

Analysis of Electrochemical Systems

1. Overview
2. Potential step method
3. Electrode kinetics and double-layer charging
4. Potential sweep method
5. Electrochemical impedance
6. Hydrodynamic method

Electrochemical instrumentation

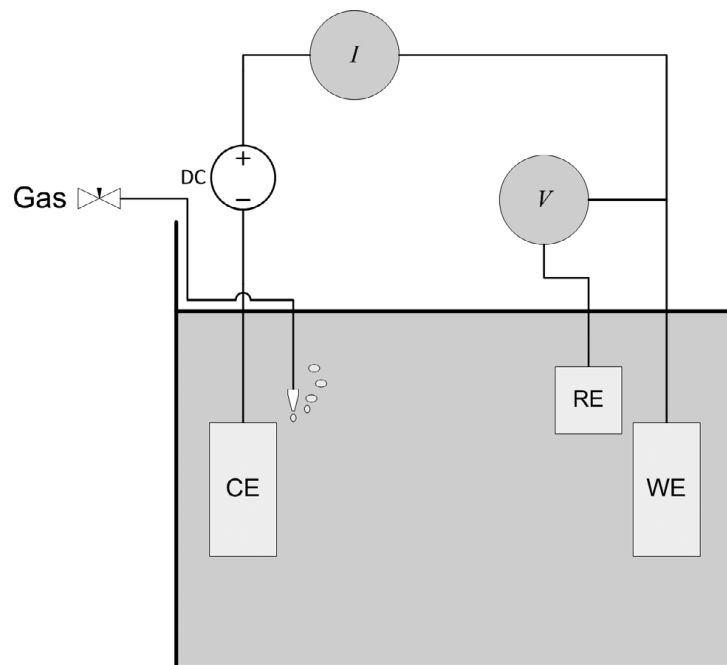
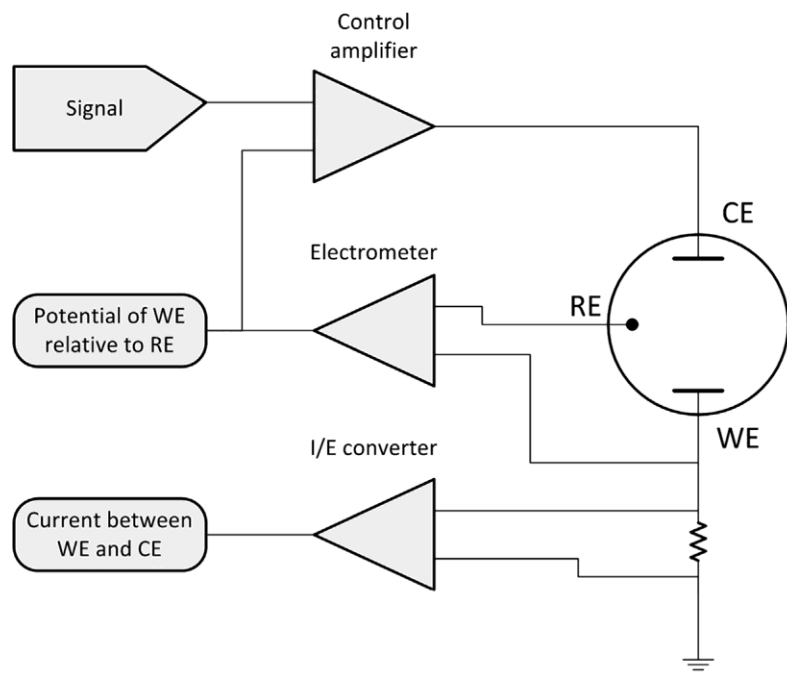


Figure 6.1 Schematic diagram of typical three-electrode setup.

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Potential step method

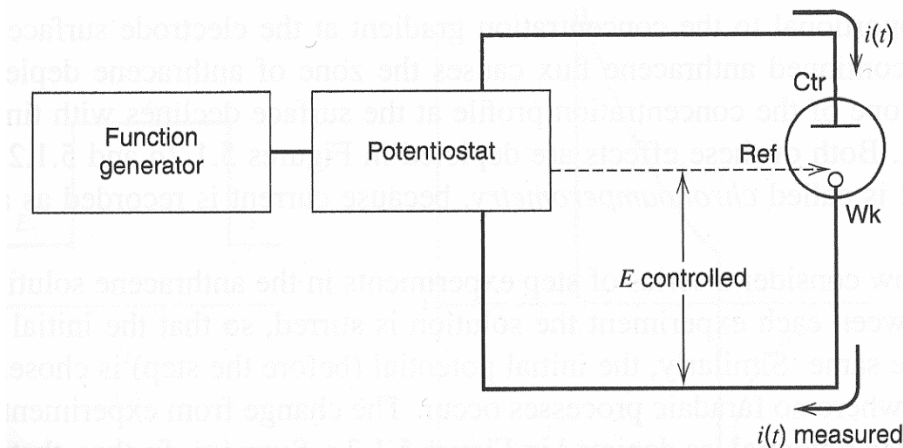


Figure 5.1.1
Experimental arrangement
for controlled-potential
experiments.

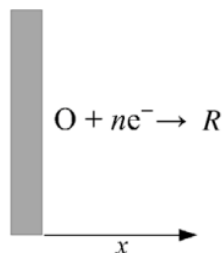


Figure 6.3 One-dimensional planar working electrode.

