

# Materials for a Sustainable Energy Future

IPAM – Tutorials

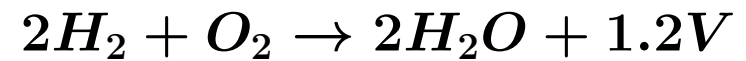
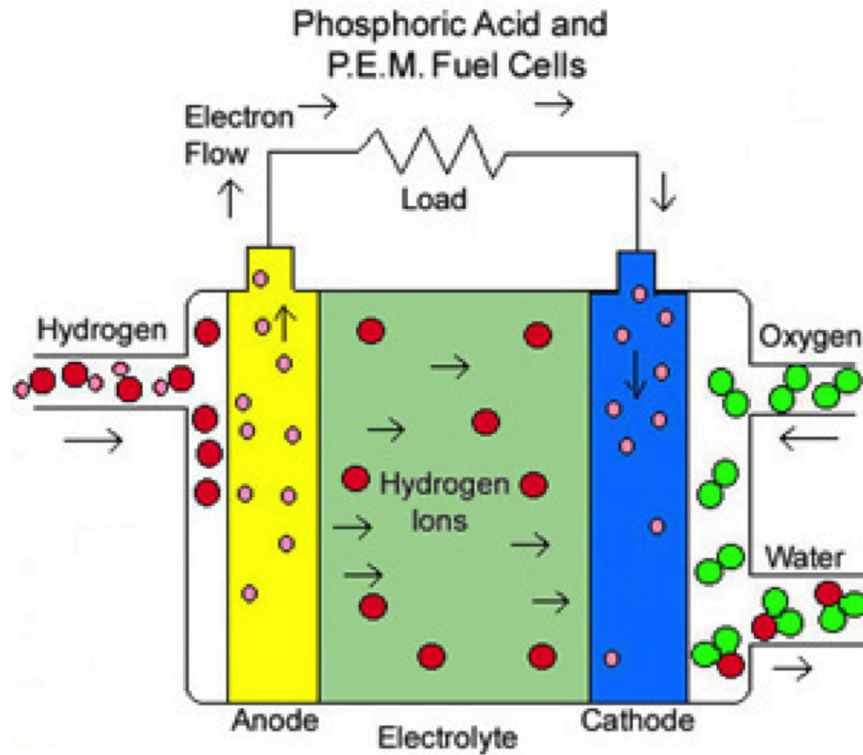
Sept 10-12, 2013

## Continuum Models of PEM Fuel Cells

Keith Promislow



## PEM Fuel Cell: Macroview



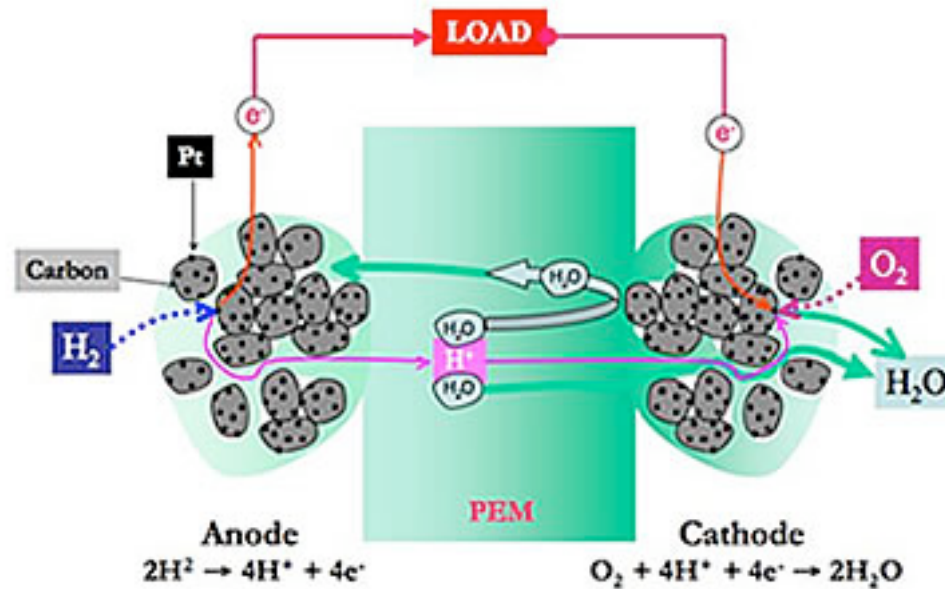
Volts = Energy/electron

This is the WRONG reaction

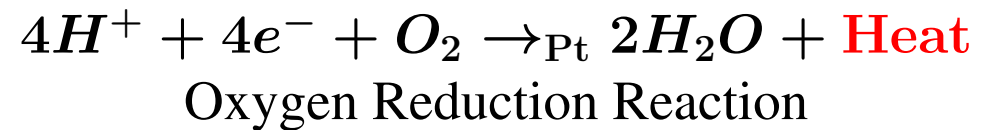
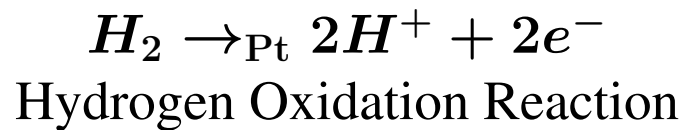
# Opps



