

Electrochemical kinetics

1. Potential on reaction rate
2. Butler-Volmer equation
3. Exchange current
4. Charge transfer resistance
5. Tafel plot

Current: expression of reaction rate

- Current (i) : the rate of the electrode reactions
- Charge (q) → extent of chemical change at each electrode. The charge required to convert N mol of starting material to product in an ne^- electrode reaction is calculated using Faraday's law of electrolysis

$$q = \int i dt = nNF = nmF / M \quad \text{for time } t$$

where F : Faraday constant (96,485 C mol⁻¹)

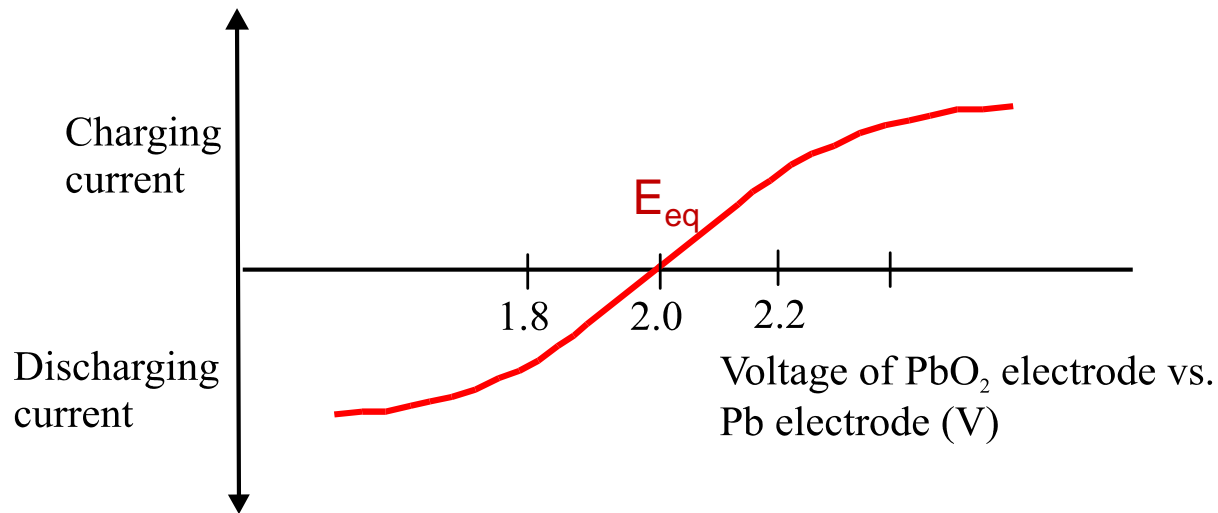
$$i(\text{amperes}) = \frac{dQ}{dt} (\text{coulombs/s})$$

$$\frac{Q}{nF} \frac{(\text{coulombs})}{(\text{coulombs/mol})} = N(\text{mol electrolyzed})$$

$$\text{Rate (mol/s)} = \frac{dN}{dt} = \frac{i}{nF}$$

I-V relation

Plot of cell currents versus the cell voltages (volt + am(pere) + mogram)



Not linear → electrochemical cells do not obey Ohm's law

Overpotential (or overvoltage, polarization) $\eta = E - E_{eq}$

$$E_{eq} = E^0$$

I-V curve : Butler-Volmer equation

Nernst equation : equilibrium expression

→ **electrode reaction rate? (kinetics)**

→ relationship between potential and rate of electrode reaction (which determine current) : **I-V curve**

I-V relation: Butler-Volmer equation, Tafel equation

One-step, one-electron kinetic relationships (Butler-Volmer approach):

$$k_f = k^0 \exp[-\alpha f(E - E^{0'})] \quad (3.3.9)$$

$$k_b = k^0 \exp[(1 - \alpha)f(E - E^{0'})] \quad (3.3.10)$$

$$i = F A k^0 [C_O(0, t) e^{-\alpha f(E - E^{0'})} - C_R(0, t) e^{(1 - \alpha)f(E - E^{0'})}] \quad (3.3.11)$$

$$i = i_0 \left[\frac{C_O(0, t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0, t)}{C_R^*} e^{(1 - \alpha)f \eta} \right] \quad (3.4.10)$$

(Cathodic Tafel equation)

$$\eta = \frac{RT}{\alpha F} \ln i_0 - \frac{RT}{\alpha F} \ln i \quad (3.4.15)$$

$E - E^0 = \eta$: overpotential

Control the magnitude of the current by changing the potential (and vice versa). Potential and current cannot be adjusted at the same time.



Electron transfer at an electrode

Reduction & oxidation at electrode are accomplished by heterogeneous electron transfer reactions since electron transfer occurs at the interface between electrode and solution → relationship between potential and rate of electrode reaction (which determine current)

→ **Butler-Volmer equation**

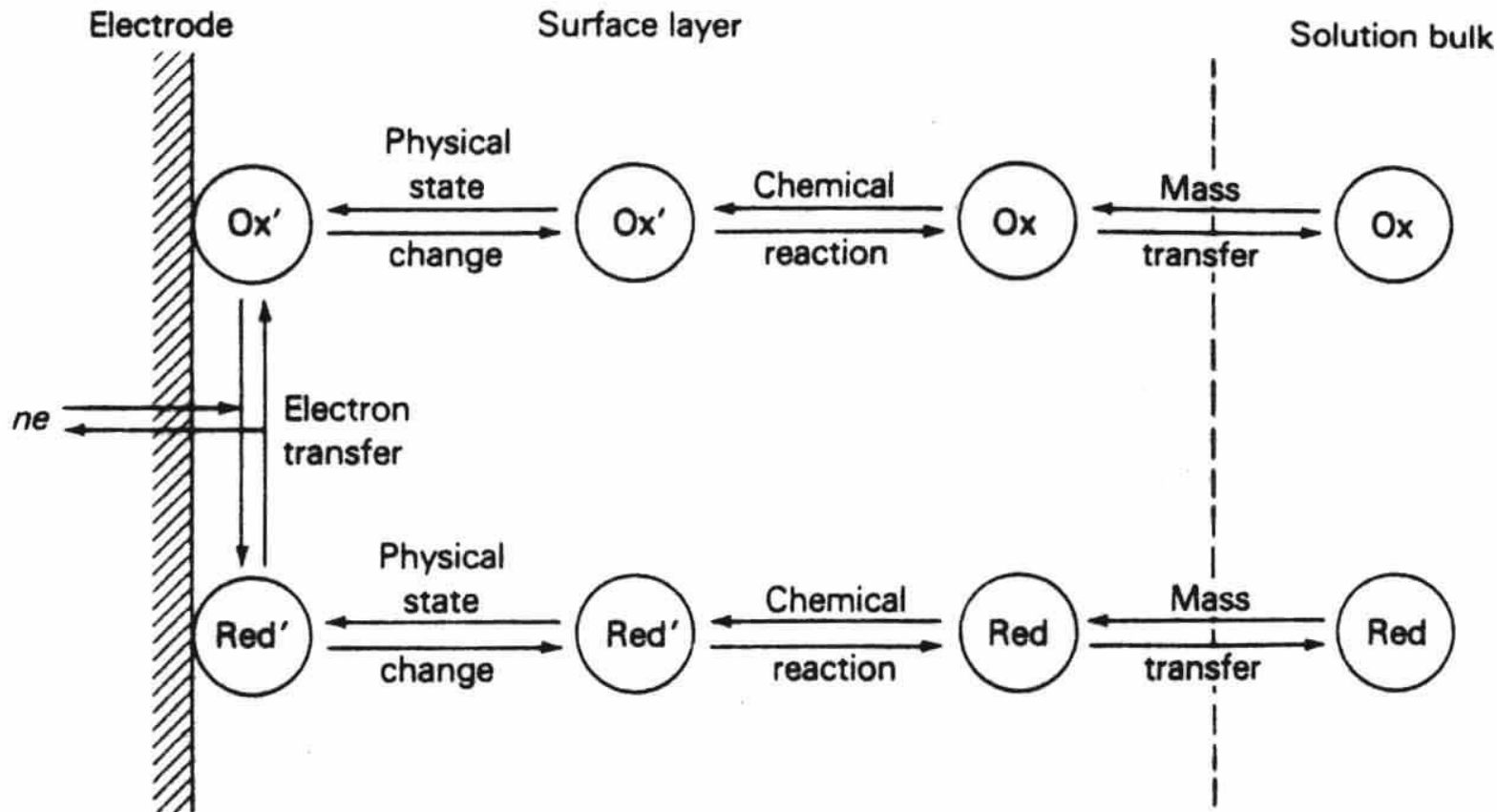
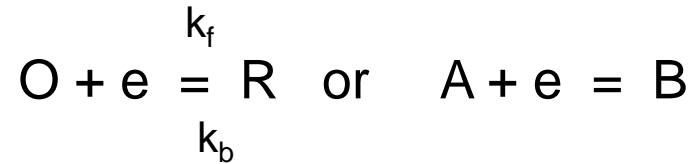


FIGURE 19-10 Steps in the reaction $\text{Ox} + ne \rightleftharpoons \text{Red}$ at an electrode. Note that the surface layer is only a few molecules thick. (Adapted from: A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, p. 21, Wiley: New York, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

Dynamic equilibrium



Rate of the forward process

$$v_f \text{ (M/s)} = k_f C_A$$

Rate of the reverse reaction

$$v_b = k_b C_B$$

Rate const, k_f, k_b : s^{-1}

Net conversion rate of A & B

$$v_{\text{net}} = k_f C_A - k_b C_B$$

At equilibrium, $v_{\text{net}} = 0$

$$k_f/k_b = K = C_B/C_A$$

*kinetic theory predicts a constant concentration ratio at equilibrium, just as thermodynamics

At equilibrium, kinetic equations \rightarrow thermodynamic ones

\rightarrow dynamic equilibrium (equilibrium: nonzero rates of k_f & k_b , but equal)

Exchange velocity

$$v_0 = k_f(C_A)_{\text{eq}} = k_b(C_B)_{\text{eq}}$$

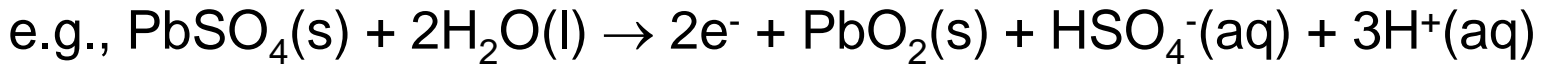
Relationship between current and heterogeneous rate constants

Faraday's law: chemical reaction → electric **current** → an indicator of **reaction rate**

Amount of electricity,

$$q = nFN$$

n: electron number, N: number of moles, F: Faraday constant (96,485 C/mol)



$$q/2F = -\Delta N_{\text{PbSO}_4} = -\Delta N_{\text{H}_2\text{O}}/2 = \Delta N_{\text{PbO}_2} = \Delta N_{\text{HSO}_4^-} = \Delta N_{\text{H}^+}/3$$

The passage of two moles of electrons = destroy one mole of PbSO_4 , destroy two moles of water, create one mole of PbO_2 ...

If we generalize this result and apply it to the oxidation reaction,



Then,

$$q/nF = -\Delta N_R = \Delta N_O$$

$$I = dq/dt = nFdN/dt$$

$$I/nF = -dN_R/dt = dN_O/dt = \text{rate}$$



$$E_n = E^0 - RT/F \ln(c_R/c_O)$$

depends on the concentrations of the two species and E^0

“=” means,



At E_n (E_{eq}), the rates

$$r_{ox}(E_n) = r_{rd}(E_n)$$

because no net reaction occurs. The rate r depend on the electrode potential E .

