

Phase Change in PEM Fuel cells

Transient Unit Cell Models

Ottawa May 10-12, 2006

Peter Berg	Univeristy of Ontario Inst. Tech.
Paul Chang	Univeristy of British Columbia
Igor Nazarov	Michigan State University
Arian Novruzi	University of Ottawa
John Stockie	Simon Fraser University
Brian Wetton	University of British Columbia

Talk Overview

I) Transient Unit Cell Models

Phase change in porous media

Multiphase flow

Comparisons to Chop-chop data

Transient simulations

II) Hysteresis and Lateral Diffusion

Benziger's STR Data

Ignition waves

Hysteresis in wet cells

Stability analysis of a toy model

III) Nanophase Models

Membrane Model

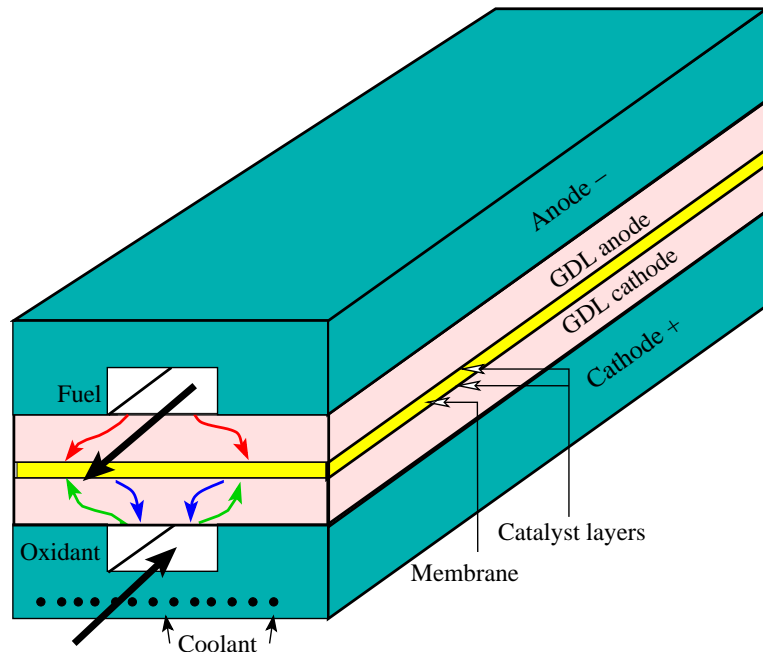
Catalyst Layer Mixing

Multiphase Performance

Carbon Corrosion/Pt dissolution

I: Transient Unit Cell Models

The PEM Unit Cell



Channels: Variation of O_2 , H_2 , and H_2O from inlet to outlet.

GDL: Oxygen and vapor counter-diffusion, two-phase flow, formation of condensation/evaporation fronts.

Catalyst Layers: Production of H_2O and heat at cathode catalyst layers. Build-up of double-layer charge at catalyst interface.

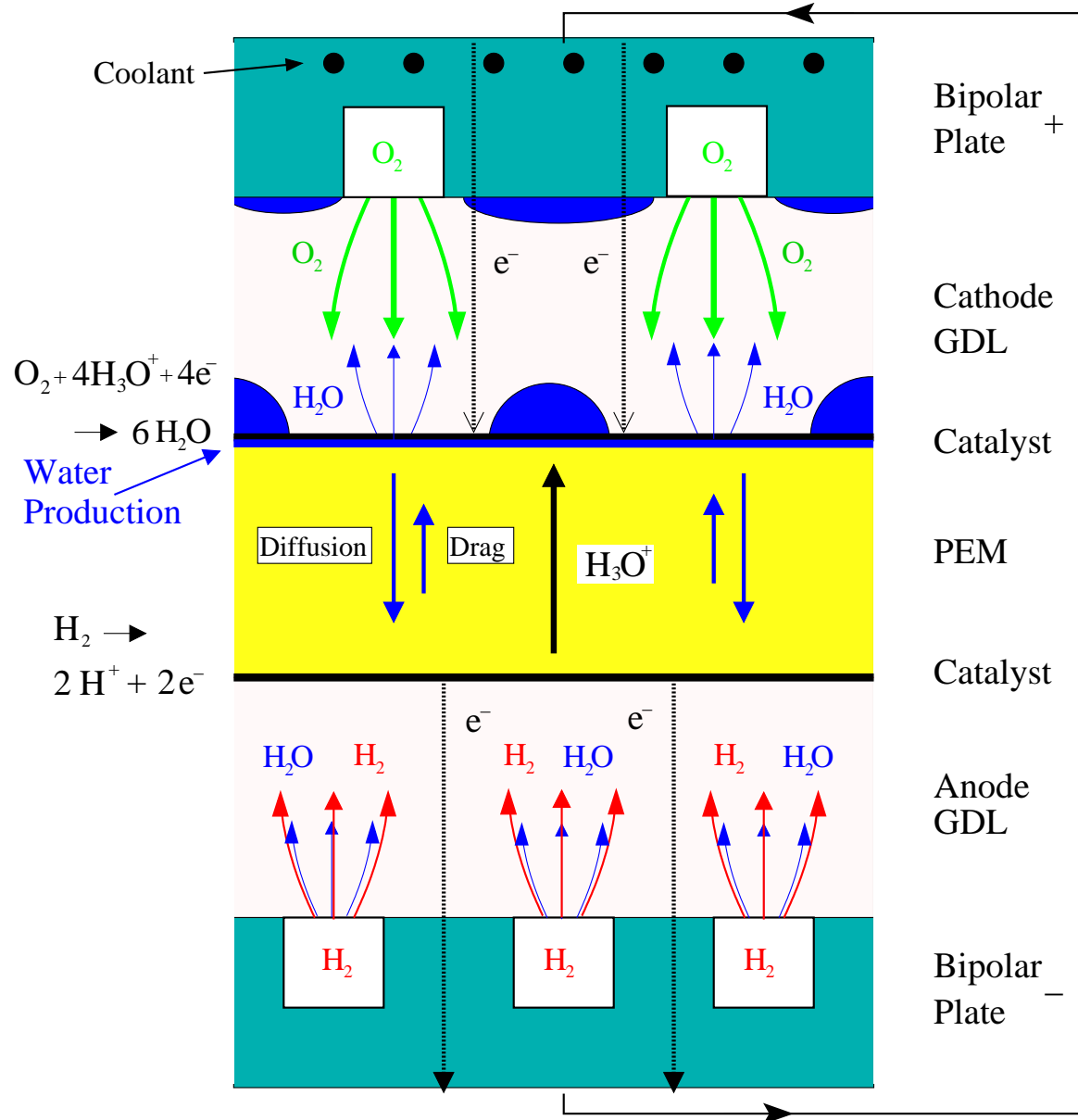
Membrane: Ion and water motion in membrane, proton conduction, forms barrier for fuel, gases, e^- .

Coolant: Dominates cell temperature in long direction.

Presence of disparate length and time-scales for lengths $> 1\mu$ meter.

Functional structure at all length scales $< 1\mu$ meter.

