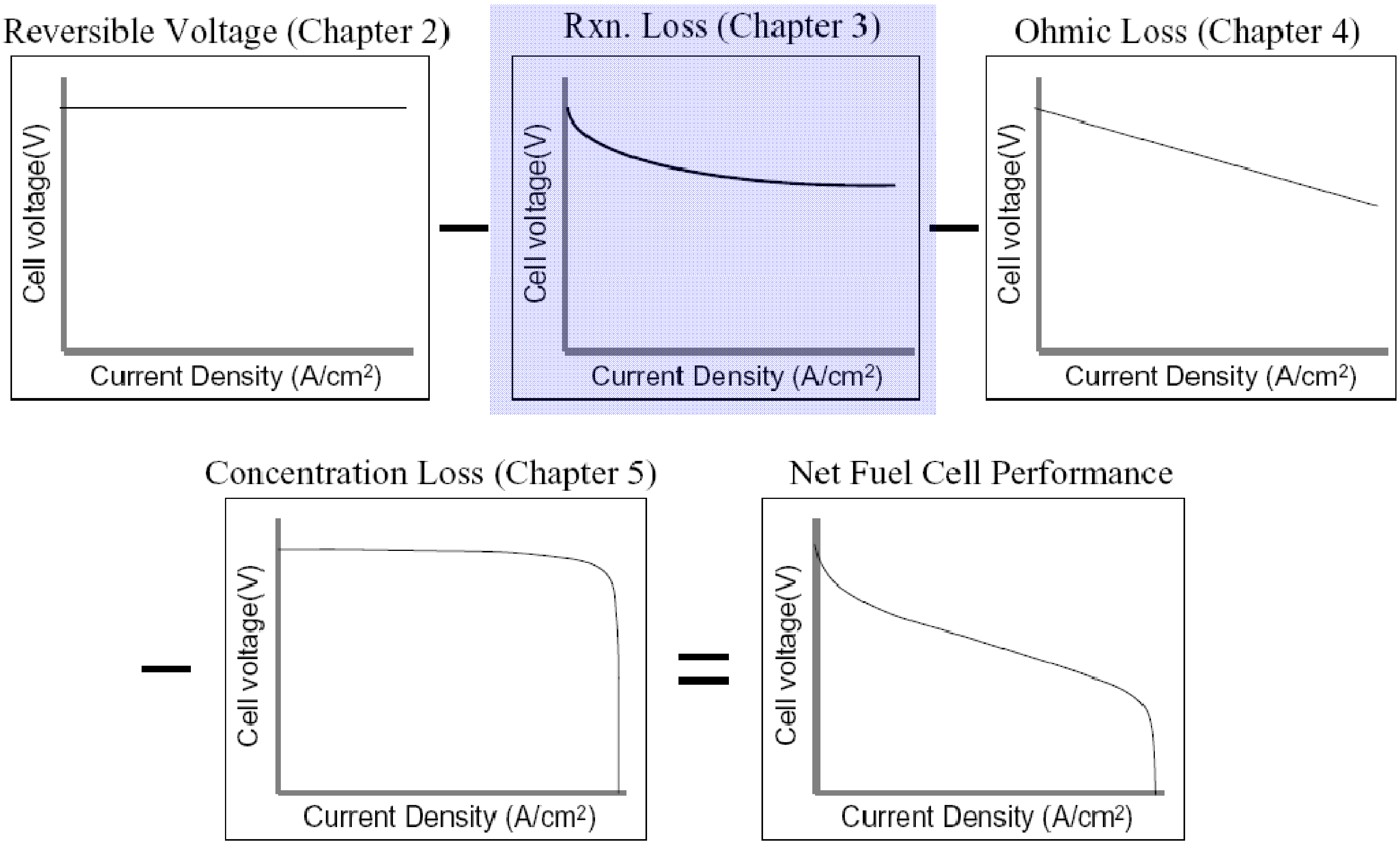
Losses in Fuel Cells



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

Fuel Cell Reaction Kinetics

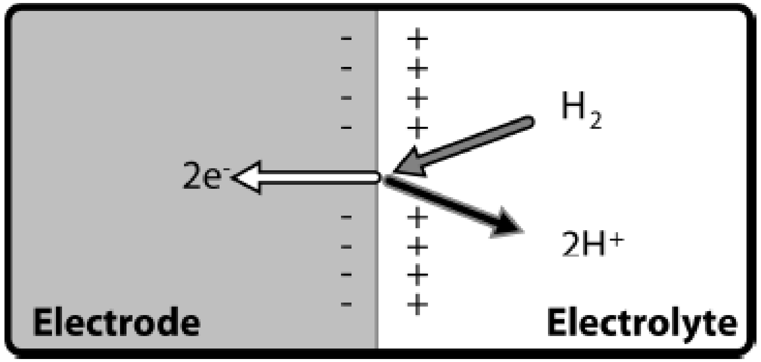
Electrode Kinetic

Current = Charge/Time

$$i = \frac{dQ}{dt} = \frac{nFdN}{dt}$$

$$\Leftrightarrow \int_0^t i dt = Q = nFN$$

$$j = \frac{i}{A} [A/cm^2]$$



Heterogeneous process

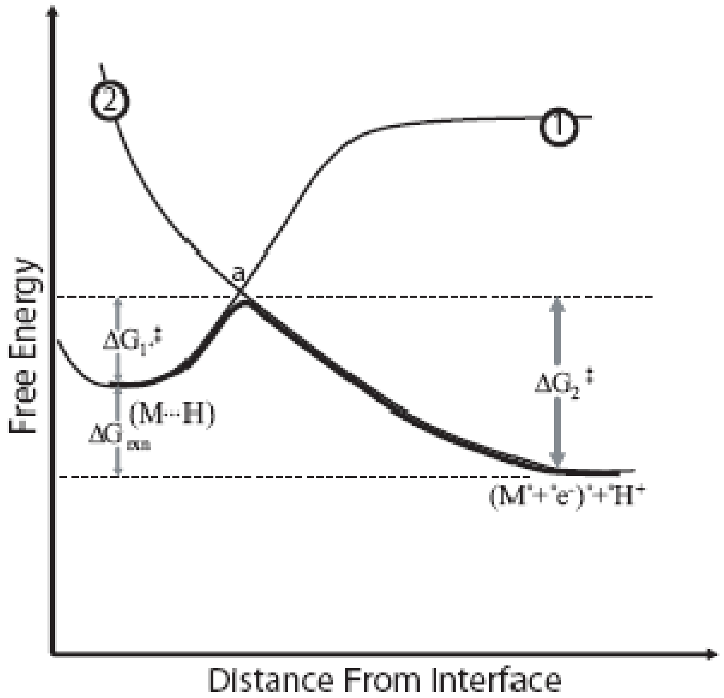
$H_2 \Leftrightarrow 2H^+ + 2e^-$

$$H_2 + M \rightarrow M \cdots H_2$$

$$M \cdots H_2 + M \rightarrow 2(M \cdots H)$$

$$M \cdots H \rightarrow M + e^- + H^+$$

Electrode Kinetic



Probability of activation $P_{act} = Ke^{\left(\frac{-\Delta G_1}{RT}\right)}$

Forward reaction rate $v_1 = Kc_R^* f_1 P_{act} = Kc_R^* f_1 e^{\left(\frac{-\Delta G_1}{RT}\right)}$

Backward reaction rate $v_2 = Kc_P^* f_2 P_{act} = Kc_P^* f_2 e^{\left(\frac{-\Delta G_2}{RT}\right)}$

Rate of reaction

$$v = v_1 - v_2 = Kc_R^* f_1 e^{\left(\frac{-\Delta G_1}{RT}\right)} - Kc_P^* f_2 e^{\left(\frac{-\Delta G_2}{RT}\right)}$$

$$= Kc_R^* f_1 e^{\left(\frac{-\Delta G_1}{RT}\right)} - Kc_P^* f_2 e^{\left(\frac{-\Delta G_1 - \Delta G_{rxn}}{RT}\right)}$$

Equilibrium Potential: Galvani Potential

Conversion to current density

$$j = nFv = nFc_R^* f_1 e^{\left(\frac{-\Delta G_1}{RT}\right)} - nFc_P^* f_2 e^{\left(\frac{-\Delta G_1 - \Delta G_{rxn}}{RT}\right)}$$
$$= j_1 - j_2$$

