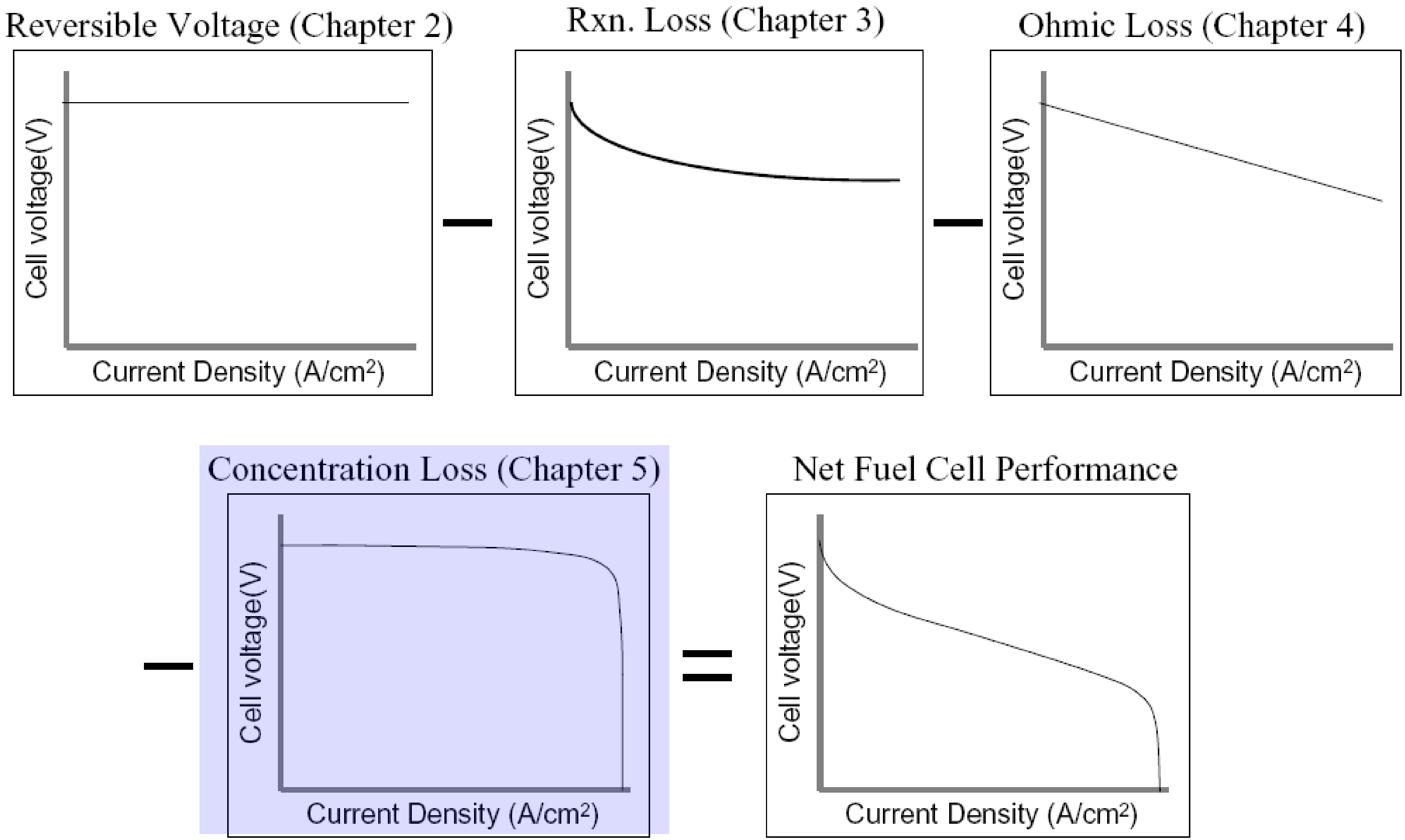
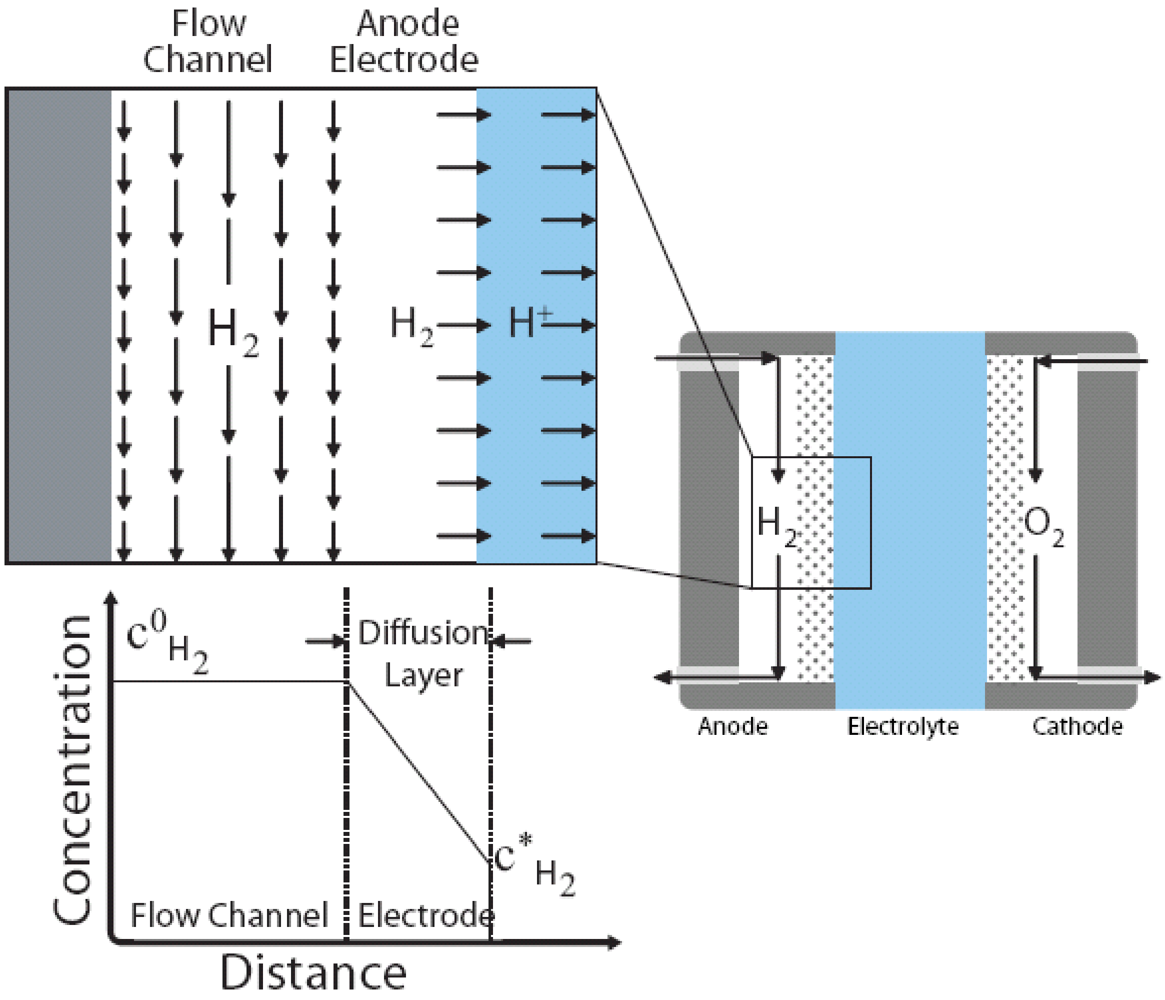
Losses in Fuel Cells



