Lecture Note #6 (Spring, 2022)

Electroanalytical Techniques & 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

Fuller & Harb (textbook), ch.6, Bard (ref.), Oh (ref.)

Electrochemical instrumentation

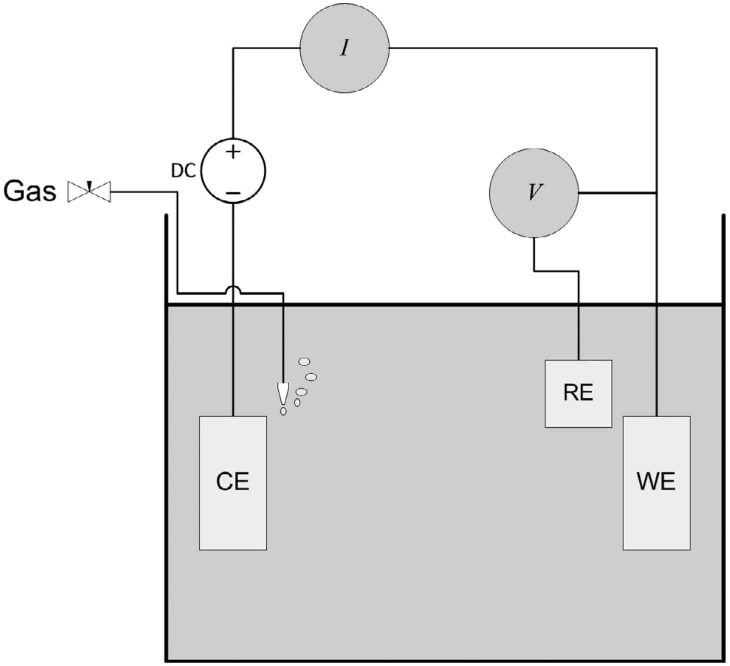

Figure 6.1 Schematic diagram of typical three-electrode setup.

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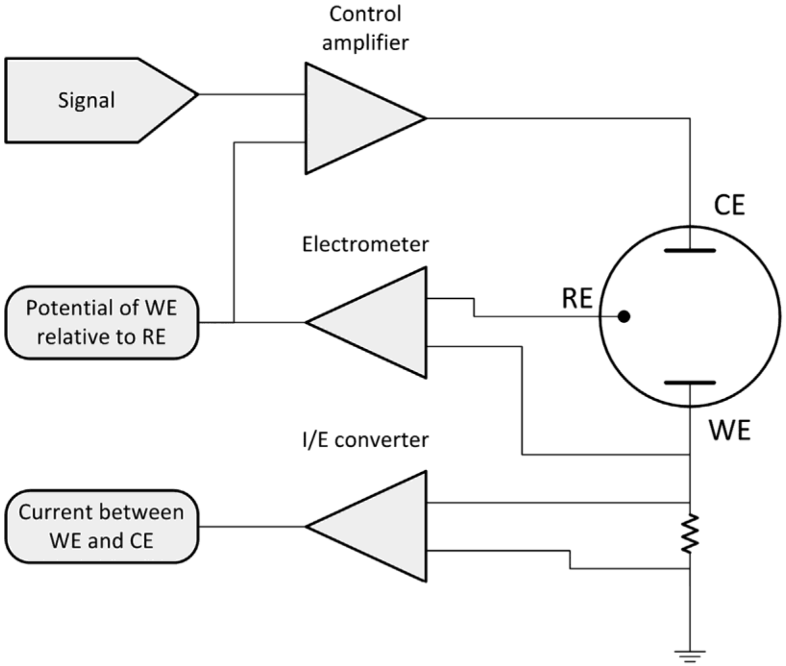

Figure 6.2 Setup and operation of a potentiostat.

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Overview

Key features of electrochemical experiment: (1) the geometry of the electrode and the systems, (2) the flow of electrolyte, (3) control of potential or current

Mass transfer has a central role in the analysis of electrochemical systems: Nernst-Planck equation, mass conservation

$$\boldsymbol{N}_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \varphi + c_i \mathbf{v} \qquad (4.3)$$

$$\partial c_i / \partial t = -\nabla \cdot \boldsymbol{N}_i + R_i \qquad (4.10)$$

Potential step method

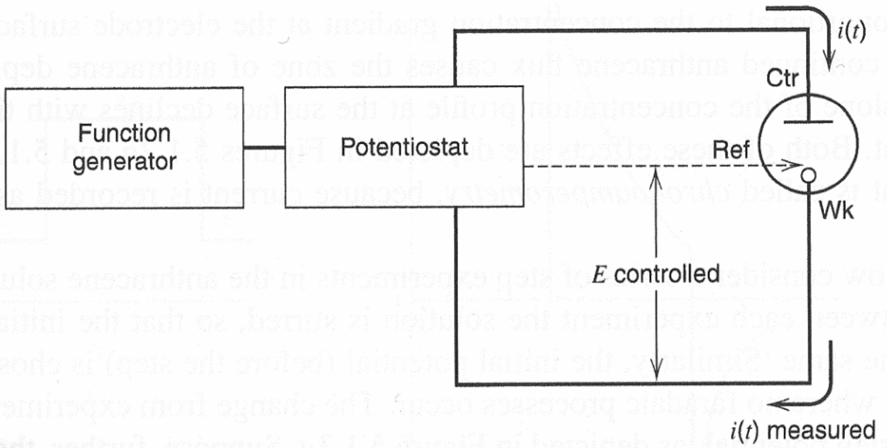

Figure 5.1.1 Experimental arrangement for controlled-potential experiments.

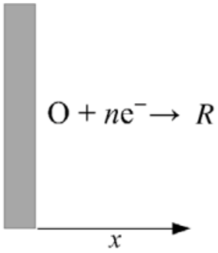

Figure 6.3 One-dimensional planar working electrode.

