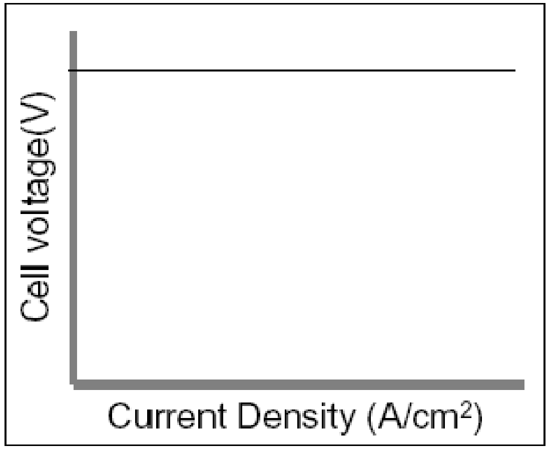
Losses in Fuel Cells

Reversible Voltage (Chapter 2)



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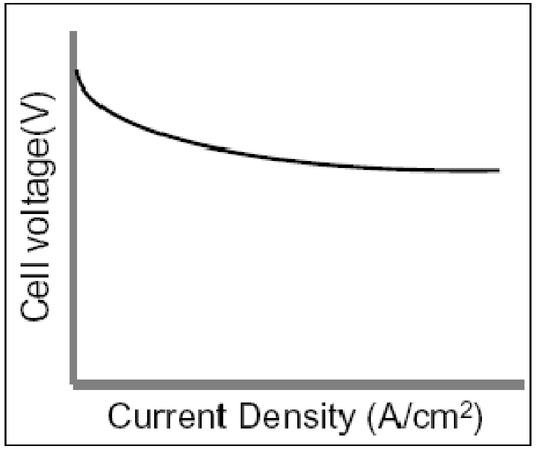
Rxn. Loss (Chapter 3)



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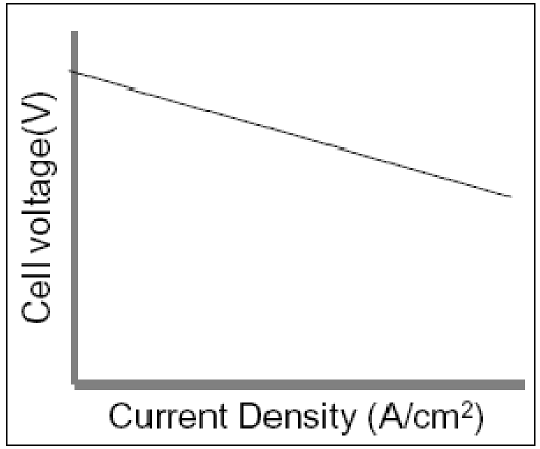
Ohmic Loss (Chapter 4)



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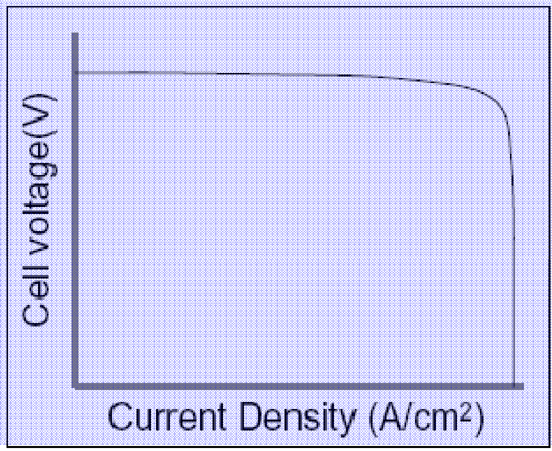
Concentration Loss (Chapter 5)



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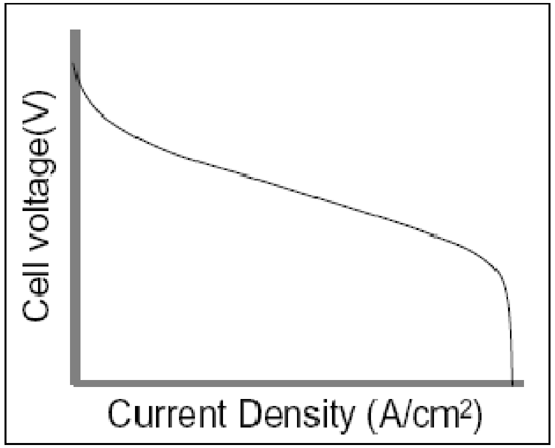
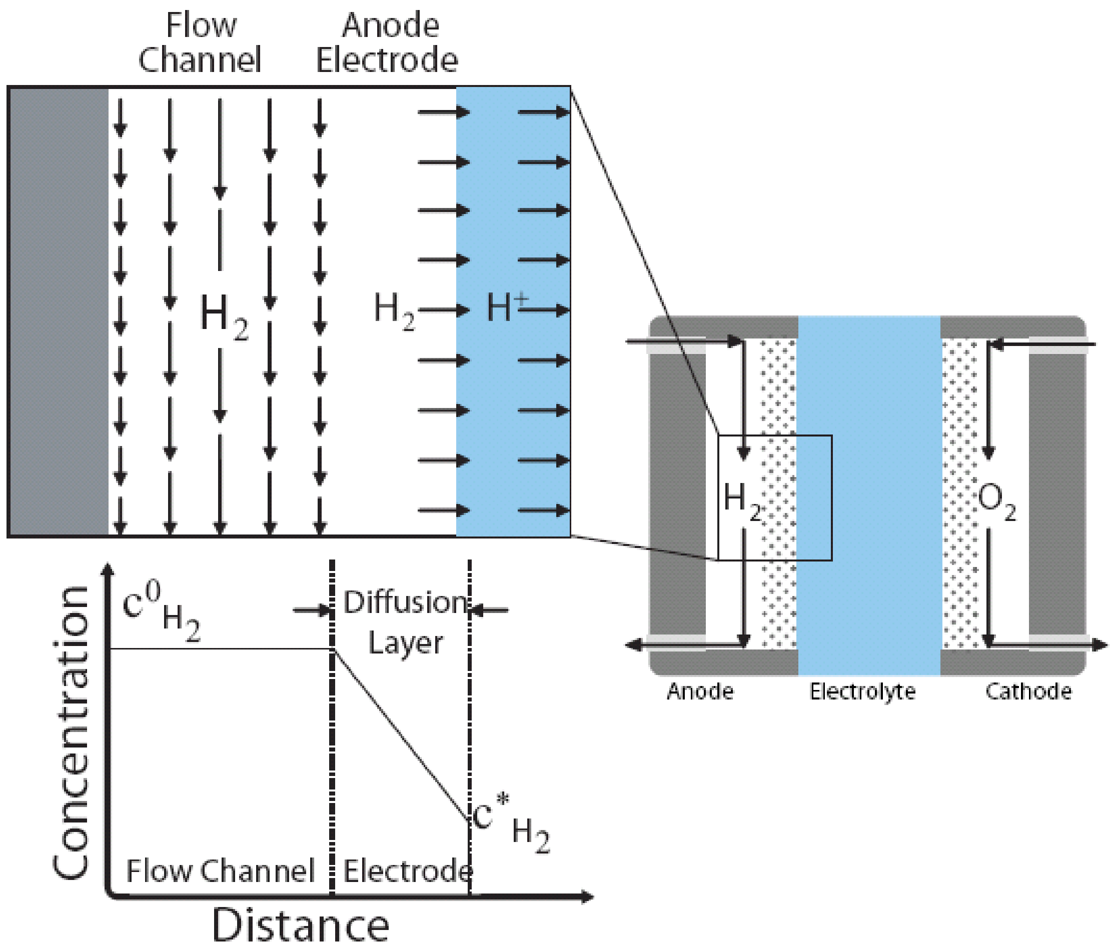
Net Fuel Cell Performance