What exactly is meant by the “rate” of an electrode reaction?

At the potential of E,

$$r_{\text{net}}(\mathbf{E}) = r_{\text{ox}}(\mathbf{E}) - r_{\text{rd}}(\mathbf{E})$$

net reaction rate: the rate at which R is destroyed , or the rate at which O is created, per unit area of electrode (unit of mol·m⁻²·s⁻¹) “heterogeneous reaction rate”

$$r_{\text{net}}(\mathbf{E}) = -(1/A)(dN_{\text{R}}/dt) = (1/A)(dN_{\text{O}}/dt)$$

$$r_{\text{ox}}(\mathbf{E}) = k_{\text{ox}}(\mathbf{E})c_{\text{R}}^{\text{s}}$$

“s” means that the concentrations at the electrode surface

$k_{\text{ox}}(\mathbf{E})$: oxidative rate constant (ms⁻¹)

$$r_{\text{rd}}(\mathbf{E}) = k_{\text{rd}}(\mathbf{E})c_{\text{O}}^{\text{s}}$$

$k_{\text{rd}}(\mathbf{E})$: reductive rate constant

$$r_{\text{net}}(\mathbf{E}) = I/nAF = i/nF$$

From $r_{\text{net}}(E) = r_{\text{ox}}(E) - r_{\text{rd}}(E)$, $r_{\text{ox}}(E) = k_{\text{ox}}(E)c_{\text{R}}$, $r_{\text{rd}}(E) = k_{\text{rd}}(E)c_{\text{O}}$

Relate the faradaic **current** and **rate constants**

$$i = nF[k_{\text{ox}}c_{\text{R}}^{\text{s}} - k_{\text{rd}}c_{\text{O}}^{\text{s}}]$$

cf) $k_{\text{ox}} = k_{\text{a}}$ of anode, $k_{\text{rd}} = k_{\text{c}}$ of cathode

when $k_{\text{ox}}(E)c_{\text{R}}^{\text{s}} = k_{\text{rd}}(E)c_{\text{O}}^{\text{s}} \rightarrow$ zero current \rightarrow equilibrium

when $k_{\text{ox}}(E)c_{\text{R}}^{\text{s}} > k_{\text{rd}}(E)c_{\text{O}}^{\text{s}} \rightarrow$ anodic current (i_{a}) \rightarrow oxidation of R to O

when $k_{\text{ox}}(E)c_{\text{R}}^{\text{s}} < k_{\text{rd}}(E)c_{\text{O}}^{\text{s}} \rightarrow$ cathodic current (i_{c}) \rightarrow reduction of O to R

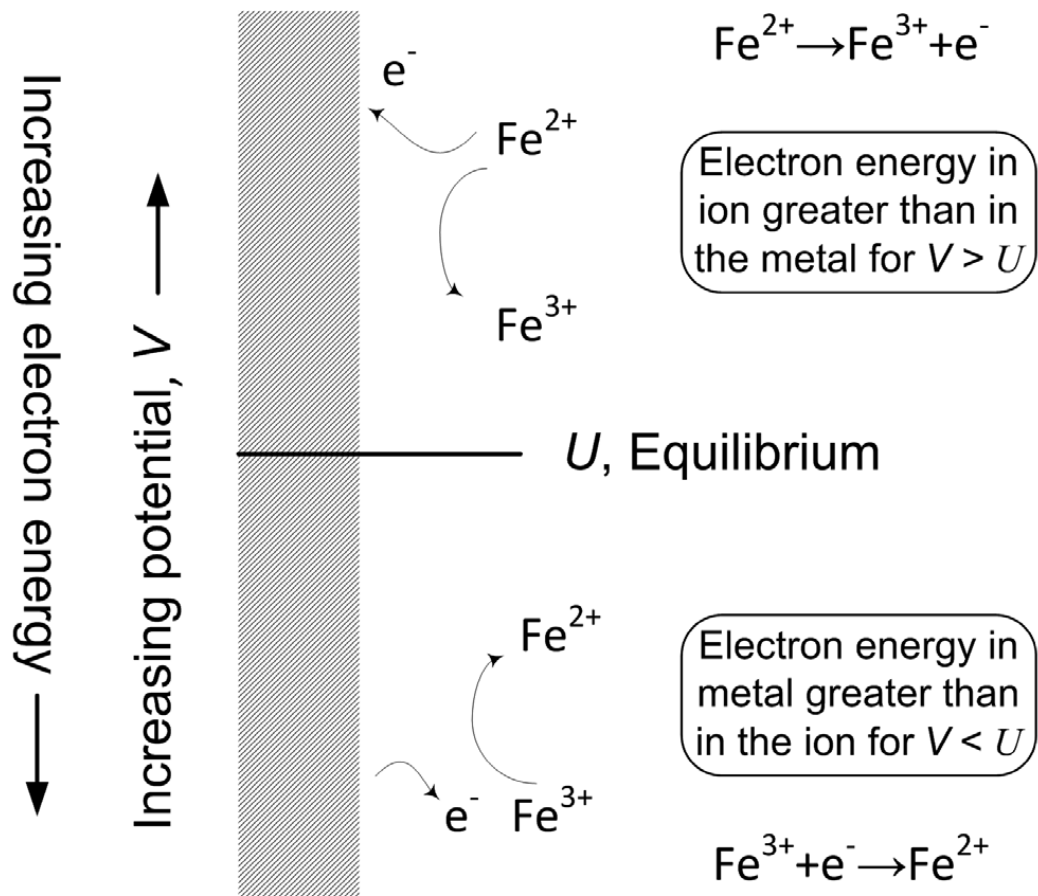


Figure 3.3 The relationship between potential, electron energy, and the direction of a faradaic reaction.

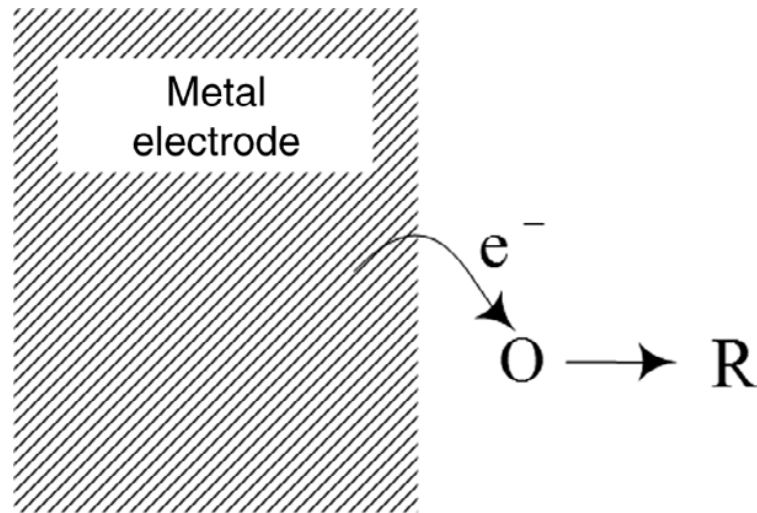


Figure 3.4 Simple electron transfer reaction at metal electrode.

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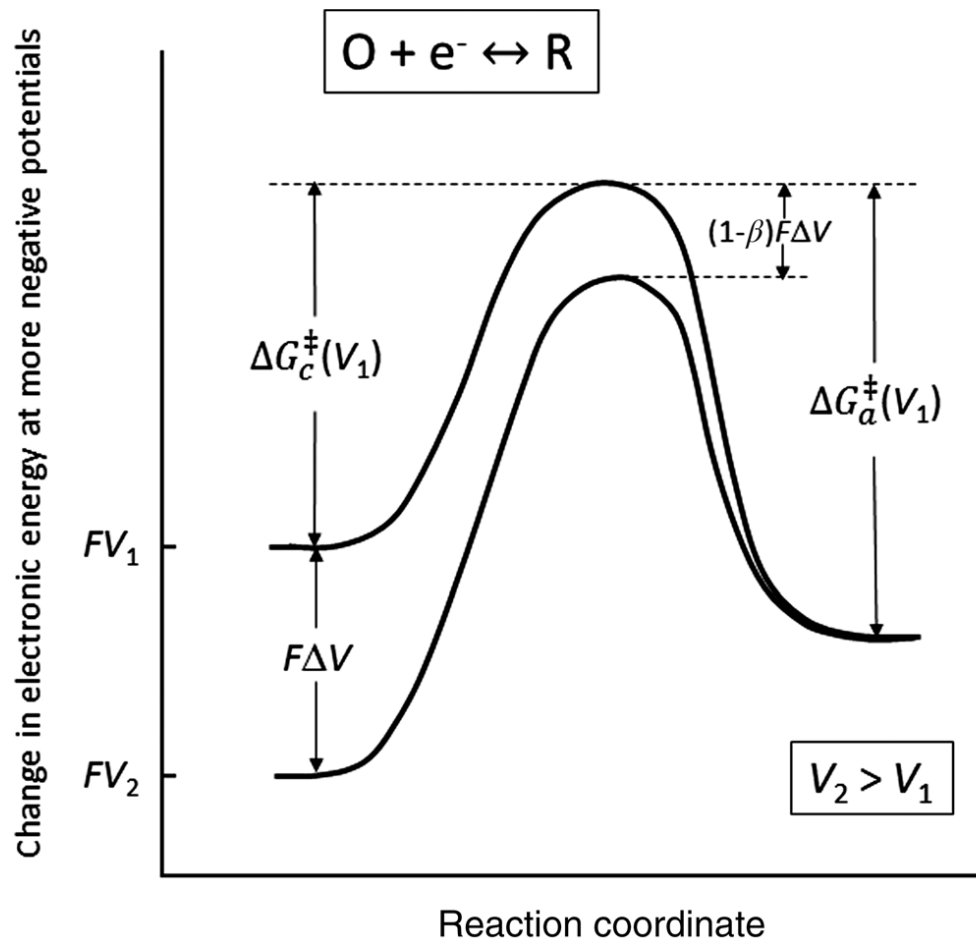
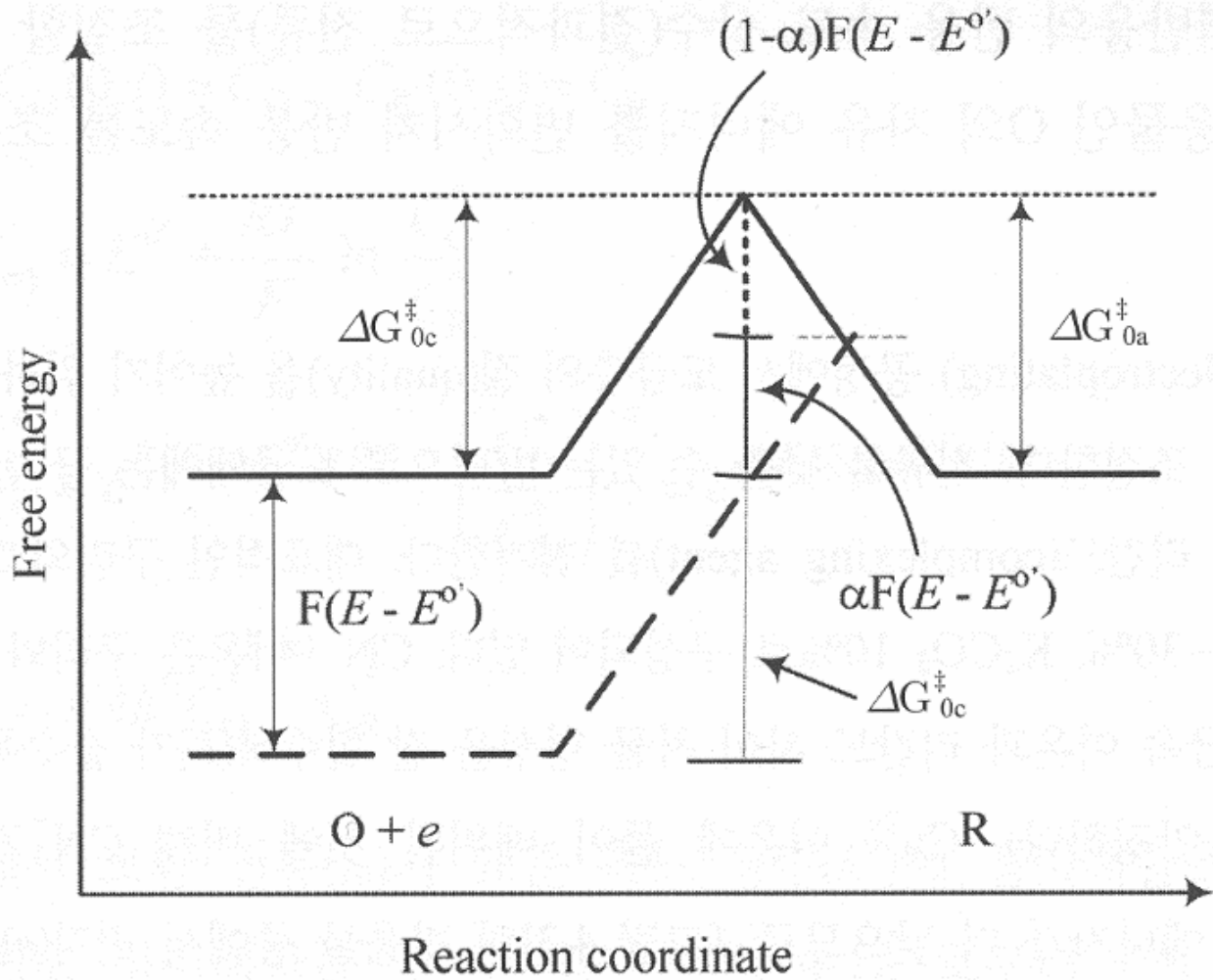