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A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 5)

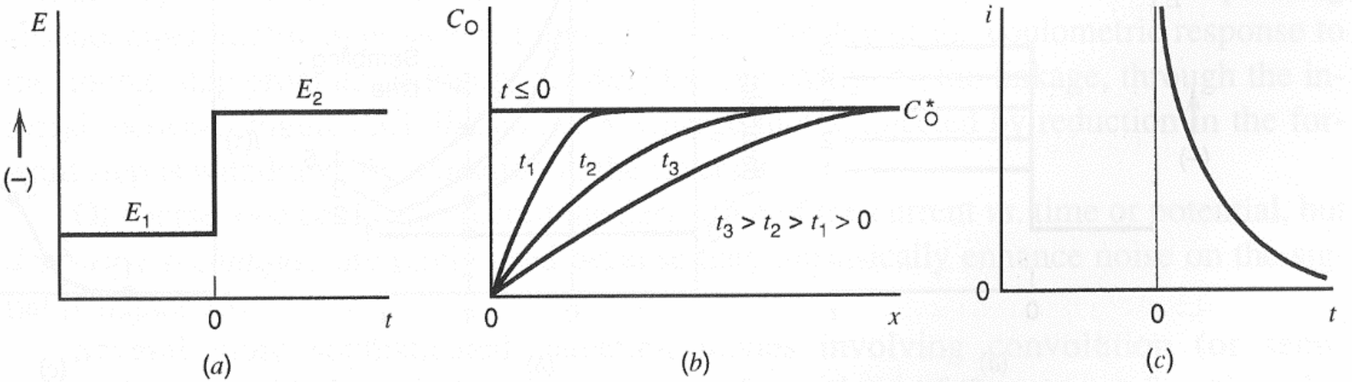
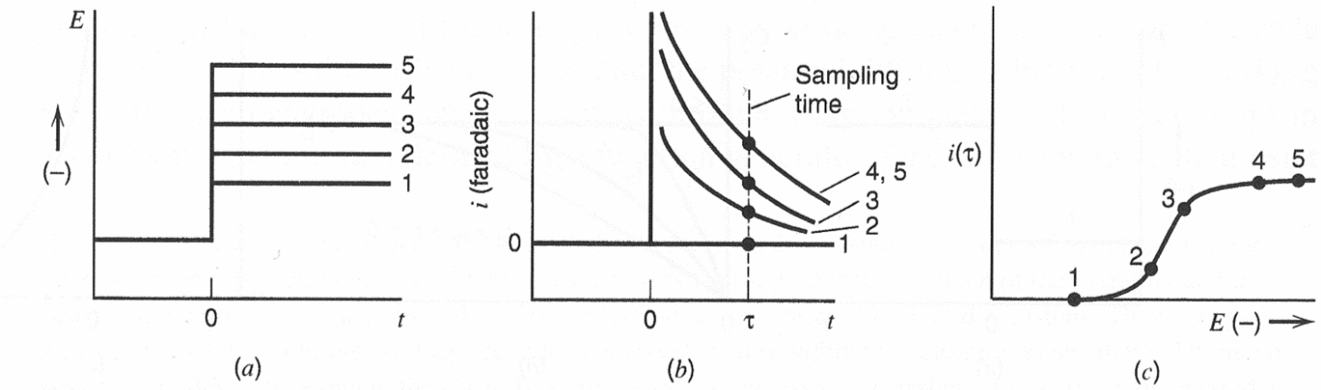


Figure 5.1.2 (*a*) Waveform for a step experiment in which species O is electroinactive at E_1, but is reduced at a diffusion-limited rate at E_2. (*b*) Concentration profiles for various times into the experiment. (*c*) Current flow *vs*. time.

Cottrell equation (a planar electrode in unstirred solution)

$$i(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}} \qquad (6.3)$$

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 5)



(*a*) (*b*) (*c*)

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)

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

Illustration 6.1

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 5)

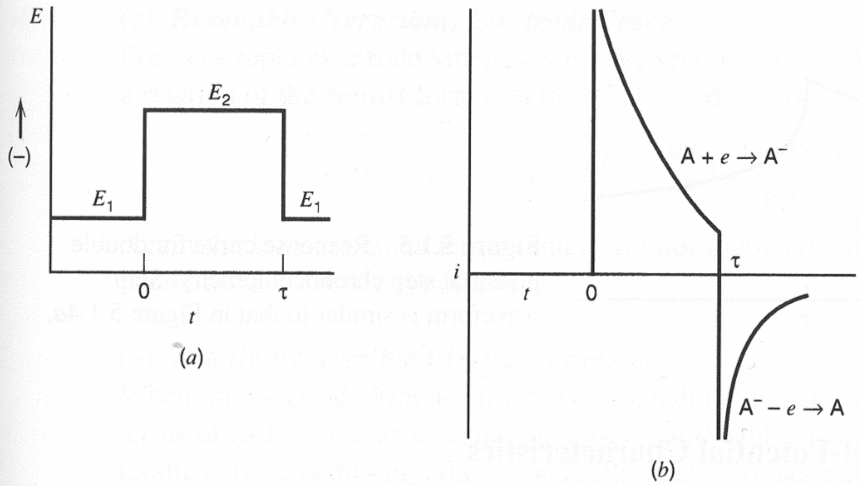


Figure 5.1.4
Double potential step chronoamperometry.
(*a*) Typical waveform.
(*b*) Current response.

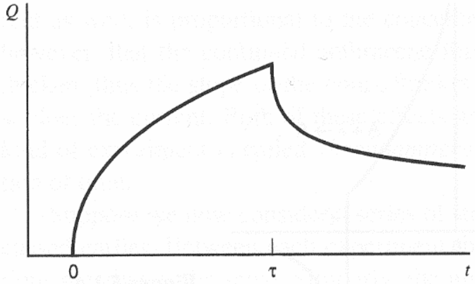


Figure 5.1.5 Response curve for double potential step chronocoulometry. Step waveform is similar to that in Figure 5.1.4*a*.

