

CFCD II - BIRS.

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# A Simple but Comprehensive PEM Unit Cell Model

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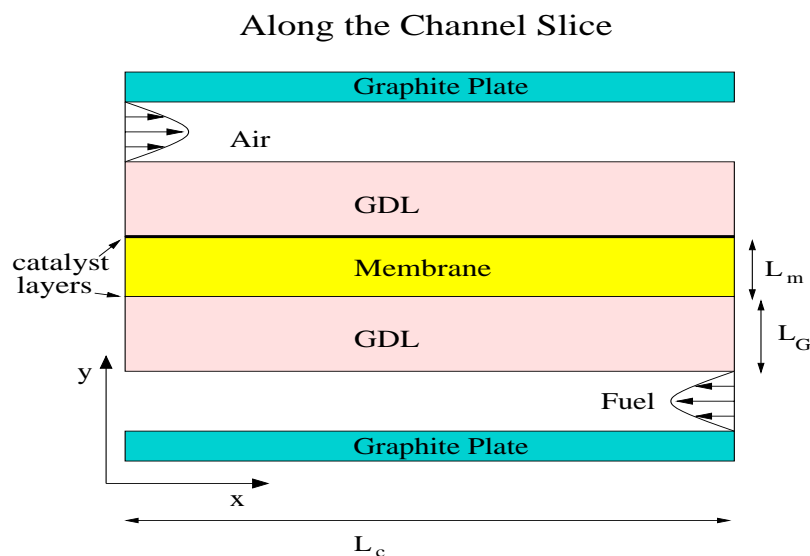
[www.math.ubc.ca/~wetton/](http://www.math.ubc.ca/~wetton/)

## Overview of the Model - I

**Unit cell:** with straight channels, run at steady state with prescribed inlet conditions (pressures, stoichs, humidifications) and total current.

**1+1 D:** Channel average fluxes are considered along the length of the channel ( $x$ ). These are coupled locally (for each  $x$ ) to 1D transport through the MEA ( $y$ ) averaged over the cell width ( $z$ ). Fuller and Newman 1993, Yi and Nguyen and White 1998.

**Outputs:** Cell voltage, local current density  $i(x)$ , local and total water crossover.



## Overview of the Model - II

**Temperature:** Assumed linear between given inlet and outlet values.

**Pressure:** Held constant at inlet value. Gasses are assumed to obey the ideal gas law.

**Voltage:** Assumed constant. Ohmic losses in GDL and plate are neglected. Anode overpotential is neglected.

**Catalyst Layers:** are treated as interfaces, exchange current  $i_0$  is fitted.

**Membrane:** nonlinear water and hydronium diffusion are considered (effective drag coefficient of 1) with local chemical equilibrium. [Thampan et. al. 2000](#). Hydronium diffusivity (membrane resistivity) minimally fitted.

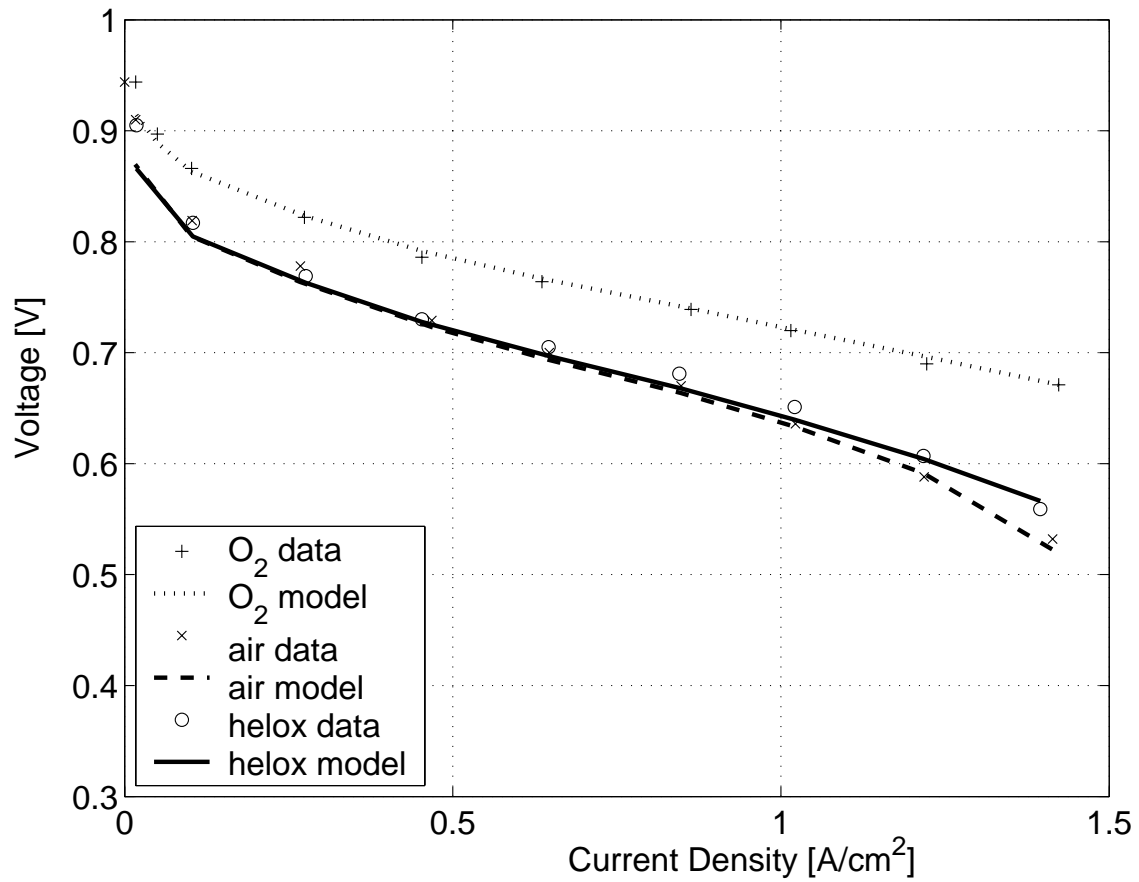
**GDL:** parametrized with fitted coefficients:  $\delta$  for oxygen transport,  $\gamma$  for water transport.

