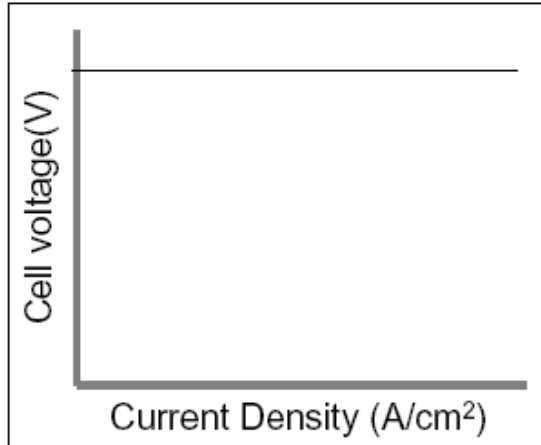
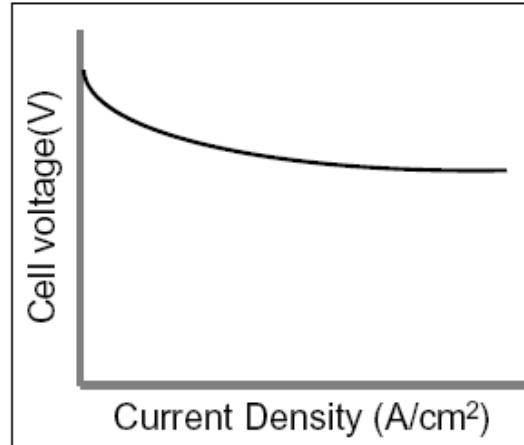


Losses in Fuel Cells

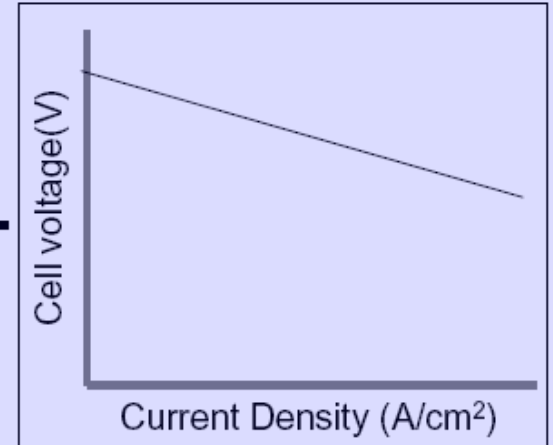
Reversible Voltage (Chapter 2)



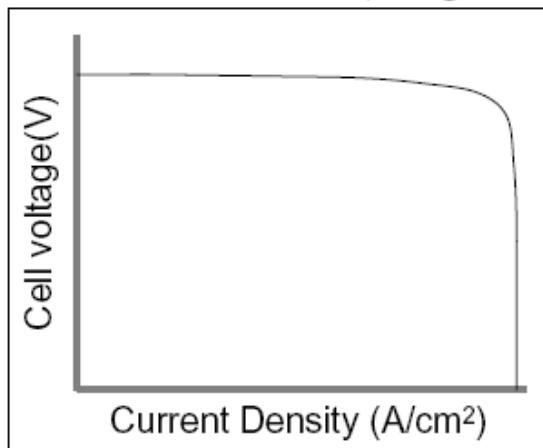
Rxn. Loss (Chapter 3)



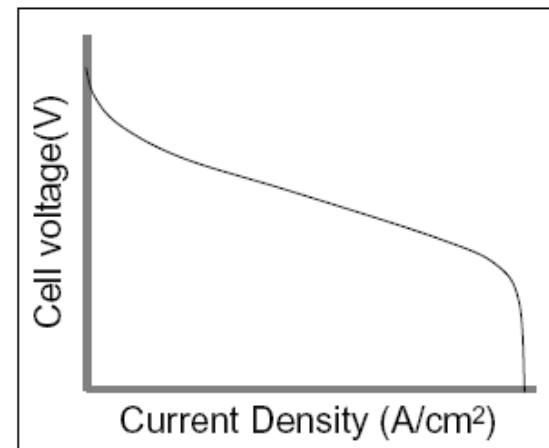
Ohmic Loss (Chapter 4)



Concentration Loss (Chapter 5)



Net Fuel Cell Performance



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

Fuel Cell Charge Transport

Charge Flux

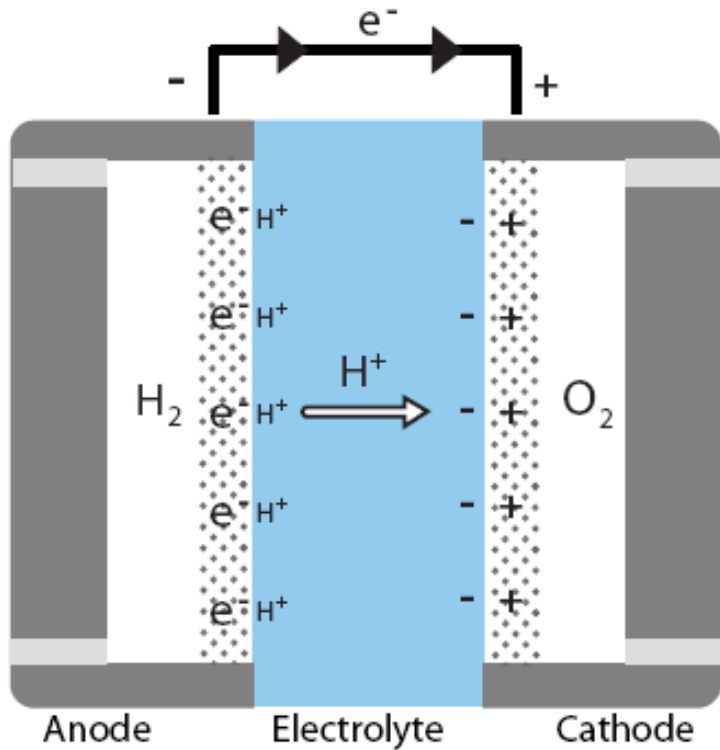
$j(\text{A}/\text{cm}^2)$, $J(\text{mol}/\text{cm}^2)$,

M : coefficient, F : dV/dx , $d\mu/dx$, dP/dx ...

$$j_i = z_i F J_i$$

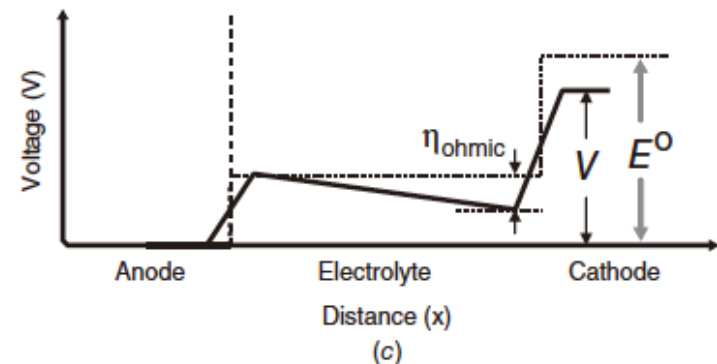
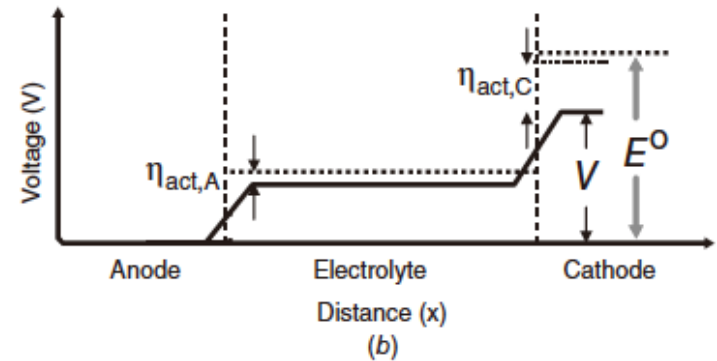
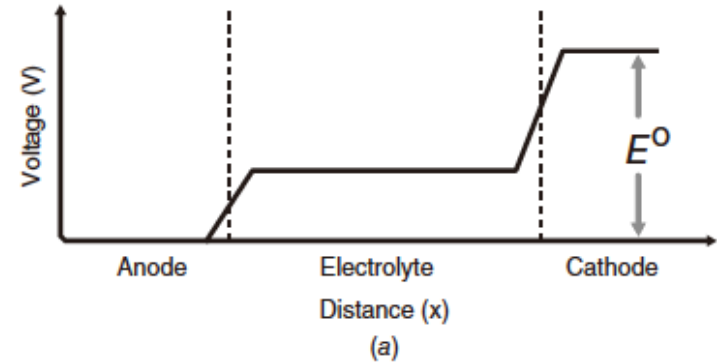
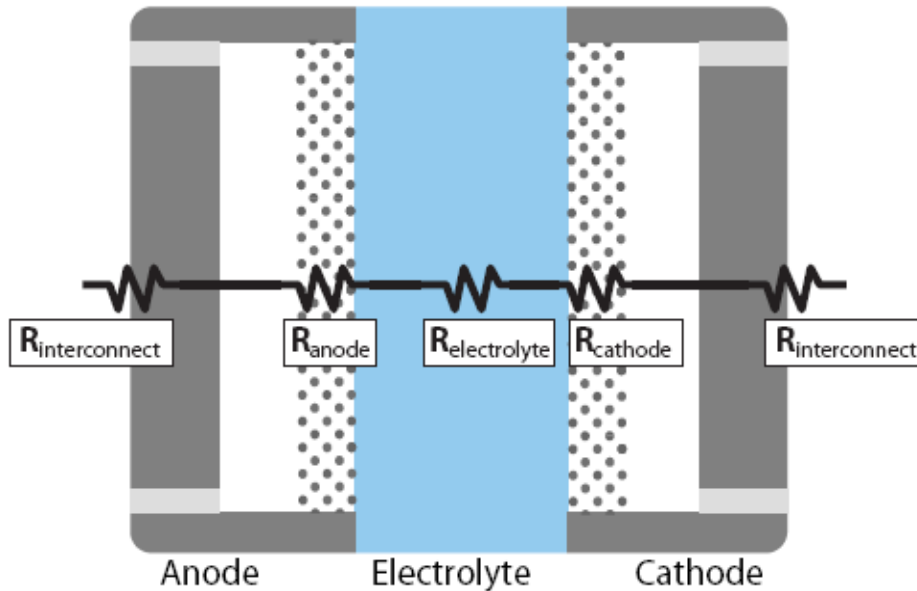
$$J_i = \sum_k M_{ik} F_k$$