Cross-sectional Slice



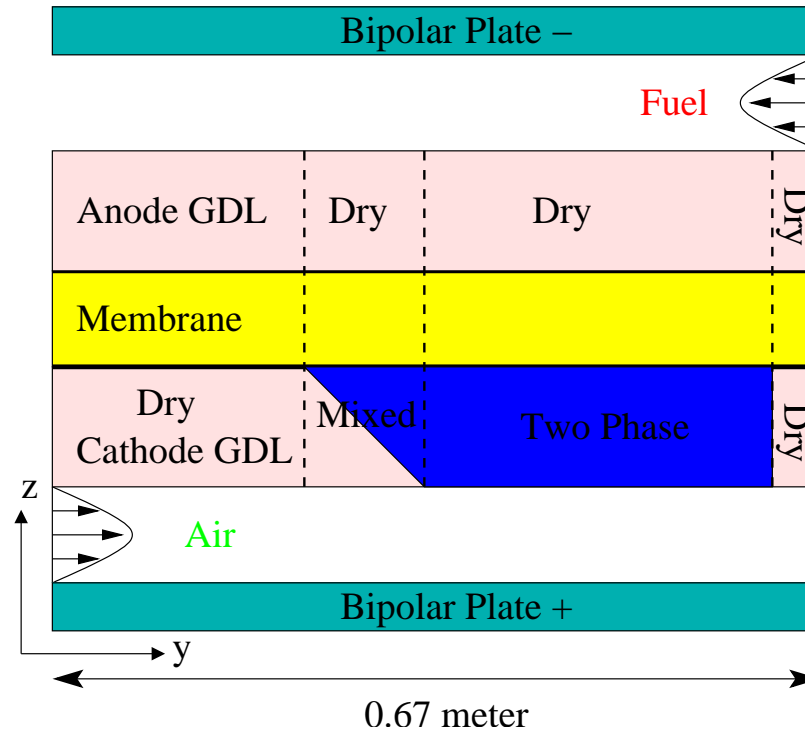
Average over the lateral direction

Average over the typical pore size in GDL

Each species has an average value at each point

Do not resolve liquid-water interface on the pore length scale

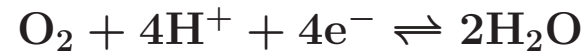
Along-the-Channel Slice



The anode reaction



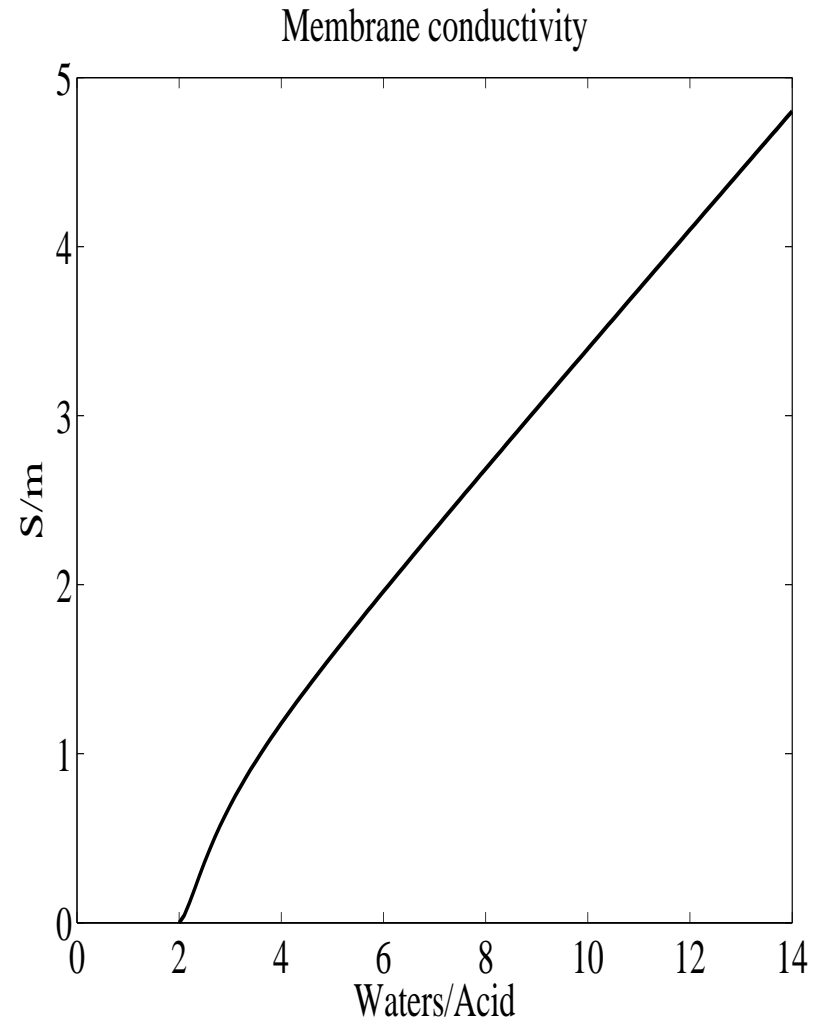
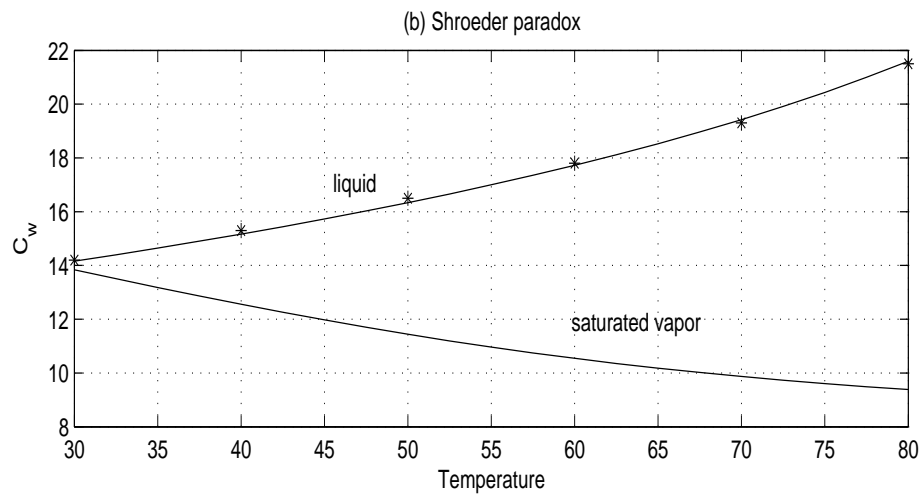
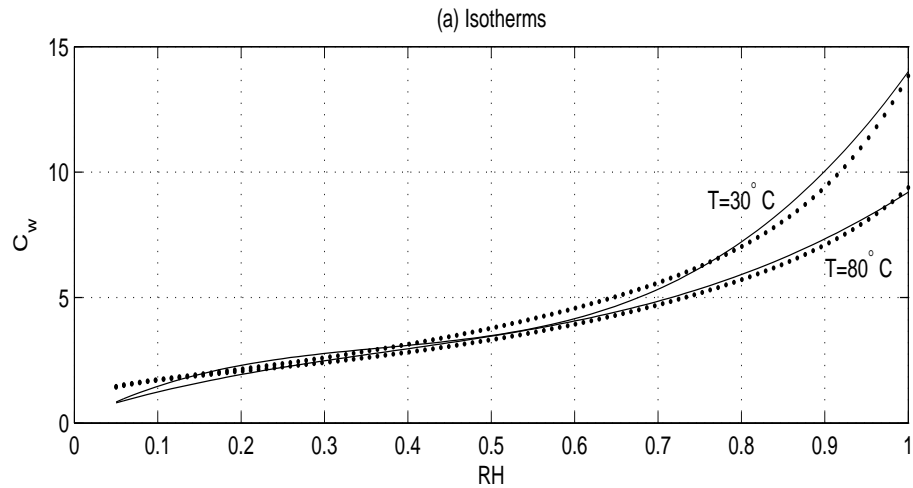
Cathode reaction (1.5 volts)



Through plane voltage balance

$$V = \underbrace{E_o}_{\text{Open circ pot.}} - \underbrace{\frac{I(y)}{\sigma}}_{\text{Ohmic Losses}} - \underbrace{\eta(I, C_o)}_{\text{overpotential}}$$

Ionomer Membrane Properties



(Left) The hydration isotherm for Nafion 117 (from Takanaka 1994).

(Right) Protonic conductivity as a function of water content.

GDL: Transient Multiphase flow

Degenerate transport of liquid water

Disparate length scales 1000 : 1

Disparate time scales:

10^{-6} s for pressure

10^3 s for liquid flow

C_o Oxygen Molar Conc. T Temperature

C_v Vapor Molar Conc. β Liquid Vol. Frac.

C_n Nitrogen Molar Conc. C Total Gas Conc.

Conservation of Energy and Mass

$$\begin{aligned} \frac{\partial}{\partial t}((1 - \beta)C) + \partial_y(\overbrace{\overline{C U_g}}^{N_g}) &= -\Gamma, \\ \frac{\partial}{\partial t}(\overline{\rho c T}) + \partial_y(\overbrace{(\overline{\rho c U})T - \tilde{\kappa} \partial_y T}^{N_T}) &= h_{lg}\Gamma, \\ \frac{\partial}{\partial t}((1 - \beta)C_o) + \partial_y(\overbrace{\overline{C_o U_g} + J_o}^{N_o}) &= 0, \\ \frac{\partial}{\partial t}((1 - \beta)C_v) + \partial_y(\overbrace{\overline{C_v U_g} + J_v}^{N_v}) &= -\Gamma, \\ \frac{\partial}{\partial t}(c_l \beta) + \partial_y(\overbrace{\overline{\beta c_l U_l}}^{N_l}) &= \Gamma. \end{aligned}$$

Constitutive Relations

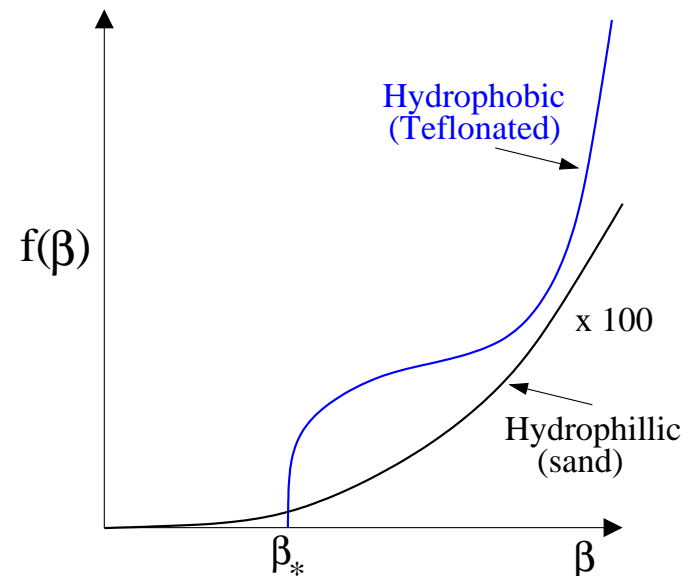
$P_g = CRT,$	Ideal Gas Law
$U_g = -\frac{Kk_{rg}(\beta)}{\mu_g}\partial_y P_g,$	Darcy's Law-Gas
$U_l = -\frac{Kk_{rl}(\beta)}{\mu_l}\partial_y P_l,$	Darcy's Law-Liquid
$[J_i] = M^{-1}[\partial_y C_i]$	Maxwell Stefan Flux
$P_c = P_g - P_l = L(\beta),$	Leveret-like Capillary Pressure.
$\Gamma = \frac{\gamma_v}{L_p}(\beta)(C_v - C_{\text{sat}}(T)),$	Condensation-Saturation

Hydrophobicity

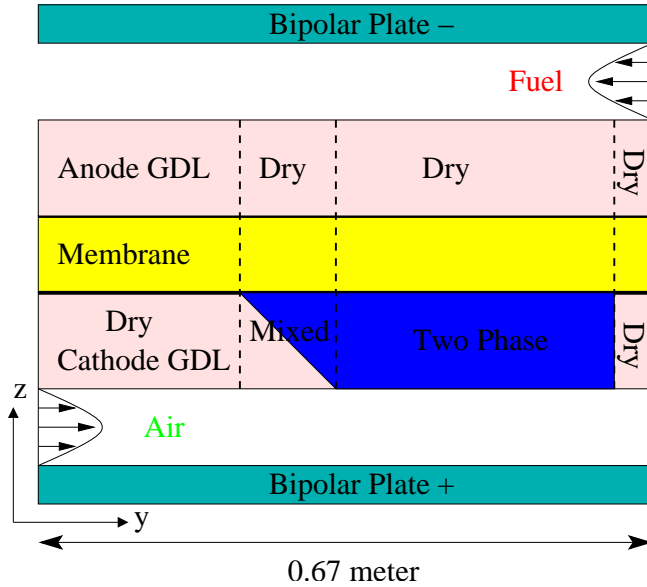
Capillary pressure and relative permeability form nonlinear diffusivity

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

$$\frac{\partial}{\partial t}(\beta) - D\partial_y(f(\beta)\partial_y\beta) = \Gamma/c_l$$