Chronocoulometry

Chronocoulometry, forward step:

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

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 5)

Potential sweep method (전위 주사 실험)

전위를 시간에 따라 변화시켜 전류를 측정

O + ne = R

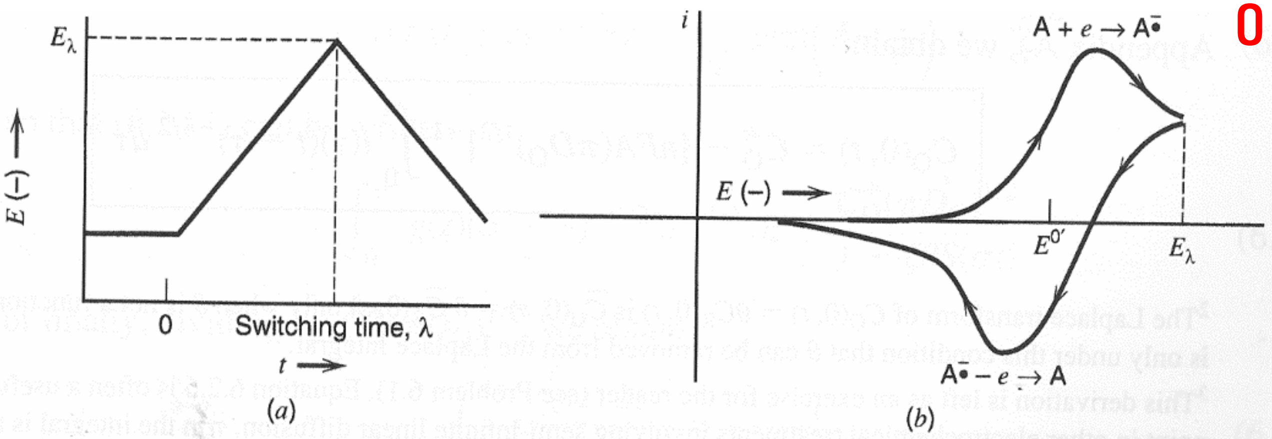
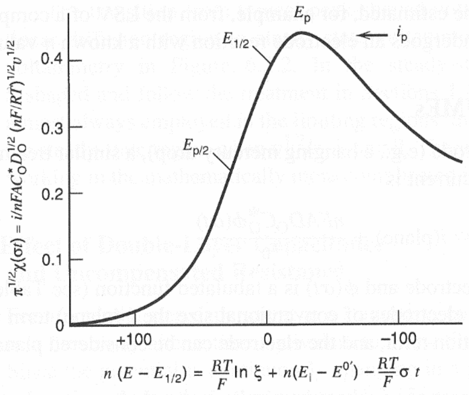


Figure 6.1.3 (*a*) Cyclic potential sweep. (*b*) Resulting cyclic voltammogram.

순환 전압-전류법



O + ne = R

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

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

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

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

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

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

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 6)

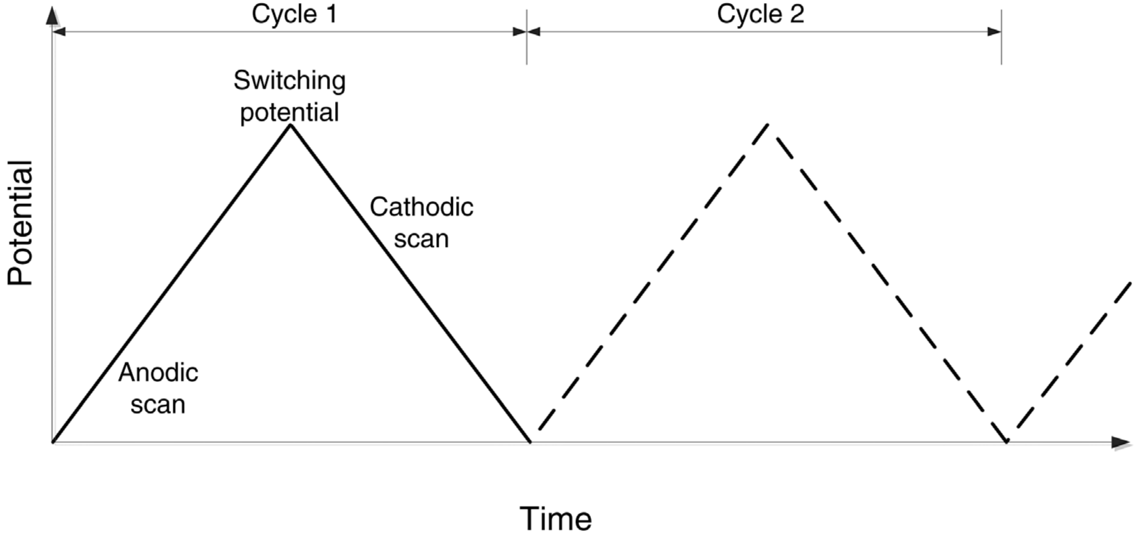


Figure 6.9 Triangle wave used in cyclic voltammetry.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

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Non-faradaic current (associated with the double-layer charging)