$$V = i \left(\frac{L}{A\sigma} \right) = iR$$



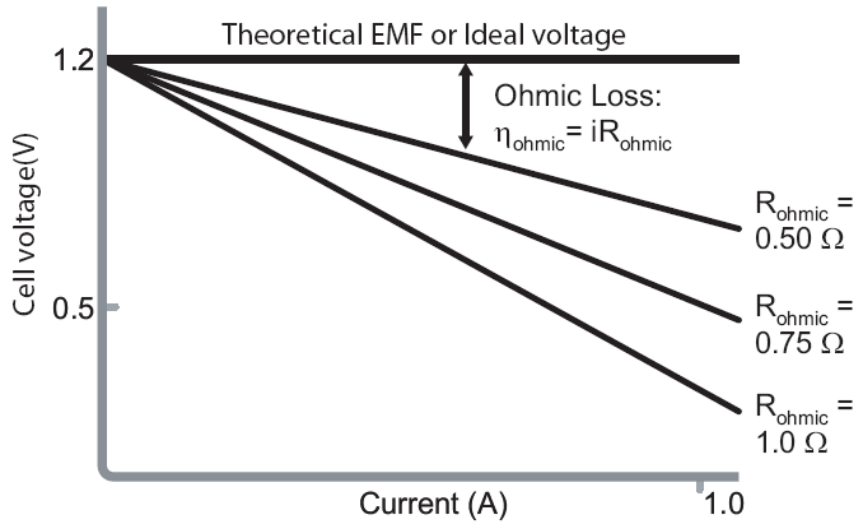
$$\eta_{ohmic} = iR_{ohmic} = i(R_{elec} + R_{ionic})$$

Ohmic Resistances in Fuel Cell



Electrolyte (ionic) resistance is dominant, since all other resistances are electronic.



Ohmic Resistance



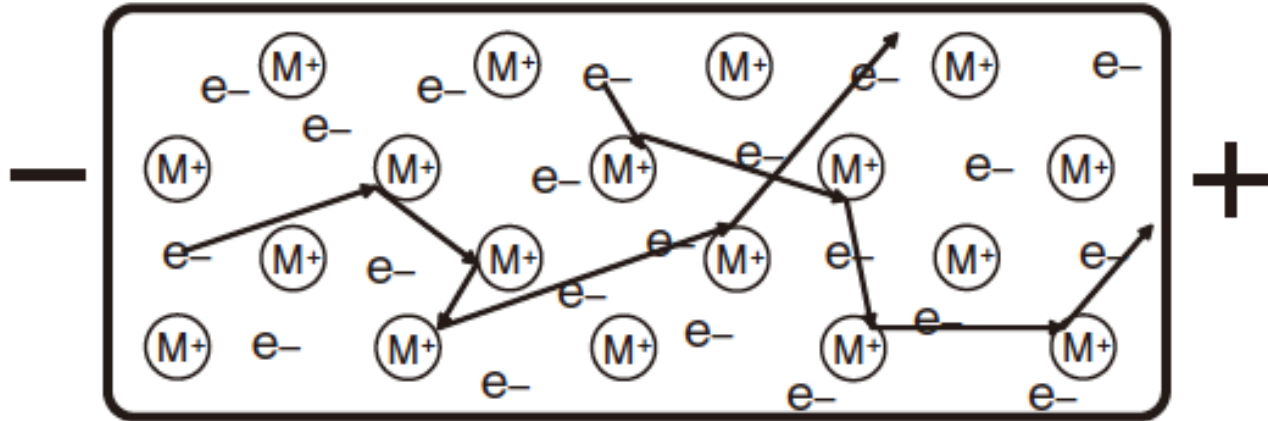
$$R = \left(\frac{L}{A\sigma} \right)$$

Thinner electrolyte has lower resistance, but has to consider

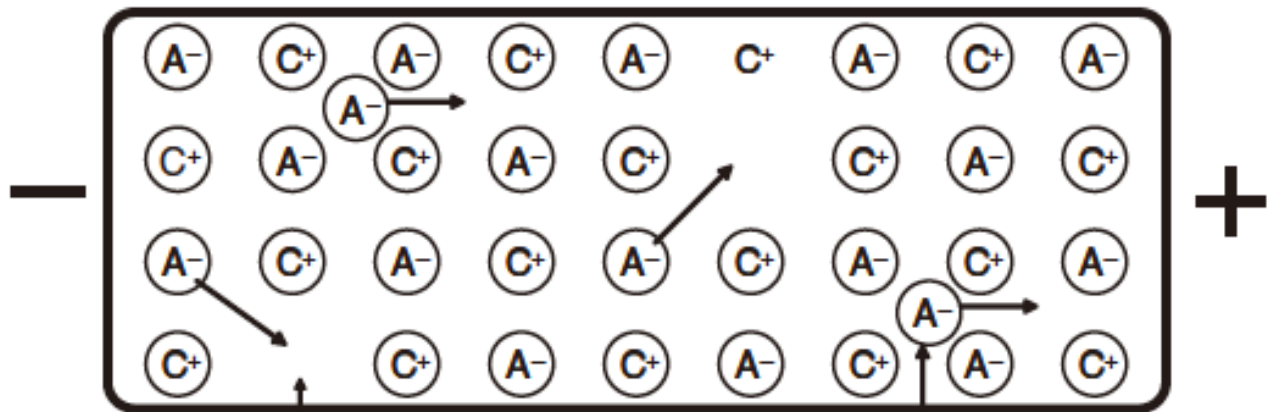
- **Mechanical weakness**
- **Non-uniformity**
- **Shorting**
- **Fuel crossover**
- **Contact resistance**
- **Dielectric breakdown**

<p><u>Fuel Cell 1</u> $A_1 = 1 \text{ cm}^2$ $R_1 = 0.1 \Omega$</p>  <p><u>Fuel Cell 1 ASR</u> $R_1 * A_1 = 0.1 \Omega \text{cm}^2$</p>	<p><u>Fuel Cell 2</u> $A_2 = 10 \text{ cm}^2$ $R_2 = 0.02 \Omega$</p>  <p><u>Fuel Cell 2 ASR</u> $R_2 * A_2 = 0.2 \Omega \text{cm}^2$</p>
--	--

Ohmic Resistance



(a)

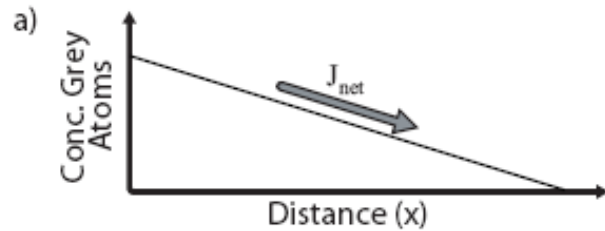


Vacancy

Interstitial

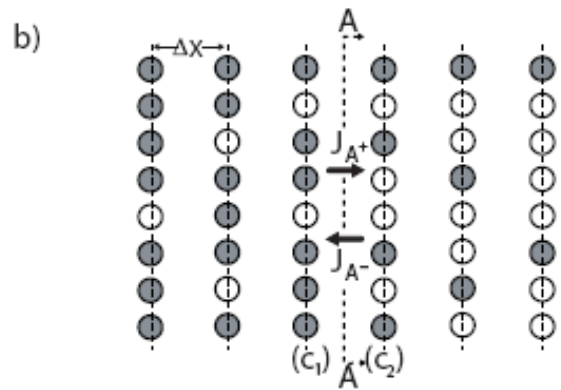
(b)