## Half-Reactions in PEM Fuel Cells

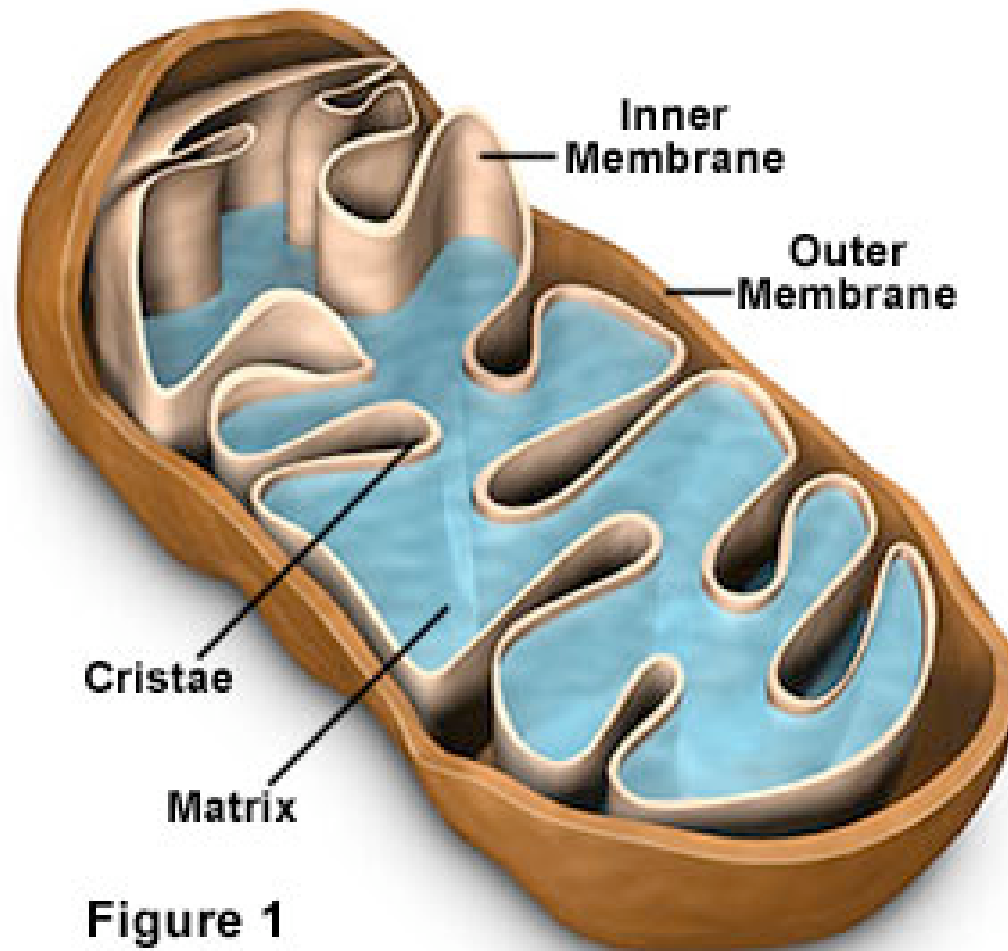


Schematic of Proton Exchange Membrane (PEM) Fuel Cell



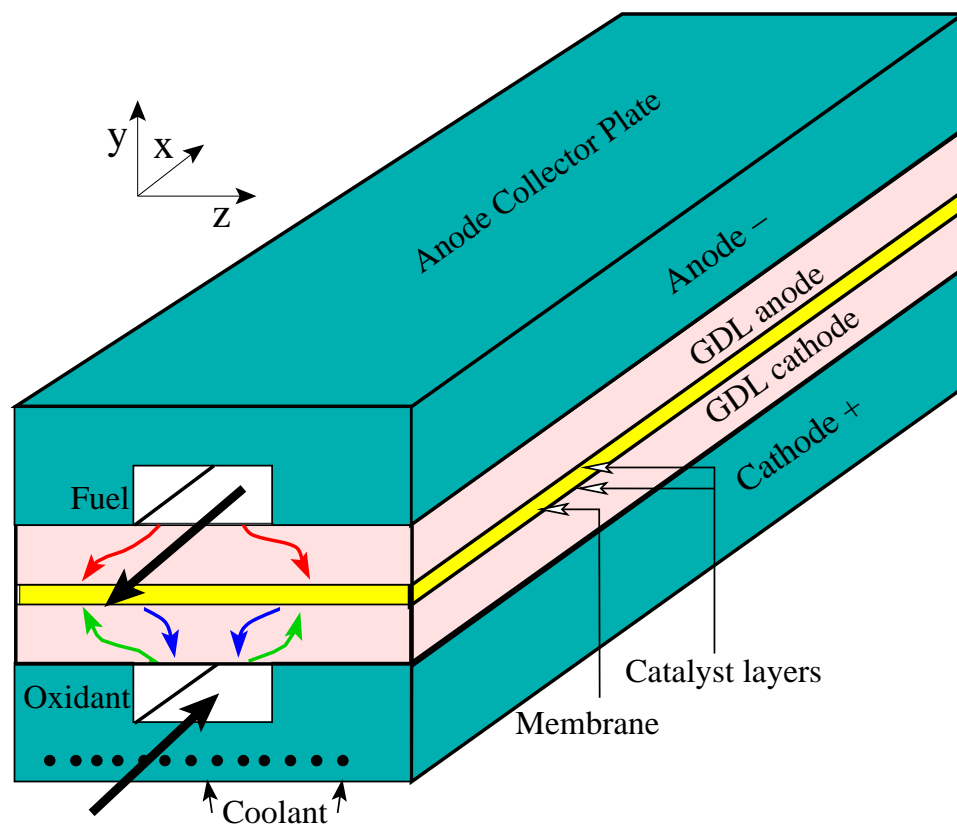
# Other Types of Fuel Cells

## Mitochondria Inner Structure



**Figure 1**

## 3D View of a PEM Fuel Cell



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

The anode reaction



The cathode reaction



## Along-the-Channel Slice

### Dimensionless Quantities

Cathode (Air) Stoich

$$S_c = \frac{Q_{O_2}}{I_T / (4F)}$$

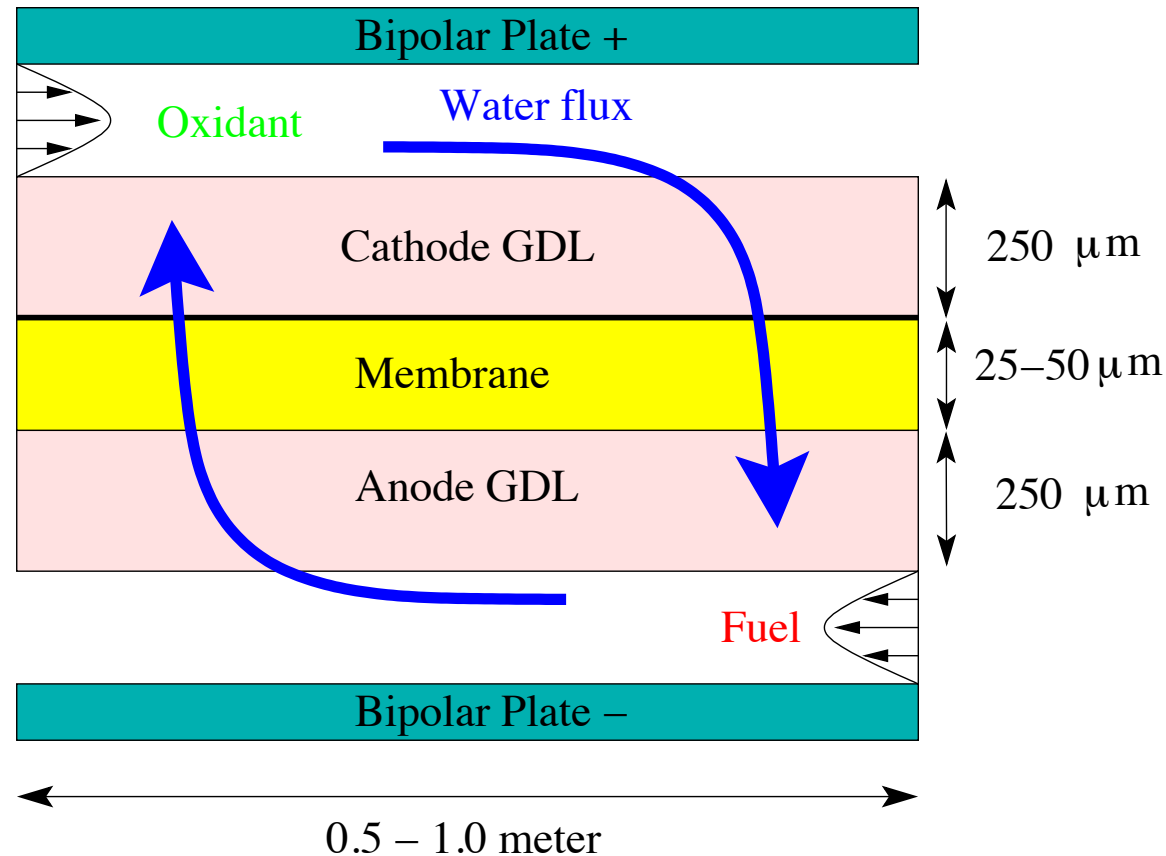
Anode (Fuel) Stoich

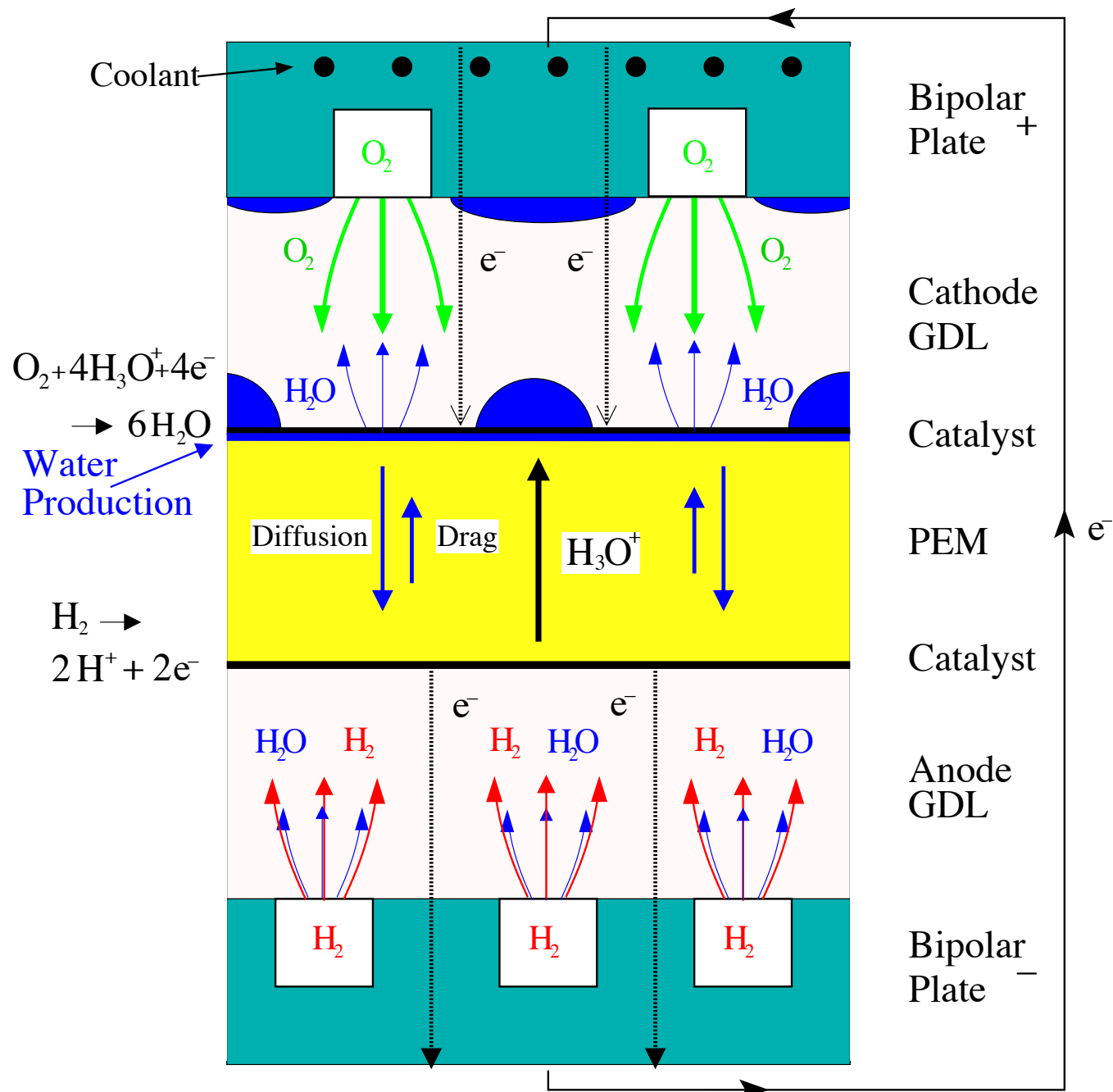
$$S_a = \frac{Q_{H_2}}{I_T / (2F)}$$

Local Water transfer

$$\alpha = \frac{J_w}{I / (2F)}$$

Aspect ratio 2000 : 1

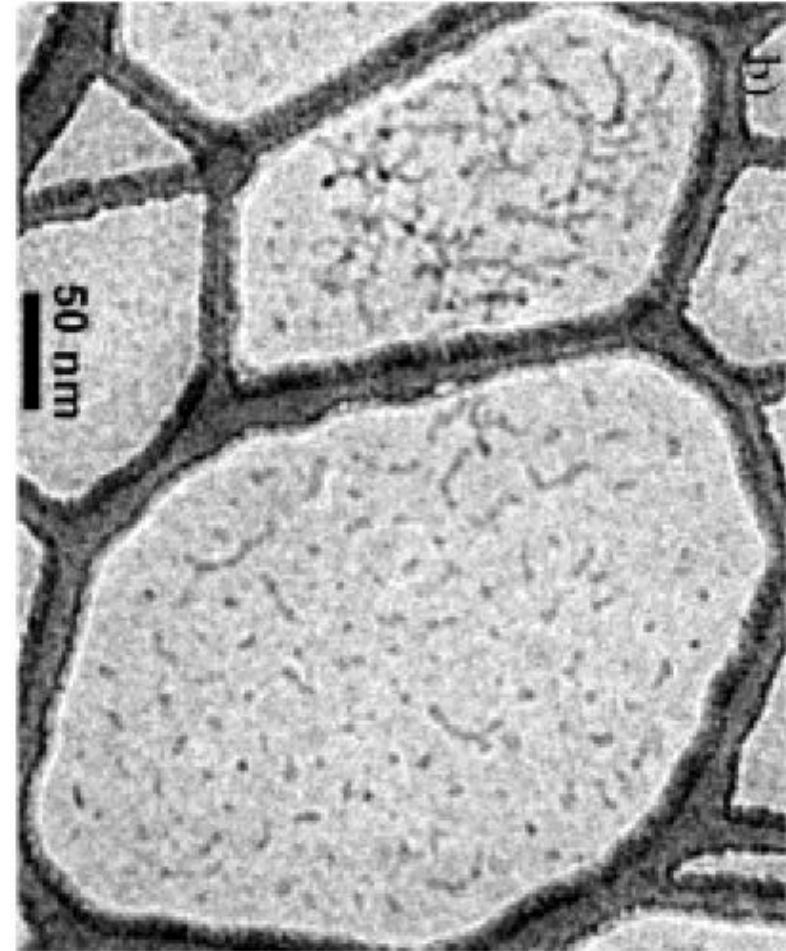
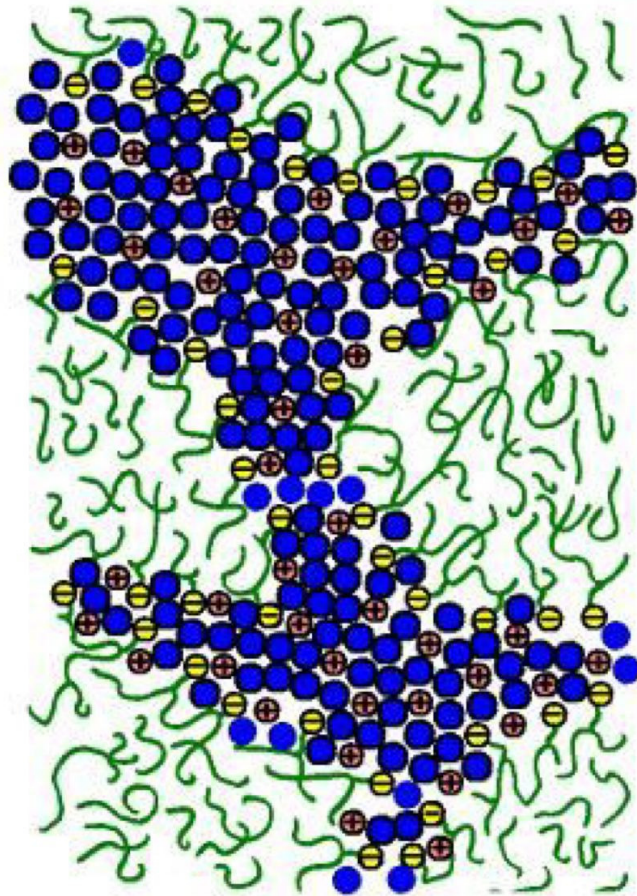
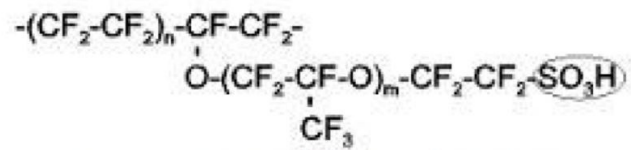




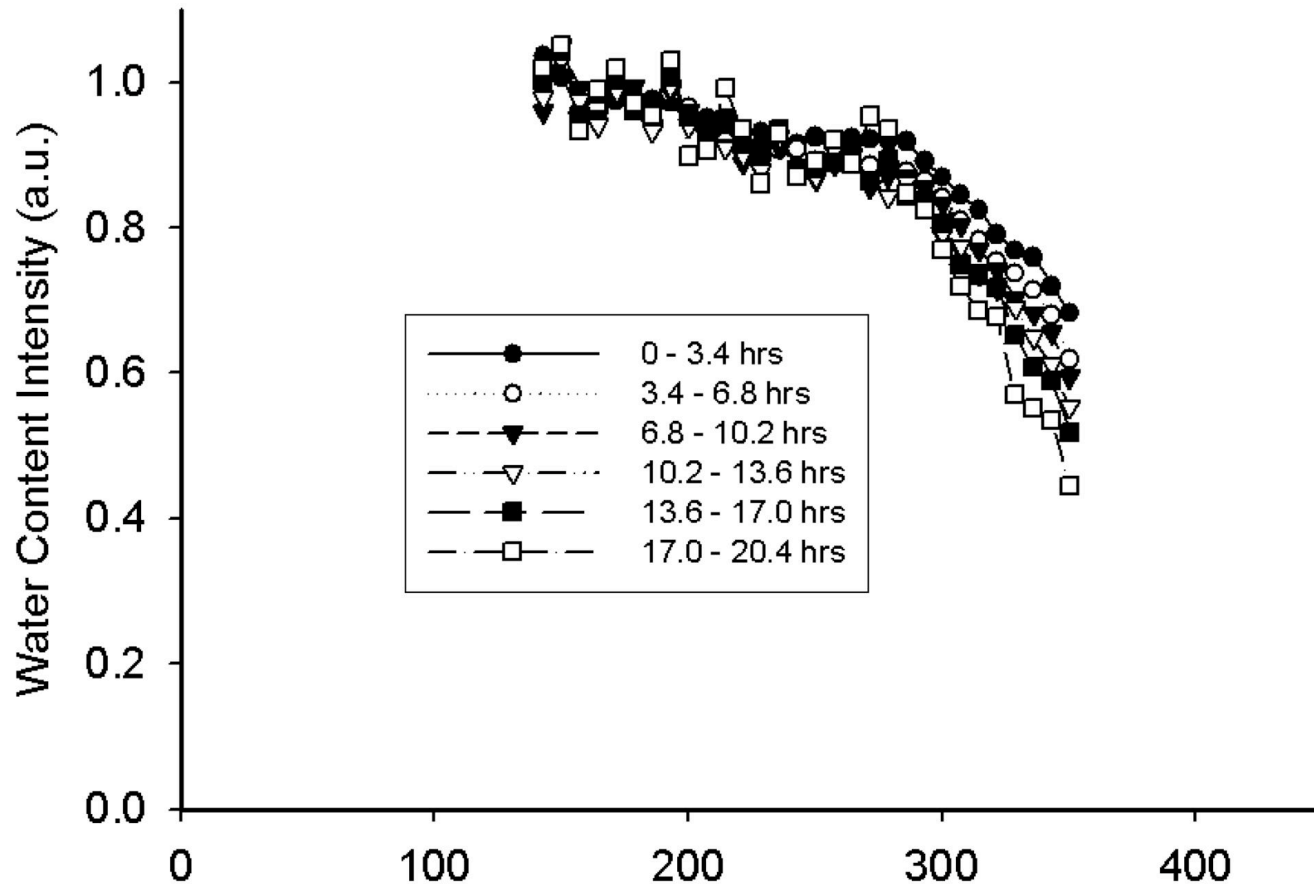


# Ionomer Membranes: Network Formation

NAFION

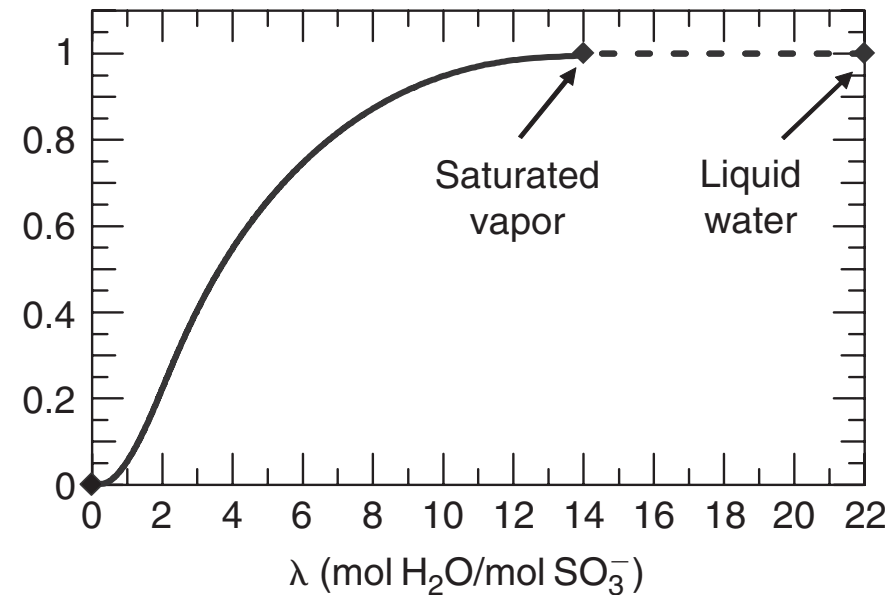
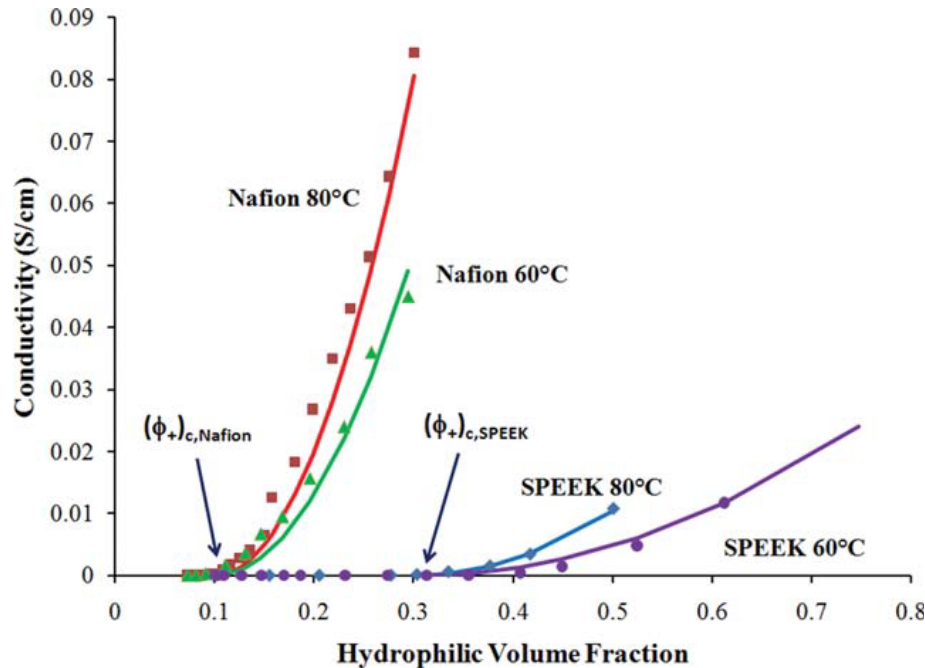


## Slow Transients in Nafion Hydration



In-situ MRI data of Nafion membrane exposed on one side to liquid water and on the other air at 20% RH.

