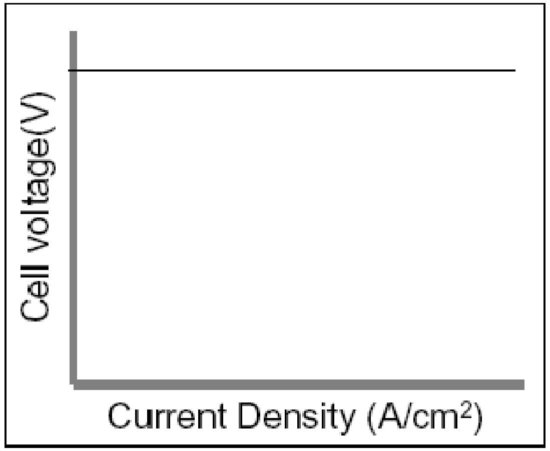
Losses in Fuel Cells

Reversible Voltage (Chapter 2)



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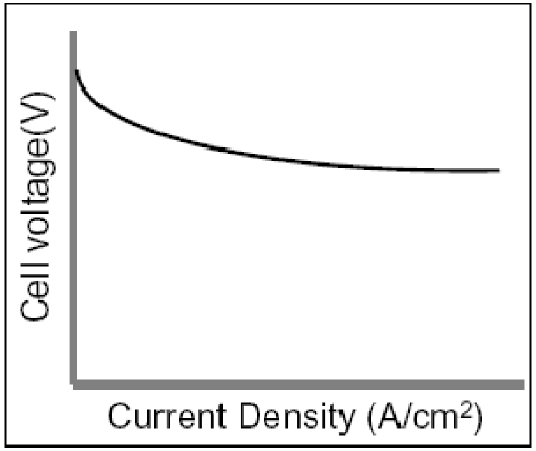
Rxn. Loss (Chapter 3)



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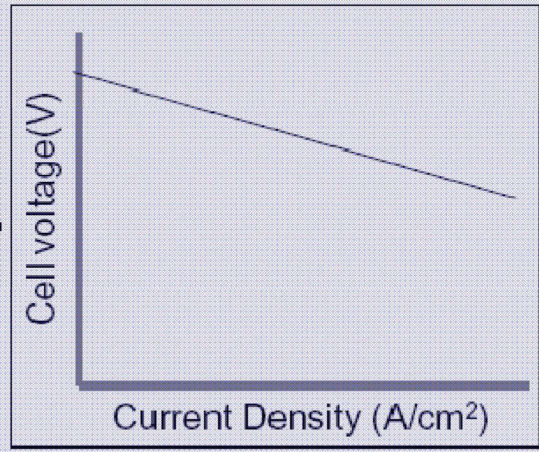
Ohmic Loss (Chapter 4)



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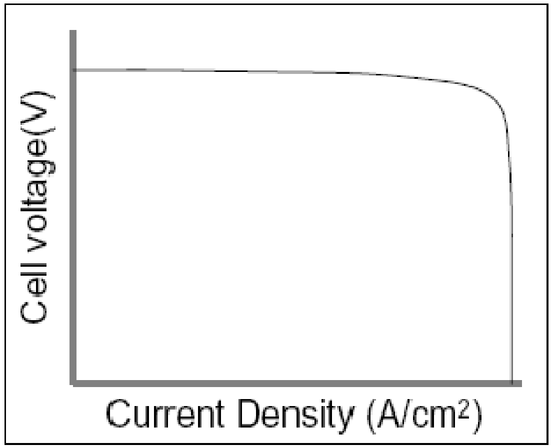
Concentration Loss (Chapter 5)



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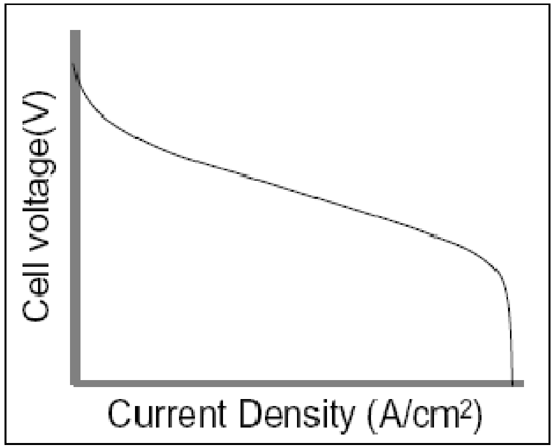
Net Fuel Cell Performance



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

Fuel Cell Charge Transport

Charge Flux

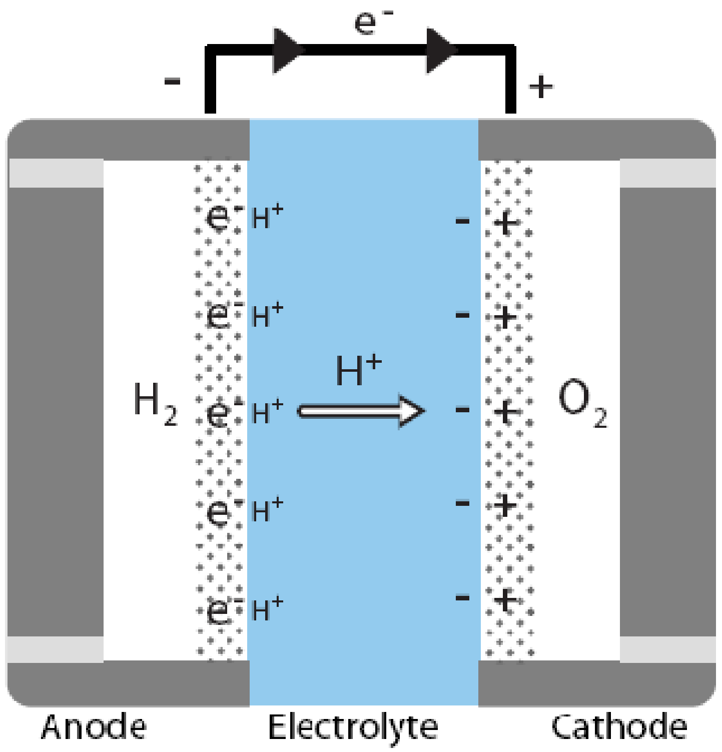
j(A/cm2), J(mol/cm2),

M: coefficient, F: dV/dx, dμ/dx, dP/dx...