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

Fuel Cell Charge Transport

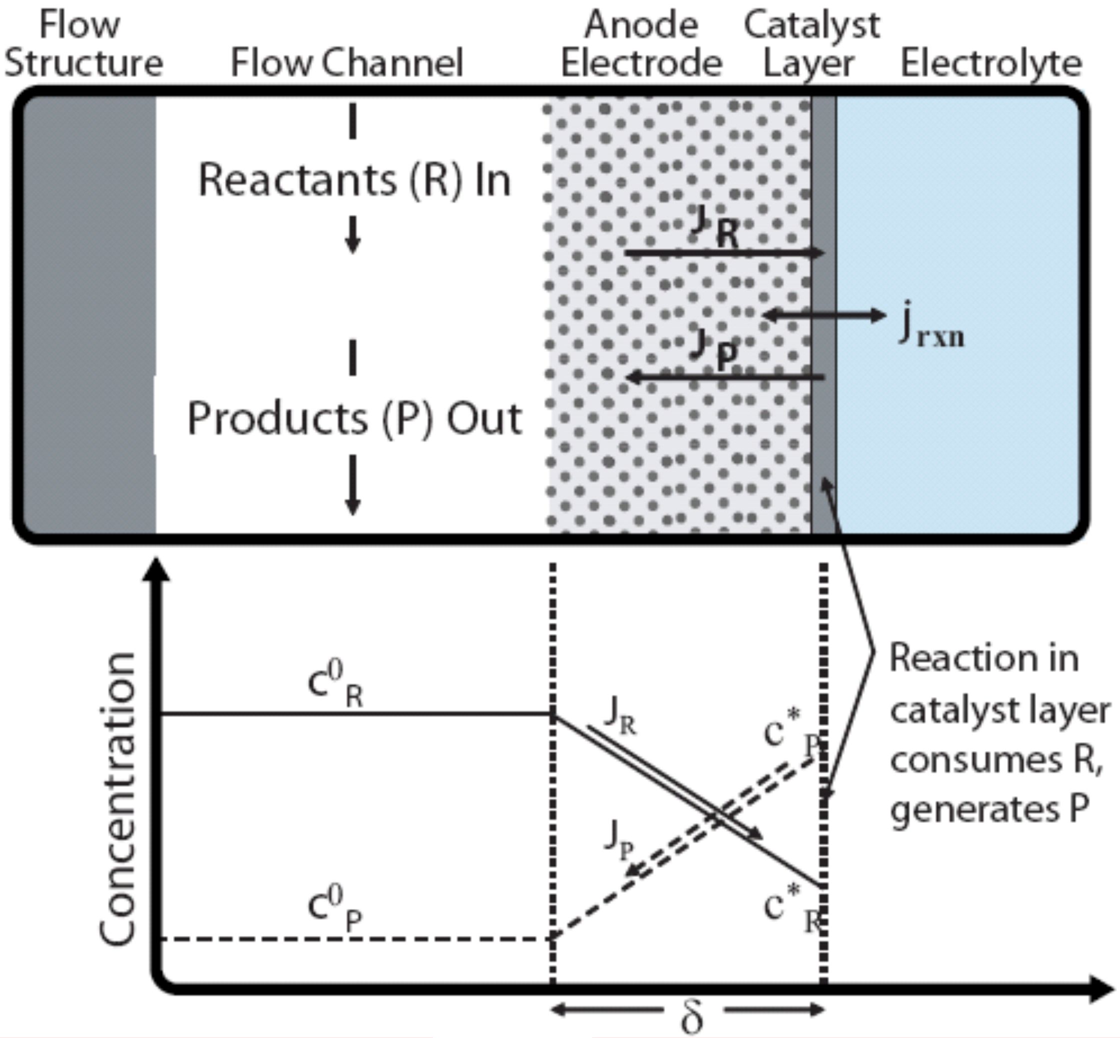
Mass Transport



Convection dominant in flow channels

Diffusion dominant in electrode

Concentration Drop



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

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

Diffusion In Electrode

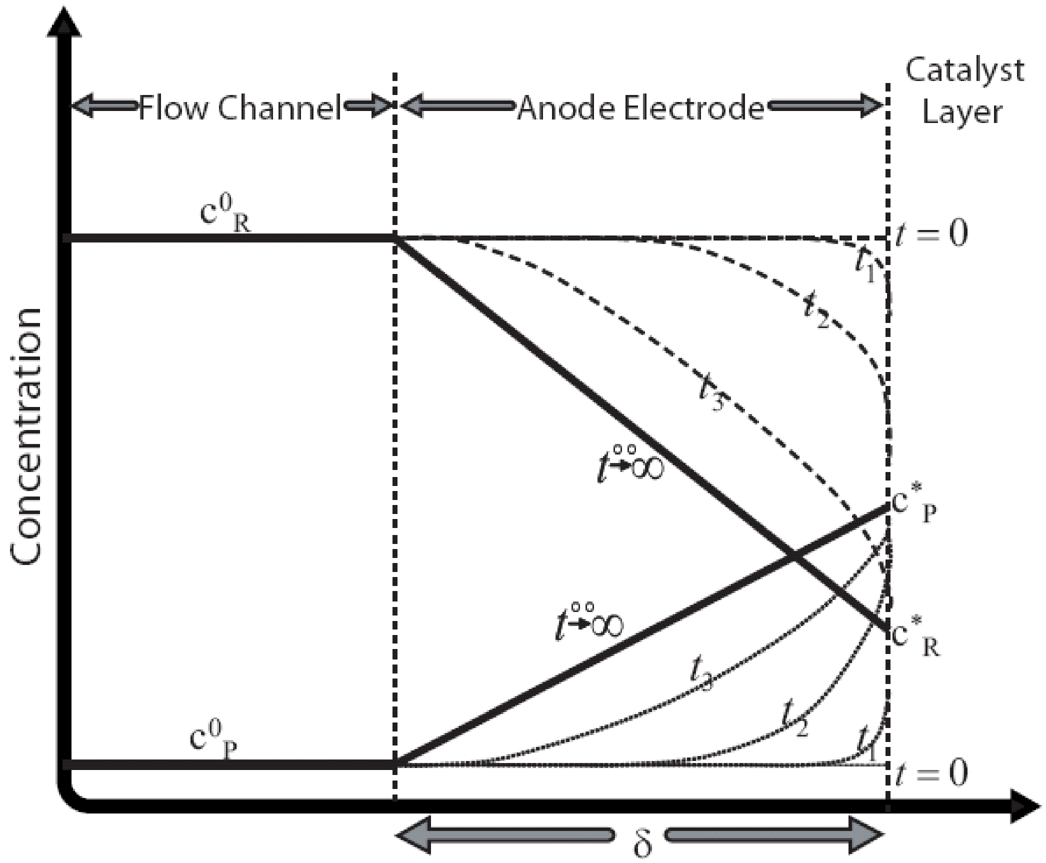
$$J_{diff} = -D\frac{dc}{dx}$$

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

$$j = nFJ_{diff}$$

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

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



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

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

$$\eta_{act} = \frac{RT}{\alpha nF}\ln\frac{jc_R^{0*}}{j_0^0 c_R^*}$$

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

$$\eta_{conc} = \left(\frac{RT}{\alpha nF}\ln\frac{jc_R^{0*}}{j_0^0 c_R^*}\right) - \left(\frac{RT}{\alpha nF}\ln\frac{jc_R^{0*}}{j_0^0 c_R^0}\right)$$

