5. Electrode Processes 2

Learning subject

1. Butler-Volmer equation
2. Tafel plot
3. Mass transport

Learning objective

1. Understanding the relation between potential and current
2. Understanding Butler-Volmer equation and Tafel plot
3. Understanding limiting current from mass transport

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

1. Butler-Volmer equation

Nernst equation : equilibrium expression → electrode reaction rate? (kinetics)

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)

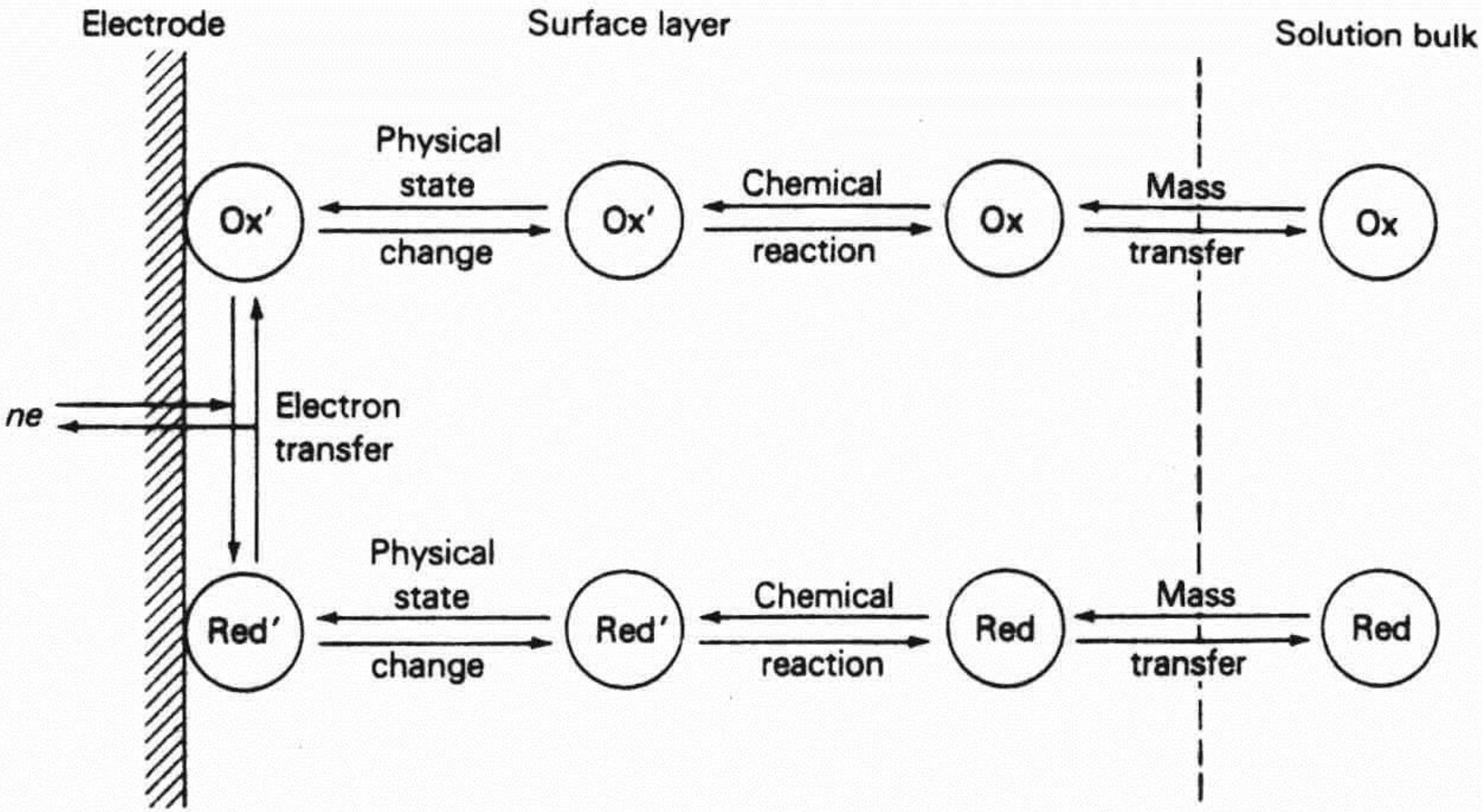


FIGURE 19–10 Steps in the reaction Ox + *ne* ⇌ Red at an electrode. Note that the surface layer is only a few molecules thick. (Adapted from: A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, p. 21, Wiley: New York, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

Review of homogeneous kinetics

Dynamic equilibrium

$$O + e \underset{k_b}{\overset{k_f}{=}} R$$

Rate of the forward process

$$v_f\ (M/s) = k_f C_A$$

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

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

At equilibrium, $v_{net} = 0$

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

*kinetic theory predicts a const conc ratio at equilibrium, just as thermodynamics

At equilibrium, kinetic equations → thermodynamic ones

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

Exchange velocity

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

Relationship between current and heterogeneous rate constants

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

Amount of electricity,

$$\mathbf{q = nFN}$$

n: electron number, N: number of moles, F: Faraday constant (96485 C/mol)

e.g., $PbSO_4(s) + 2H_2O(l) \rightarrow 2e^- + PbO_2(s) + HSO_4^-(aq) + 3H^+(aq)$

$$q/2F = -\Delta N_{PbSO4} = -\Delta N_{H2O}/2 = \Delta N_{PbO2} = \Delta N_{HSO4-} = \Delta N_{H+}/3$$