**Fitting:** to Ballard Mk9 hardware experimental sub-cell data. [Stumper et. al. 1998](#).

**Liquid Water:** ignored.

**Co- and Counter-flow**

## Results - Polarization Curves



**Pressures:** 2.2/2.0 barg (anode/cathode)

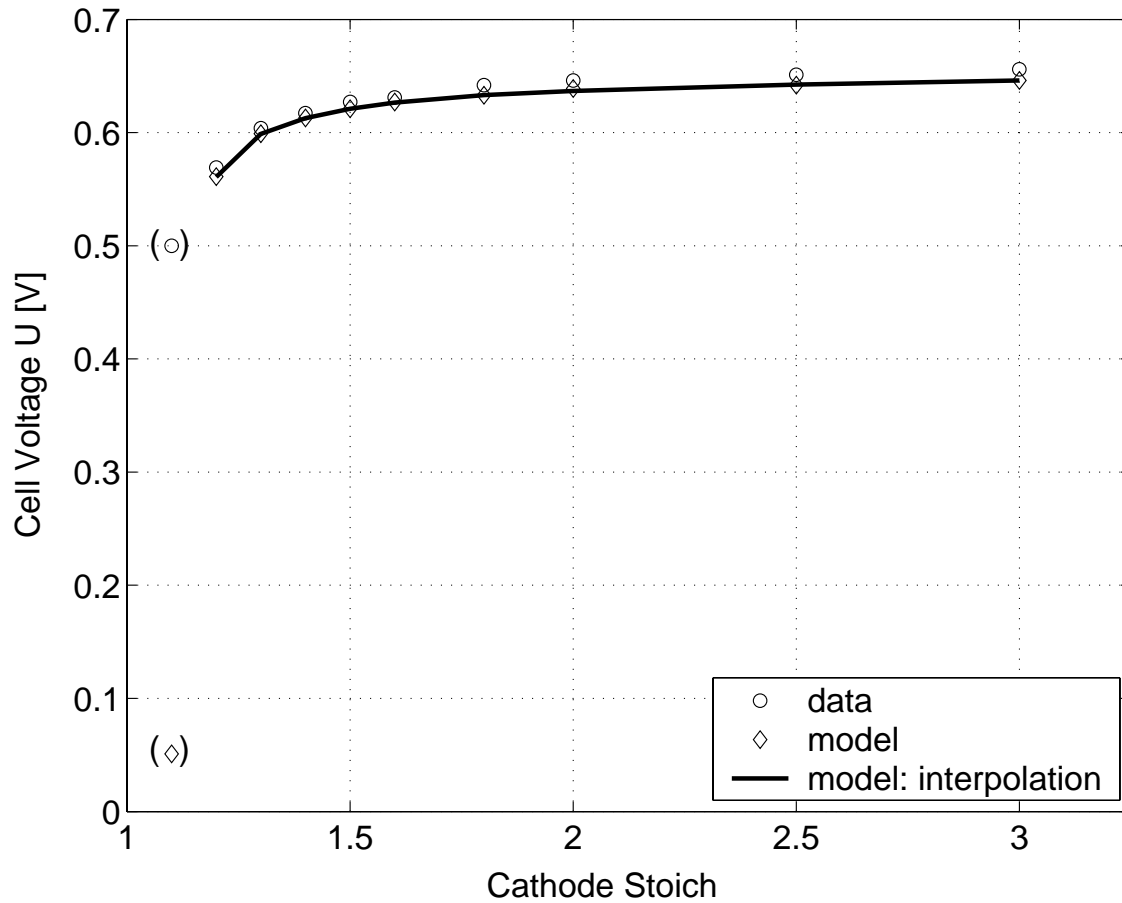
**Stoichs:** 1.2/1.8

**Inlet Dew Points:** 66/66 ° C

**Temperatures:** 70° C → 80° C

**Configuration:** Counterflow

## Results - Air Stoich Sensitivity



**Current:**  $1\text{A}/\text{cm}^2$ .

