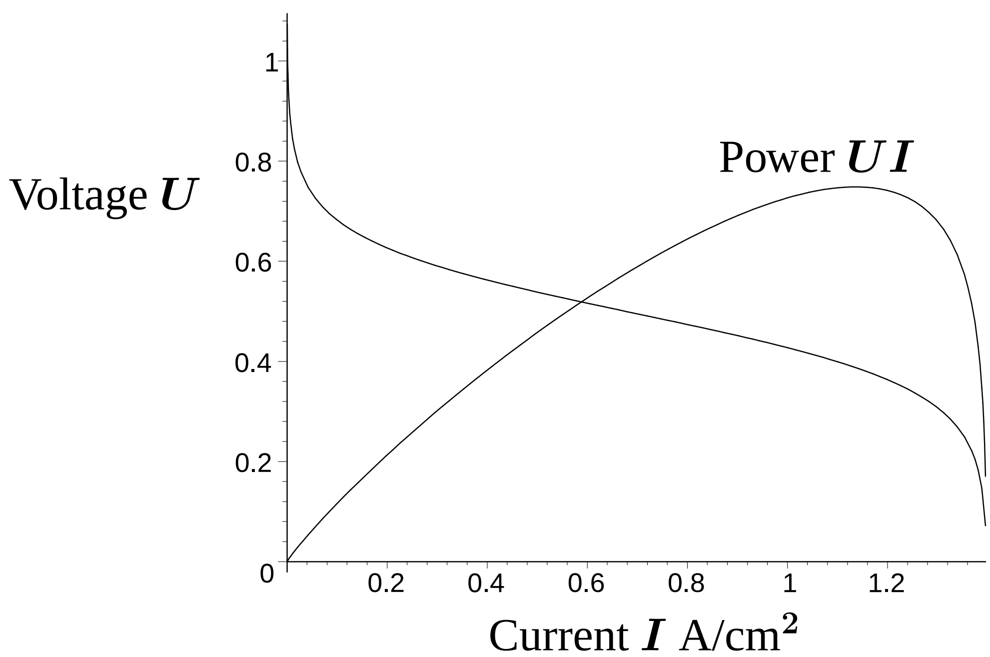
$$\eta_c \approx \overbrace{\frac{RT}{\alpha_c F}}^{\text{TafelSlope}} \ln\left(\frac{I}{i_{o,c}}\left(\frac{c_{O,\mathrm{ref}}}{c_O(\,\text{channel}\,) - \delta I}\right)^{e_c}\right)$$

the membrane potential losses

$$\phi_m \approx I/\sigma$$

the polarization curve relates potential U to current I.

$$U = E_o - \frac{RT}{\alpha_c F}\ln\left(\frac{I}{i_{o,c}}\left(\frac{c_{O,\mathrm{ref}}}{c_O(\,\text{channel}\,) - \delta I}\right)^{e_c}\right) - I/\sigma_m.$$



Membrane Issues

Unknowns

$c_w = [H_2O]/a$	Water Molar Conc.	T	Temperature
$c_+ = [H_3O^+]/a$	Free Proton Conc.	ϕ	Electric Potential
$c_b = [SO_3^- H^+]/a$	Bound Proton Conc.	a	Acid Weight