$$j_i = z_i F J_i$$

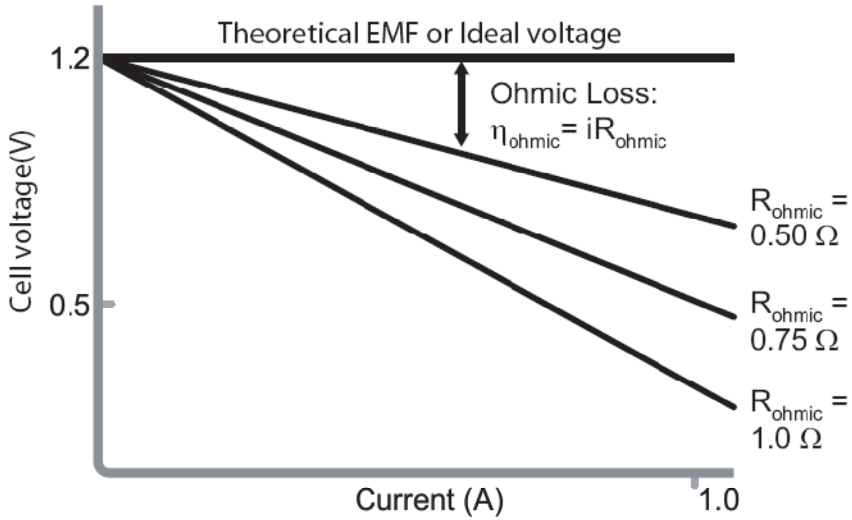
$$J_i = \sum_k M_{ik} F_k$$

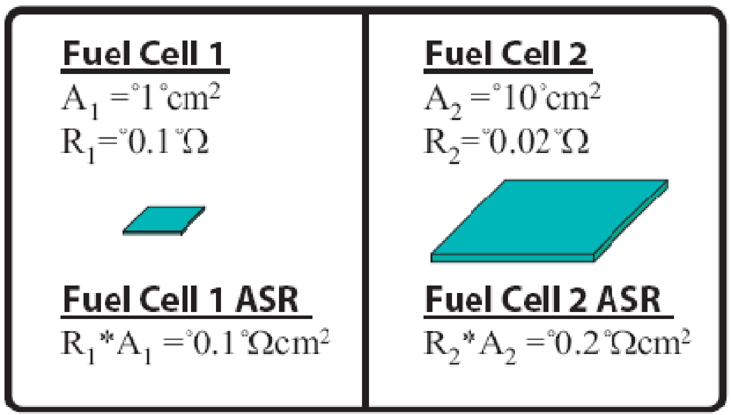
$$V = i\left(\frac{L}{A\sigma}\right) = iR$$



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

Ohmic Resistance



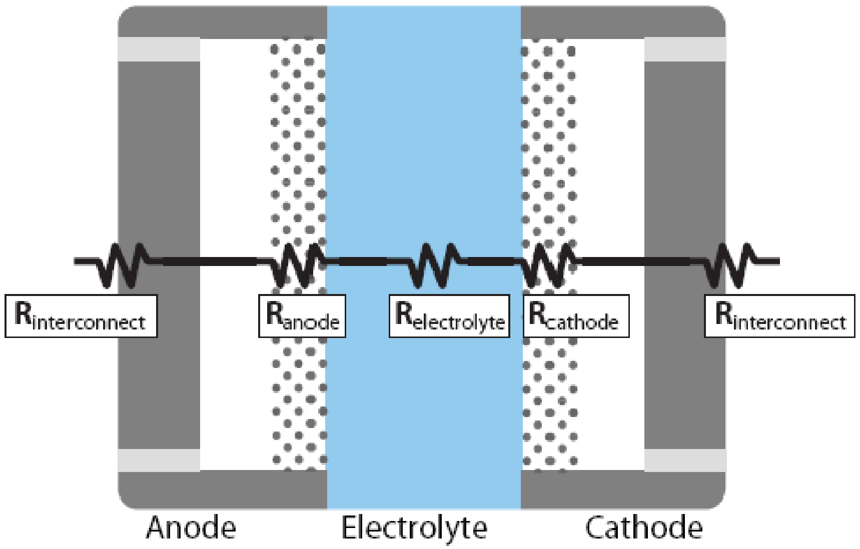


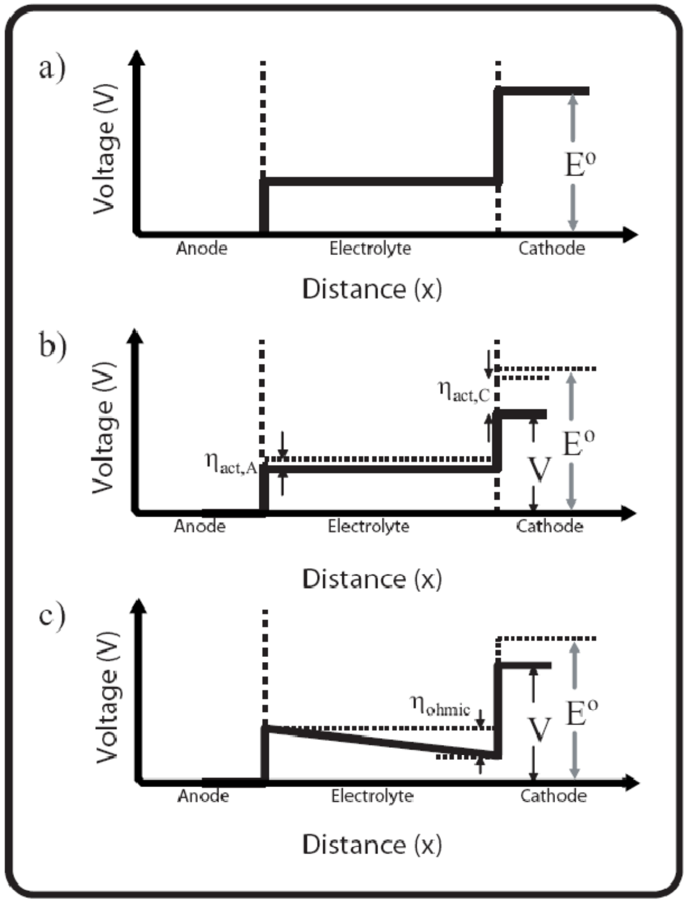
$$R = \left(\frac{L}{A\sigma}\right)$$

Thinner electrolyte has lower resistance, but has to consider

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

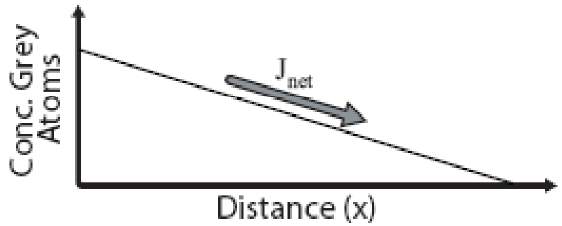
Ohmic Resistances in Fuel Cell





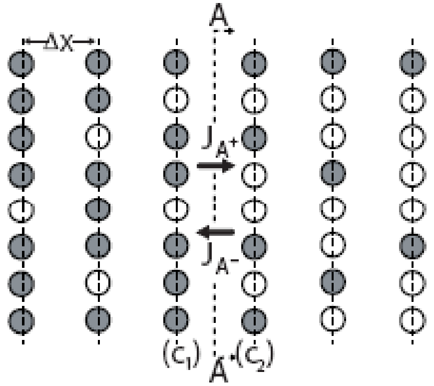
Electrolyte (ionic) resistance is dominant, since all other resistances are electronic.