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

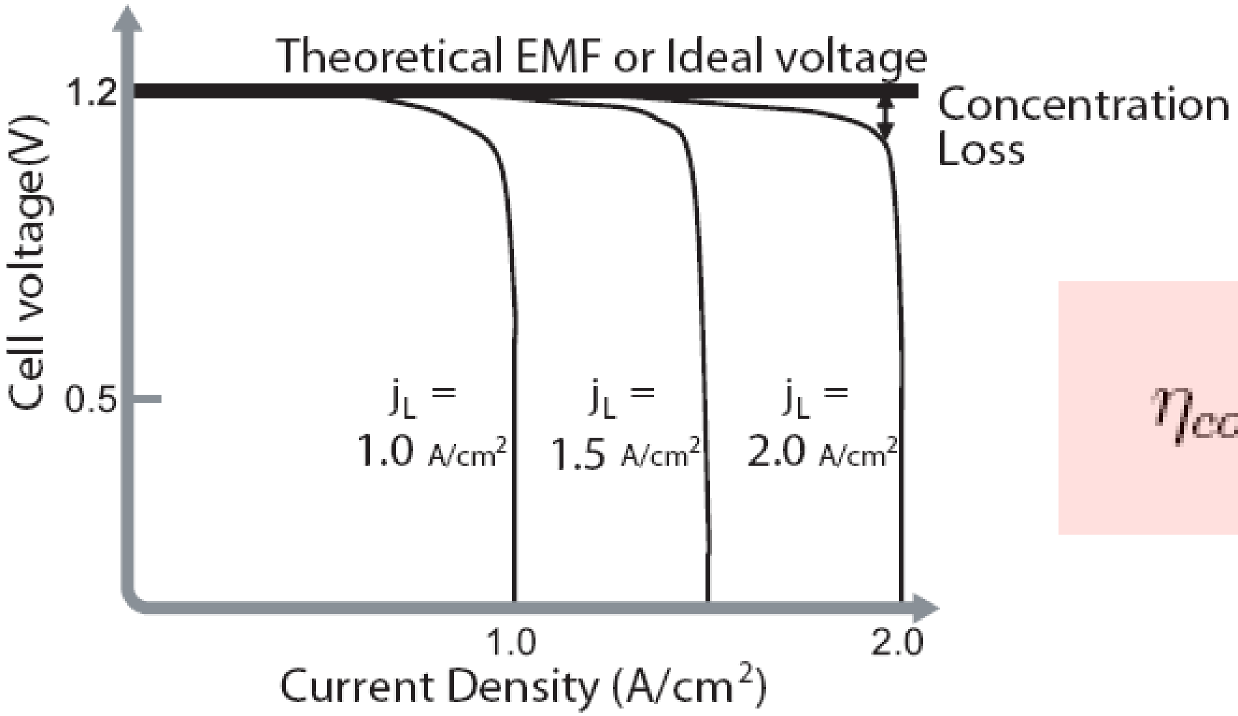
$$\eta_{conc} = \frac{RT}{\alpha nF}\ln\frac{j_L}{j_L - j}$$

Mass Transportation Loss

Adding two losses

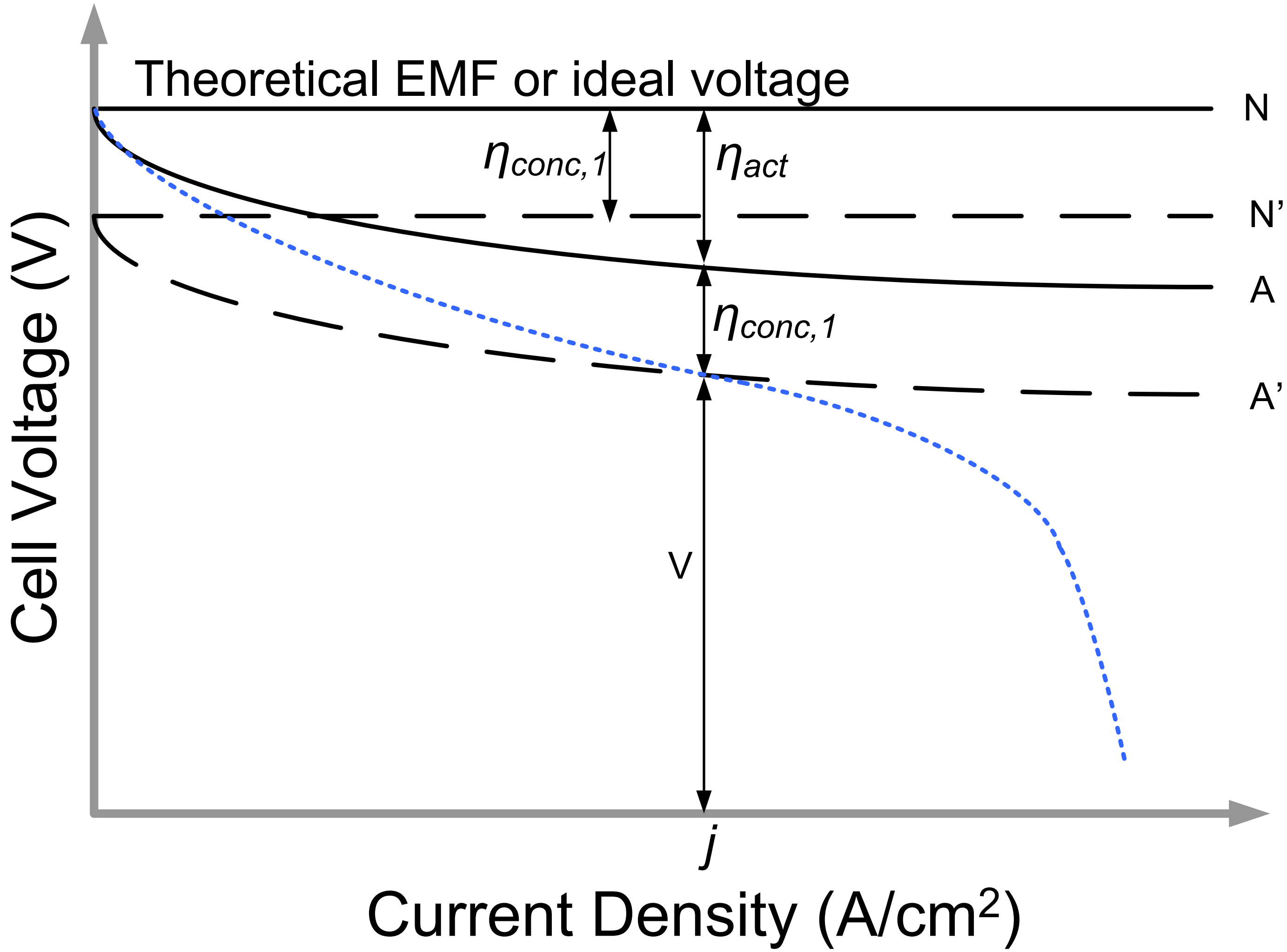
$$\eta_{conc} = \frac{RT}{nF}\ln\frac{j_L}{j_L - j} + \frac{RT}{\alpha nF}\ln\frac{j_L}{j_L - j}$$