$$i_c = C_{DL}(dV/dt) = vC_{DL} \qquad (6.11)$$

$$i = i_f + i_c$$

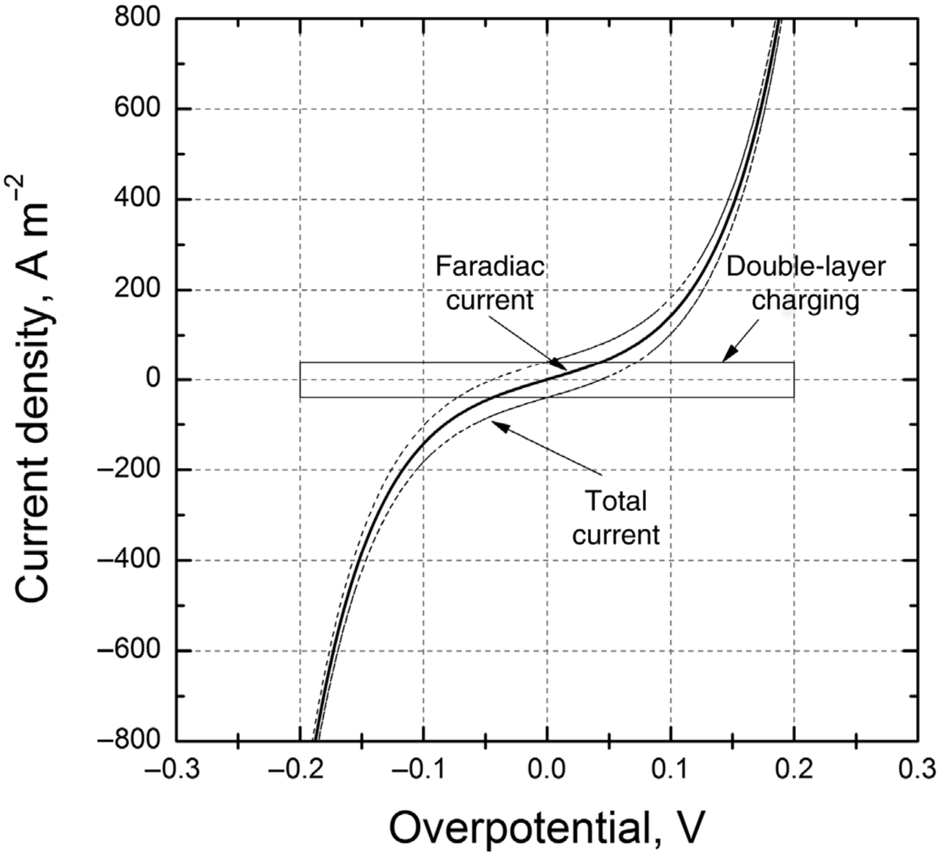

Figure 6.10 Cyclic voltammogram in the absence of mass transfer.

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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 cm^2, D_O in cm^2/s, C_O^* in mol/cm^3, 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

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

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

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

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

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

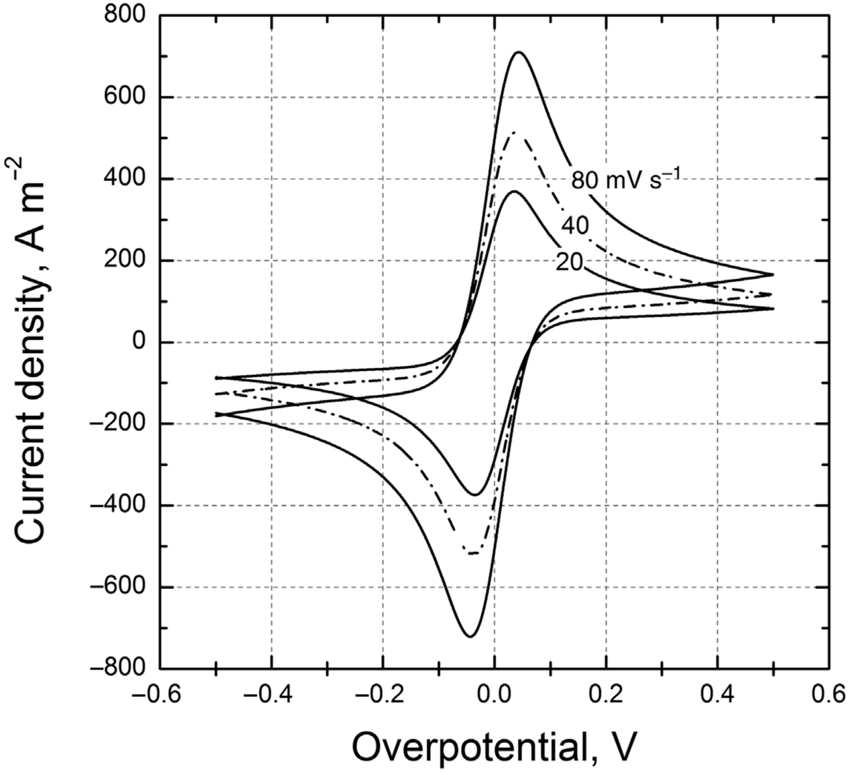

Figure 6.13 Effect of scan rate for a reversible reaction. Double-layer charging has been removed.

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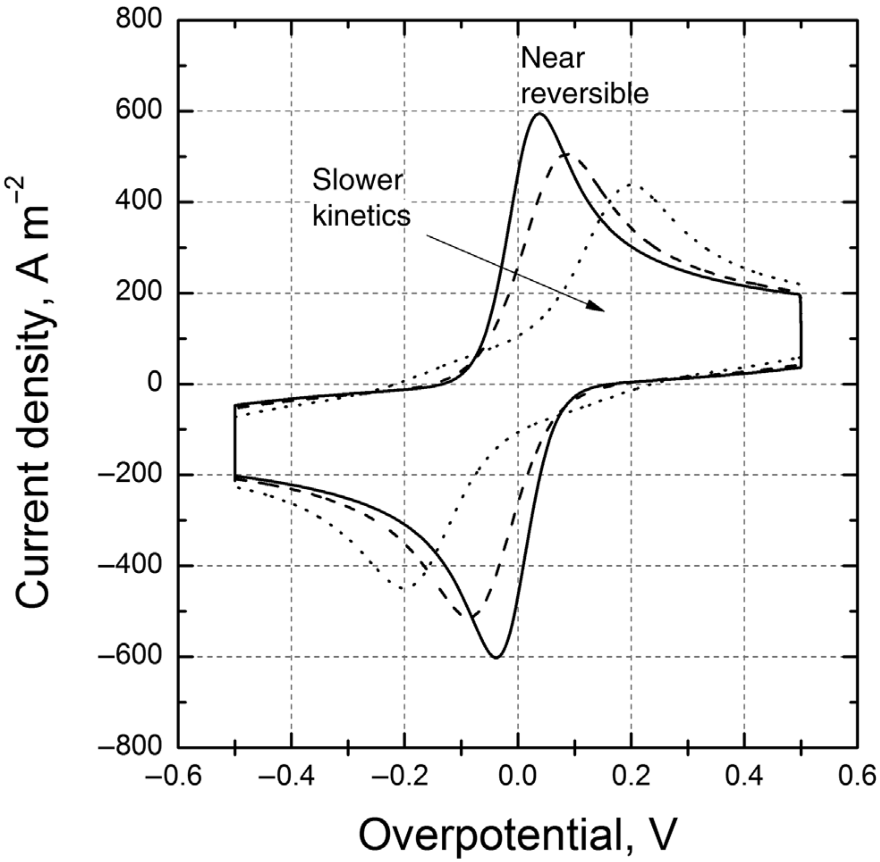

Figure 6.14 Effect of the exchange-current density on the cyclic voltammogram when kinetic limitations are important.