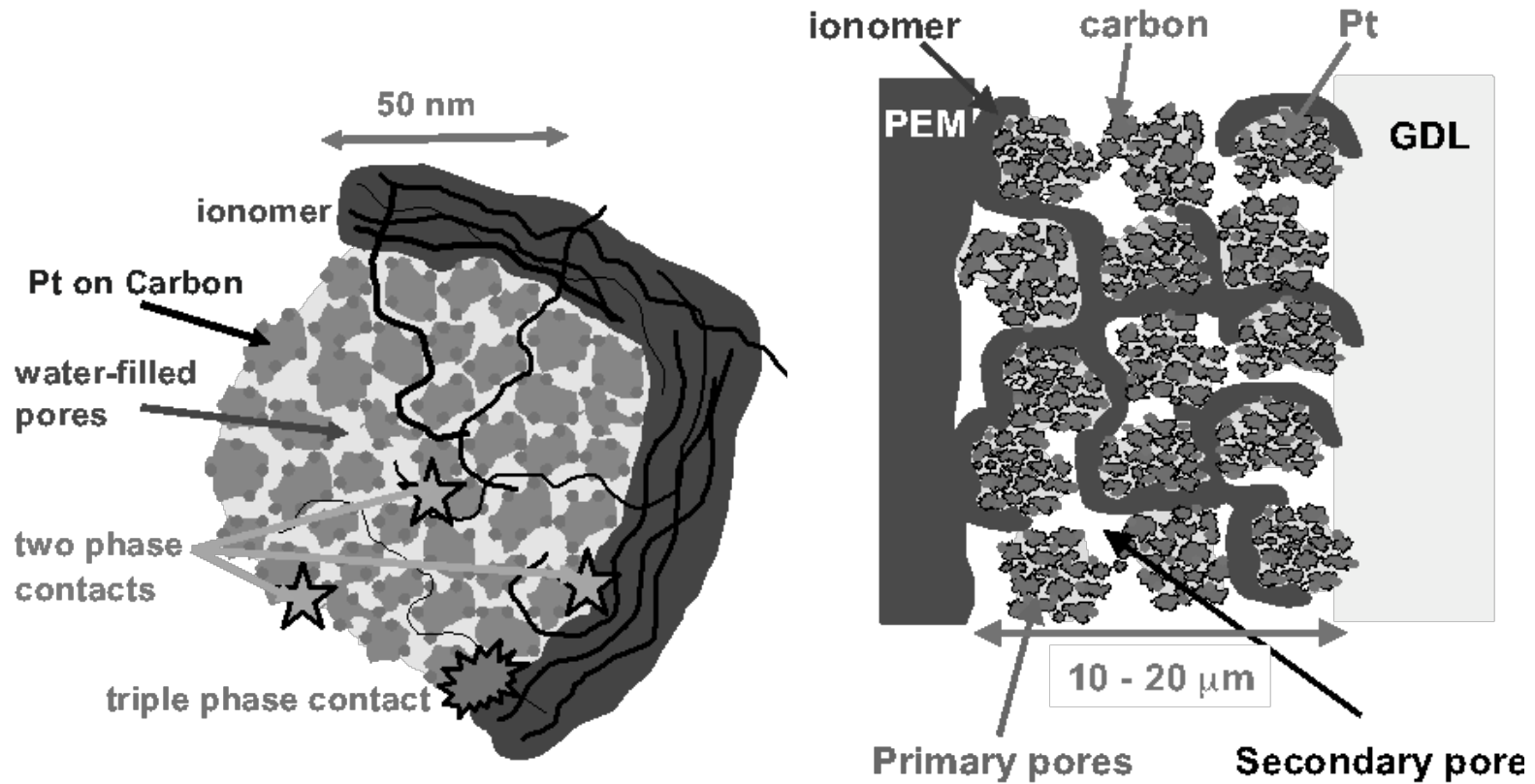
# Membrane Macroscopic Properties



(left) Conductivity of Nafion is sensitive to pre-treatment, water uptake, and temperature, but generally exceeds that of other ionic conducting membranes.

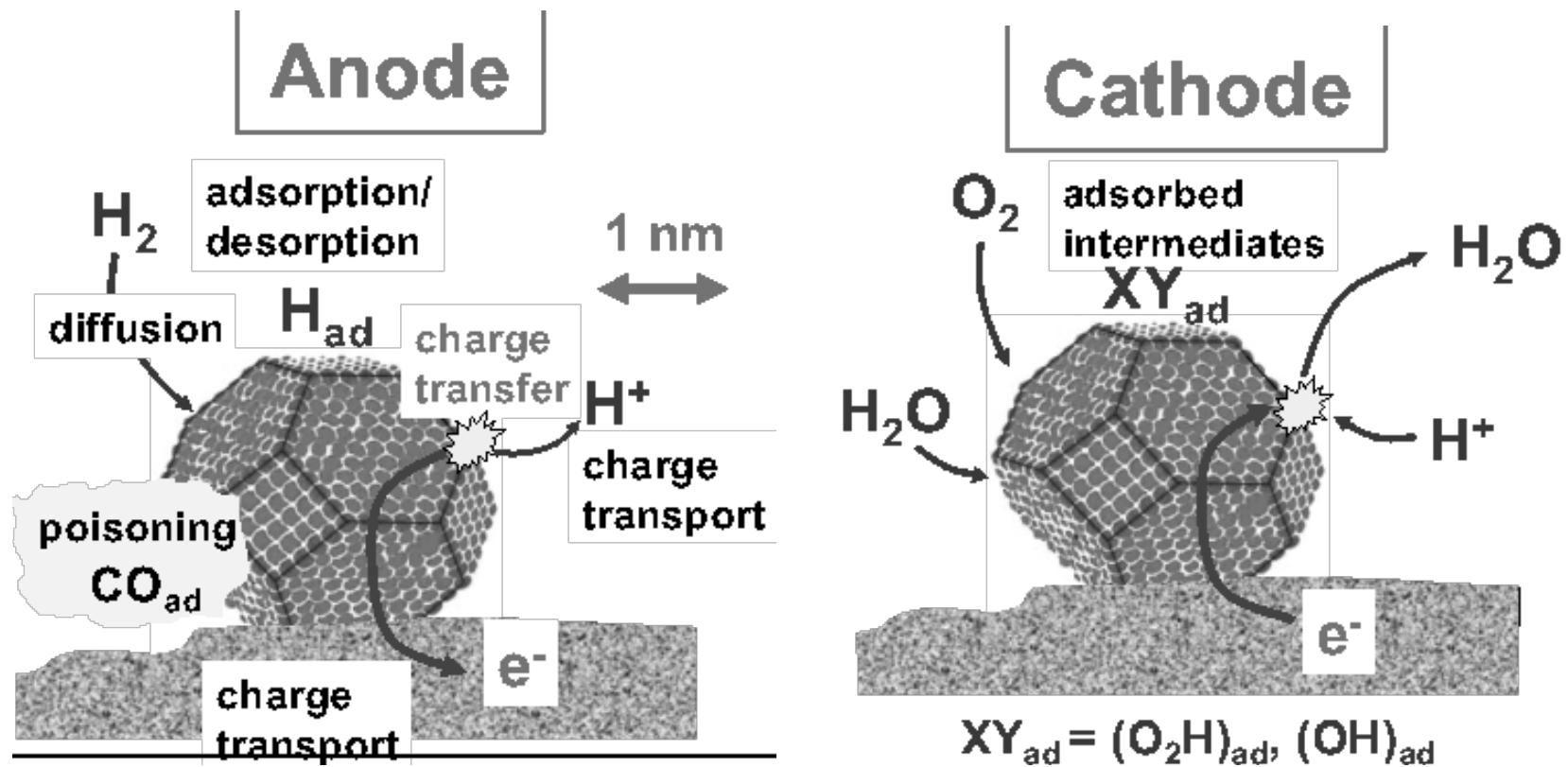
(right) Water uptake of Nafion increases with ambient RH, and is discontinuous from saturated vapor to liquid water.

# Catalyst Layer



Carbon support material forms agglomerates (left) which are interpenetrated by ionomer material (right).

# Platinum Catalyst

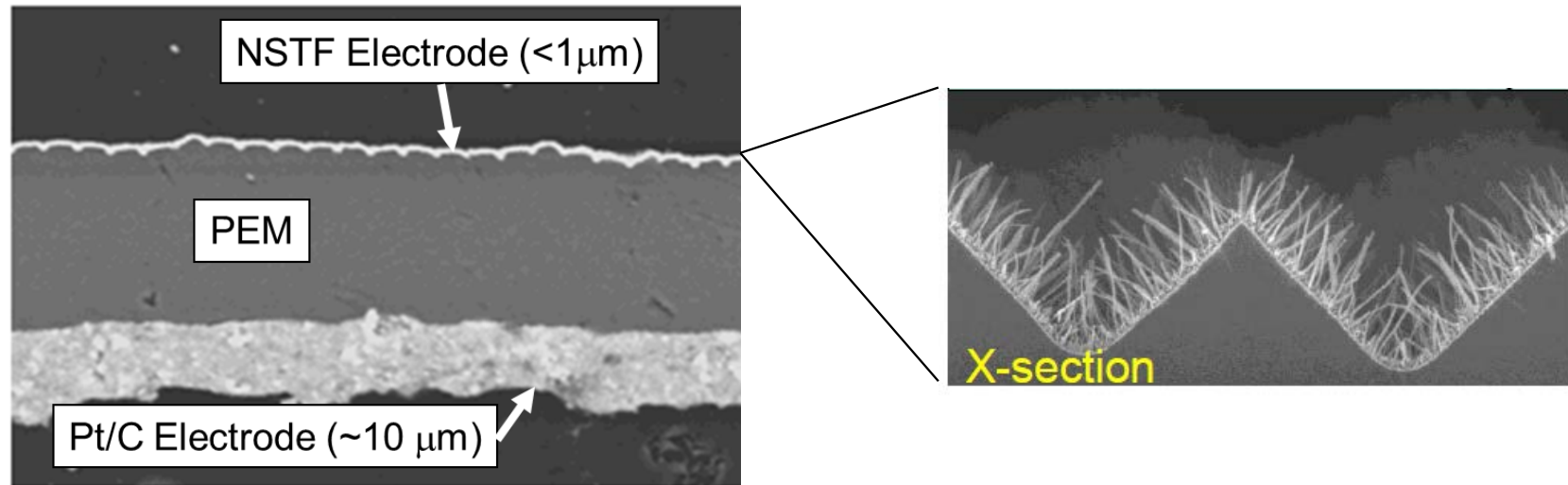


At the anode  $H_2$  is catalyzed into  $H^+$ , which is conducted by the ionomer and  $e^-$  which travels through the Pt and carbon support.

At the cathode  $H^+$  from the ionomer,  $e^-$  from the external circuit, and  $O_2$  from the GDL meet on the Pt surface, completing the reaction.

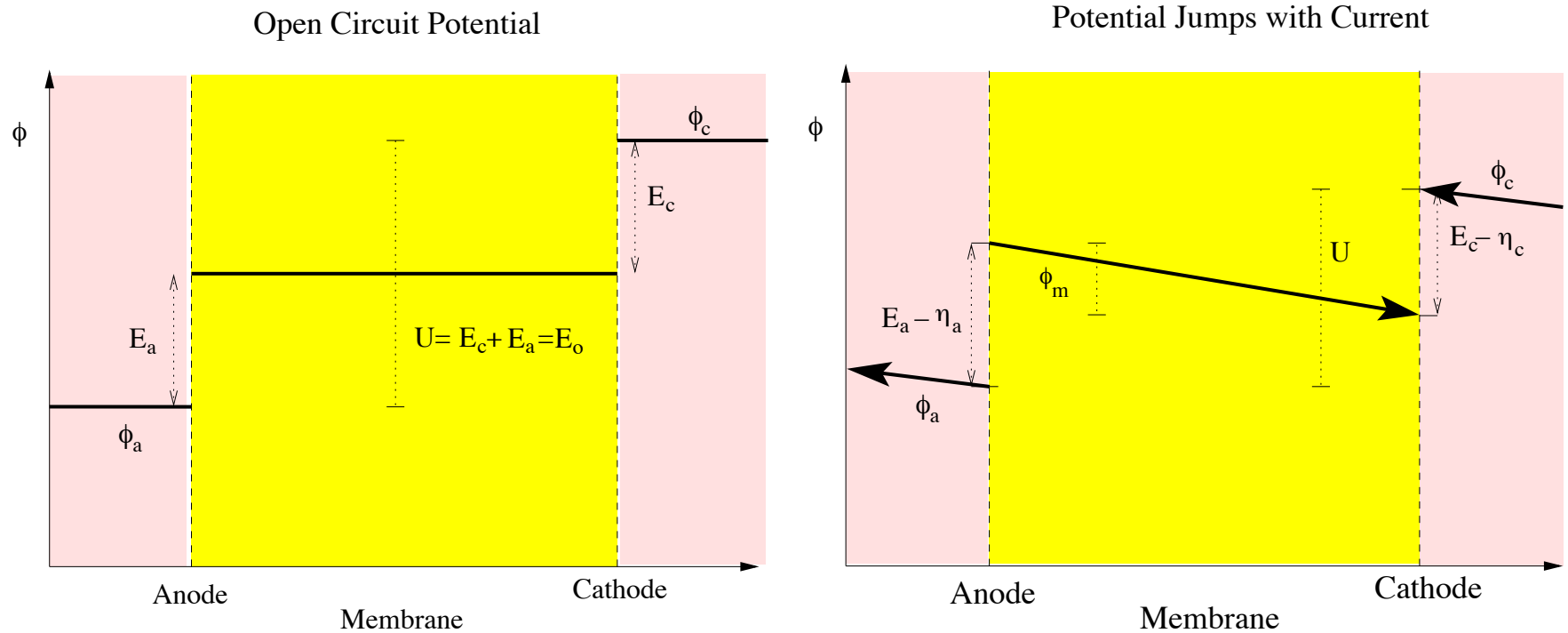


## MEA and 3M Anode Catalyst



Cross-sectional view of Membrane-Electrode Assembly (MEA) showing the ionomer flanked by the anode and cathode catalyst layers. The cathode catalyst is a traditional carbon-support/Pt agglomerate while the anode catalyst is the 3M Nanostructured thin film (NSTF) from Pt-Ni alloy.