$$V = E_{thermo} - \eta_{act} - \eta_{ohmic} - \eta_{conc}$$

Fuel Cell Charge Transport

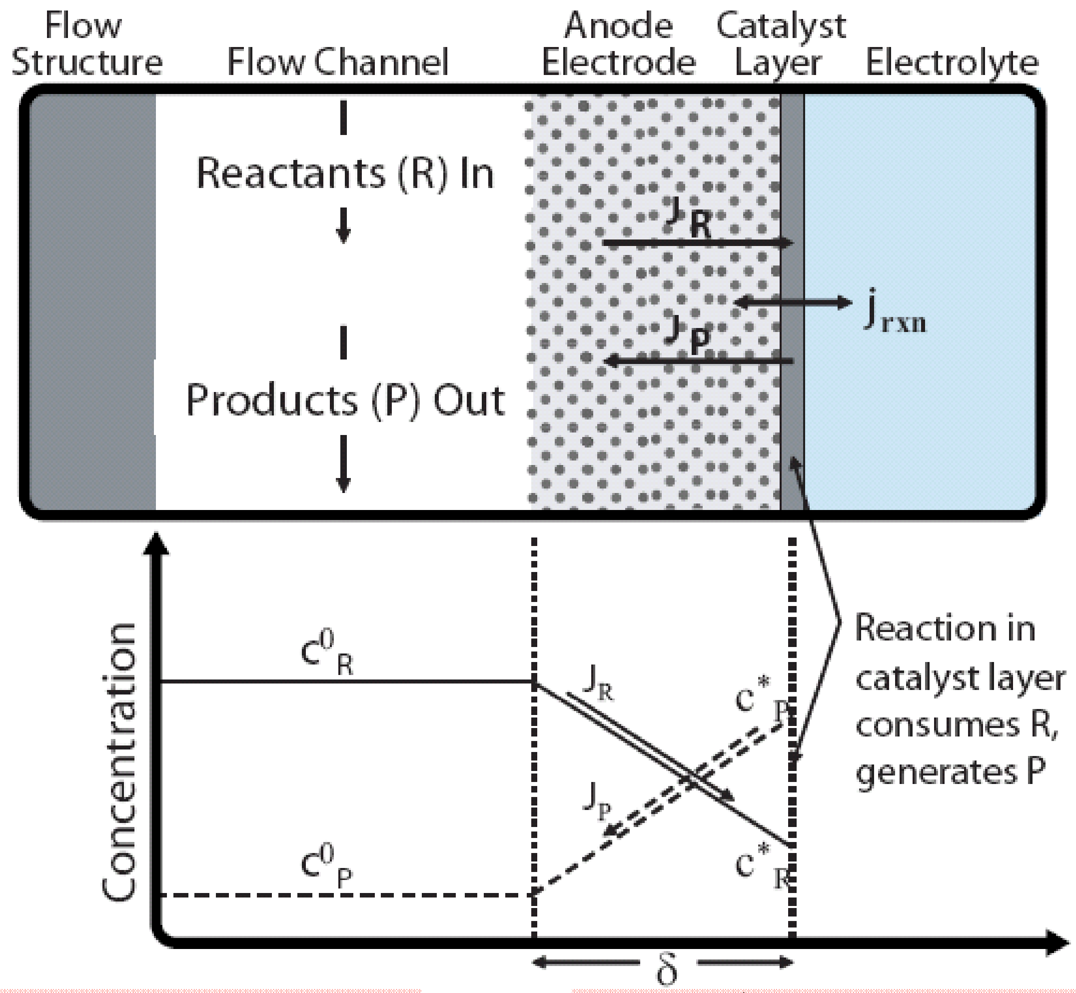
Mass Transport



Convection dominant in flow channels

Diffusion dominant in electrode

Concentration Drop



$$E = E^0 - \frac{RT}{nF}\ln\frac{\Pi p_{\text{Product}}^{v_i}}{\Pi p_{\text{Reactants}}^{v_i}}$$

$$j = j_0\left(\frac{C_R}{C_R^0}e^{\left(\frac{\alpha nF\eta}{RT}\right)} - \frac{C_P}{C_P^0}e^{-\left(\frac{(1-\alpha)nF\eta}{RT}\right)}\right)$$

Diffusion In Electrode

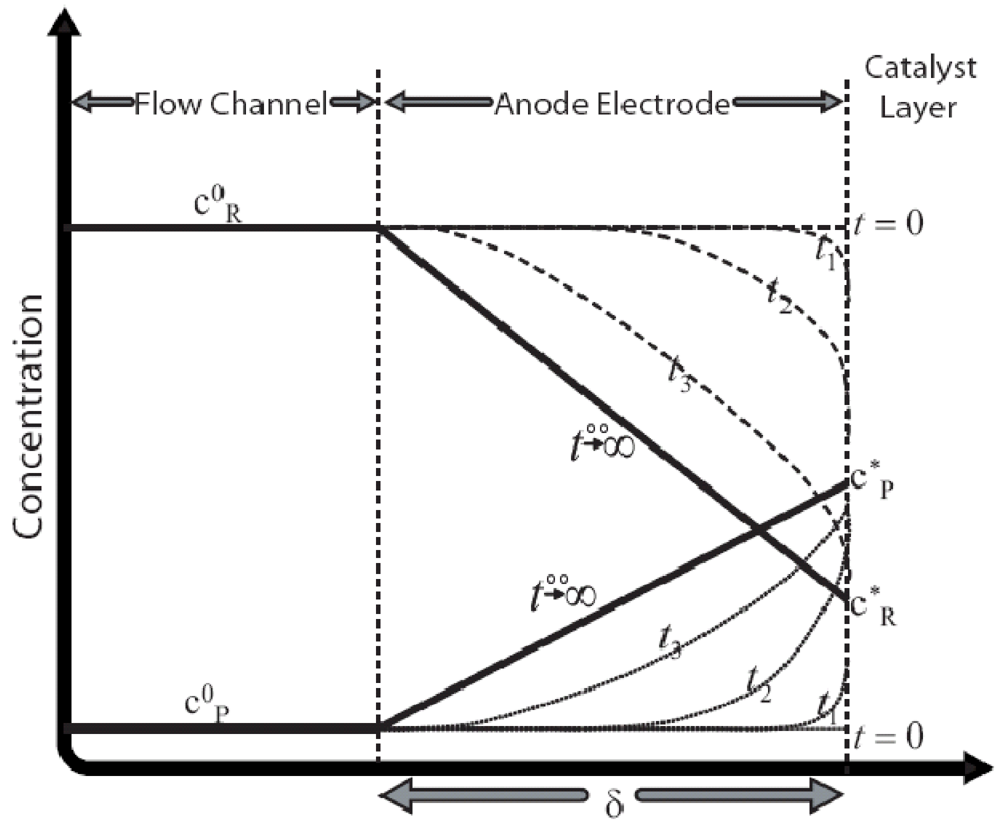
$$J_{diff} = -D\frac{dc}{dx}$$

$$J_{diff} = -D^{eff}\frac{c_R^* - c_R^0}{\delta}$$

$$j = nFJ_{diff}$$

$$j = -nFD^{eff}\frac{c_R^* - c_R^0}{\delta}$$

$$c_R^* = c_R^0 - \frac{j\delta}{nFD^{eff}}$$



Limiting Current Density

$$j_L = nFD^{eff}\frac{c_R^0}{\delta}$$

Typical values for δ are around $100-300\mu m$ and D^{eff} are around $10^{-2}cm^2/s$. Therefore typical limiting current densities are on order of $1-10A/cm^2$. This

– To increase j_L

1. Ensuring a high c_R^0 (by designing good flow structures that evenly distribute reactants).

2. Ensuring that D^{eff} is large and δ is small (by carefully optimizing fuel cell operating conditions, electrode structure, and diffusion layer thickness).

Q: Are 1 & 2 are easy?

Q: Does anode has larger j_L?

Diffusivity & Effective Diffusivity

Diffusivity from kinetic theory

$$p \cdot D_{ij} = a \left(\frac{T}{\sqrt{T_{ci} T_{cj}}} \right)^b (p_{ci} p_{cj})^{1/3} (T_{ci} T_{cj})^{5/12} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}$$

Substance	Molecular Weight, M	$T_c(K)$	p_c(atm)
H_2	2.016	33.3	12.80
Air	28.964	132.4	37.0
N_2	28.013	126.2	33.5
O_2	31.999	154.4	49.7
CO	28.010	132.9	34.5
CO_2	44.010	304.2	72.8
H_2O	18.015	647.3	217.5

Effective diffusivity

$$D_{ij}^{eff} = \epsilon^{1.5} D_{ij}$$

$$D_{ij}^{eff} = \epsilon^{\tau} D_{ij}$$

$$D_{ij}^{eff} = D_{ij} \frac{\epsilon}{\tau}$$

Nernst Effect

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod a_{PRODUCTS}^{v_i}}{\prod a_{REACTANTS}^{v_i}}$$

$$\eta_{conc} = E_{Nernst}^0 - E_{Nernst}^*$$

$$\eta_{conc} = (E^0 - \frac{RT}{nF} \ln \frac{1}{c_R^0}) - (E^0 - \frac{RT}{nF} \ln \frac{1}{c_R^*})$$

$$\eta_{conc} = \frac{RT}{nF} \ln \frac{c_R^0}{c_R^*}$$

$$c_R^* = c_R^0 - \frac{j\delta}{nFD^{eff}}$$

$$c_R^* = \frac{j_L\delta}{nFD^{eff}} - \frac{j\delta}{nFD^{eff}}$$

$$\frac{c_R^0}{c_R^*} = \frac{\frac{j_L\delta}{nFD^{eff}}}{\frac{j_L\delta}{nFD^{eff}} - \frac{j\delta}{nFD^{eff}}}$$

$$\frac{c_R^0}{c_R^*} = \frac{j_L}{j_L - j}$$

$$\eta_{conc} = \frac{RT}{nF} \ln \frac{j_L}{j_L - j}$$

Concentration Effect

B-V for high current density

$$j = j_0^0\left(\frac{c_R^*}{c_R^{0*}}e^{\left(\frac{\alpha n F \eta_{act}}{RT}\right)}\right)$$

$$\eta_{act} - \frac{RT}{\alpha n F}\ln\frac{j c_R^{0*}}{j_0^0 c_R^*}$$

$$\eta_{conc} = \eta_{act}^* - \eta_{act}^0$$

$$\eta_{conc} - \left(\frac{RT}{\alpha n F}\ln\frac{j c_R^{0*}}{j_0^0 c_R^*}\right) - \left(\frac{RT}{\alpha n F}\ln\frac{j c_R^{0*}}{j_0^0 c_R^0}\right)$$