Basic Equations: Diffusivity

a)


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

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

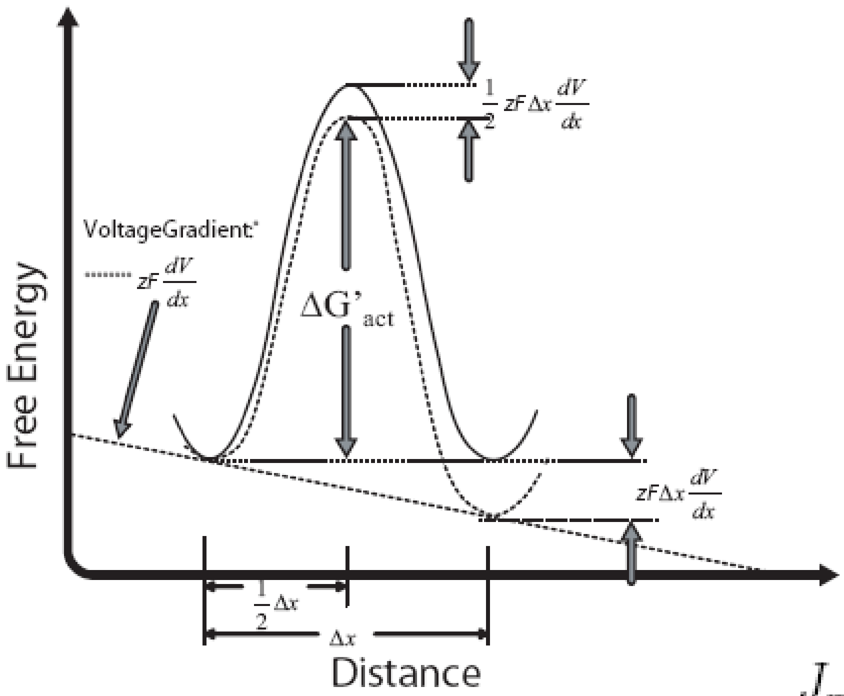
b)


$$\begin{aligned} J_{net} &= -\frac{1}{2}\upsilon(\Delta x)^2 \frac{(c_2 - c_1)}{\Delta x} \\ &= -\frac{1}{2}\upsilon(\Delta x)^2 \frac{\Delta c}{\Delta x} \\ &= -\frac{1}{2}\upsilon(\Delta x)^2 \frac{dc}{dx} \qquad (for\ small\ x) \end{aligned}$$

$$D = \frac{1}{2}\upsilon(\Delta x)^2 \qquad \upsilon = \upsilon_0 e^{\frac{-\Delta G_{act}}{RT}} \qquad D = \frac{1}{2}(\Delta x)^2 \upsilon_0 e^{\frac{-\Delta G_{act}}{RT}}$$

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

Basic Equations: Conductivity



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

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

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

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

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

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

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

$$J_{net} = \frac{czFD}{RT}\frac{dV}{dx} \qquad J = \frac{\sigma}{zF}\frac{dV}{dx},$$

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

Ionic Conduction

Basic equations

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

Liquid electrolyte

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

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}

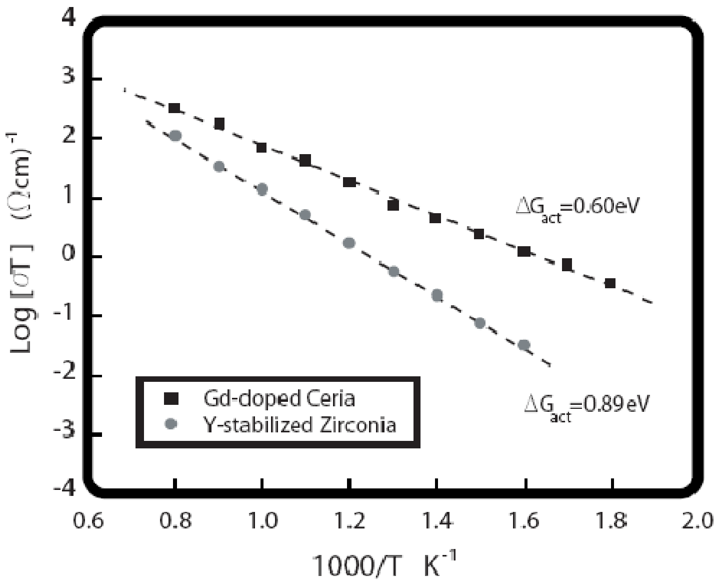
Calculated conductivity may be valid only for dilute solutions

Ionic Conduction in Ceramic

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

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

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

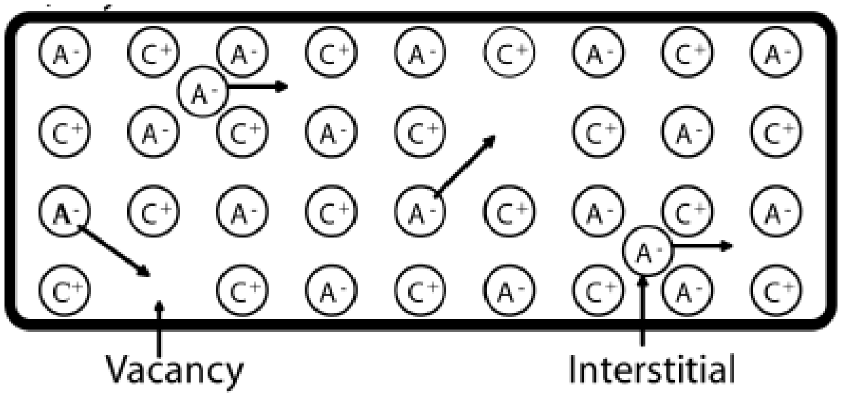


Commonly,

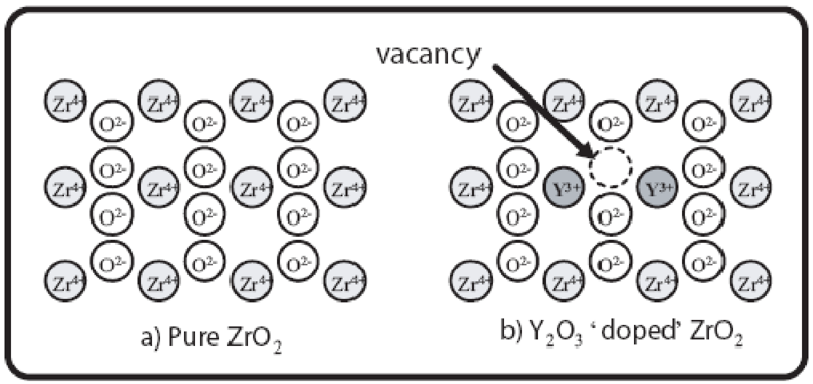
$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