# Butler-Volmer Equations



Over-potentials  $\eta_a$  and  $\eta_c$  describe non-equilibrium loss of voltage

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

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

## Cell Voltage– Polarization Curve

The membrane resistance is a function of membrane water content

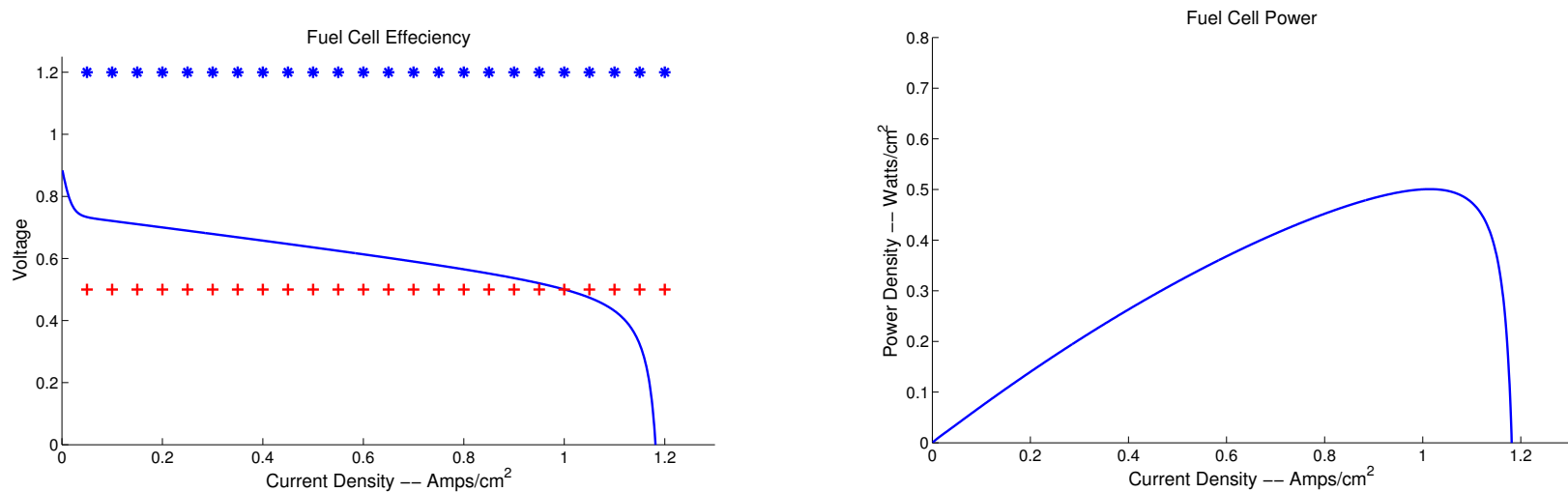
$$R_m = R_m(\lambda),$$

The catalyst oxygen conc. is a function of current and water content (flooding)

$$C_O(cat) = C_O(ch) - I\delta.$$

The cell voltage is given by

$$U = E_o - R_m(\lambda)I - \eta(I, C_O(ch)).$$

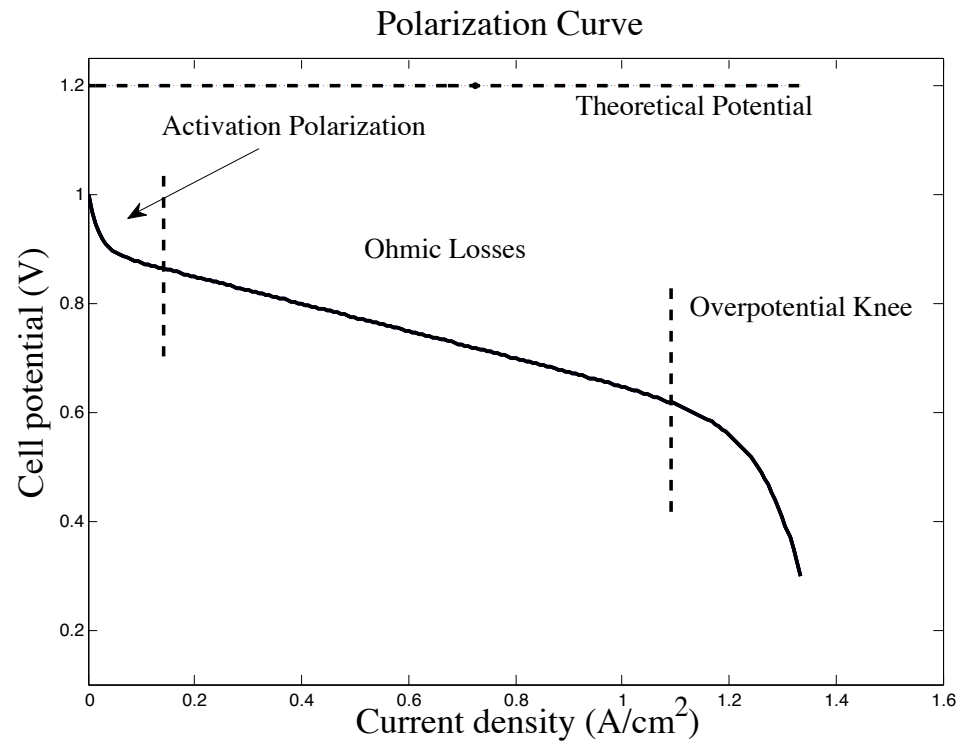


Below the red line is the **Cheetah** regime

Fuel Cell Power:  $0.5 \text{ Watts/cm}^2 \times 300 \text{ cm}^2 = 150 \text{ Watts/cellt}$



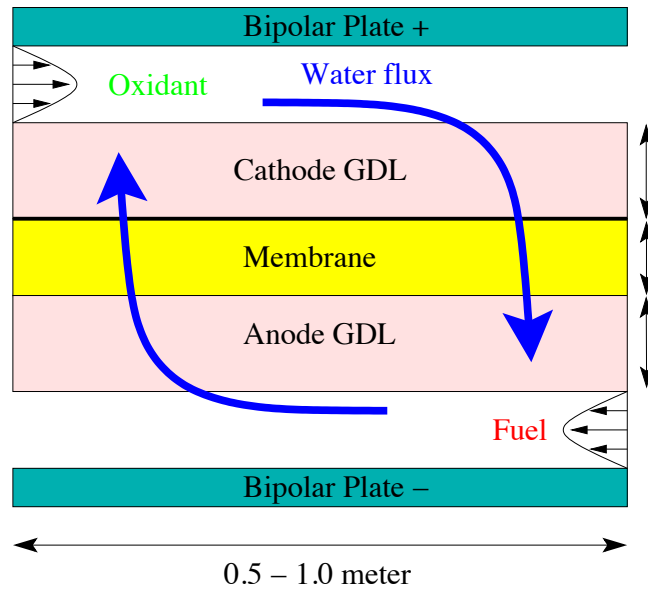
# Cathode Overpotential



At non-zero currents the cathode over potential takes the form

$$\eta_c \approx \overbrace{\frac{RT}{\alpha_c F}}^{\text{Tafel Slope}} \ln \left( \frac{I}{i_{o,c}} \left( \frac{c_{O,\text{ref}}}{c_{O}(\text{ch}) - \delta I} \right) \right)$$

# 1+1D Unit Cell Models – 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.	$T_r$

Ignore build up of liquid water in channels.

Exploit aspect ratio: couple 1D, steady-state transport for gas phases in channel with time dependent, 1D transport through MEA and accumulation of heat in coolant phase.

## Channel Equations at Equilibrium

The through-plane current  $I = I(x)$  drives the gas composition in channel

$$\begin{aligned}
 \frac{dQ_{c,o}}{dx} &= -\frac{I(x)L_w}{4F}, & C_{c,o} &= \frac{P_c}{\mathcal{R}T_c(x)} \frac{Q_{c,o}}{Q_{c,o}+Q_{c,v}+Q_{c,n}}, \\
 \frac{dQ_{c,v}}{dx} &= (1 + \alpha(x)) \frac{I(x)L_w}{2F}, & C_{c,v} &= \text{Min} \left\{ \frac{P_c}{\mathcal{R}T_c(x)} \frac{Q_{c,v}}{Q_{c,o}+Q_{c,v}+Q_{c,n}}, \frac{P_{\text{sat}}(T_c)}{\mathcal{R}T_c(x)} \right\}, \\
 \frac{dQ_{c,n}}{dx} &= 0, & C_{c,n} &= \frac{P_c}{\mathcal{R}T_c(x)} \frac{Q_{c,n}}{Q_{c,o}+Q_{c,v}+Q_{c,n}}, \\
 \frac{dQ_{a,h}}{dx} &= \pm \frac{I(x)L_w}{2F}, & C_{a,h} &= \frac{P_a}{\mathcal{R}T_a(x)} \frac{Q_{c,h}}{Q_{a,h}+Q_{a,v}}, \\
 \frac{dQ_{a,v}}{dx} &= \pm \alpha \frac{I(x)L_w}{2F}, & C_{a,v} &= \text{Min} \left\{ \frac{P_a}{\mathcal{R}T_a(x)} \frac{Q_{a,v}}{Q_{a,h} + Q_{a,v}}, \frac{P_{\text{sat}}(T_a)}{\mathcal{R}T_a(x)} \right\},
 \end{aligned}$$

The coolant temperature is transient and coupled to resevoir

$$\begin{aligned}
 \frac{\partial}{\partial t} (\rho c T_{\text{col}}) + \partial_x (\rho c T_{\text{col}} v_g) &= N_T L_w, & T_{\text{col}}(0, t) &= T_r(t), \\
 \frac{dT_r}{dt} &= q(T_{\text{col}}^{\text{out}} - T_r) - r(T_r - T_{\text{amb}})
 \end{aligned}$$

## GDL: Transient Multiphase flow

Degenerate transport of liquid water

Disparate time scales:

$10^{-6}$  s for pressure

$10^3$  s for liquid flow

$C_o$  Oxygen Molar Conc.

$C_v$  Vapor Molar Conc.

$C_n$  Nitrogen Molar Conc.

$T$  Temperature

$\beta$  Liquid Vol. Frac.

$C$  Total Gas Conc.

Conservation of Energy and Mass: ( $\Gamma$  denotes liquid-vapor phase change rate)

$$\frac{\partial}{\partial t}((1 - \beta)C) + \partial_y(\overbrace{CU_g}^{N_g}) = -\Gamma,$$

$$\frac{\partial}{\partial t}(\overline{\rho c T}) + \partial_y(\overbrace{(\overline{\rho c U})T - \tilde{\kappa} \partial_y T}^{N_T}) = h_{lg}\Gamma,$$

$$\frac{\partial}{\partial t}((1 - \beta)C_o) + \partial_y(\overbrace{C_o U_g + J_o}^{N_o}) = 0,$$

$$\frac{\partial}{\partial t}((1 - \beta)C_v) + \partial_y(\overbrace{C_v U_g + J_v}^{N_v}) = -\Gamma,$$

$$\frac{\partial}{\partial t}(c_l \beta) + \partial_y(\overbrace{\beta c_l U_l}^{N_l}) = \Gamma.$$

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

$$P_c = P_g - P_l = L(\beta),$$

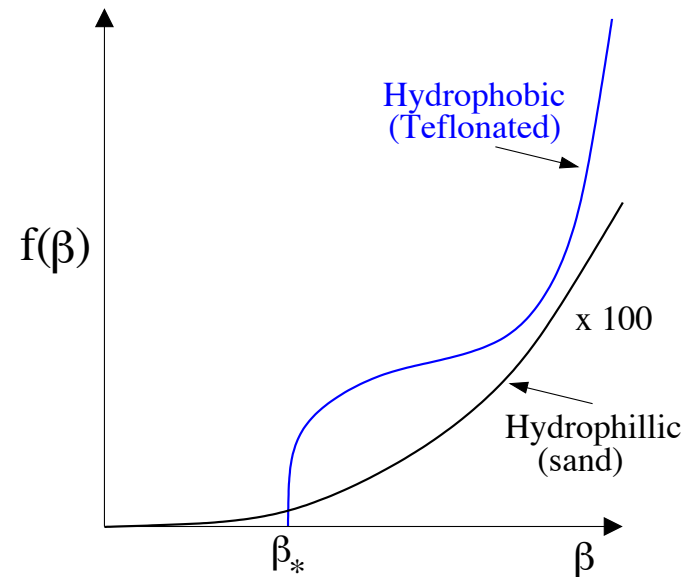
Leveret-like Capillary Pressure.

$$\Gamma = H(\beta)(C_v - C_{\text{sat}}(T)), \text{ Condensation-Saturation}$$

Capillary pressure and relative permeability form nonlinear diffusivity

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

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



## Non-dimensional Form of GDL equations

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

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

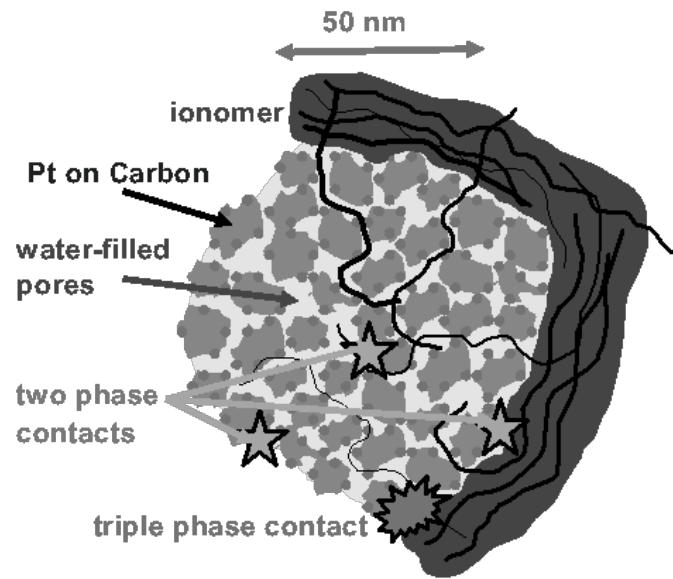
where  $\vec{S} = (-1, 1, 0, -1, 1)^t$  is the scaled stoichiometry vector for phase change and the matrix  $\mathcal{D}$  is given by