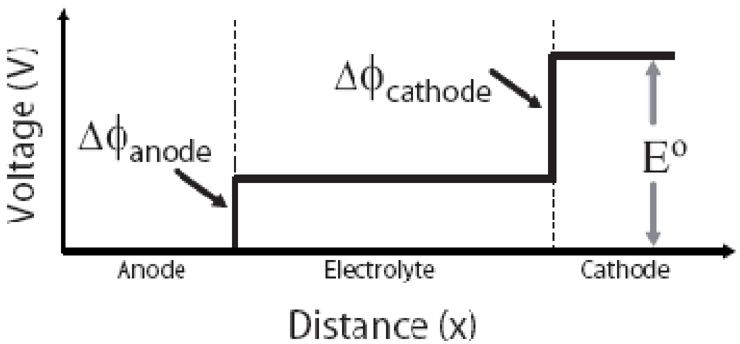
At equilibrium

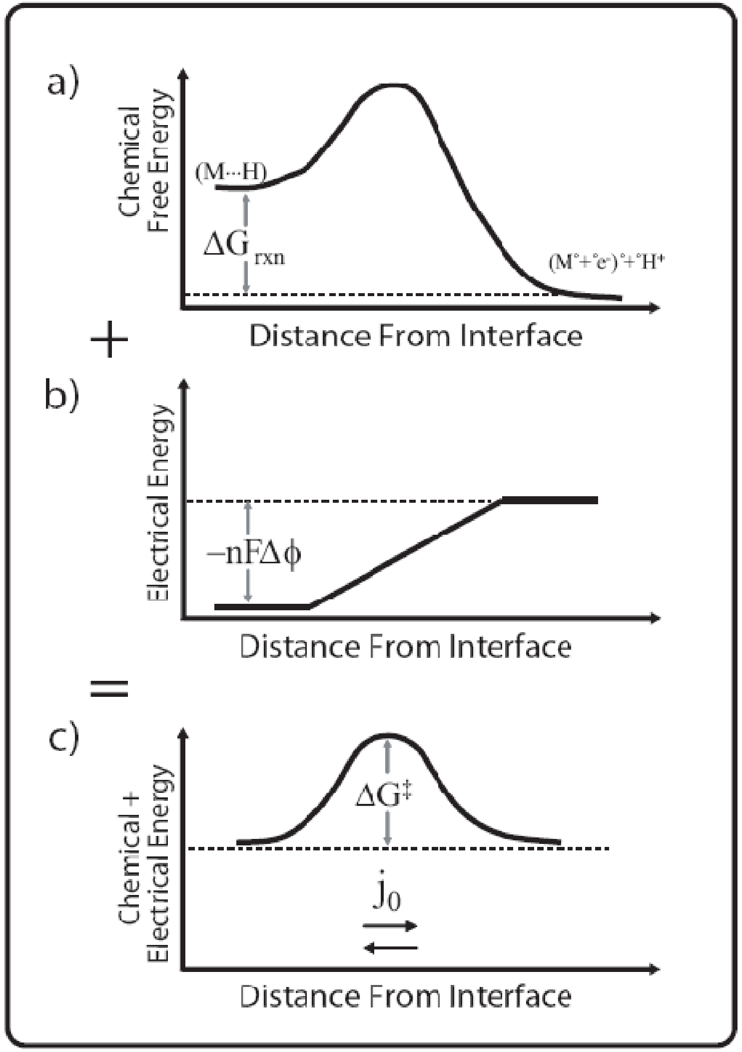
$$j = j_1 - j_2 = 0$$

$j_1 = j_2 = j_0$:Exchange Current Density

$$j_1 = nFc_R^* f_1 e^{\left(\frac{-\Delta G_1}{RT} + \alpha nF\Delta\phi\right)} = nFc_R^* f e^{\left(\frac{-\Delta G^{++}}{RT}\right)}$$

$$j_2 = nFc_P^* f_2 e^{\left(\frac{-\Delta G_1 - \Delta G_{rxn}}{RT} + nF\Delta\phi\right)} = nFc_P^* f e^{\left(\frac{-\Delta G^{++}}{RT}\right)}$$





Bultler-Volmer Equation: Non-Equilibrium

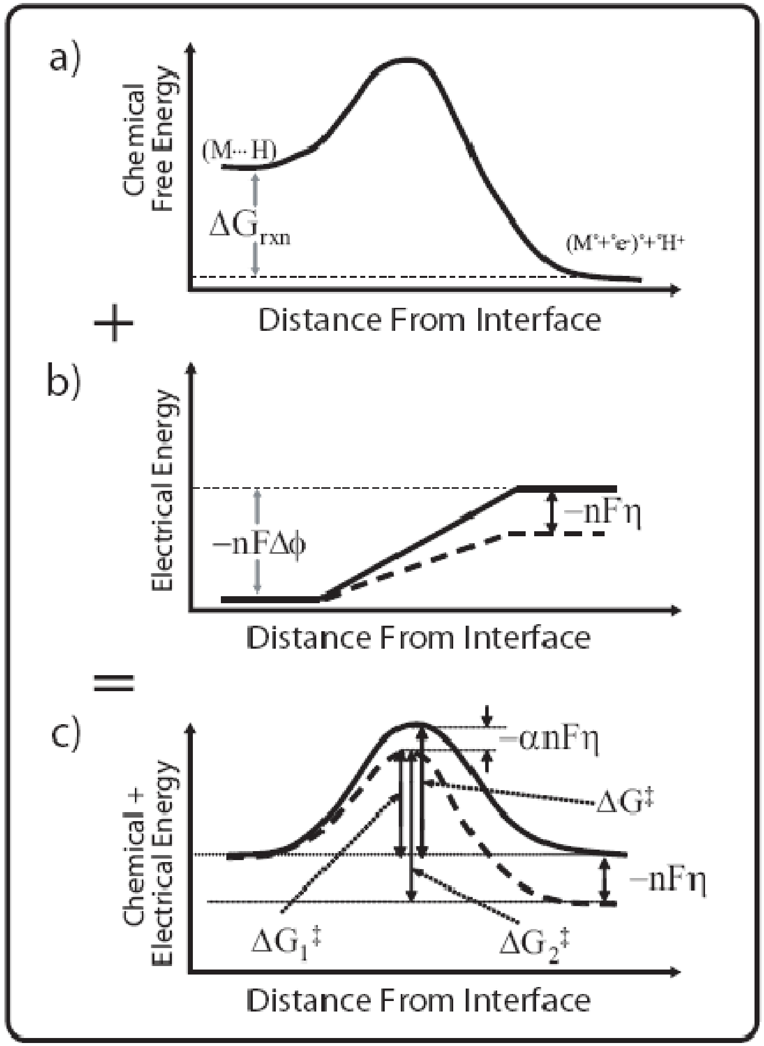
$$j_1 = j_0 e^{\left(\frac{\alpha n F \eta}{RT}\right)}$$