Boundary Conditions



Boundary I: Membrane-GDL	Boundary II: Channel-GDL
$\tilde{N}_o = \frac{\tilde{I}(x)}{4F}$	$\tilde{r}(\tilde{C}_o(0) - \bar{C}_o) = -\tilde{N}_o(0)$
$\tilde{N}_v = \tilde{N}_v^m$	$\tilde{r}(\tilde{C}_v(0) - \bar{C}_v) = -\tilde{N}_v(0)$
$\tilde{N}_n = 0$	$\tilde{r}(\tilde{C}_n(0) - \bar{C}_n) = -\tilde{N}_n(0)$
$\tilde{N}_l = \tilde{N}_w^m - \tilde{N}_v^m$	$\beta = 0$
$\tilde{N}_T = \tilde{N}_T^m - h_v \tilde{N}_v^m$	$\tilde{r}_T(\tilde{T}(0) - \bar{T}_c) = -\tilde{N}_T(0)$

Driving forces computed at higher iteration:

\tilde{N}_v^m	Flux of vapor into GDL
\tilde{N}_w^m	Total flux of water out of catalyst layer
\tilde{N}_T^m	Total heat production in catalyst layer
\tilde{I}	Local current density

Non-dimensional Forms

Nondimensionalize the variables. Choose temperature scale $T_* = \frac{h_v \bar{C}}{\rho_l c_l}$ so heat flux produced by evaporation balances the fluxes of water, setting the coefficient of Γ in the heat equation to one. Distance is scaled by the thickness L of the diffusion layer, time is scaled by $\tau_* = \frac{\epsilon L^2}{D}$, the characteristic diffusive time.

$$\begin{aligned} C_o &= \tilde{C}_o / \bar{C} & C_v &= \tilde{C}_v / \bar{C} & C_n &= \tilde{C}_n / \bar{C}, \\ T &= \tilde{T} / T_* & \tau &= t / \tau_* & z &= \tilde{z} / L, \end{aligned}$$

Collect the fluxes and unknowns

$$\vec{N} = (N_g, N_T, N_o, N_v, N_l)^t \quad \text{and} \quad \vec{V} = (C, T, C_o, C_v, \beta)^t$$

The full problem can be written as

$$\left(M(\vec{V}) \vec{V} \right)_\tau + \nabla \cdot \left(\mathcal{D}(\vec{V}) \nabla \vec{V} \right) = \vec{S} \Gamma,$$

where $\vec{S} = (-1, 1, 0, -1, 1)^t$ is the scaled stoichiometry vector for phase change and the matrix \mathcal{D} is given by

$$\mathcal{D} = - \left(\begin{array}{ccccc} R_g k_{rg} T C & R_g k_{rg} C^2 & 0 & 0 & 0 \\ \delta_l C_{lg} T^2 & \delta_l C_{lg} C T + R_T & 0 & 0 & R_c T f(\beta) \\ \left(R_g k_{rg} T - \frac{1}{C} \right) C_o & R_g k_{rg} C C_o & 1 & 0 & 0 \\ \left(R_g k_{rg} T - \frac{1}{C} \right) C_v & R_g k_{rg} C C_v & 0 & 1 & 0 \\ R_l \beta k_{rl}(\beta) T & R_l \beta k_{rl}(\beta) C & 0 & 0 & R_c f(\beta) / \delta_l \end{array} \right)$$

Scalings

$$I = \frac{\tilde{I}L}{4F\bar{C}D} \ll 1$$

Scaled current density approximately 10^{-2}

$$H = \frac{L^2\gamma_v}{D\bar{L}_p} \gg 1$$

Scaled phase change rate approximately 10^6

$$\delta_l = \frac{\bar{C}}{C_l} \ll 1$$

Ratio of gas to liquid molar concentrations 10^{-3}

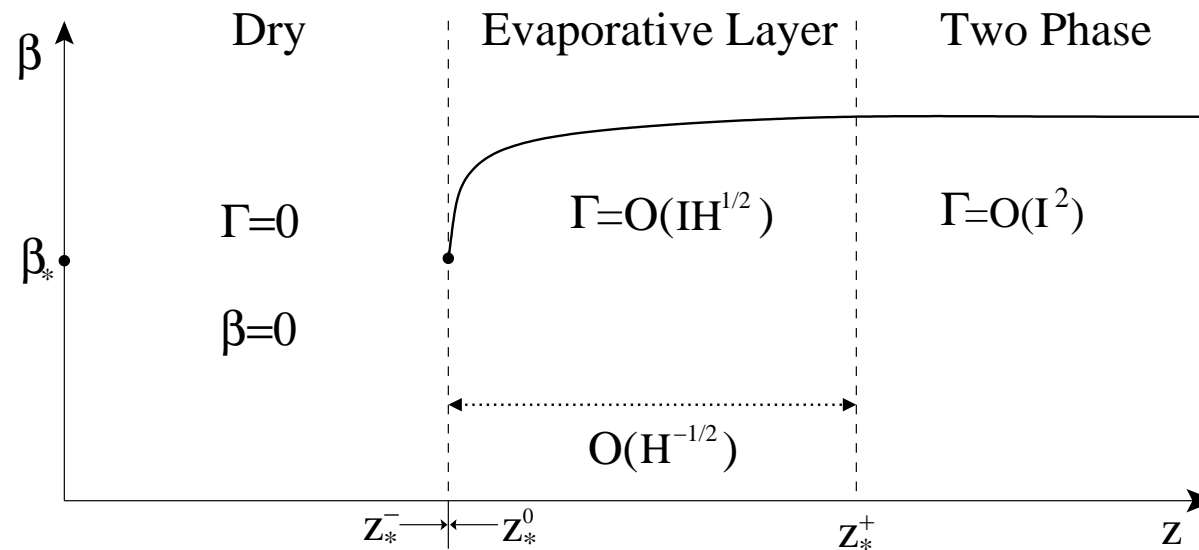
$$N_\alpha = \frac{L}{D\bar{C}}\tilde{N}_\alpha = O(I)$$

Scaled gas or liquid flux

$$N_T = \frac{L}{h_v\bar{C}D}\tilde{N}_T = O(I)$$

Scaled heat flux

Break domain into dry, two-phase, and boundary layer $O(I/\sqrt{H})$



Dry Regime

No liquid water ($\beta = 0$) and no phase change $\Gamma = 0$. The unknowns $\vec{V} = (C, T, C_o, C_v)^t$ are expanded

$$\vec{V} = \vec{V}(0) + I\vec{V}^1 + O(I^2).$$

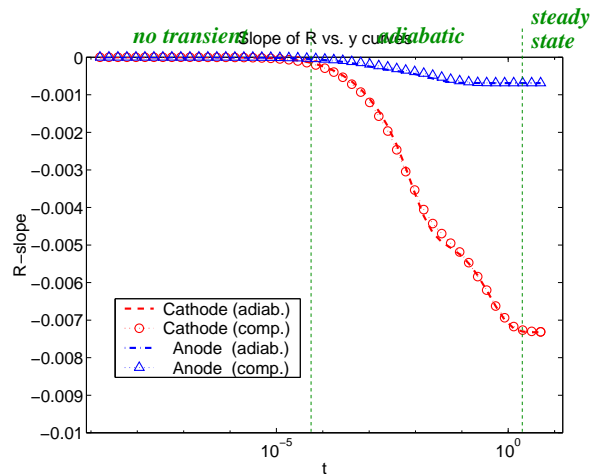
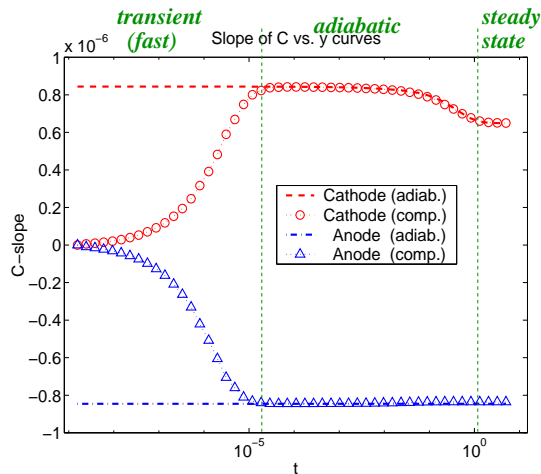
The conservation laws

$$(M(\vec{V})\vec{V})_\tau + \nabla \cdot (\mathcal{D}(\vec{V})\nabla\vec{V}) = 0,$$

are expanded as

$$M(\vec{V}(0))\vec{V}_\tau^1 + \mathcal{D}(\vec{V}(0))\Delta\vec{V}^1 = O(I).$$

The matrix $M^{-1}\mathcal{D}(\vec{V}(0))$ has eigenvalues with ratio $O(10^5)$. Time scales from 10^{-6} seconds down to 10^{-1} second.



Convection dominates the gas flow, but balances diffusion at equilibrium

Two-Phase Regime

In the two-phase regime the liquid water is everywhere greater than the immobile volume fraction, β_* , and the gas is saturated to leading order. As in the dry regime, the scaled variables $\vec{V}^w = (C^1, T^1, C_o^1, C_v^1, \beta^1)^t$ describe variations from the channel values, except for the scaled water vapor and water volume fractions, which describe variations from the saturation pressure and the immobile volume fraction respectively,

$$\begin{aligned} C &= 1 + C^1 I / T_c, & T &= T_c + T^1 I, & C_o &= X_o + C_o^1 I, \\ C_v &= C_{sat}(T) + C_v^1 I / H, & \beta &= \beta_* + \beta^1 (I \delta_l)^{\frac{2}{3}}. \end{aligned}$$

The equation for vapor flux is degenerate at leading order – At steady-state

- Phase change is $O(I^2)$ in the two-phase layer – fluxes are constant
- The vapor flux within the two-phase region is determined at leading order by the temperature profile

$$N_v = -D \nabla C_v \approx -D C'_{sat}(T) \nabla T$$

but

$$-\kappa \nabla T = N_T \approx \alpha_h I$$

while

$$N_w^m = \frac{I}{2F}$$

so that

$$\frac{N_v}{N_w^m} \approx \frac{D}{\kappa} C'_{sat}(T) \alpha_h 2F$$

The Evaporative Layer

- The leading order phase change occurs in the evaporative layer.
- The free boundary evolution is determined by the total phase change, expressed in terms of Θ_* , the degree of vapor undersaturation at the two-phase point z_*^-

$$\Theta_* = \frac{\sqrt{H}}{I} \left(C_{sat}(T(z_*^-)) - C_v(z_*^-) \right)$$

Rescale as in the two-phase region, except for the water vapor molar concentration

$$\begin{aligned} C &= 1 + \frac{C^1 I}{T_c}, & T &= T_c + T^1 I, & C_o &= X_o + C_o^1 I, \\ C_v &= C_{sat}(T) + \frac{C_v^1 I}{\sqrt{H}}, & \beta &= \beta_* + (\delta_l I)^{\frac{2}{3}} \beta^1, & \tilde{z} &= (z - z_0^*) \sqrt{H}. \end{aligned}$$

