Potential Sweep Methods (Ch. 6)

Nernstian (reversible) systems
Totally irreversible systems
Quasireversible systems
Cyclic voltammetry
Multicomponent systems & multistep charge transfers

Introduction

Linear sweep voltammetry (LSV)

Cyclic voltammetry (CV)

Nernstian (reversible) systems

Solution of the boundary value problem

O + ne = R (semi-infinite linear diffusion, initially O present)

$$E(t) = E_i - vt$$

Sweep rate (or scan rate): v (V/s)

Rapid e-transfer rate at the electrode surface

$$C_O(0, t)/C_R(0, t) = f(t) = \exp[nF\,(E_i - vt - E^{0'})/RT]$$

$$i = nFAC_O^*(\pi D_O \sigma)^{1/2}\chi(\sigma t)$$

$\sigma = (nF/RT)v$

Peak current and potential

Peak current: $\pi^{1/2}\chi(\sigma t) = 0.4463$

$$i_p = 0.4463(F^3/RT)^{1/2}n^{3/2}AD_O^{1/2}C_O^*v^{1/2}$$

At 25°C, for A in cm², D_O in cm²/s, C_O^* in mol/cm³, v in V/s → i_p in amperes

$$i_p = (2.69 \times 10^5)n^{3/2}AD_O^{1/2}C_O^*v^{1/2}$$

Peak potential, E_p

$$E_p = E_{1/2} - 1.109(RT/nF) = E_{1/2} - 28.5/n \quad \text{mV at } 25°\text{C}$$

Half-peak potential, $E_{p/2}$

$$E_{p/2} = E_{1/2} + 1.09(RT/nF) = E_{1/2} + 28.0/n \quad \text{mV at } 25°\text{C}$$

$E_{1/2}$ is located between E_p and $E_{p/2}$

$$|E_p - E_{p/2}| = 2.20(RT/nF) = 56.5/n \quad \text{mV at } °\text{C}$$

For reversible wave, <u>E_p is independent of scan rate, i_p is proportional to $v^{1/2}$</u>

Spherical electrodes and UMEs

Spherical electrode (e.g., a hanging mercury drop)

$$i = i(\text{plane}) + nFAD_O C_O{}^{*}\phi(\sigma t)/r_0$$

$\phi(\sigma t)$: tabulated function (Table 6.2.1)

For large v in conventional-sized electrode → i(plane) >> 2^{nd} term
Same for hemispherical & UME at fast scan rate

For UME at very small v: r_0 is small → i(plane) << 2^{nd} term
→ voltammogram is a steady-state response independent of v
→ $v \ll RTD/nFr_0^2$
r_0 = 5 μm, D = 10^{-5} cm^2/s, T = 298 K → steady-state voltammogram at v < 1 V/s
r_0 = 0.5 μm → steady-state behavior up to 10 V/s

Transition from typical peak-shaped voltammograms at fast v to steady-state voltammograms at small v cf. For potential sweep (Ch.1)

Linear potential sweep with a sweep rate v (in V/s)

$$E = vt$$

$E = E_R + E_C = iR_s + q/C_d$

$$vt = R_s(dq/dt) + q/C_d$$

If $q = 0$ at $t = 0$, $\quad i = vC_d[1 – \exp(-t/R_sC_d)]$

- Current rises from 0 and attains a steady-state value (vC_d): <u>measure C_d</u>

Effect of double-layer capacitance & uncompensated resistance

Charging current at potential sweep

$$|i_c| = AC_d v$$

Faradaic current measured with baseline of i_c

i_p varies with $v^{1/2}$, i_c varies with $v \rightarrow$ $\underline{i_c \text{ more important at faster } v}$

$$|i_c|/i_p = [C_d v^{1/2}(10^{-5})]/[2.69 n^{3/2} D_O^{1/2} C_O^*]$$

At high v & low $C_O^* \rightarrow$ severe distortion of the LSV wave

R_u cause E_p to be a function of v

Totally irreversible systems

Solution of the boundary value problem

Totally irreversible one-step, one-electron reaction: $O + e \xrightarrow{k_f} R$