**Pressures:** 2.2/2.0 barg (anode/cathode)

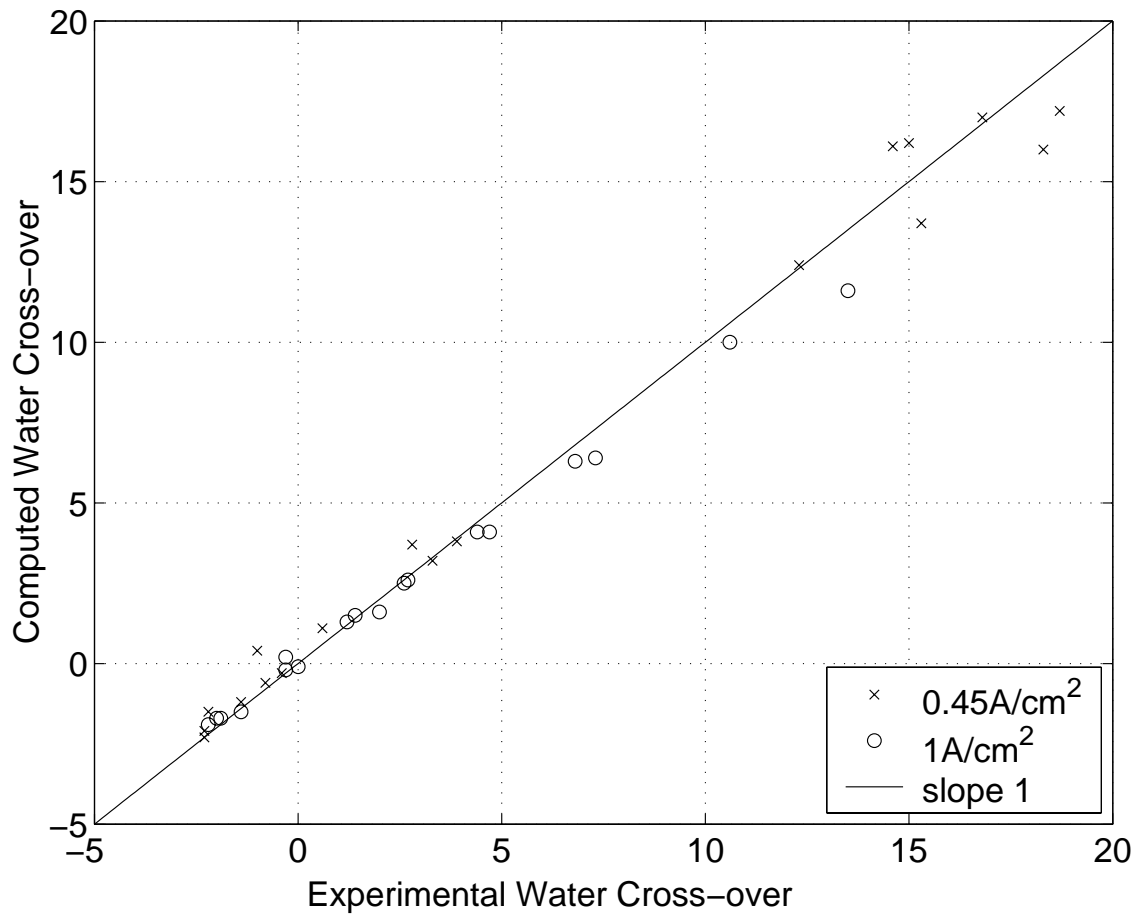
**Stoichs:** 1.2/ varied

**Inlet Dew Points:** 66/66 ° C

**Temperatures:** 70° C  $\rightarrow$  80° C

**Configuration:** Counterflow

## Results - Total Water Crossover (Anode → Cathode)



**Pressures:** 1.5, 2.0 barg (low, high current)

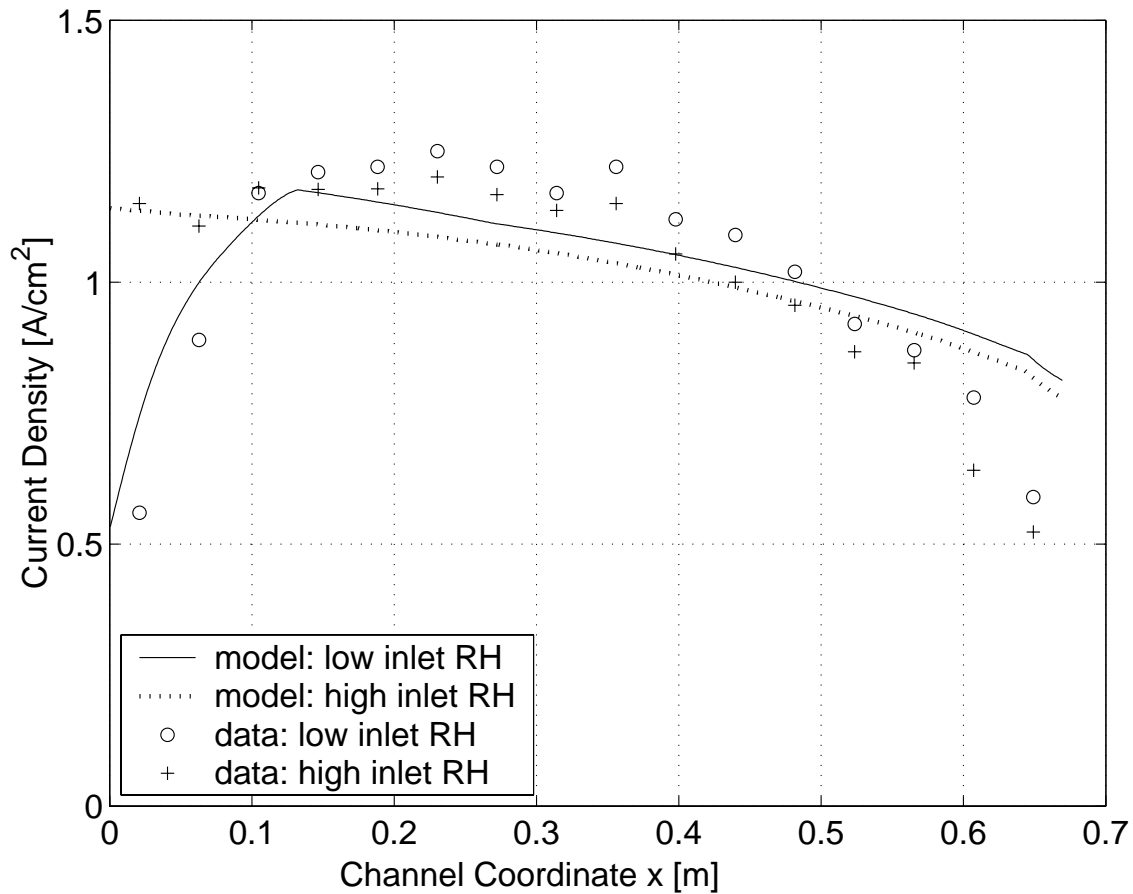
**Temperatures:** 70° C → 72° C, 70° C → 80° C.