Basic Equations: Diffusivity



$$J_{A+} = \frac{1}{2} v c_1 \Delta x \quad J_{A-} = \frac{1}{2} v c_2 \Delta x$$

$$J_{net} = \frac{1}{2} v \Delta x (c_1 - c_2)$$



$$J_{net} = -\frac{1}{2} v (\Delta x)^2 \frac{(c_2 - c_1)}{\Delta x}$$

$$= -\frac{1}{2} v (\Delta x)^2 \frac{\Delta c}{\Delta x}$$

$$= -\frac{1}{2} v (\Delta x)^2 \frac{dc}{dx} \quad (\text{for small } x)$$

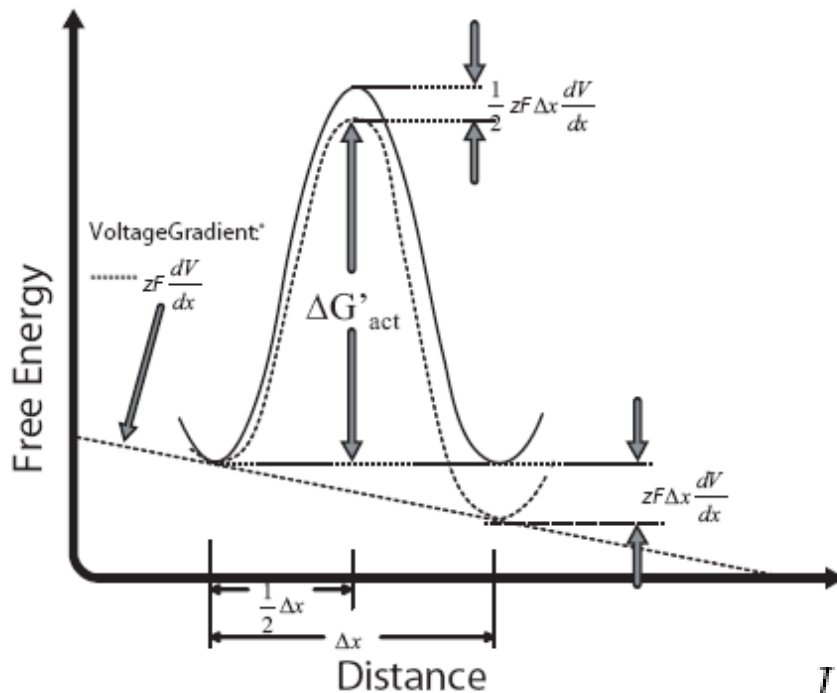
$$D = \frac{1}{2} v (\Delta x)^2$$

$$v = v_0 e^{\frac{-\Delta G_{act}}{RT}}$$

$$D = \frac{1}{2} (\Delta x)^2 v_0 e^{\frac{-\Delta G_{act}}{RT}}$$

$$D = D_0 e^{\frac{-\Delta G_{act}}{RT}}$$

Basic Equations: Conductivity



$$v_+ = v_0 e^{\frac{-(\Delta G_{act} - \frac{1}{2} zF \Delta x \frac{dV}{dx})}{RT}}$$

$$v_- = v_0 e^{\frac{-(\Delta G_{act} + \frac{1}{2} zF \Delta x \frac{dV}{dx})}{RT}}$$

$$\frac{1}{2} \frac{zF}{RT} \Delta x \frac{dV}{dx} \ll 1$$

$$v_+ \approx v_0 e^{\frac{-\Delta G_{act}}{RT}} \left(1 + \frac{1}{2} \frac{zF}{RT} \Delta x \frac{dV}{dx} \right)$$

$$v_- \approx v_0 e^{\frac{-\Delta G_{act}}{RT}} \left(1 - \frac{1}{2} \frac{zF}{RT} \Delta x \frac{dV}{dx} \right)$$

$$J_{net} = J_{A+} - J_{A-} = \frac{1}{2} \Delta x (c_1 v_+ - c_2 v_-)$$

$$J_{net} = \frac{1}{2} \Delta x v_0 e^{\frac{-\Delta G_{act}}{RT}} \left(\frac{czF}{RT} \Delta x \frac{dV}{dx} \right)$$

$$= \frac{1}{2} \Delta x^2 v_0 e^{\frac{-\Delta G_{act}}{RT}} \left(\frac{czF}{RT} \frac{dV}{dx} \right)$$

$$J_{net} = \frac{czFD}{RT} \frac{dV}{dx}$$

$$J = \frac{\sigma}{zF} \frac{dV}{dx}$$

$$\sigma = \frac{c(zF)^2 D}{RT}$$

Requirements for Electrolyte

- High ionic conductivity
- Low electronic conductivity
- High stability (in both oxidizing and reducing environments)
- Low fuel crossover
- Reasonable mechanical strength (if solid)
- Ease of manufacturability

Ionic Conduction

Basic equations

$$\sigma_i = (|z_i|F)c_i u_i \quad u = \frac{|z_i|FD}{RT} \quad \sigma = \frac{c(z_i F)^2 D}{RT}$$

Liquid electrolyte

$$F_E = n_i q \frac{dV}{dx} \quad F_D = 6\pi\mu r v \quad u_i = \frac{v}{\frac{dV}{dx}} = \frac{n_i q}{6\pi\mu r}$$

Cation	Mobility, u ($\frac{cm^2}{Vs}$)	Anion	Mobility, u ($\frac{cm^2}{Vs}$)
$H^+(H_3O^+)$	3.63×10^{-3}	OH^-	2.05×10^{-3}
K^+	7.62×10^{-4}	Br^-	8.13×10^{-4}
Ag^+	6.40×10^{-4}	I^-	7.96×10^{-4}
Na^+	5.19×10^{-4}	Cl^-	7.91×10^{-4}
Li^+	4.01×10^{-4}	HCO_3^-	4.61×10^{-4}

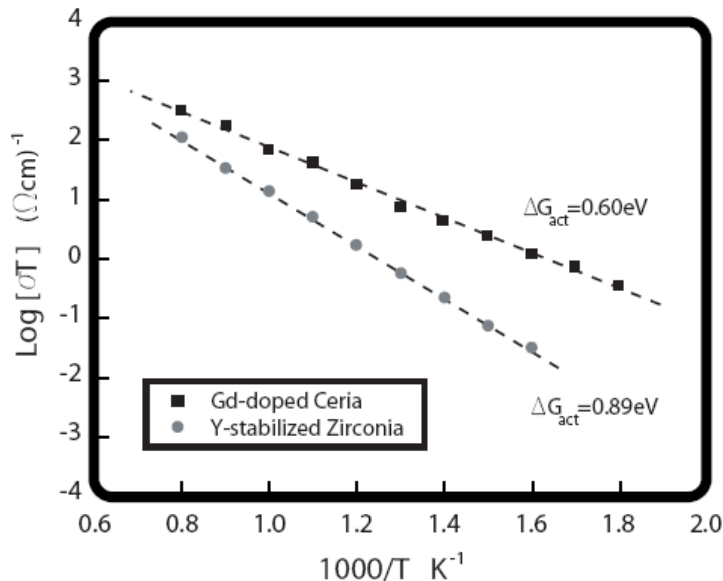
Calculated conductivity may be valid only for dilute solutions

Ionic Conduction in Ceramic

Using $\sigma = \frac{c(z_i F)^2 D}{RT}$ and $D = D_0 e^{-\frac{\Delta G_{act}}{RT}}$

$$\sigma = \frac{c(zF)^2 D_0 e^{-\frac{\Delta G_{act}}{RT}}}{RT} \quad : \text{ extrinsic}$$

$$\sigma = \frac{c_{sites} (zF)^2 D_0 e^{-\frac{\Delta H_v}{2kT}} e^{-\frac{\Delta G_{act}}{RT}}}{RT} \quad : \text{ intrinsic}$$