Thinness of bdry layer leads to very fast relaxation time scales. The quasi-steady version of the conservation laws

$$\vec{N}_{\tilde{z}} = \frac{\Gamma}{\sqrt{H}} \vec{S} = I H^{\frac{1}{2}-\alpha} C_v^1 h_* \vec{S}.$$

Fluxes are related to the scaled variables $\vec{V}^b = (C^1, T^1, C_o^1, C_v^1, \beta^1)$ through the constitutive laws as

$$\vec{N} = I \sqrt{H} \mathcal{D}^b \vec{V}_{\tilde{z}}^b + O(I^2 \sqrt{H})$$

where the 5×5 matrix \mathcal{D}^b is given by

$$\mathcal{D}^b = - \begin{pmatrix} R_g k_{rg} & R_g k_{rg} & 0 & 0 & 0 \\ C_{lg} \delta_l T_c & C_{lg} \delta_l T_c + R_T & 0 & 0 & R_c T_c \delta_l \\ \left(R_g k_{rg} - \frac{1}{T_c} \right) C_o & R_g k_{rg} C_o & 1 & 0 & 0 \\ \left(R_g k_{rg} - \frac{1}{T_c} \right) X_s & R_g k_{rg} X_s + X'_s & 0 & \frac{1}{H^\alpha} & 0 \\ 0 & 0 & 0 & 0 & R_c \end{pmatrix}$$

The conservation laws and the constitutive relations yield a 5×5 system

$$\mathcal{D}^b \vec{V}_{\tilde{z}\tilde{z}} = \frac{h_* C_v^1}{H^\alpha} \vec{S} + O(I).$$

Observe that

$$\frac{1}{H^\alpha} [\mathcal{D}^b]^{-1} \vec{S} = \xi_v \vec{S}_0 + O(H^{-\alpha})$$

where $\vec{S}_0 = (0, 0, 0, 1, 0)^t$ and the parameter ξ_v is independent of H and strictly positive.

The equation for C_v^1 **uncouples at leading order**,

$$\begin{aligned} (C_v^1)_{\tilde{z}\tilde{z}} &= \xi_v h_* C_v^1, \\ \lim_{\tilde{z} \rightarrow \infty} C_v^1(\tilde{z}) &= 0, \\ C_v^1(0) &= \frac{H^\alpha \Theta_*}{I}. \end{aligned}$$

This has a classic boundary layer solution,

$$C_v^1 = C_v^1(0) e^{-\sqrt{h_* \xi_v} \tilde{z}}.$$

The jump in fluxes across the boundary layers is determined as function of undersaturation, Θ_* , at dry edge

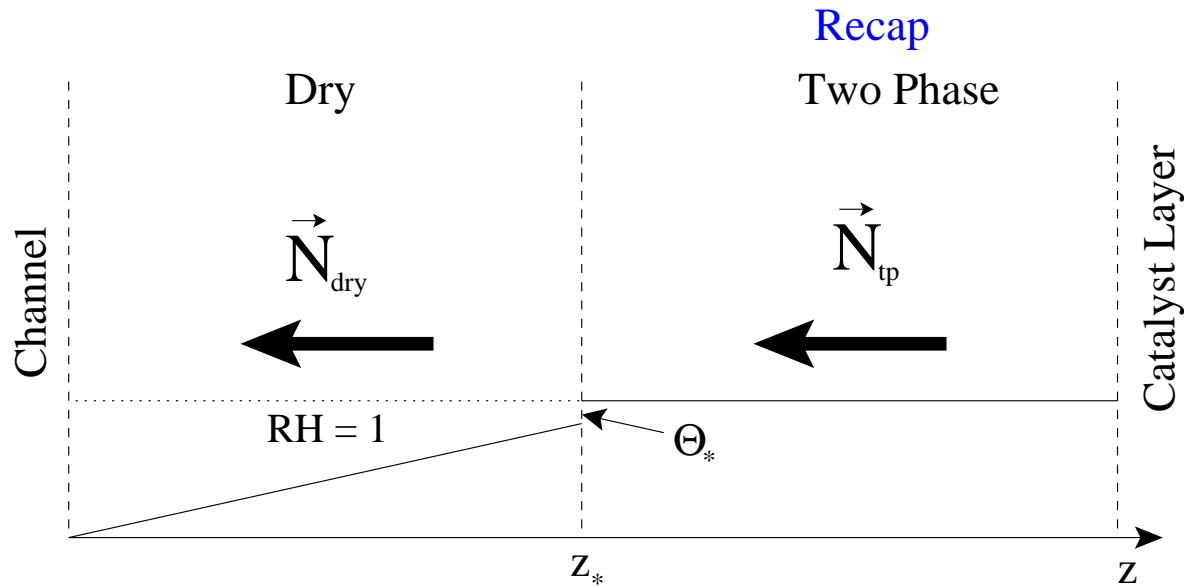
$$[[\vec{N}]] = -I\Theta_* \sqrt{\frac{h_*}{\xi_v}} \vec{S}.$$

Taking the dry and two-phase problem at quasi-steady state, obtain the interface motion as a degenerate Rankine-Hugoniot relation

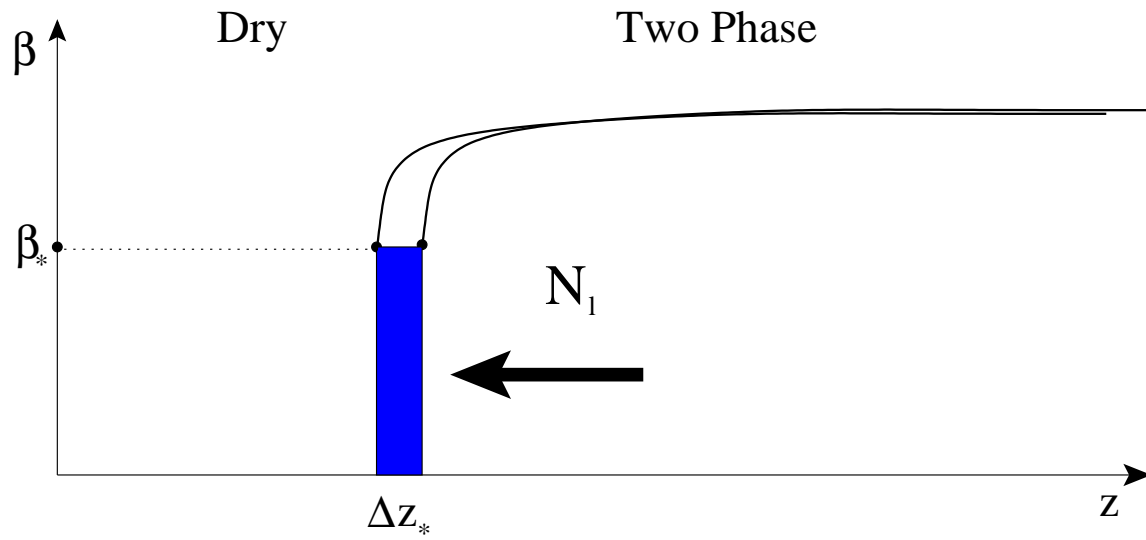
$$\frac{dz_*}{d\tau} = \delta_l \frac{[[N_l]]}{[[\beta]]} = \frac{\delta_l N_l(z_*^0)}{\beta_*}$$

The liquid flux into the front serves to propagate the front.

The front propagation is the slowest time scale in the system, as it requires the production of quantities of liquid water.

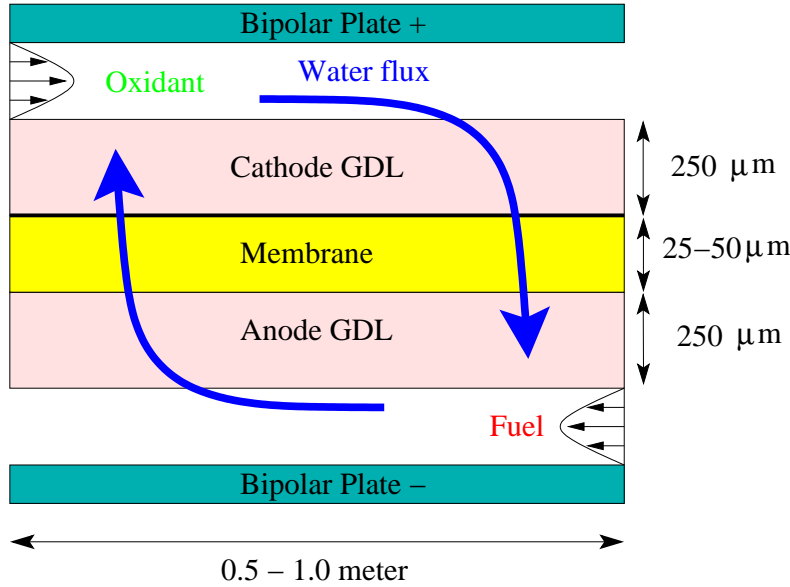


Jump in fluxes across bdry layer is determined by the undersaturation on dry side of two-phase interface



$$\beta_* \Delta z_* = N_1 \Delta \tau \delta_1$$

Quasi-Steady Along the Channel



Cathode Oxygen flux	$Q_{c,o}(x)$
Cathode Vapor flux	$Q_{c,v}(x)$
Cathode Nitrogen flux	$Q_{c,n}(x)$
Water cross-over/proton	$\alpha(x)$ (An. \rightarrow Cath.)
Anode Hydrogen flux	$Q_{a,h}$
Anode Vapor flux	$Q_{a,v}$
Coolant Temp.	T_{col}
Reservoir Temp.	T_r

$$\frac{dQ_{c,o}}{dx} = -\frac{I(x)L_w}{4F},$$

$$C_{c,o} = \frac{P_c}{\mathcal{R}T_c(x)} \frac{Q_{c,o}}{Q_{c,o} + Q_{c,v} + Q_{c,n}},$$