$$j_2 = j_0 e^{-\left(\frac{(1-\alpha) n F \eta}{RT}\right)}$$

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

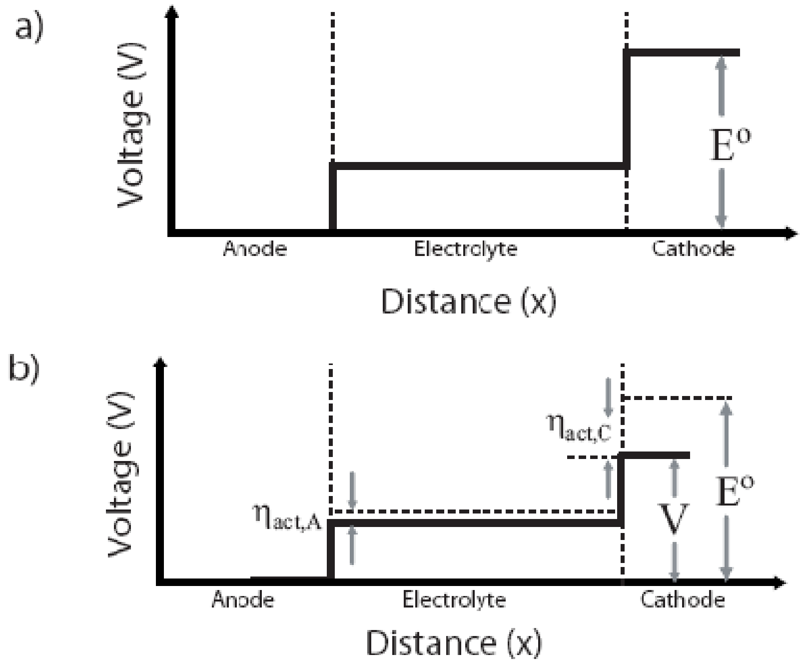
$$j = j_0 \left(\frac{C_R}{C_R^0} e^{\left(\frac{\alpha n F \eta}{RT}\right)} - \frac{C_P}{C_P^0} e^{-\left(\frac{(1-\alpha) n F \eta}{RT}\right)} \right)$$

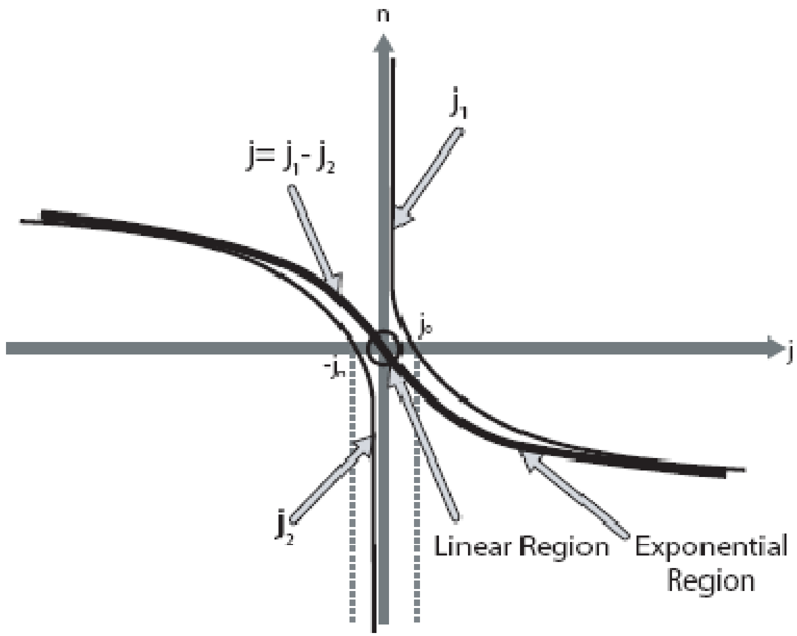
Bulter-Volmer Equation



Bultler-Volmer Equation: Non-Equilibrium

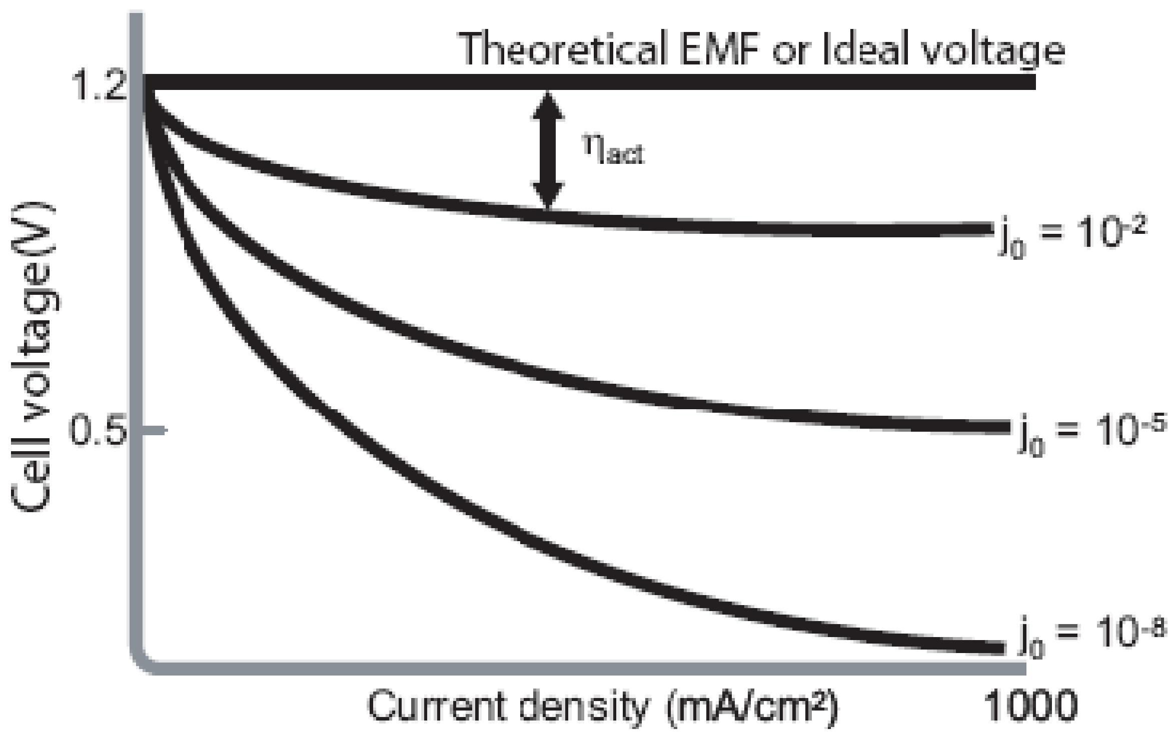
$$j = j_0\left(\frac{C_R}{C_R^0}e^{\left(\frac{\alpha nF\eta}{RT}\right)} - \frac{C_P}{C_P^0}e^{-\left(\frac{(1-\alpha)nF\eta}{RT}\right)}\right)$$