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

The local current production  $I$  is the driving force: fluxes at membrane proportional to  $I$ . A large charge flow is a small *molar* flux:

$$I = O(10^{-2})$$

# Membrane-Catalyst Layer Coupling (Boundary conditions)



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

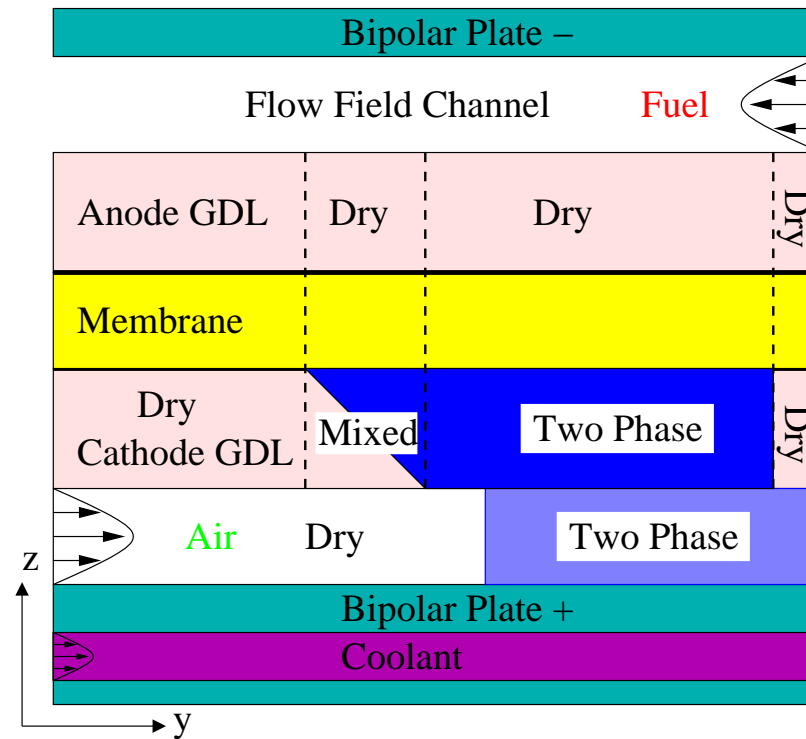
$$\gamma(c_w) \overbrace{(c_{w,a}^* - c_{w,a})}^{\text{disequilibrium}} = \overbrace{J_{w,a}^{GDL}}^{\text{Flux}} = J_{w,a}^m + \frac{I}{F},$$

$$\gamma(c_w)(c_{w,c} - c_{w,c}^*) = J_{w,c}^{GDL} = J_{w,c}^m + \frac{3I}{2F}.$$

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

Heat Production in Catalyst

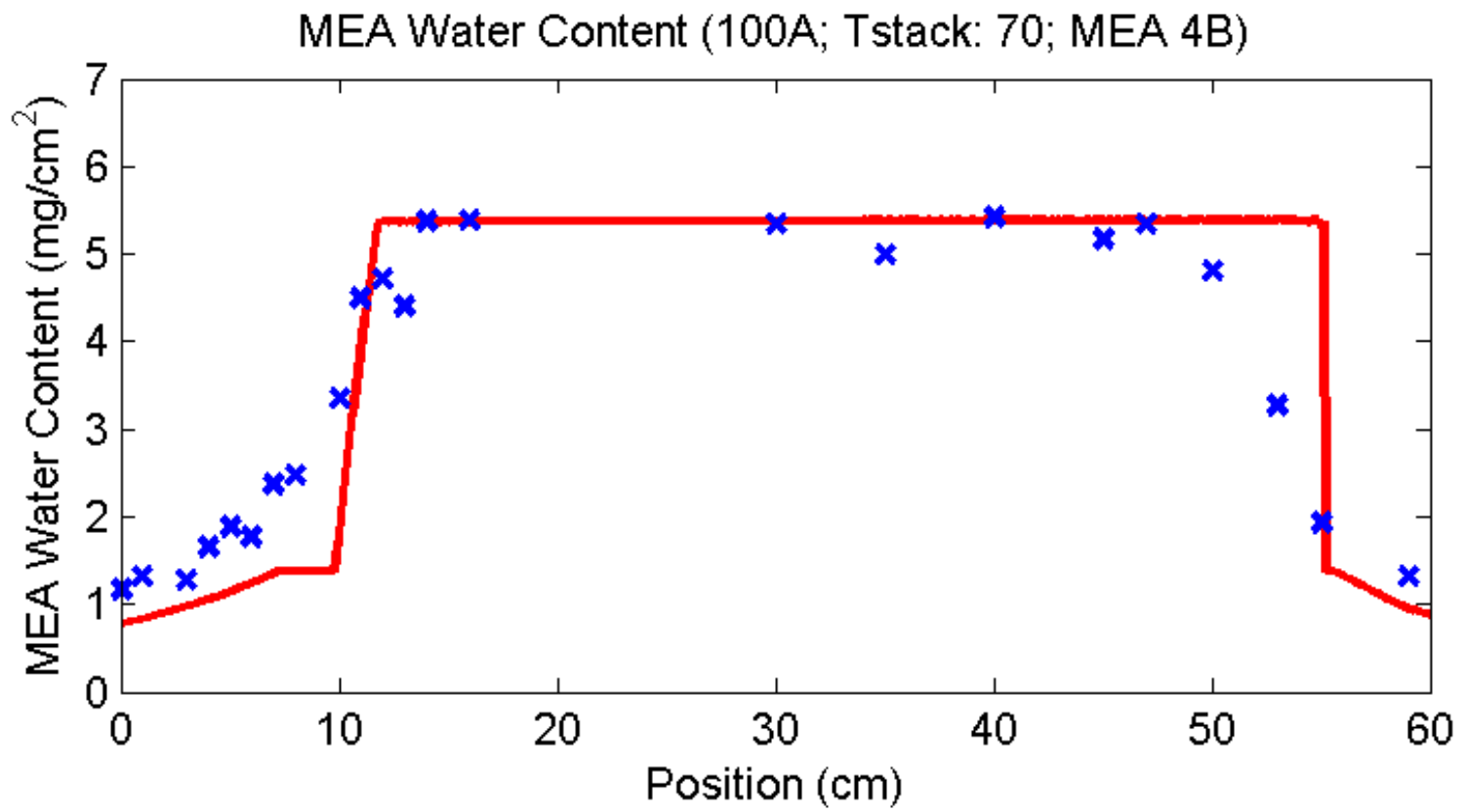
$$Q_{\text{heat}} = \left( \frac{Th_{rc}}{4F} + \eta_c \right) I_c - h_v \gamma (c_T - c_T^*(r)).$$

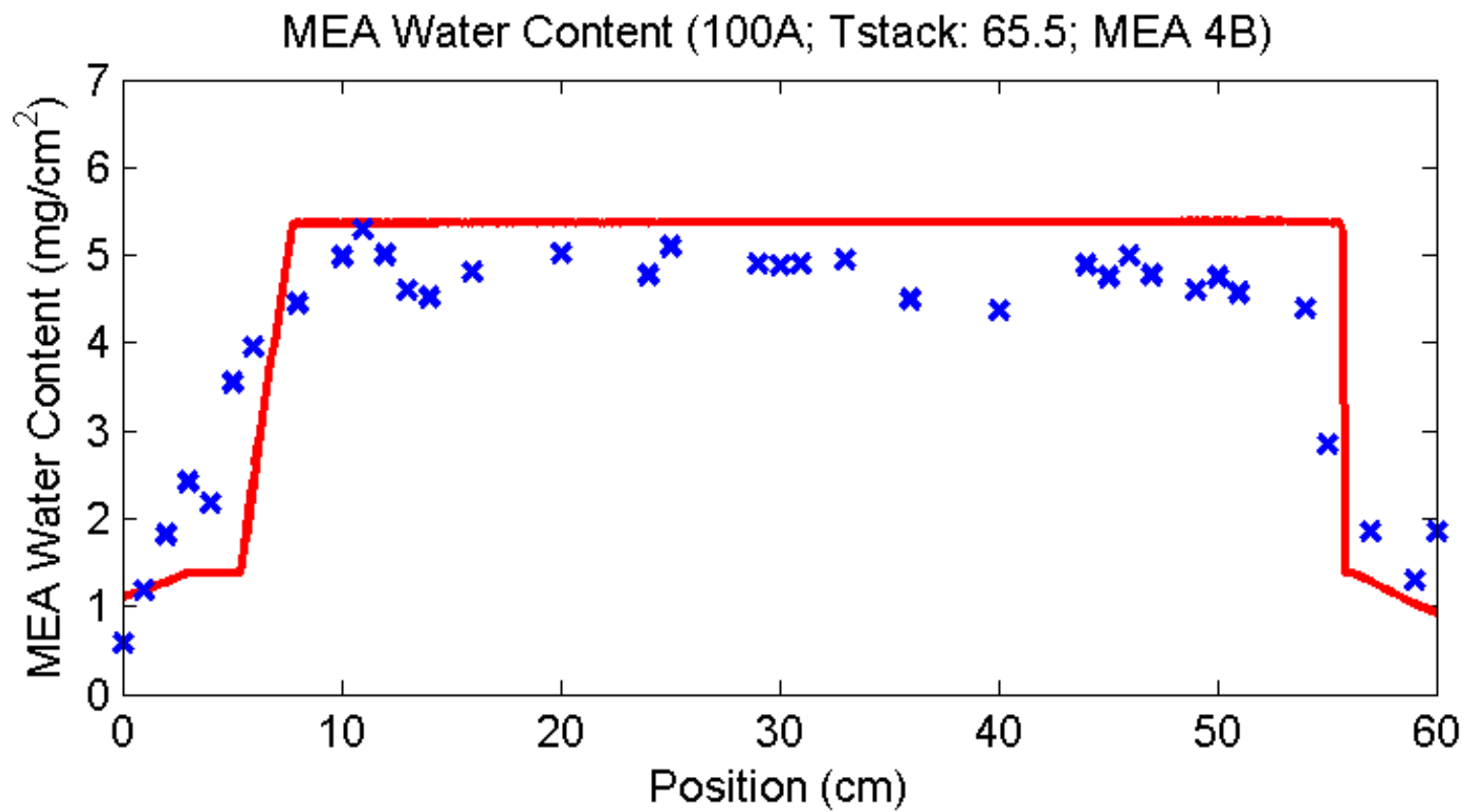


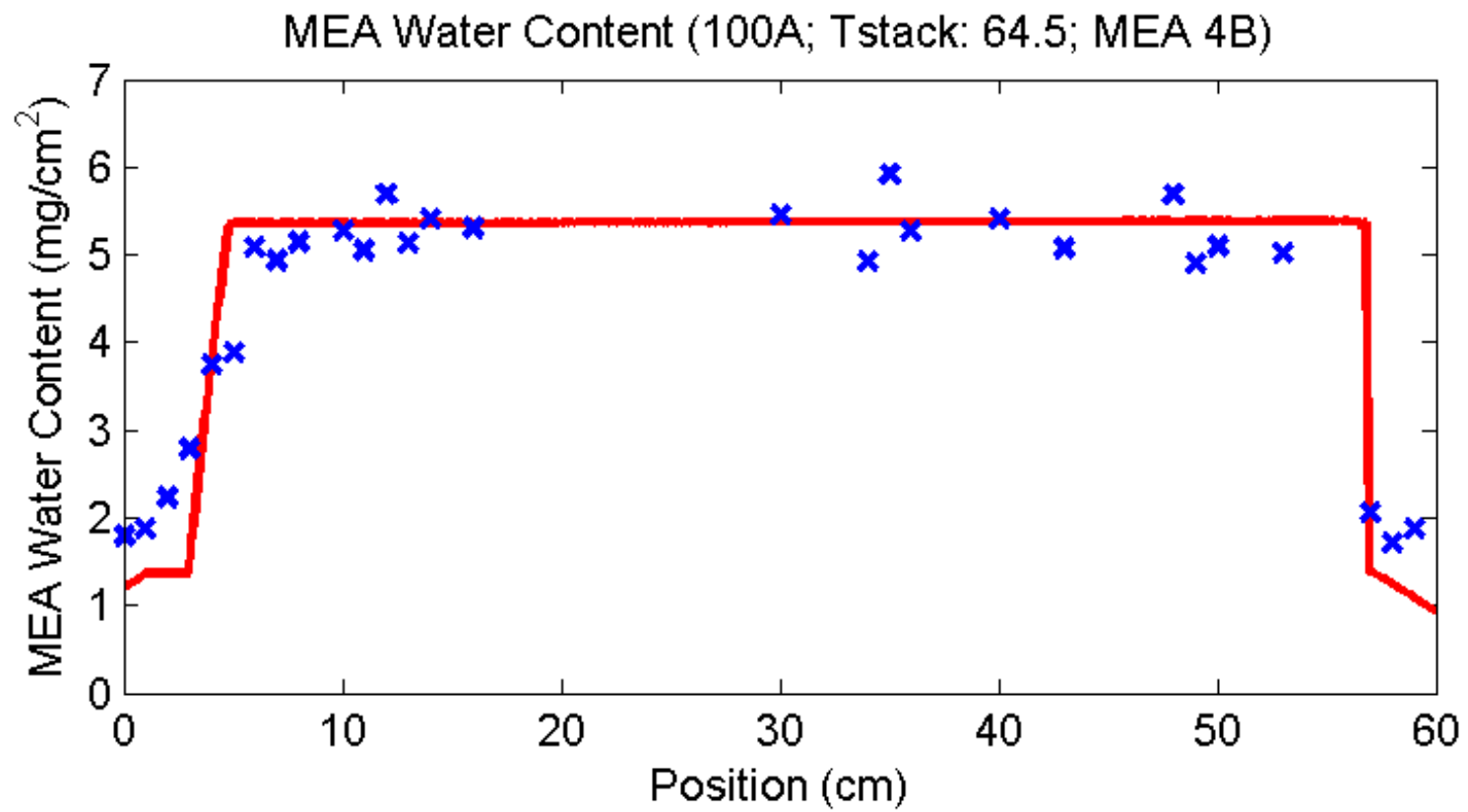
Break PDE into Dry, Two-phase, and a Boundary Layer regime  $O\left(\frac{I}{\sqrt{H}}\right)$ .  
 Exact solutions in Dry and Two-phase yield flux imbalance at wet-dry interface.  
 Leads to explicit ODE for slow front evolution.