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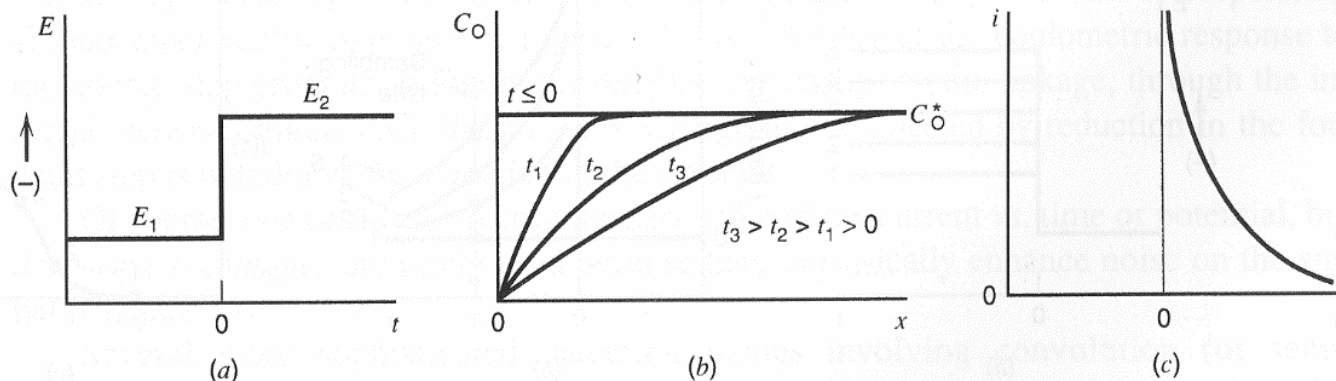


Figure 5.1.2 (a) Waveform for a step experiment in which species O is electroinactive at E_1 , but is reduced at a diffusion-limited rate at E_2 . (b) Concentration profiles for various times into the experiment. (c) Current flow vs. time.

Cottrell equation (a planar electrode in unstirred solution)

$$i(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}} \quad (5.2.11)$$

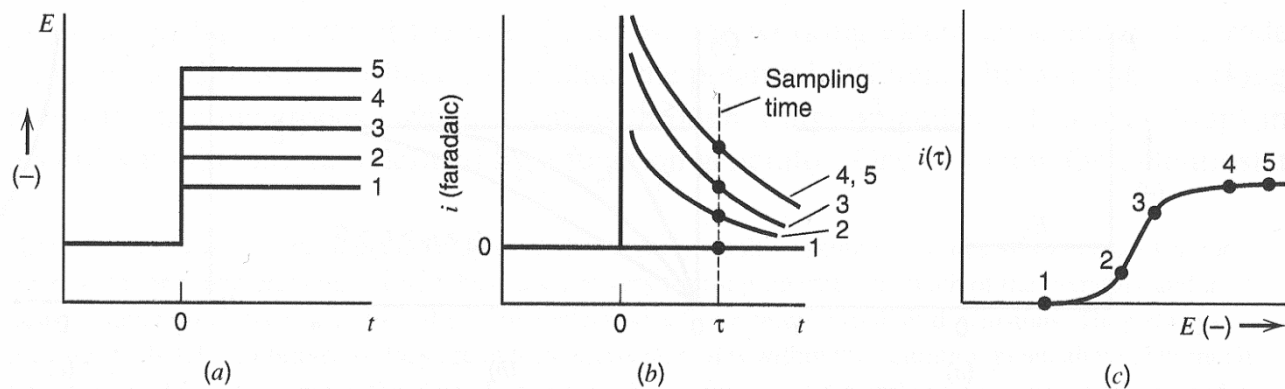
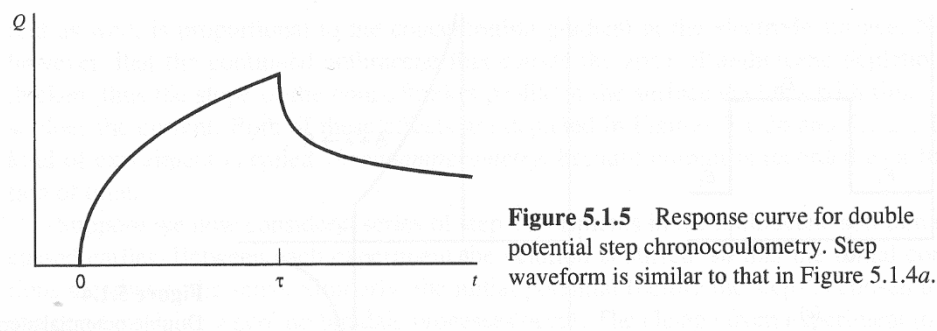
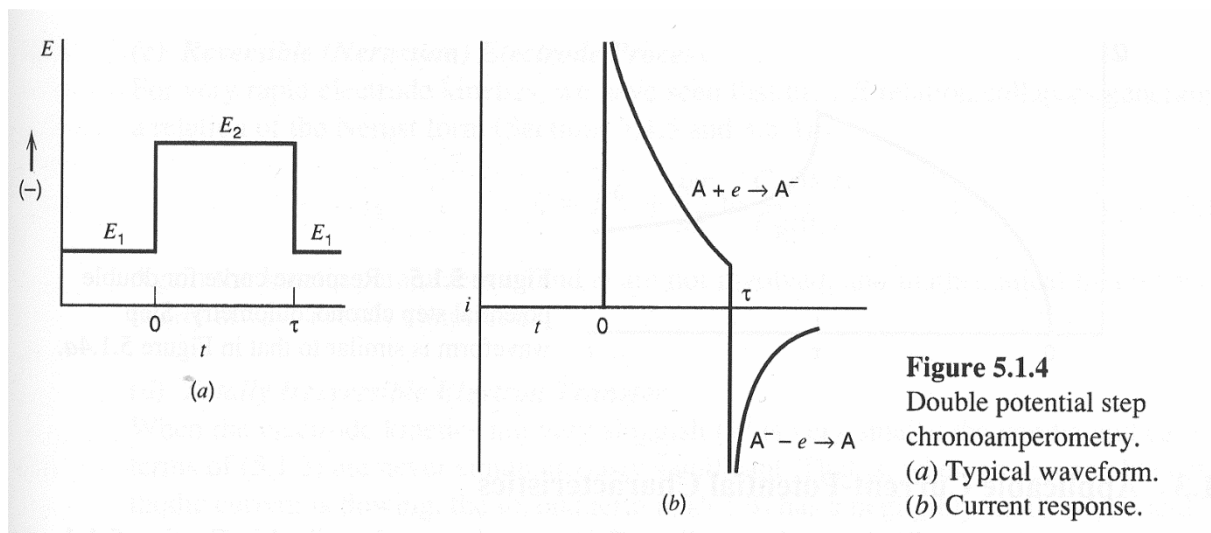


Figure 5.1.3 Sampled-current voltammetry. (a) Step waveforms applied in a series of experiments. (b) Current-time curves observed in response to the steps. (c) Sampled-current voltammogram.