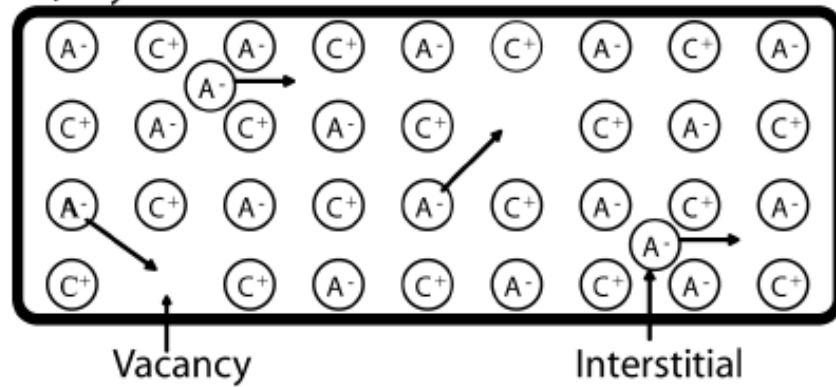


Commonly,

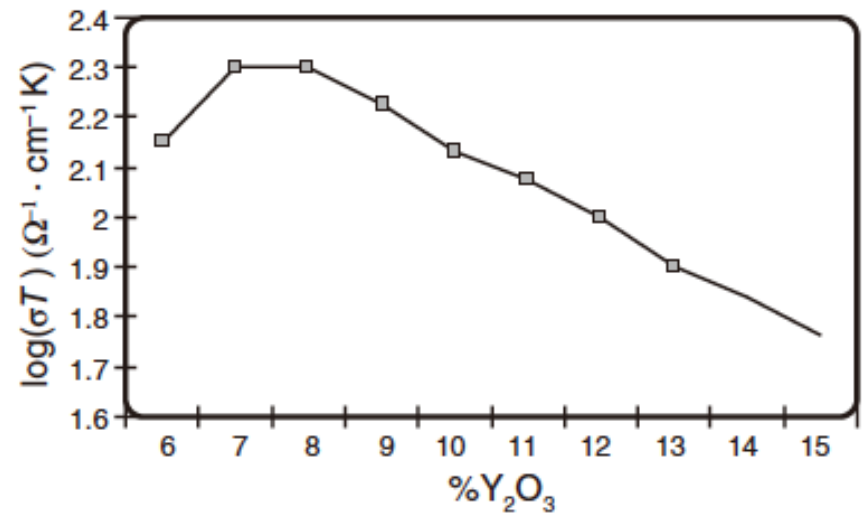
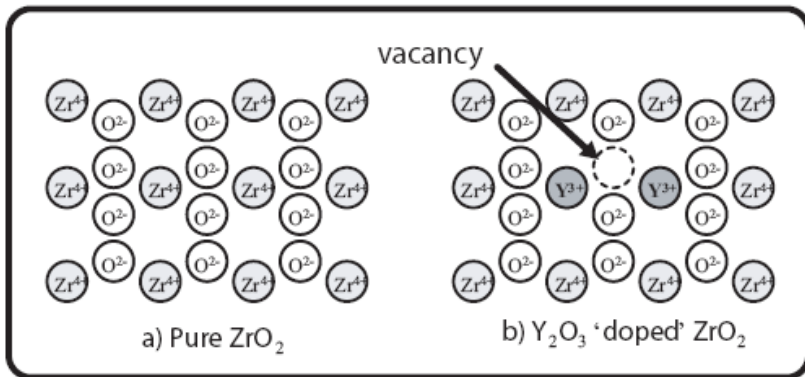
$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

Extrinsic vs Intrinsic

Intrinsic vacancy

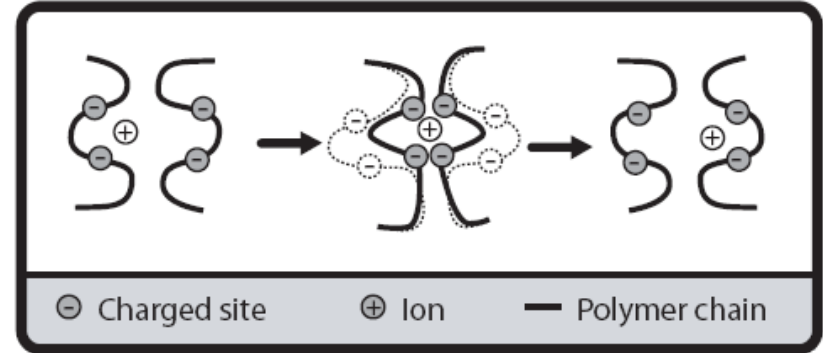


extrinsic vacancy

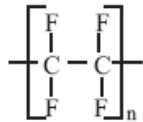


Ion Conduction in Polymers

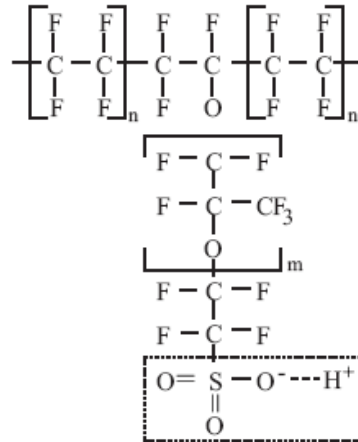
$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$



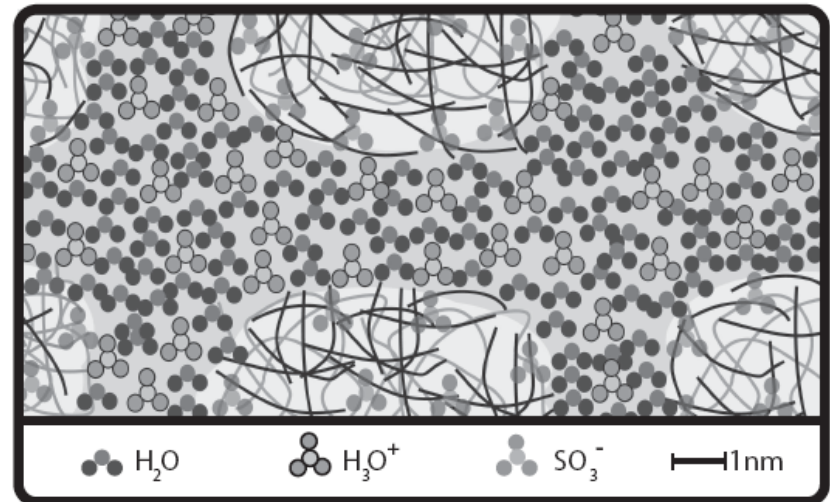
Polytetrafluoroethylene (PTFE)



Nafion



Nafion

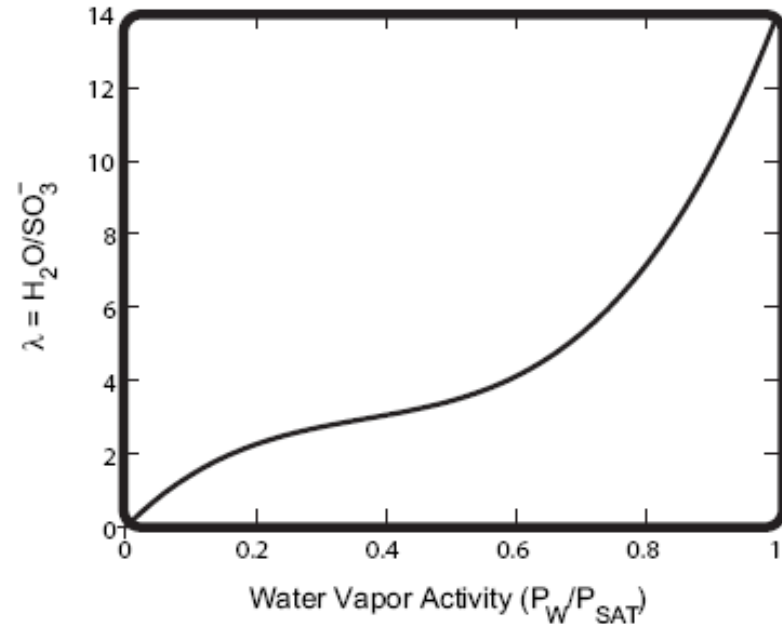


Nafion Characteristics 1

Water absorption

$$a_W = \frac{p_W}{p_{SAT}}$$

$$\lambda = \frac{[H_2O]}{[SO_3^- H^+]} : 0 \leq \lambda \leq 22$$



$$\begin{aligned} \lambda &= 0.0043 + 17.81a_W - 39.85a_W^2 + 36.0a_W^3 \quad \text{for } 0 < a_W \leq 1 \\ \lambda &= 14 + 1.4(a_W - 1) \quad \text{for } 1 < a_W \leq 3 \end{aligned} \quad (4)$$

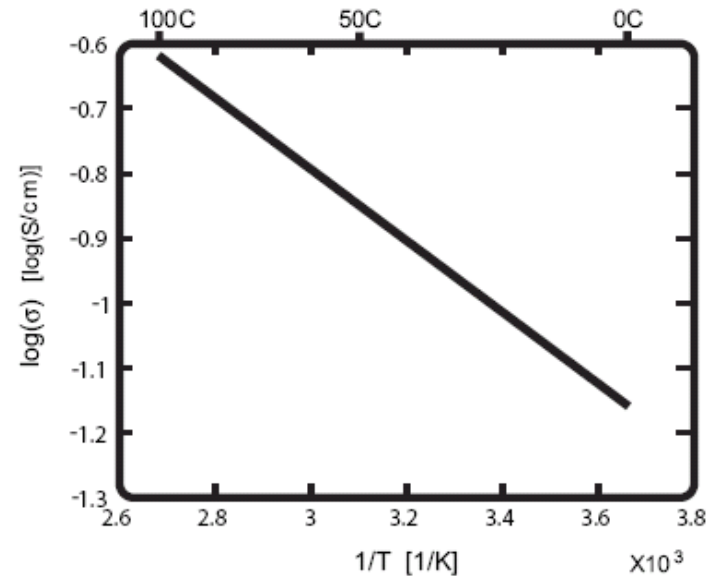
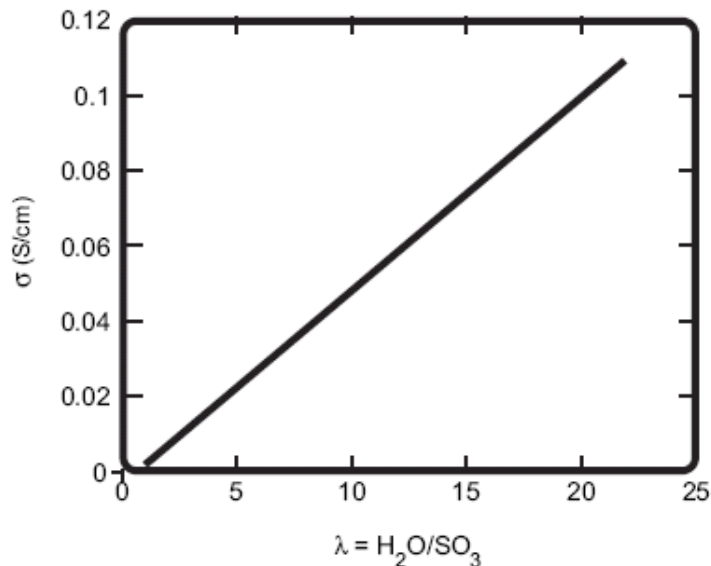
Nafion Characteristics 2