Figure 3.5 Change in energy associated with reaction at an electrode surface (subscript a = anodic and c = cathodic).



Potential dependence of heterogeneous rate constants

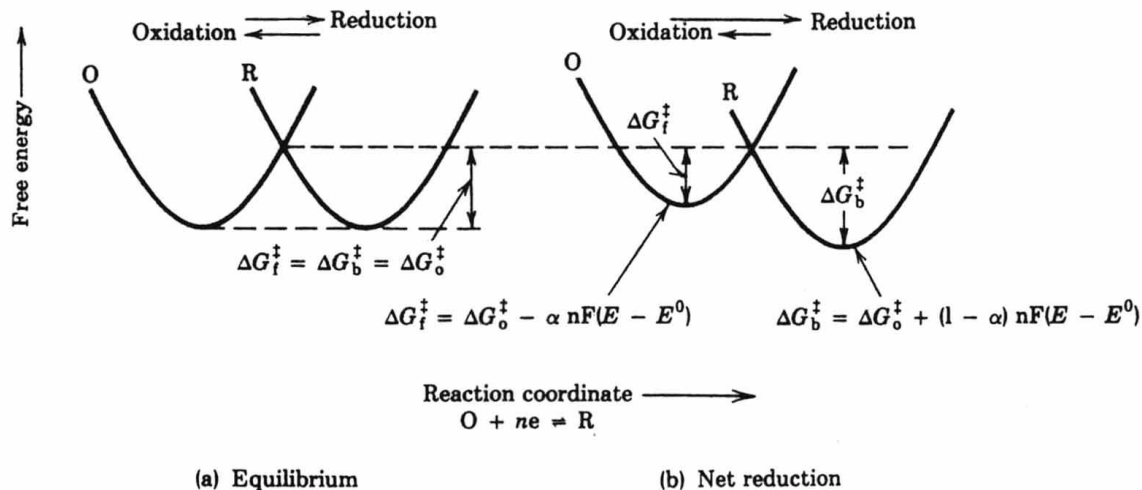


Transition state model,

$$k_{rd} = k_f = A \exp(-\Delta G_f^\ddagger / RT)$$

where ΔG_f^\ddagger is the free energy of activation and A is a frequency factor which accounts for the rate of collision of the electroactive molecule with the electrode surface

cf) $k_{ox} = k_b$ of anode, $k_{rd} = k_f$ since forward direction (\rightarrow) is reduction one.



(a) equilibrium between O and R

O \rightarrow R: pass over the activation free energy barrier, ΔG_f^\ddagger

R \rightarrow O: pass over the activation free energy barrier, ΔG_b^\ddagger

At equilibrium, $\Delta G_f^\ddagger = \Delta G_b^\ddagger \rightarrow$ probability of electron transfer is the same in each direction \rightarrow no net current $\rightarrow i_c + i_a = 0$

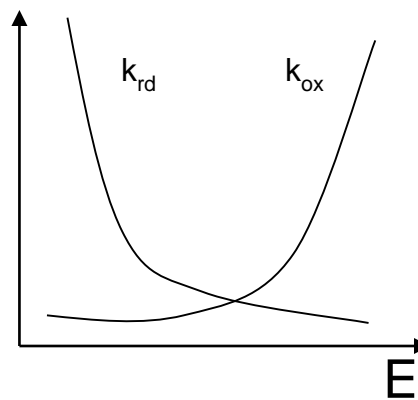
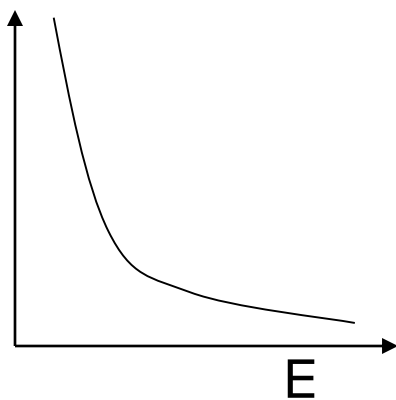
No net current means same rates between forward and backward (not zero current) \rightarrow **exchange current i_0** at equilibrium; $i_0 = i_c = -i_a$

$i_0 \uparrow$ as $\Delta G \downarrow$

(b) net reduction

applying negative potentials

reduction: more negative potential $\rightarrow k_f$ (or k_{rd}) \uparrow , k_b \downarrow



Negative potential $E \rightarrow$ lower ΔG_f^\ddagger and raise ΔG_b^\ddagger

Potential change $E - E^0 \rightarrow$ free energy change $-nF(E-E^0) \Rightarrow$ part of this energy change (factor α) \rightarrow decrease in the activation barrier for reduction (forward reaction) ; part (factor $(1 - \alpha)$) \rightarrow increase in the activation barrier for oxidation

$$\Delta G_f^\ddagger = \Delta G^{0\ddagger} - \alpha nF(E-E^0)$$

$$\Delta G_b^\ddagger = \Delta G^{0\ddagger} + (1-\alpha)nF(E-E^0)$$

Applying potential to the electrode \rightarrow activation free energy barrier α ; “**transfer coefficient**” or “**symmetry factor**” since α is a measure of the symmetry of the energy barrier \rightarrow a symmetrical energy barrier ($\alpha = 0.5$), real systems: 0.3 ~ 0.7 semiconductor: ~ 0 or ~ 1



Actually,



$\alpha, -(1-\alpha)$; orders of the reductive and oxidative processes

another interpretation of α : increasing electrochemical activity of electrons
 \rightarrow it accelerates the reductive process and retards the oxidative process \rightarrow
 α is the fraction of the increase r_{rd} , $(1-\alpha)$ is the fraction that diminishes r_{ox}
 $\alpha = 0.5$; perfect symmetric, these fractions are equal

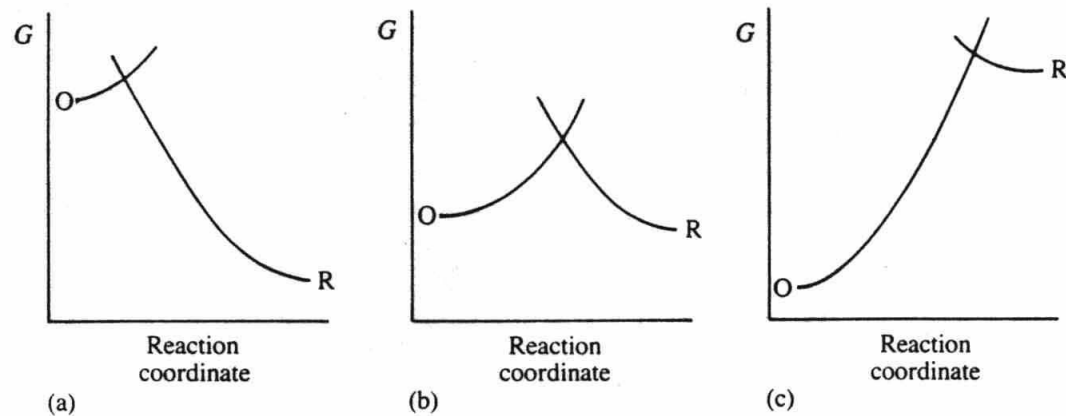


Fig. 4.4 Energy profiles for the cases (a) $\alpha_c \approx 0$; (b) $\alpha_c \approx \frac{1}{2}$; (c) $\alpha_c \approx 1$.

Arrhenius form,

$$k_f = k^0 \exp[-\alpha n F (E - E^0) / RT]$$

$$k_b = k^0 \exp[(1 - \alpha) n F (E - E^0) / RT]$$

Where k^0 is the standard rate constant, $k_f = k_b = k^0$ at E^0 . k^0 , $\alpha \rightarrow$ rate constant. Relationship between potential and rate

Relationship between current and potential

$$i_c = nF c_O^s k_f \quad \text{and} \quad i_a = -nF c_R^s k_b$$

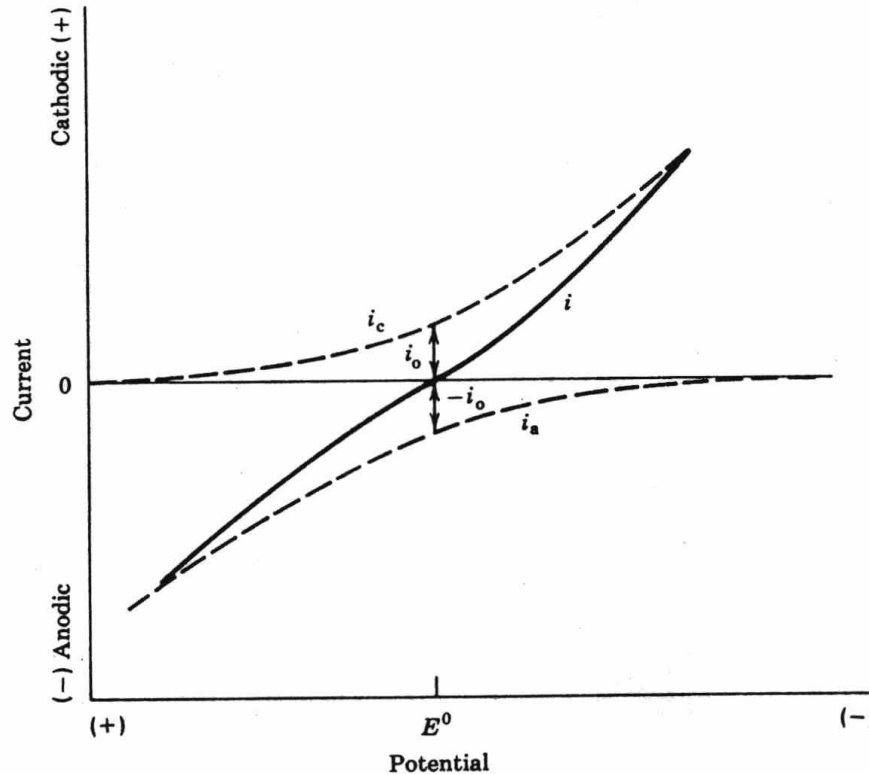
$$i_c = nF k^0 c_O^s \exp\{-\alpha nF(E-E^0)/RT\}$$
$$i_a = -nF k^0 c_R^s \exp\{(1-\alpha)nF(E-E^0)/RT\}$$

$$i = i_c + i_a$$

Butler-Volmer equation

$$i = nF k^0 [c_O^s \exp\{-\alpha nF(E-E^0)/RT\} - c_R^s \exp\{(1-\alpha)nF(E-E^0)/RT\}]$$