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



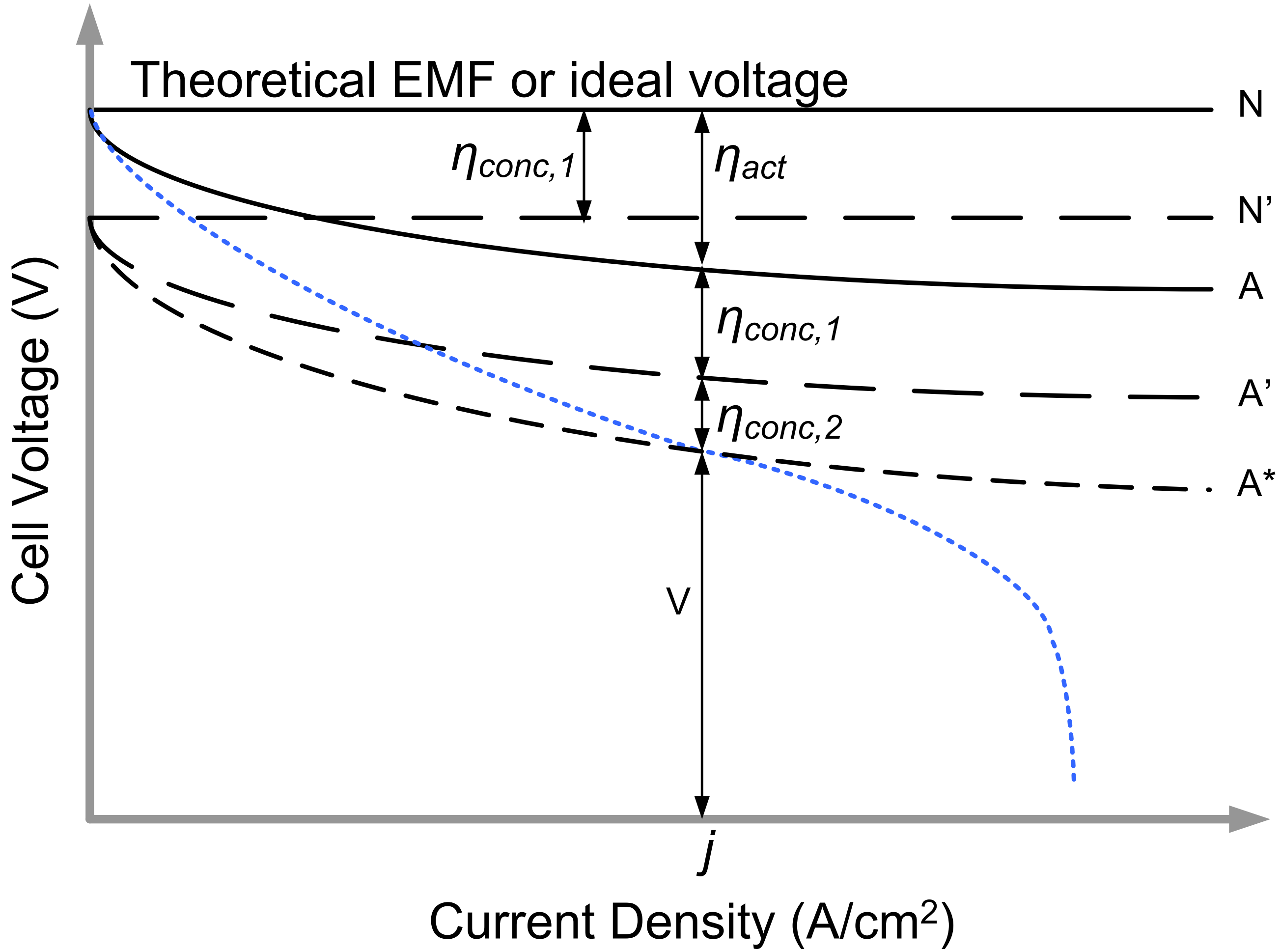
$$\eta_{conc} = c\ln\frac{j_L}{j_L - j}$$