$$i/FA = D_O(\partial C_O(x, t)/\partial x)_{x=0} = k_f(t)C_O(0, t)$$

Where $k_f = k^0 e^{-\alpha f(E(t) - E0')}$, $E(t) = E_i - vt$

$\rightarrow$ $$k_f(t)C_O(0, t) = k_{fi}C_O(0, t)e^{bt}$$

Where $b = \alpha fv$ & $k_{fi} = k^0\exp[-\alpha f(E_i - E^{0'})]$

$$i = FAC_O^*D_O^{1/2}v^{1/2}(\alpha F/RT)^{1/2}\chi(bt)$$

$\chi(bt)$ (Table 6.3.1). i varies with $v^{1/2}$ and C_O^*

For spherical electrodes

$$i = i(\text{plane}) + FAD_OC_O^*\phi(bt)/r_0$$

Peak current and potential

Maximum $\chi(bt)$ at $\pi^{1/2}\chi(bt) = 0.4958$

Peak current

$$i_p = (2.99 \times 10^5)\alpha^{1/2}AC_O^*D_O^{1/2}v^{1/2}$$

n-electron process with RDS: n in right side

Peak potential

$$\alpha(E_p - E^{0\prime}) + (RT/F)\ln[(\pi D_O b)^{1/2}/k^0] = -0.21(RT/F) = -5.34 \text{ mV at } 25^\circ\text{C}$$

Or

$$E_p = E^{0\prime} - (RT/\alpha F)[0.780 + \ln(D_O^{1/2}/k^0) + \ln(\alpha Fv/RT)^{1/2}]$$

$$|E_p - E_{p/2}| = 1.857RT/\alpha F = 47.7/\alpha \text{ mV at } 25^\circ\text{C}$$

E_p: ftn of v → for reduction, $1.15RT/\alpha F$ (or $30/\alpha$ mV at 25°C) negative shift for tenfold increase in v

$$i_p = 0.227FAC_O^*k^0\exp[-\alpha f(E_P - E^{0\prime})]$$

→ i_p vs. $E_p - E^{0\prime}$ plot at different v: slope of $-\alpha f$ and intercept proportional to k^0
n-electron process with RDS: n in right side

Quasireversible systems

For one-step, one-electron system

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

For the quasireversible one-step, one-electron case (5.5.3, p. 191)

$$i/FA = D_O(\partial C_O(x, t)/\partial x)_{x=0} = k_f C_O(0, t) - k_b C_R(0, t)$$

Where $k_f = k^0 e^{-\alpha f(E - E0')}$ & $k_b = k^0 e^{(1-\alpha) f(E - E0')}$, $f = F/RT$

The shape of peak & peak parameters → ftns of α & Λ

$$\Lambda = k^0/(D_O^{1-\alpha} D_R^{\alpha} f v)^{1/2}$$

Or for $D_O = D_R = D$

$$\Lambda = k^0/(Dfv)^{1/2}$$

Current

$$i = FAD_O^{1/2} C_O^* f^{1/2} v^{1/2} \Psi(E)$$

$\Psi(E)$ (Fig. 6.4.1): <u>$\Lambda > 10$ → approach to the reversible</u>

Cyclic voltammetry

$(0 < t \leq \lambda)$ $E = E_i - vt$

$(t > \lambda)$ $E = E_i - 2v\lambda + vt$

Nernstian systems

i-t curve at different E_λ

i-E curve (CV) at different E_λ

(1) E_λ (1) $E_{1/2}$ – 90/n, (2) $E_{1/2}$ – 130/n, (3) $E_{1/2}$ – 200/n mV, (4) after $i_{pc} \to 0$

i_{pa}/i_{pc} = 1 for nernstian regardless of scan rate, E_λ (> 35/n mV past E_{pc}), D

$i_{pa}/i_{pc} \rightarrow$ kinetic information

If actual baseline cannot be determined,

$$i_{pa}/i_{pc} = (i_{pa})_0/i_{pc} + 0.485(i_{sp})_0/i_{pc} + 0.086$$

Reversal charging current is same as forward scan, but opposite sign

$\Delta E_p = E_{pa} - E_{pc} \sim 2.3RT/nF$ (or 59/n mV at 25°C)

Quasireversible systems

Wave shape & $\Delta E_p \rightarrow$ ftns of v, k^0, α & E_λ

If E_λ > 90/n mV beyond cathodic peak $\rightarrow$ small E_λ effect

$$\Psi = \Lambda\pi^{-1/2} = [k^0(D_O/D_R)^\alpha]/(\pi D_O f v)^{1/2}$$

(1) $\Psi = 0.5$, $\alpha = 0.7$, (2) $\Psi = 0.5$, $\alpha = 0.3$, (3) $\Psi = 7$, $\alpha = 0.5$, (4) $\Psi = 0.25$, $\alpha = 0.5$

For $0.3 < \alpha < 0.7 \rightarrow \Delta E_p$ independent of α; depend only on Ψ
$\rightarrow$ estimating k^0 in quasireversible systems

ΔE_p vs. $v \rightarrow \Delta E_p$ vs Ψ

Multicomponent systems & Multistep charge transfers

O & O´ system

Method for obtaining baselines

Constant E after 1

Sweep stop beyond E_{p1}

In vivo applications of LSV & CV
e.g., rat brain