**Stoichs:** 1.2/1.8 (anode/cathode)

**Inlet Dew Points:** -24 to 77 ° C range.

**Configuration:** Counterflow

## Results - Local Current



**Current:** 1A/cm<sup>2</sup>

**Pressures:** 2.2/2.0 barg (anode/cathode)

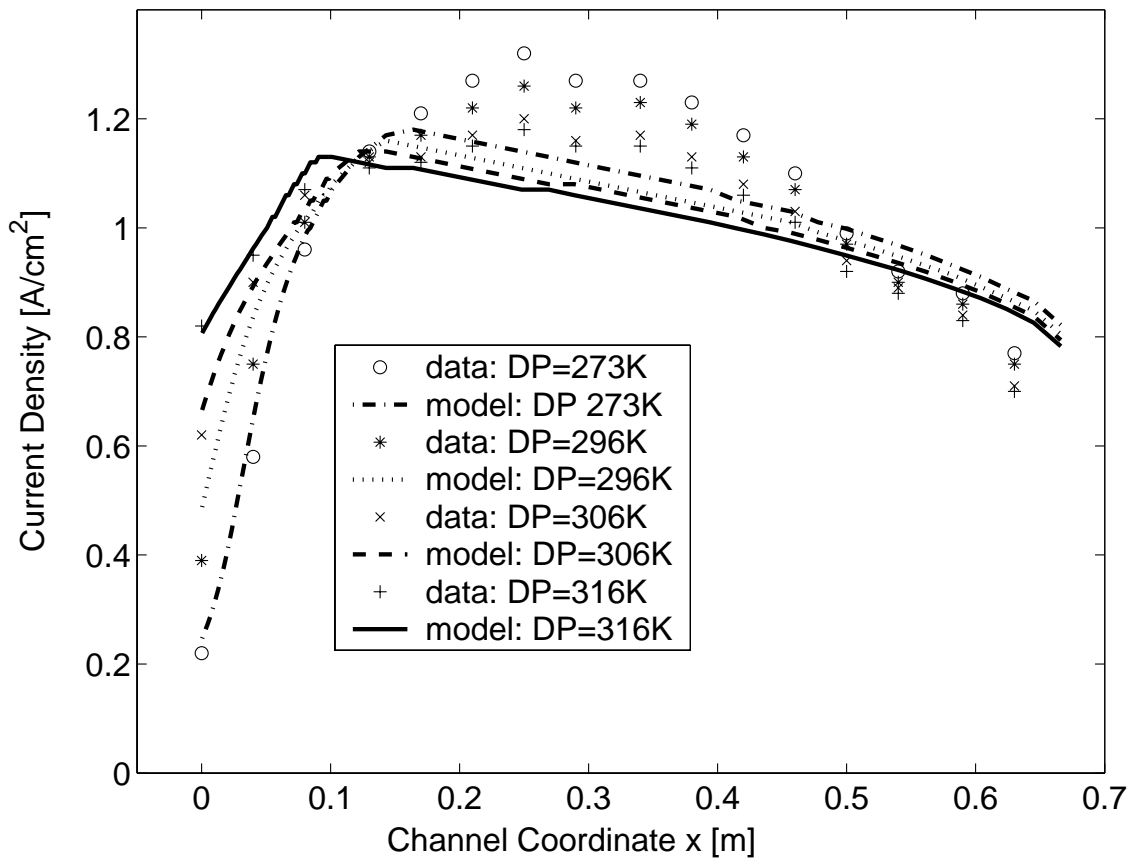
**Stoichs:** 1.2/1.8

**Inlet Dew Points:** 63° C / 63° C (high), 23° C (low)

**Temperatures:** 70° C → 80° C.

**Configuration:** Counterflow

## Results - Local Current Dependence on Cathode Inlet Humidification