Pictorial View



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

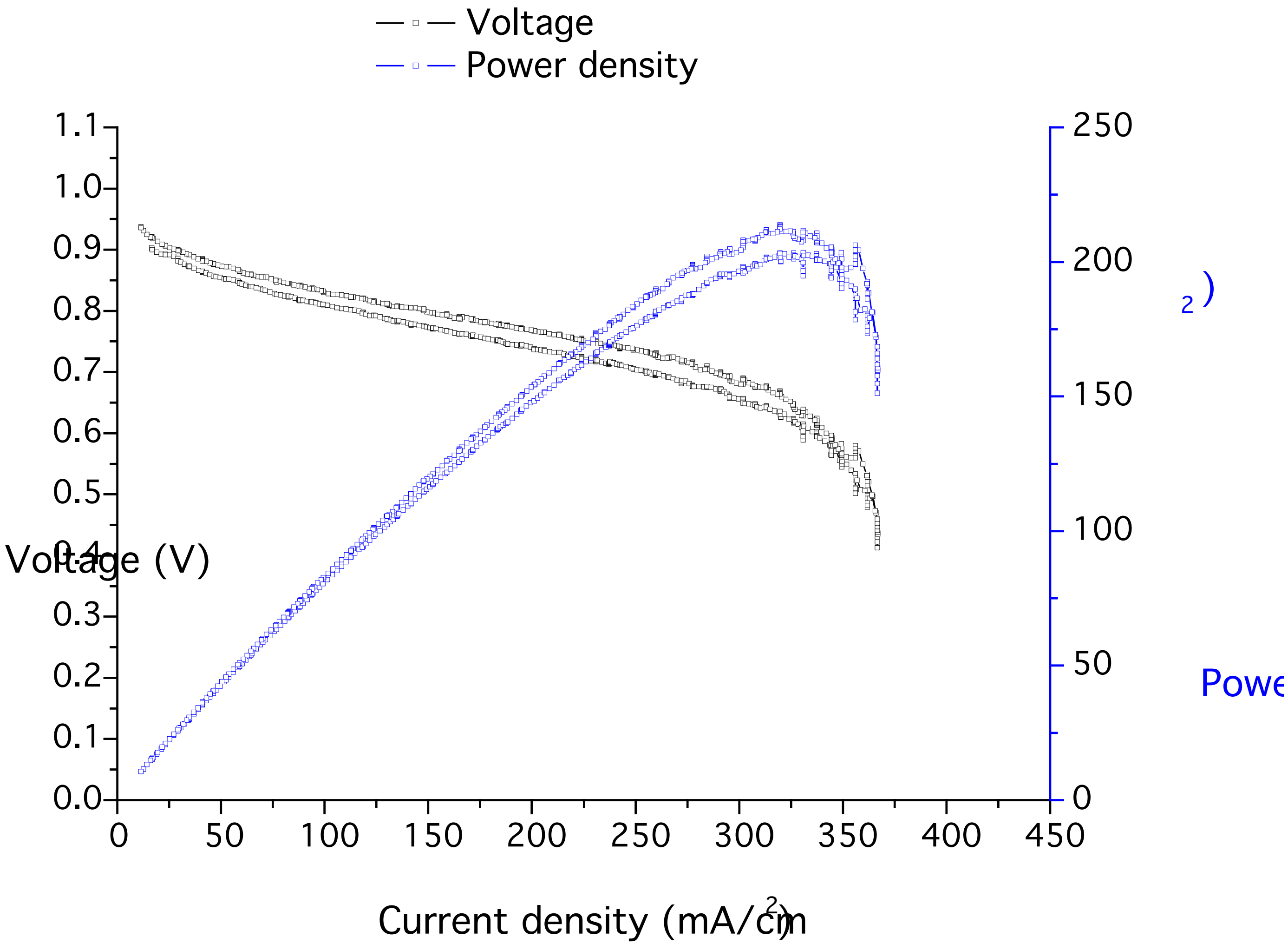
Pictorial View



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

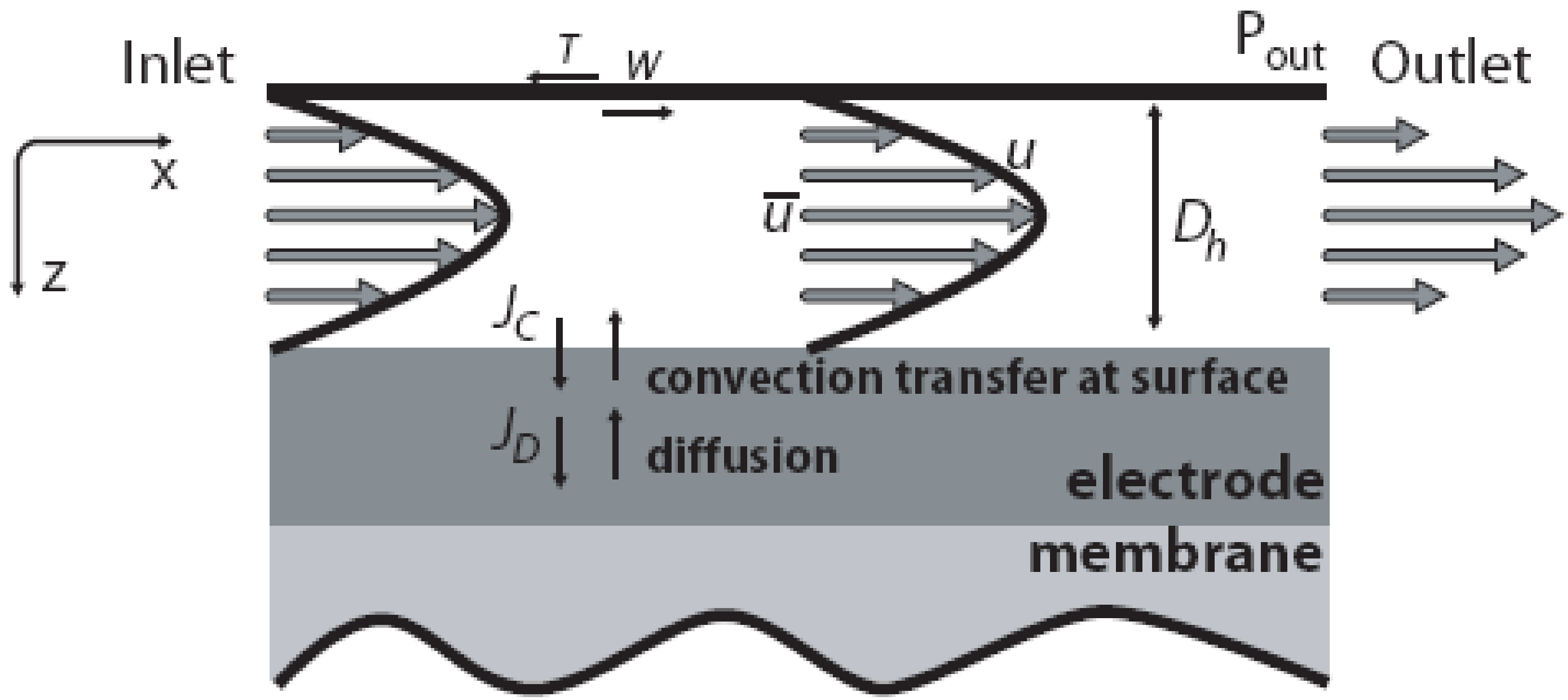
$$j = j_0^0 \left(\frac{c_R^*}{c_R^{0*}} e^{\left(\frac{\alpha n F \eta_{act}}{RT} \right)} \right)$$

A Very³ Tricky Example



PEMFC with or without temperature control

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

$$\frac{\mu}{\mu_0} \approx (\frac{T}{T_0})^n$$

or

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

Gas	$\mu_0 (10^{-6}$(kg/m·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

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

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

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.*

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

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

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

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

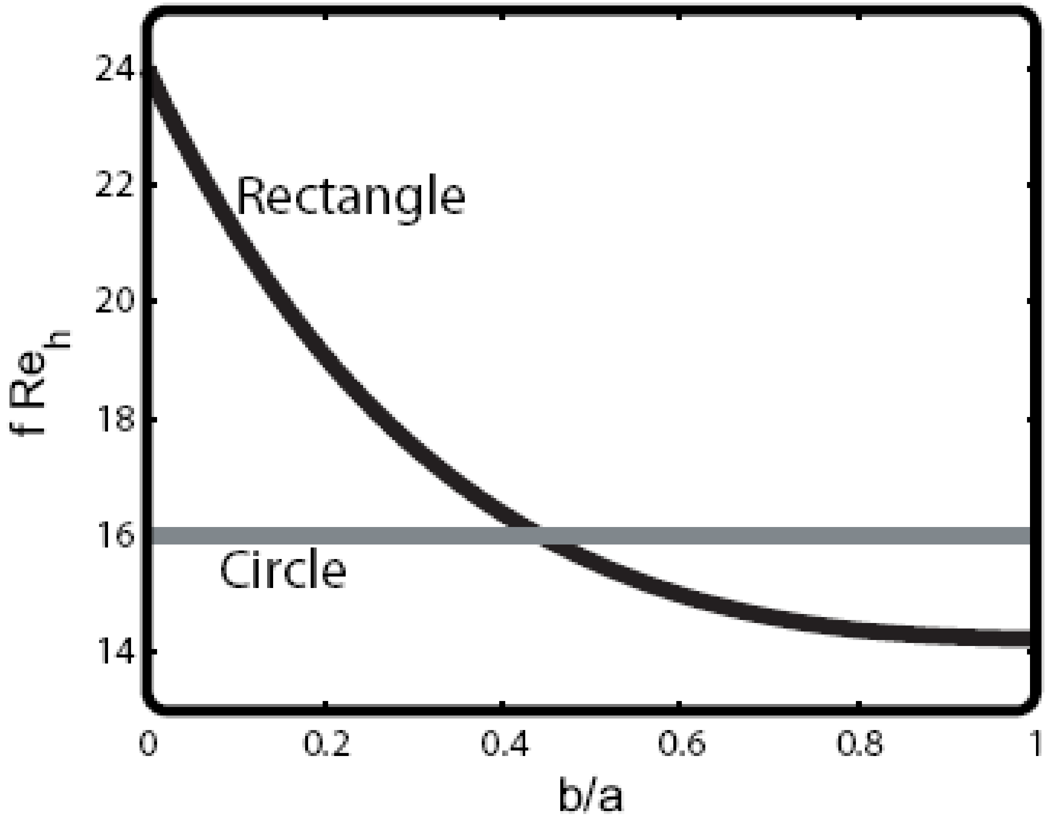
Roughly, laminar flow holds for Re$\sim$ 2000, *thus:*