Ion Balance

The ion disassociation process

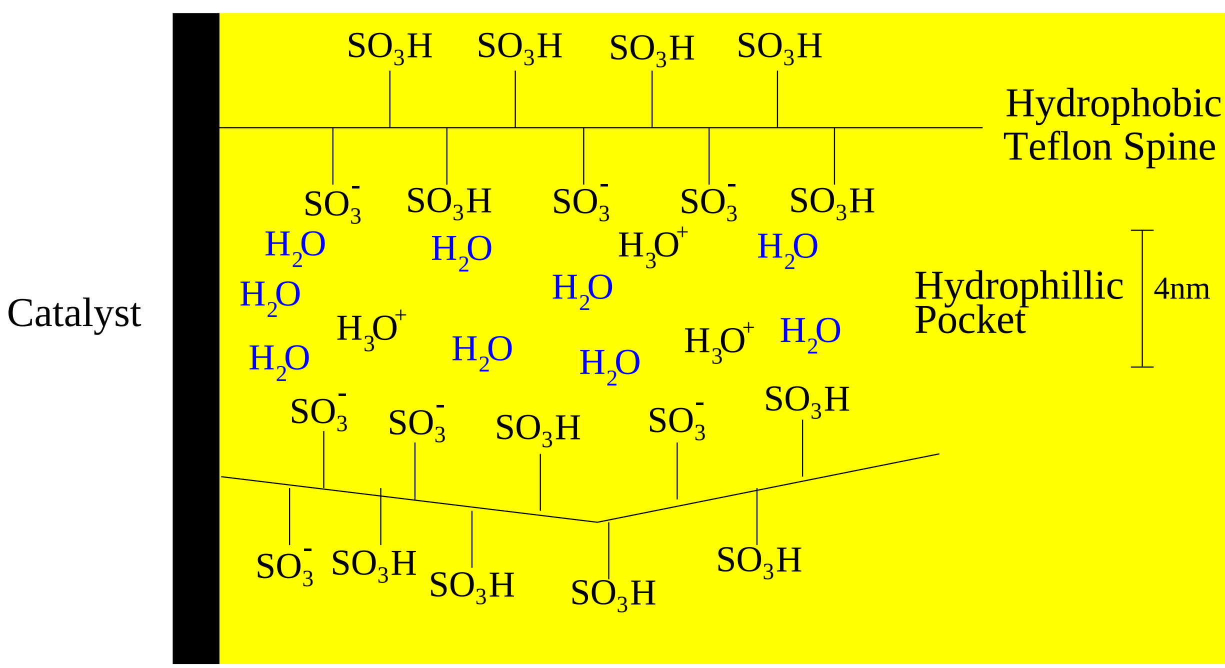
$$SO_3^- H^+ + H_2O \rightleftharpoons SO_3^- + H_3O^+, \tag{1}$$

Hydronium production rate

$$S = a^2 \left(K_1 c_b c_w - K_2 (1 - c_b) c_+ \right), \tag{2}$$

with rate constants

$$K_i = K_{i0} \exp[\frac{-H_{i0}}{RT}] \gg 1. \tag{3}$$



Governing Equations

Poisson's equation

$$\epsilon^2 \Delta\phi = -(\overbrace{c_+}^{\rho_+} - \overbrace{(1-c_b)}^{\rho_-}), \qquad \epsilon^2 = d/(4a\pi F), \tag{4}$$

Conservation of Mass

$$\frac{\partial}{\partial t} c_w + \nabla\cdot(J_w + U_l c_w) = -\bar{S}/\delta, \tag{5}$$

$$\frac{\partial}{\partial t} c_+ + \nabla\cdot(J_+ + U_l c_+) = \bar{S}/\delta, \tag{6}$$

$$\frac{\partial}{\partial t} c_b + \nabla\cdot(J_b + U_b c_b) = -\bar{S}/\delta. \tag{7}$$

Outer Approximation

- Bound ions do not flux: $\nabla\cdot(J_b + U_b c_b) = 0$,
- $\bar{S} = 0 + \delta S_1 + O(\delta^2) \qquad \delta \ll 1$
- $\rho = 0 + \epsilon^2 \rho_1 + O(\epsilon^4) \qquad \epsilon \ll 1$

Outer Equations: Parabolic-Elliptic-Algebraic

$$c_b c_w - \frac{K_2}{K_1}(1-c_b)c_+ = 0, \qquad \text{Ion Equilibrium}$$

$$c_+ - (1-c_b) = 0, \qquad \text{LEN}$$

$$\frac{\partial}{\partial t}(c_T) + \nabla\cdot(J_T + U_l(c_T)) = 0, \qquad \text{Cons. Total water}$$

$$\nabla\cdot J_+ = 0, \qquad (6) + (7) + \text{LEN}$$

Ion Balance

LEN and Ion Equilibrium yield

$$c_+ = c_+(c_w, T) = -\frac{K(T)c_w}{2} + \sqrt{\left(\frac{K(T)c_w}{2}\right)^2 + Kc_w}, \quad (8)$$

where

$$K(T) = K_1(T)/K_2(T) = O(1).$$

Parabolic for c_w and elliptic for ϕ.