$$\eta_{conc} = \frac{RT}{\alpha n F}\ln\frac{c_R^0}{c_R^*}$$

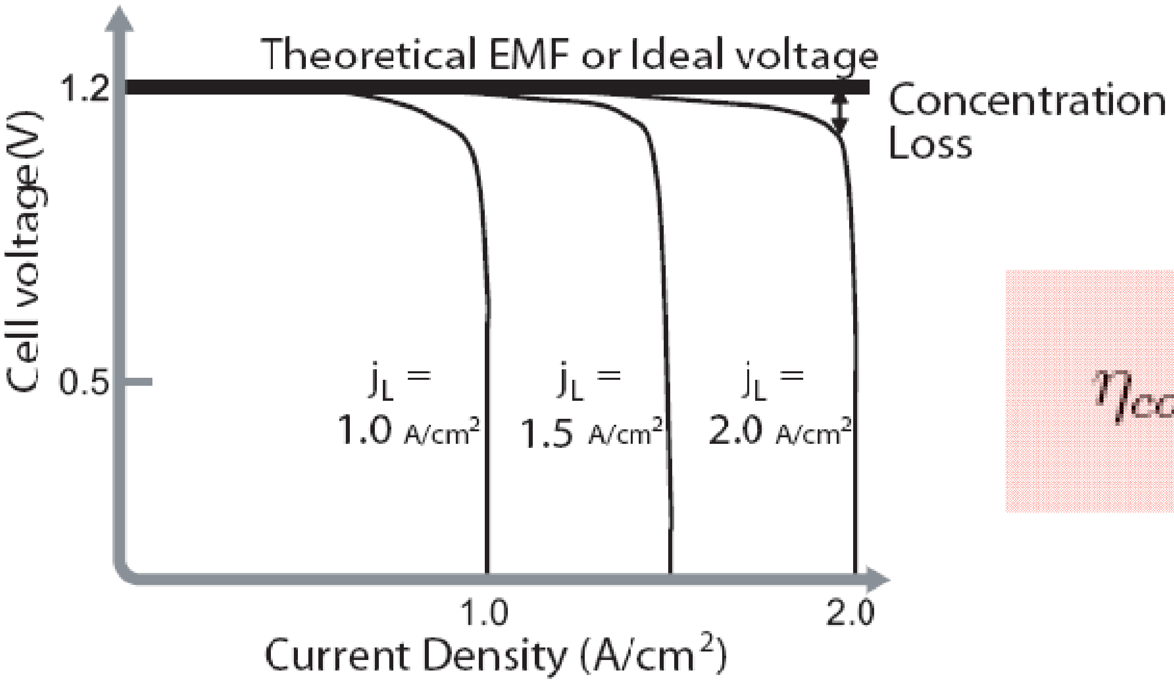
$$\eta_{conc} = \frac{RT}{\alpha n F}\ln\frac{j_L}{j_L - j}$$

Mass Transportation Loss

Adding two losses

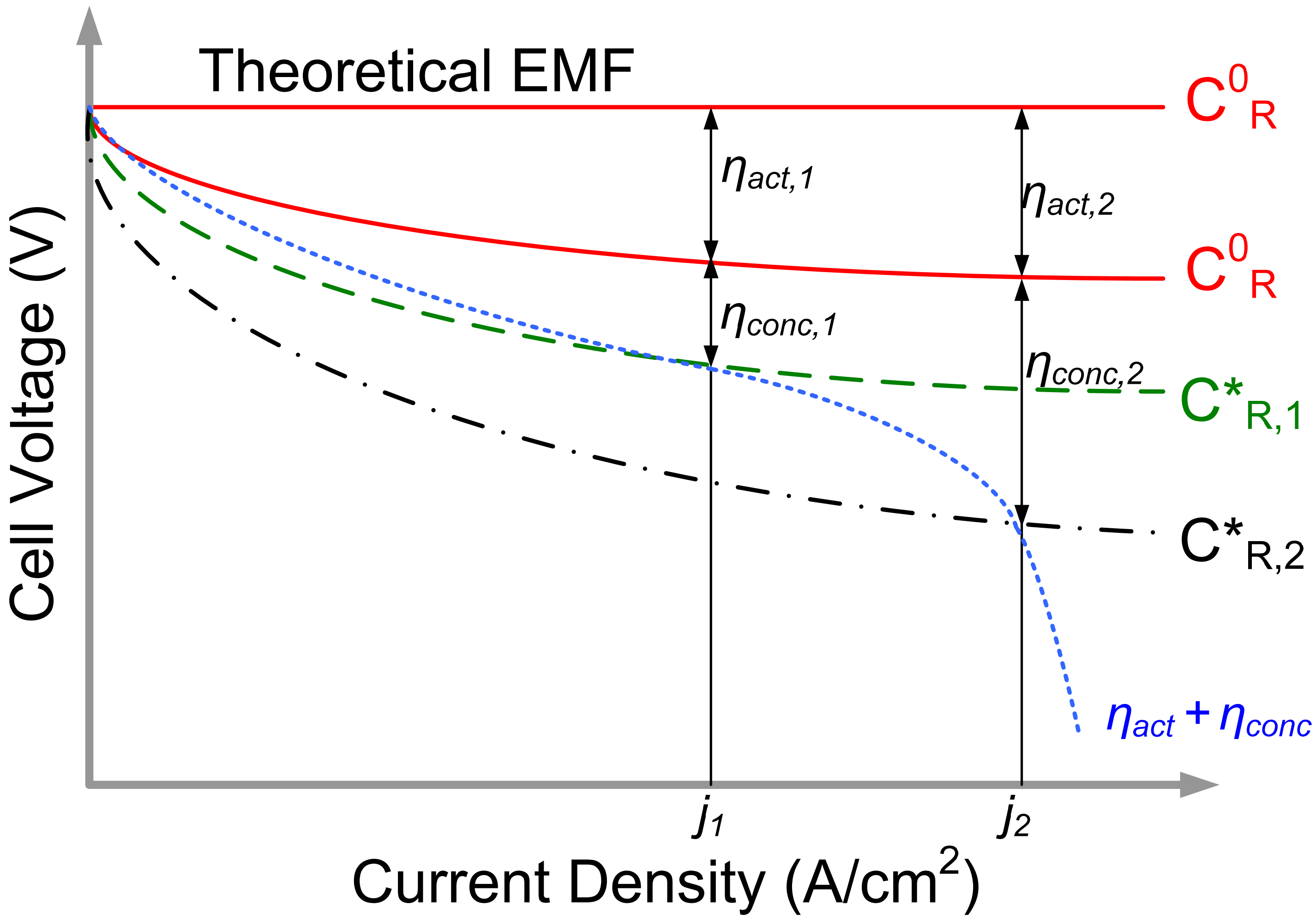
$$\eta_{conc} = \frac{RT}{nF} \ln \frac{j_L}{j_L - j} + \frac{RT}{\alpha nF} \ln \frac{j_L}{j_L - j}$$