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

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



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

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

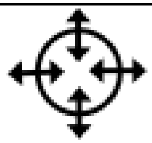
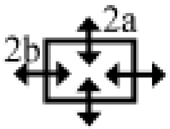
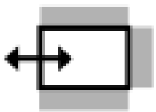
$$Re_h = \frac{\rho\bar{u}D_h}{\mu}$$

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

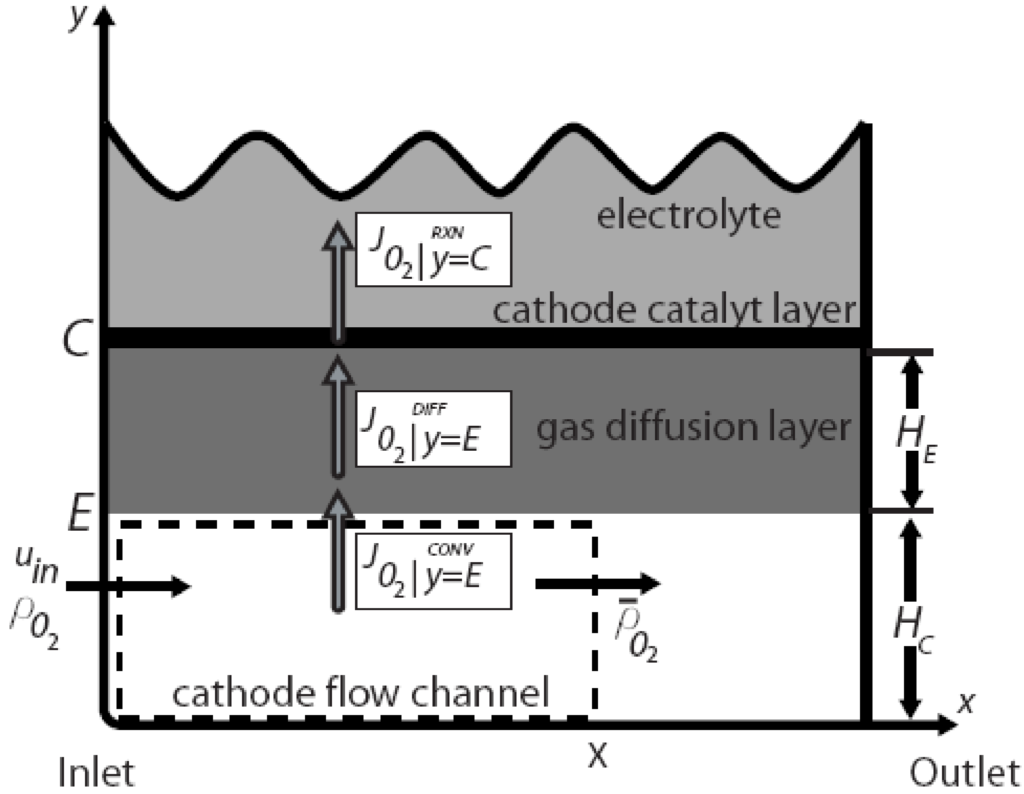
Convective Mass Transport

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

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

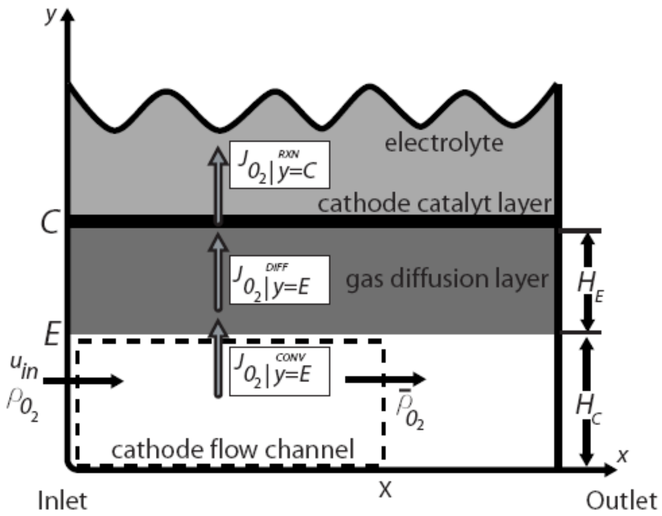
Cross section		α^* 0.2	0.4	0.7	1.0	2.0	2.5	5.0	10.0
	Sh_D				4.36				
	Sh_F				3.66				
	Sh_D	4.80	3.67	3.08	2.97	3.38	3.67	4.80	5.86
	Sh_F	5.74	4.47	3.75	3.61	4.12	4.47	5.74	6.79
	Sh_D	0.83	1.42	2.02	2.44	3.19	3.39	3.91	4.27
	Sh_F	0.96	1.60	2.26	2.71	3.54	3.78	4.41	4.85

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



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

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

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

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

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

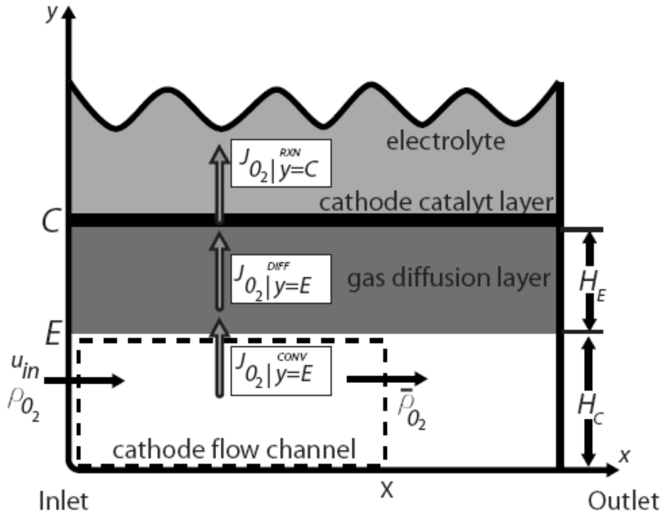
$$\rho_{O_2}|_{x=X,y=C} = \rho_{O_2}|_{x=X,y=E} - M_{O_2}\frac{j(X)}{4F}\frac{H_E}{D^{eff}_{O_2}}$$

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

Convective Mass Transport in PEMFC

$$u_{in} H_C \bar{\rho}_{O_2}|_{x=0,y=channel} - u_{in} H_C \bar{\rho}_{O_2}|_{x=X,y=channel} = \int_0^{X} \left(\hat{J}_{O_2}|_{y=E}^{conv} \right) dx \quad (5.60)$$

Amount of gas entering from left — *Amount of gas leaving from right* — *Amount of gas leaving out the top*