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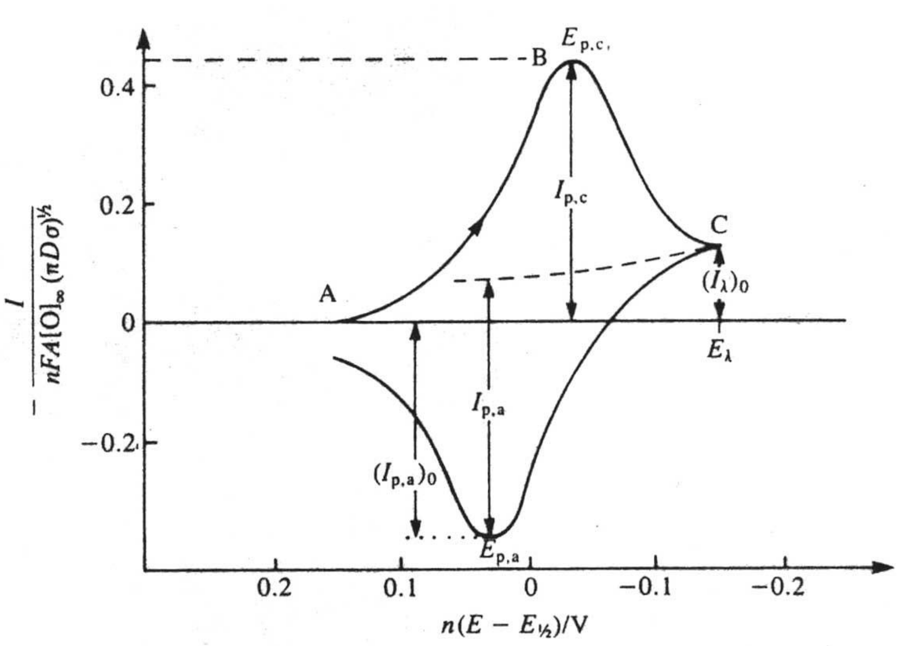
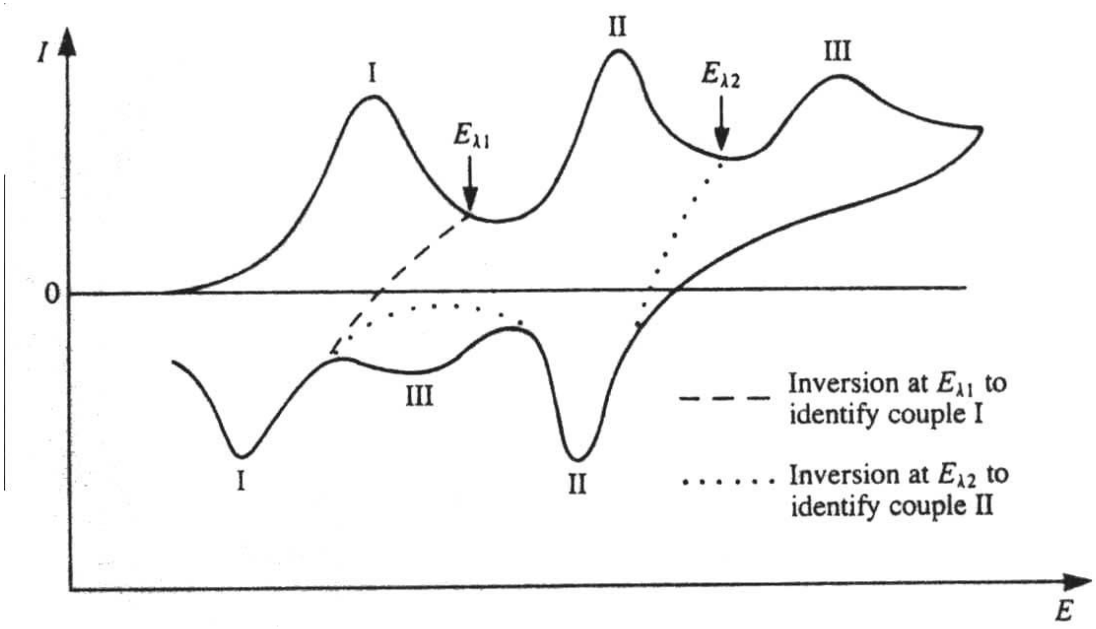
Illustration 6.2



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

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



Stripping analysis

$CO_{ads} + H_2O_{ads} \rightarrow CO_2(g) + 2H^+ + 2e^-$ ($E^0 = -0.11$ V)

$Q_{CO} = \int (I - vC)dt$

Electrochemically active surface area (ECSA)

