13. Charge transfer kinetics 2

① Preview

→ Charge transfer rate ($i = i_c - i_a = nFA[k_f C_O(0,t) - k_b C_R(0,t)]$, $k_f = A_f e^{-\Delta G_f^{\ddagger}/RT}$) … ①

→ Energy barrier & current ($\Delta G_f^{\ddagger} = \Delta G_{f,a}^{\ddagger} - (1-\alpha)F(E-E^{o'})$] … ②

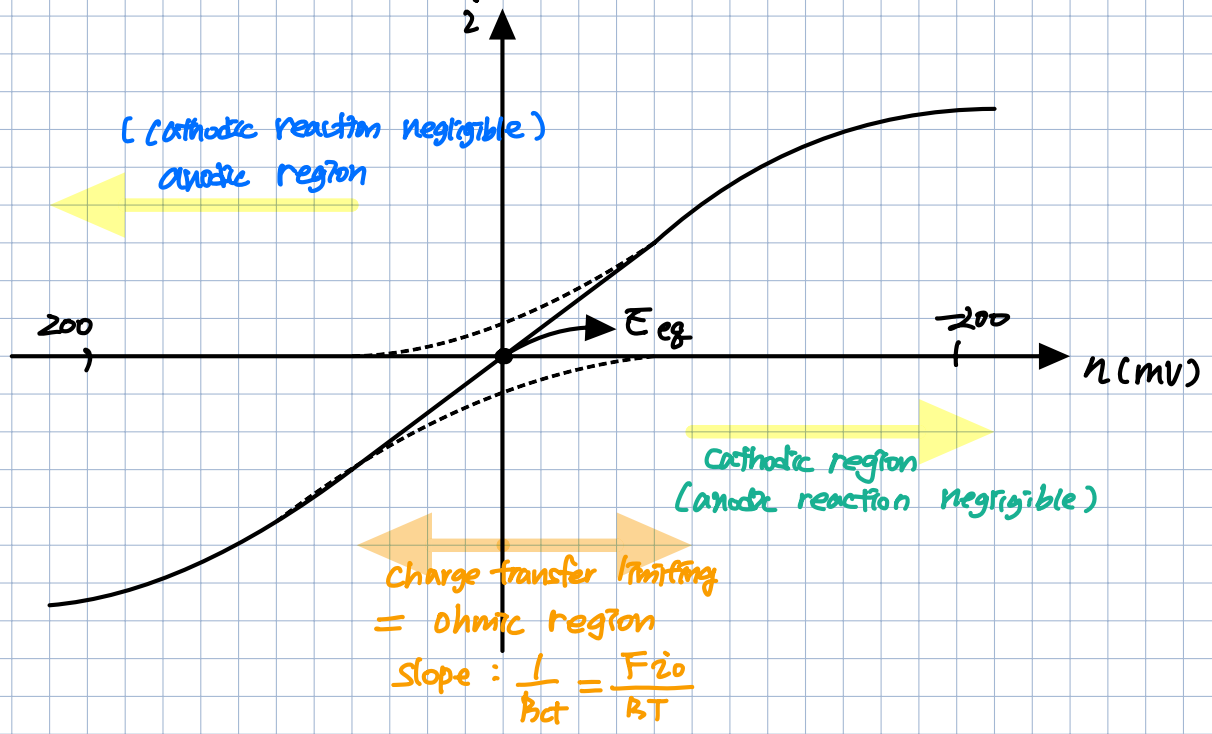
→ ① + ② = current - potential relation ($i = FAk^{o}\{C_O(0,t)\, e^{-\alpha f(E-E^{o'})} - C_R(0,t)\, e^{(1-\alpha)f(E-E^{o'})}\}$) … ③

→ using exchange current (i_o) & $C_O^{*} = C_O(0,t)$ & ③,

current - overpotential eqn. : $i = i_o \left[\frac{C_O(0,t)}{C_O^{*}} e^{-\alpha f\eta} - \frac{C_R(0,t)}{C_R^{*}} e^{(1-\alpha)f\eta} \right]$

② Current-overpotential curve

→ $i = i_o \left[\underbrace{\frac{C_O(0,t)}{C_O^{*}} e^{-\alpha f\eta}}_{\text{cathodic}} - \underbrace{\frac{C_R(0,t)}{C_R^{*}} e^{(1-\alpha)f\eta}}_{\text{anodic}} \right]$



3 Butler - Volmer equation & Tafel plot

→ mass transfer > charge transfer 이면, $C_O(0,t) \approx C_O^*$ & $C_R(0,t) \approx C_R^*$

$$i = i_o \left[\frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \eta} \right]$$

$$\therefore i = i_o \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right] \quad : \text{Butler - Volmer eqn.}$$

→ for small η, ohmic region

(using $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots = 1 + x$)

$$i = i_o \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right]$$

$$= i_o \left[1 - \alpha f \eta - \{ 1 + (1-\alpha) f \eta \} \right]$$

$$= -i_o f \eta \quad \text{where } f = \frac{F}{RT}$$

$$= \frac{i_o F}{RT} \cdot (-\eta)$$

$$\Rightarrow i = \frac{1}{R_{ct}} \cdot (-\eta) \quad (R_{ct}: \text{charge transfer resistance})$$

→ for large η, tafel region

1) at large negative overpotential,

$$i = i_o \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right] = i_o e^{-\alpha f \eta}$$

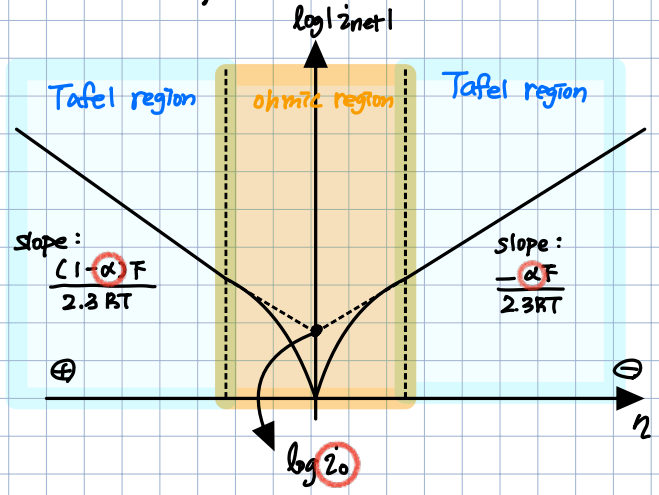
$$\therefore \log |i_{net}| = \log i_o - \frac{\alpha F}{2.303 RT} \eta$$

2) at large positive overpotential.

$$i = i_o \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right] = -i_o e^{(1-\alpha) f \eta}$$

$$\therefore \log |i_{net}| = \log i_o + \frac{(1-\alpha) F}{2.303 RT} \eta$$

→ Tafel plot



⊕ $i_o = FAk^\circ C_O^{*(1-\alpha)} C_R^{*\alpha}$

⊕ $R_{ct} = \frac{RT}{i_o F}$