$$\frac{dQ_{c,v}}{dx} = (1 + \alpha(x)) \frac{I(x)L_w}{2F},$$

$$C_{c,v} = \text{Min} \left\{ \frac{P_c}{\mathcal{R}T_c(x)} \frac{Q_{c,v}}{Q_{c,o} + Q_{c,v} + Q_{c,n}}, \frac{P_{\text{sat}}(T_c)}{\mathcal{R}T_c(x)} \right\},$$

$$\frac{dQ_{c,n}}{dx} = 0,$$

$$C_{c,n} = \frac{P_c}{\mathcal{R}T_c(x)} \frac{Q_{c,n}}{Q_{c,o} + Q_{c,v} + Q_{c,n}},$$

$$\frac{dQ_{a,h}}{dx} = \pm \frac{I(x)L_w}{2F},$$

$$C_{a,h} = \frac{P_a}{\mathcal{R}T_a(x)} \frac{Q_{a,h}}{Q_{a,h} + Q_{a,v}},$$

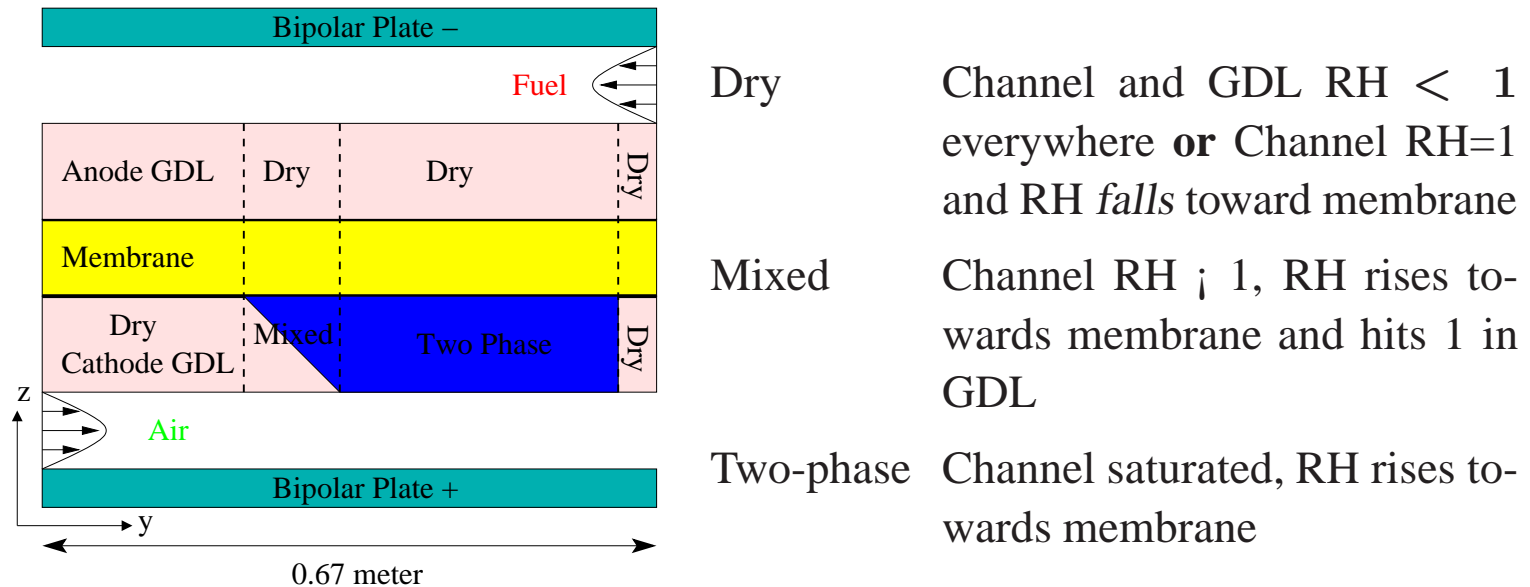
$$\frac{dQ_{a,v}}{dx} = \pm \alpha \frac{I(x)L_w}{2F},$$

$$C_{a,v} = \text{Min} \left\{ \frac{P_a}{\mathcal{R}T_a(x)} \frac{Q_{a,v}}{Q_{a,h} + Q_{a,v}}, \frac{P_{\text{sat}}(T_a)}{\mathcal{R}T_a(x)} \right\},$$

$$\frac{\partial}{\partial t} (\rho c T_{col}) + \partial_x (\rho c T_{col} v_g) = N_T L_w, \quad T_{col}(0, t) = T_r(t),$$

$$\frac{dT_r}{dt} = q(T_{col}^{\text{out}} - T_r) - r(T_r - T_{\text{amb}})$$

Steady-State Regimes

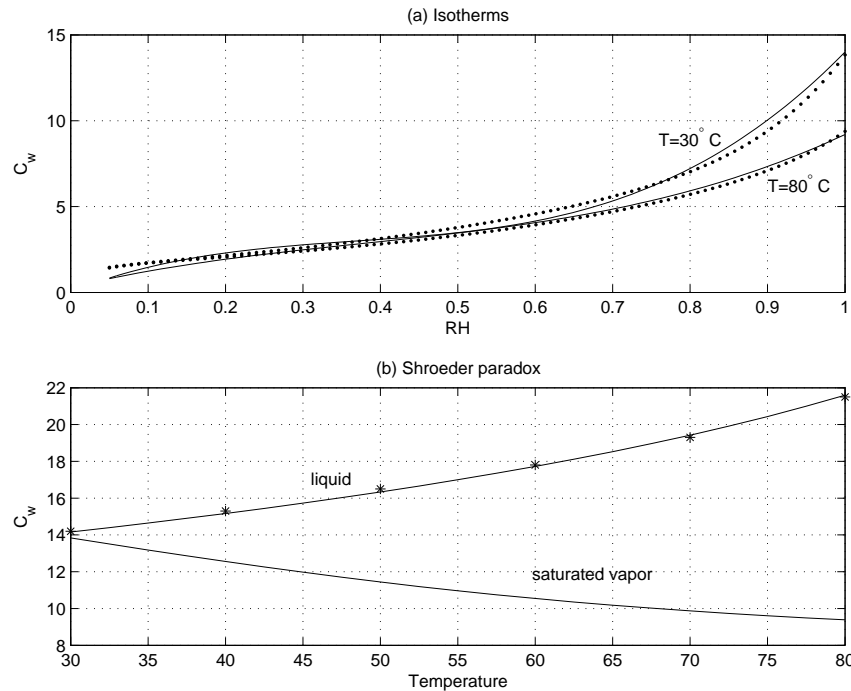


Transients

All transients are associated to build up of liquid water, $\delta_l \ll 1$ or to accumulation of heat in the external radiator. All other processes at steady-state.

- Slow motion of wetting front in GDL
- Build up of water in membrane
- Build up of heat in reservoir

Major Open Issue



If the anode channel is dry but almost saturated (typical) and the cathode channel is saturated and the GDL is two-phase (typical) then most models predict a water flux across the membrane, from cathode to anode, that is sufficiently high to saturate the anode.

Fixes

- Degenerate diffusion (Weber or Brutal)
- Artificially constrain membrane water content (Ugly)
- Increase the water drag, and include impact of membrane compression on water uptake (Igor – related to Ugly)

References

P. Berg, K. P., J. St. Pierre, J. Stumper, B. Wetton, “Water management in PEM fuel cells”, *J. Electrochem. Soc.* **151** (No. 3) (2004) A341-A354.

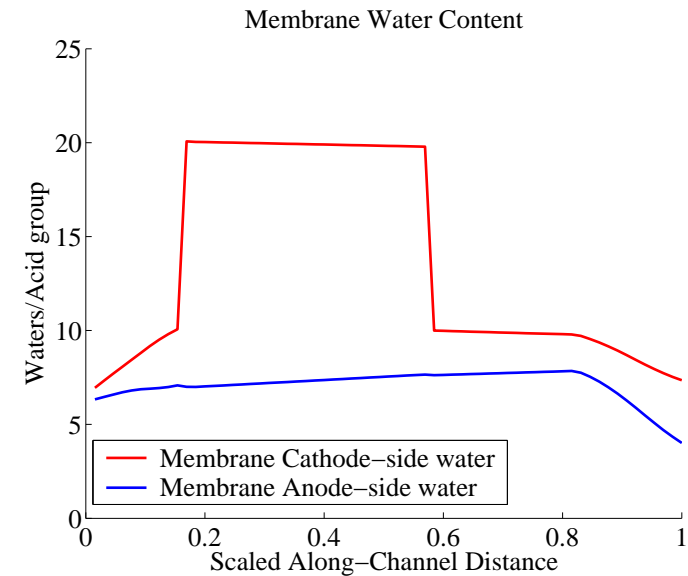
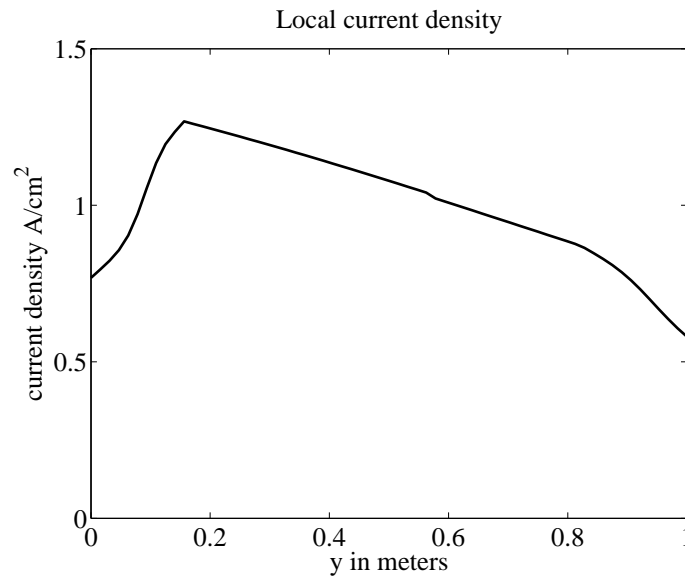
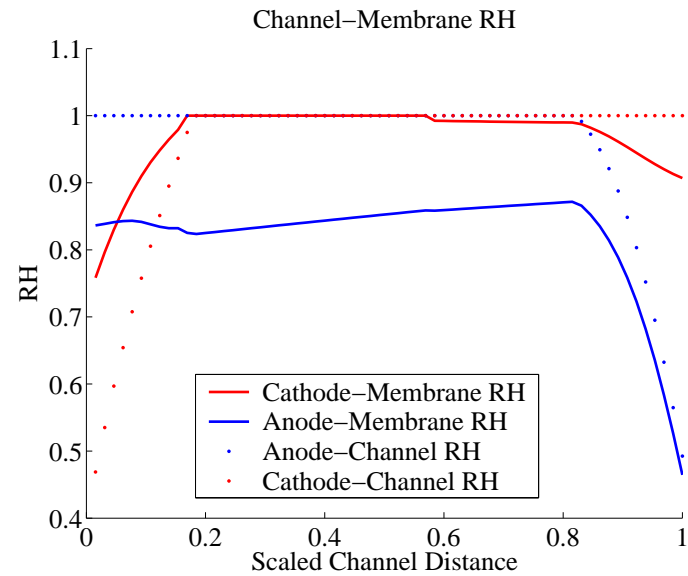
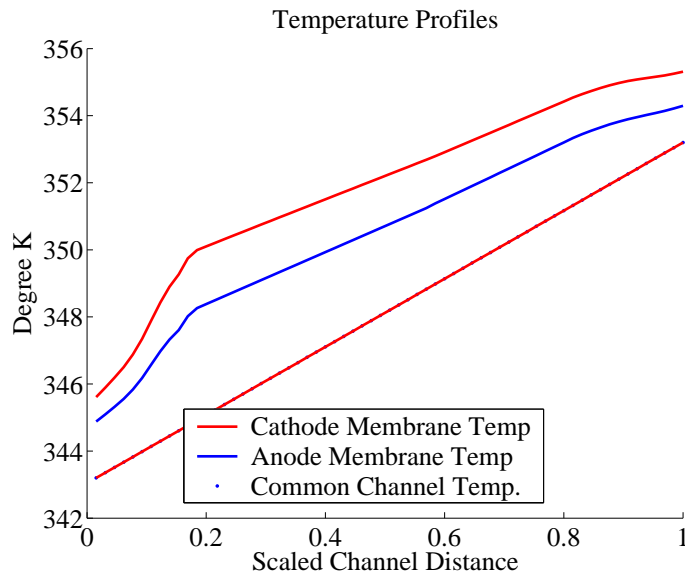
K. P., J. Stockie, B. Wetton, “A Sharp Interface Reduction for Multiphase flow in a Porous PEM Fuel Cell Electrode”, *Proc. Roy. Soc. London: Series A* **462** No. 2067 (2006).