Sampled-current voltammetry (reversible reaction)

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d(\tau) - i(\tau)}{i(\tau)} \quad (5.4.22)$$



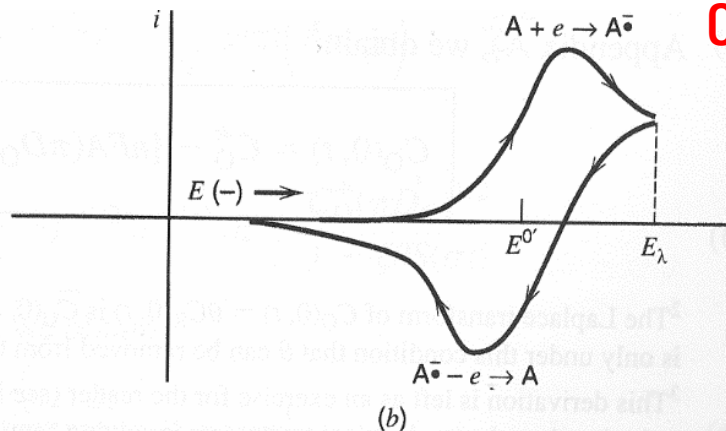
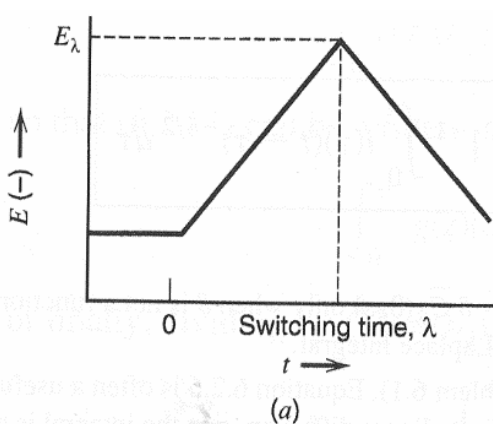
Chronocoulometry

Chronocoulometry, forward step:

$$Q = \frac{2nFAD_O^{1/2}C_O^*t^{1/2}}{\pi^{1/2}} + Q_{dl} + nFA\Gamma_O \quad (5.8.2)$$

Potential sweep method (전위 주사 실험)

전위를 시간에 따라 변화시켜 전류를 측정



순환 전압-전류법

Figure 6.1.3 (a) Cyclic potential sweep. (b) Resulting cyclic voltammogram.

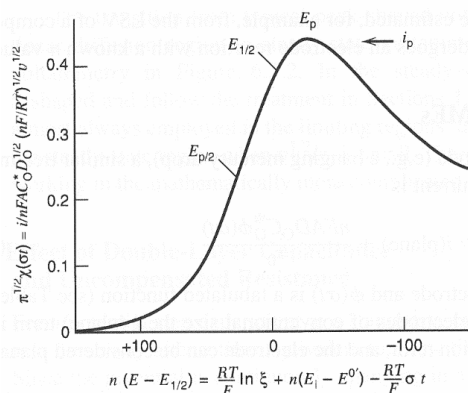


Figure 6.2.1 Linear potential sweep voltammogram in terms of dimensionless current function. Values on the potential axis are for 25°C

$$E_{1/2} = E^0 + (nF/RT)\ln(D_R/D_O)^{1/2} \sim E^0$$

- $E_{p,c} - E_{1/2} = -28.8/n, \text{ mV}$
- $E_{p/2,c} - E_{1/2} = -28.0/n, \text{ mV}$
- $E_{p,c} - E_{p/2,c} = 56.6/n, \text{ mV}$

Linear sweep voltammetry, forward peak current for a reversible system:

$$i_p = (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C_O^* v^{1/2} \quad (6.2.19)$$

$$i_p \sim 200 \mu\text{A/cm}^2 \text{ area/mM} \quad (n = 1, v = 0.1 \text{ V/s})$$

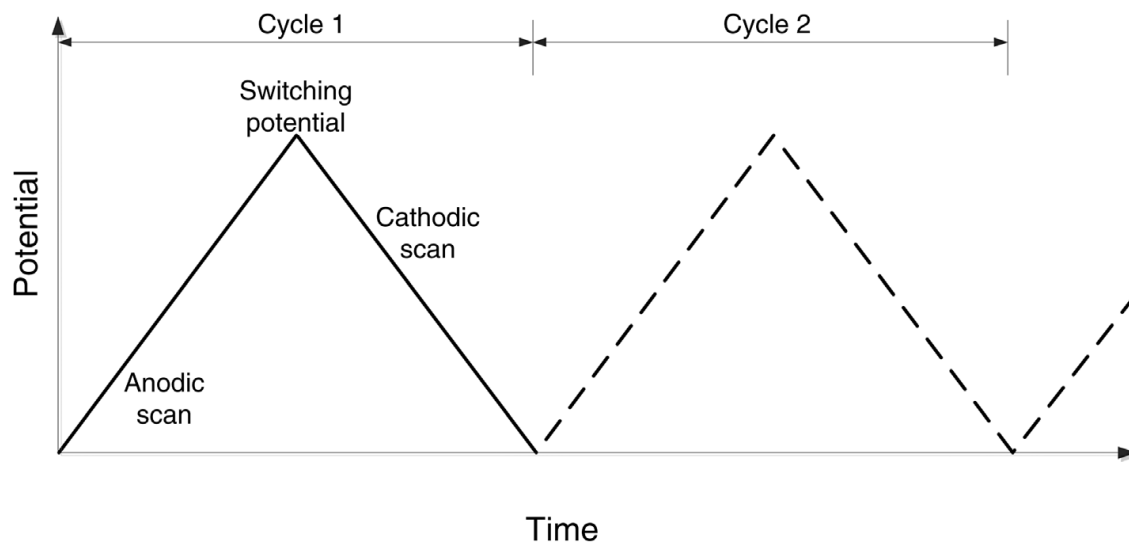


Figure 6.9 Triangle wave used in cyclic voltammetry.