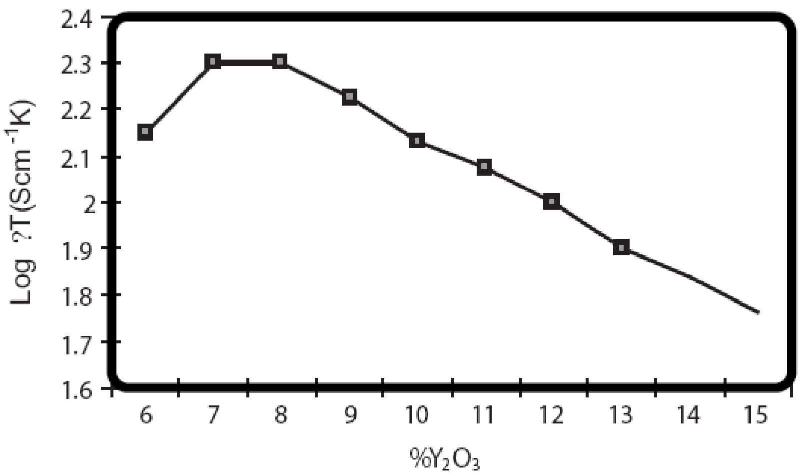
Extrinsic vs Intrinsic

Intrinsic vacancy



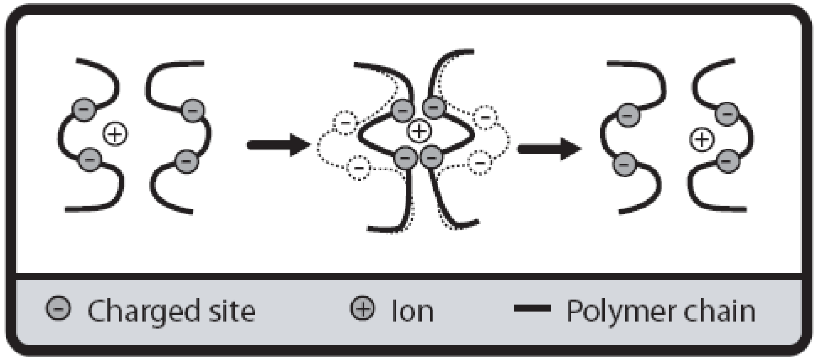
extrinsic vacancy



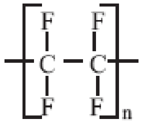


Ion Conduction in Polymers

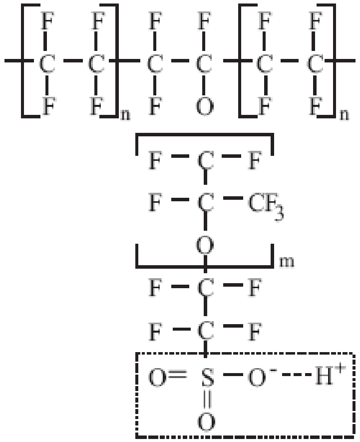
$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$



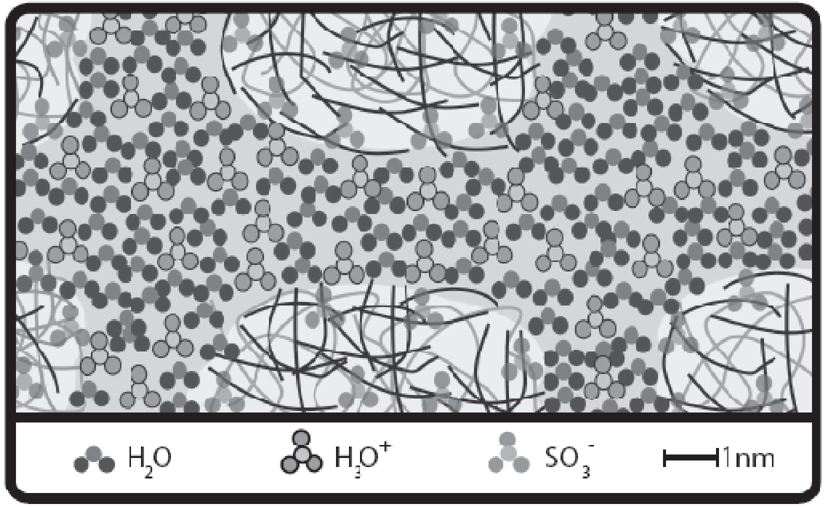
Polytetraflouroethylene (PTFE)



Nafion



Nafion

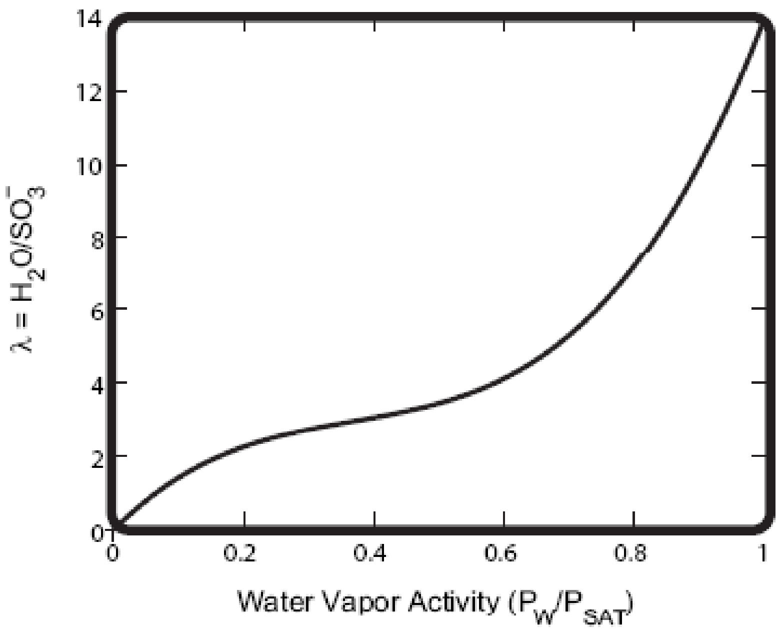


Nafion Characteristics 1

Water absorption

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

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



$$\lambda = 0.0043 + 17.81 a_W - 39.85 a_W^2 + 36.0 a_W^3 \quad \text{for} \quad 0 < a_W \le 1$$

$$\lambda = 14 + 1.4(a_W - 1) \quad \text{for} \quad 1 < a_W \le 3$$

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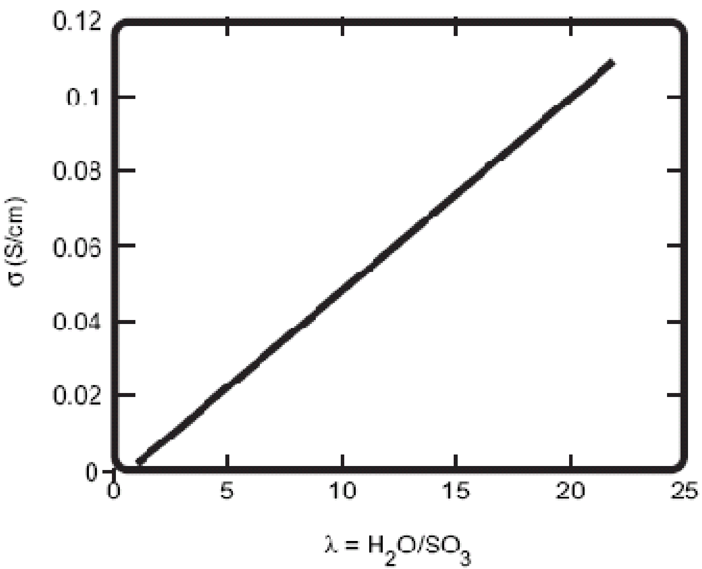
Nafion Characteristics 2