Exchange Current Density Effect

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



Improving Kinetic

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

1. C_R: Increase reactant concentration
2. Increase j_0

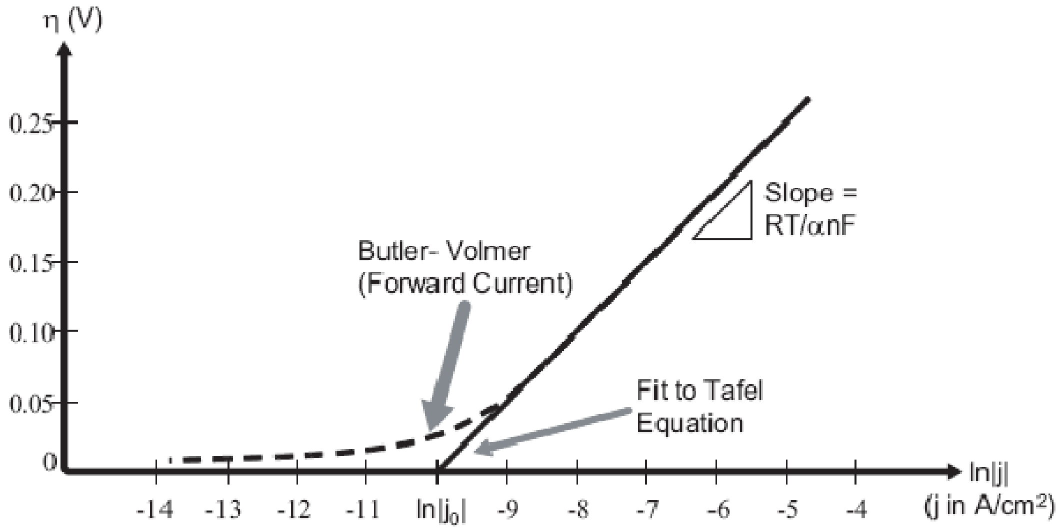
$$j_0 = nFC^* fe^{\left(\frac{-\Delta G^{++}}{RT}\right)}$$

- Decrease the activation energy (G^{++})
- Increase T
- Increase reaction site (equivalent to C^*)

Simplified B-V Equation

1. When η_{act} is very small

$$j = j_0 \frac{nF\eta_{act}}{RT}$$



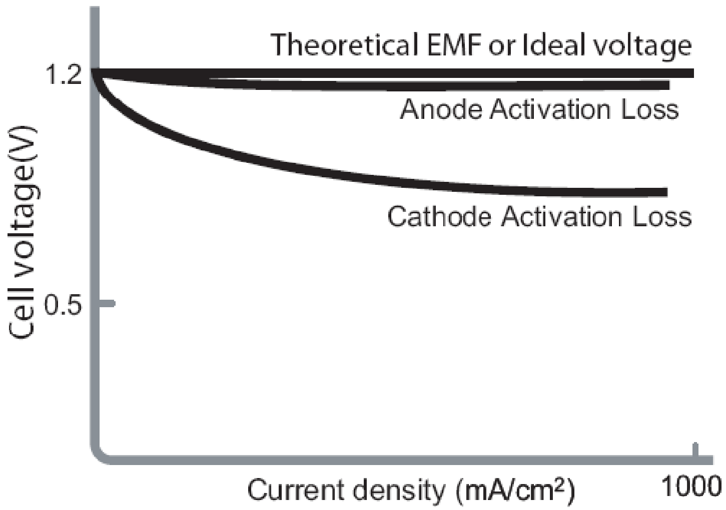
1. When η_{act} is large

$$j = j_0 e^{\frac{\alpha nF\eta_{act}}{RT}} \quad or \quad \eta_{act} = -\frac{RT}{\alpha nF}\ln j_0 + \frac{RT}{\alpha nF}\ln j$$

$$= a + b\log j$$

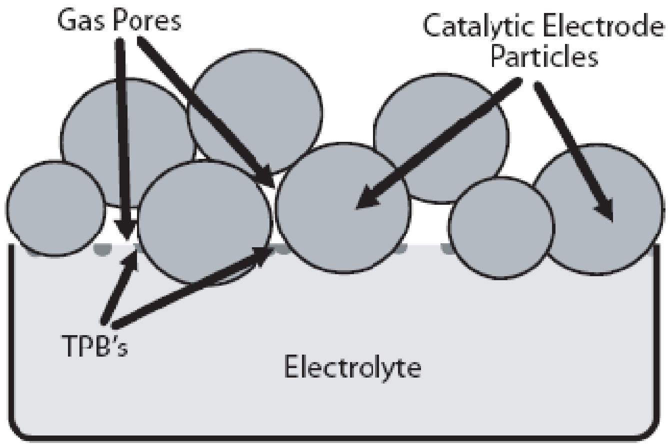
Tafel Equation

B-V Equation: Practical Consideration



Hydrogen

Surface	Electrolyte	j_0' (A/cm^2)
Pt	Acid	10^{-3}
Pt	Alkaline	10^{-4}
Pd	Acid	10^{-4}
Rh	Alkaline	10^{-4}
Ir	Acid	10^{-4}
Ni	Alkaline	10^{-4}
Ni	Acid	10^{-5}