Conductivity
vs T & water contents

$$\sigma(T, \lambda) = \sigma_{303K}(\lambda) \exp \left[1268 \left(\frac{1}{303} - \frac{1}{T} \right) \right]$$

where $\sigma_{303K}(\lambda) = (0.005193\lambda - 0.00326)$

$$R_m = \int_0^{t_m} r(z) dz = \int_0^{t_m} \frac{dz}{\sigma(\lambda(z))}$$



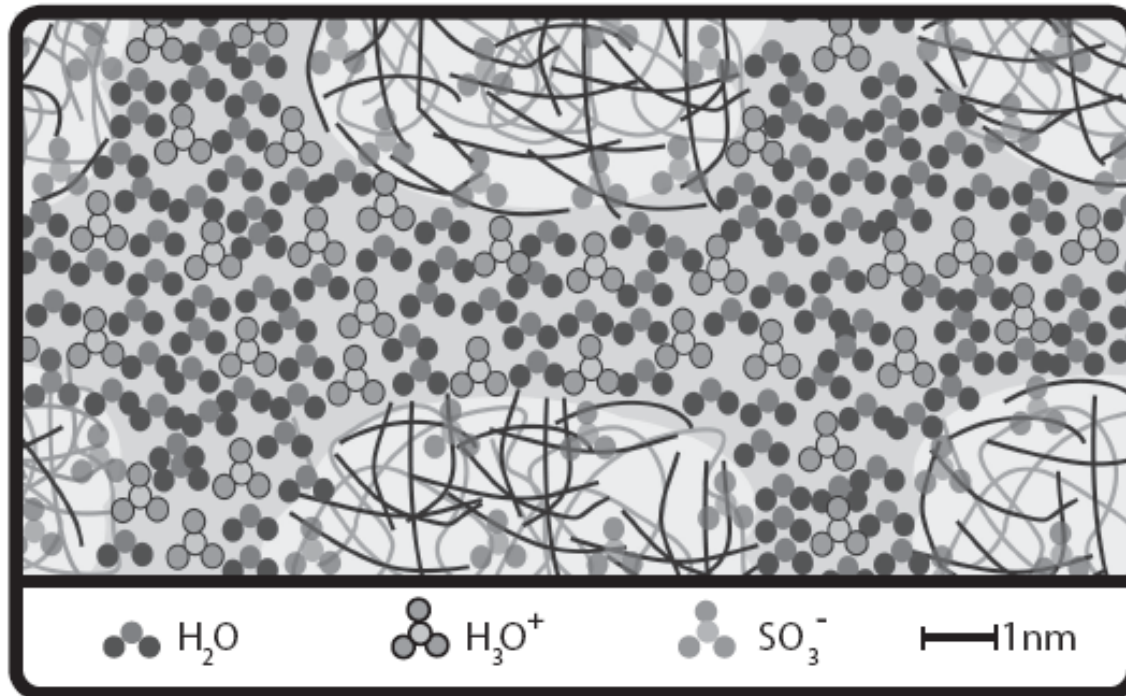
Nafion Characteristics 3

Electro-osmotic drag

$$n_{drag} = n_{drag}^{SAT} \frac{\lambda}{22} \quad \text{for } 0 \leq \lambda \leq 22$$

$$n_{drag}^{SAT} \approx 2.5.$$

$$J_{H_2O,drag} = 2n_{drag} \frac{j}{2F}$$



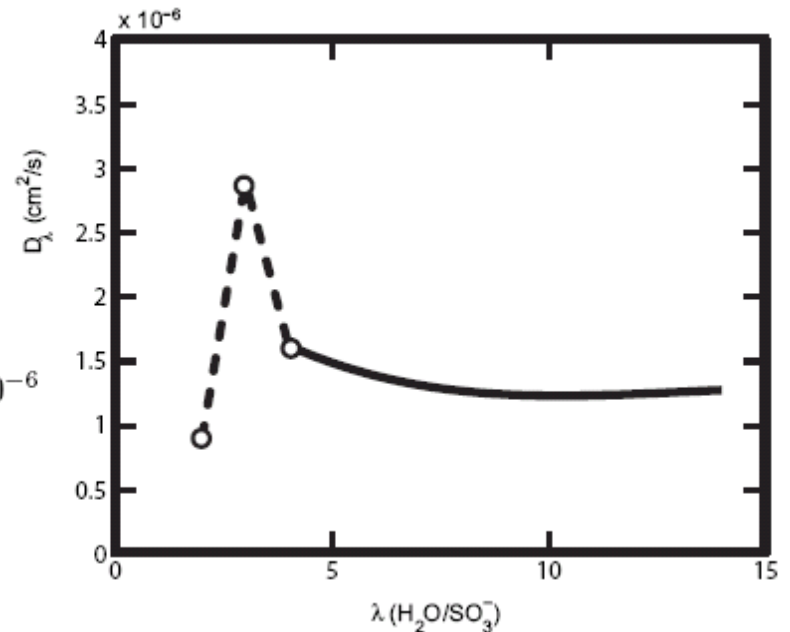
Nafion Characteristics 4

Back Diffusion

$$J_{H_2O, backdiffusion} = -\frac{\rho_{dry}}{M_m} D_\lambda \frac{d\lambda}{dz}$$

$$D_\lambda = \exp \left[2416 \left(\frac{1}{303} - \frac{1}{T} \right) \right] \times (2.563 - 0.33\lambda + 0.0264\lambda^2 - 0.000671\lambda^3) \times 10^{-6}$$

in $[cm^2/s]$ for $\lambda > 4$



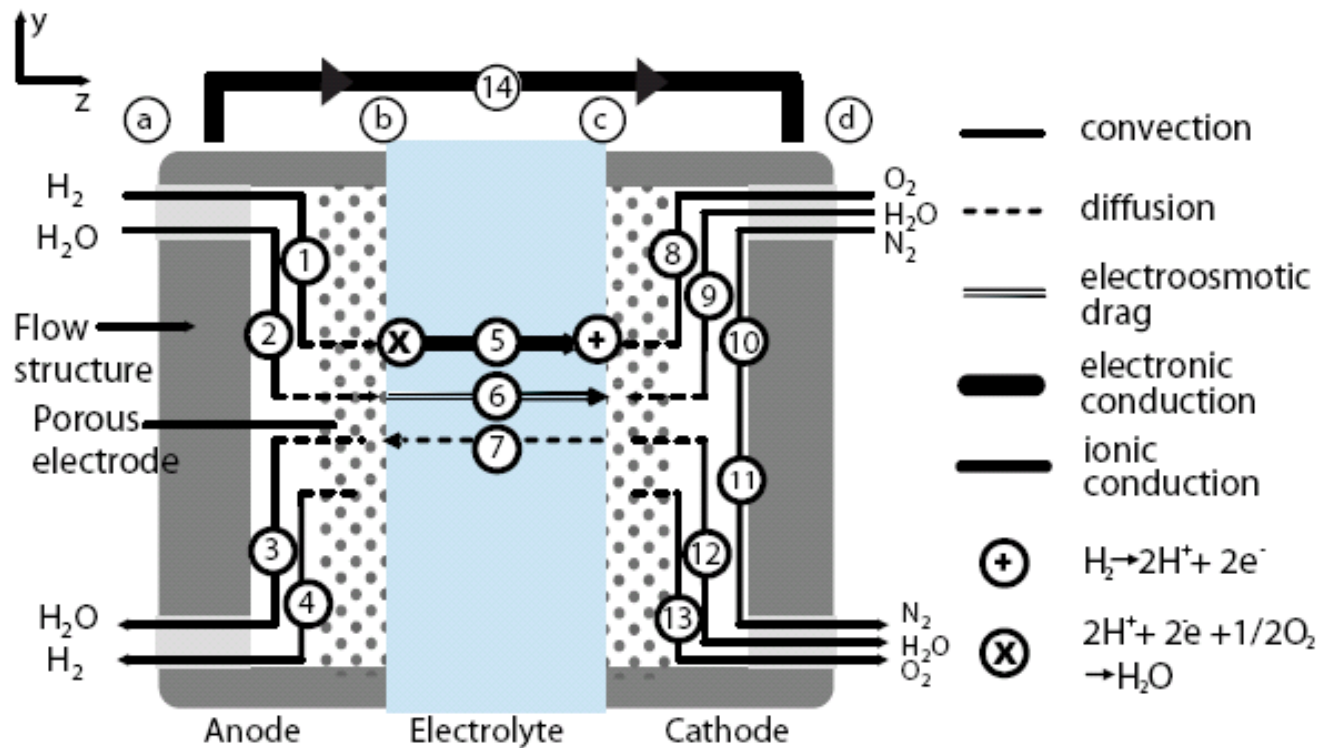
$$\text{Equivalent weight} = \frac{\text{Atomic(Formula) weight}}{\text{Valance}}$$

$$C_{SO_3^-} (\text{mol}/m^3) = \frac{\rho_{dry} (\text{kg}/m^3)}{M_m (\text{kg}/\text{mol})}$$

$$C_{H_2O} (\text{mol}/m^3) = \lambda \frac{\rho_{dry} (\text{kg}/m^3)}{M_m (\text{kg}/\text{mol})}$$