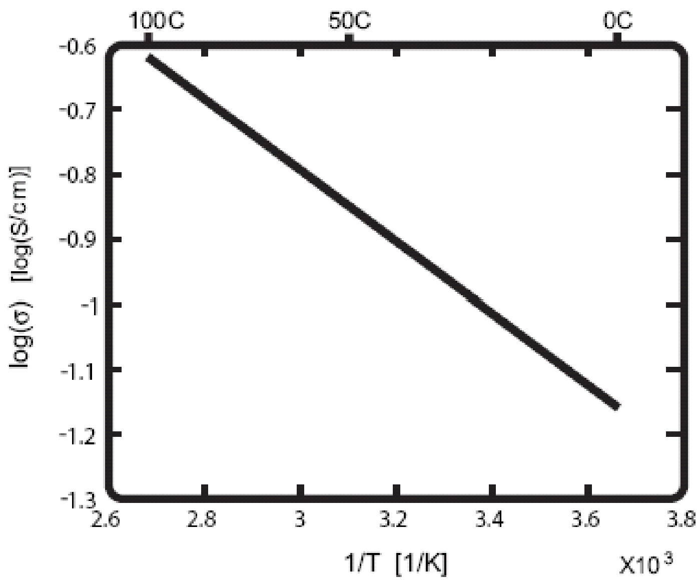
Conductivity
vs T & water contents

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

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

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





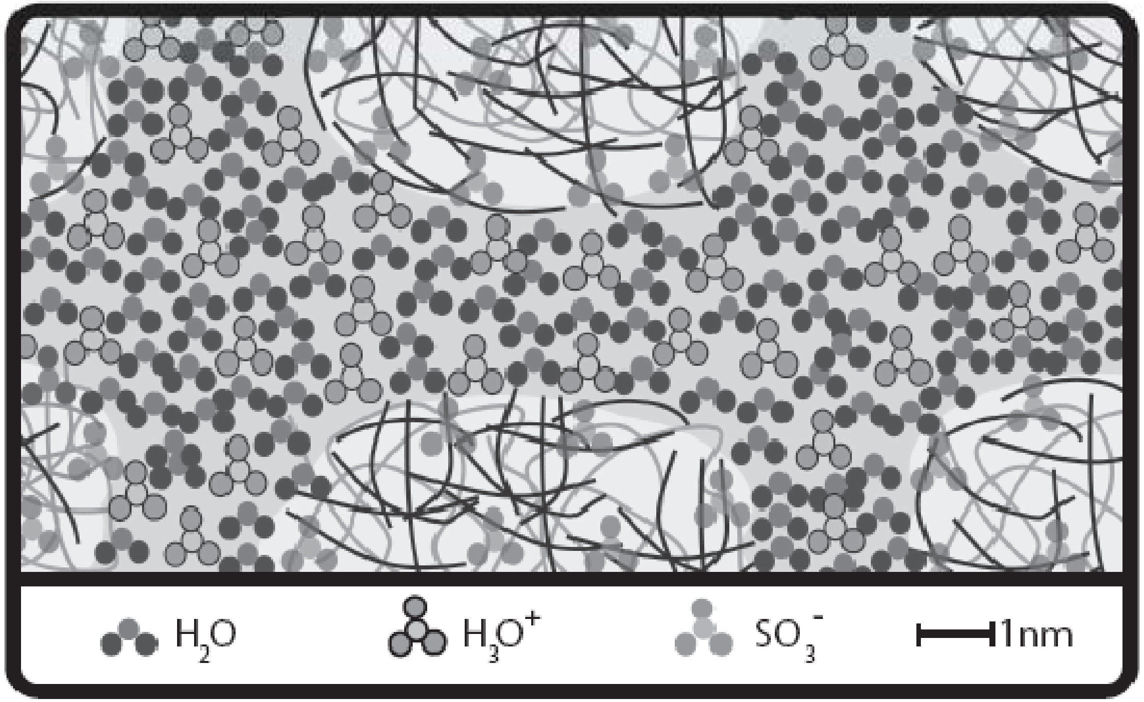
Nafion Characteristics 3

Electro-osmotic drag

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

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

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

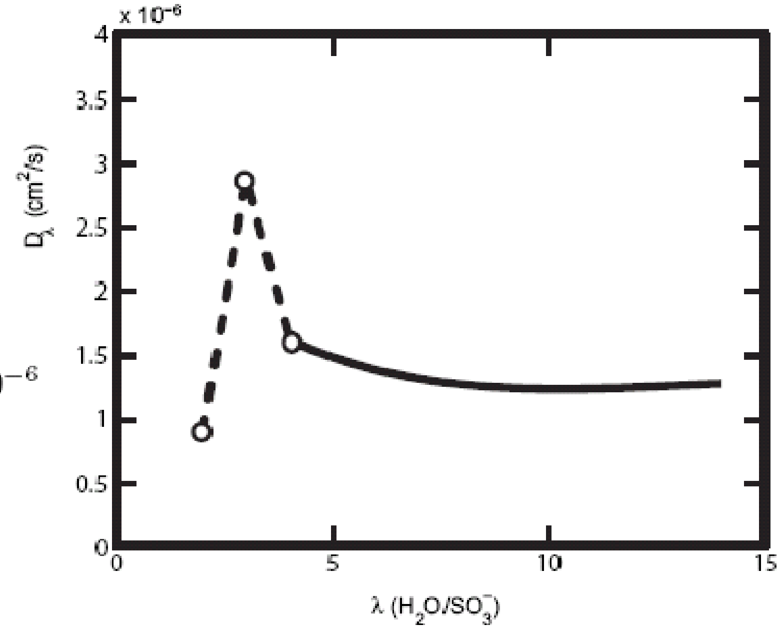


Nafion Characteristics 4

Back Diffusion

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

$$D_\lambda = \exp\left[2416\left(\frac{1}{303} - \frac{1}{T}\right)\right] \times \left(2.563 - 0.33\lambda + 0.0264\lambda^2 - 0.000671\lambda^3\right) \times 10^{-6} \quad in\ [cm^2/s] \quad for\ \lambda > 4$$