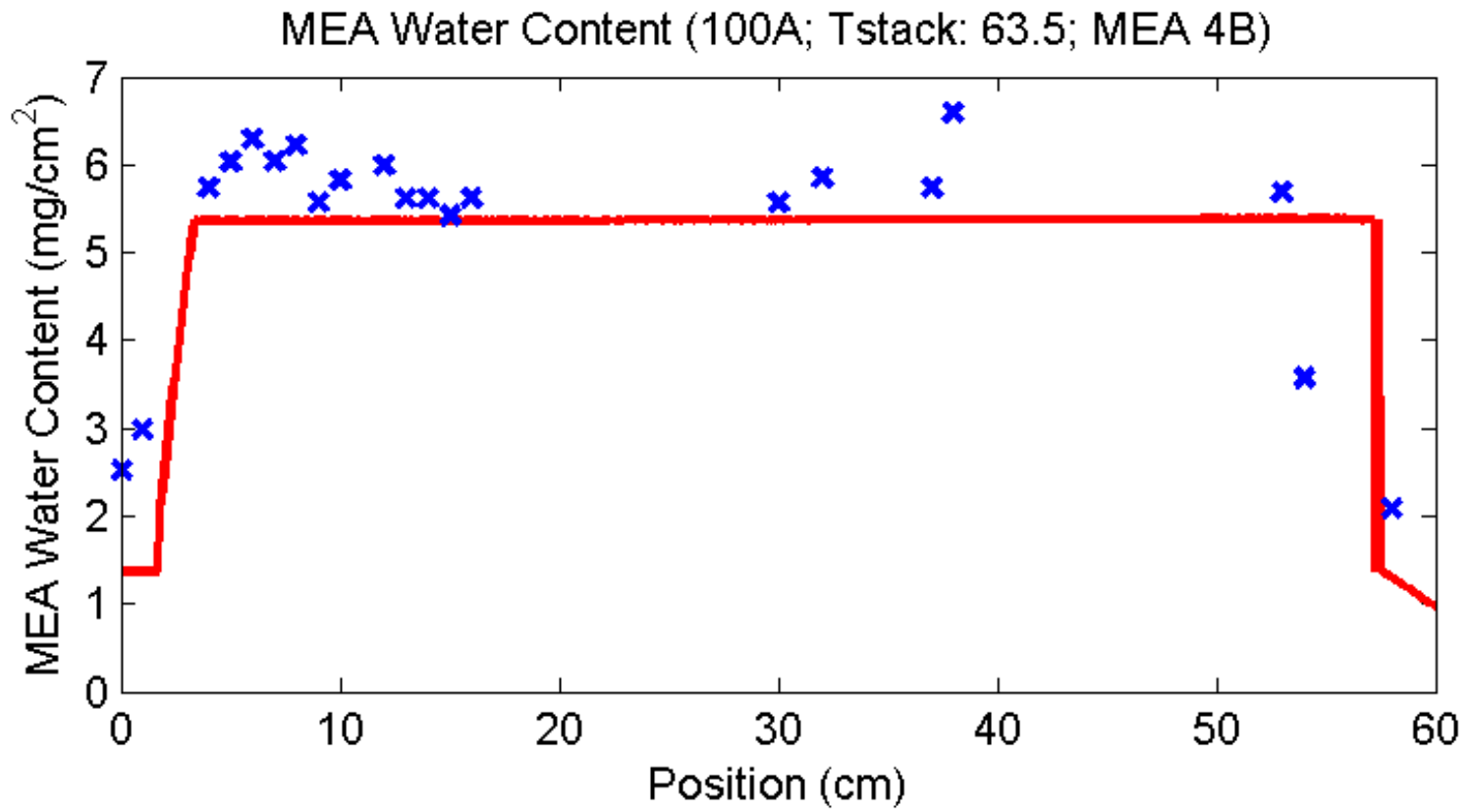
K.P., J. Stockie, B. Wetton, *Proc. Roy. Soc. London: Series A* **462** (2006).