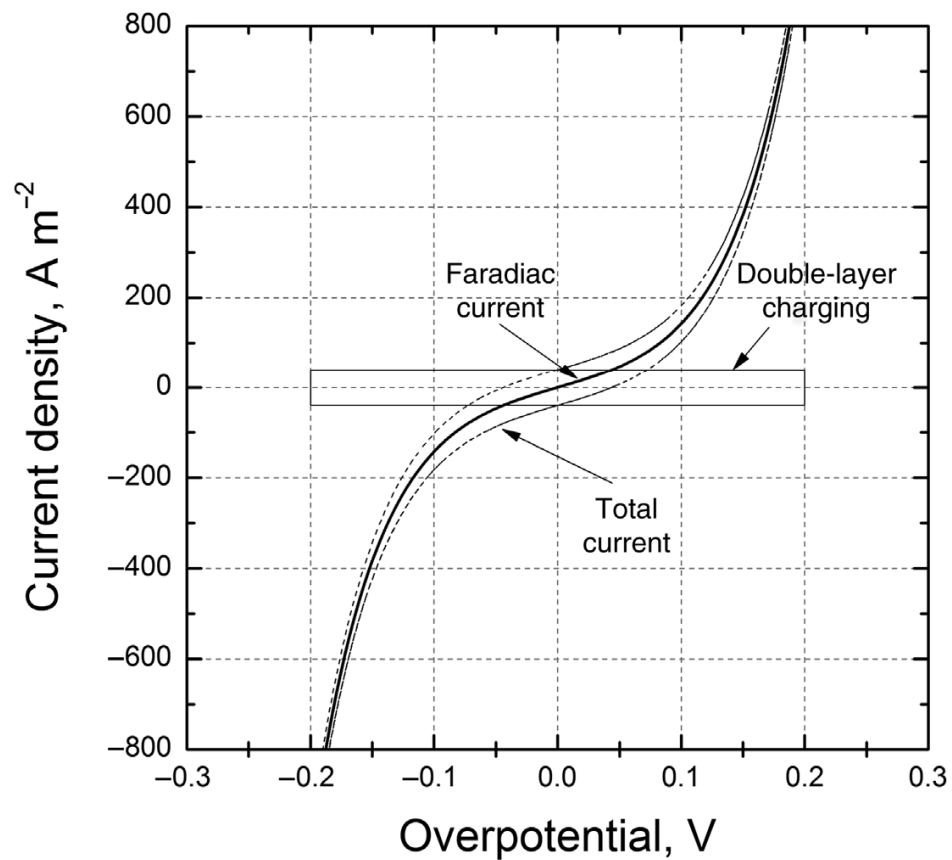


Figure 6.10 Cyclic voltammogram in the absence of mass transfer.

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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

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

Half-peak potential, E_{p/2}

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

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

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

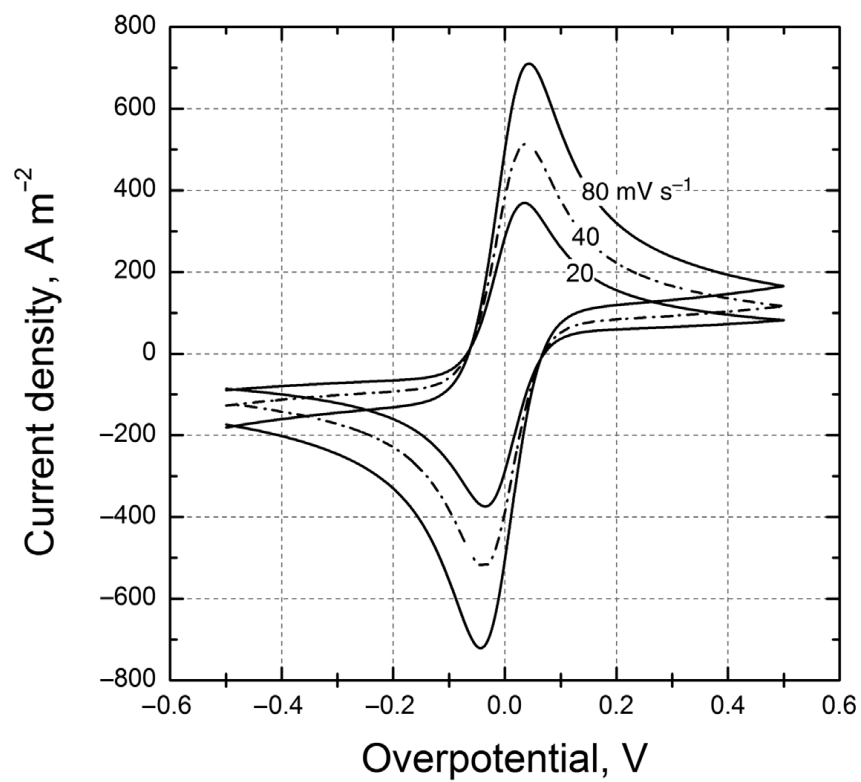


Figure 6.13 Effect of scan rate for a reversible reaction. Double-layer charging has been removed.