Maxwell-Stefan Equations

Water, hydronium, methanol:

$$\begin{pmatrix} J_+ \\ J_w \\ J_{\text{meth}} \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} & L_{13} \\ L_{12} & L_{22} & L_{23} \\ L_{13} & L_{23} & L_{33} \end{pmatrix} \begin{pmatrix} \nabla\mu_+ \\ \nabla\mu_w \\ \nabla\mu_{\text{meth}} \end{pmatrix}$$

Off diagonal terms represent interspecies friction

The chemical potential of species i

$$\nabla\mu_i = RT\nabla \ln c_i + \overbrace{z_i}^{\text{charge}} F\nabla\phi.$$

The average velocity U_l is given by a Darcy type relation

$$U_l = -\frac{K}{\mu}\nabla P$$

where the Pressure gradient arises from

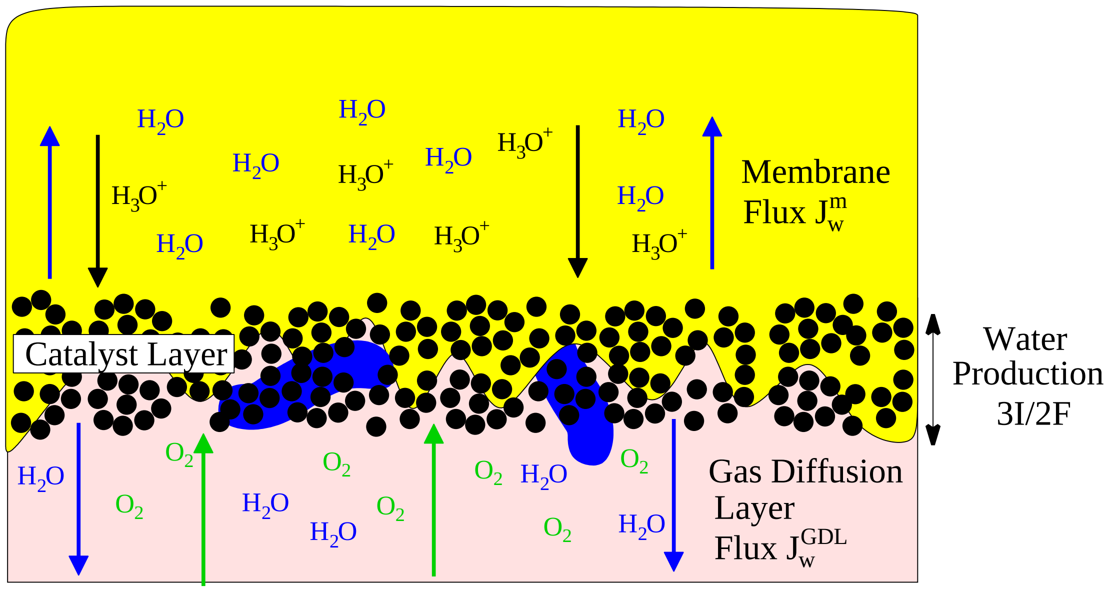
Capillary effects: hydrophilic/hydrophobic phase separation

Membrane swelling

External pressure differences

Membrane-GDL Coupling

Membrane-Catalyst Layer water transfer



Membrane equilibrium hydration levels function of GDL RH level r,

$$c^*(r) = 0.043 + 17.81r - 39.85r^2 + 36.0r^3.$$

Flux out of membrane proportional to disequilibrium

$$\gamma(c_w)\overbrace{(c^*_{w,a} - c_{w,a})}^{\text{disequilibrium}} = \overbrace{J^{GDL}_{w,a}}^{\text{Flux}}/a = (J^m_{w,a} + I/F)/a,$$

$$\gamma(c_w)(c_{w,c} - c^*_{w,c}) = J^{GDL}_{w,c}/a = (J^m_{w,c} + 3I/2F)/a.$$

$\gamma \ll 1$ controls membrane water loss.

Heat Production in Catalyst

$$Q_{\text{heat}} = \left(\frac{Th_{rc}}{4F} + \eta_c\right) I_c - h_v\gamma(c_T - c^*_T(r)).$$

Numerical Issues: GDL Multiphase flow

Degenerate transport of liquid water
Disparate length scales $\mathbf{1000 : 1}$
Disparate time scales:

$\mathbf{10^{-6}} \boldsymbol{s}$ for pressure
$\mathbf{10^{3}} \boldsymbol{s}$ for liquid flow

Degenerate Multiphase Flow

Unknowns

C_o	Oxygen Molar Conc.	T	Temperature
C_v	Water Vapour Molar Conc.	P_l	Liquid Pressure
C_n	Nitrogen Molar Conc.	β	Liquid Water Volume Frac.
C	Total Gas Conc.	α	Gas Volume Frac.