$$\eta_{conc} = (\frac{RT}{nF})(1 + \frac{1}{\alpha}) \ln \frac{j_L}{j_L - j}$$



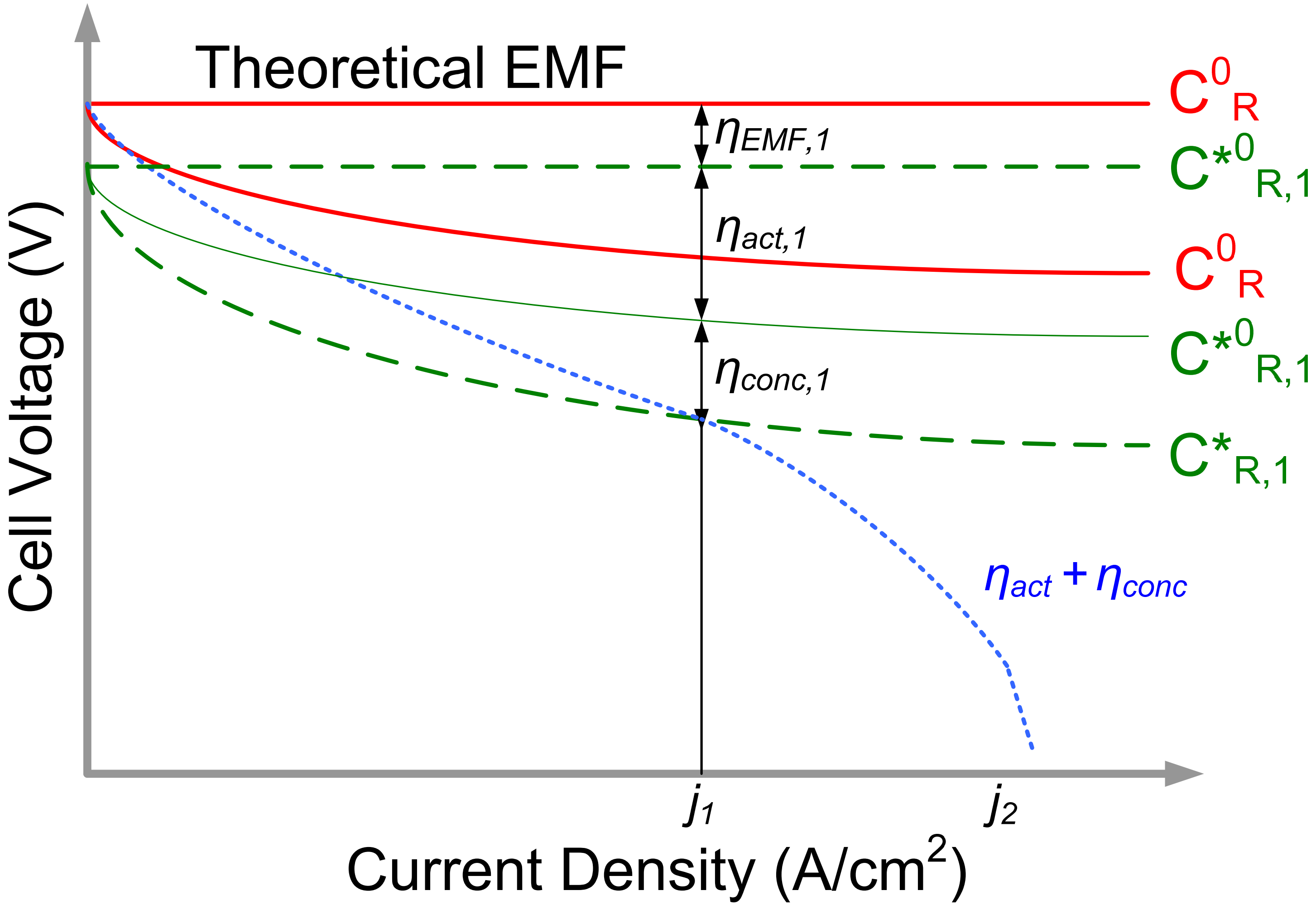
$$\eta_{conc} = c \ln \frac{j_L}{j_L - j}$$

Pictorial View



$$j = j_0^0 \left(\frac{c_R^*}{c_R^{0*}} e^{\left(\frac{\alpha n F \eta_{act}}{RT} \right)} \right)$$

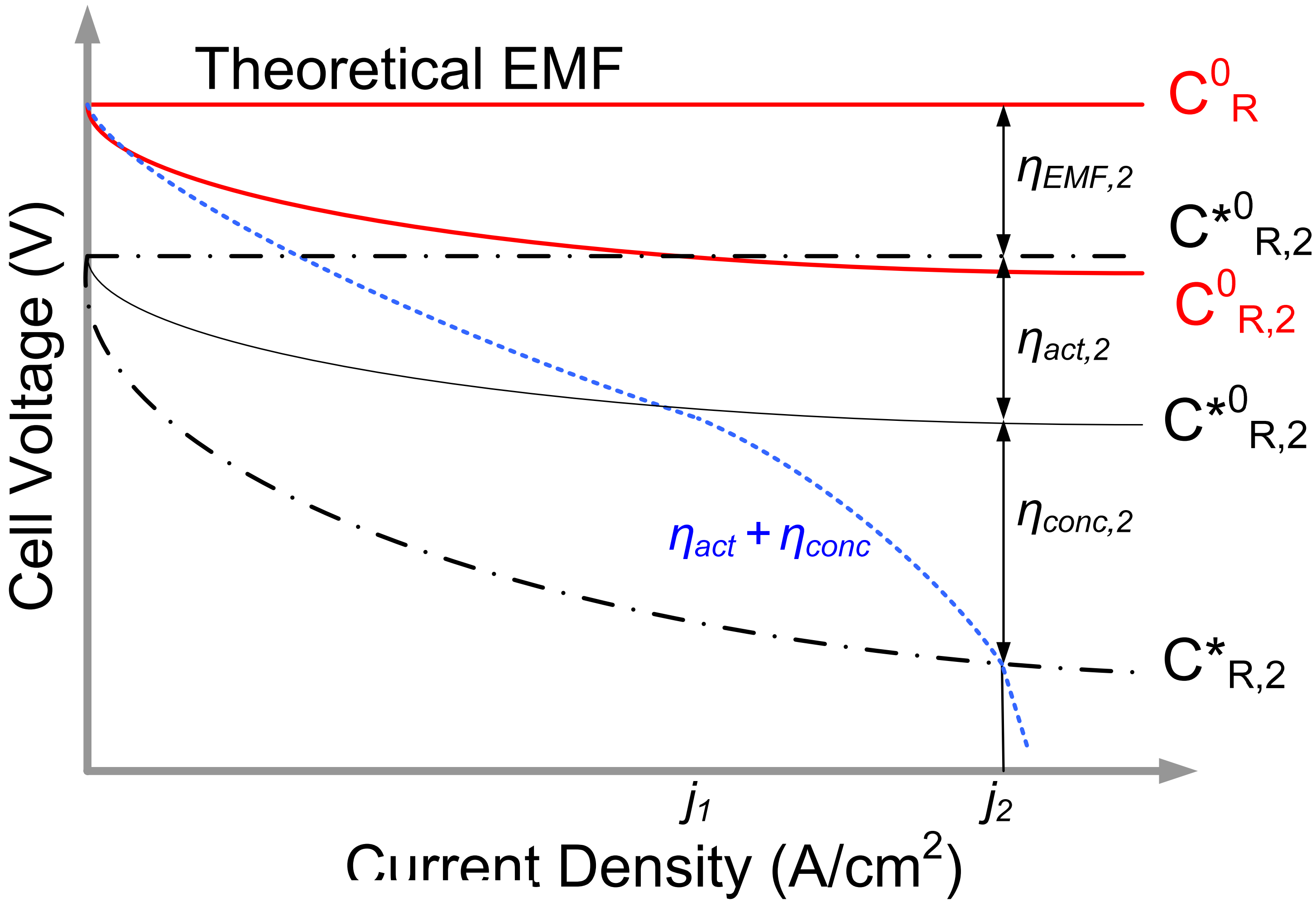
Pictorial View



$$j = j_0^0 \left(\frac{C_R^*}{c_R^{0*}} e^{\left(\frac{\alpha n F \eta_{act}}{RT} \right)} \right)$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod a_{PRODUCTS}^{v_i}}{\prod a_{REACTANTS}^{v_i}}$$

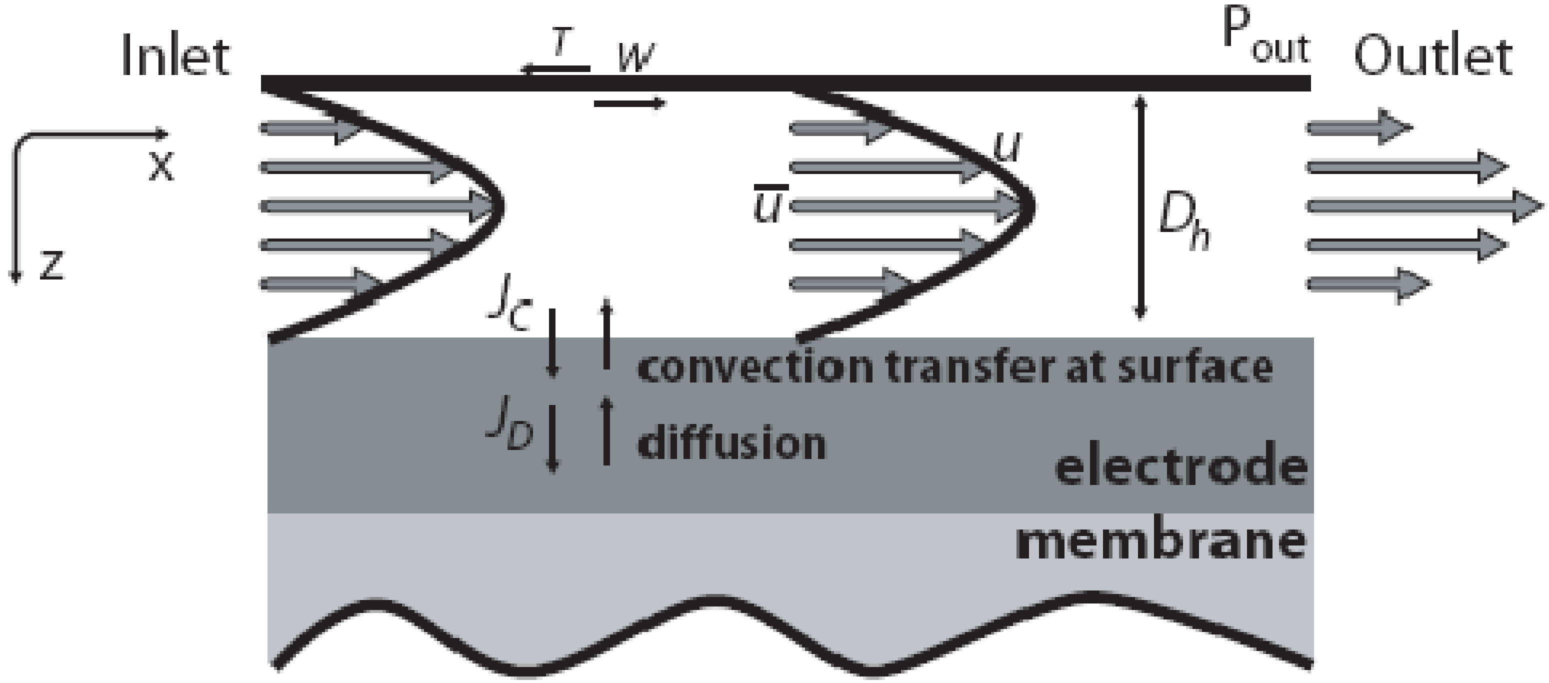
Pictorial View



$$j = j_0^0 \left(\frac{C_R^*}{C_R^{0*}} e^{\left(\frac{\alpha n F \eta_{act}}{RT} \right)} \right)$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod a_{PRODUCTS}^{v_i}}{\prod a_{REACTANTS}^{v_i}}$$