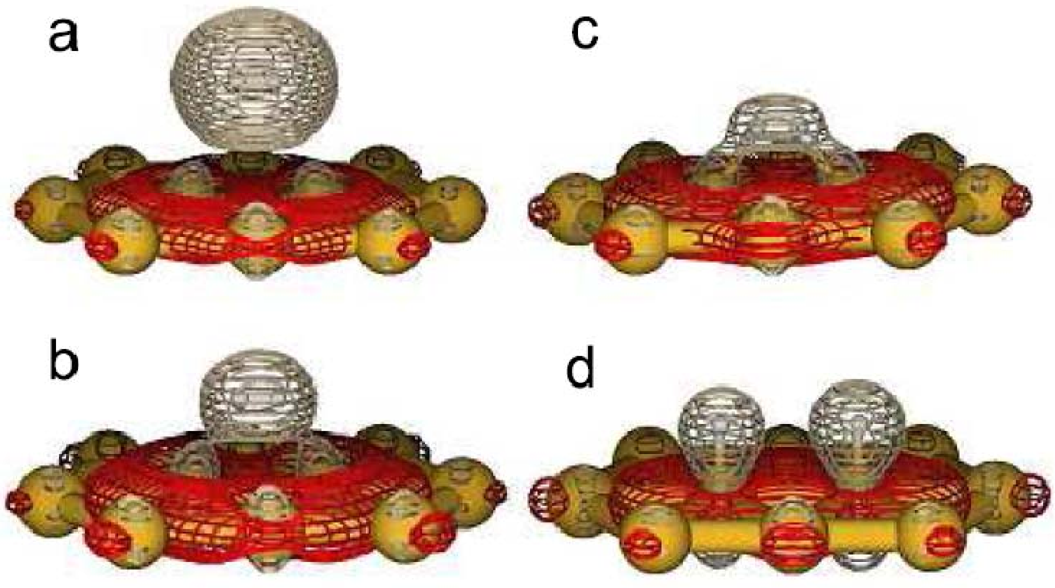


Triple Phase Boundary

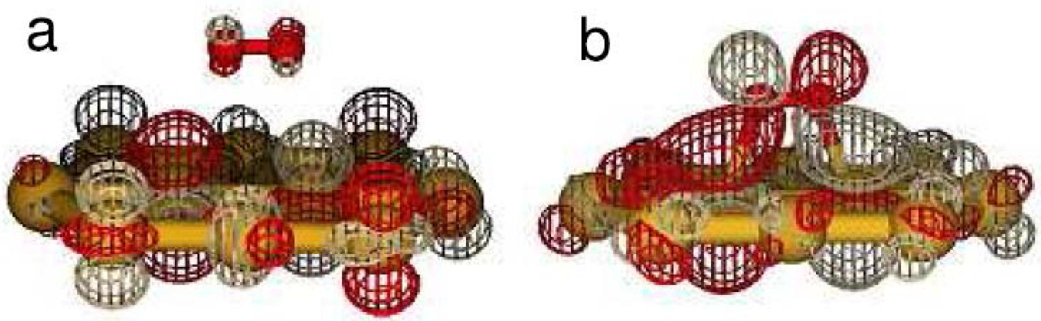
Oxygen

Surface	Electrolyte	j_0' (A/cm^2)
	Metal Surfaces in Acid Electrolyte	
Pt	Acid	10^{-9}
Pd	Acid	10^{-10}
Ir	Acid	10^{-11}
Rh	Acid	10^{-11}
Au	Acid	10^{-11}
	Pt-Alloys in PEM Fuel Cell	
Pt/C	Nafion	3×10^{-9}
PtMn/C	Nafion	6×10^{-9}
PtCr/C	Nafion	9×10^{-9}
PtFe/C	Nafion	7×10^{-9}
PtCo/C	Nafion	6×10^{-9}
PtNi/C	Nafion	5×10^{-9}