This relationship links the faradaic current, electrode potential, the concentrations of electroactive species at the electrode surface



i and i_c and i_a as a function of potential E ; negative $E \uparrow \rightarrow i_c \uparrow$ (forward reaction), positive $E \uparrow \rightarrow i_a \uparrow$ (backward)

k^0 ; $1 \sim 50 \text{ cm}\cdot\text{s}^{-1}$ for very fast reactions, $10^{-9} \text{ cm}\cdot\text{s}^{-1}$ for very slow reactions.

Exchange current density i_0 ; $10 \text{ A}\cdot\text{cm}^{-2} \sim 1 \text{ pA}\cdot\text{cm}^{-2}$

I-V: Electroless deposition

■ Electrochemical Point of View: Mixed Potential Theory (혼성전위)

- Mixed potential theory: overlap of two independent electrochemical reaction

Metal ion reduction



$$i_c = f(E)$$

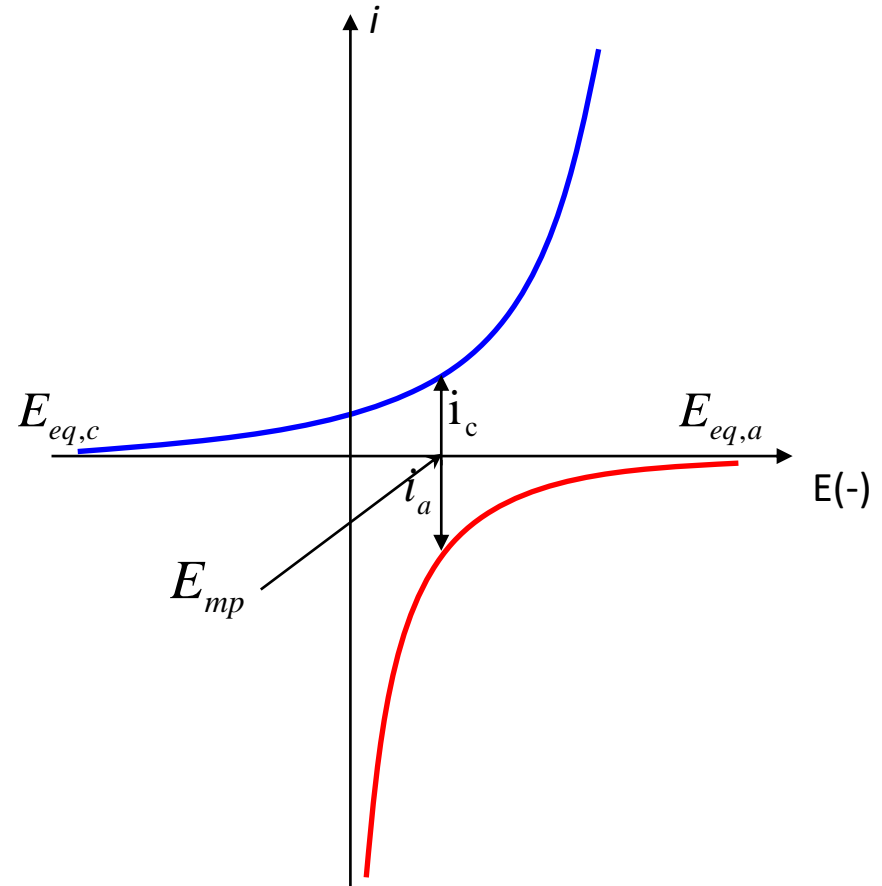
Reducing agent oxidation



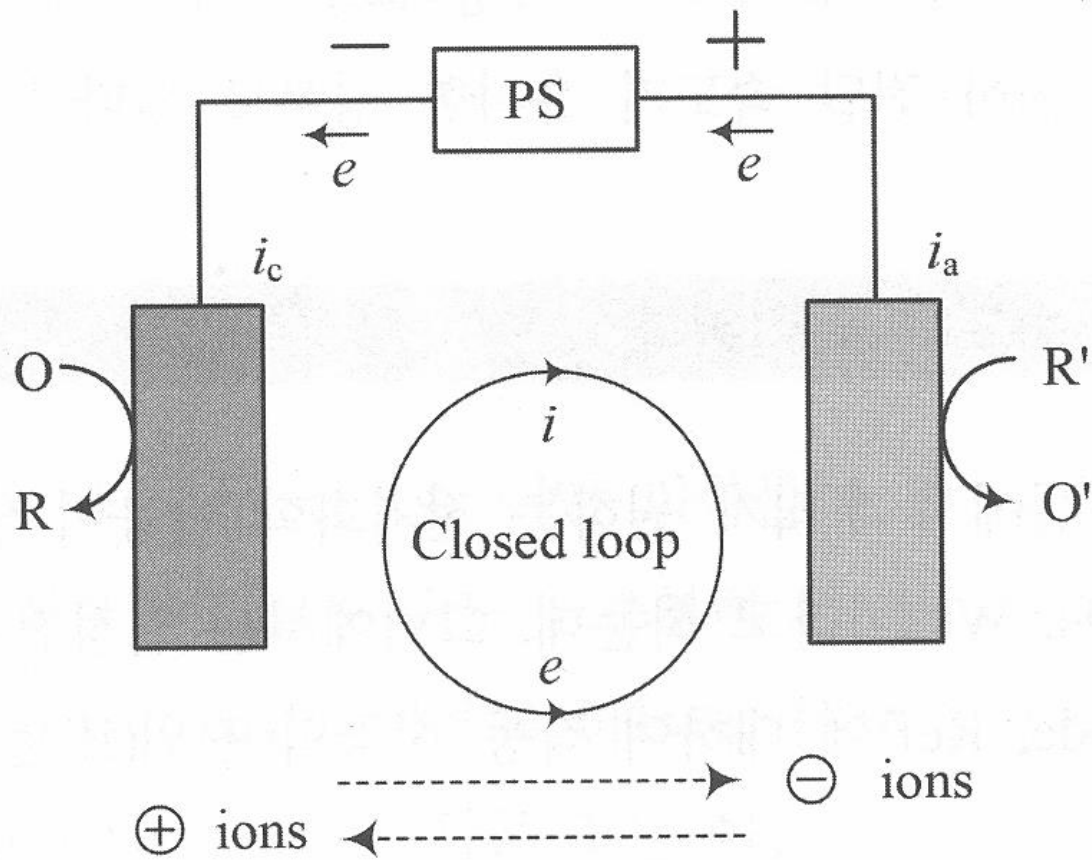
$$i_a = f(E)$$

- The potential where the total current becomes 0 is the mixed potential.

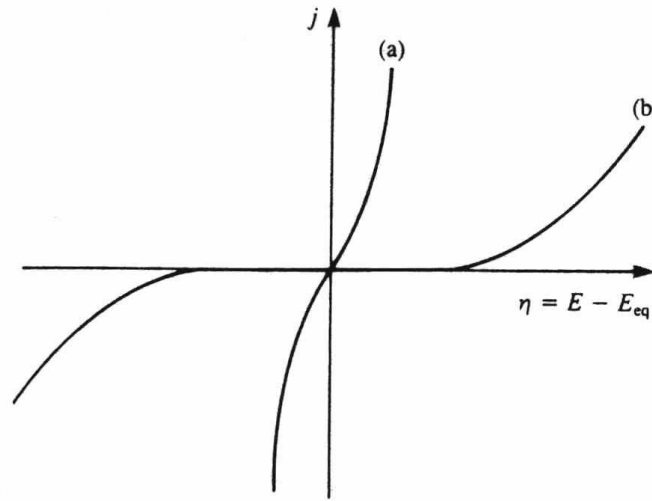
$$i_{total} = i_c + i_a$$



Electrochemistry as closed loop: $i_a = i_c$



$$i_c = |i_a| = i \text{ (electrolyte)}$$



The effect of the value of k_0 on the current density close to E_{eq} (a) k_0 large (b) k_0 smaller

At equilibrium, zero net current, $i_c = -i_a$

Butler-Volmer equation (kinetics) → Nernst equation (thermodynamics)

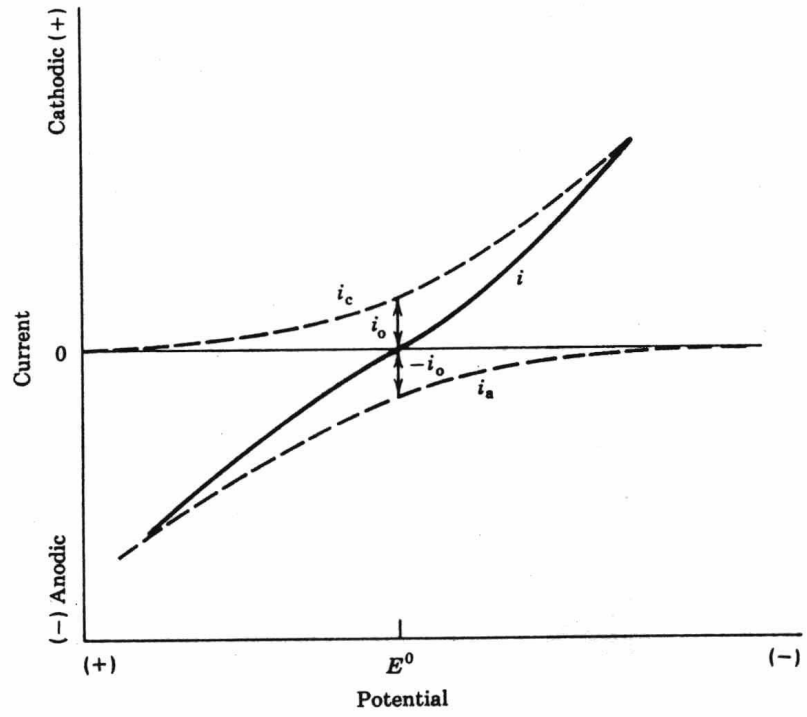
$$E = E^0 - (RT/nF)\ln(c_R^s/c_O^s)$$

$$i_0 = i_c = nFk^0c_O^s\exp\{-\alpha nF(E-E^0)/RT\} = i_a = -nFk^0c_R^s\exp\{(1-\alpha)nF(E-E^0)/RT\}$$