**Current:** 1A/cm<sup>2</sup>

**Pressures:** 2.2/2.0 barg (anode/cathode)

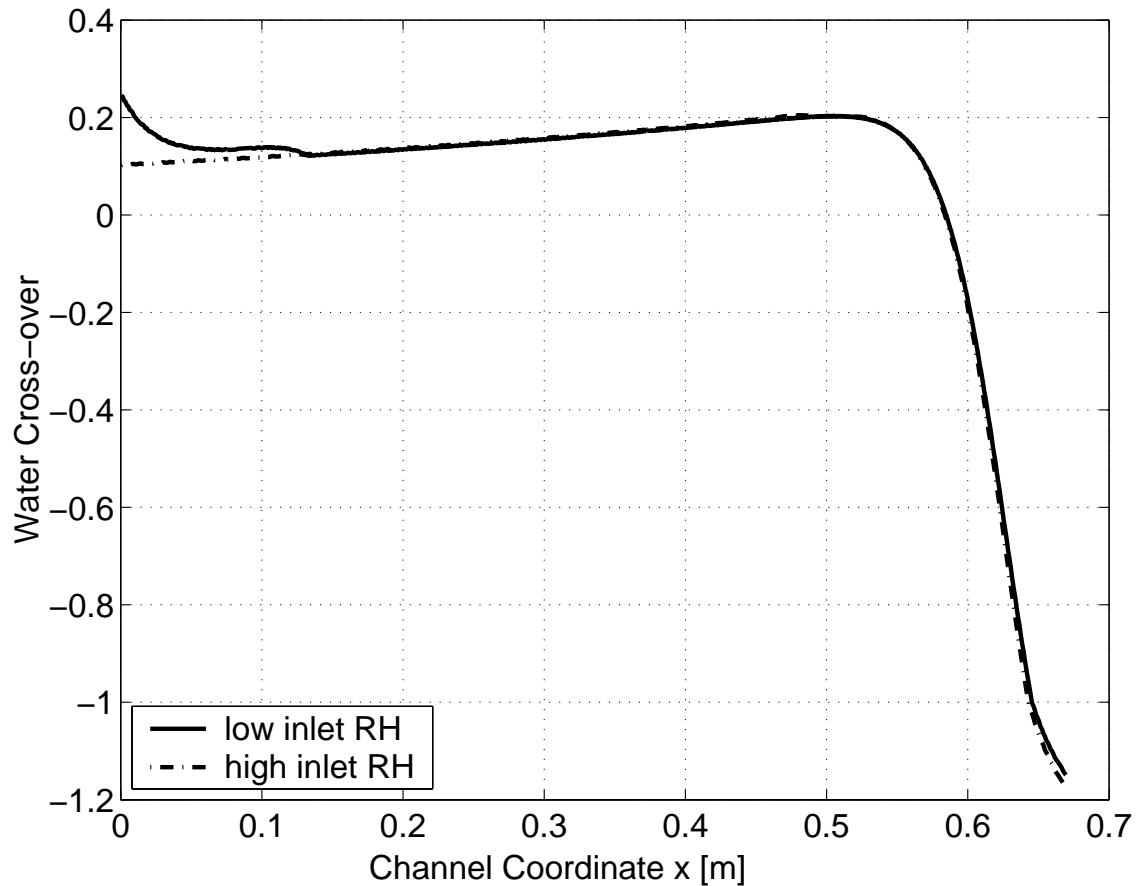
**Stoichs:** 1.2/1.8

**Inlet Dew Points:** 63° C / varied

**Temperatures:** 70° C → 80° C.

**Configuration:** Counterflow

## Results - Local Water Crossover



**Current:**  $1\text{A}/\text{cm}^2$

**Pressures:** 2.2/2.0 barg (anode/cathode)

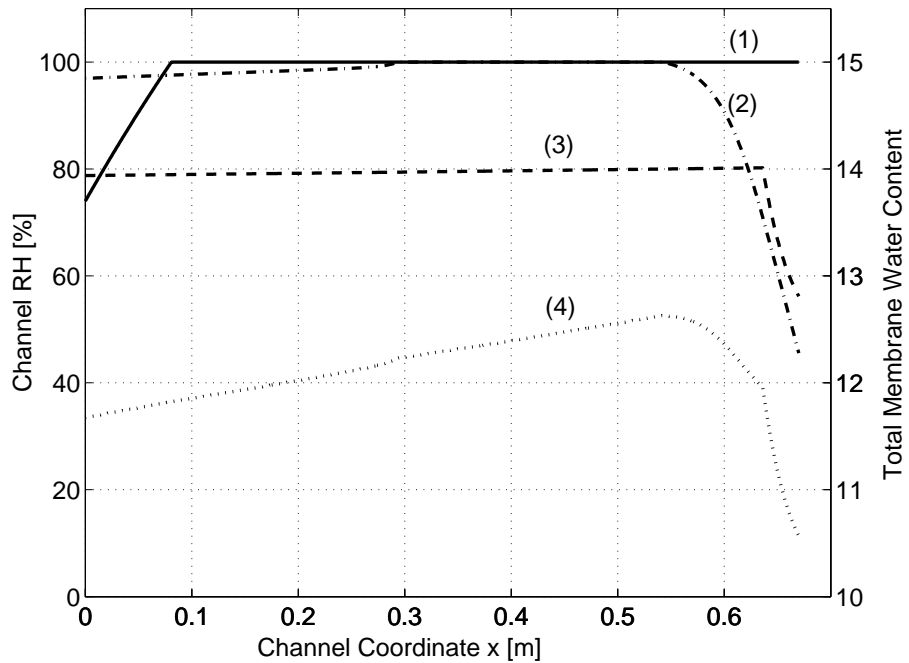
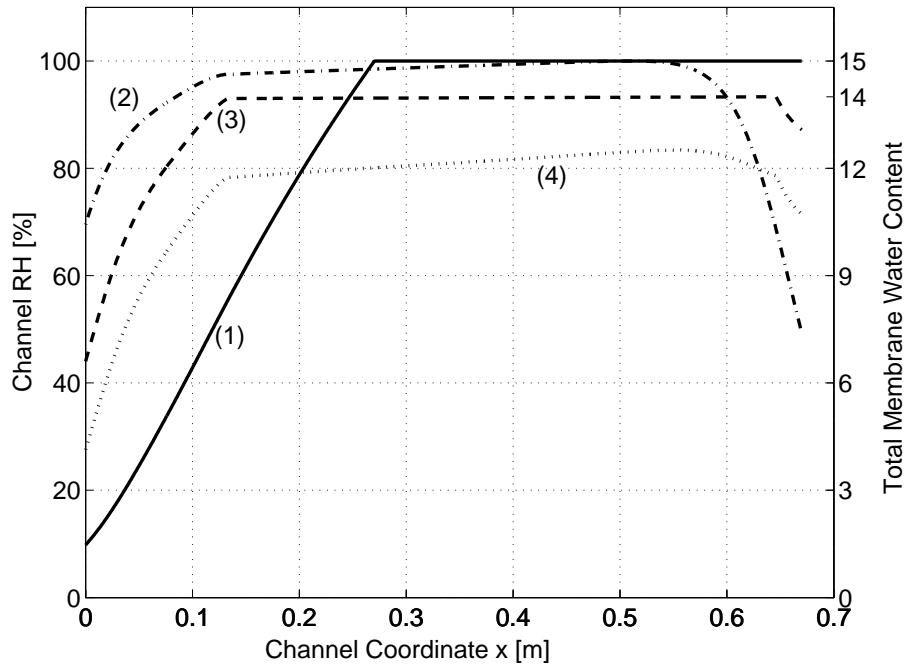
**Stoichs:** 1.2/1.8