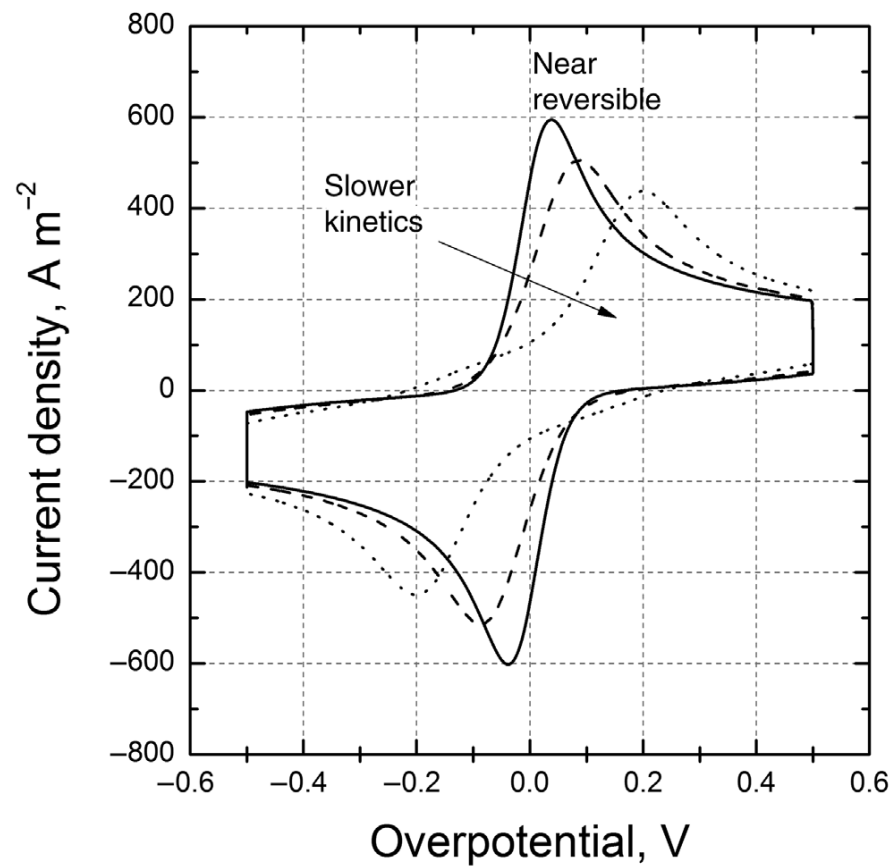
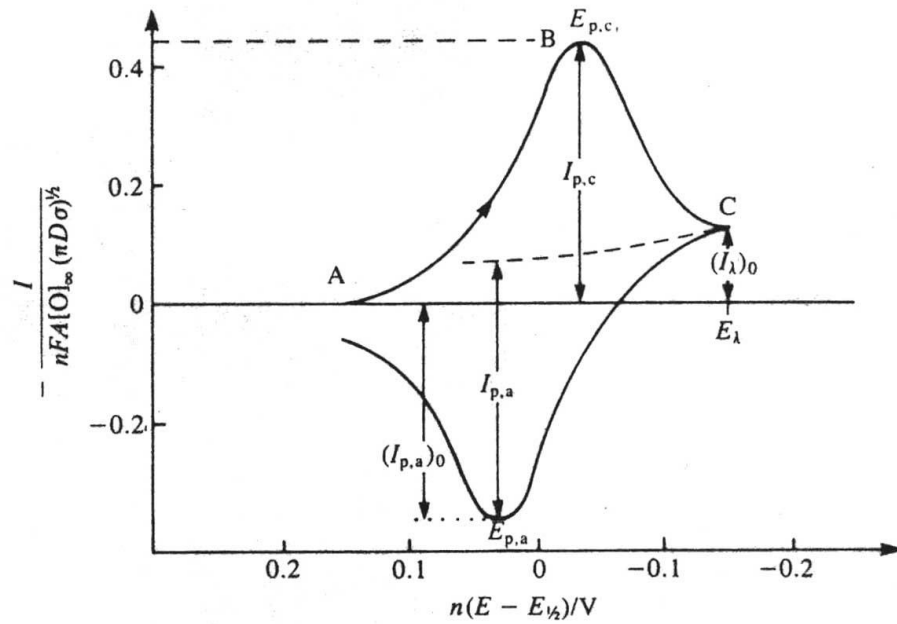
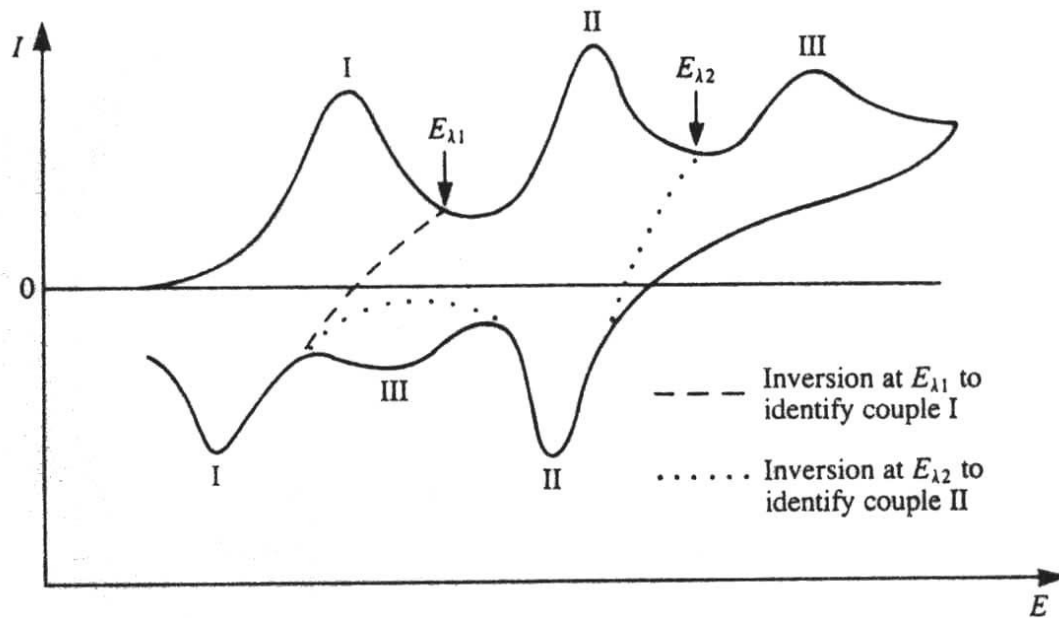


Figure 6.14 Effect of the exchange-current density on the cyclic voltammogram when kinetic limitations are important.