Nafion Resistance Example

Example 4.4 Consider a hydrogen PEM fuel cell powering an external load at $0.7\text{A}/\text{cm}^2$. The activities of water vapor on the anode and cathode sides of the membrane are measured to be 0.8 and 1.0 respectively. The temperature of the fuel cell is 80°C . If the Nafion[®] membrane thickness is 0.125mm , estimate the ohmic overvoltage loss across the membrane.



Nafion Resistance Example

Water flux in Nafion

$$J_{H_2O} = 2n_{drag}^{SAT} \frac{j}{2F} \frac{\lambda}{22} - \frac{\rho_{dry}}{M_m} D_\lambda(\lambda) \frac{d\lambda}{dz}$$

$$\frac{d\lambda}{dz} = \left[2n_{drag}^{SAT} \frac{\lambda}{22} - \alpha \right] \frac{j M_m}{2F \rho_{dry} D_\lambda} \quad J_{H_2O} = \alpha N_{H_2} = \alpha \frac{j}{2F}$$

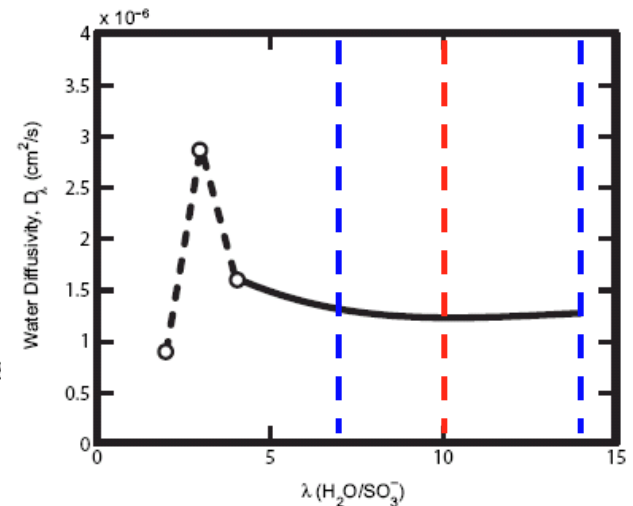
Find B.C.

$$\lambda^A = 0.0043 + 17.81 \times 0.8 - 39.85 \times 0.8^2 + 36.0 \times 0.8^3 = 7.22$$

$$\lambda^C = 0.0043 + 17.81 \times 1.0 - 39.85 \times 1.0^2 + 36.0 \times 1.0^3 = 14.0$$

Find water diffusivity

$$\begin{aligned} D_\lambda &= 10^{-6} \exp \left[2416 \left(\frac{1}{303} - \frac{1}{353} \right) \right] \\ &\times (2.563 - 0.33 \times 10 + 0.0264 \times 10^2 - 0.000671 \times 10^3) \\ &= 3.81 \times 10^{-6} \text{ [cm}^2/\text{s]} \end{aligned}$$



Nafion Resistance Example

Water profile in Nafion

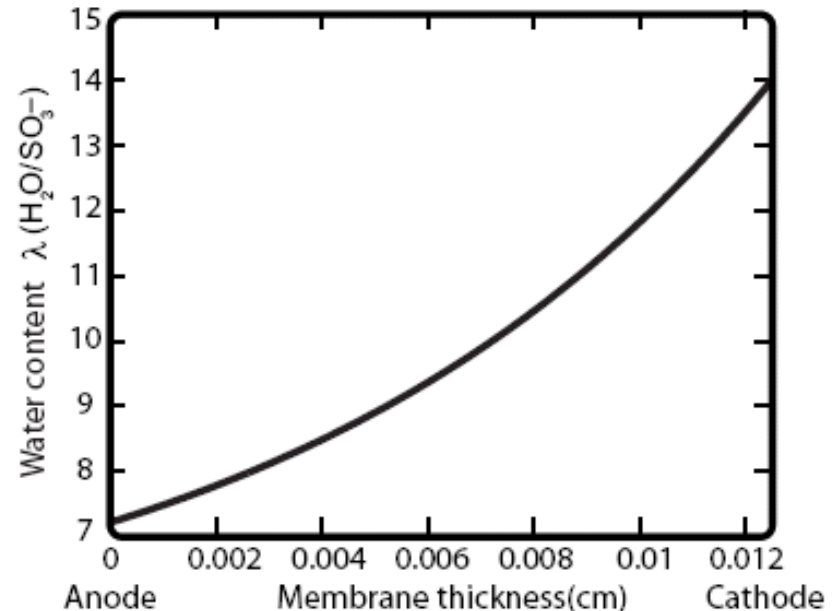
$$\begin{aligned} \lambda(z) &= \frac{11\alpha}{n_{drag}^{SAT}} + C \exp \left[\frac{jM_m n_{drag}^{SAT}}{22F\rho_{dry}D_\lambda} z \right] = \frac{11\alpha}{2.5} \\ &+ C \exp \left[\frac{0.7(A/cm^2) \times 1.0(kg/mol) \times 2.5}{22 \times 96500 C/mol \times 0.00197(kg/cm^3) \times 3.81(cm^2/s)} z \right] \\ &= 4.4\alpha + C \exp(109.8z) \quad \text{where } z \text{ in [cm]} \end{aligned} \quad (4.53)$$

B.C.

$$\lambda(0) = 7.22 \quad \text{and} \quad \lambda(0.0125) = 14$$

$$\lambda(z) = 4.4\alpha + 2.30 \exp(109.8z)$$

$$\text{where } \alpha = 1.12$$

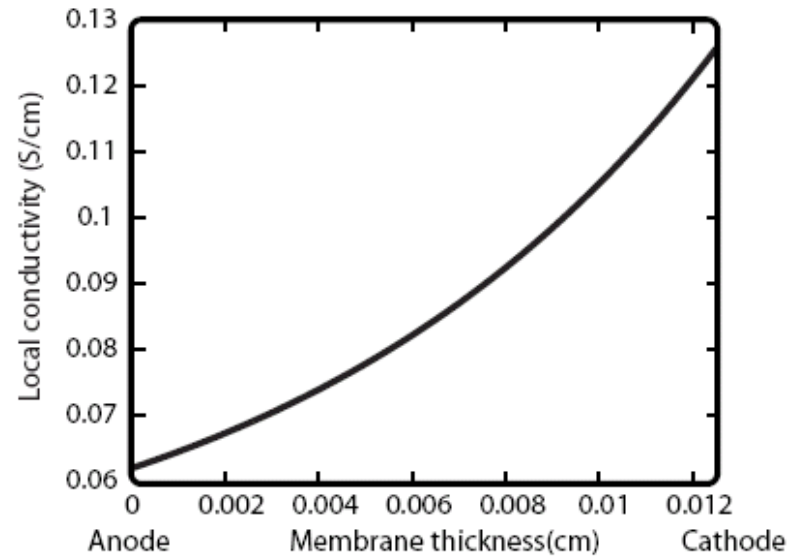


(a) Water content profile across the Nafion[®] membrane

Nafion Resistance Example

Conductivity profile

$$\begin{aligned}\sigma(z) &= [0.005193(4.4\alpha + 2.30 \exp(109.8z)) - 0.00326] \\ &\quad \times \exp \left[1268 \left(\frac{1}{303} - \frac{1}{353} \right) \right] \\ &= 0.0404 + 0.0216 \exp(109.8z)\end{aligned}$$