**Inlet Dew Points:**  $63^\circ\text{C}$  /  $63^\circ\text{C}$  (high),  $23^\circ\text{C}$  (low)

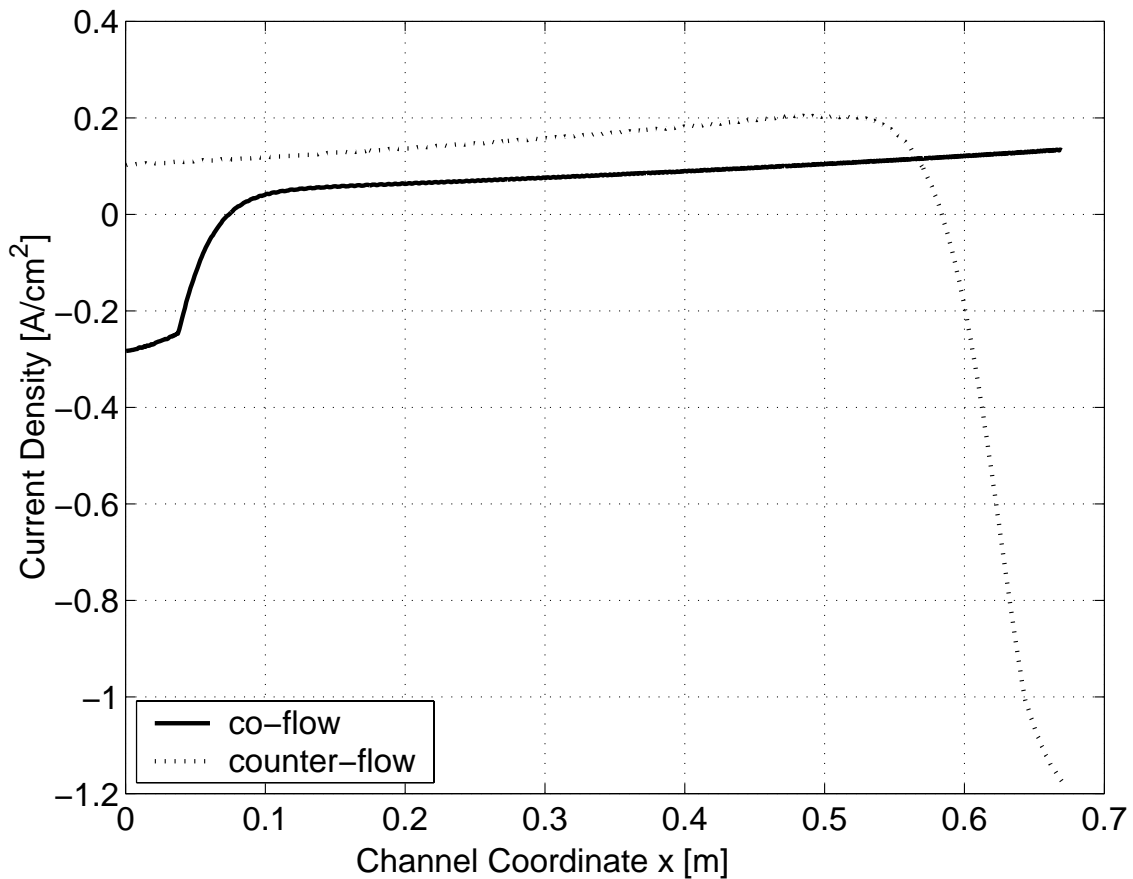
**Temperatures:**  $70^\circ\text{C} \rightarrow 80^\circ\text{C}$ .

**Configuration:** Counterflow

## Results - Water Crossover Details



## Results - Local Water Crossover Co- vs Counter-Flow



**Current:** 1A/cm<sup>2</sup>

**Pressures:** 2.2/2.0 barg (anode/cathode)

**Stoichs:** 1.2/1.8

**Inlet Dew Points:** 63/63° C

**Temperatures:** 70° C → 80° C.

## Model Details - Channel Fluxes

Average (per unit length  $z$ ) channel fluxes are considered:

$Q_1(x)$ : oxygen flux

$Q_2(x)$ : total water flux (liquid and vapour)

$Q_3$ : nitrogen flux, constant

In terms of the local current density  $I(x)$  and the total water flux  $J$  (anode to cathode) we can write:

$$\begin{aligned}\frac{dQ_1}{dx} &= -\frac{I}{4F} \\ \frac{dQ_2}{dx} &= \frac{I}{2F} + J\end{aligned}$$

Note that “initial” conditions for anode fluxes are given at the opposite end of the cell for counterflow operation.

## Model Details - Channel Molar Concentrations

Assuming the gases are ideal and that diffusion down the channel can be neglected we obtain:

$$C_j = \frac{P}{\mathcal{R}T} \frac{Q_j}{Q_1 + Q_2 + Q_3} \quad , \quad j = 1, 2, 3$$

where  $P$  is the cathode pressure, assumed constant in  $x$ . This result is valid if the channel is undersaturated (if  $\mathcal{R}TC_{c,2} < P_{sat}(T)$ ).

Otherwise

$$C_2 = P_{sat}(T)/\mathcal{R}T$$

and

$$C_j = \frac{P - P_{sat}(T)}{\mathcal{R}T} \frac{Q_j}{Q_1 + Q_3} \quad , \quad j = 1, 3.$$

We have so far:

- Cathode channel oxygen concentration
- Channel activities

in terms of the channel fluxes.

## Model Details - Oxygen Concentration at Catalyst - I

The oxygen concentration at the catalyst sites is influenced by mass transport limitations from

- inter-species diffusion in the GDL.
- inter-species diffusion in the channel flow.
- pore blockage of the GDL due to liquid water.