$$E_{p,a} - E_{p,c} = 57/n, \text{ mV}$$

$$|I_{p,a}/I_{p,c}| = 1$$



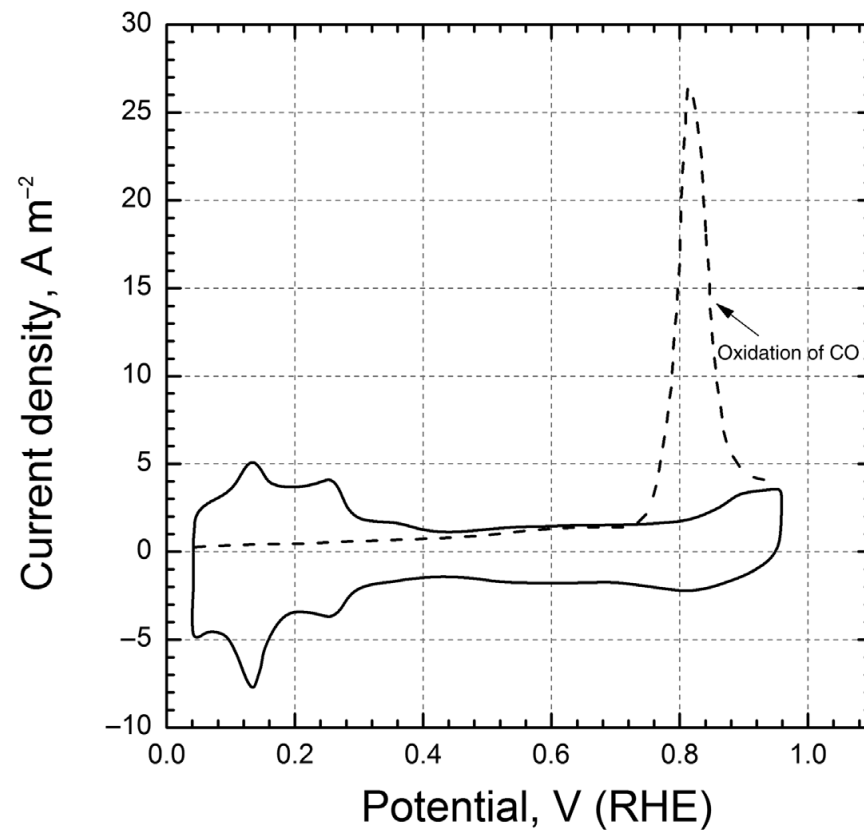
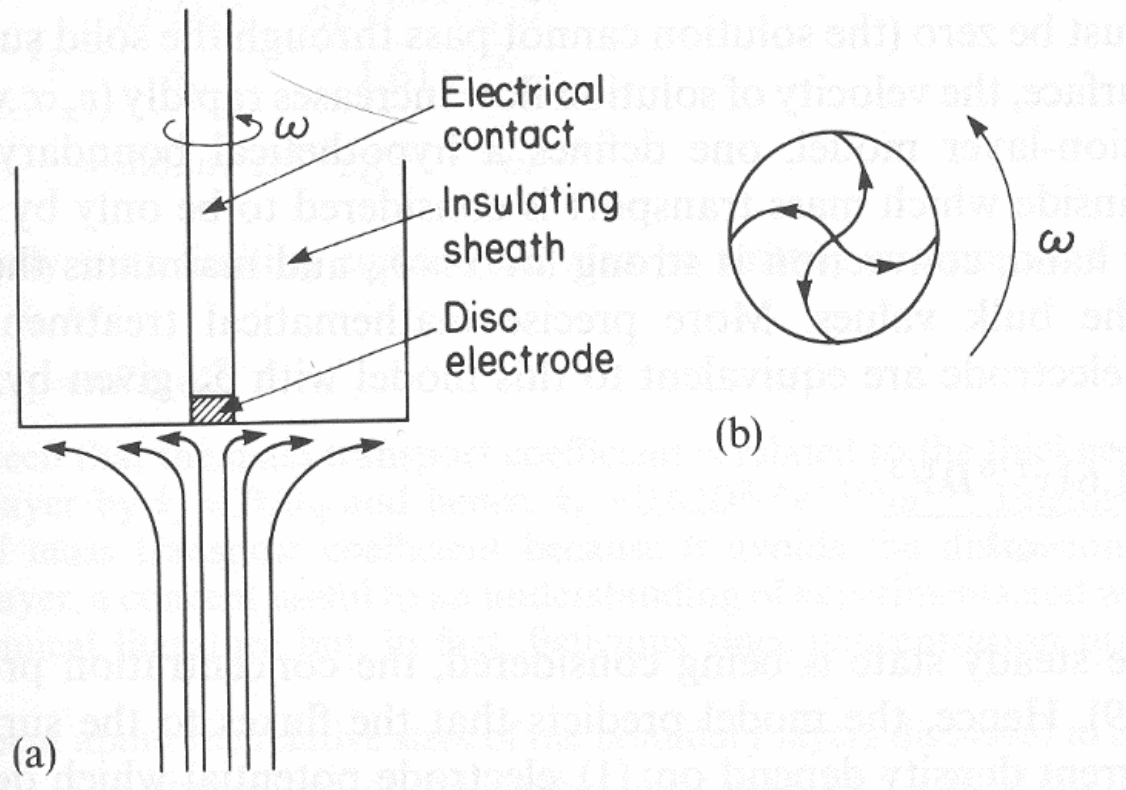


Figure 6.15 Oxidation of adsorbed CO on Pt surface during linear sweep.

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Hydrodynamic methods: rotating disk electrode



$$\delta = (1.61\nu^{1/6}D^{1/3}) / \omega^{1/2}$$
$$I_l = (nFD/\delta)C_o^*$$

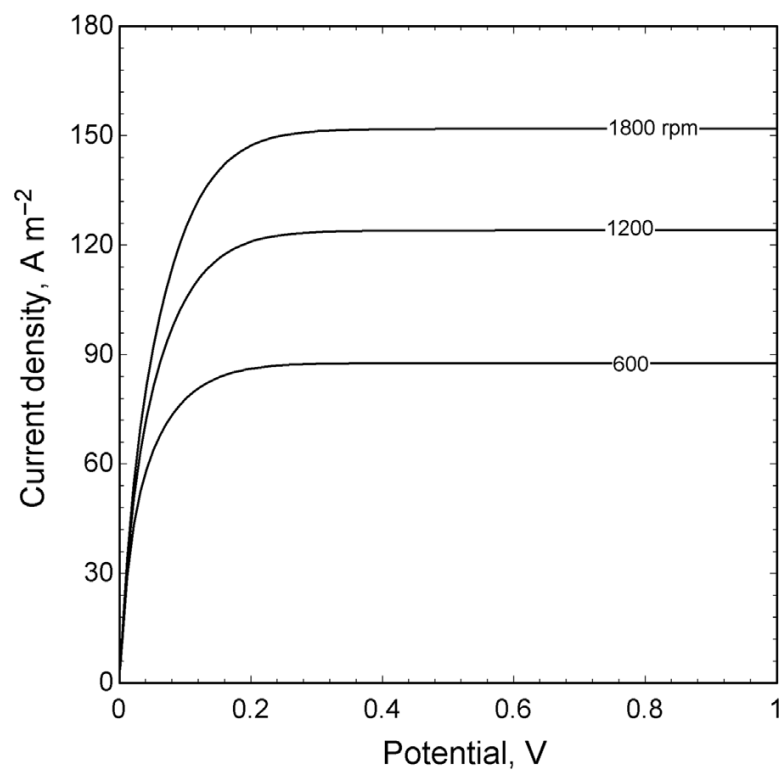


Figure 6.21 Linear potential sweep with RDE.