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,

$$R \rightarrow ne^- + O$$

Then,

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

$I = dq/dt = nFdN/dt$

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

$$O + e^- = R$$

$$E_n = E^0 – RT/F \ln(c_R/c_O)$$

depends on the concentrations of the two species and $E^{0’}$

“=” means,

$$R \rightarrow e^- + O$$
$$O + e^- \rightarrow R$$

At E_n (E_{eq}), the rates

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

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,

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

<u>net reaction rate</u>: the rate at which R is destroyed , or the rate at which O is created, per unit area of electrode (unit of molm^{-2}s^{-1}) “heterogeneous reaction rate”

$$r_{net}(E) = -(1/A)(dN_R/dt) = (1/A)(dN_O/dt)$$

$$\mathbf{r_{ox}(E) = k_{ox}(E)c_R{}^s}$$

“s” means that the concentrations at the electrode surface

k_{ox}(E): oxidative rate constant (ms^{-1})

$$\mathbf{r_{rd}(E) = k_{rd}(E)c_O{}^s}$$

k_{rd}(E): reductive rate constant

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

From $r_{net}(E) = r_{ox}(E) - r_{rd}(E)$, $r_{ox}(E) = k_{ox}(E)c_R$, $r_{rd}(E) = k_{rd}(E)c_O$

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

$$\mathbf{i = nF[k_{ox}c_R^{\,s} - k_{rd}c_O^{\,s}]}$$

cf) $k_{ox} = k_a$ of anode, $k_{rd} = k_c$ of cathode

when $k_{ox}(E)c_R^{\,s} = k_{rd}(E)c_O^{\,s}$ → zero current → equilibrium

when $k_{ox}(E)c_R^{\,s} > k_{rd}(E)c_O^{\,s}$ → anodic current (i_a) → oxidation of R to O

when $k_{ox}(E)c_R^{\,s} < k_{rd}(E)c_O^{\,s}$ → cathodic current (i_c) → reduction of O to R

Potential dependence of heterogeneous rate constants

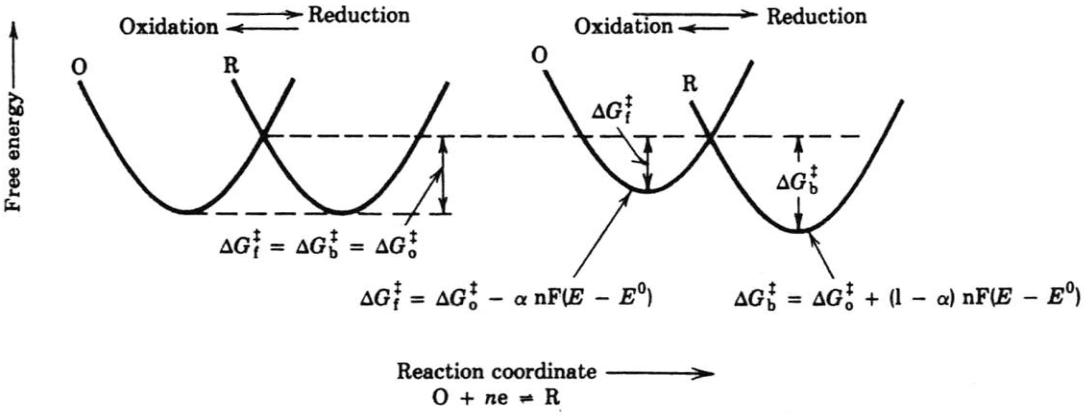
$$O + ne^- = R$$

Transition state model,

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

where $\Delta G_f^{\ddagger}$ 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 (→) is reduction one.



(a) Equilibrium (b) Net reduction

(a) equilibrium between O and R

O → R: pass over the activation free energy barrier, $\Delta G_f^{\ddagger}$

R → O: pass over the activation free energy barrier, $\Delta G_b^{\ddagger}$

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

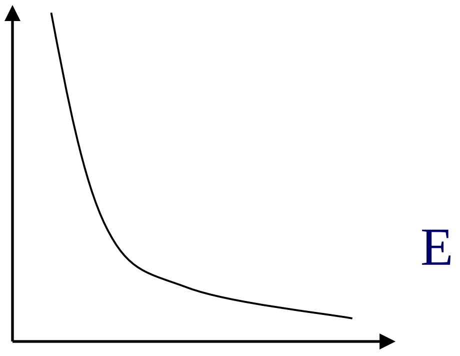
No net current means same rates between forward and backward (not zero current) → **exchange current i_0** at equilibrium; $i_0 = i_c = -i_a$

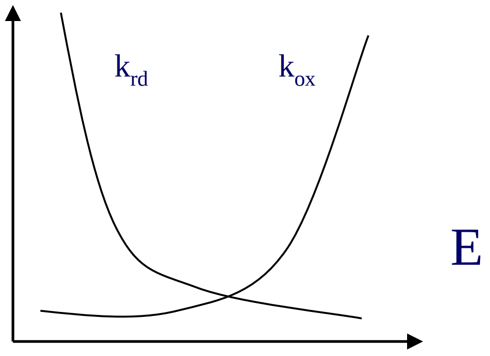
$$i_0 \uparrow \text{ as } \Delta G \downarrow$$

(b) net reduction

<u>applying negative potentials</u>

reduction: more negative potential → $k_f \uparrow, k_b \downarrow$





Negative potential E → lower $\Delta G_f^{\ddagger}$ and raise $\Delta G_b^{\ddagger}$
Potential change $E - E^0$ → free energy change $-nF(E-E^0)$ ⇒ part of this energy change (factor α) → decrease in the activation barrier for reduction (forward reaction) ; part (factor (1 - α)) → increase in the activation barrier for oxidation