The first two effects are incorporated into the model via an effective GDL diffusivity  $D_o^{eff}$  through the mass transport condition

$$\frac{I(x)}{4F} = \frac{D_o^{eff}}{L_G}(C_1(x) - \hat{C}(x))$$

where  $L_G$  is the width of the GDL and  $\hat{C}(x)$  is the oxygen concentration at GDL-side of the catalyst layer.

We rewrite this as

$$\hat{C}(x) = C_1(x) - \delta I$$

where the parameter

$$\delta = \frac{L_G}{4F D_o^{eff}}$$

has been introduced.  $\delta$  will be fit to experimental data.

## Model Details - Oxygen Concentration at Catalyst - II

We further assume that the active catalyst sites are inside the membrane material. The water must dissolve into this medium, which is assumed to occur at a equilibrium similar to oxygen in water giving

$$C(x) = \frac{RT}{H_o} C(\hat{x})$$

(Henry's law) where  $C(x)$  is the oxygen concentration at the catalyst sites.

Now we have the oxygen concentration at catalyst sites in terms of the channel concentration and the local current.

## Model Details - Voltage Balance

The external potential  $U$  (independent of  $x$ ) is given by

$$U = E_0 - \eta - I/\sigma$$

at each  $x$  where  $E_0$  is the open circuit voltage,  $\eta_c$  is the cathode overpotential (electrochemical losses) and  $\sigma$  is the (water content dependent) membrane proton conductivity.

Standard electrochemistry literature approximates

$$\eta \simeq \frac{\mathcal{R}T}{\alpha F} \ln \left( \frac{I(x)C_o^{ref}}{i_0 C(x)} \right)$$

(Tafel equation) where  $C_o^{ref}$  is taken to be pure oxygen at 1 Atm, the exchange current  $i_0$  is fitted to data, and we take  $\alpha = 1$  (leading to a Tafel slope of about 67mV per decade).

The voltage balance above now determines  $I$  implicitly in terms of the channel oxygen concentration, provided  $\sigma$  is known.

## Model Details - Membrane Equilibrium

We assume only hydronium and free water are present in the membrane. Equilibrium between the the local free water content  $c_w$ , the protons bound to the fixed charge (acid) groups  $c_b$ , and hydronium  $c_+$ ,



leads to

$$c_b c_w K_e(T) = c_+(1 - c_b)$$

with

$$K_e(T) = K_0 \exp \left[ -\frac{H_0}{\mathcal{R}} \left( \frac{1}{T} - \frac{1}{298} \right) \right].$$

with  $K_0 = 6.2$  [Thampan et al. 2000](#).

The assumption of local electro-neutrality gives

$$1 - c_b - c_+ = 0$$

which leads to

$$c_+(c_w, T) = -\frac{K_e c_w}{2} + \sqrt{\left( \frac{K_e c_w}{2} \right)^2 + K_e c_w}$$

Thus, the membrane free water content locally determines the hydronium concentration  $c_+$ , and hence the total water concentration  $c_T = c_w + c_+$ , as a function of temperature.

## Model Details - Membrane Diffusion

We neglect frictional effects between hydronium and free water and assume they are subject to nonlinear diffusion:

$$\begin{aligned} -D_+ \frac{dc_+}{dy} - \frac{F}{\mathcal{R}T} D_+ c_+ \frac{d\phi}{dy} &= I/(Fa) \\ -D_w \frac{dc_w}{dy} &= J_w/a. \end{aligned}$$

where  $a$  is the sulfonic acid group concentration,  $I$  is the (as yet undetermined) local current density and  $J_w$  is the (as yet undetermined) diffusive free water flux. The total water flux is

$$J = I/F + J_w$$

The second equation above will be solved for  $c_w(y)$  and then the first can be integrated to give voltage losses across the membrane (effect is like a water dependent conductivity).

The diffusion coefficients are chosen to be

$$\begin{aligned} D_+(c_w, T) &= d_+ \exp(-1683/T) c_w, \\ D_w(c_w, T) &= d_w \exp(-2436/T) c_w, \end{aligned}$$

following the literature [Bernardi and Verbrugge 1992](#), [Motupally et. al 2000](#). The value of  $d_+$  is (minimally) fit to the experimental data.

## Model Details - Catalyst/Membrane Interface

Membrane equilibrium water sorption value  $c_w^*$  as a function of water activity  $a_w$  (relative humidity) of its environment:

$$c_T^* = 0.043 + 17.81a_w - 39.85a_w^2 + 36a_w^3,$$

fit for Nafion 117 at 30°C [Zawodinski et al. 1993](#). We neglect Shroeder's paradox and limit water contents to 14.

Incorrect results occur when  $c_T^*$  (based on channel activities) is taken to be the total water content at the inner boundary of the membrane (conductivity is too sensitive to channel activities).

We take

$$\begin{aligned} \text{anode} : (J_w + \frac{I}{F})/a &= -\gamma [c_T^a - c_{T,a}^*], \\ \text{cathode} : (J_w + \frac{3I}{2F})/a &= \gamma [c_T^c - c_{T,c}^*]. \end{aligned}$$

where  $\gamma$  is a fitted water mass transport parameter.

$J_w$  can be determined analytically in terms of  $c_T^a$  and  $c_T^c$ . We can (after some algebra) solve analytically for the  $c_T$ 's in terms of the channel predicted values  $c_T^*$  and the local current  $I$ .

## Model Details - Implementation

The code is written in MATLAB and is a nested sequence of iterations:

- The cell voltage  $U$  is varied until the target current is reached.
- The cathode and anode fluxes are updated at (1000) points along the channel sequentially from inlet to outlet. The technique is called “back and forth shooting” [Eirola 1983](#). 10 iterations are sufficient.
- At each channel location, the local current density is found by the iterative solution of

$$U = E_o - \frac{\mathcal{R}T}{\alpha_c F} \ln \left( \frac{C_o^{ref} H_0}{i_{o,c} \mathcal{R}T} \frac{I}{(C_1(x) - \delta I)} \right) - I/\sigma$$

where  $C_1(x)$  is the local channel oxygen concentration. Recall  $\sigma$  depends on water content so also on  $I$ .