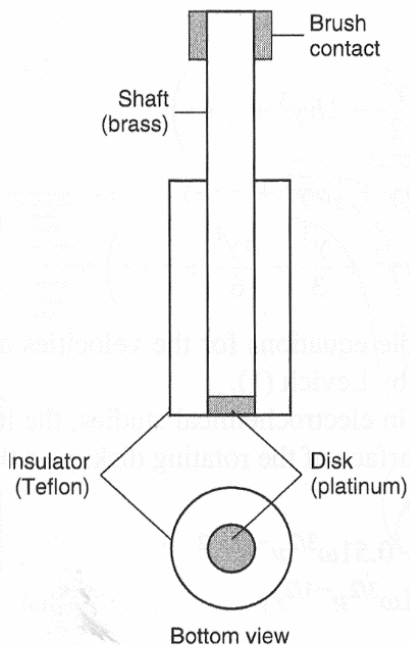


Figure 9.3.1 Rotating disk electrode.

Levich equation (rotating disk electrode)

Levich equation (rotating disk electrode)

$$i_l = 0.62nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}C_O^* \quad (9.3.22)$$

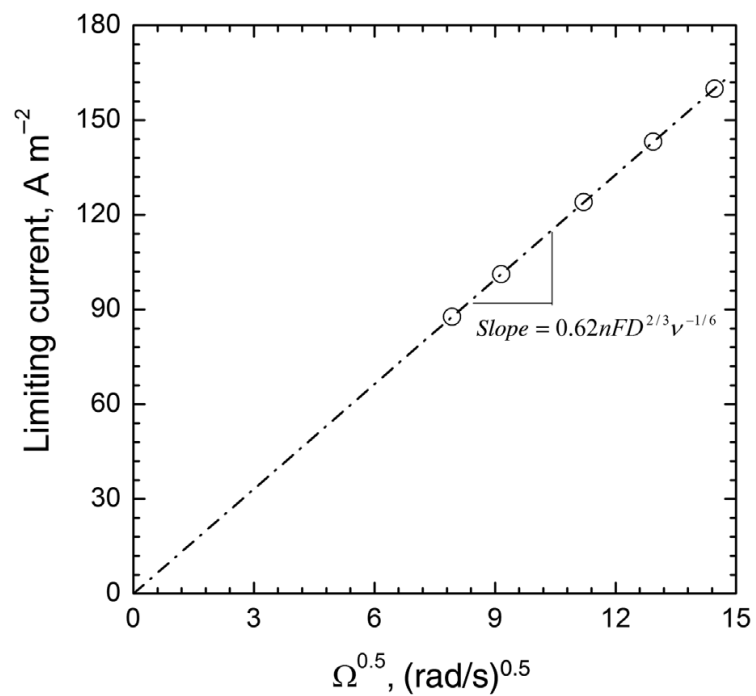
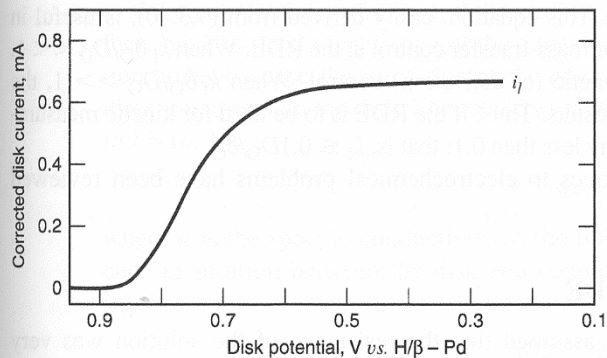
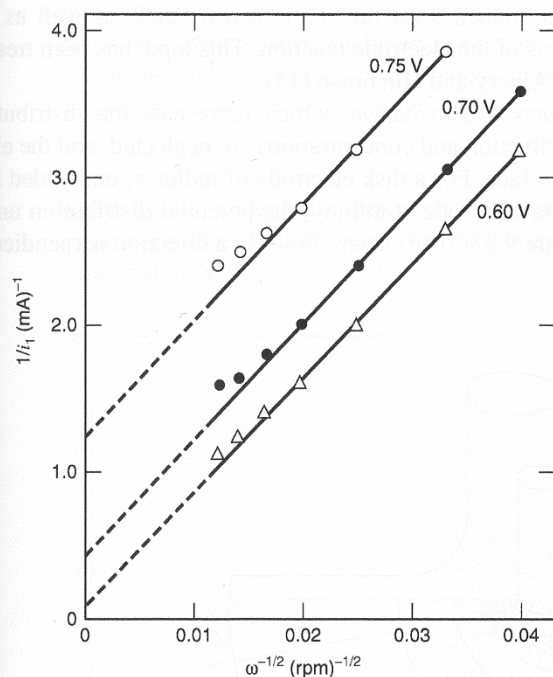


Figure 6.22 Levich plot.