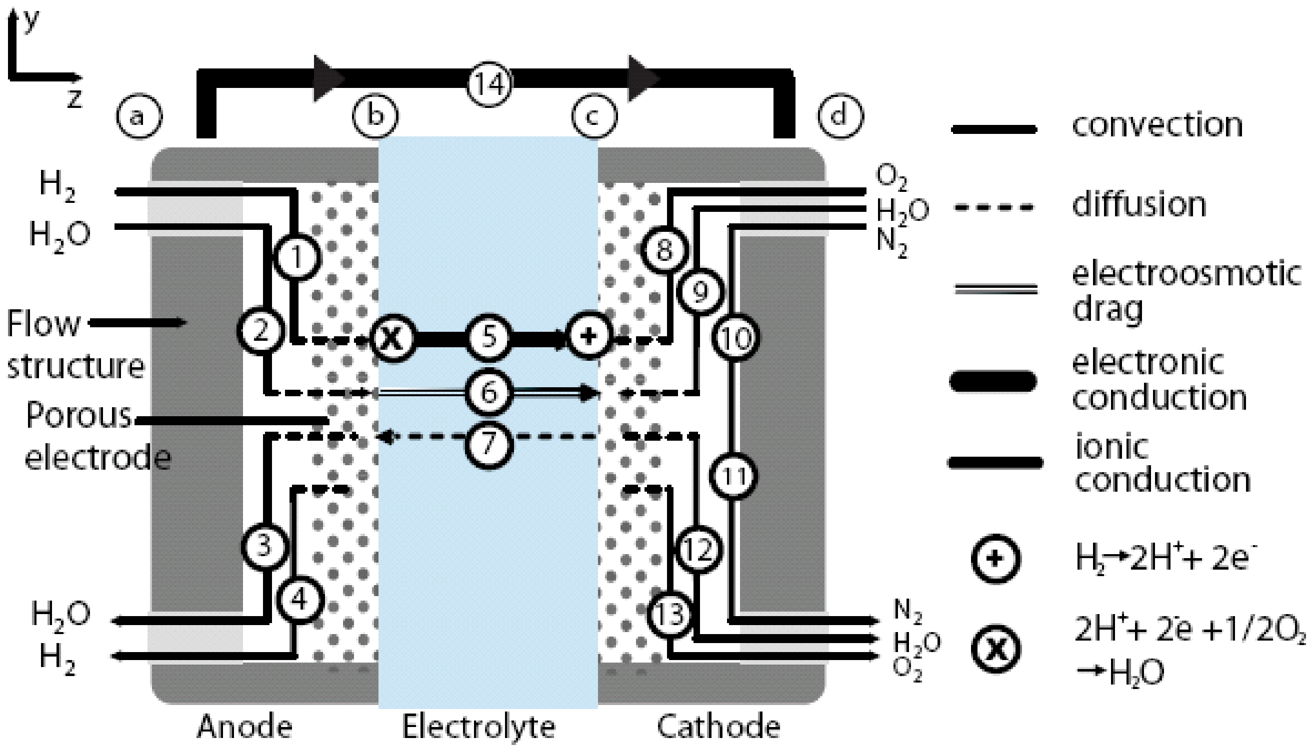
$$Equivalent\ weight = \frac{Atomic(Formula)\ weight}{Valance}$$

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

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

Nafion Resistance Example

Example 4.4 *Consider a hydrogen PEM fuel cell powering an external load at 0.7A/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

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

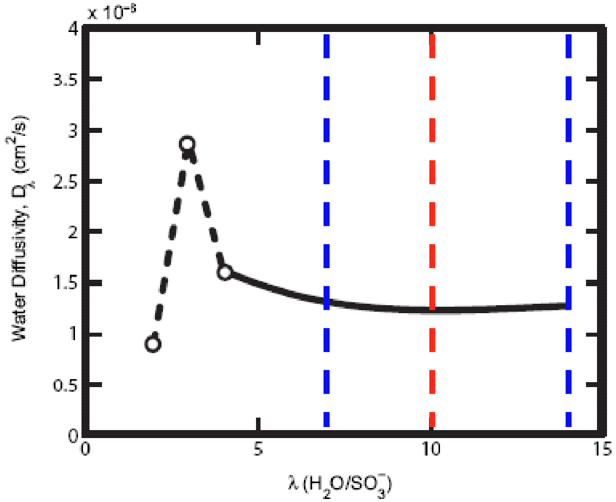
$$\frac{d\lambda}{dz} = \left[2n_{drag}^{SAT}\frac{\lambda}{22} - \alpha\right]\frac{jM_m}{2F\rho_{dry}D_\lambda} \qquad J_{H_2O} = \alpha N_{H_2} = \alpha\frac{j}{2F}$$

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

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



Nafion Resistance Example

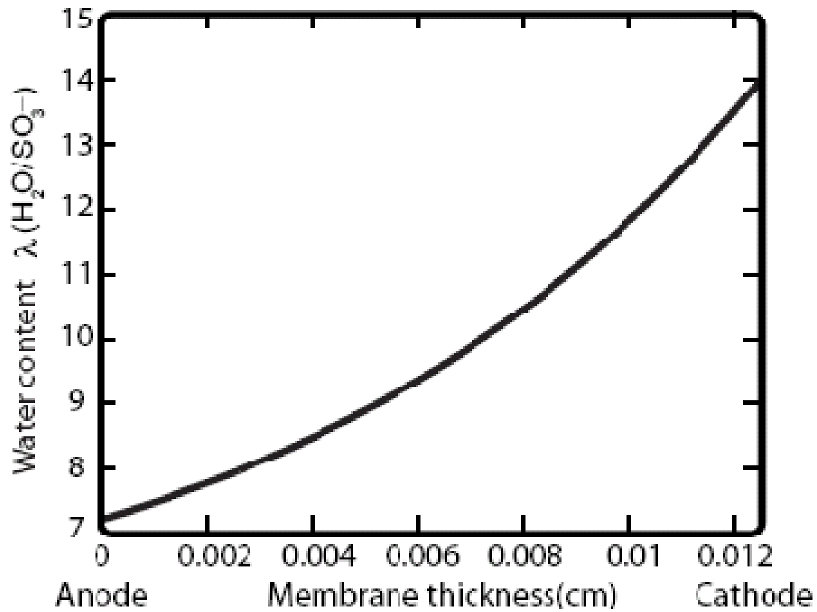
Water profile in Nafion

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

B.C.

