14. Mass transfer kinetics

1 Review

→ Current – overpotential curve

→ Butler–Volmer equation & Tafel plot : $i = i_0[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}]$

2 mass transfer (under mass transfer limiting condition)

→ charge transfer > mass transfer

↳ Nernst – Planck equation :

$$\underbrace{J_i(x)}_{(\text{flux})} = \underbrace{\boxed{-D_i\frac{dC_i(x)}{dx}}}_{\text{diffusion}} \underbrace{\boxed{-\frac{z_iF}{RT}D_iC_i\frac{d\phi(x)}{dx}}}_{\text{migration}} + \underbrace{\boxed{C_i v(x)}}_{\text{Convection }(=0)} \quad \left[\frac{\text{mol}}{\text{cm}^2\cdot\text{sec}}\right]$$

↳ $$J_i(x) = -D_i\frac{dC_i(x)}{dx} - \frac{z_iF}{RT}D_iC_i\frac{d\phi(x)}{dx}$$

$$= -\frac{i_{d,i}}{z_iFA} - \frac{i_{m,i}}{z_iFA}$$

$$= -\frac{i_i}{z_iFA}$$

3 In the bulk solution

→ $$J_i(x) = -\cancel{D_i\frac{dC_i(x)}{dx}} - \frac{z_iF}{RT}D_iC_i\frac{d\phi(x)}{dx}$$

$$\therefore \frac{i_{m,i}}{z_iFA} = \frac{z_iF}{RT}D_iC_i\frac{d\phi(x)}{dx} \Rightarrow i_i = \frac{z_i^2F^2A\,D_iC_i}{RT}\frac{d\phi}{dx}$$

$\frac{d\phi}{dx} = \frac{\Delta E}{l}$ (linear E-field)

→ $u_i = \frac{|z_i|FD_i}{RT}$ (즉, $D_i = \frac{u_iRT}{|z_i|F}$) 를 대입하면, $i_i = |z_i|FAu_iC_i\frac{d\phi}{dx} = \frac{|z_i|FAu_iC_i\Delta E}{l}$

$$\therefore i = \sum_i i_i = \frac{FA\Delta E}{l}\sum_i |z_i|u_iC_i$$

→ 즉, $t_i = \frac{i_i}{i} = \frac{|z_i|u_iC_i}{\sum|z_j|u_jC_j} = \frac{|z_i|C_i\lambda_i}{\sum|z_j|u_jC_j}$ [$\because \Lambda = F(u_+ + u_-) = \lambda_+ + \lambda_-$, $\therefore \lambda_i = Fu_i$]

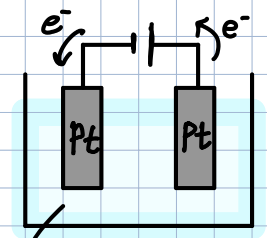
4 near the electrode

→ diffusion + migration ($\Leftrightarrow i = i_d + i_m$)

→ i_d & i_m 의 방향은 서로 같을수도 & 다를수도 있으며 $i = i_d$ ($\Leftrightarrow i_m = 0$)일수도 있다. ⇒ "balance sheet"