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(a)



(b)

Figure 9.3.8 (a) i_D vs. E at 2500 rpm and (b) Koutecký–Levich plots for the reduction of O_2 to HO_2^- at a gold electrode in O_2 -saturated (~ 1.0 mM) 0.1 M NaOH at an RDE ($A = 0.196$ cm²). The potential was swept at 1 V/min. $T = 26^\circ\text{C}$. (i_l represents the corrected current attributable to O_2 reduction.) [From R. W. Zurilla, R. K. Sen, and E. Yeager, *J. Electrochem. Soc.*, **125**, 1103 (1978). Reprinted by permission of the publisher, The Electrochemical Society, Inc.]

one obtains the *Koutecký–Levich equation*:

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_{l,c}} = \frac{1}{i_K} + \frac{1}{0.62nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}C_O^*} \quad (9.3.39)$$

Microelectrodes

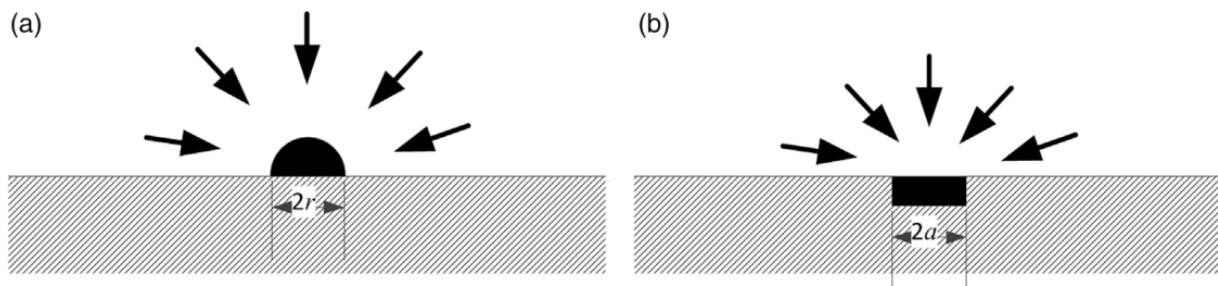


Figure 6.28 Hemispherical and disk microelectrodes.

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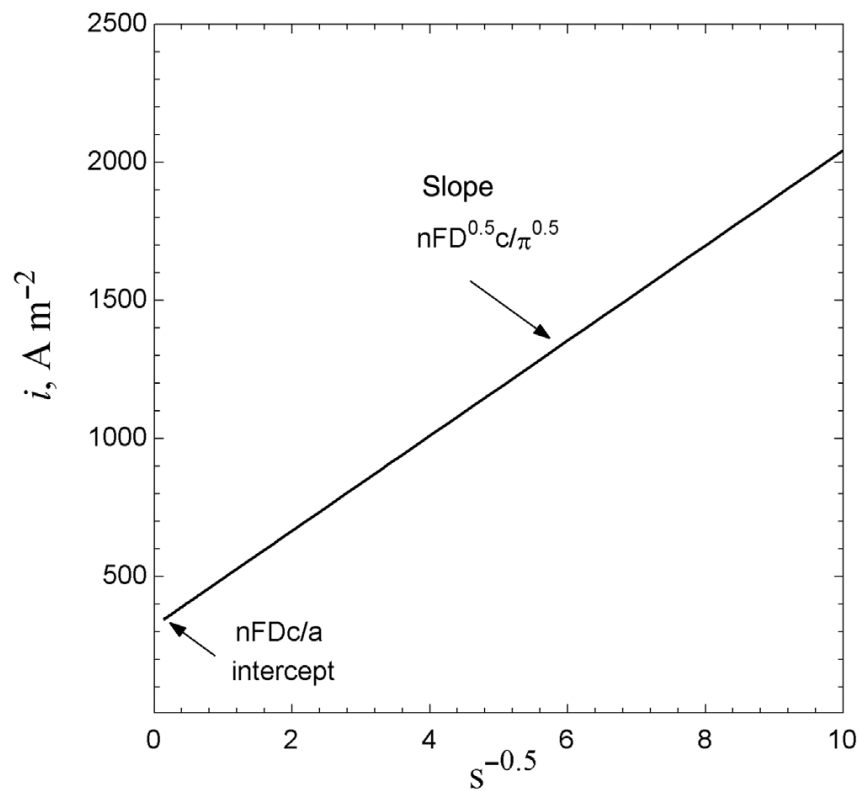


Figure 6.29 Transient behavior at microelectrode under mass-transfer control.

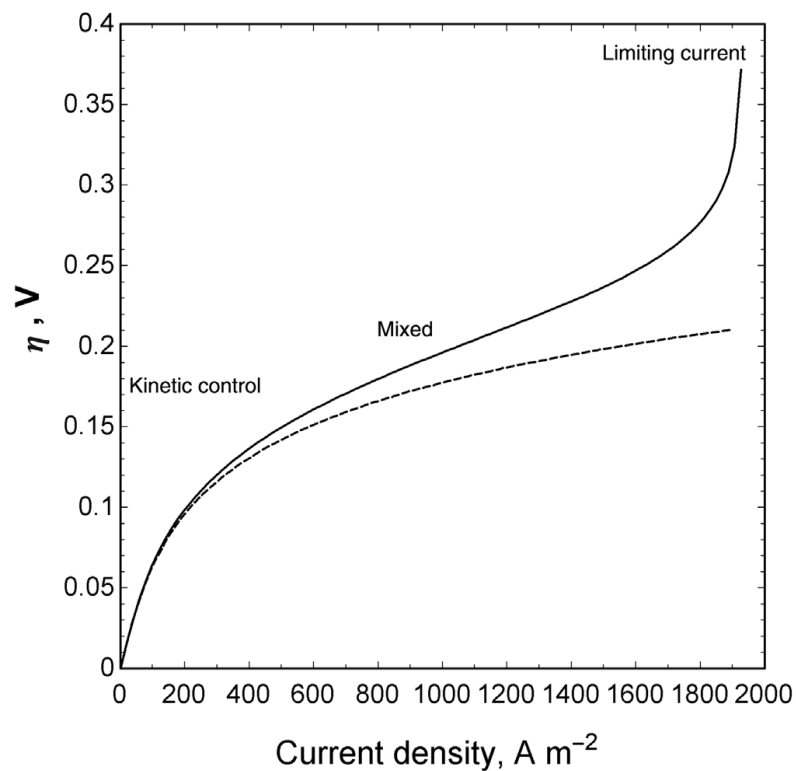


Figure 6.30 Current–voltage relationship for a spherical electrode showing regions of kinetic, mixed, and mass-transfer control. The dashed line is for pure kinetic control with no mass-transfer effect.