Convection



$$\tau_{xy} = 2\mu\dot{\epsilon}_{xy} = 2\mu \cdot \frac{1}{2}(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x})$$

Viscosity

Temperature effect

$$\frac{\mu}{\mu_0} \approx \left(\frac{T}{T_0}\right)^n \quad \text{or}$$

$$\frac{\mu}{\mu_0} \approx \left(\frac{T}{T_0}\right)^{1.5} \frac{T_0 + S}{T + S}$$

Gas	$\mu_0(10^{-6}(\mathrm{kg/m \cdot s})$	T_0(K)	**n**	S
Air	17.16	273	0.666	111
CO_2	13.7	273	0.79	222
CO	16.57	273	0.71	136
N_2	16.63	273	0.67	107
O_2	19.19	273	0.69	139
H_2	8.411	273	0.68	97
H_2O(vapor)	11.2	350	1.15	1064

Mixture

$$\mu_{mix} = \sum_{i=1}^{N} \frac{x_i \mu_i}{\sum_{j=1}^{N} x_j \Phi_{ij}}$$

$$\Phi_{ij} = \frac{1}{\sqrt{8}}\left(1 + \frac{M_i}{M_j}\right)^{-1/2}\left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{1/2}\left(\frac{M_i}{M_j}\right)^{1/4}\right]^2$$

Viscosity: Example

Example 5.1 *Consider a fuel cell operating at 80°C. In the cathode, humidified air at 1 atm is supplied with a water vapor mole fraction of 0.2. If the fuel cell employs circular channels with a diameter of 1 mm, find the maximum tolerable air velocity that still ensures laminar flow.*

$$\mu_{N_2}|_{80^\circ C} = \mu_0\left(\frac{T}{T_0}\right)^n = 16.63\left(\frac{353.15}{273}\right)^{0.67} = 19.76 \times 10^{-6}\ kg/m \cdot s \quad (5.37)$$

Similarly, we can obtain $\mu_{O_2}|_{80^\circ C} - 22.92 \times 10^{-6}\ kg/m \cdot s$ *and* $\mu_{H_2O}|_{80^\circ C} - 11.32 \times 10^{-6}\ kg/m\cdot$.

Species	*Mole fraction,* x_i	*Molecular Weight,* M_i	*Viscosity,* $\mu_i(10^{-6} kg/m \cdot s)$
1. N_2	*0.8×0.79=0.632*	*28.02*	*19.76*
2. O_2	*0.8×0.21=0.168*	*32.00*	*22.92*
3. H_2O	*0.200*	*18.02*	*11.32*

Viscosity: Example

Species i	Species j	M_i/M_j	μ_i/μ_j	Φ_{ij}	$x_j\Phi_{ij}$	$\sum_{j=1}^{3} x_j\Phi_{ij}$
1. N_2	1. N_2	1.000	1.000	1.000	0.632	
	2. O_2	0.876	0.862	0.930	0.156	1.059
	3. H_2O	1.555	1.746	1.356	0.271	
2. O_2	1. N_2	1.142	1.160	1.079	0.682	
	2. O_2	1.000	1.000	1.000	0.168	1.146
	3. H_2O	1.776	2.025	1.482	0.296	
3. H_2O	1. N_2	0.643	0.573	0.776	0.491	
	2. O_2	0.563	0.494	0.732	0.123	0.814
	3. H_2O	1.000	1.000	1.000	0.200	

$$\mu_{mix} = \left(\frac{0.632 \times 19.76}{1.059} + \frac{0.168 \times 22.92}{1.146} + \frac{0.200 \times 11.32}{0.814}\right) \times 10^{-6}$$
$$= 17.93 \times 10^{-6}\ kg/m \cdot s$$

Viscosity: Example

$$M_{mix} = \sum_{i=1}^{N} x_i M_i = 0.632 \times 28.02 + 0.168 \times 32.00 + 0.200 \times 18.02 = 26.69\ g/mol$$

$$\rho = \frac{p}{\frac{R}{M_{mix}}} = \frac{101325\ Pa}{\frac{8.314 J/mol \cdot K}{0.02669 kg/mol}\ (273.15 + 80)T} = 0.921\ kg/m^3$$

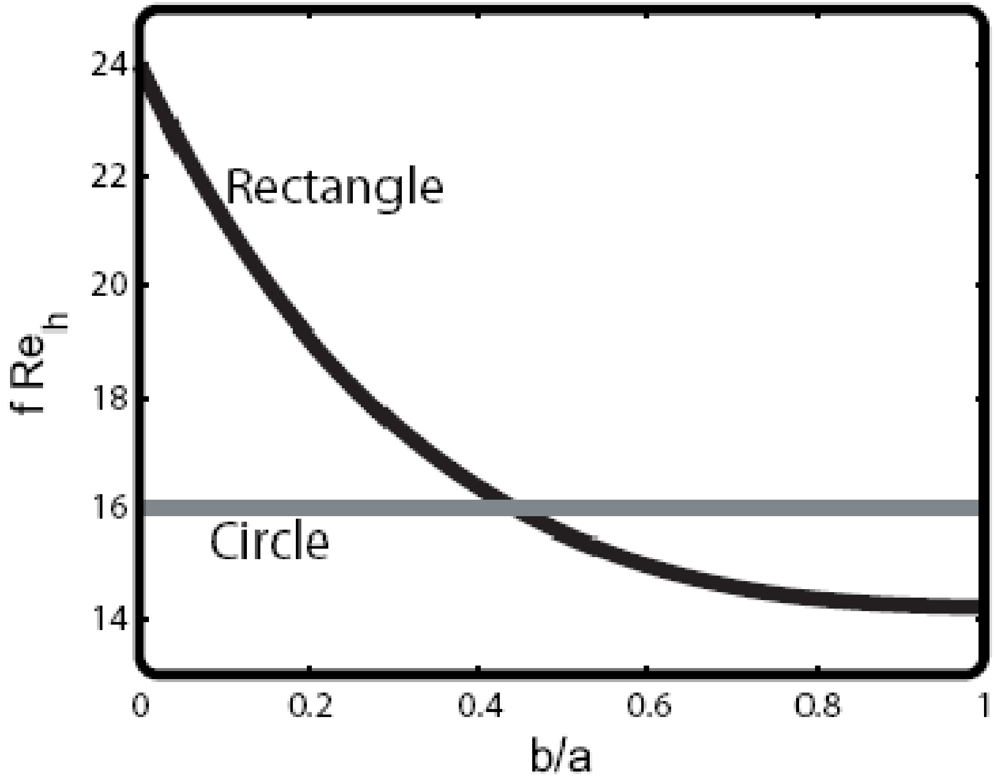
Roughly, laminar flow holds for Re~ 2000, thus:

$$V\ max = \frac{Re^{max}\ \mu_{mix}}{\rho\ L} = \frac{2000 \times (17.93 \times 10^{-6}\ kg/m \cdot s)}{(0.921\ kg/m^3) \times (0.001\ m)} = 38.03\ m/s \tag{5.39}$$

This is very fast flow considering the channel is only 1 mm in diameter.

In general, flow in fuel cell is laminar.