$ECSA = Q_{CO} / 4.17\ Cm^{-2}$

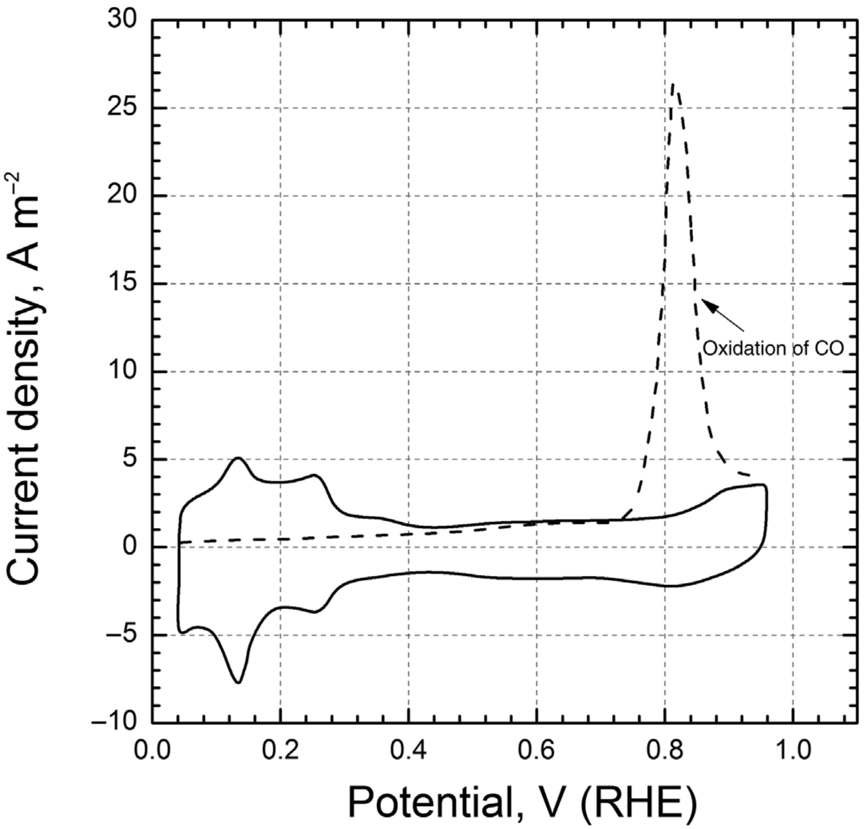


Figure 6.15 Oxidation of adsorbed CO on Pt surface during linear sweep.

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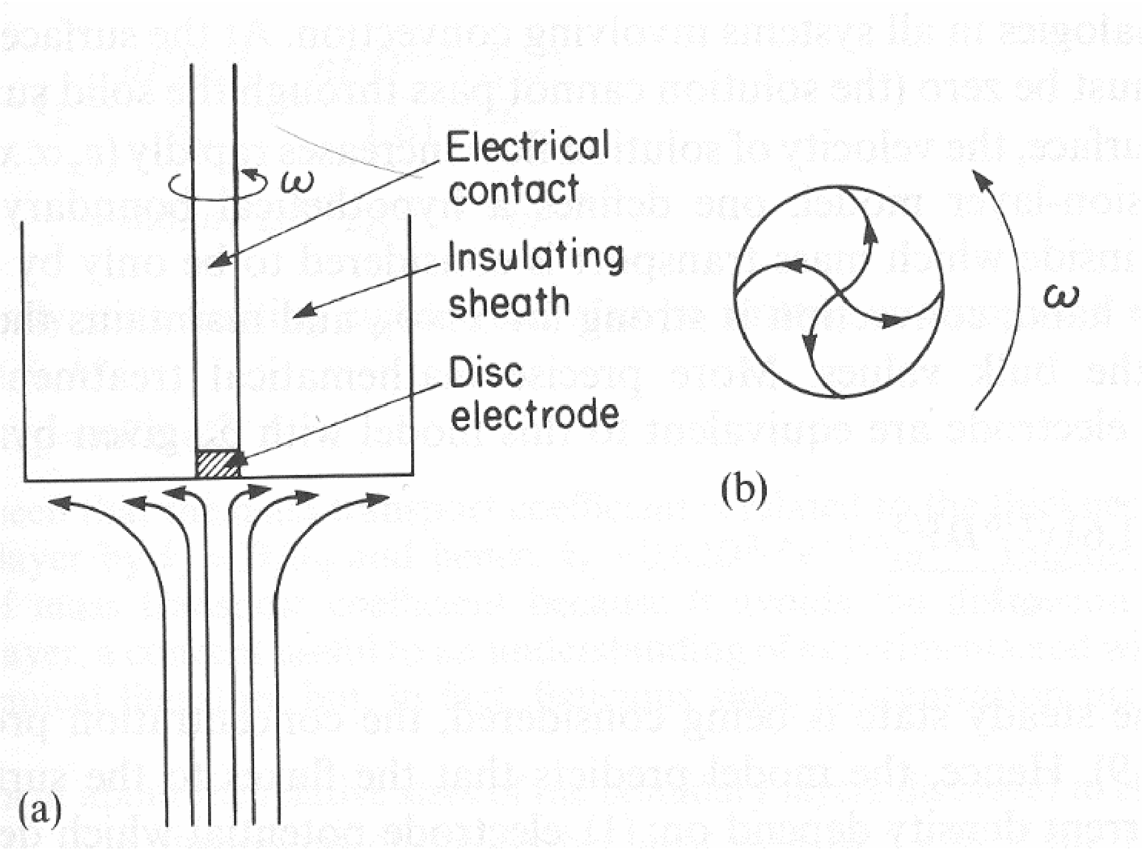
Illustration 6.3

Hydrodynamic methods: rotating disk electrode



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

$I_l = (nFD/\delta)C_O^*$

Pletcher, Fig. 1.8

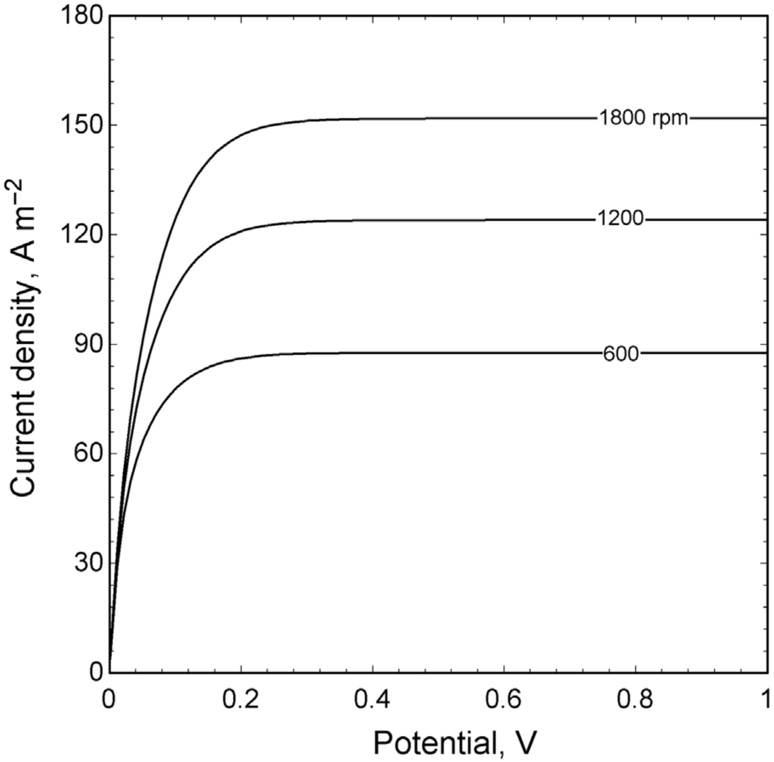


Figure 6.21 Linear potential sweep with RDE.