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

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

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

$$O + ne^- \rightarrow R$$

Actually, $O + \alpha ne- \rightarrow R - (1 - \alpha)ne-$

α, -(1-α); orders of the reductive and oxidative processes another interpretation of α: increasing electrochemical activity of electrons → it accelerates the reductive process and retards the oxidative process → 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

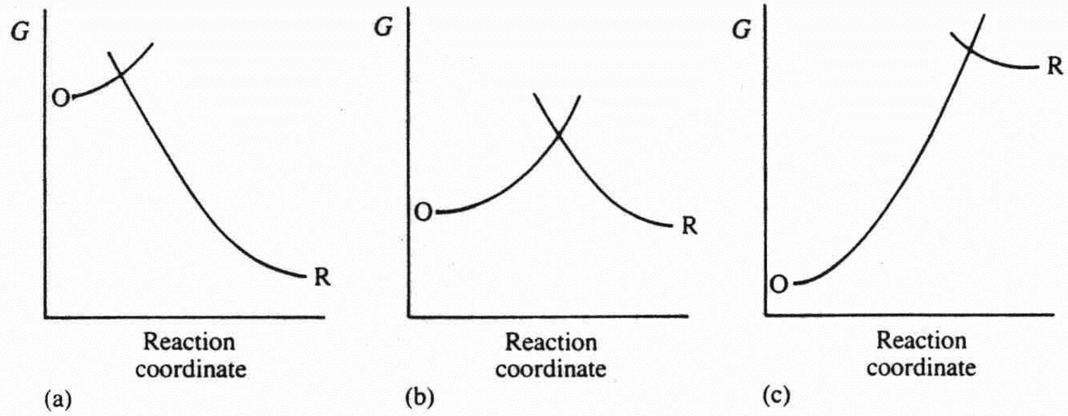


Fig. 4.4 Energy profiles for the cases (a) $\alpha_c \approx 0$; (b) $\alpha_c \approx \frac{1}{2}$; (c) $\alpha_c \approx 1$.

Arrhenius form,

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

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

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

Relationship between current and potential

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

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

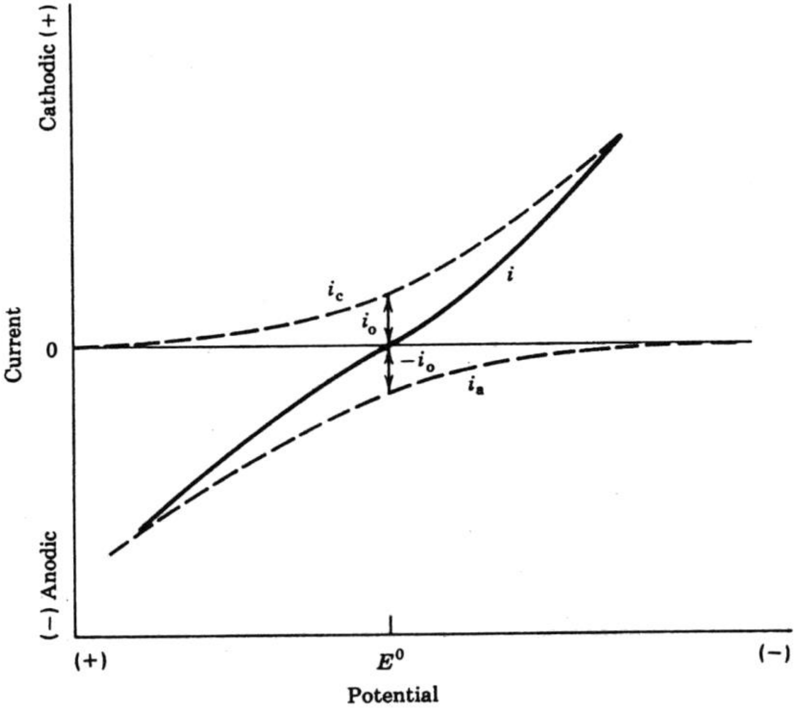
$$i_a = -\, nFk^0 c_R^s \exp\{(1-\alpha)nF(E-E^0)/RT\}$$

$$i = i_c + i_a$$

Butler-Volmer equation

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

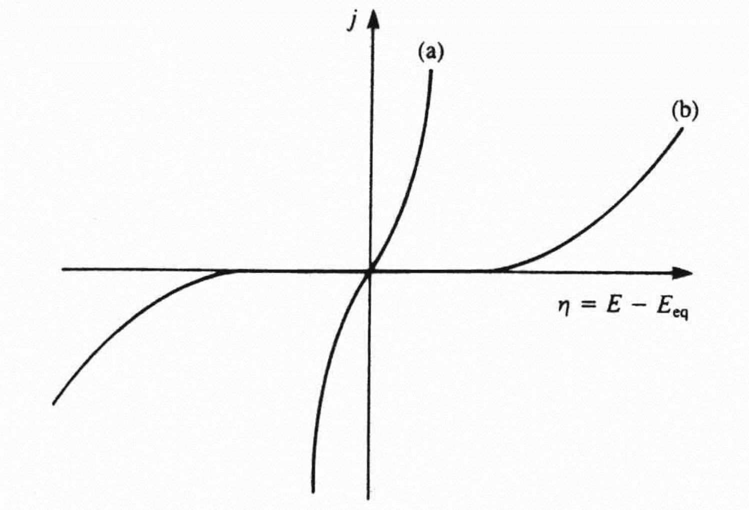
This relationship links the faradaic current, electrode potential, the concentrations of electroactive species at the electrode surface



i and i_c and i_a as a function of potential E; negative E ↑→ i_c ↑ (forward reaction), positive E ↑→ i_a ↑ (backward)

k^0; 1 ~ 50 cm s^{-1} for very fast reactions, 10^{-9} cm s^{-1} for very slow reactions.