Pressure Drop In Flow Channels



$$\frac{dp}{dx} = \frac{4}{D}\bar{\tau}_w$$

$$f = \frac{\bar{\tau}_w}{1/2\rho\bar{u}^2}$$

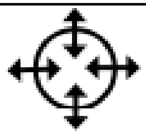
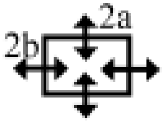
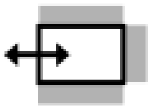
$$Re_h = \frac{\rho\bar{u}D_h}{\mu}$$

$$D_h = \frac{4A}{P} = \frac{4 \times cross\ section\ area}{perimeter}$$

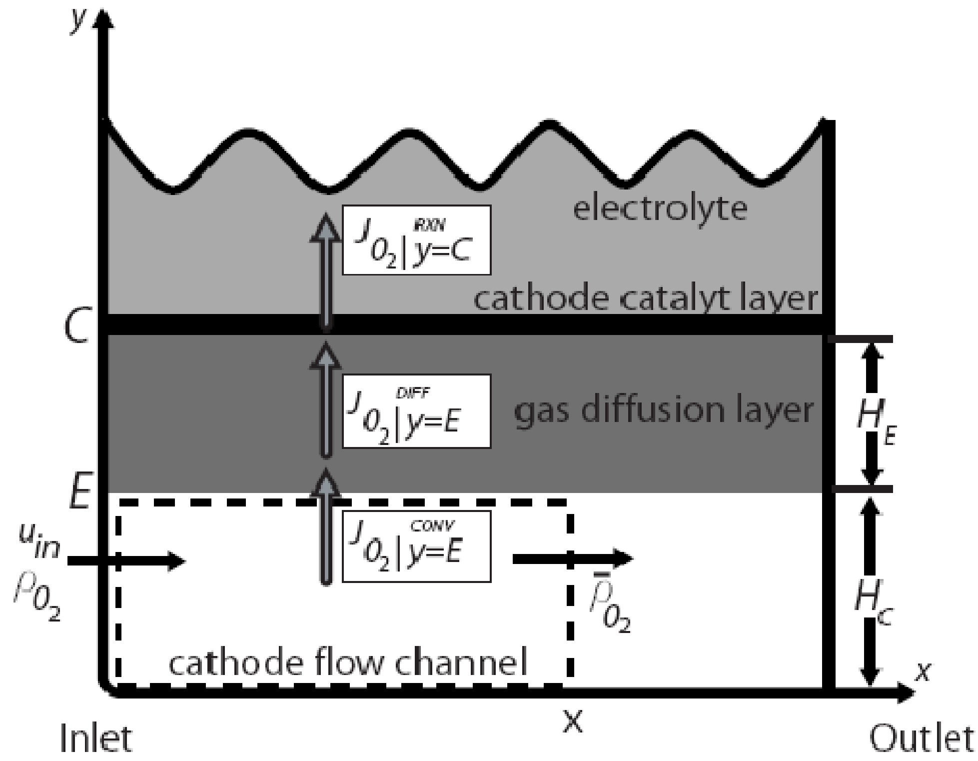
Convective Mass Transport

$$J_{C,i} = h_m(\rho_{i,s} - \bar{\rho}_i)$$

$$h_m = Sh\frac{D_{ij}}{D_h}$$

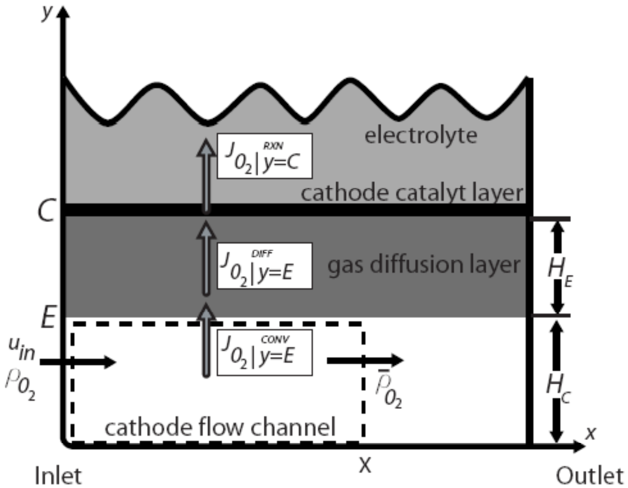
Cross section		α^*							
		0.2	0.4	0.7	1.0	2.0	2.5	5.0	10.0
	Sh_D	4.36							
	Sh_F	3.66							
	Sh_D	4.80	3.67	3.08	2.97	3.38	3.67	4.80	5.86
	Sh_F	5.74	4.47	3.75	3.61	4.12	4.47	5.74	6.79
	Sh_D	0.83	1.42	2.02	2.44	3.19	3.39	3.91	4.27
	Sh_F	0.96	1.60	2.26	2.71	3.54	3.78	4.41	4.85

Convective Mass Transport in PEMFC



1. The catalyst layer is infinitely thin.[1]
2. Water exists only in the vapor form.
3. Diffusive mass transport dominates in the diffusion layer. Furthermore, only y-direction diffusion in considered.
4. Convection dominates in the flow channel.
5. Flow velocity in the channel is constant.

Convective Mass Transport in PEMFC



$$\hat{J}_{O_2}|^{rxn}_{x=X,y=C} = M_{O_2}\frac{j(X)}{4F}$$

$$\hat{J}_{O_2}|^{diff}_{x=X,y=E} = -D^{eff}_{O_2}\frac{\rho_{O_2}|_{x=X,y=C} - \rho_{O_2}|_{x=X,y=E}}{H_E}$$

$$\hat{J}_{O_2}|^{conv}_{x=X,y=E} = -h_m\left(\rho_{O_2}|_{x=X,y=E} - \bar{\rho}_{O_2}|_{x=X,y=channel}\right)$$

$$\hat{J}_{O_2}|^{rxn}_{x=X,y=C} = \hat{J}_{O_2}|^{diff}_{x=X,y=E} = \hat{J}_{O_2}|^{conv}_{x=X,y=E}$$

$$\hat{J}_{O_2}|^{conv}_{x=X,y=E} = M_{O_2}\frac{j(X)}{4F}$$

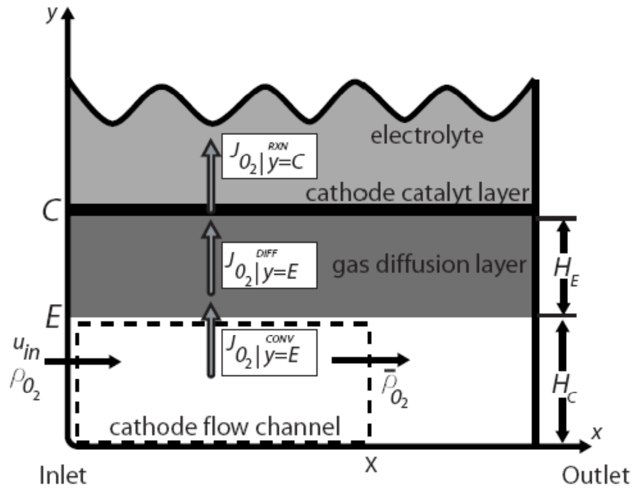
$$\rho_{O_2}|_{x=X,y=C} = \rho_{O_2}|_{x=X,y=E} - M_{O_2}\frac{j(X)}{4F}\frac{H_E}{D^{eff}_{O_2}}$$

$$\rho_{O_2}|_{x=X,y=E} = \bar{\rho}_{O_2}|_{x=X,y=channel} - M_{O_2}\frac{j(X)}{4F}\frac{\mathbf{1}}{h_m}$$

Convective Mass Transport in PEMFC

$$u_{in} H_C \bar{\rho}_{O_2}|_{x=0,y=channel} - u_{in} H_C \bar{\rho}_{O_2}|_{x=X,y=channel} = \int_0^{X} \left(\hat{J}_{O_2}|^{conv}_{y=E} \right) dx \quad (5.6$$

$$\begin{matrix} Amount\ of\ gas & Amount\ of\ gas & Amount\ of\ gas \\ entering\ from\ left & leaving\ from\ right & leaving\ out\ the\ top \end{matrix}$$

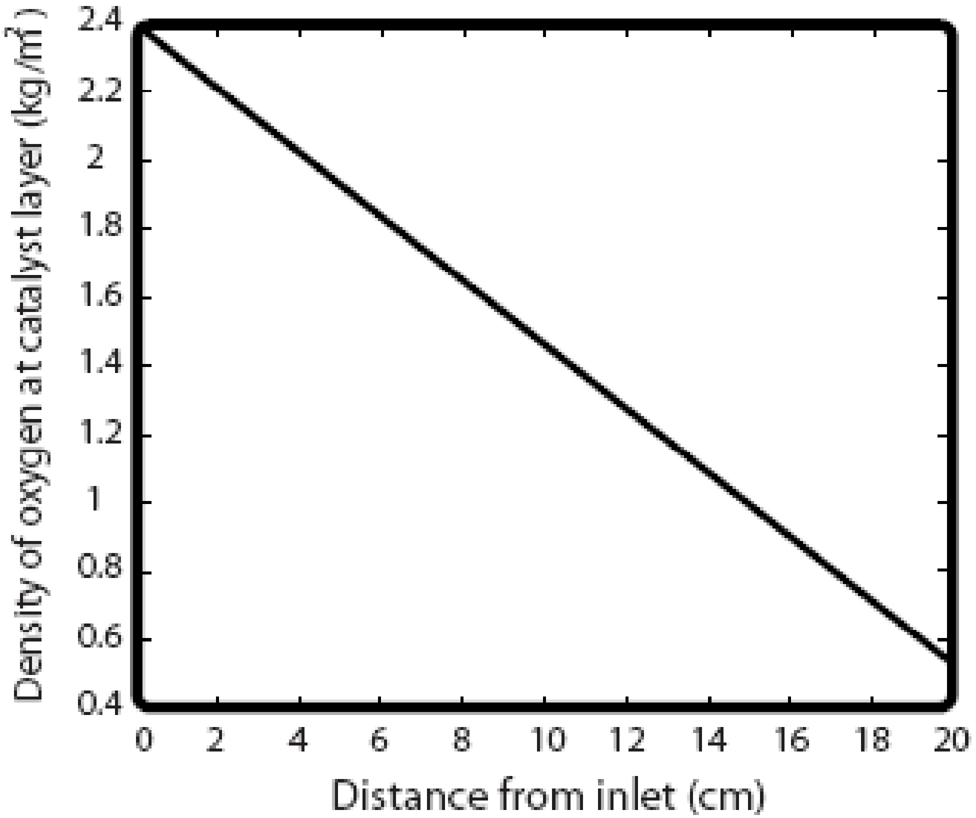


$$\int_0^X \left(\hat{J}_{O_2}|^{conv}_{y=E} \right) dx = \int_0^X \frac{M_{O_2} j(x)}{4F} dx$$