Understanding Catalyst via DFT

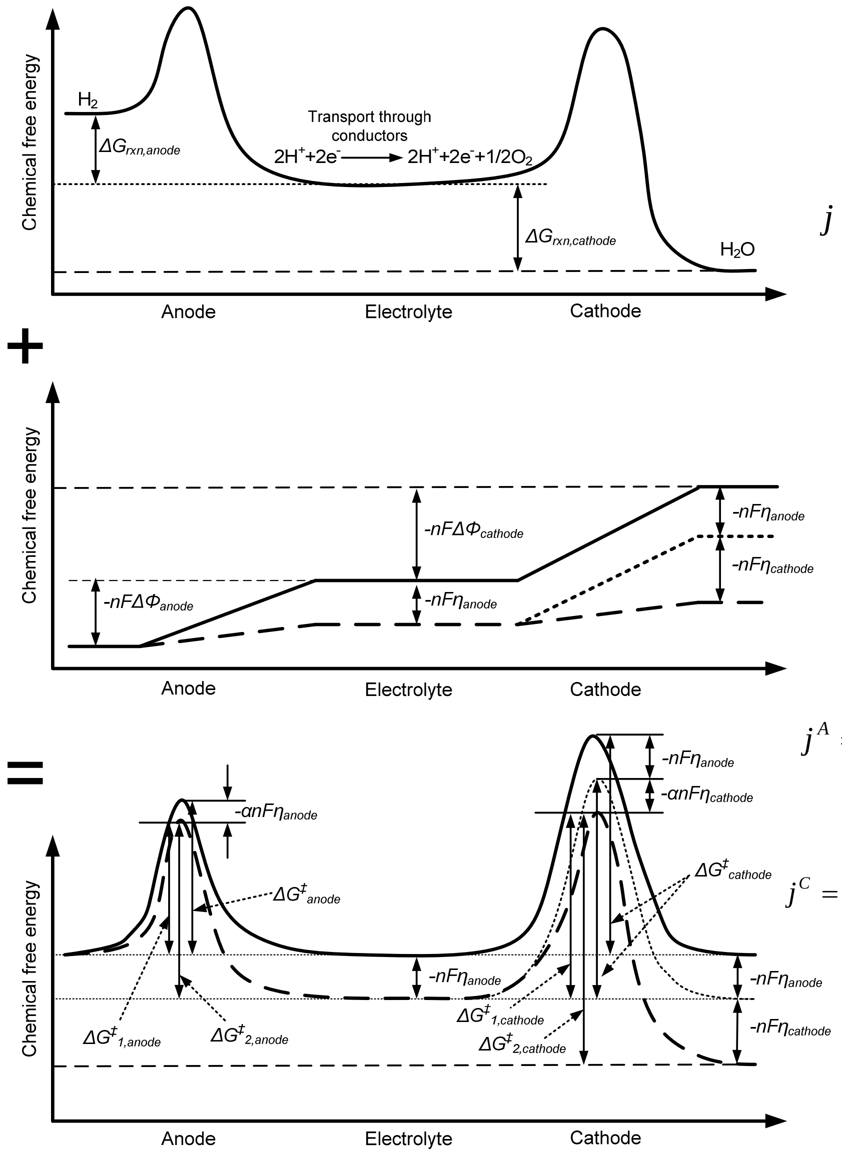


Hydrogen dissociation



Oxygen dissociation

Anode and Cathode



$$j = j_0\left(\prod\left(\frac{C^*_{R,i}}{C^{0*}_{R,i}}\right)^{\nu_i}\exp\left(\alpha nF\eta/(RT)\right)-\prod\left(\frac{C^*_{P,i}}{C^{0*}_{P,i}}\right)^{\nu_i}\exp\left(-(1-\alpha)nF\eta/(RT)\right)\right)$$

$$H_2 \leftrightarrow 2H^+ + 2e^-$$

$$2H^+ + 2e^- + \frac{1}{2}O_2 \leftrightarrow H_2O$$

$$j^A = j_0^A\left(\frac{C^{*,A}_{H_2}}{C^{0*,A}_{H_2}}\exp\left(2\alpha^A F\eta^A/(RT)\right)-\left(\frac{C^{*,A}_{H^+}}{C^{0*,A}_{H^+}}\right)^2\left(\frac{C^{*,A}_{e^-}}{C^{0*,A}_{e^-}}\right)^2\exp\left(-2(1-\alpha^A)F\eta^A/(RT)\right)\right)$$

$$j^C = j_0^C\left(\left(\frac{C^{*,C}_{H^+}}{C^{0*,C}_{H^+}}\right)^2\left(\frac{C^{*,C}_{e^-}}{C^{0*,C}_{e^-}}\right)^2\left(\frac{C^{*,C}_{O_2}}{C^{0*,C}_{O_2}}\right)^{\frac{1}{2}}\exp\left(2\alpha^C F\eta^C/(RT)\right)-\frac{C^{*,C}_{H_2O}}{C^{0*,C}_{H_2O}}\exp\left(-2(1-\alpha^C)F\eta^C/(RT)\right)\right)$$

$$j^A = j^C = j$$

Anode and Cathode at Equilibrium

$$0 = j_0^A\left(\frac{C_{H_2}^{*,A}}{C_{H_2}^{0*,A}}\exp\left(2\alpha F\eta^A/(RT)\right)-\left(\frac{C_{H^+}^{*,A}}{C_{H^+}^{0*,A}}\right)^2\left(\frac{C_{e^-}^{*,A}}{C_{e^-}^{0*,A}}\right)^2\exp\left(-2(1-\alpha^A)F\eta^A/(RT)\right)\right)$$

$$\frac{C_{H_2}^{*,A}}{C_{H_2}^{0*,A}}\exp\left(2\alpha F\eta^A/(RT)\right)=\left(\frac{C_{H^+}^{*,A}}{C_{H^+}^{0*,A}}\right)^2\left(\frac{C_{e^-}^{*,A}}{C_{e^-}^{0*,A}}\right)^2\exp\left(-2(1-\alpha^A)F\eta^A/(RT)\right)$$

$$\log\left(\frac{C_{H_2}^{*,A}}{C_{H_2}^{0*,A}}\right)+\frac{2\alpha^A F\eta^A}{RT}=\log\left(\frac{C_{H^+}^{*,A}}{C_{H^+}^{0*,A}}\right)^2+\log\left(\frac{C_{e^-}^{*,A}}{C_{e^-}^{0*,A}}\right)^2-\frac{2(1-\alpha^A)F\eta^A}{RT}$$

$$\frac{2F\eta^A}{RT}=-\log\left(\frac{C_{H_2}^{*,A}}{C_{H_2}^{0*,A}}\right)+\log\left(\frac{C_{H^+}^{*,A}}{C_{H^+}^{0*,A}}\right)^2+\log\left(\frac{C_{e^-}^{*,A}}{C_{e^-}^{0*,A}}\right)^2$$