Exchange current density i_0; 10 Acm^{-2} ~ 1 $pAcm^{-2}$



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)

$$E = E^0 – (RT/nF)\ln(c_R{}^s/c_O{}^s)$$

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

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

high exchange current density → high reaction rate

2. Tafel plot

Essentials of electrode reactions

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

$$\mathrm{O} + n\mathrm{e} \underset{k_b}{\overset{k_f}{=}} \mathrm{R}$$

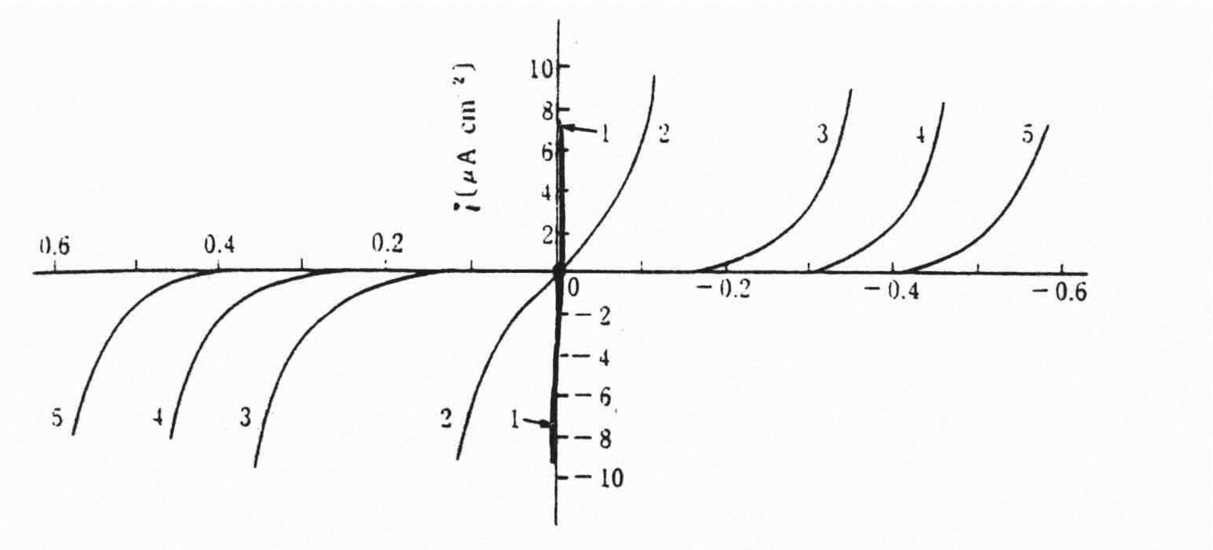
Equilibrium is characterized by the Nernst equation

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

bulk conc

Kinetic: dependence of current on potential

Overpotential $\eta = a + b\log i$ Tafel equation



The effect of exchange current density on overpotential

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

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

$\eta >> 0$ (oxidation, only O in bulk) $\rightarrow \exp(-\alpha nf\eta) << \exp((1-\alpha)nf\eta)$