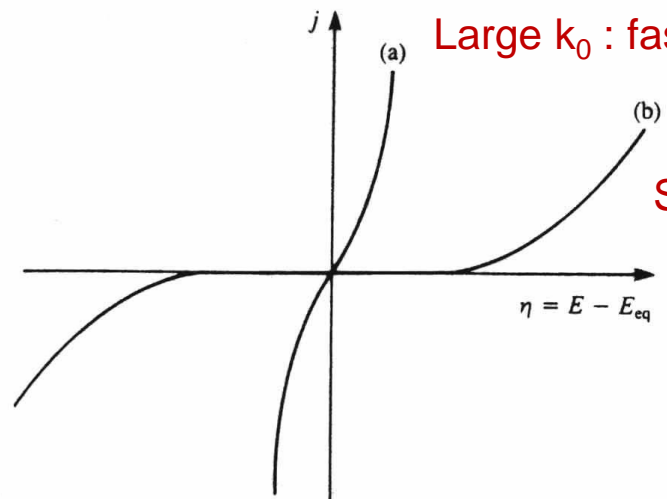
⇒

$$i_0 = nFk^0(c_O^s)^{1-\alpha}(c_R^s)^\alpha$$

high exchange current density → high reaction rate



i_0 : 교환전류
(exchange current)



Large k_0 : fast reaction rate

Small k_0 : slow reaction rate

교환전류 (i_0)

Plot I-V relation using Butler-Volmer equation if charge-transfer is rate-determining step:

어떤 전기화학 반응($O + e = R$)에서 전하 전달이 전체 속도를 결정한다고 가정하고, 다음의 조건이 주어졌을 때 버틀러-볼머 식을 이용하여 전압과 전류의 관계를 그리시오; $A = 0.1 \text{ cm}^2$, $E^0 = -0.15 \text{ V (vs. SCE)}$, $k^0 = 10^{-4} \text{ cm/sec}$, $T = 298 \text{ K}$, $\alpha = 0.5$, $C_O^* = 5.0 \text{ mM}$, $C_R^* = 1.0 \text{ mM}$

풀이 버틀러-볼머 식을 이용하여 전압에 따른 전류를 모사하기 위해서 먼저 평형 전압 (E_{eq})과 교환 전류(i_0)를 알아야 한다. 평형 전압(E_{eq})을 계산하면 다음과 같다.

$$\begin{aligned} E_{eq} &= E^0 + \frac{RT}{F} \ln \frac{C_O^*}{C_R^*} \\ &= (-0.15 \text{ V}) + \frac{(8.314 \text{ J/mol} \cdot \text{K})(298\text{K})}{(9.65 \times 10^4 \text{ C/equiv.})} \ln \frac{(5 \times 10^{-3} \text{ M})}{(10^{-3} \text{ M})} = -0.11 \text{ V} \end{aligned}$$

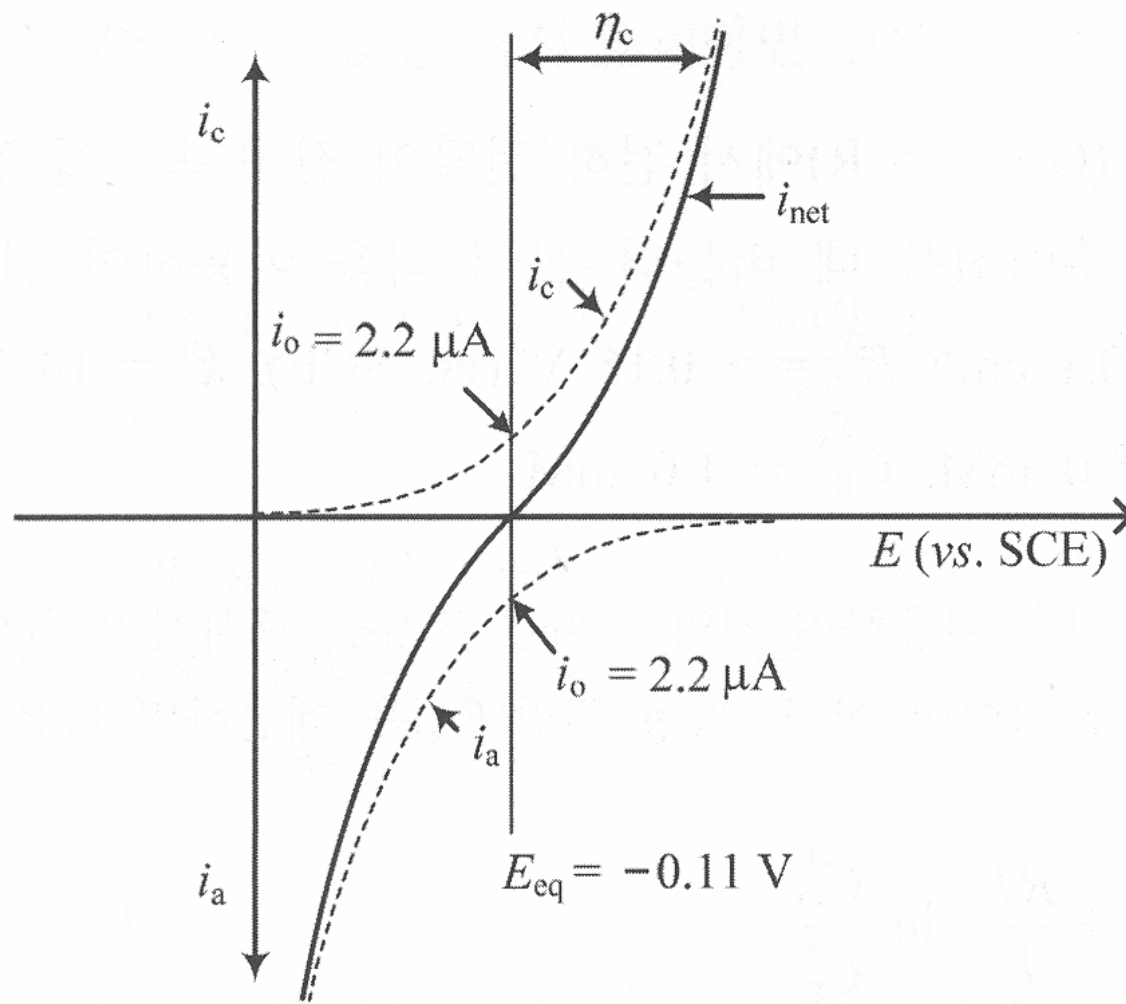
주어진 조건에서 i_0 는 다음과 같이 계산된다.

$$\begin{aligned} i_0 &= F A k^0 C_O^{(1-\alpha)} C_R^{\alpha} \\ &= (9.65 \times 10^4 \text{ Coul/equiv}) \times (0.1 \text{ cm}^2) \times (10^{-4} \text{ cm/sec}) \\ &\quad \times (5 \times 10^{-6} \text{ mol/cm}^3)^{0.5} \times (1 \times 10^{-6} \text{ mol/cm}^3)^{0.5} \\ &= 2.2 \mu\text{A} \end{aligned}$$

위 계산에서 각 변수를 cgs 단위로 표현하고 농도의 단위를 반드시 mol/cm^3 로 사용하여야 전류가 암페어(amperes)의 단위를 갖게 된다.

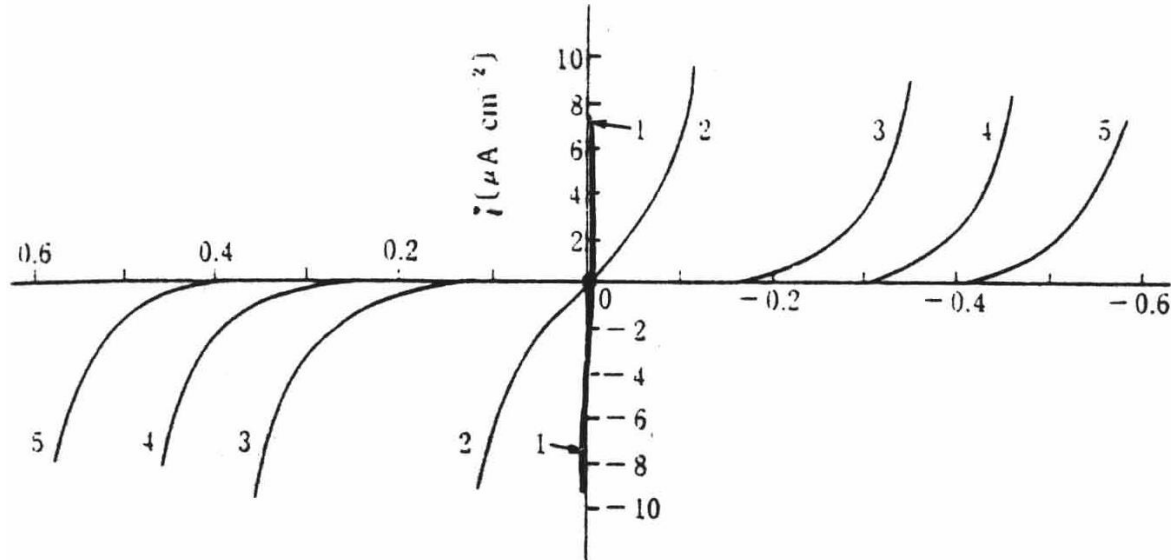
$$\left(\frac{\text{Coul}}{\text{equiv.}} \right) (\text{cm}^2) \left(\frac{\text{cm}}{\text{sec}} \right) \left(\frac{\text{mol}}{\text{cm}^3} \right)^{0.5} \left(\frac{\text{mol}}{\text{cm}^3} \right)^{0.5} = \frac{\text{Coul}}{\text{sec}} = \text{Amperes}$$

i_a , i_c , i_{net} , η_c , η_a , E_{eq}



The effect of exchange current density on overpotential

교환전류 (i_0)



Butler-Volmer equation/ i_0

$$i = nFk^0[c_o^s \exp\{-\alpha nF(E-E^0)/RT\} - c_R^s \exp\{(1-\alpha)nF(E-E^0)/RT\}]$$

and let $F/RT = f$, overpotential $\eta = E - E^0 \Rightarrow$ current-overpotential equation

$$i = i_0[\exp(-\alpha nf\eta) - \exp((1-\alpha)nf\eta)]$$

Table 3.1 i_o for Different Reactions

| Reaction | i_o [$A \cdot m^{-2}$] |
|--|----------------------------|
| $O_2 + 4H^+ + 4e^- = 2H_2O$ on Pt | 4×10^{-9} |
| $NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$ | 6.1×10^{-1} |
| $H_2 = 2H^+ + 2e^-$ on Pt in 1 N HCl | 10 |
| $Fe^{3+} + e^- = Fe^{2+}$ | 20 |
| $Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$ | 600 |
| Ferri/ferrocyanide, 0.001 M | 230 |

Illustration 3.2

Table 3.2 i_o for Hydrogen Reaction in 1 m H_2SO_4 at 25 °C, values provide order of magnitude estimates

| Metal | i_o [$A \cdot m^{-2}$] |
|----------------|----------------------------|
| Pb, Hg | 10^{-8} |
| Zn | 10^{-7} |
| Sn, Al, Be | 10^{-6} |
| Ni, Ag, Cu, Cd | 10^{-3} |
| Fe, Au, Mo | 10^{-2} |
| W, Co, Ta | 10^{-1} |
| Rh, Ir | 2.5 |
| Pd, Pt | 10 |