5 balance sheet example

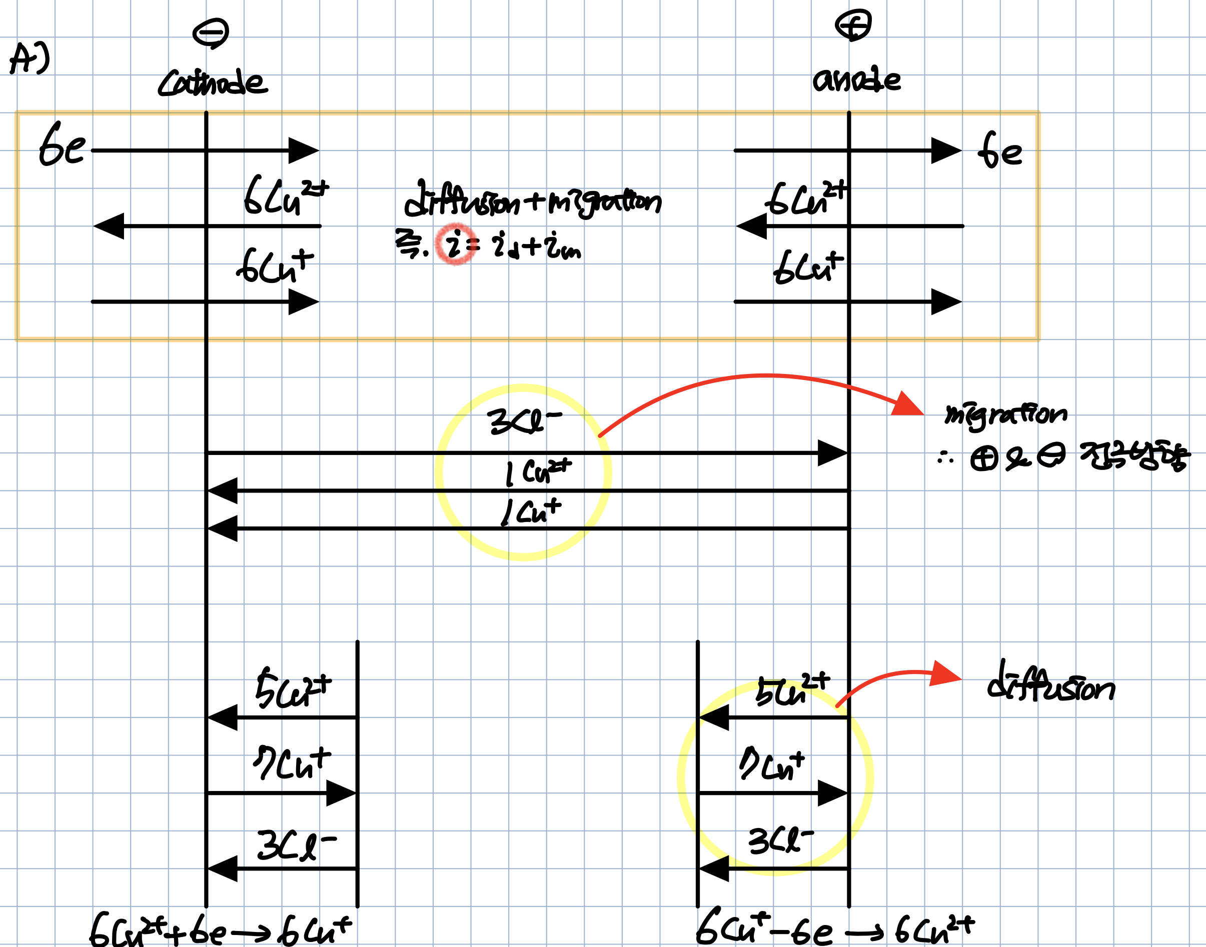
→ a)



$Cu(NH_3)_4^{2+}$: $10^{-3}M$
$Cu(NH_3)_2^{+}$: $10^{-3}M$
Cl^- : $3\times10^{-3}M$
NH_3 : $0.1M$

⊛ assuming : $\lambda_{Cu^{2+}} = \lambda_{Cu^+} = \lambda_{Cl^-}$
6e per unit time

A)



↳ bulk : "electrolyte conductivity" ∴ t_i

ex)
$$t_{Cu^{2+}} = \frac{|z_{Cu^{2+}}|\cancel{\lambda_{Cu^{2+}}}C_{Cu^{2+}}}{|z_{Cu^{2+}}|\cancel{\lambda_{Cu^{2+}}}C_{Cu^{2+}} + |z_{Cu^+}|\cancel{\lambda_{Cu^+}}C_{Cu^+} + |z_{Cl^-}|\cancel{\lambda_{Cl^-}}C_{Cl^-}} = \frac{2\times1}{2\times1+1+3}$$
$$t_{Cu^+} = \frac{1}{6}$$
$$t_{Cl^-} = \frac{3}{6} = \frac{1}{2} \rightarrow 6\times\frac{1}{2} = 3$$