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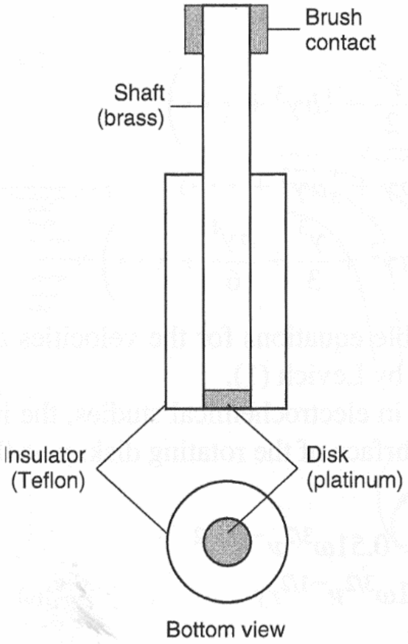

Figure 9.3.1 Rotating disk electrode.

Levich equation (rotating disk electrode)

Levich equation (rotating disk electrode)

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

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 9)

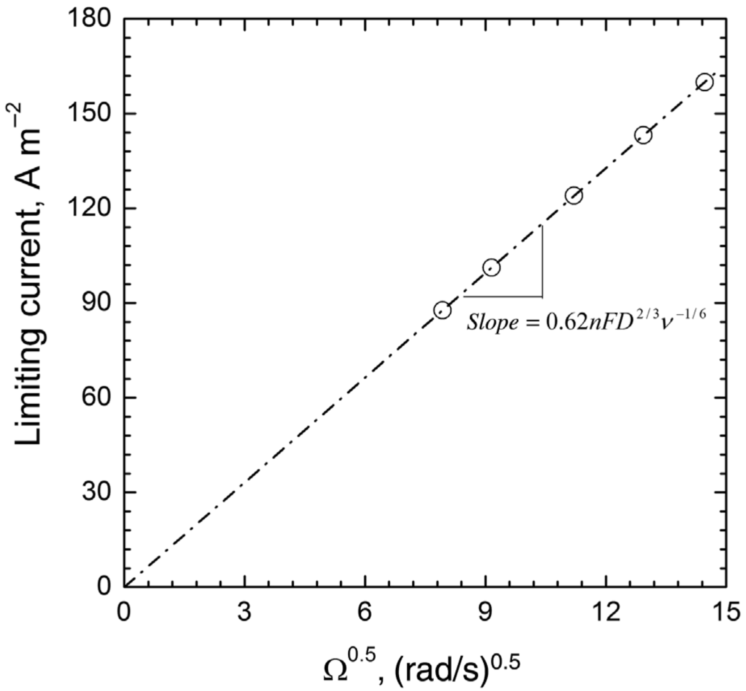

Figure 6.22 Levich plot.

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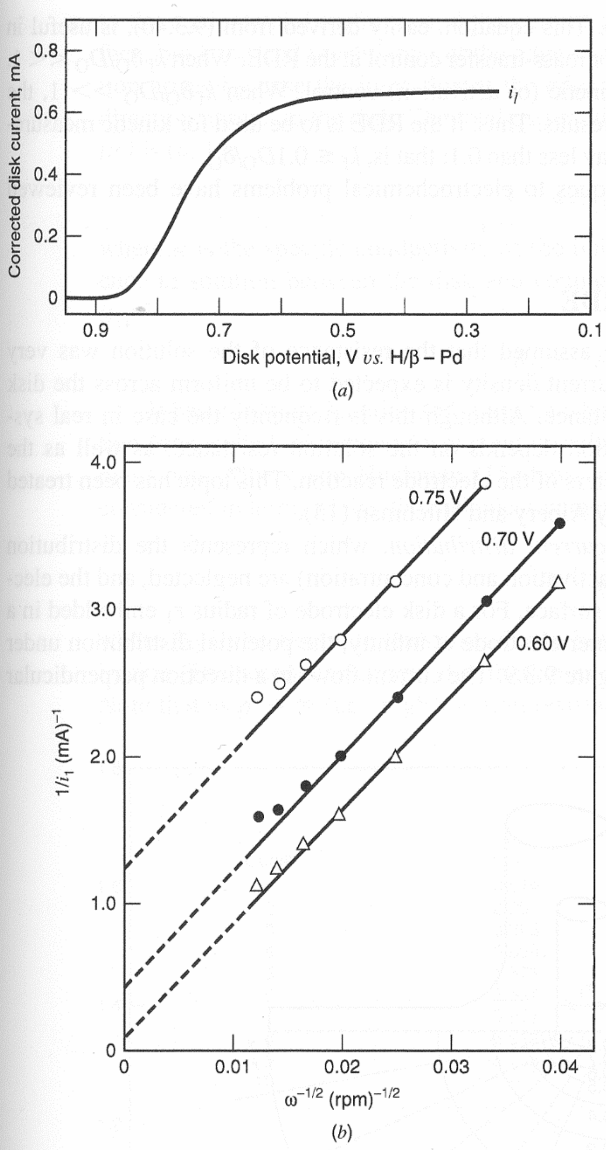

Figure 9.3.8 (*a*) i_D *vs. E* at 2500 rpm and (*b*) Koutecký–Levich plots for the reduction of O_2 to HO_2^- at a gold electrode in O_2-saturated (~1.0 m*M*) 0.1 *M* NaOH at an RDE ($A = 0.196$ cm^2). The potential was swept at 1 V/min. $T = 26$°C. (i_1 represents the corrected current attributable 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*:

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

Illustration 6.6

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 9)