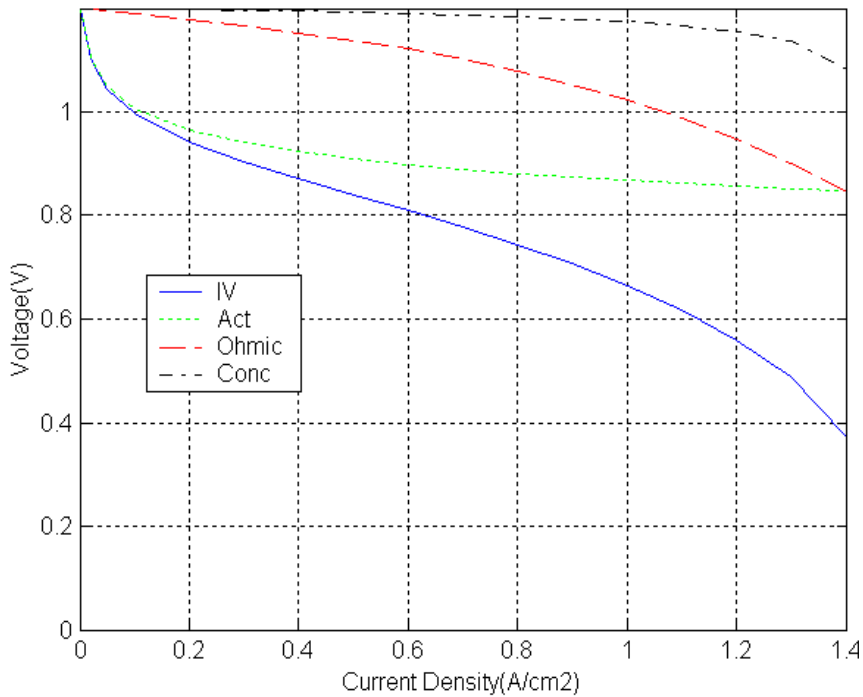
(b) Local conductivity profile across the Nafion[®] membrane

Ohmic resistance

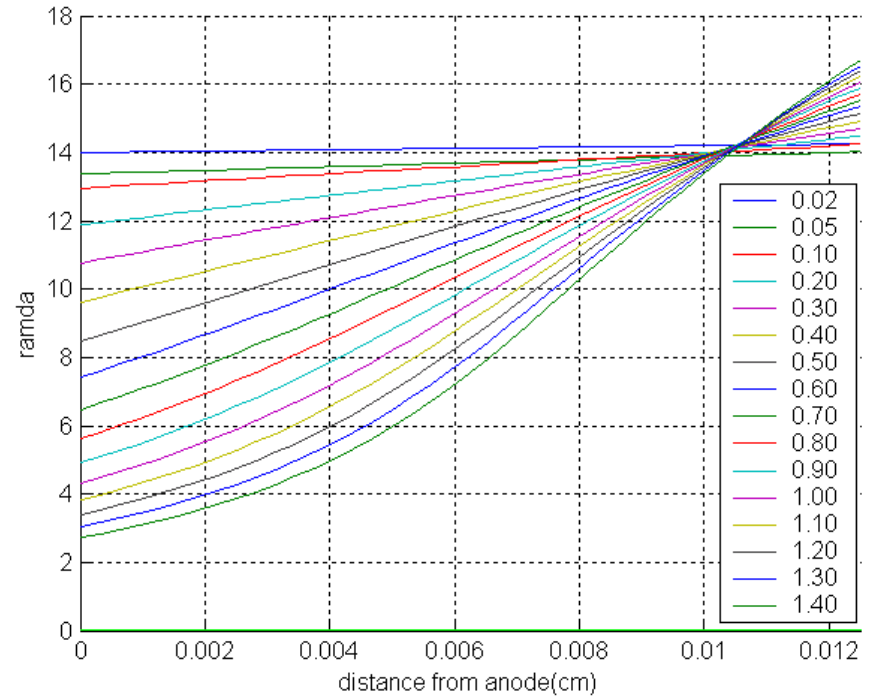
$$\begin{aligned}R_m &= \int_0^{t_m} \frac{dz}{\sigma(\lambda(z))} = \int_0^{0.0125} \frac{dz}{0.0404 + 0.0216 \exp(109.8z)} \\ &= 0.150 \Omega \text{cm}^2\end{aligned}$$

$$V_{ohm} = j \times R_m = 0.7 (\text{A/cm}^2) \times 0.15 (\Omega \text{cm}^2) = 0.105 \text{V}$$

Ohmic Resistance



Overpotentials in PEMFC's



Water profile through membrane

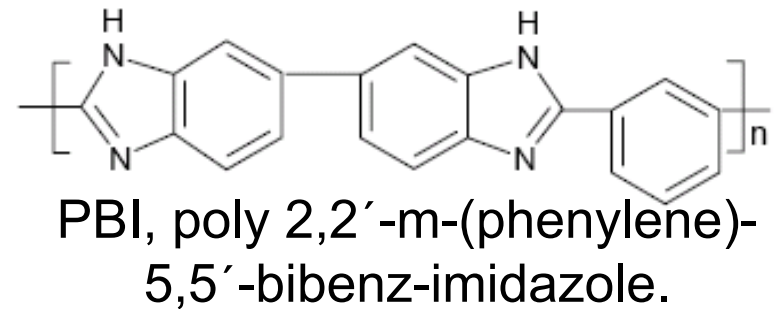
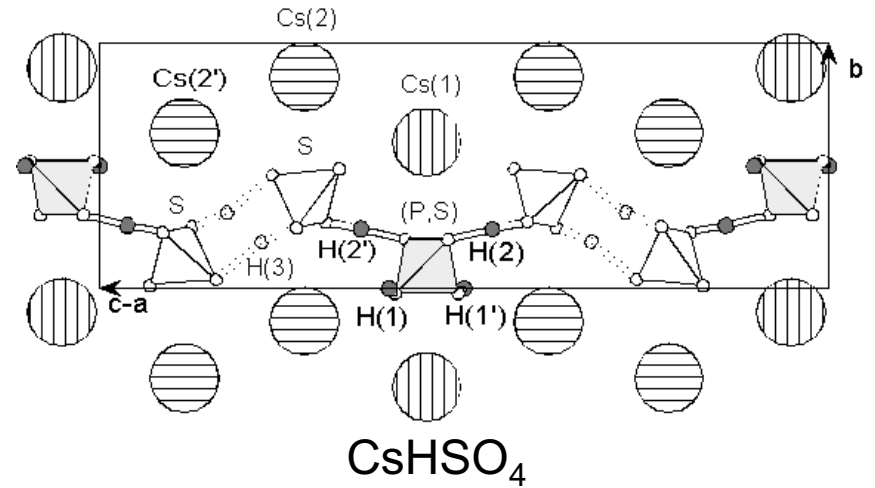
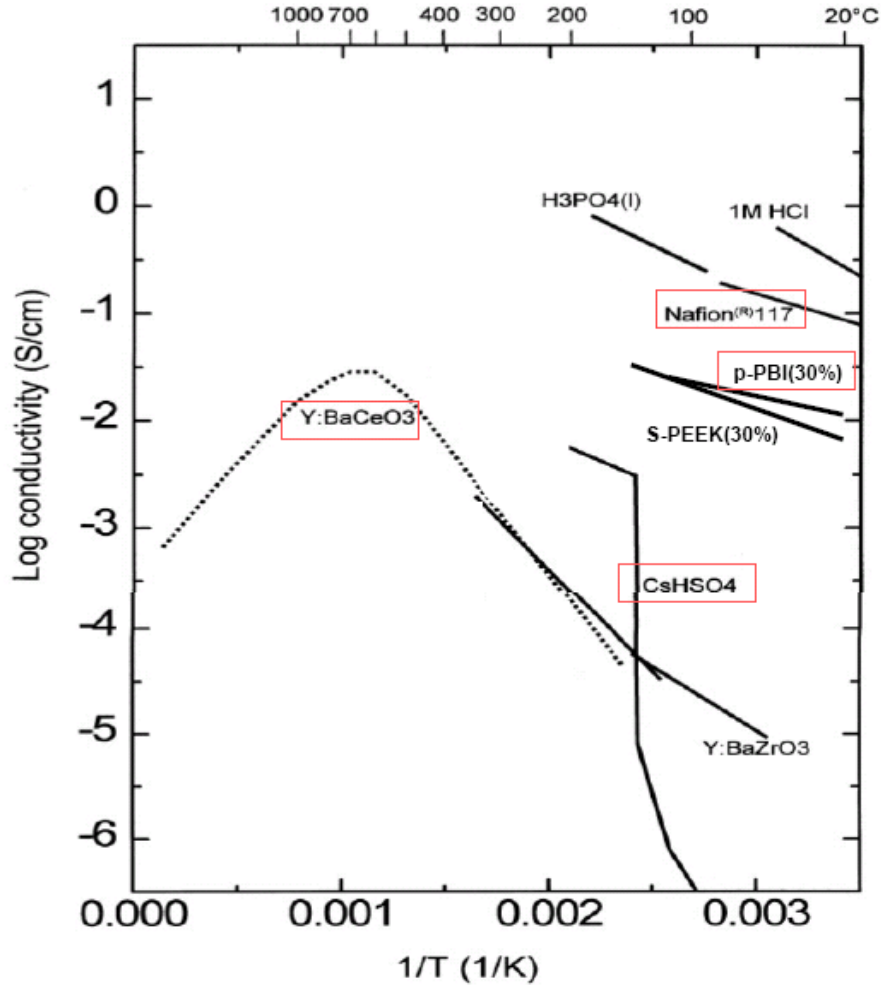
Reference:

$P_a = 3 \text{ atm}$, $P_c = 3 \text{ atm}$, $T = 80 \text{ C}$, $v_{H_2} = 1.5 \text{ A}$, $v_{O_2} = 1.5 \text{ A}$

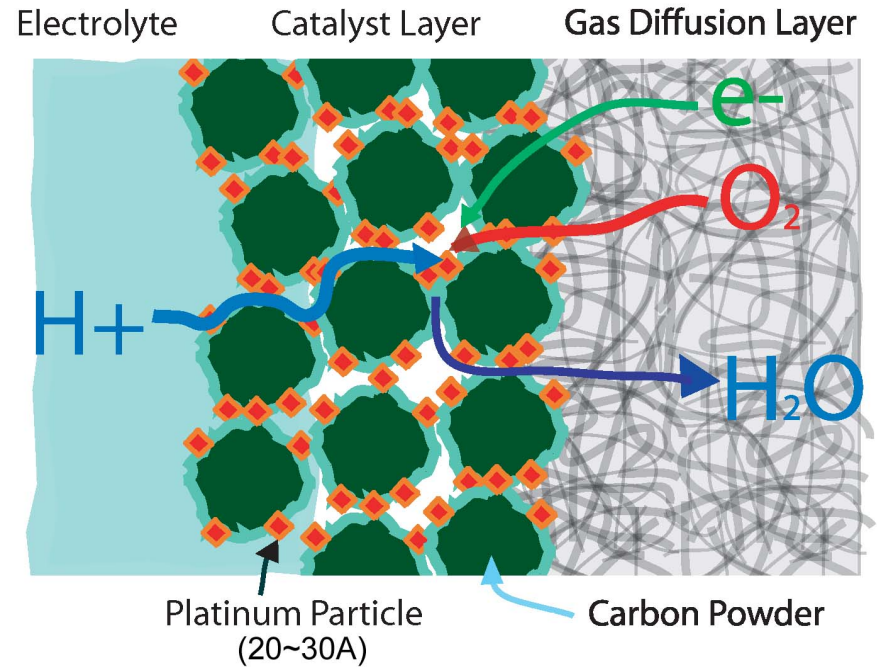
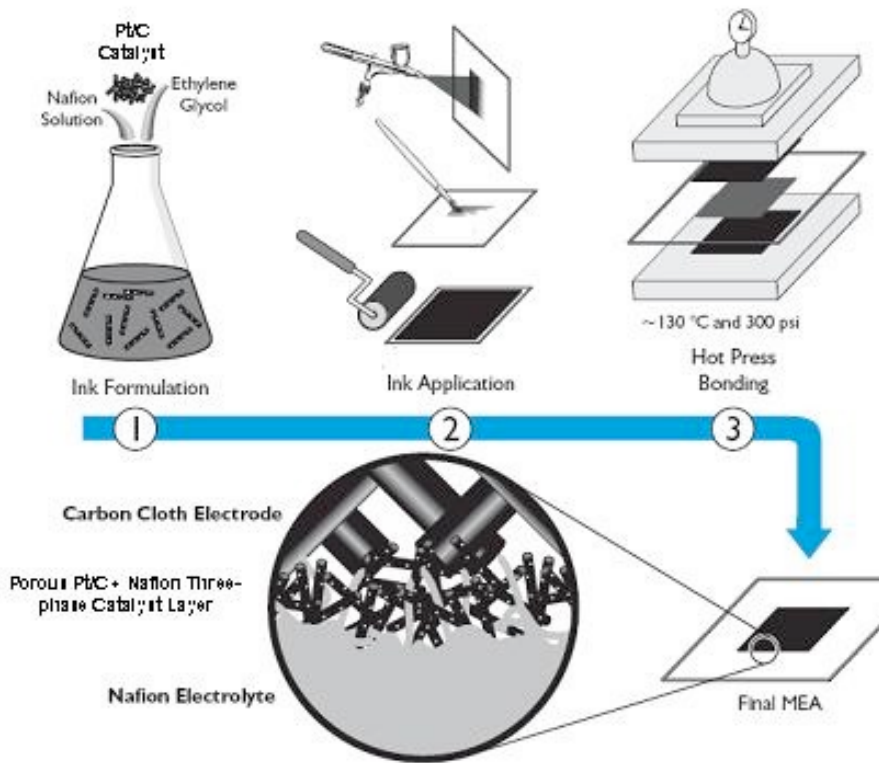
$t_m = 0.0125 \text{ cm}$, $t_c = 0.0365 \text{ cm}$, $t_a = 0.0365 \text{ cm}$

$n_{drag} = 2.5$, $poro = 0.4$, Relative Humidity = 100%

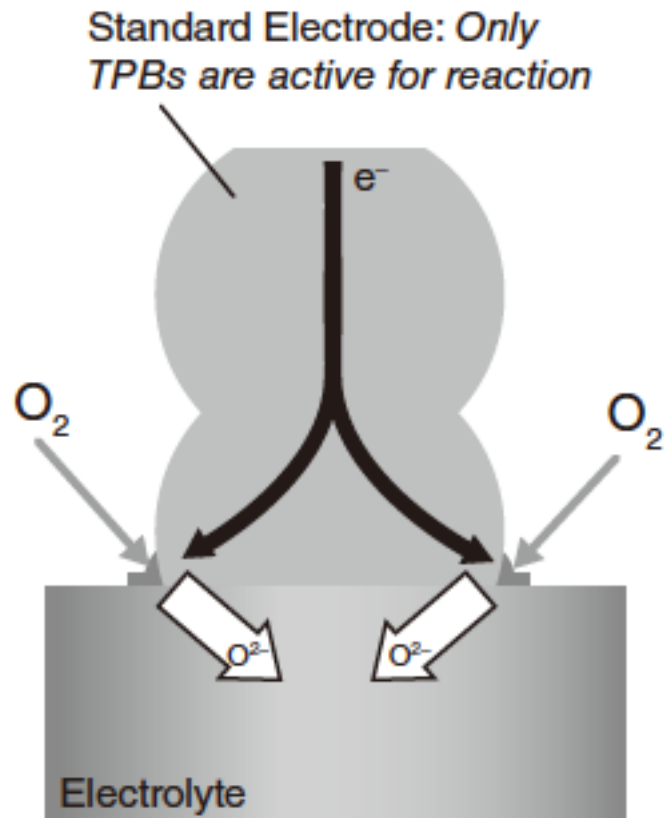
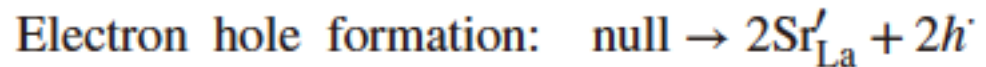
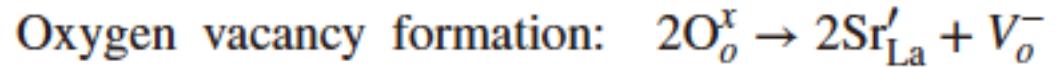
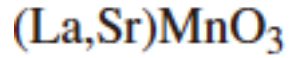
Electrolytes



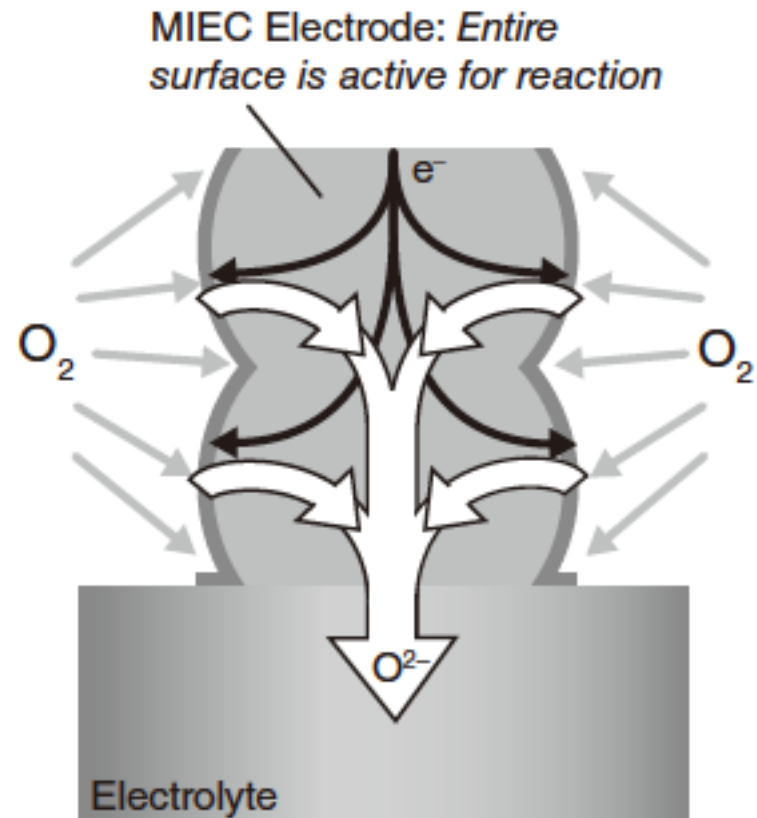
More on TBP(PEMFC)



More on TBP(SOFC)



(a)



(b)