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

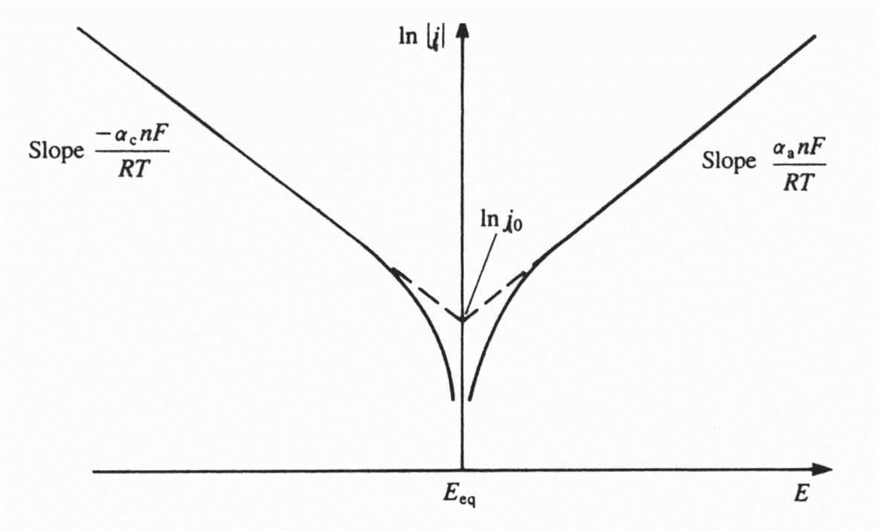
apply log,

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

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

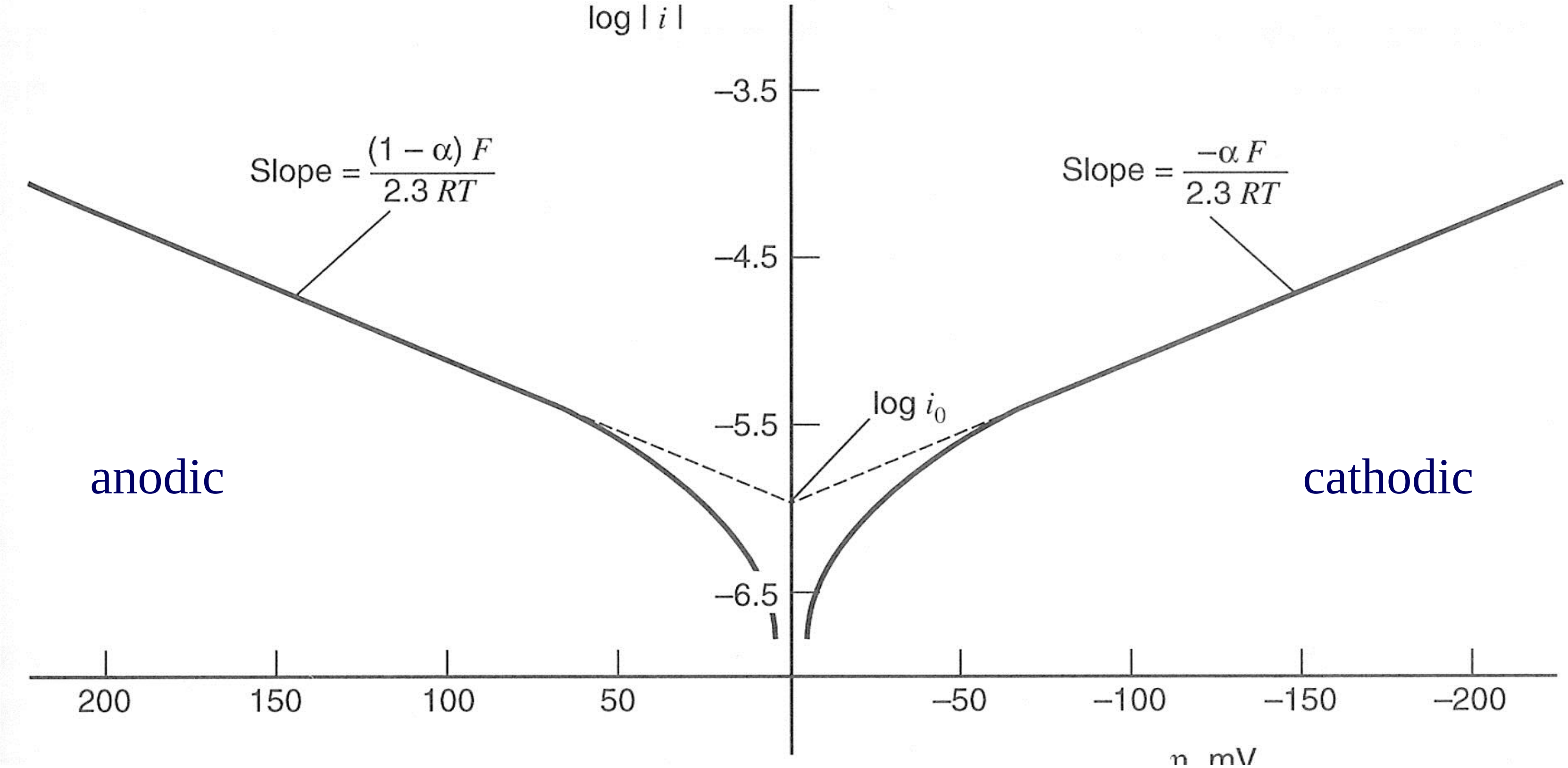
Tafel plot → measure i_0 and α

$$\mathbf{E - E^0 = \eta = a}\boldsymbol{ln}\,\mathbf{i_0 \pm b}\boldsymbol{ln}\,\mathbf{|i|}$$



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)