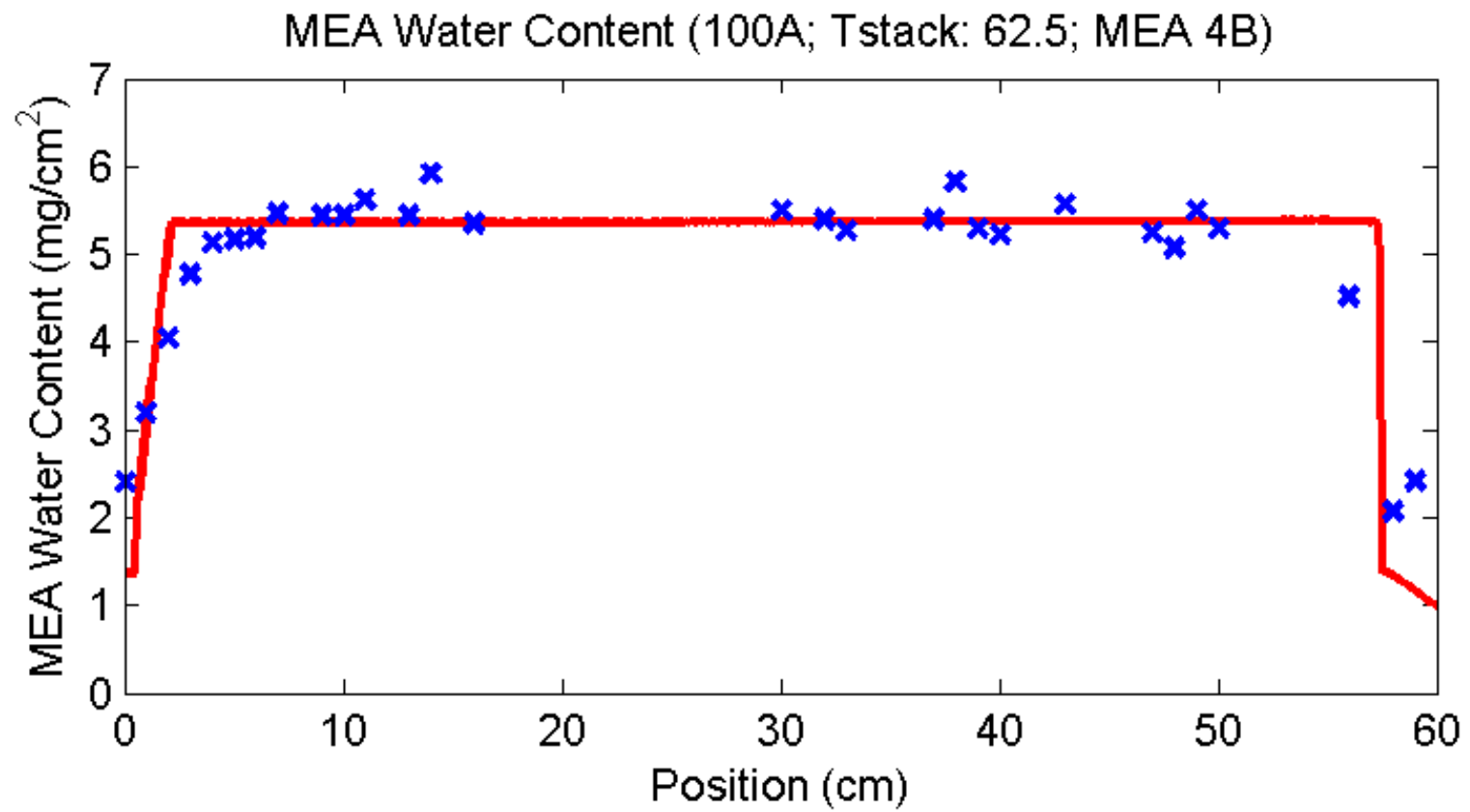


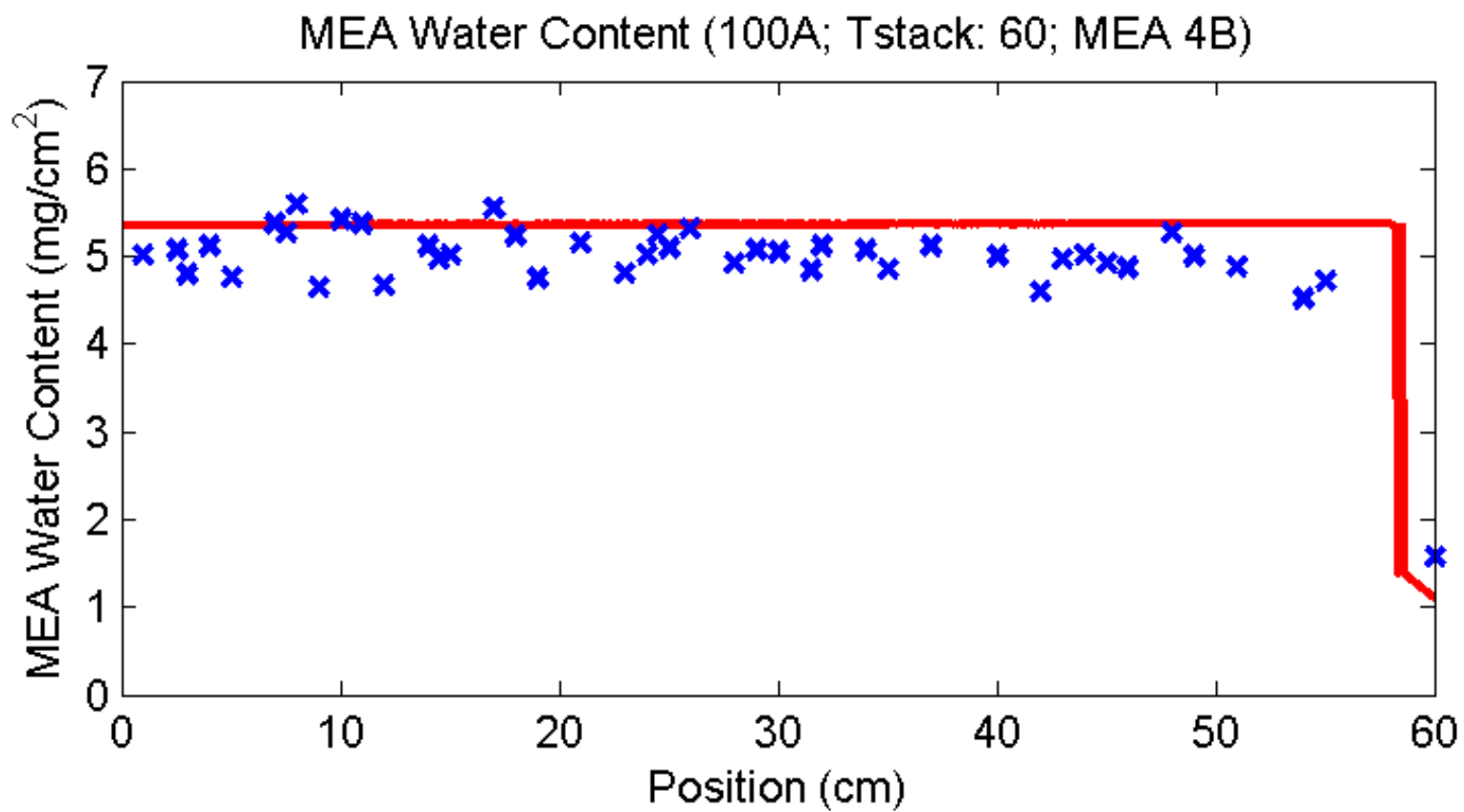




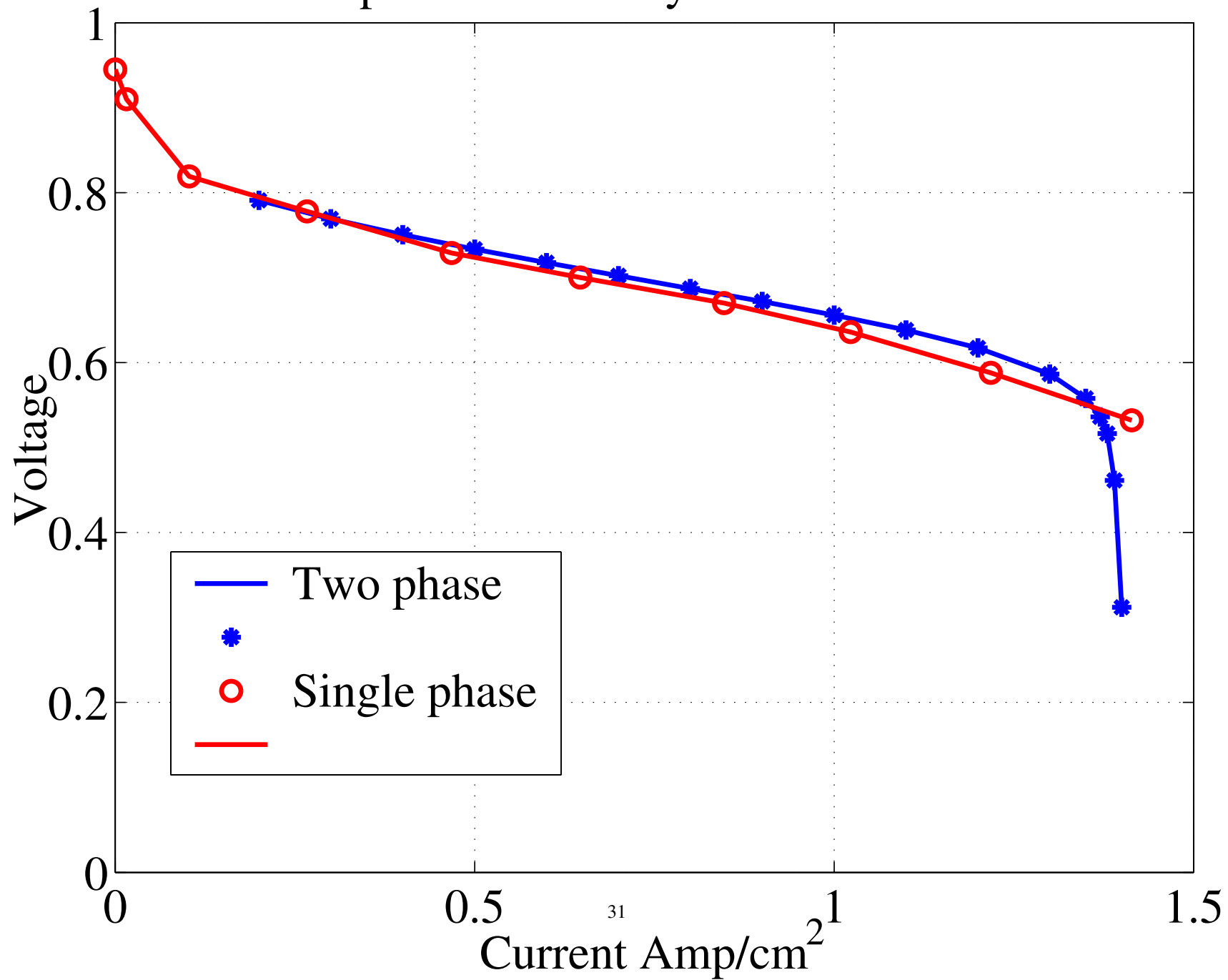






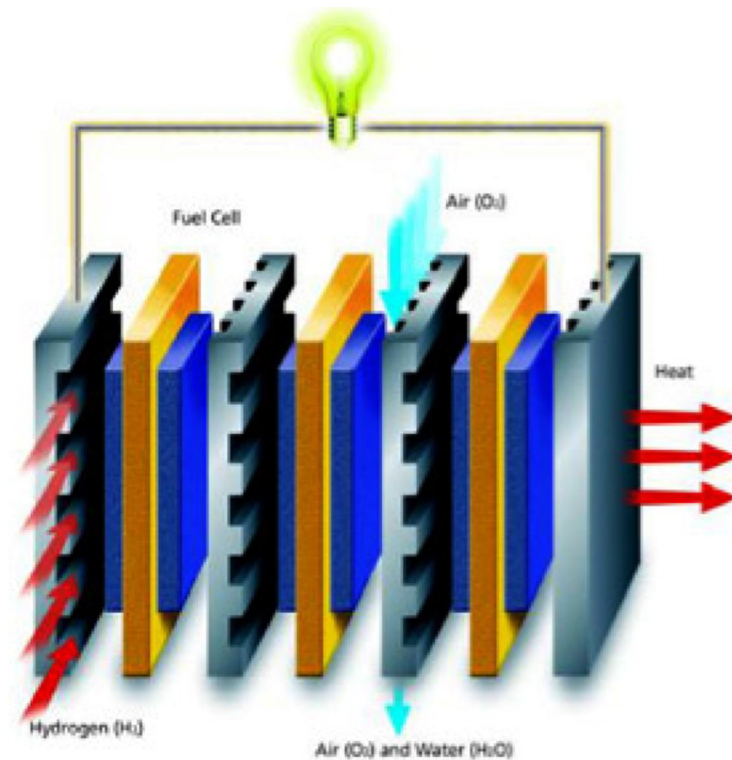
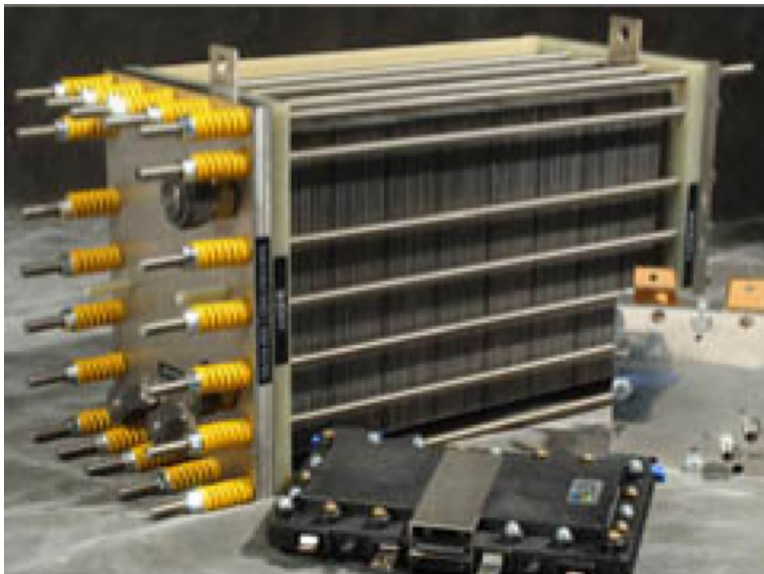


# Two-phase versus Dry Polarization Curve



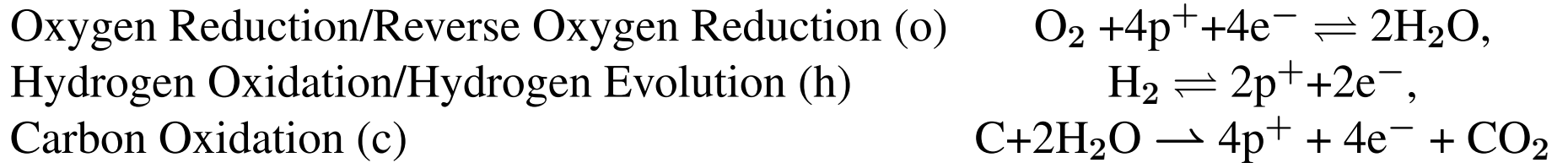
## Fuel Cell Stacks

A single  $60\text{cm} \times 30\text{cm}$  cell, operating at  $1 \text{ Amp}/\text{cm}^2$  and  $0.6 \text{ Volts}$  produces about a kilowatt in power. Automotive applications, which require almost a MegaWatt of power require **Stacks**.





## Carbon Corrosion



Common Electrode potential, for reaction r=o, h, c, at anode/cathode

$$E_{a/c} = E_{r,ref} + N_r(C_o, C_h) + \eta_r(i_r),$$

$$V_{cell} = E_c - E_a - R_{\Omega}I,$$

$$i_r = i_{r,ref} \left\{ \exp\left(\frac{\alpha_r \mathcal{F} \eta_r}{RT}\right) - \exp\left(-\frac{(1 - \alpha_r) \mathcal{F} \eta_r}{RT}\right) \right\},$$

Small current  $i_r \approx \eta_r / R_r,$

Large current  $\eta_r \approx \frac{RT}{\alpha_r \mathcal{F}} \ln \frac{i_r}{i_{r,ref}}$

Each reaction competes to provide the local current  $I(x)$

$$I(x) = i_c(x) + i_o(x) + i_h(x)$$

Oxidation reactions (producing electrons)  $i > 0$  and  $\eta > 0,$

Reduction reactions (consuming electrons)  $i < 0$  and  $\eta < 0$

## Kinetic Parameters

Reaction	Nerst	$E_{ref}$	$i_{ref}$	$\alpha_r$
Carbon Ox. (c)	-	0.207V	$1.1 \cdot 10^{-5} \frac{A}{m^2}$	0.324
Hydrogen Ev. (h)	$C_{H_2}^{ref} = 100 \frac{mol}{m^3}$	0	$\eta_h = R_h i_h$	$R_h = 0.10 \Omega\text{-cm}^2$
Oxygen Red. (o)	$C_{O_2}^{ref} = 40.9 \frac{mol}{m^3}$	1.28V	$9.3 \cdot 10^{-4} \frac{A}{m^2}$	1.0
Rev. Ox. Red. $i_o > 0$	-		$\eta_o = R_o i_o$	$R_o = 0.01 \Omega\text{-cm}^2$

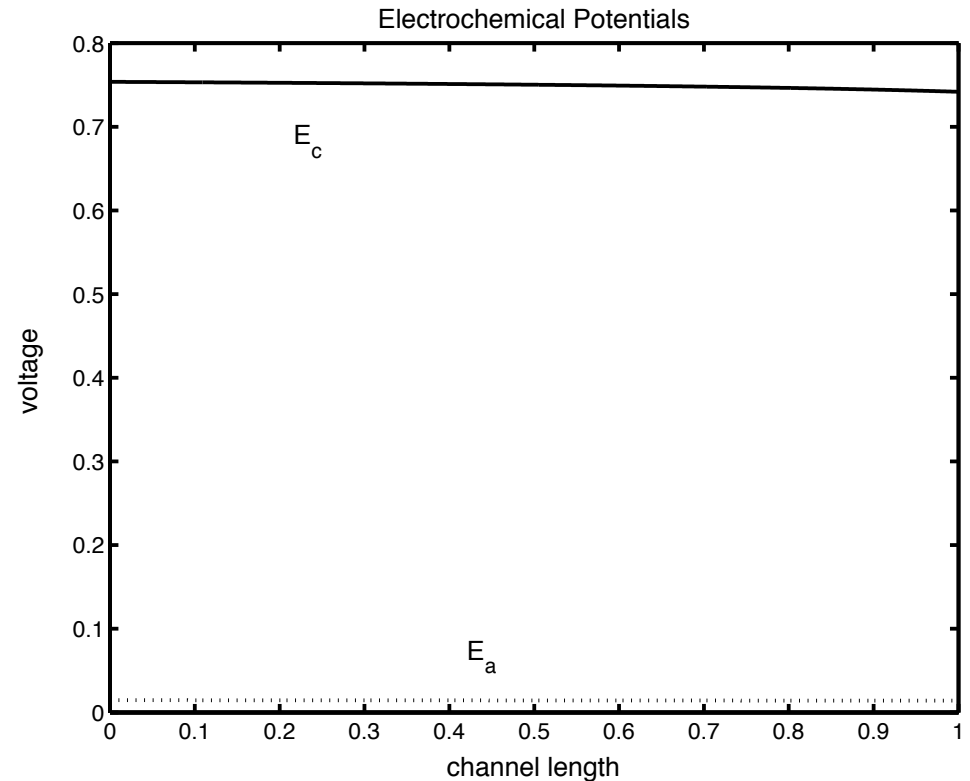
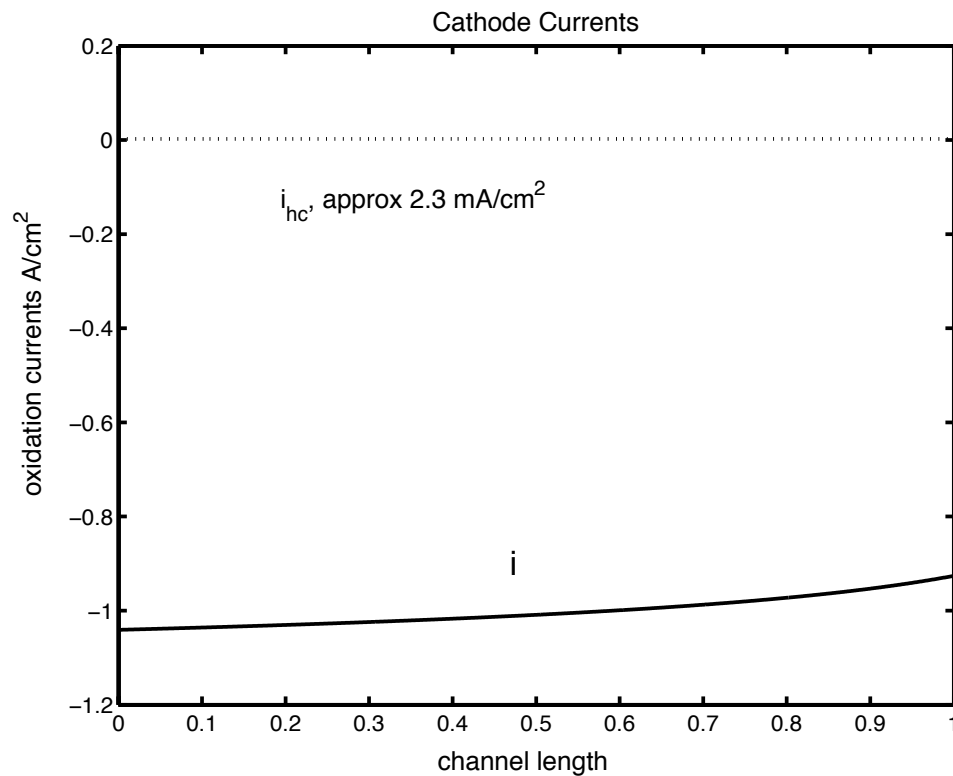
Oxygen/Hydrogen cross over,  $A = 3 \times 10^{-3}$  m/s,

$$J_r = A(C_{r,a} - C_{r,c})$$

Unknowns

Anode and Cathode catalyst layer conc.	$C_{o,a}, C_{h,a}$	$C_{o,c}, C_{h,c}$
Partial currents	$i_{o,a}, i_{h,a}, i_{c,a}$	$i_{o,c}, i_{h,c}, i_{c,c}$
Local current	$I(x)$	$I(x)$
Anode and Cathode potentials	$E_{an}$	$E_{cat}$