$$\rho_{O_2}|_{x=X,y=C} = \bar{\rho}_{O_2}|_{x=0,y=channel} - \frac{M_{O_2}}{4F} \left(\frac{j(X)}{h_m} + \frac{H_E j(X)}{D^{eff}_{O_2}} + \int_0^X \frac{j(x)}{u_{in} H_C} dx \right)$$

$$\rho_{O_2}|_{x=X,y=C} = \bar{\rho}_{O_2}|_{x=0,y=channel} - M_{O_2} \frac{j}{4F} \left(\frac{1}{h_m} + \frac{H_E}{D^{eff}_{O_2}} + \frac{X}{u_{in} H_C} \right)$$

Convective Mass Transport in PEMFC

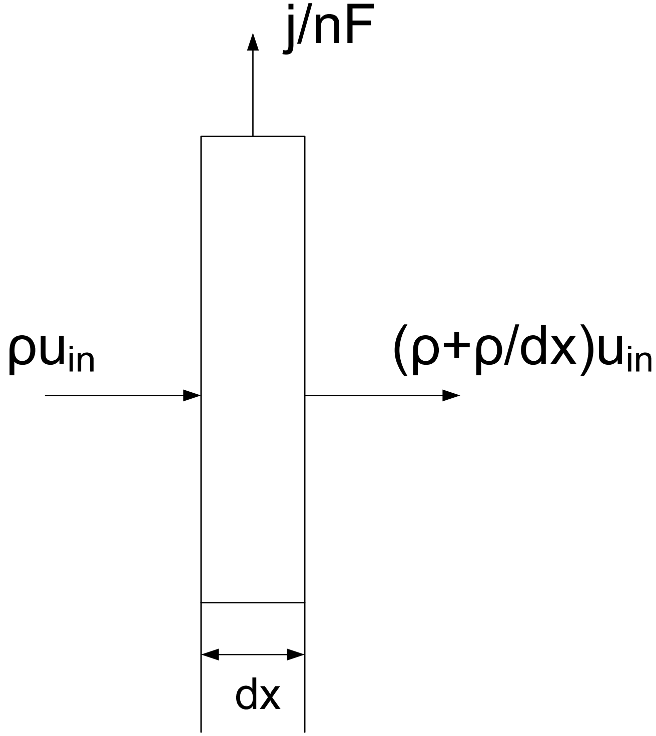


$$\rho_{O_2}|_{x=X,y=C} = \bar{\rho}_{O_2}|_{x=0,y=channel} - M_{O_2}\frac{j}{4F}\left(\frac{H_C}{Sh_F D_{O_2}} + \frac{H_E}{D_{O_2}^{eff}} + \frac{X}{u_{in}H_C}\right)$$

$$h_m = \frac{Sh_F D_{O_2}}{H_C} \qquad N_{total} = u_{in}H_C = constant$$

A More Realistic Alternative Solution

$$\rho_{O_2}\big|_{x=X,y=C} = \bar{\rho}_{O_2}\big|_{x=0,y=channel} - \frac{M_{O_2}}{4F}\left(\frac{j(X)}{h_m} + \frac{H_E j(X)}{D_{O_2}^{eff}} + \int_0^X \frac{j(x)}{u_{in}H_C}dx\right)$$



$$u_{in}\rho - u_{in}\left(\rho + \frac{\rho}{dx}\right) = \frac{j(x)}{nF}dx$$

$$\frac{d\rho}{dx} = -\frac{j(x)}{u_{in}nF}$$

$$\frac{dC(x)}{dx} = -Bj(x)$$

A More Realistic Alternative Solution

If constant Voltage instead of constant current is assumed

$$j = j_0^0 \frac{c_R^*}{c_R^{0*}} e^{\alpha n F \eta / RT}$$

$$\frac{dc(x)}{dx} = -Bj(x) = -Bj_0^0 \frac{c(x)}{c^0} e^{\alpha n F \eta / RT} = ac(x)$$

$$c(x) = Ae^{-ax}$$

$$c(0) = c_{in} = A$$

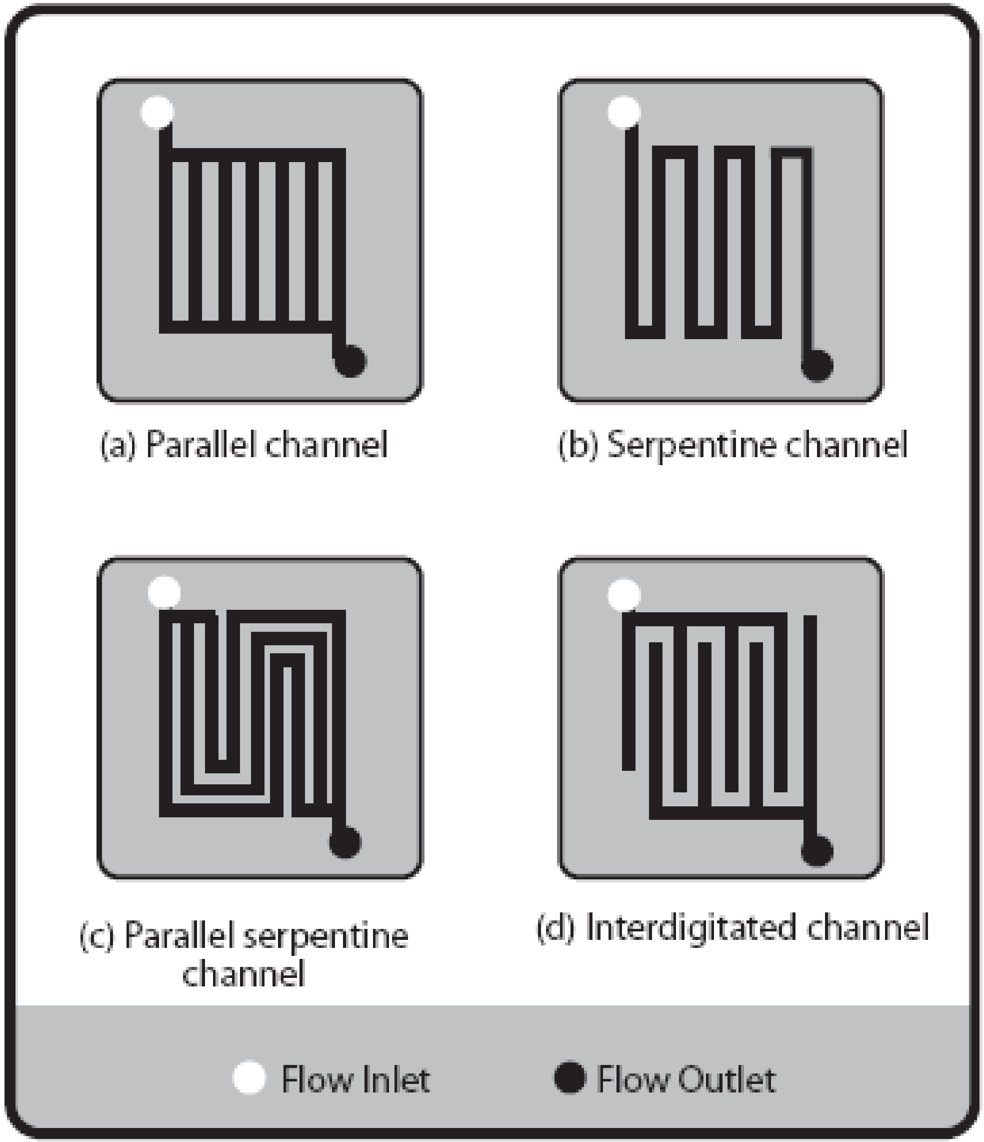
$$j(x) = Ke^{-ax}$$

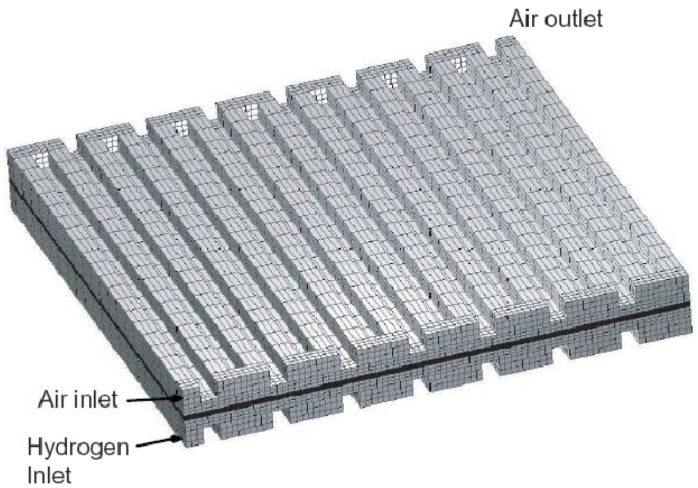
- Current drop Exponentially
- Concentration also drop exponentially
- HW 5.10

