Relationship of Limiting Current to Concentration

UCI MAE 212 - Prof. Madou

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Fick's Law of Diffusion

Describes material transport due to diffusion. Relates flux to concentration gradient.

3D: $J = -D(\nabla C)$

1D: $J = -D(\partial C/\partial x)$

J: diffusion flux [m^2/s]

C: concentration [mol/m^3]

D: diffusion coefficient [m^2/s]

Faraday's Law of Electrolysis

Rearranging Faraday's Law to get the current in an electrolytic cell.

$$I = nFAJ$$

I: current [A]

n: moles of electrons / mole of reactant

F: Faraday's constant [C/mol]

A: electrode surface area [m^2]

Plugging Fick's Law into Faraday's Law...

$$I = nFA\left(-D\frac{C_{x=\delta} - C_{x=0}}{\delta - 0}\right)$$

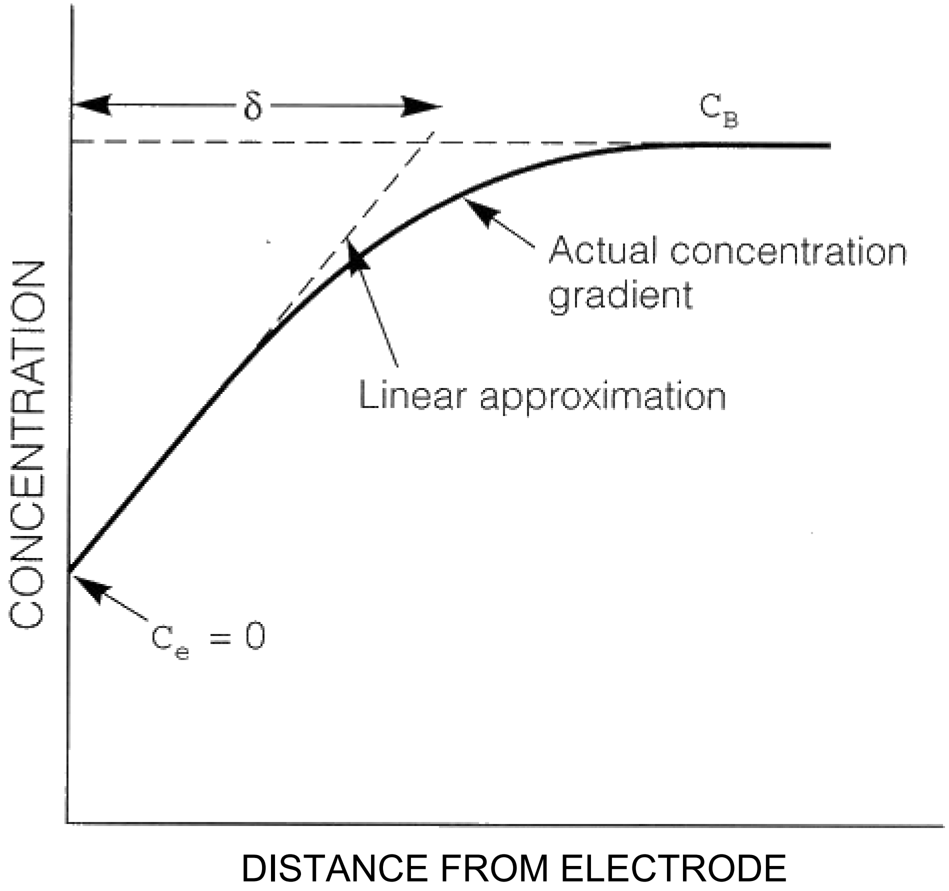
$$= -nFAD\left(\frac{C_b - C_{x=0}}{\delta}\right)$$

For small applied voltages:

$I(x=0) \approx 0$ b/c C_b-C_e is very small

For large applied voltages:

$I(x>\delta) = I_L$ b/c C_b-C_e is maximum



$$C_{x=0} = 0$$

$$I_l = nFAD\left(\frac{C_b}{\delta}\right)$$

$$j_l = \frac{I_l}{A} = nFD\left(\frac{C_b}{\delta}\right)$$

At the limiting current, the concentration near the electrode drops to zero, so the current depends only on the bulk concentration.

The limiting current density is proportional to the bulk concentration.

Concentration Polarization:

$$\eta_c = \frac{RT}{nF}\ln\left(\frac{C_e}{C_b}\right) \Rightarrow C_e = C_b e^{\frac{nF\eta_c}{RT}}$$

Plugging this into Faraday's Law

$$j_{total} = j_{\lim iting} - j_{polarization}$$

$$j_t = nFAD\left(\frac{C_b}{\delta} - \frac{C_e}{\delta}\right)$$

$$j_t = nFAD\left(\frac{C_b}{\delta} - \frac{C_b}{\delta}e^{\frac{nF\eta_c}{RT}}\right)$$

$$j_t = j_l\left(1 - e^{\frac{nF\eta_c}{RT}}\right)$$