Conservation of Energy and Mass

$$\frac{\partial}{\partial t}(\alpha C) + \nabla \cdot (C U_g) = -\Gamma, \tag{9}$$

$$\frac{\partial}{\partial t}(\alpha C_o) + \nabla \cdot (C_o U_g + J_o) = 0, \tag{10}$$

$$\frac{\partial}{\partial t}(\alpha C_v) + \nabla \cdot (C_v U_g + J_v) = -\Gamma \tag{11}$$

$$\frac{\partial}{\partial t}(\beta) + \nabla \cdot (\beta U_l) = \Gamma / c_l \tag{12}$$

$$\frac{\partial}{\partial t}(\tilde{\rho} c T) + \nabla \cdot ((\widetilde{\rho c U}) T - \tilde{\kappa} \nabla T) = h_{lg} \Gamma. \tag{13}$$

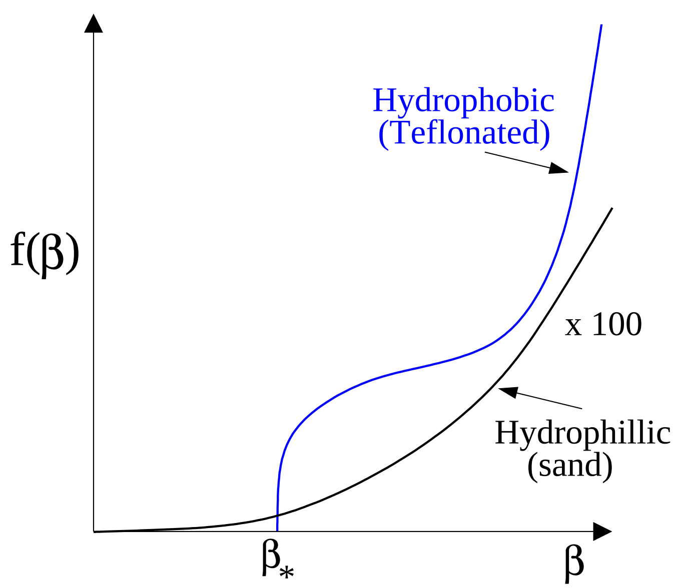
Constitutive Relations

$\alpha + \beta + \epsilon = 1,$	Volume Fraction relation
$C = C_o + C_v + C_n,$	Total Concentration
$P_g = CRT,$	Ideal Gas Law
$U_g = -\frac{K k_{rg}(\beta)}{\mu_g} \nabla P_g,$	Darcy's Law-Gas
$U_l = -\frac{K k_{rl}(\beta)}{\mu_l} \nabla P_l,$	Darcy's Law-Liquid
$[J_i] = M^{-1}[\nabla C_i]$	Maxwell Stefan Flux
$P_c = P_g - P_l = L(\beta),$	Leveret-like Capillary Pressure.
$\Gamma = H(\beta)(C_v - C_{\text{sat}}(T)),$	Condensation-Saturation

Capillary pressure and relative permeability form nonlinear diffusivity

$$f(\beta) = \beta k_{rl}(\beta) L'(\beta).$$

$$\frac{\partial}{\partial t}(\beta) + D\nabla \cdot (f(\beta)\nabla\beta) = \Gamma / c_l$$