$$\lambda(0) = 7.22 \ \ and\ \lambda(0.0125) = 14$$

$$\lambda(z) = 4.4\alpha + 2.30\exp(109.8z)$$
$$where\ \alpha = 1.12$$

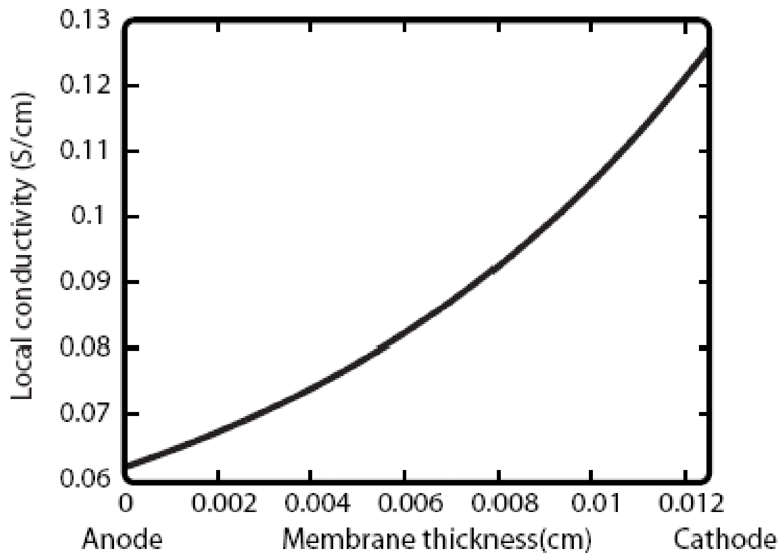


(a) Water content profile across the Nafion® membrane

Nafion Resistance Example

Conductivity profile

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



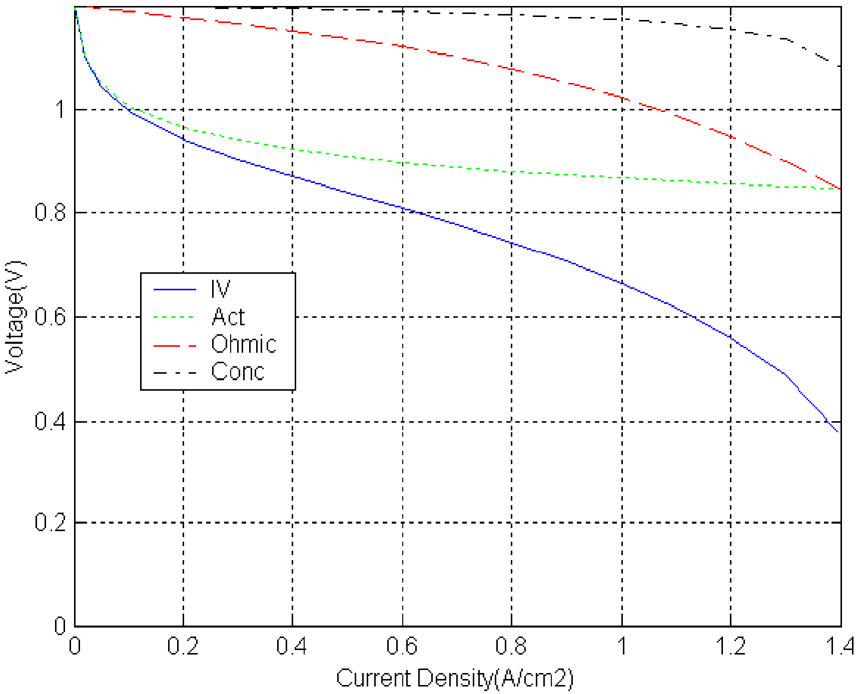
(b) Local conductivity profile across the Nafion® membrane

Ohmic resistance

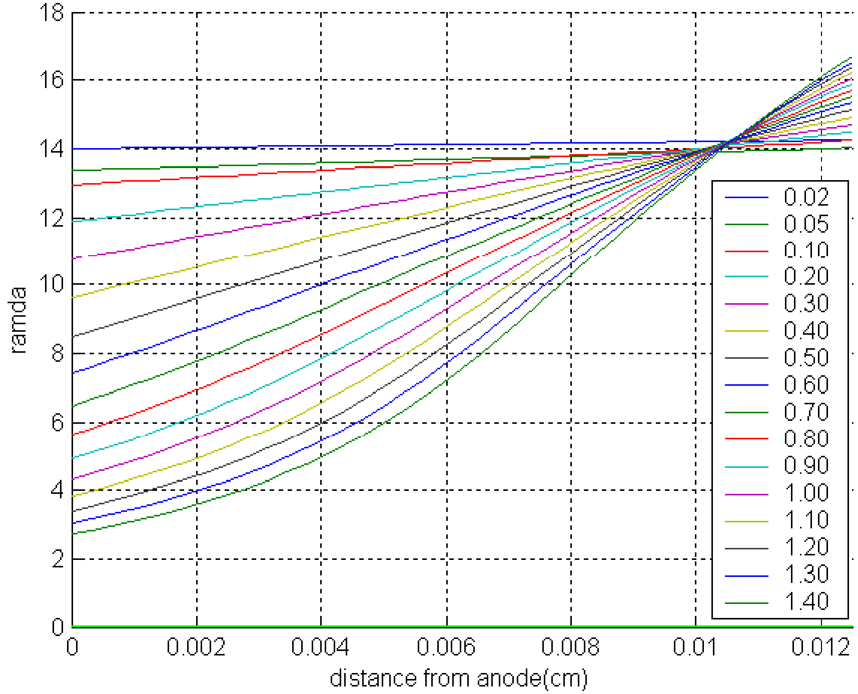
$$R_m = \int_0^{t_m} \frac{dz}{\sigma(\lambda(z))} = \int_0^{0.0125} \frac{dz}{0.0404 + 0.0216\exp(109.8z)} = 0.150\Omega cm^2$$

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

Ohmic Resistance



Overpotentials in PEMFC's



Water profile through membrane

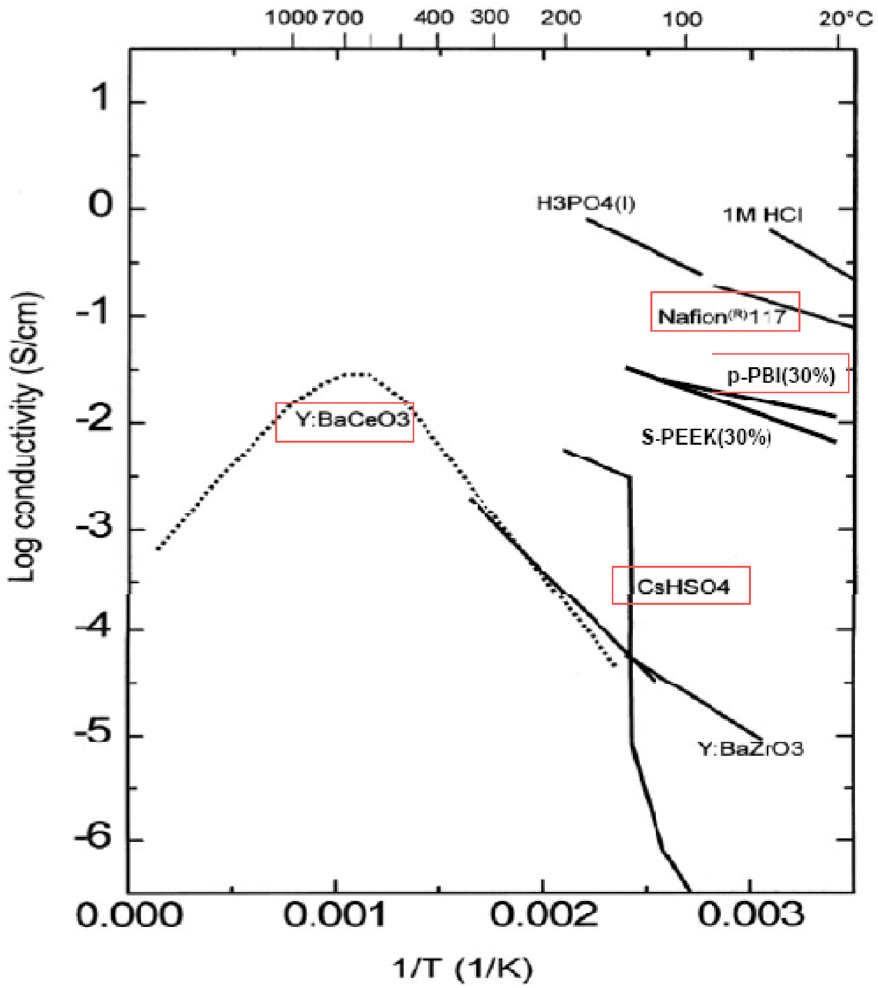
Reference:

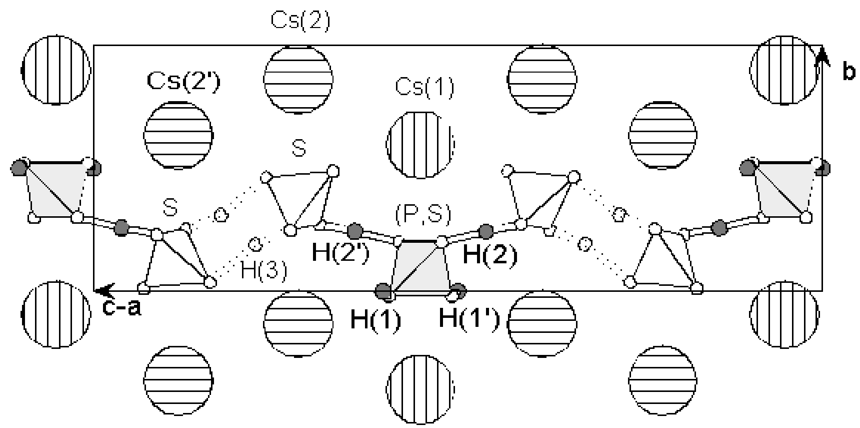
Pa=3atm, Pc = 3atm, T = 80C, v_{H2}=1.5A, v_{O2}=1.5A

tm = 0.0125cm, tc = 0.0365cm, ta = 0.0365cm

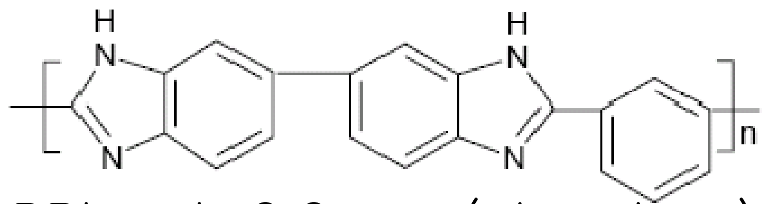
ndrag = 2.5, poro = 0.4, Relative Humidity = 100%

Electrolytes



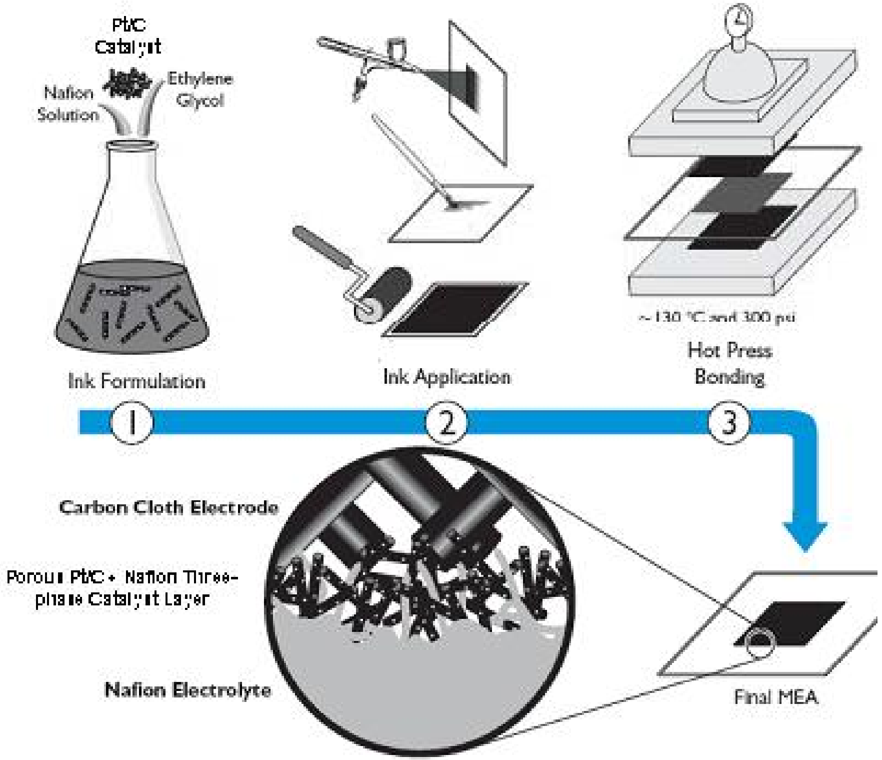


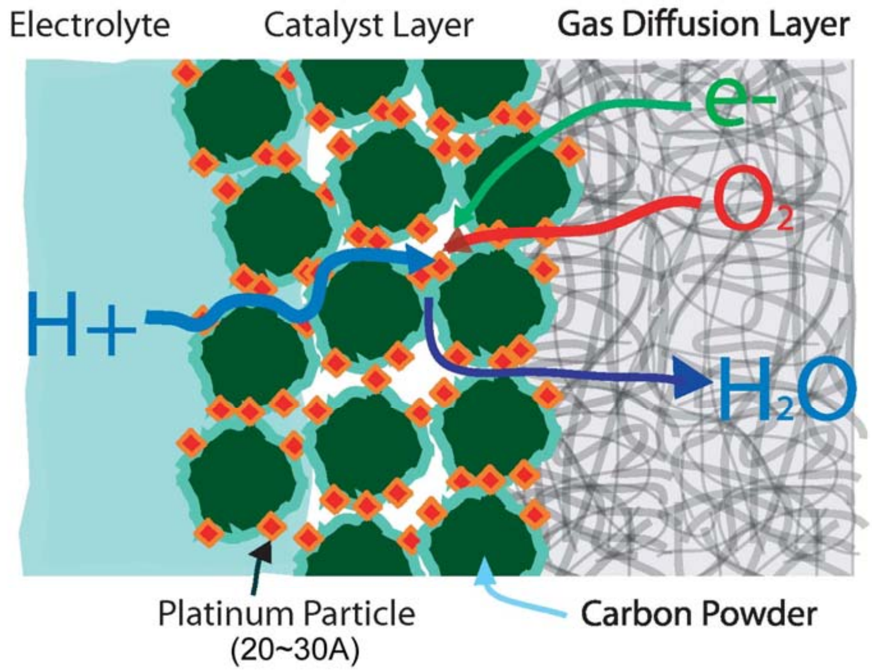
$CsHSO_4$



PBI, poly 2,2′-m-(phenylene)-5,5′-bibenz-imidazole.

More on TBP(PEMFC)





More on TBP(SOFC)