Steady-State Simulations

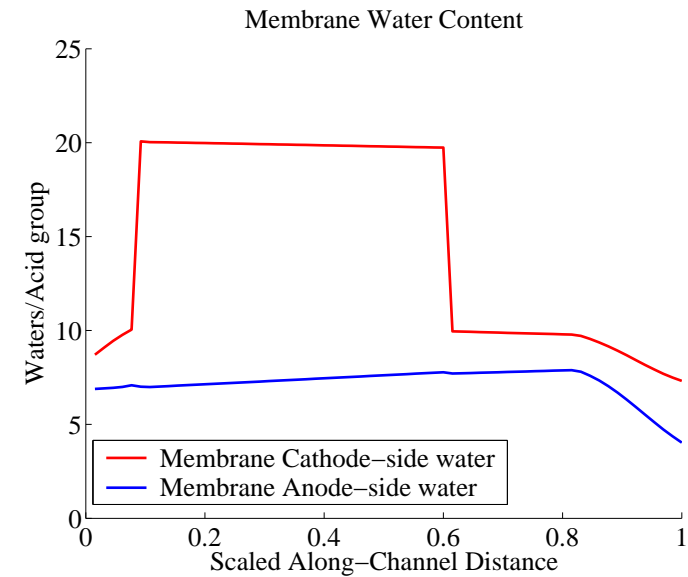
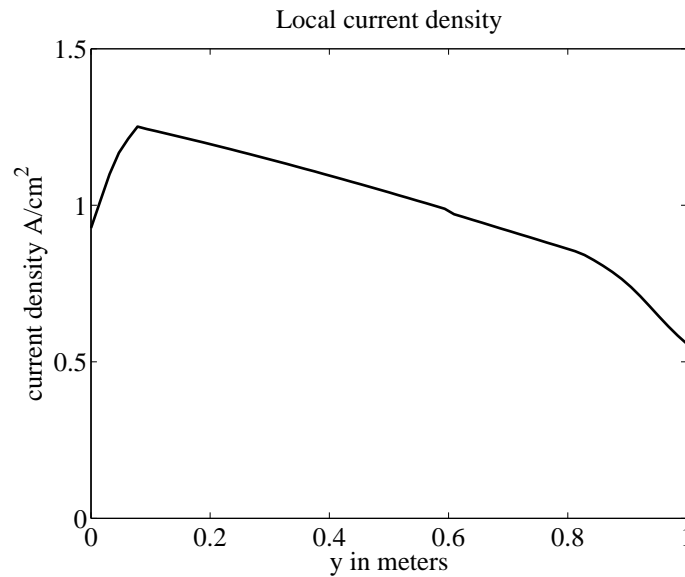
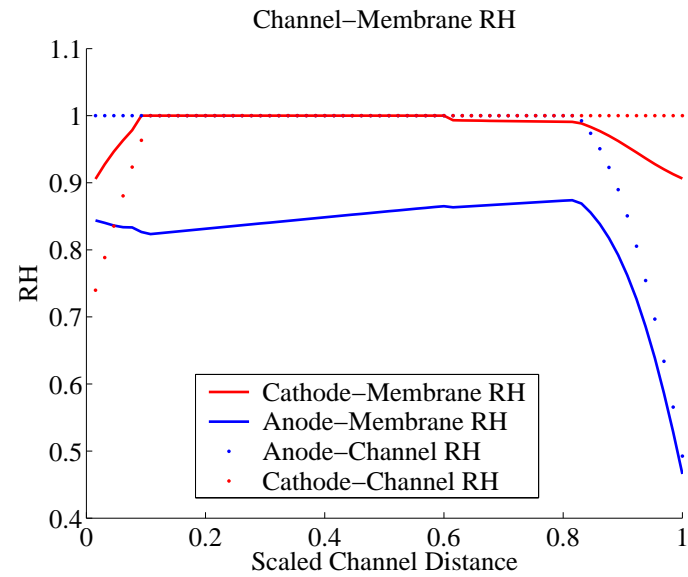
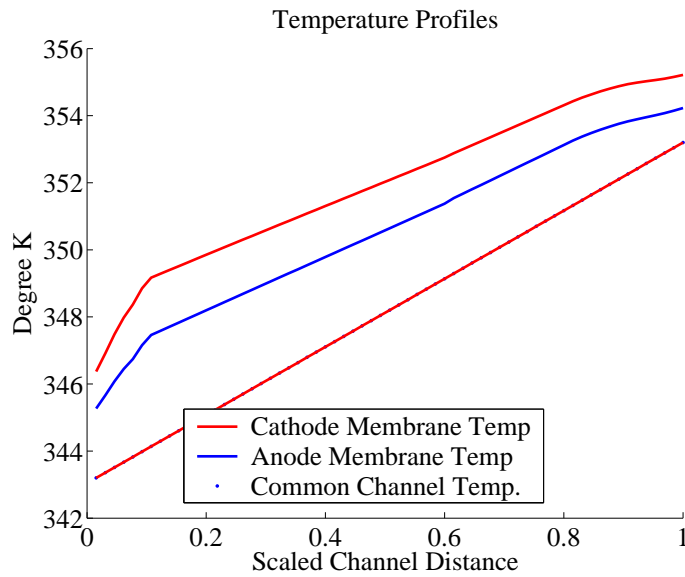
Use degenerate diffusion in membrane

Do not include membrane compression effects

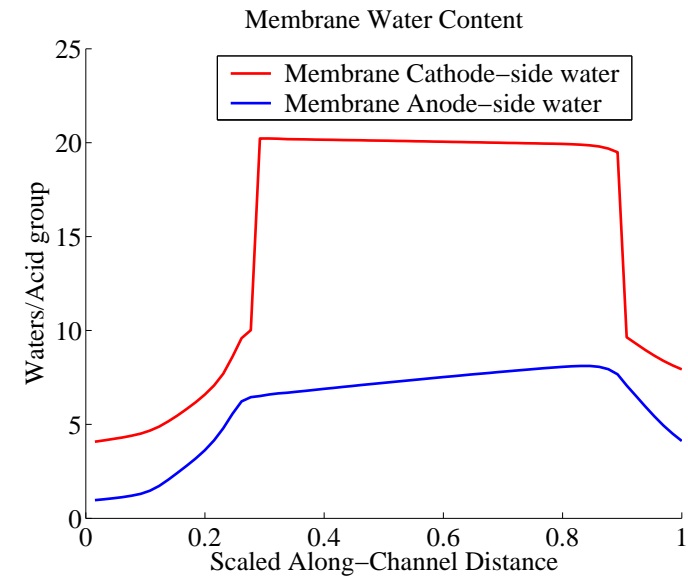
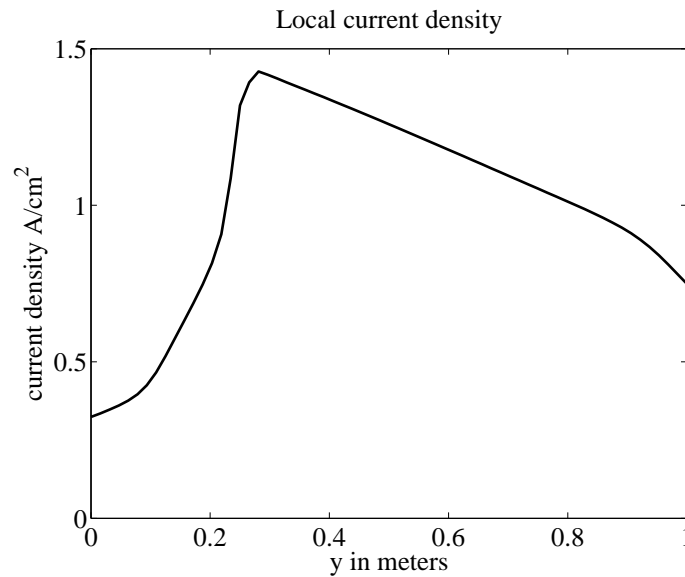
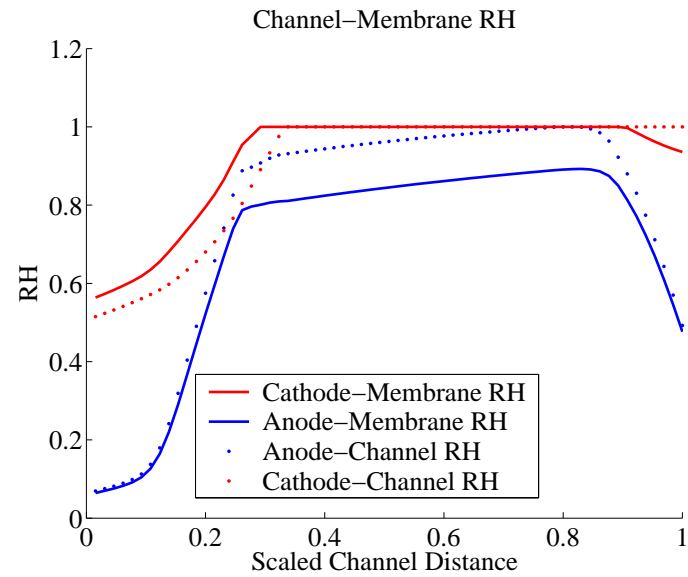
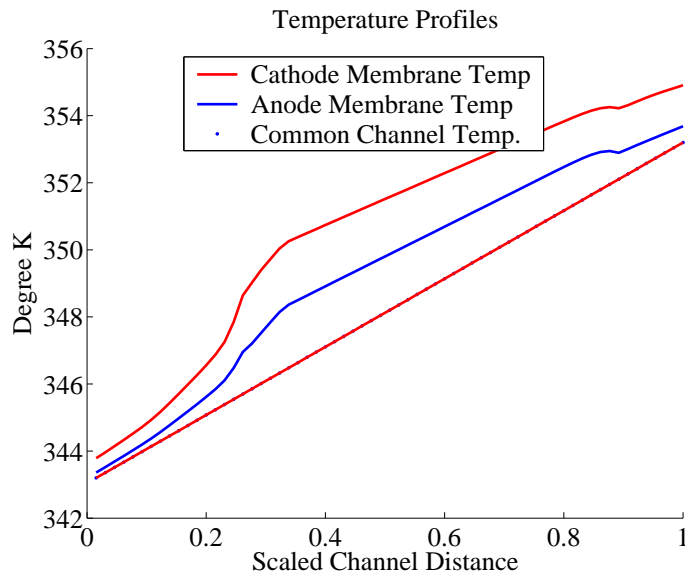
Prescribes coolant thermal profile



