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: \( J = -D(\frac{\partial C}{\partial x}) \)

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:

\[ I(x=0) \approx 0 \quad b/c \ C_b - C_e \text{ is very small} \]

For large applied voltages:

\[ I(x>\delta) = I_L \quad b/c \ C_b - C_e \text{ is maximum} \]
At the limiting current, the concentration near the electrode drops to zero, so the current depends only on the bulk concentration.

\[ C_{x=0} = 0 \]

\[ I_l = nF AD\left(\frac{C_b}{\delta}\right) \]

\[ j_l = \frac{I_l}{A} = nF D\left(\frac{C_b}{\delta}\right) \]

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

\[ j_{total} = j_{limiting} - j_{polarization} \]

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

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

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