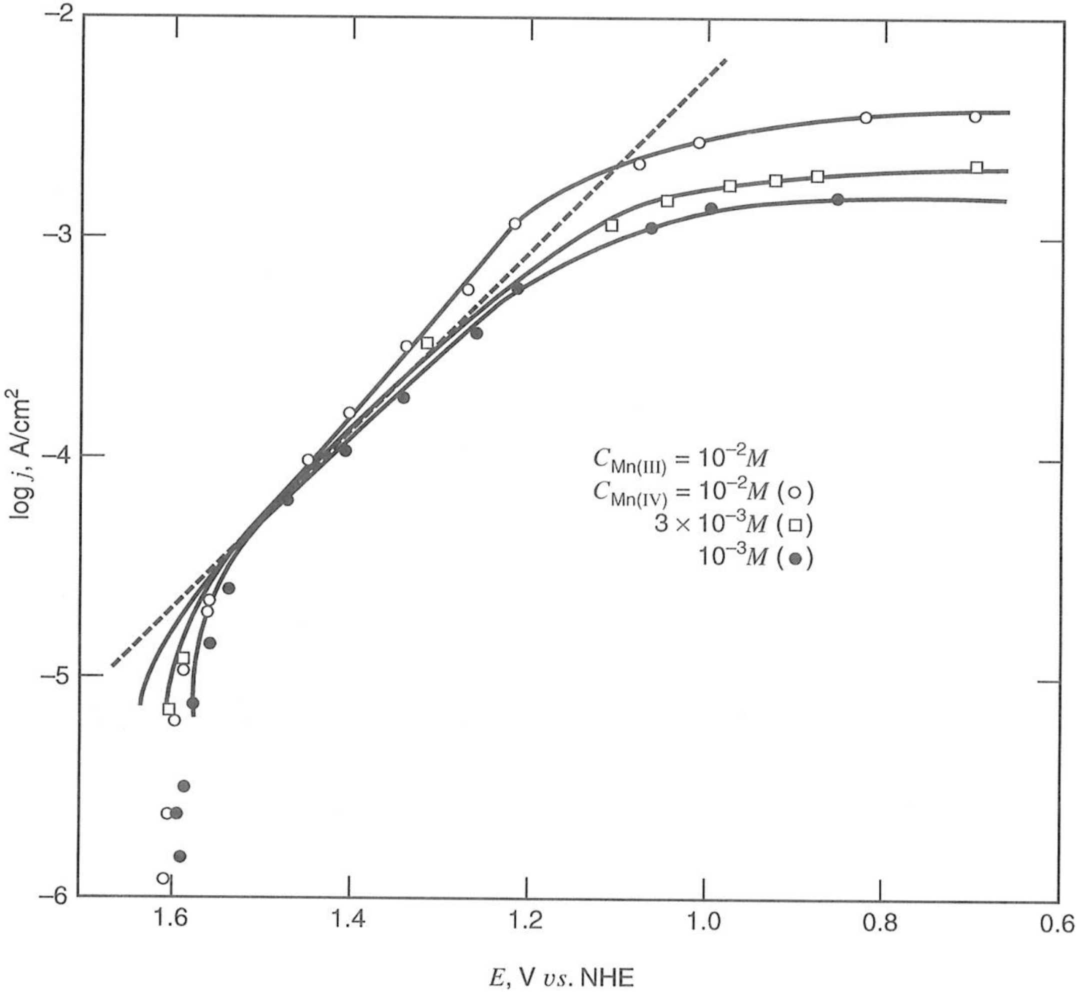


anodic

cathodic

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

- At very large overpotential: mass transfer limitation



Summary of Butler–Volmer Kinetics and Useful Simplifications

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

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

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

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

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

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

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

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

3. Mass Transport

Mass transport

$$\text{rate} = k_a \mathbf{C_R}^{\mathbf{s}} - k_c \mathbf{C_O}^{\mathbf{s}}$$

Electrochemical reaction at electrode/solution interface: molecules in bulk solution must be transported to the electrode surface → "mass transfer"

$$C_O^b = C_O^s = C_R^s = C_R^b$$

<u>Mechanisms for mass transport</u>:

(a) Migration: movement of a charged body under the influence of an electric field (a gradient of electric potential)

(b) Diffusion: movement of species under the influence of gradient of chemical potential (i.e., a concentration gradient)

(c) Convection: stirring or hydrodynamic transport

Nernst-Planck equation (diffusion + migration + convection)

$$J_i(x) = -D_i(\partial C_i(x)/\partial x) - (z_i F/RT) D_i C_i(\partial \phi(x)/\partial x) + C_i v(x)$$

Where $J_i(x)$; the flux of species i ($\text{molsec}^{-1}\text{cm}^{-2}$) at distance x from the surface, D_i; the diffusion coefficient (cm^2/sec), $\partial C_i(x)/\partial x$; the concentration gradient at distance x, $\partial \phi(x)/\partial x$; the potential gradient, z_i and C_i; the charge and concentration of species i, v(x); the velocity (cm/sec)

1. Steady state mass transfer

steady state, $(\partial C/\partial t) = 0$; the rate of transport of electroactive species is equal to the rate of their reaction on the electrode surface

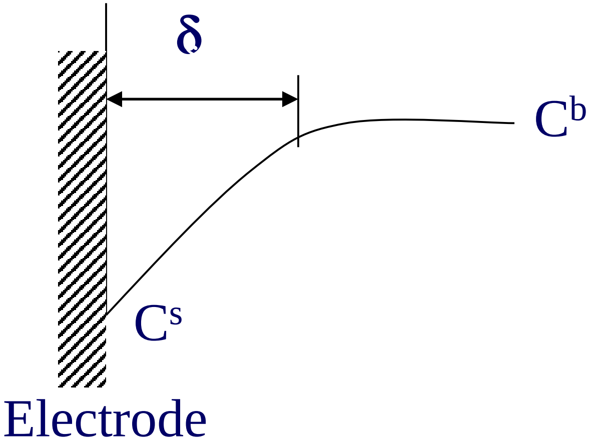
In the absence of migration,

$$R = O + ne^-$$

The rate of mass transfer,

$$v_{mt} \propto (\partial C_R(x)/\partial x)_{x=0} = (C_R^{\,b} - C_R^{\,s})/\delta$$

where x is distance from the electrode surface & δ: diffusion layer



$$v_{mt} = m_R[C_R^{\,b} – C_R^{\,s}]$$

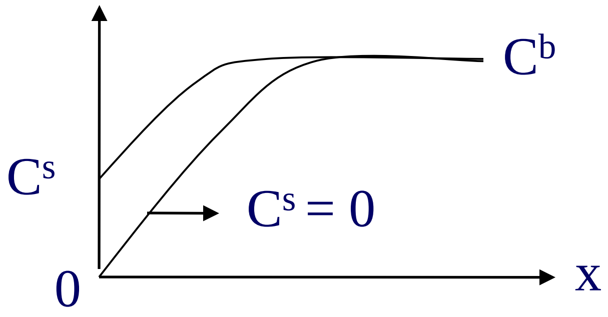
where $C_R^{\,b}$ is the concentration of R in the bulk solution, $C_R^{\,s}$ is the concentration at the electrod surface
m_R is “mass transfer coefficient”

$$i = nFm_R[C_R^{\,b} – C_R^{\,s}]$$

$$i = -nFm_O[C_O^{\,b} – C_O^{\,s}]$$

largest rate of mass transfer of R when $C_R^s = 0$ → “limiting current”