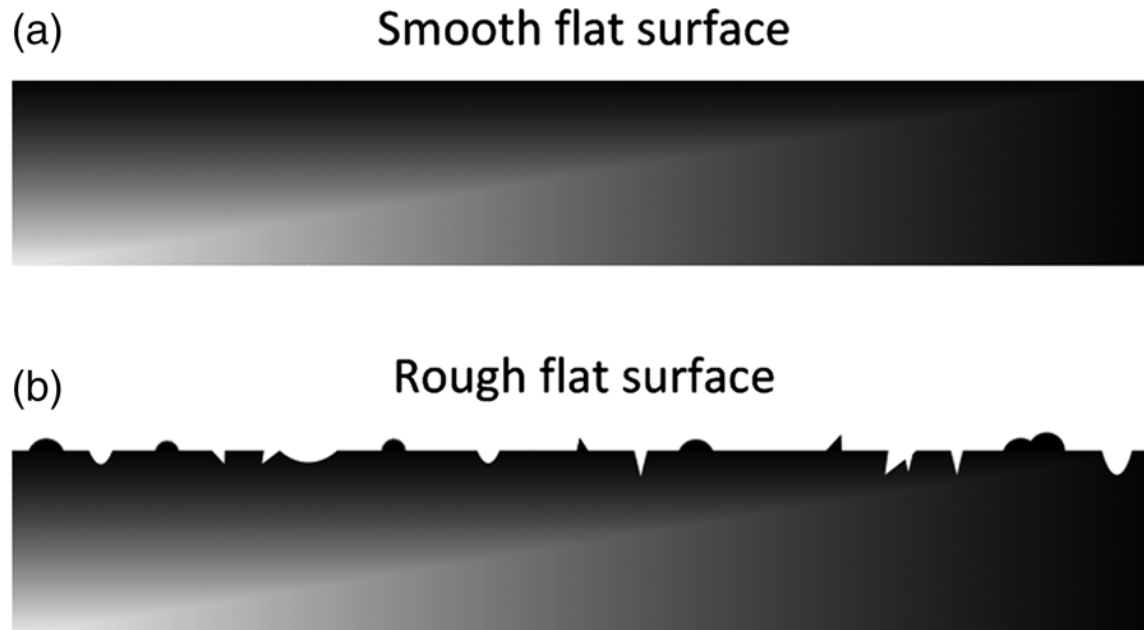
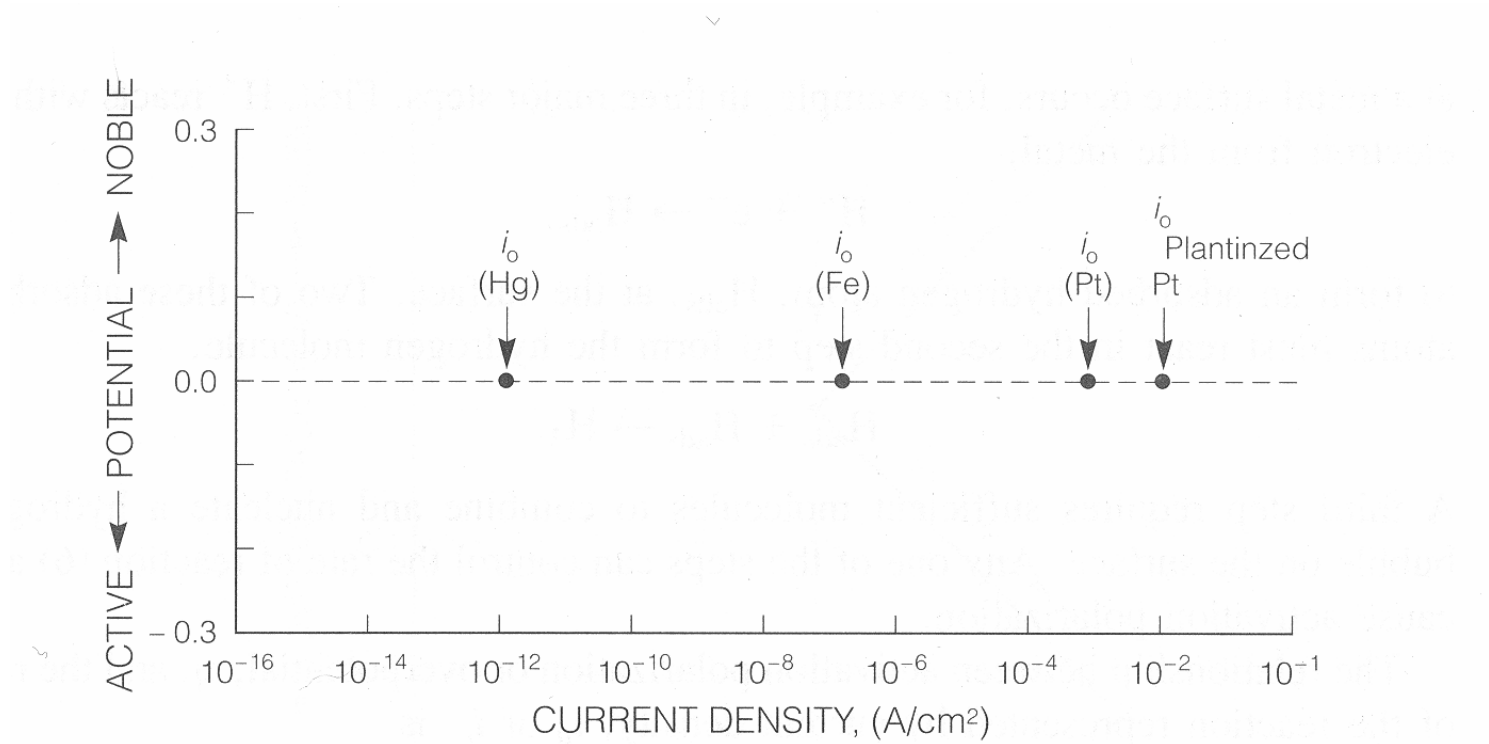


Figure 3.6 The area of the electrode with a rough surface is much larger than that of the one with the smooth surface.

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Exchange current density (i_0)



hydrogen oxidation reaction (HOR)

Corrosion

TABLE 1.1 Galvanic Series in Seawater

Cathodic (noble)

↑

platinum
gold
graphite
titanium
silver
zirconium

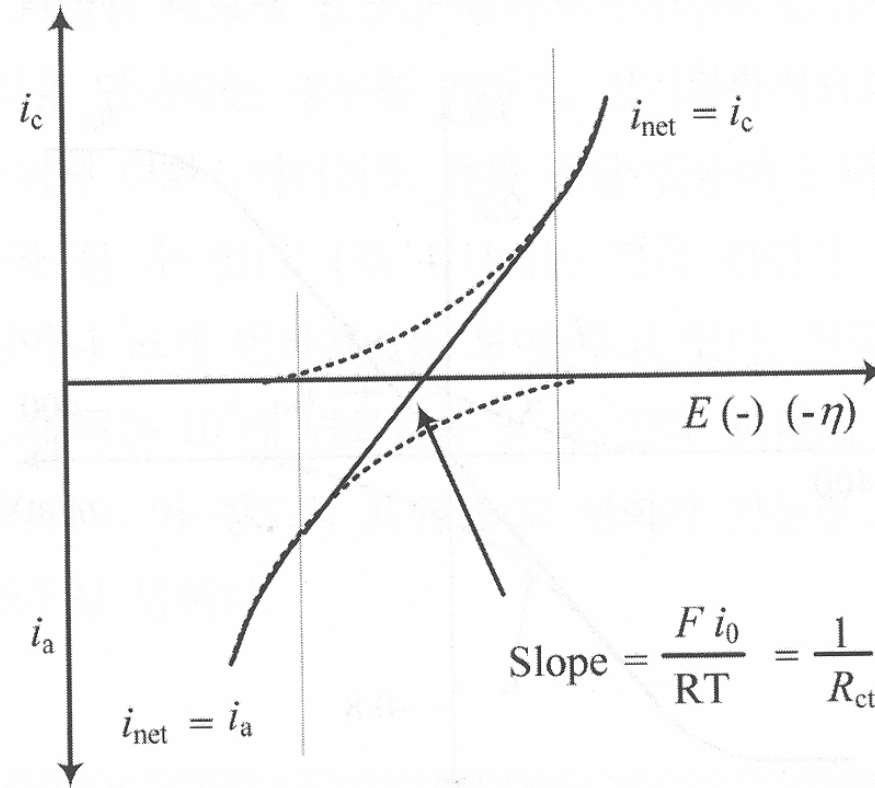
AISI Type 316, 317 stainless steels (passive)
AISI Type 304 stainless steel (passive)
AISI Type 430 stainless steel (passive)
nickel (passive)
copper-nickel (70-30)
bronzes
copper
brasses
nickel (active)
naval brass
tin
lead

AISI Type 316, 317 stainless steels (active)
AISI Type 304 stainless steel (active)
cast iron
steel or iron
aluminum alloy 2024
cadmium
aluminum alloy 1100
zinc
magnesium and magnesium alloys

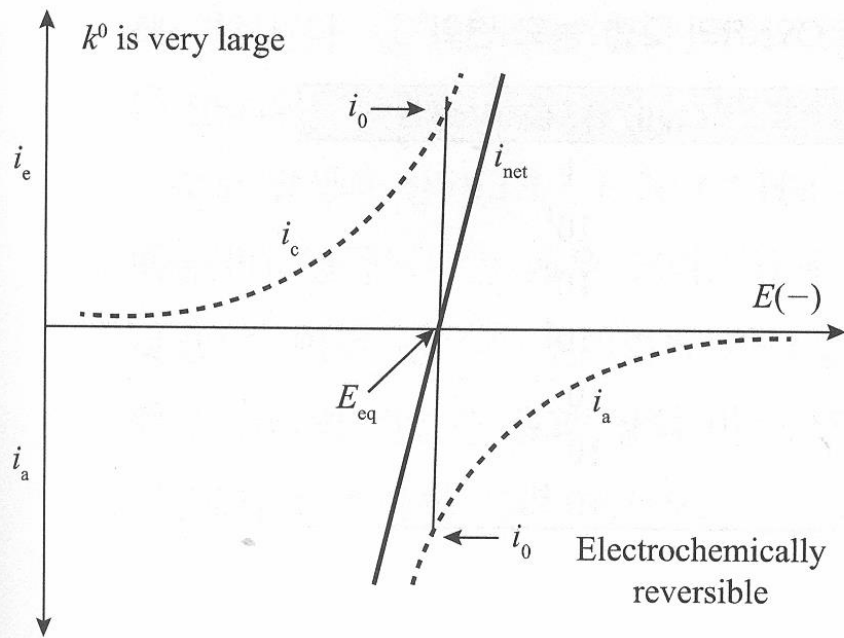
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Anodic (active)