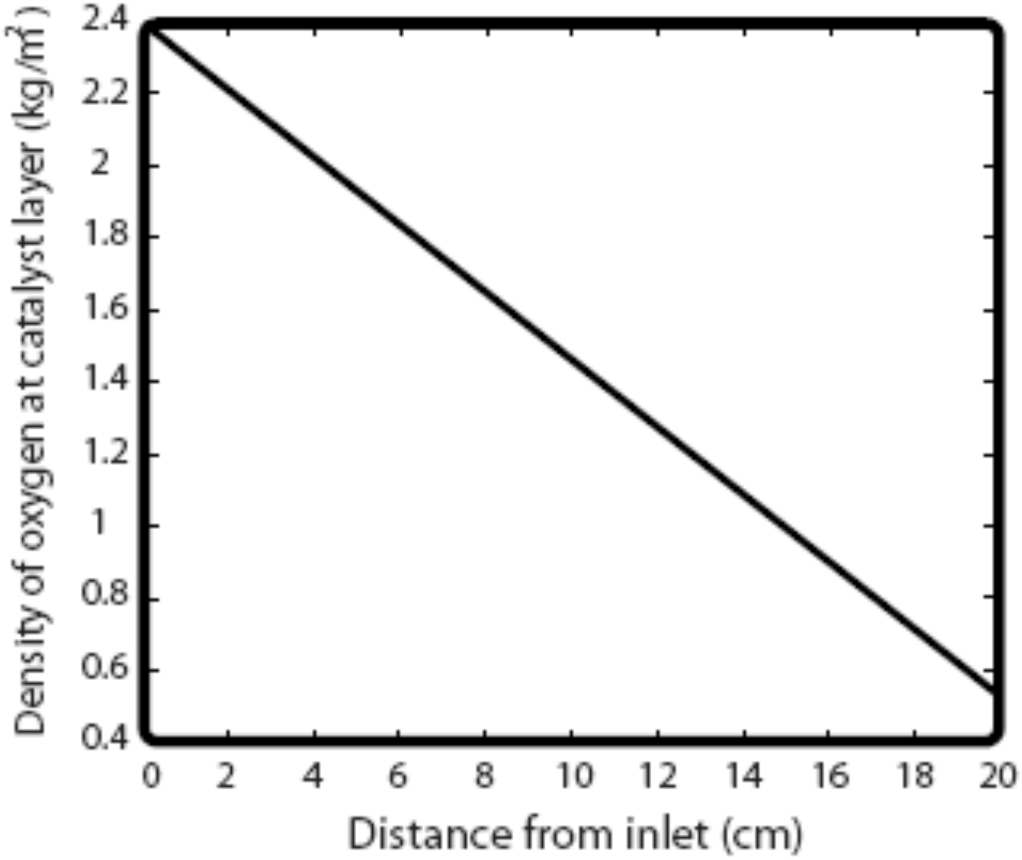


$$\int_0^X \left(\hat{J}_{O_2}|_{y=E}^{conv} \right) dx = \int_0^X \frac{M_{O_2} j(x)}{4F} dx$$

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

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

Convective Mass Transport in PEMFC

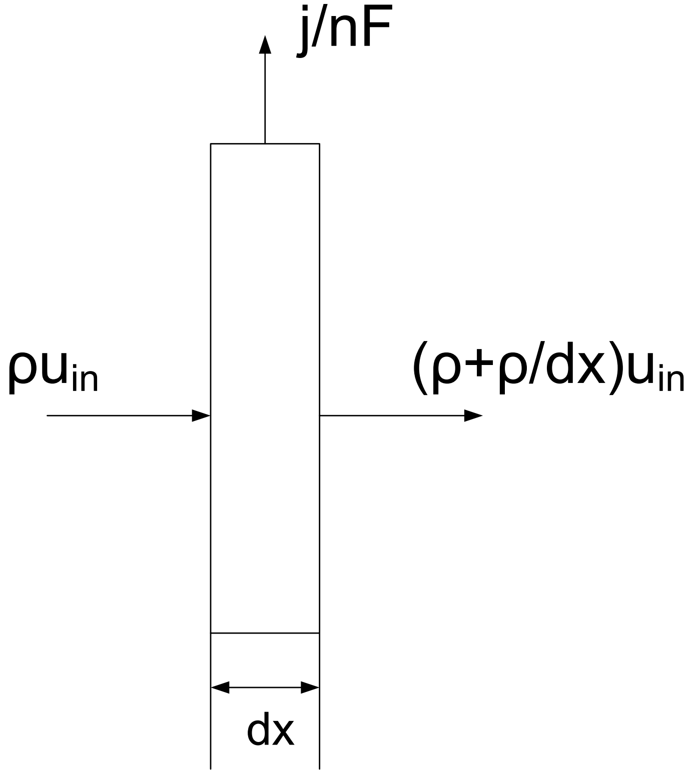


$$\rho_{O_2}|_{x=X,y=C} = \bar{\rho}_{O_2}|_{x=0,y=channel} - M_{O_2}\frac{j}{4F}\left(\frac{H_C}{Sh_F D_{O_2}} + \frac{H_E}{D_{O_2}^{eff}} + \frac{X}{u_{in}H_C}\right)$$