Microelectrodes

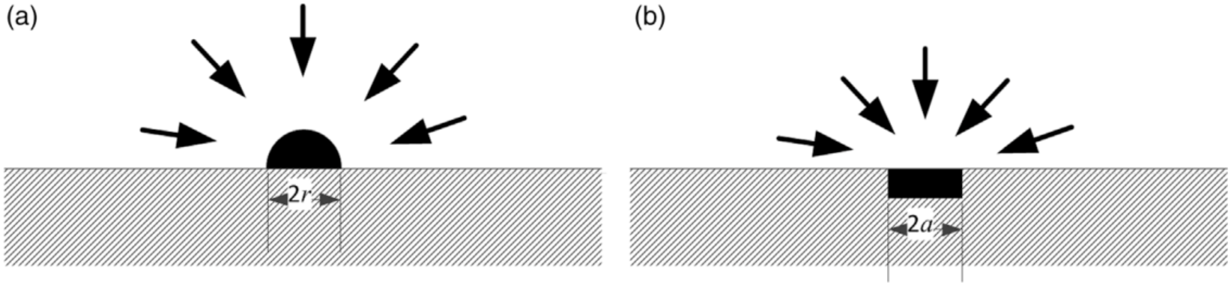

Figure 6.28 Hemispherical and disk microelectrodes.

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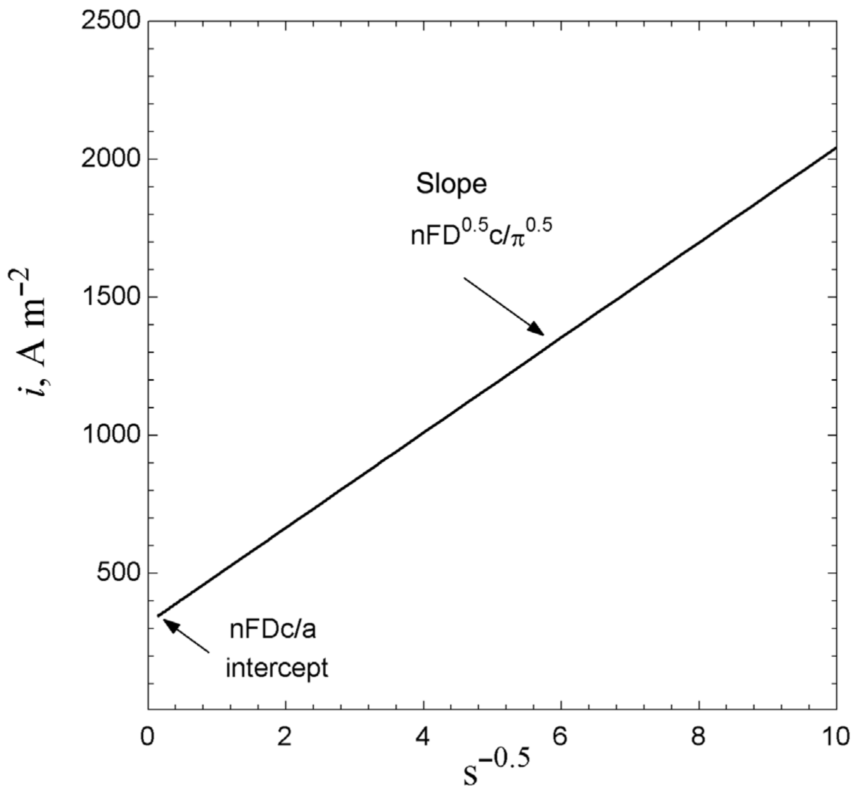

Figure 6.29 Transient behavior at microelectrode under mass-transfer control.

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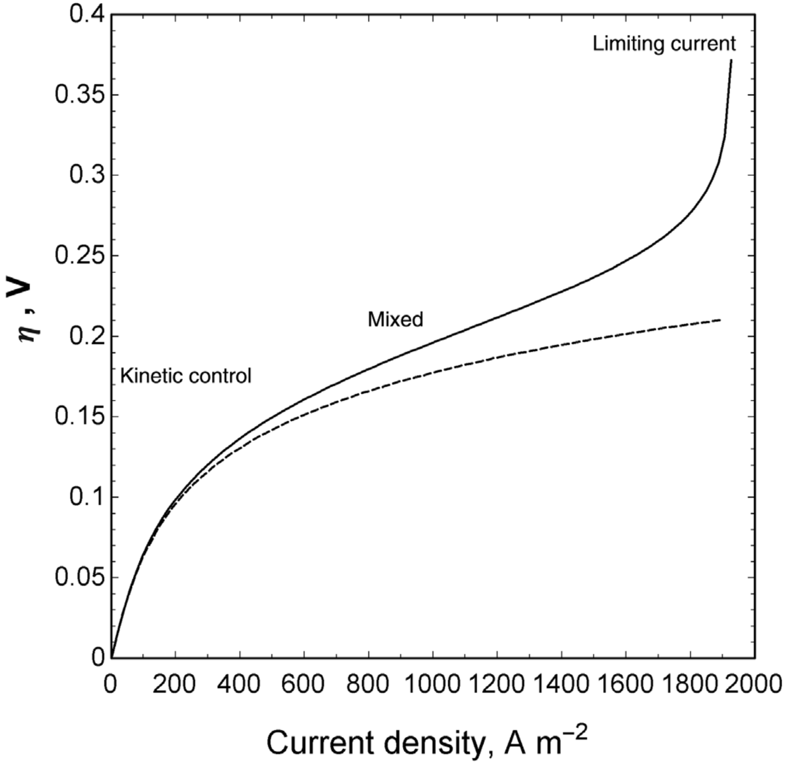

Figure 6.30 Current–voltage relationship for a spherical electrode showing regions of kinetic, mixed, and mass-transfer control. The dashed line is for pure kinetic control with no mass-transfer effect.

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Illustration 6.7

- ✓ The midterm exam is scheduled for April 18th on Monday.

- ✓ Lecture Note #7(ch.7. Battery, ~Midterm Exam range) & HW#5 will be uploaded today.

- ✓ I will record Wednesday lecture today and upload because of Korean Electrochemical Society.