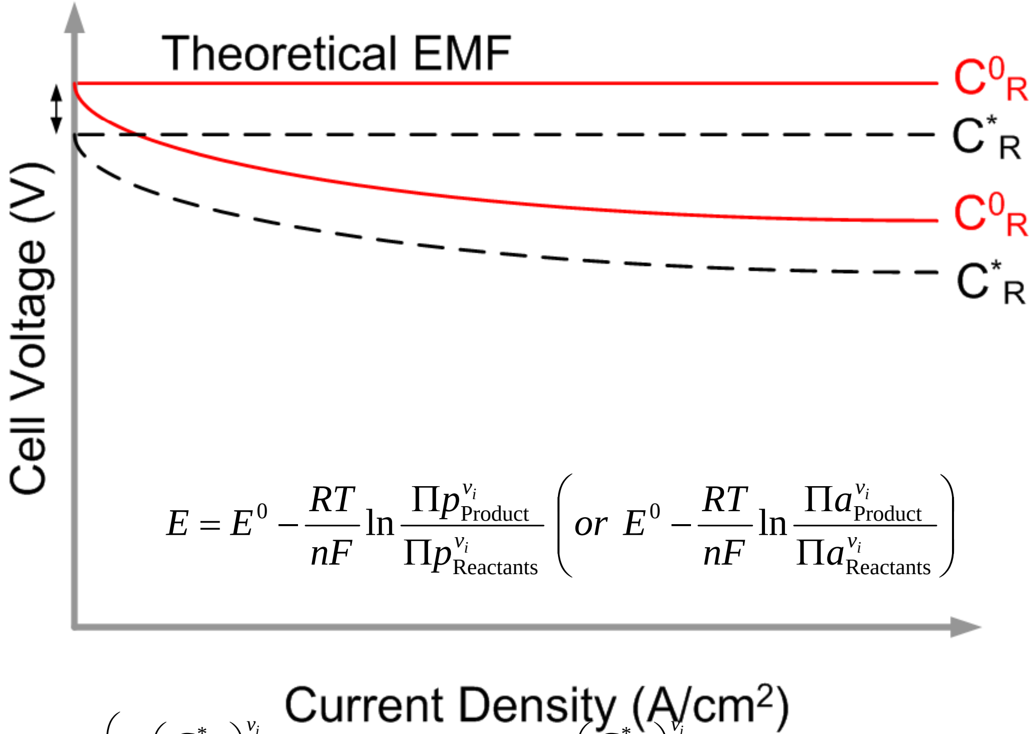
$$\eta^A=\frac{RT}{2F}\left(-\log\left(a_{H_2}^{*,A}\right)+\log\left(a_{H^+}^{*,A}\right)^2+\log\left(a_{e^-}^{*,A}\right)^2\right)$$

$$\eta^C=\frac{RT}{2F}\left(-\log\left(a_{H^+}^{*,C}\right)^2-\log\left(a_{e^-}^{*,C}\right)^2-\log\left(a_{O_2}^{*,C}\right)^{\frac{1}{2}}+\log\left(a_{H_2O}^{*,C}\right)\right)$$

$$\eta^A+\eta^C=\frac{RT}{2F}\left(\log\frac{a_{H_2O}^{*,C}}{a_{H_2}^{*,A}\left(a_{O_2}^{*,A}\right)^{\frac{1}{2}}}-\log\left(\frac{a_{H^+}^{*,C}}{a_{H^+}^{*,A}}\right)^2-\log\left(\frac{a_{e^-}^{*,C}}{a_{e^-}^{*,A}}\right)^2\right)$$

$$\eta^A+\eta^C=E^0-E$$

$$\therefore E=E^0-\frac{RT}{2F}\left(\log\frac{a_{H_2O}^{*,C}}{a_{H_2}^{*,A}\left(a_{O_2}^{*,A}\right)^{\frac{1}{2}}}-\log\left(\frac{a_{H^+}^{*,C}}{a_{H^+}^{*,A}}\right)^2-\log\left(\frac{a_{e^-}^{*,C}}{a_{e^-}^{*,A}}\right)^2\right)$$



$$E=E^0-\frac{RT}{nF}\ln\frac{\Pi p_{\text{Product}}^{v_i}}{\Pi p_{\text{Reactants}}^{v_i}}\left(or\ E^0-\frac{RT}{nF}\ln\frac{\Pi a_{\text{Product}}^{v_i}}{\Pi a_{\text{Reactants}}^{v_i}}\right)$$

$$j=j_0\left(\prod\left(\frac{C_{R,i}^{*}}{C_{R,i}^{0*}}\right)^{v_i}\exp\left(\alpha nF\eta/(RT)\right)-\prod\left(\frac{C_{P,i}^{*}}{C_{P,i}^{0*}}\right)^{v_i}\exp\left(-(1-\alpha)nF\eta/(RT)\right)\right)$$