- At each iteration above, the conductivity is determined by numerical integration.

## Fitting - I

- oxygen mass transfer coefficient  $\delta$
- exchange current density  $i_0$
- average membrane conductivity  $\sigma$

$n$  runs of experimental  $i(x)$  (at 16 stations) is used in the channel model (neglecting water crossover) to generate  $16n$  data ( $k = 1 \dots 16$  and  $m = 1 \dots n$ ):

- Oxygen concentrations  $C_{k,m}$
- Current Densities  $I_{k,m}$  (data)
- Temperatures  $T_{k,m}$  (linear)
- Voltage  $U_m$  (data)

Then

$$RES = \sum_{m=1}^n \sum_{k=1}^{16} (res_{k,m})^2$$

is minimized where

$$res_{k,m} = E_o - U_m - I_{k,m}/\sigma - \frac{RT_{k,m}}{F\alpha_c} \ln \left( \frac{I_{k,m}}{i_{o,c}} \frac{c_{o,ref}}{C_{k,m} - \delta I_{k,m}} \right).$$

The procedure yields

$$\begin{aligned} \text{Air} : i_{o,c} &= 426.7 \text{ A/m}^2, \\ \delta &= 0.8993 \times 10^{-3} \text{ s mole m}^{-1} \text{ C}^{-1} \\ \sigma^{-1} &= 0.09373 \text{ } \Omega \text{ cm}^2, \end{aligned}$$

## Fitting - Discussion of $\delta$

If  $\delta$  was due entirely to oxygen diffusivity in the GDL then this would correspond to:

$$D_o = \frac{4F}{L_G \delta} = 7.2^{-7} \text{m}^2/\text{s}$$

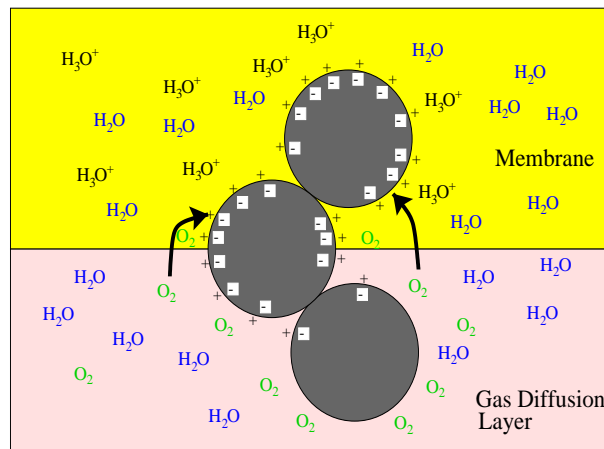
in Nitrogen, an order of magnitude from the actual value  $1.04 \times 10^{-5}$ .

Also, the fitting procedure yields

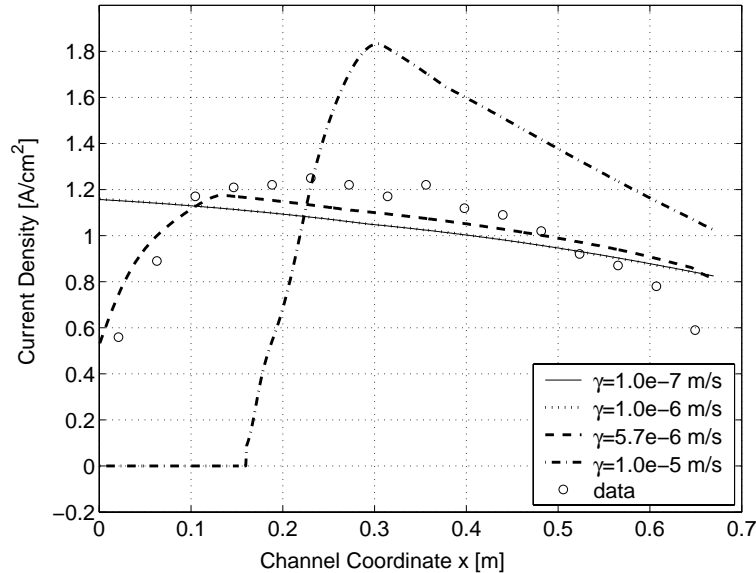
$$\delta = 0.7939 \times 10^{-3}$$

for Helox, and if  $\delta$  was due entirely to binary diffusivity in the channel and GDL, there should be a factor of 3 difference to the air value of  $0.8993 \times 10^{-3}$ .

Other diffusive processes are clearly important in the overall parameter  $\delta$ .



## Fitting - II



- $\gamma$  chosen to match the inlet blip of the lowest RH cathode inlet data. We find  $\gamma = 0.57 \times 10^{-5}$  m/s.
- Performance is very sensitive to the choice of  $\gamma$ . Order of magnitude estimates can be found from membrane drying data [Basura 2000](#).
- If  $\gamma$  was due entirely to vapour diffusivity in the DGL, this would correspond to

$$D_v = 1.43 \times 10^{-9}$$

four orders of magnitude too small!

- Water transfer from the membrane to the channel is dominated by processes occurring at the boundary of the membrane.

## End Remarks

A simple steady state computational model of a unit cell is presented capable of predicting:

- polarization curves
- stoich sensitivities
- local and total water crossover
- local current density profiles
- sensitivity to inlet humidities
- co- and counter-flow operation

Minimal fitting is required.

The model can be extended to include

- Thermal effects.
- Pressure drops driving the flow in the channels.
- Transient effects.

It can be used to investigate and fit MEA models used in large 3D CFD codes.