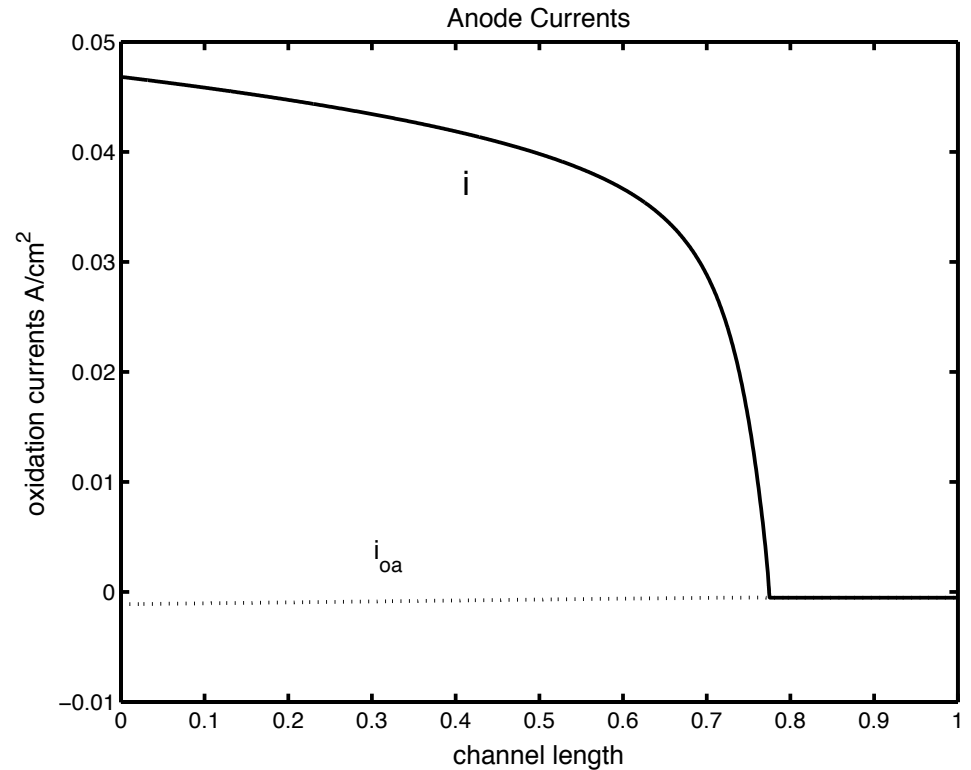
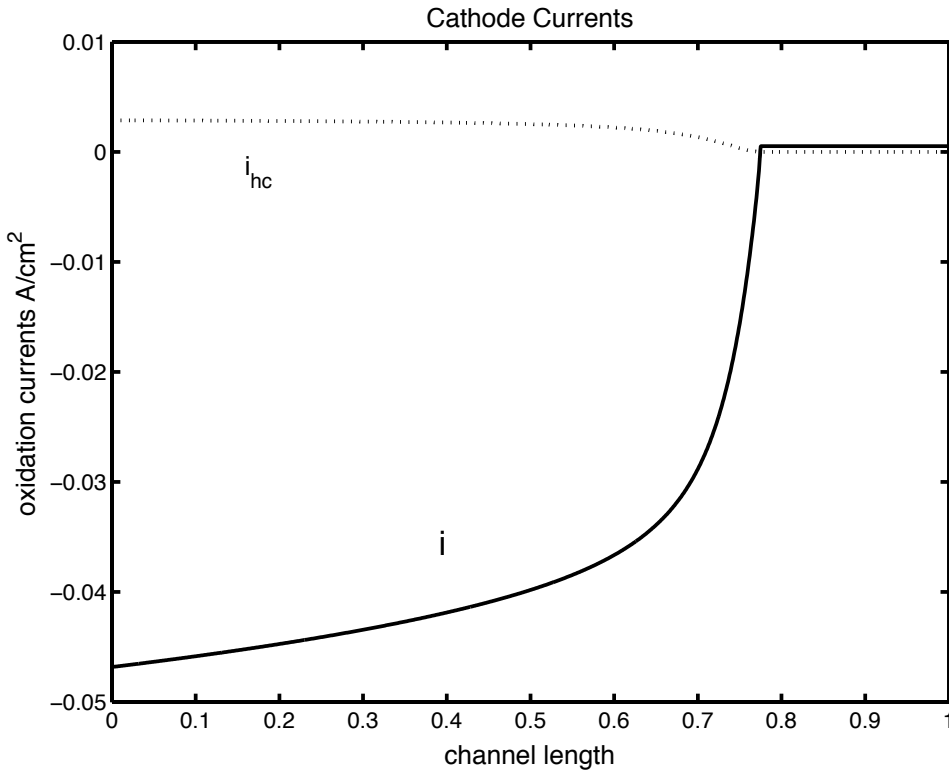
## Base case– Coflow



An/Cat 2.2/2.0 barg, stoich=1.2/1.8,  $I_T = 1 \text{ A/cm}^2$ ,  $V_{\text{cell}} = 0.635 \text{ V}$ .

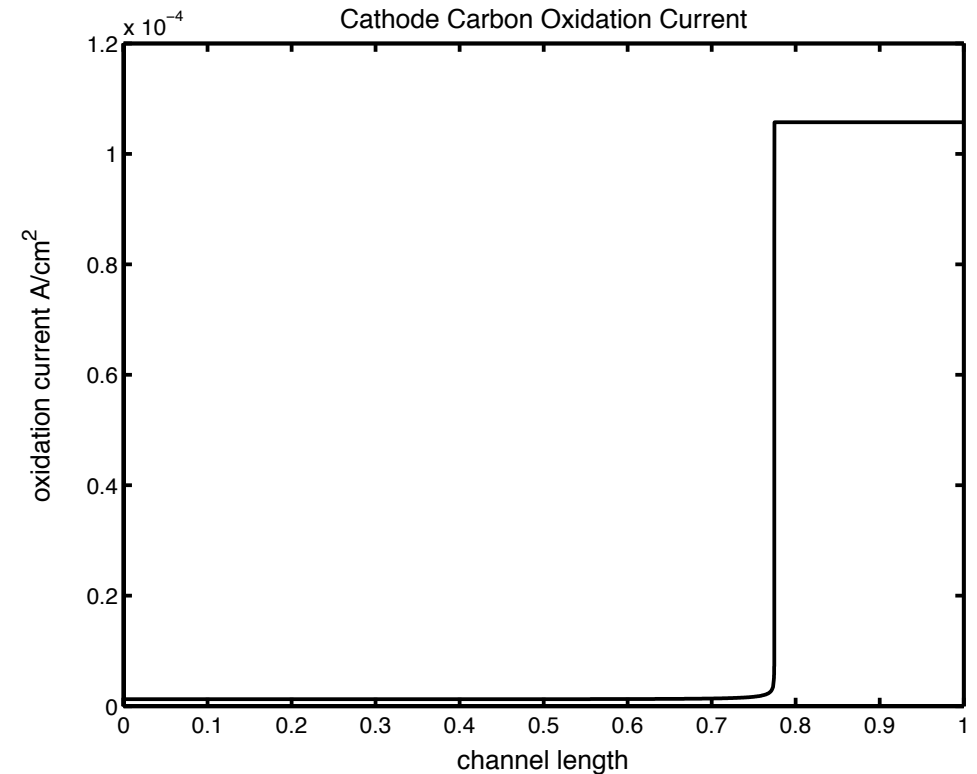
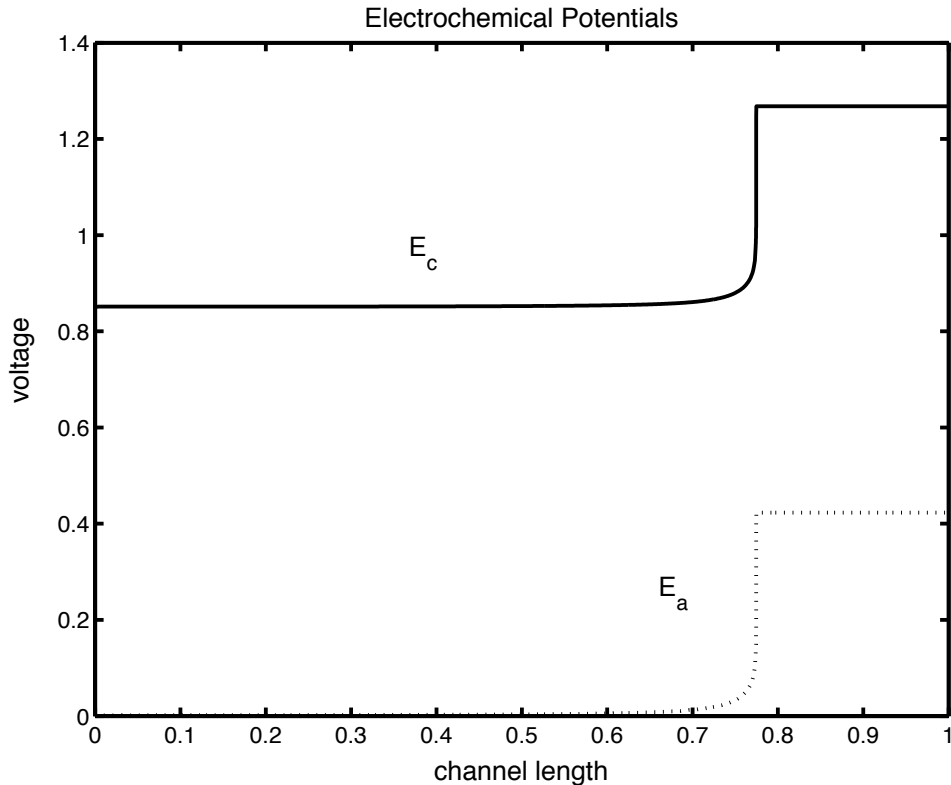
Small hydrogen oxidation current (2.3 mA/cm<sup>2</sup>) on cathode due to hydrogen crossover. This current is present at open circuit and causes the drop in open circuit voltage from 1.28 to 0.95V.

## Partial Anode Understoich (idle)



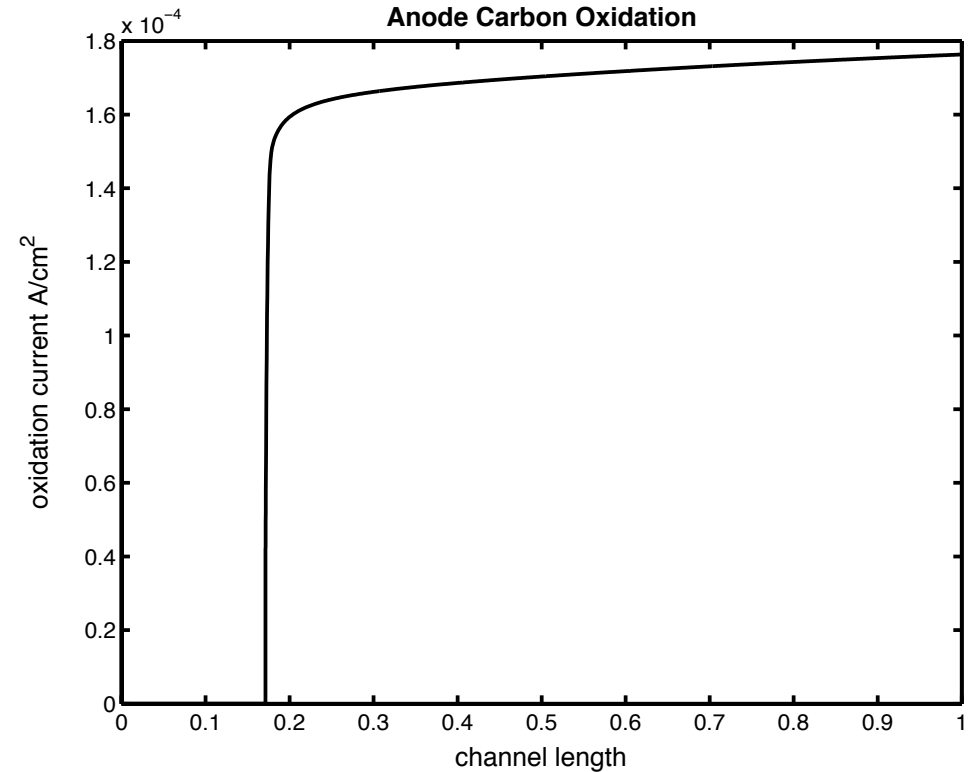
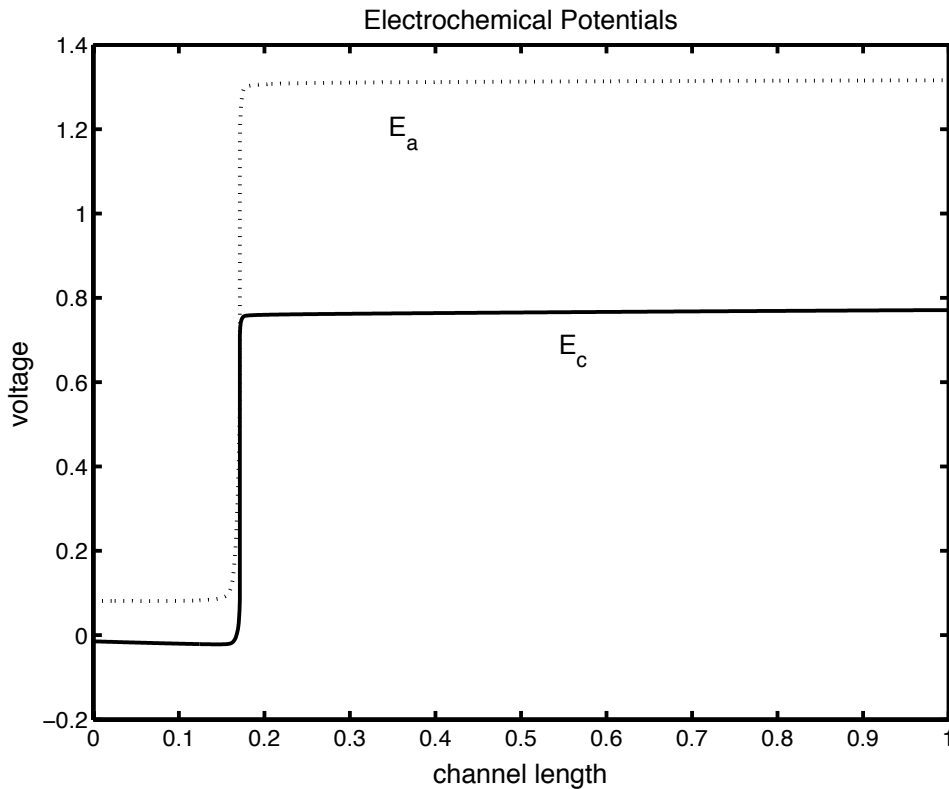
An/Cat 2.2/2.0 barg, stoich=1.1/1.8,  $I_T = 30 \text{ mA/cm}^2$ ,  $V_{\text{cell}} = 0.845 \text{ V}$ .  
 Hydrogen cross-over drives cell to anode understoich. Oxygen reduction at anode (from crossover) and Reverse Oxygen reduction at cathode. Elevated cathode pot leads to sig. carbon corrosion. (1 mg of carbon/hour =  $6 \times 10^{-4} \text{ A}$ ).

## Partial Anode Understoich (idle)



An/Cat 2.2/2.0 barg, stoich=1.1/1.8,  $I_T = 30 \text{ mA/cm}^2$ ,  $V_{\text{cell}} = 0.845 \text{ V}$ .  
Hydrogen cross-over drives cell to anode understoich. Oxygen reduction at anode (from crossover) and Reverse Oxygen reduction at cathode. Elevated cathode pot leads to sig. carbon corrosion. ( $1 \text{ mg of carbon/hour} = 6 \times 10^{-4} \text{ A}$ ).

# Anode Understoich – Coflow



An/Cat 2.2/2.0 barg, stoich=0.8/1.8,  $I_T = 1 \text{ A/cm}^2$ ,  $V_{\text{cell}} = -0.575 \text{ V}$ .

Current near inlet is limited only by hydrogen mass transfer on anode. On cathode oxygen reduction (at mass transfer limit) plus hydrogen evolution. After depletion of hydrogen, anode and cathode pot. rise, leading to reverse oxygen reduction on anode, hydrogen oxidation and oxygen reduction on cathode.

## Fuel Cell Issues

Would like higher temperature operation to avoid *CO* poisoning, reduce the Cheetah effect, and improve the performance of non-precious metal (cheaper) catalysts.

Requires the development of new (cheaper, higher temperature) polymer electrolyte membranes

Lower Pt loading ( $\text{mg}/\text{cm}^2$ ). Catalyst layers can degrade when run at high voltage, mostly due to understoich (Carbon Corrosion). Pt dissolution is also a long-term degradation worry.

Liquid water builds up in catalyst layers and clogs oxygen transport (Flooding). Also freeze-thaw issues.