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

A More Realistic Alternative Solution

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



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

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

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

A More Realistic Alternative Solution

If constant Voltage instead of constant current is assumed

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

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

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

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

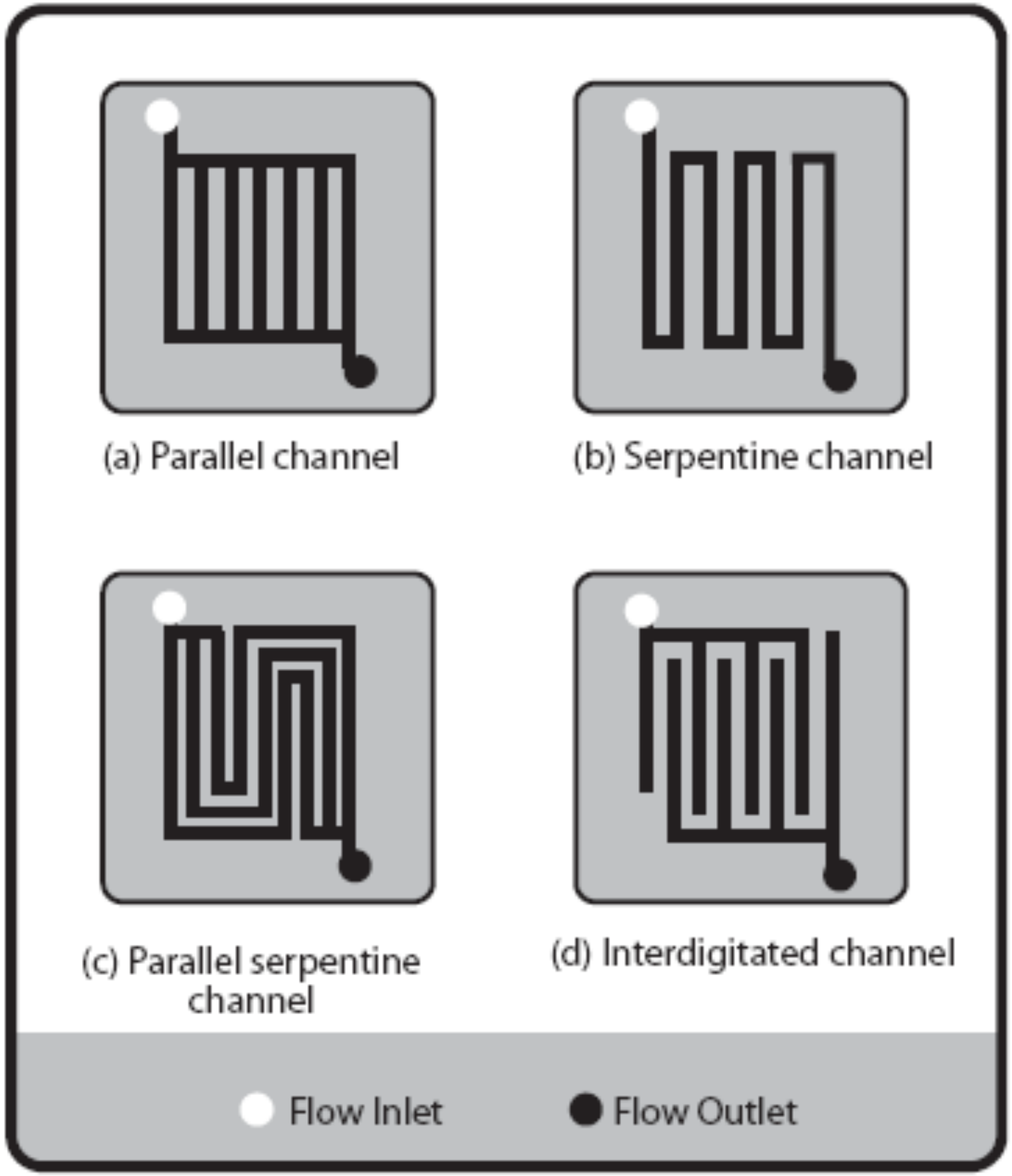
$$j(x) = Ke^{-ax}$$

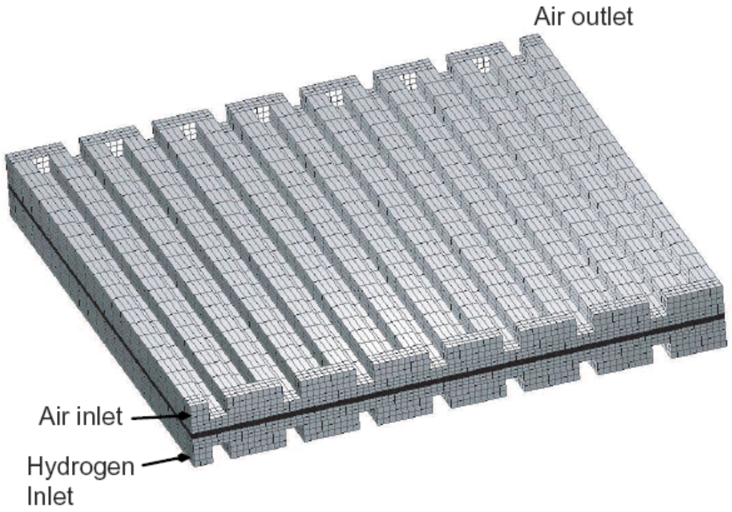
- Current drop Exponentially
- Concentration also drop exponentially
- HW 5.10

Flow Channel Design

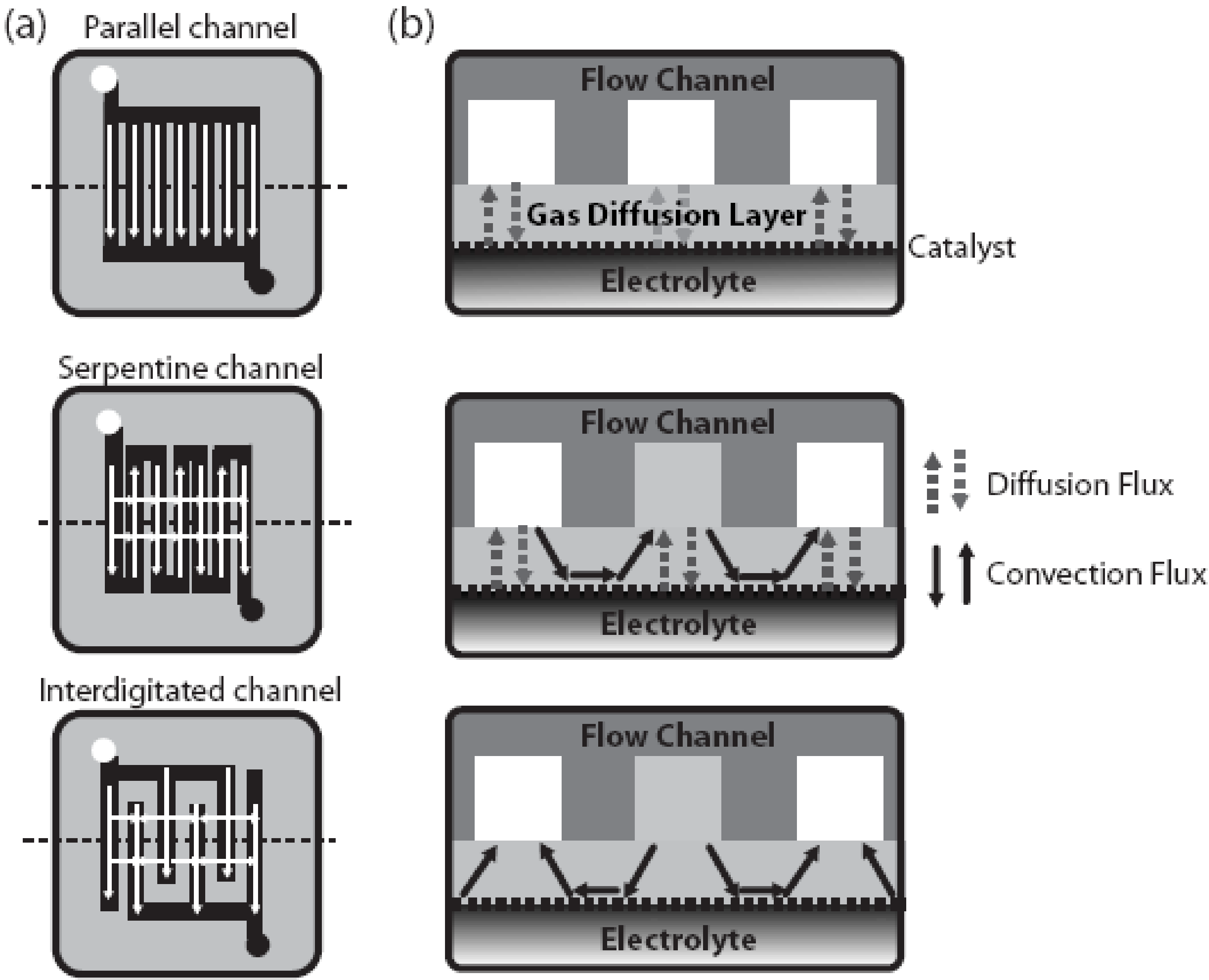
- High electrical conductivity
- High corrosion resistance
- High chemical compatibility
- High thermal conductivity
- High gas tightness
- High mechanical strength
- Low weight and volume
- Ease of manufacturability
- Cost effectiveness

PEMFC Flow Channel Design





PEMFC Flow Channel Design



Toyota Metal Mesh Flow Field