Flow Channel Design

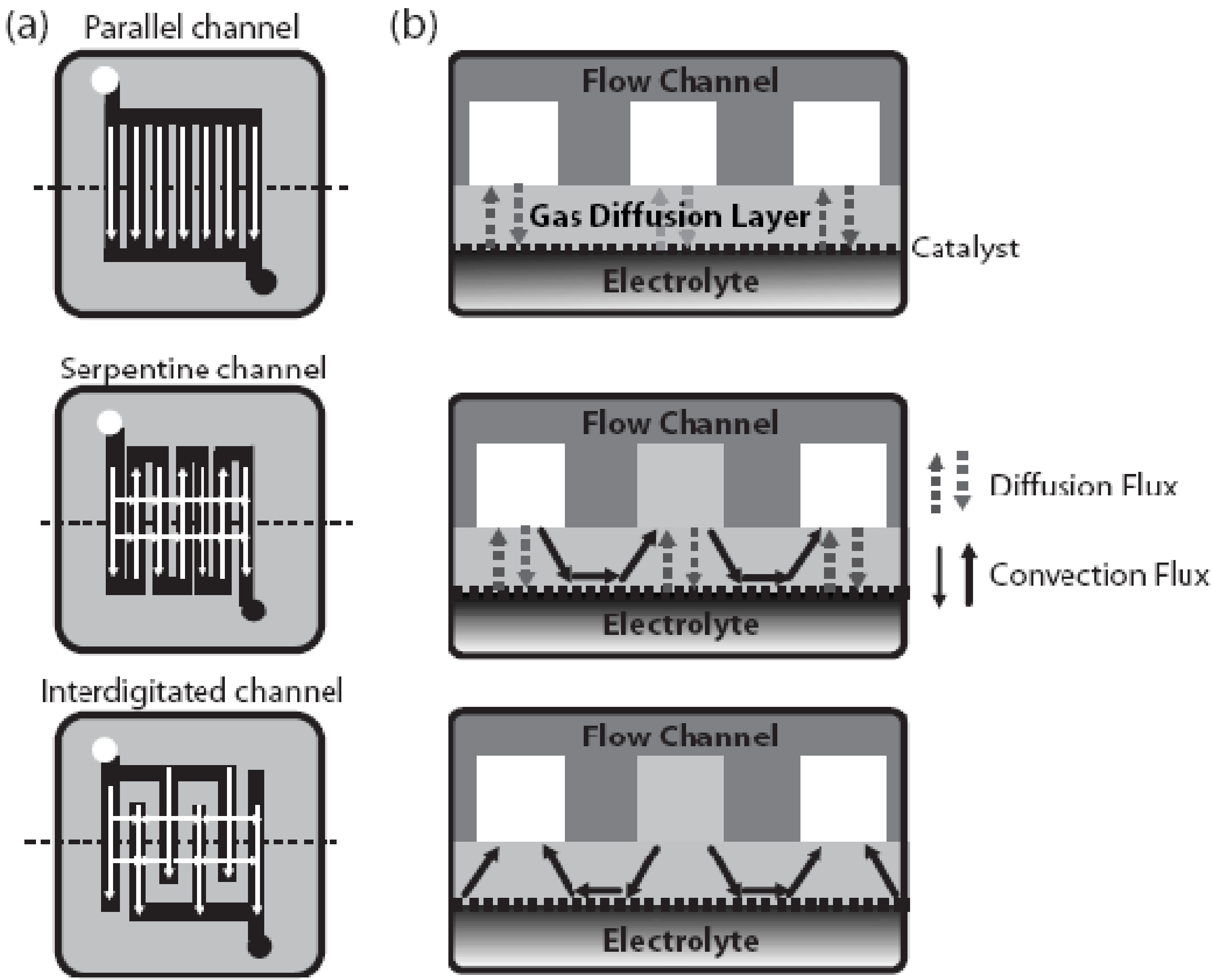
- High electrical conductivity
- High corrosion resistance
- High chemical compatibility
- High thermal conductivity
- High gas tightness
- High mechanical strength
- Low weight and volume
- Ease of manufacturability
- Cost effectiveness

PEMFC Flow Channel Design

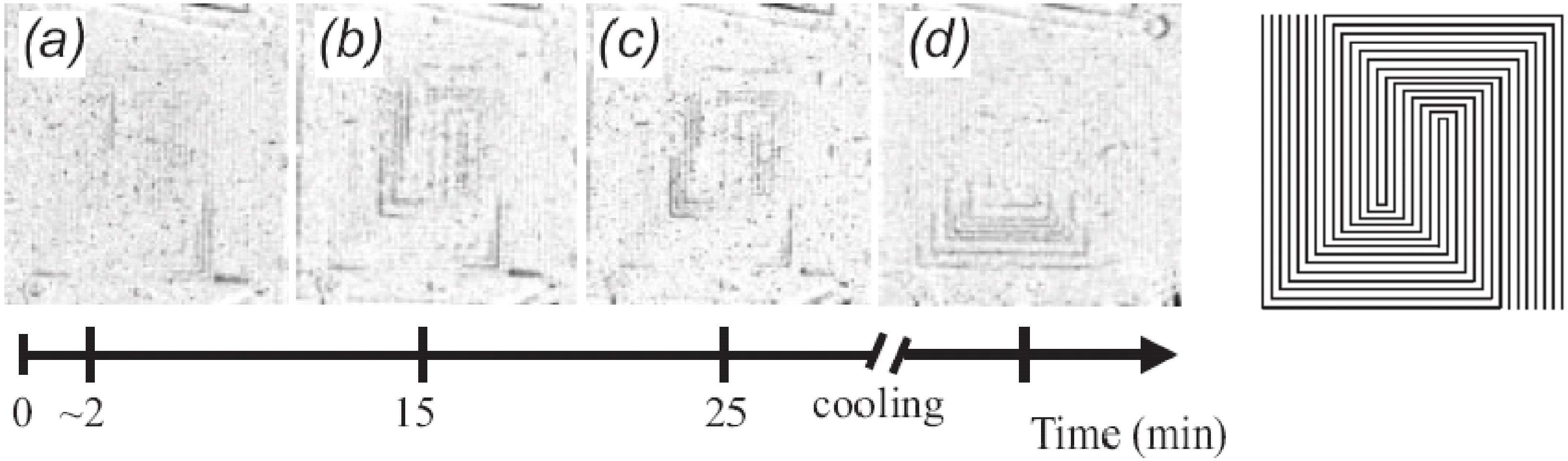




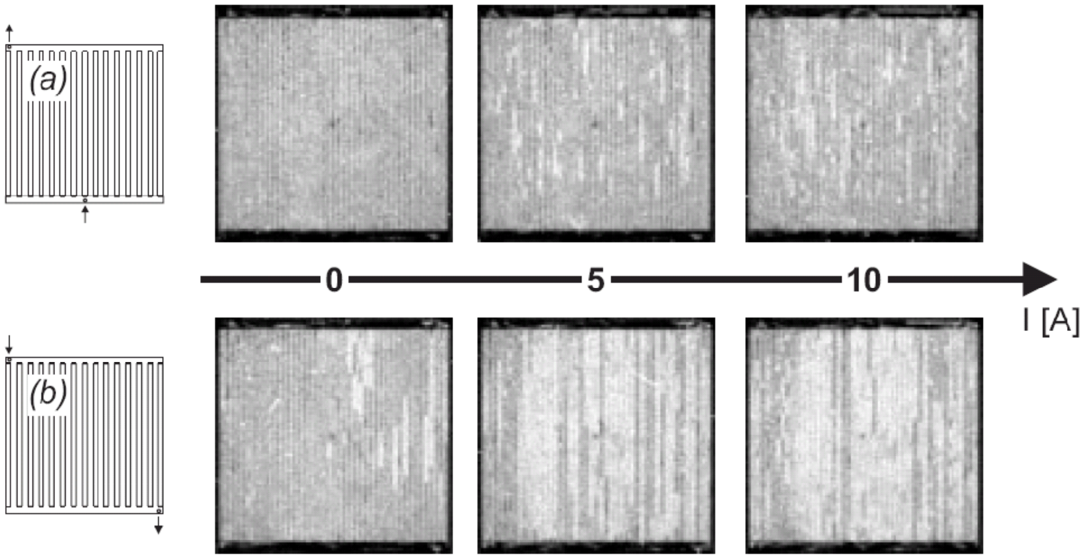
PEMFC Flow Channel Design



Flow Visualization (Neutron Radiography)



PEMFC serpentine cathode channels. Dark area is liquid filled.



DMFC parallel anode channels. Bright area is CO2 filled

Flow Visualization