$$\mathbf{i_{l,a} = nFm_RC_R^b}$$



$$C_R^s/C_R^b = 1 – (i/i_{l,a})$$

And

$$C_R^s = [1 – (i/i_{l,a})]\ [\ i_{l,a}/nFm_R] = (i_{l,a} – i)/(nFm_R)$$

Same method,

$$C_O^s/C_O^b = 1 – (i/i_{l,c})$$

$$i_{l,c} = nFm_OC_O^b$$

$$C_O^s = [1 – (i/i_{l,c})]\ [\ i_{l,c}/nFm_O] = (i_{l,c} – i)/(nFm_O)$$

Put these equations to $E = E^0 - (RT/nF)\ln(C_R^s/C_O^s)$

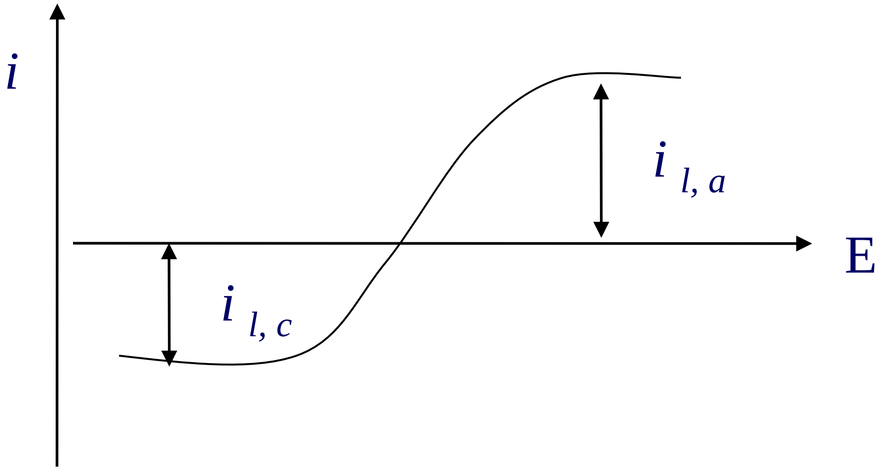
$$\mathbf{E = E^0 - (RT/nF)\ln(m_O/m_R) - (RT/nF)\ln[(i_{l,a} - i)/(i - i_{l,c})]}$$

Let

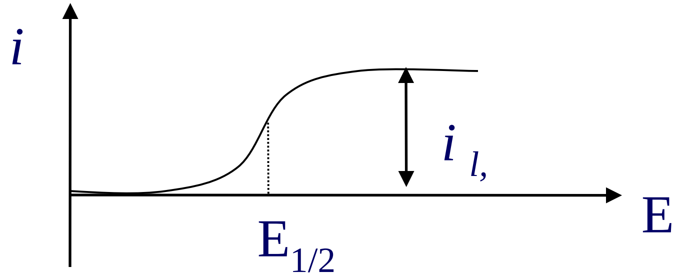
$$E_{1/2} = E^0 - (RT/nF)\ln(m_O/m_R)$$

Then,

$$E = E_{1/2} - (RT/nF)\ln[(i_{l,a} - i)/(i - i_{l,c})]$$



$E_{1/2}$, half-wave potential, independent of C_O^b and C_R^b → characteristic of the R/O system.



Reversibility:

<u>reversible</u>: $k^0 >> m_O$ or m_R → kinetic rate constant >> mass transport rate constant → system is at equilibrium at the electrode surface and it is possible to apply the Nernst equation at any potential

<u>irreversible</u>: $k^0 << m_O$ or m_R

2. Non-steady state mass transport: diffusion control

The rate of diffusion depends on the concentration gradients

$$J = -D(\partial C/\partial x) \quad \text{Fick's first law}$$

D: diffusion coefficient (cm^2/sec)

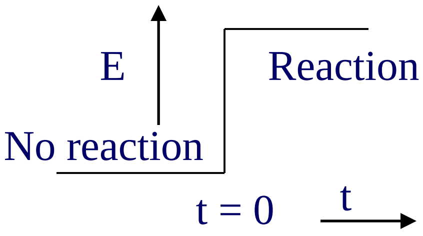
The variation of concentration with time due to diffusion → Fick's second law

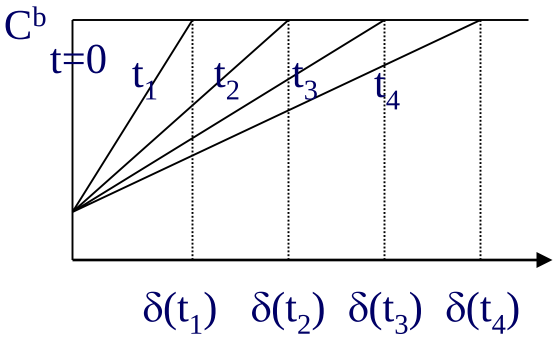
$$\partial C/\partial t = -D(\partial^2 C/\partial x^2) \qquad \text{1-D}$$

$$J = -D(\partial C/\partial x) = i/nF$$

$$D(\partial C/\partial x) = D(C^b - C^s)/\delta = i/nF$$

Time-dependent, applying potential step E





Moles of species in diffusion layer = $\int i\,dt/nF \approx [C^b - C^s](A\delta(t)/2)$