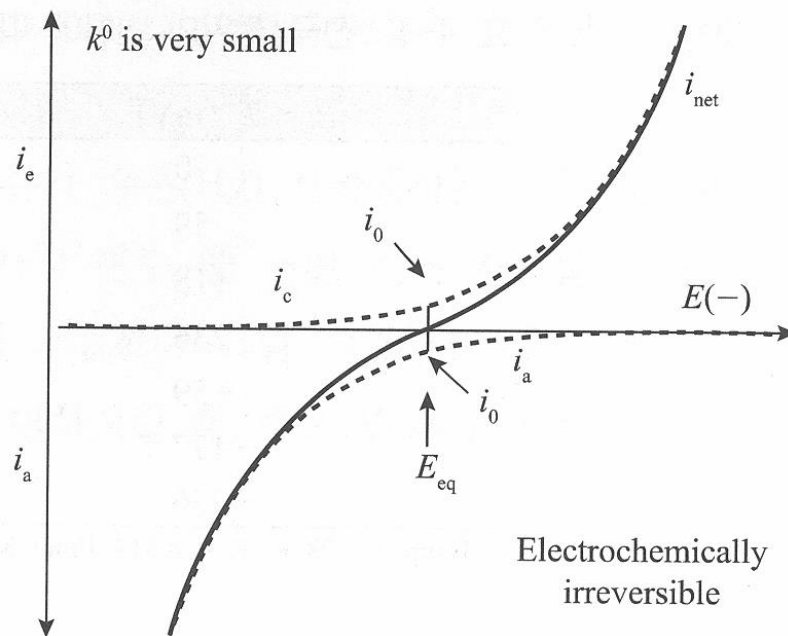
Low polarization region ($\eta < \pm(118/n) \text{ mV}$)



As the current and overvoltage are proportional, following Ohm's law, so they are called **ohmic regions** → slope = **Charge transfer resistance**, $R_{\text{ct}} = RT/i_0F$



(a)



(b)



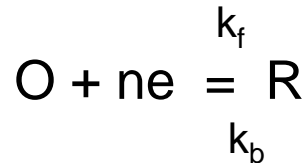
Tafel plot

High polarization region ($\eta > \pm(118/n)$ mV)

$\rightarrow i_{\text{net}} \sim i_a$ or $i_{\text{net}} \sim i_c$

Essentials of electrode reactions

*accurate kinetic picture of any dynamic process must yield an equation of the thermodynamic form in the limit of equilibrium



Equilibrium is characterized by the Nernst equation

$$E = E^{0'} + (RT/nF)\ln(C_o^*/C_R^*)$$

bulk conc

Kinetic: dependence of current on potential

Overpotential

$$\eta = a + b/\log i$$

Tafel equation
(경험식)

Butler-Volmer equation/ i_0

$$i = nFk^0[c_O^s \exp\{-\alpha nF(E-E^0)/RT\} - c_R^s \exp\{(1-\alpha)nF(E-E^0)/RT\}]$$

and let $F/RT = f$, overpotential $\eta = E - E^0 \Rightarrow$ current-overpotential equation

$$i = i_0[\exp(-\alpha n f \eta) - \exp((1-\alpha)n f \eta)]$$

$\eta \gg 0$ (oxidation, only O in bulk) $\rightarrow \exp(-\alpha n f \eta) \ll \exp((1-\alpha)n f \eta)$

$$i = -i_0 \exp((1-\alpha)n f \eta)$$

apply log,

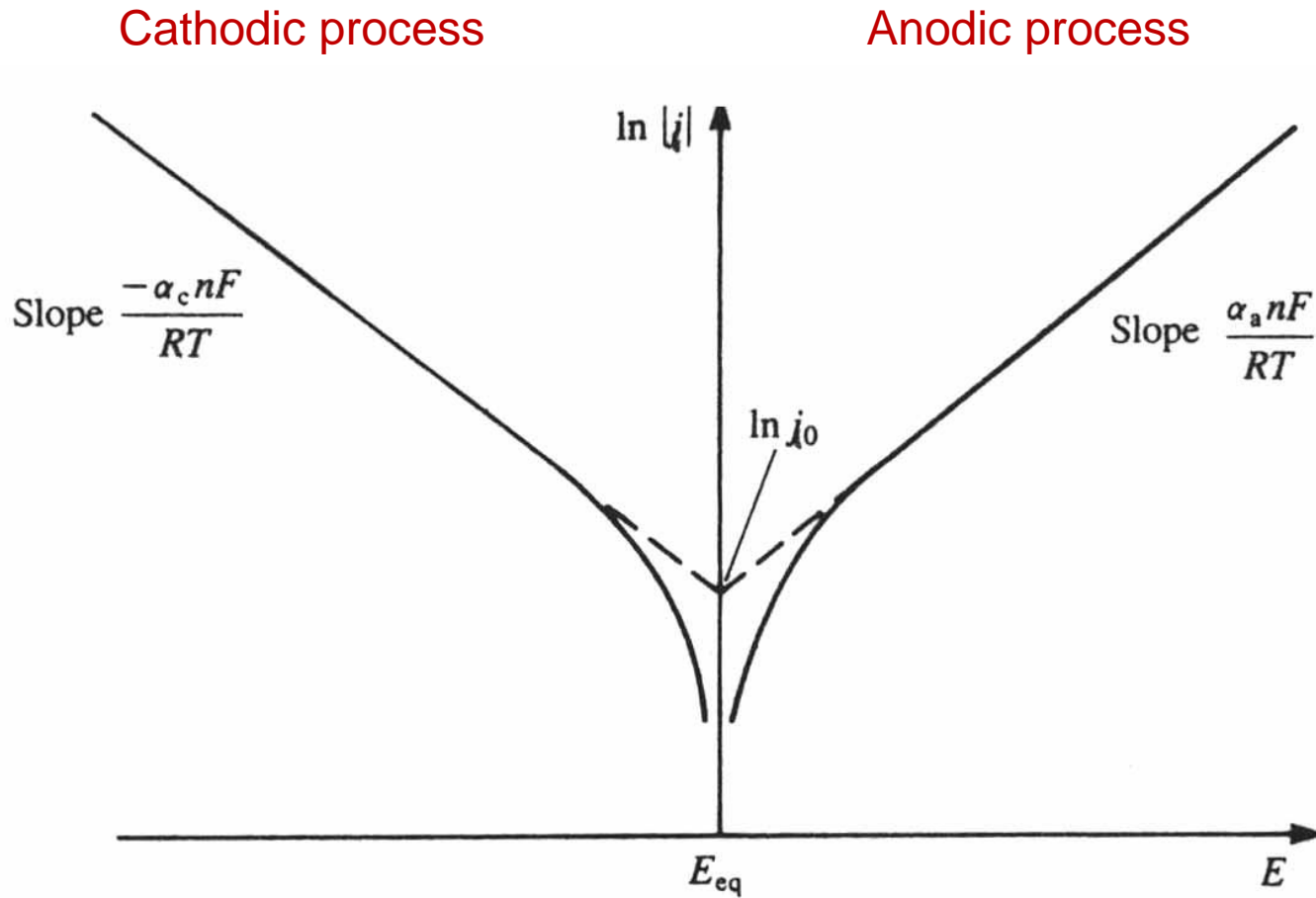
$$\eta = -(RT/(1-\alpha)nF) \ln i_0 + (RT/(1-\alpha)nF) \ln |i|$$

for $\eta \ll 0$ (reduction), $\eta = (RT/\alpha nF) \ln i_0 - (RT/(\alpha nF)) \ln |i|$

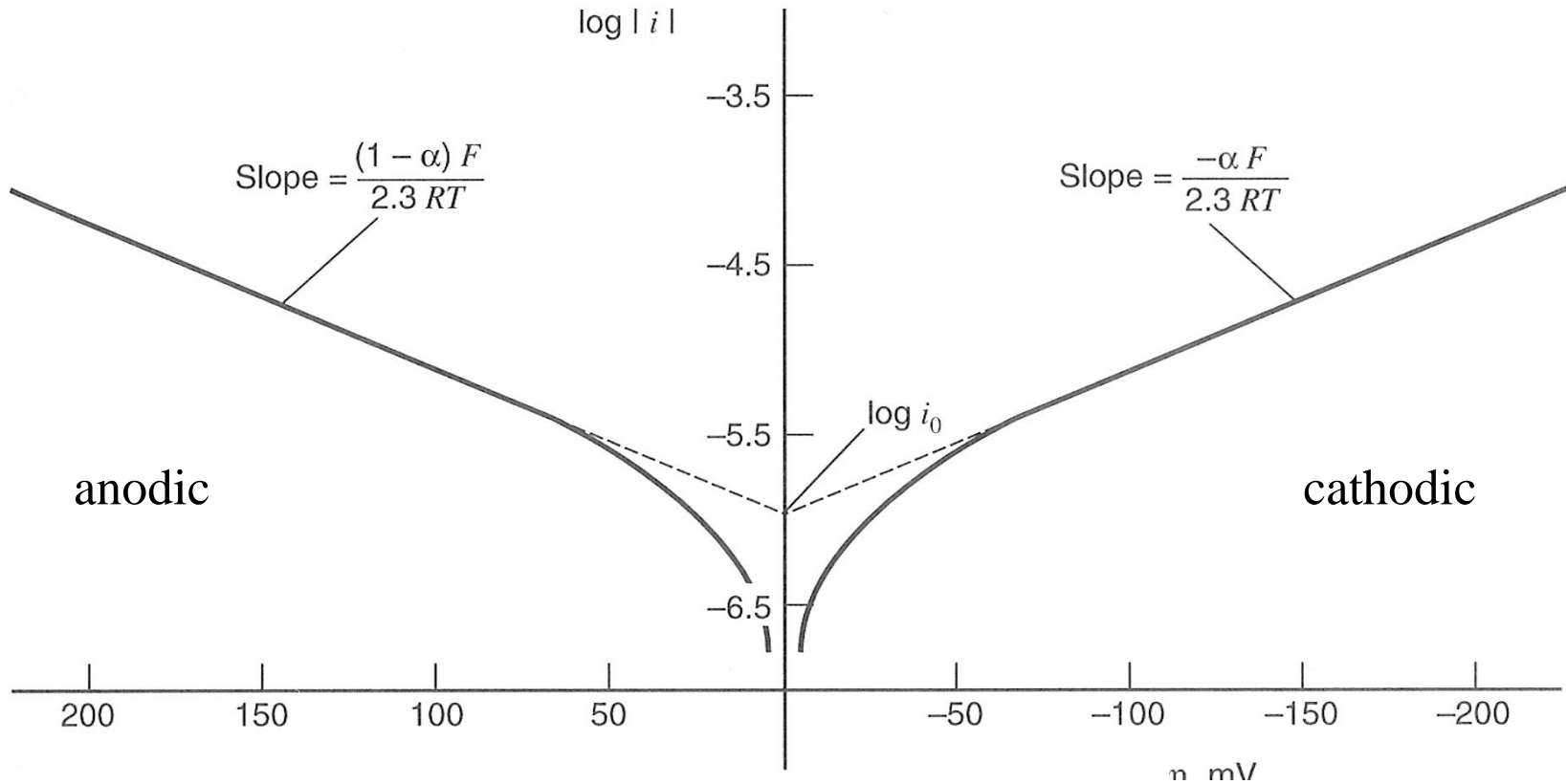
Tafel plot \rightarrow measure i_0 and α

$$E - E^0 = \eta = a/ni_0 \pm b/ln|i|$$

Plot of $\ln |i|$ vs. E showing how to measure i_0 and α from the slopes of the lines



Tafel plots (i vs. η) → evaluating kinetic parameters (e.g., i_0 , α)