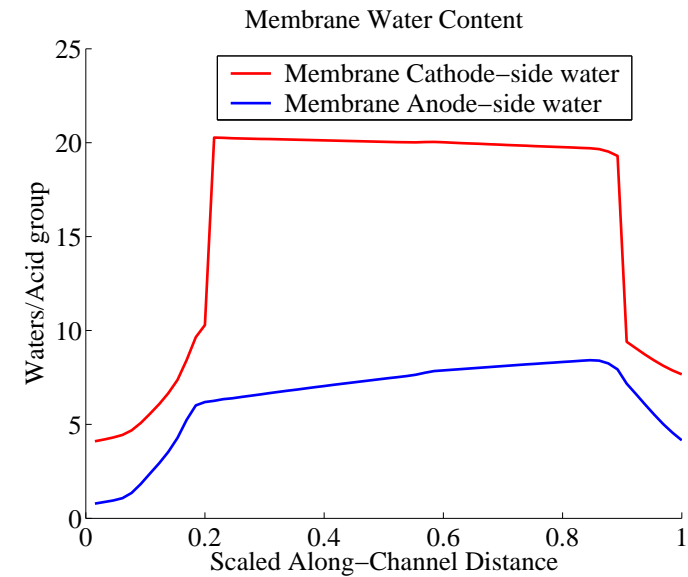
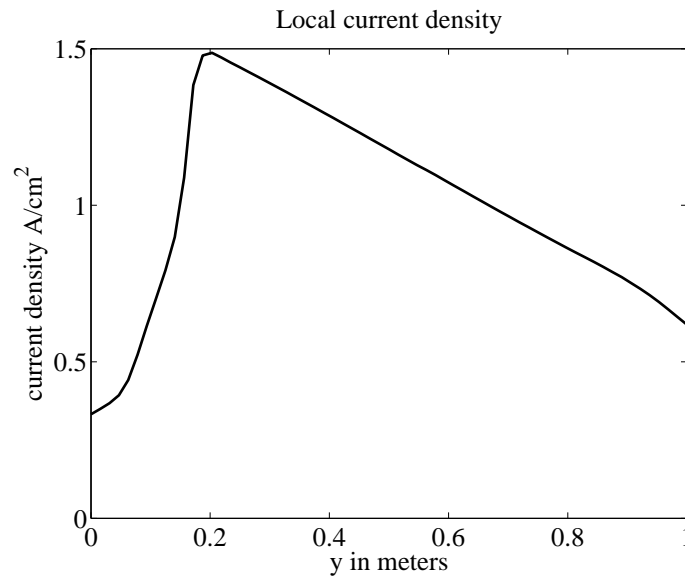
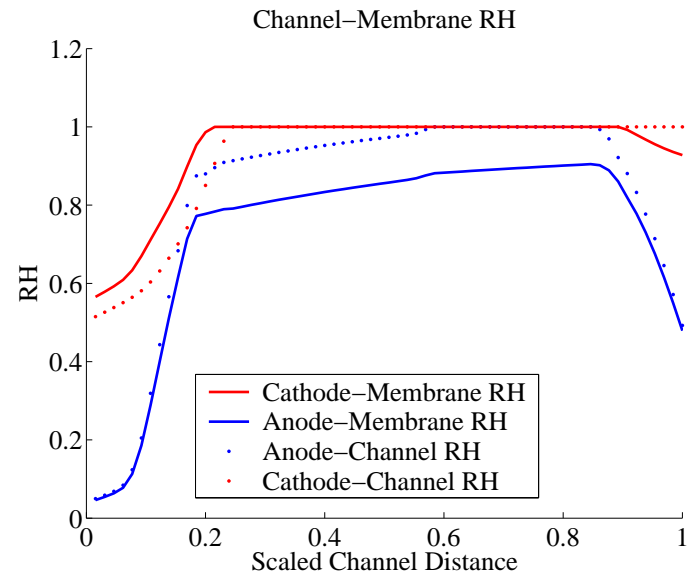
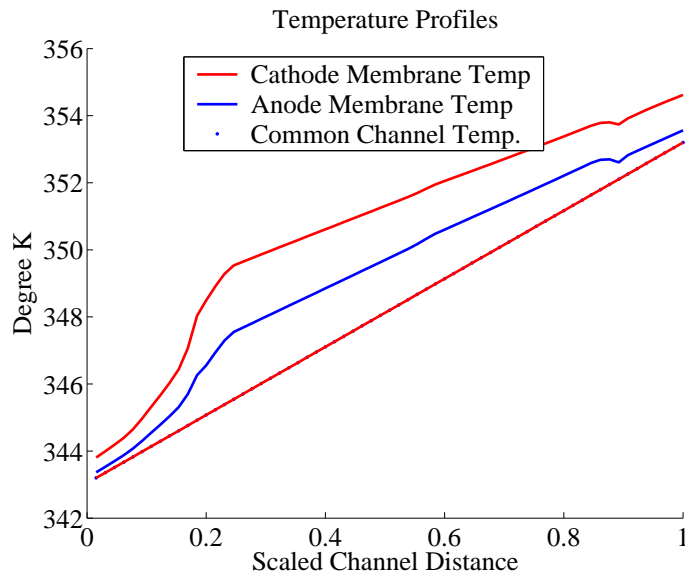
An/Cat. inlet dew point 63/53C. GDL thermal cond. 1W/(m K).
 Voltage 0.6489 at 1 Amp/cm².
 An/Cat. stoich 1.2/1.8, Pressure 2.2/2.0 barg.