Differentiating,

$i/nF = [C^b - C^s](A d\delta(t)/2dt) = D(C^b - C^s)/\delta(t)$

$d\delta(t)/dt = 2D/\delta(t)$, $\delta(t) = 0$ at $t = 0$

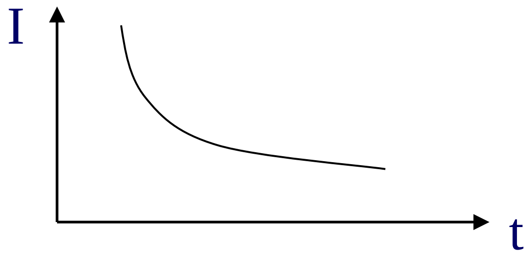
$\delta(t) = 2\sqrt{(Dt)}$

$$i/nF = (D^{1/2}/2t^{1/2})\,[C^b - C^s]$$

diffusion layer grows with $t^{1/2}$ and current decays with $t^{-1/2}$

potential step (chronoamperometry), planar electrode: <u>Cottrell equation</u> (in Table)

constant current → potential variation at time (chronopotentiometry): <u>Sand equation</u> (t = τ (transition time) at $C^s = 0$)



1. Polarization curve

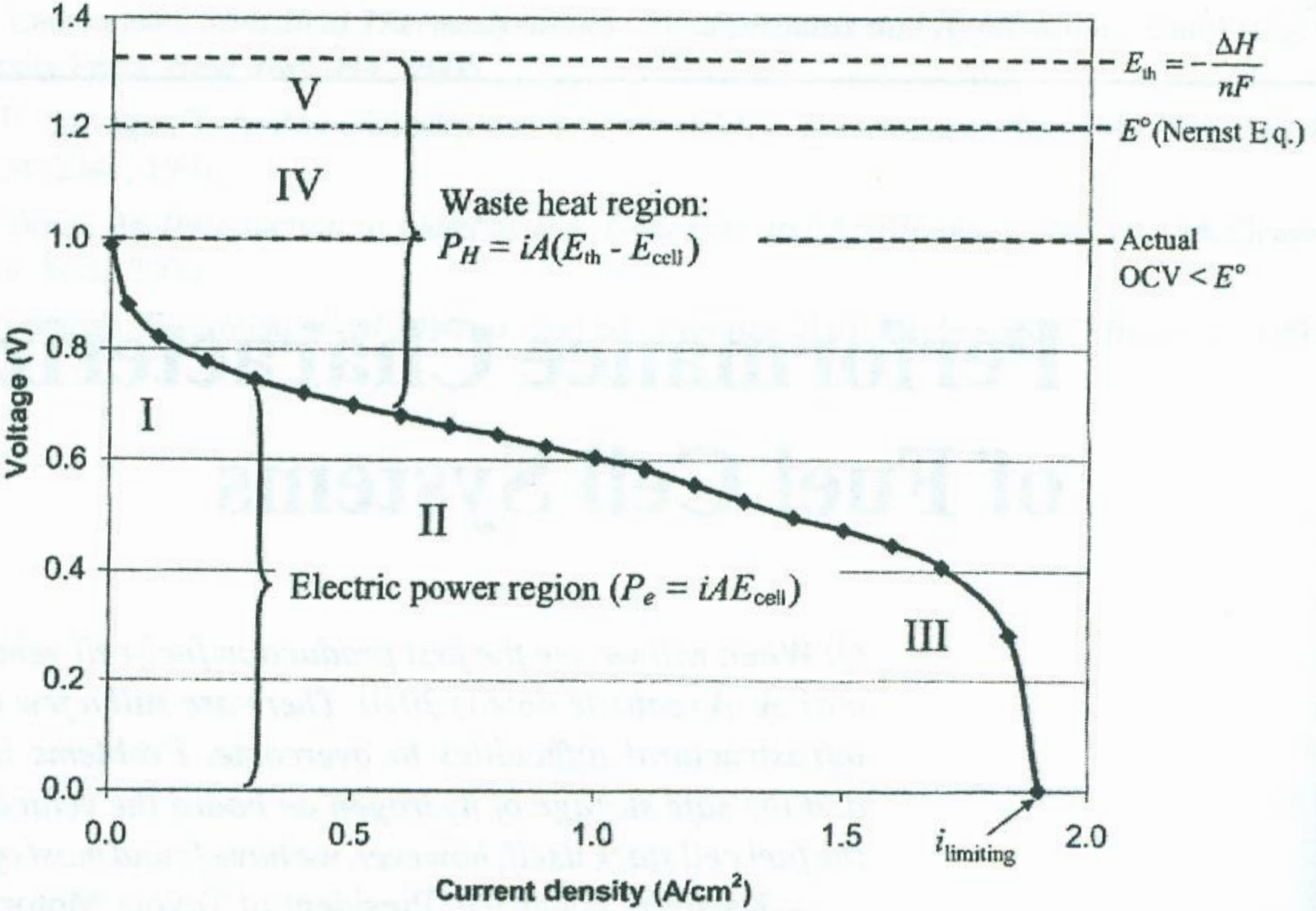


Figure 4.1 Typical polarization curve for fuel cell with significant kinetic, ohmic, concentration, and crossover potential losses.

hydrogen-air FC

-5 regions

(i) Region I: activation (kinetic) overpotential at the electrodes

(ii) Region II: ohmic polarization. Electric & ionic conduction loss

(iii) Region III: concentration polarization. Mass transport limitations

(iv) Region IV. Departure from Nernst thermodynamic equilibrium
potential; undesired species crossover through
electrolyte, internal currents from electron leakage,
other contamination or impurity

(v) Region V: the departure from the maximum thermal voltage; a
result of entropy change which cannot be engineered

-Regions I, II, III are not discrete → all modes of loss contribute throughout the entire current range

-Heat: current x (thermal voltage – FC voltage)

& electrical generation: cell current x FC voltage

-FC voltage:

$$E_{\text{cell}} = E^{\circ}(T, P) - \eta_{a,a} - |\eta_{a,c}| - \eta_r - \eta_{m,a} - |\eta_{m,c}| - \eta_x \qquad (4.1)$$