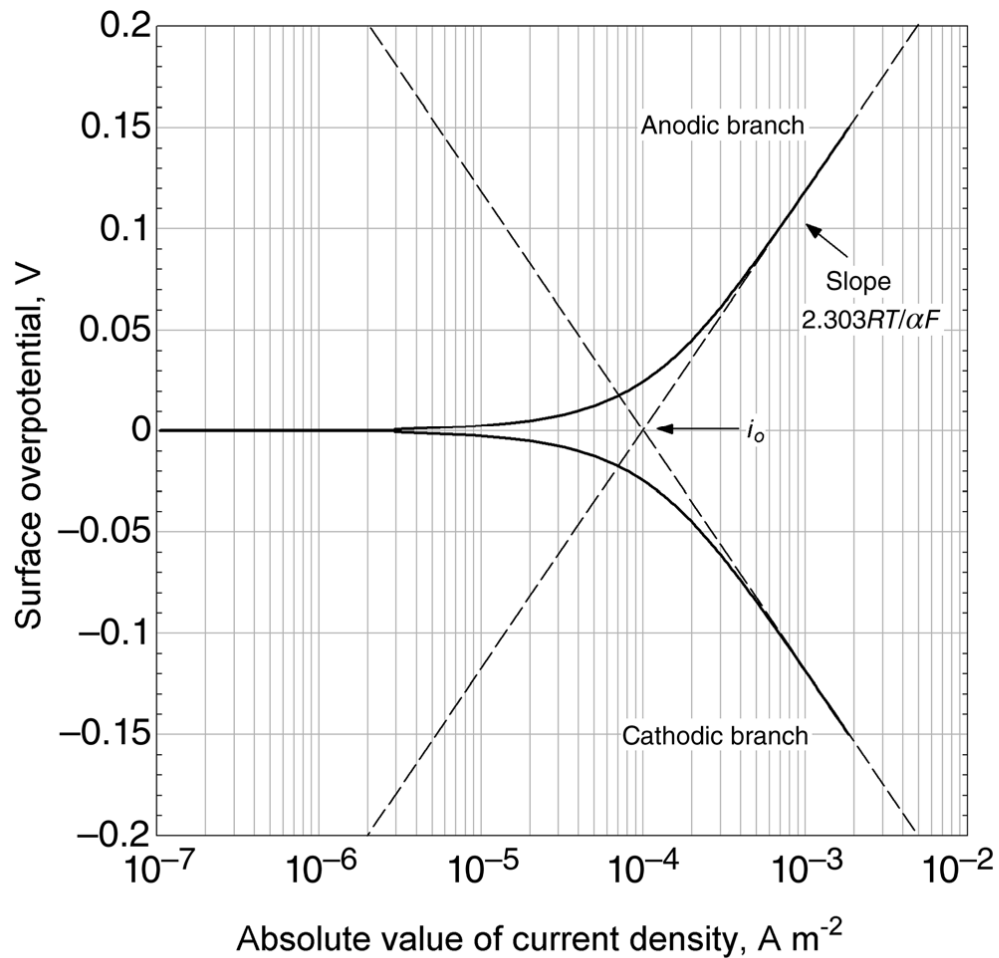
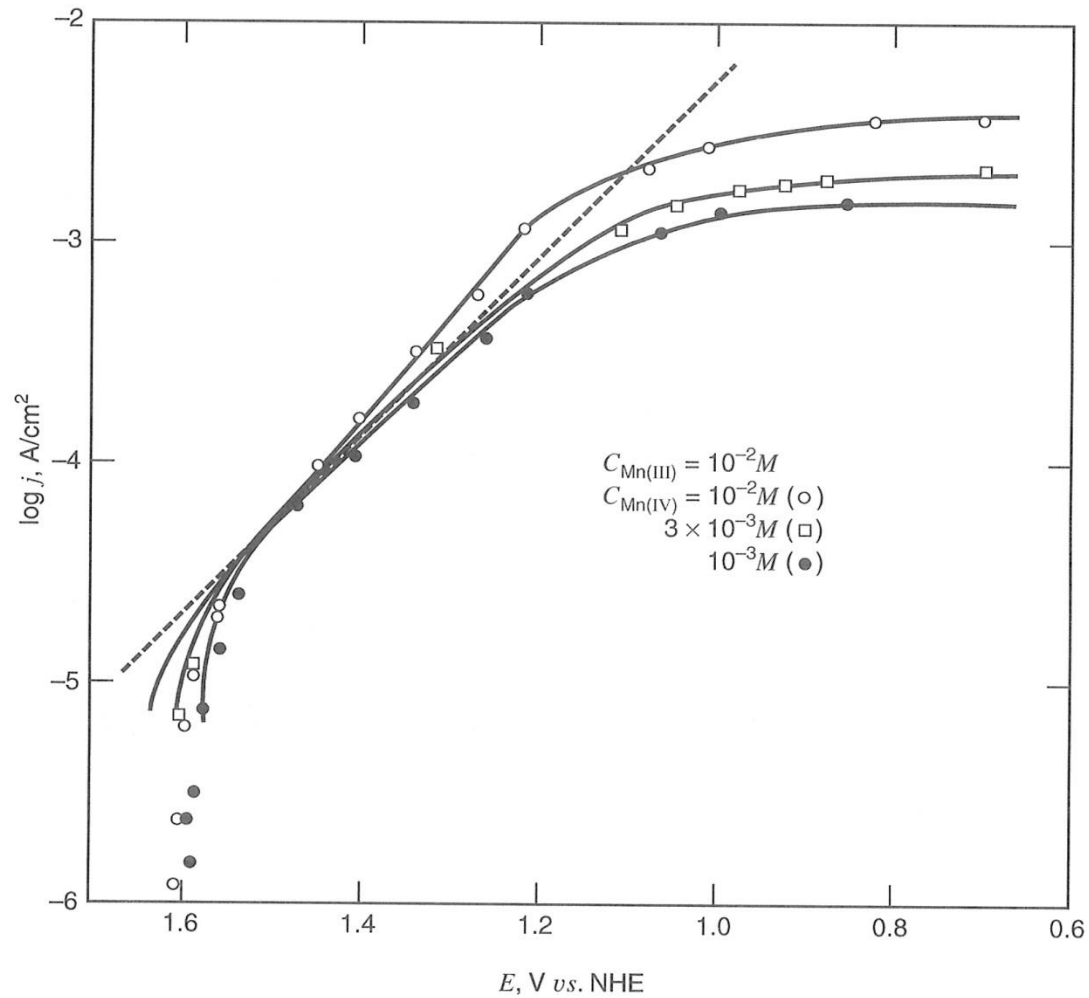


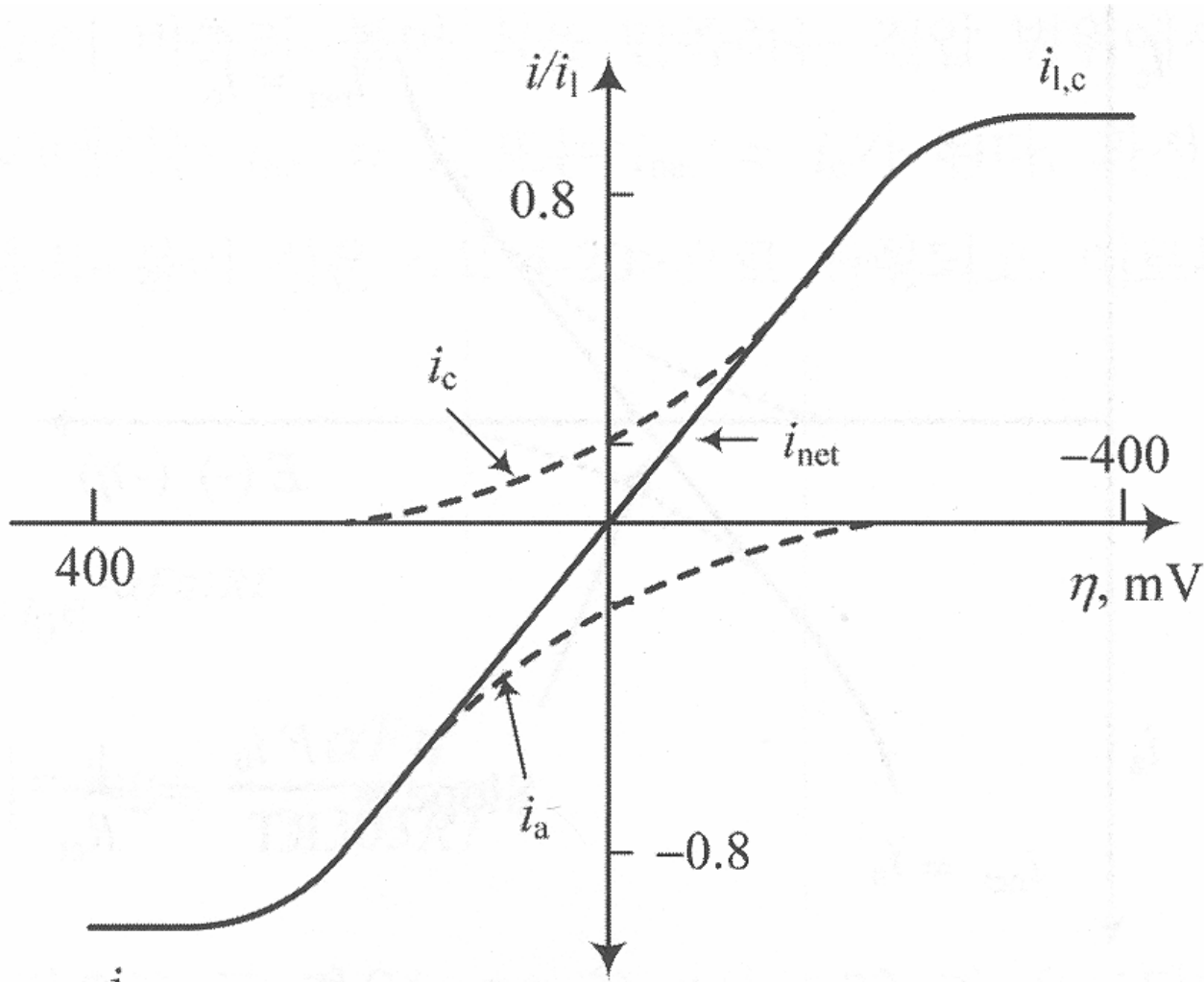
Figure 3.7 Classic Tafel plot. Parameters used are $i_0 = 10^{-4} \text{ A} \cdot \text{m}^{-2}$, 25°C , $\alpha = 0.5$.

e.g., real Tafel plots for Mn(IV)/Mn(III) system in concentrated acid

- At very large overpotential: mass transfer limitation



Determination of reaction rate (current) by mass transport (next Lecture)



Summary of Butler–Volmer Kinetics and Useful Simplifications

1. General kinetics, applicable under all current density conditions; the general BV expression for η (solve numerically):

$$i_{\text{cell}} = i_o \left\{ \exp \left(\frac{\alpha_a F}{R_u T} \eta \right) - \exp \left(\frac{-\alpha_c F}{R_u T} \eta \right) \right\} \quad (4.52) \quad 3.17$$

2. Low polarization, facile kinetics, linearized BV approximation (explicit η expression):

$$\eta = \pm \frac{i}{i_o} \frac{R_u T}{(\alpha_a + \alpha_c) F} \quad (4.53)$$

3. High polarization, Tafel approximation (explicit η expression):

$$\eta = \frac{R_u T}{\alpha_j F} \ln \left(\frac{i}{i_o} \right) \quad (4.54)$$

4. Both regions, $\alpha_a = \alpha_c$ sinh simplification (explicit η expression):

$$\frac{R_u T}{\alpha F} \sinh^{-1} \left(\frac{i_{\text{cell}}}{2i_o} \right) = \eta \quad (4.55)$$

Illustration 3.3, 3.4



Current efficiency

$$\eta_c = \frac{\text{current of desired reaction}}{\text{total current}}$$

Illustration 3.5