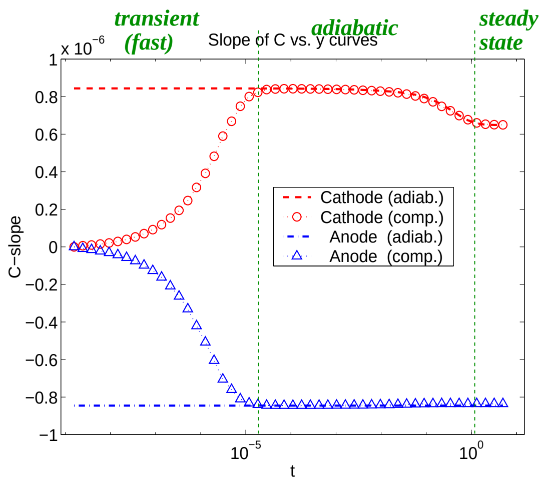


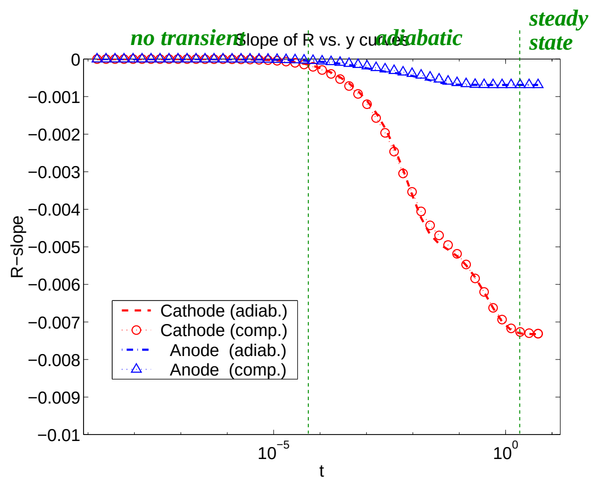
Non-dimensional Forms

$$
\begin{aligned}
\frac{\partial}{\partial \bar t}(\alpha \bar C_v) + \bar\nabla\cdot(\,\mathrm{Sc}\,\bar C_v \bar U_g + \bar J_v) &= -\bar\Gamma,\\
\frac{\partial}{\partial \bar t}(\alpha \bar C_o) + \bar\nabla\cdot(\,\mathrm{Sc}\,\bar C_o \bar U_g + \bar J_o) &= 0,\\
\frac{\partial \beta}{\partial \bar t} + \delta_\beta\left(\bar\nabla\cdot(f(\beta)\nabla\beta) - \bar\Gamma\right) &= 0,\\
\frac{\partial \bar T}{\partial \bar t} + \bar\nabla\cdot(\,\mathrm{Ra}\,\bar U \bar T - \bar\nabla \bar T) &= \delta_T \bar\Gamma
\end{aligned}
$$

Schmidt	$\mathrm{Sc} = O(10^2 - 10^3)$
Raleigh	$\mathrm{Ra} = O(10^2 - 10^3)$
Heat of Vaporization	$\delta_T = O(10^{-1} - 10^{-2})$.
Water time-scale	$\delta_\beta = O(10^{-2} - 10^{-3})$.

Convection dominates the gas flow, but balances diffusion at equilibrium
Liquid on slow time scale $\tau = \delta_\beta t$



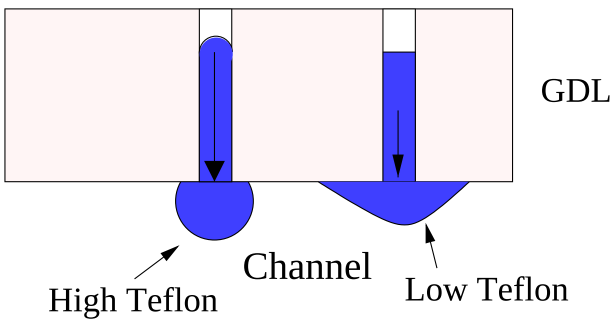


GDL-Channel Liquid exchange

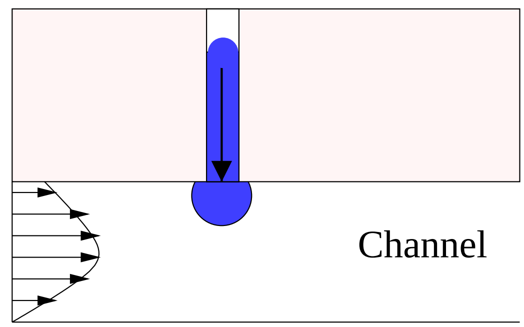
Proper modeling of liquid water exchange between porous carbon fiber paper and open channel is non-trivial

Water transport in channel flow truly multi-phase flow

Teflon and Capillary Pressure



Shearing force on a Droplet



Open Problems in Electro-Chemistry + Ion Transport

Electrocatalysis

- Modeling of mechanisms and kinetics of electrocatalysis
  - Proton surface diffusion on Pt
  - Percolation of conducting phase in catalysis layer
  - Liquid water inhibition of reaction
  - CO poisoning of catalyst
- Reaction kinetics for methanol

Polymer Membranes

- Hydrophilic-hydrophobic phase separation in membrane
  - Impact on proton and water transport (osmotic drag)
- Dielectric effects: Bound and free water
- Membrane swelling and water transport

Computational Issues

- Model stiffness
- Moving fronts
- Temporal and spatial boundary layers