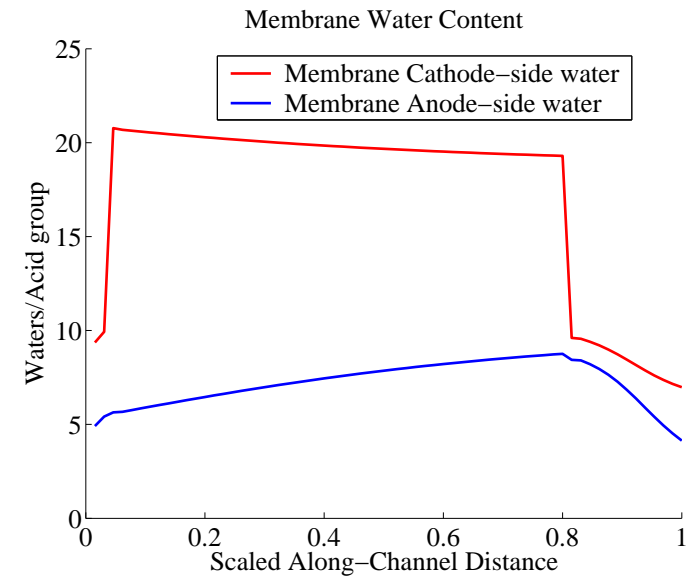
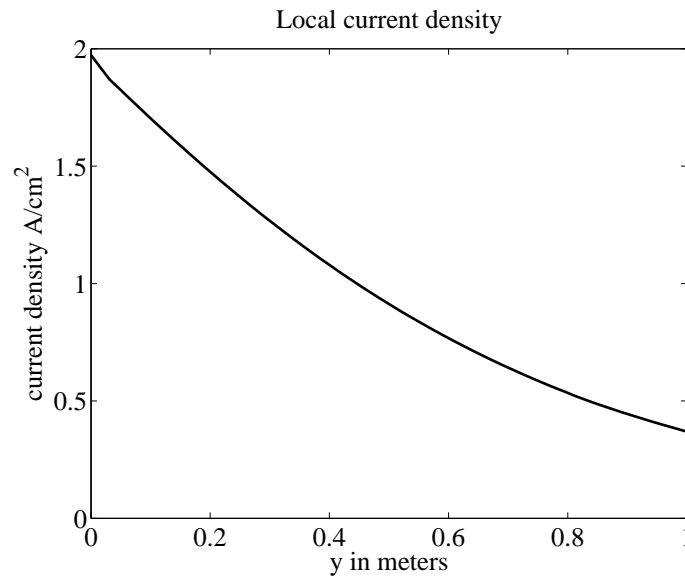
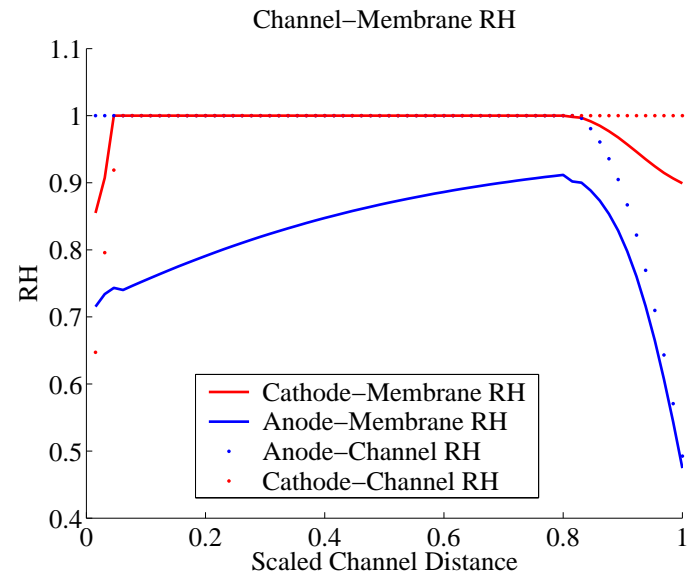
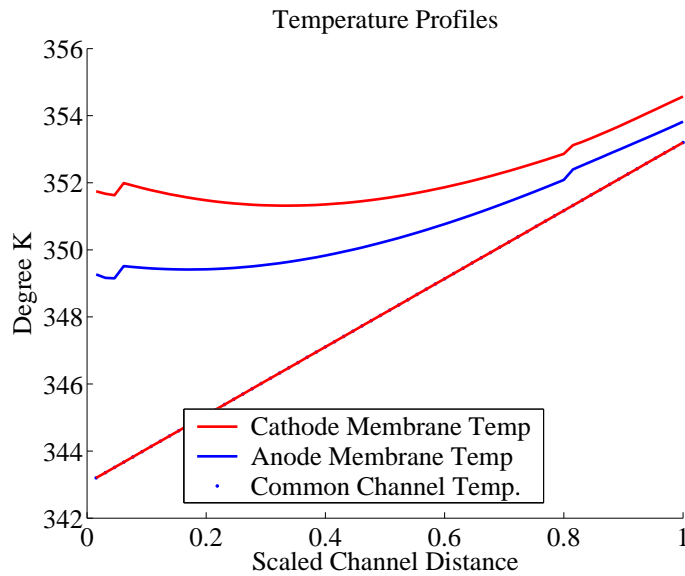
An/Cat. inlet dew point 63/63C. GDL thermal cond. 1W/(m K).
 Voltage 0.6539 at 1 Amp/cm².
 An/Cat. stoich 1.2/1.8, Pressure 2.2/2.0 barg.



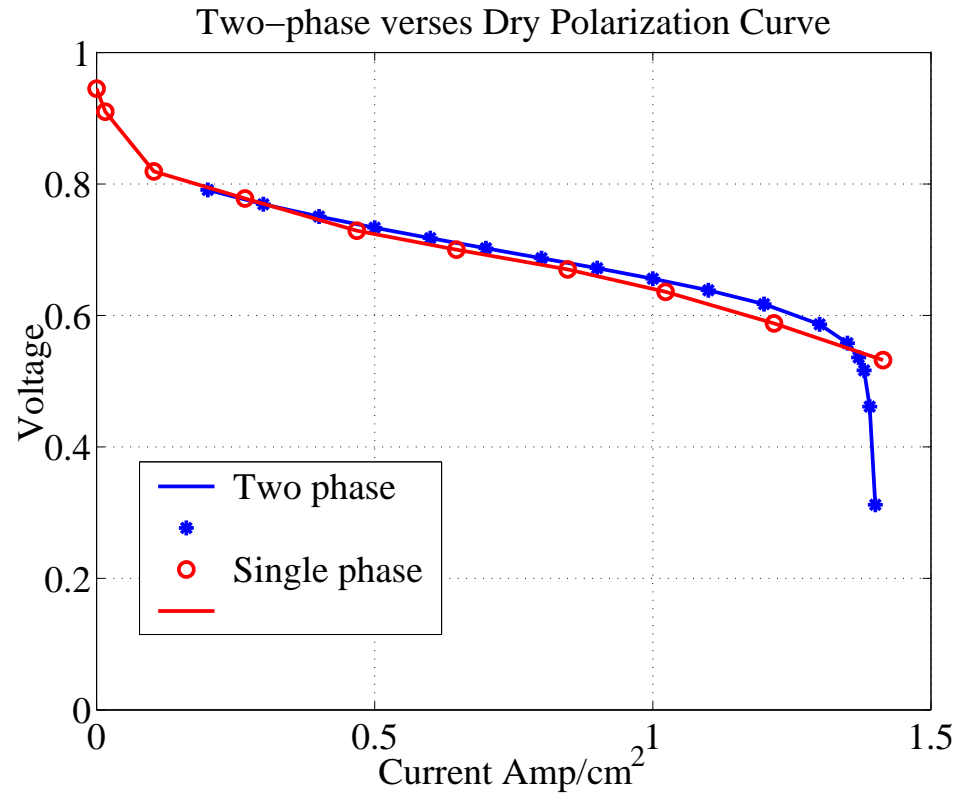
An/Cat. inlet dew point 63/55C, GDL thermal cond. 2W/(m K).
 Voltage 0.6261 at 1 Amp/cm².
 An/Cat. stoich 1.2/1.8, Pressure 2.2/2.0 barg.



An/Cat. inlet dew point 63/55C, GDL thermal cond. 2W/(m K).
 Voltage 0.6179 at 1 Amp/cm².
 An/Cat. stoich 1.2/1.5, Pressure 2.2/2.0 barg. (Slower gas flow)

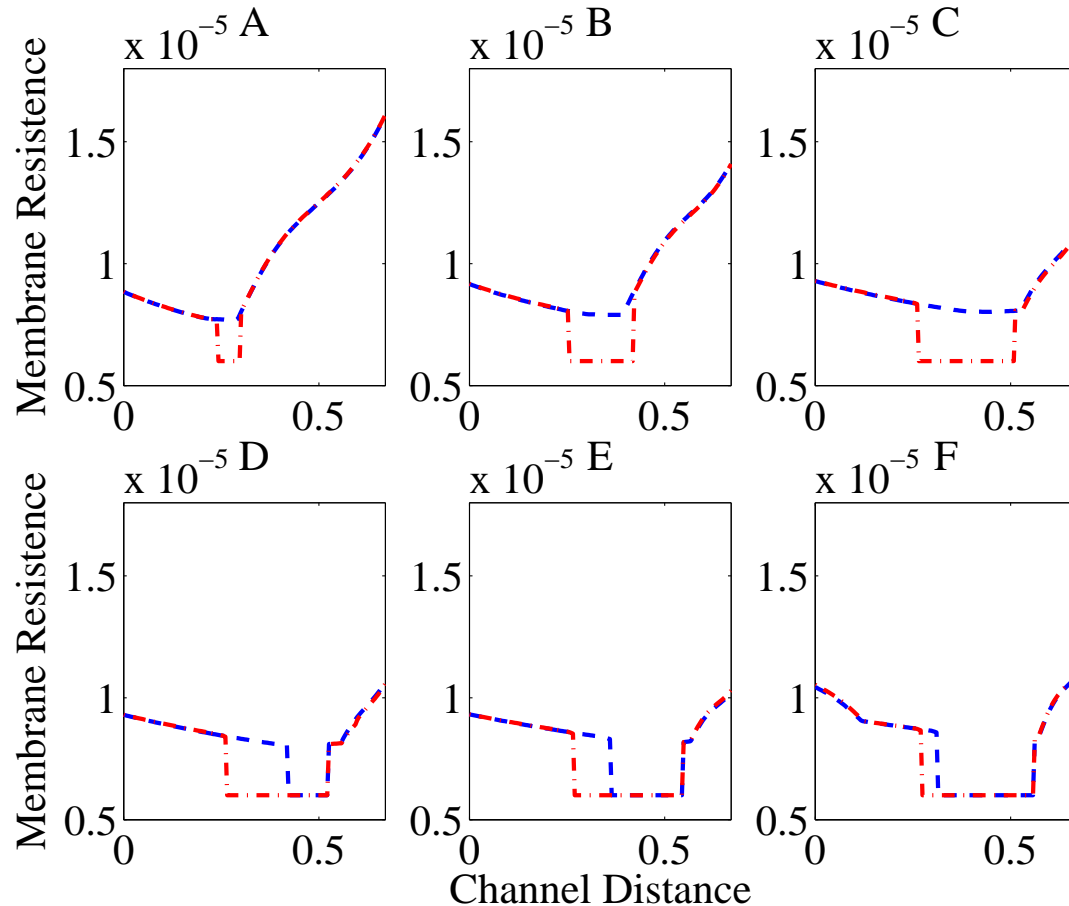


An/Cat. inlet dew point 63/60C. GDL thermal cond. 2W/(m K).
 Voltage 0.4108 at 1 Amp/cm².
 An/Cat. stoich 1.2/1.2, Pressure 2.2/2.0 barg.



Polarization curves for Cathode/Anode dew point 66C. The mobility of the two-phase region within the unit cell enhances current non-uniformity and induces an earlier knee.

Steady-State Hysteresis & Lateral Diffusion



Membrane resistance versus channel position for six different current densities, running from 1.6 A/cm^2 (A) down to 0.7 A/cm^2 . Figures show two different steady-state configurations. Low membrane resistance corresponds to liquid equilibrated membrane

Transient Unit Cell Simulation

$T_r(0) = 70C, T_{amb} = 25C, I = 1A/cm^2, An/Cath\ press.=2.2/2\ barg, Stoich\ 1.2/1.8$

40C 0 to 100 seconds

Inlet Dew Point 65C 100 to 200 seconds

40C 200 to 400 seconds

