6. Electrochemical Methods

Learning subject

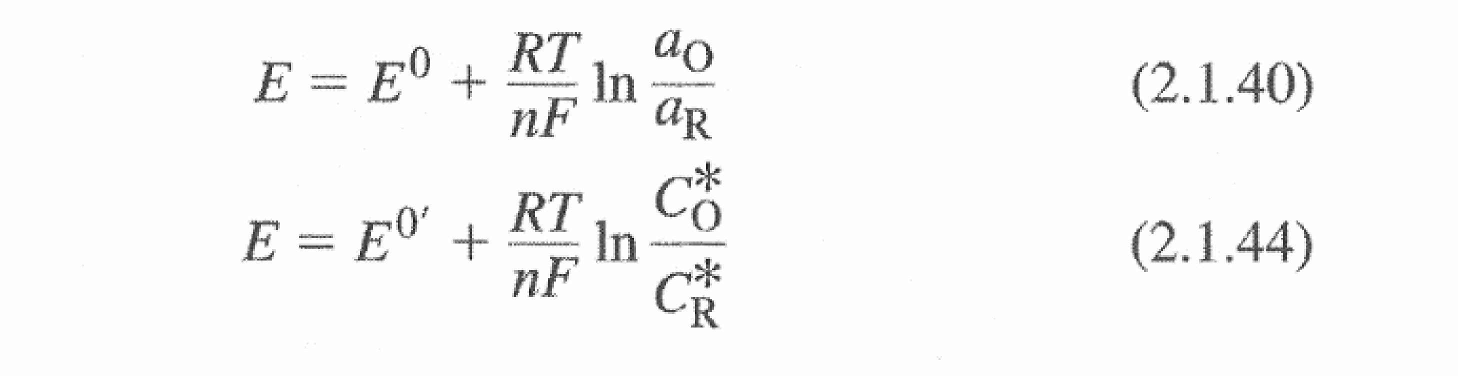
1. Electrochemical methods
2. Equations in electrochemistry

Learning objective

1. Understanding electrochemical methods
2. Understanding the equations in electrochemical methods

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (front inside cover)

Nernst equation for O + ne = R

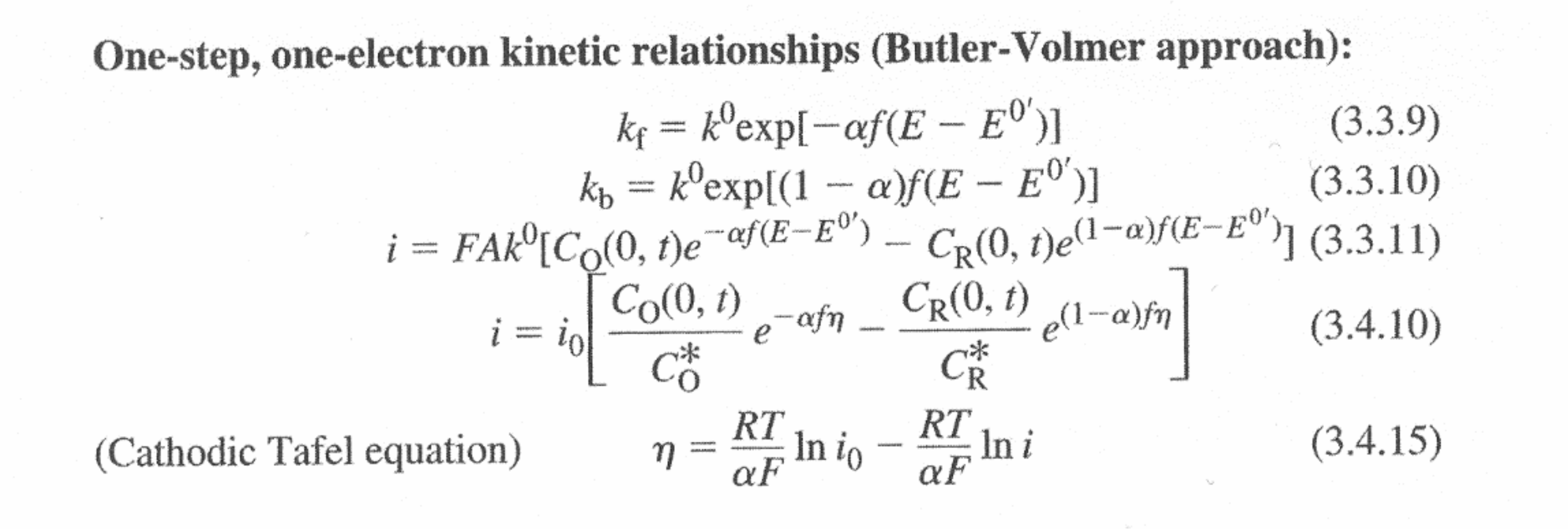


$$E = E^0 + \frac{RT}{nF} \ln \frac{a_\mathrm{O}}{a_\mathrm{R}} \tag{2.1.40}$$

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_\mathrm{O}^*}{C_\mathrm{R}^*} \tag{2.1.44}$$

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 2)

Butler-Volmer equation



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

$$k_{\mathrm{f}} = k^0 \exp[-\alpha f(E - E^{0'})] \tag{3.3.9}$$

$$k_{\mathrm{b}} = k^0 \exp[(1 - \alpha) f(E - E^{0'})] \tag{3.3.10}$$

$$i = FAk^0[C_{\mathrm{O}}(0, t)e^{-\alpha f(E - E^{0'})} - C_{\mathrm{R}}(0, t)e^{(1-\alpha) f(E - E^{0'})}] \tag{3.3.11}$$

$$i = i_0 \left[\frac{C_{\mathrm{O}}(0, t)}{C_{\mathrm{O}}^*} e^{-\alpha f \eta} - \frac{C_{\mathrm{R}}(0, t)}{C_{\mathrm{R}}^*} e^{(1-\alpha) f \eta} \right] \tag{3.4.10}$$

(Cathodic Tafel equation)

$$\eta = \frac{RT}{\alpha F} \ln i_0 - \frac{RT}{\alpha F} \ln i \tag{3.4.15}$$

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 3)

Potential step method

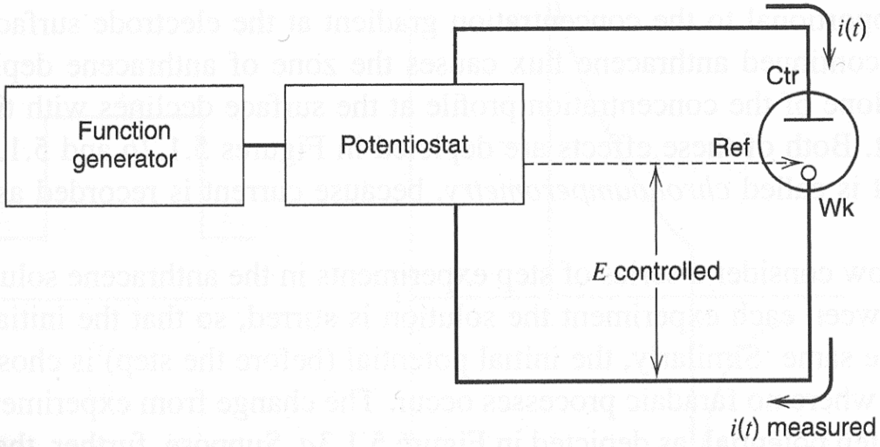


Figure 5.1.1 Experimental arrangement for controlled-potential experiments.

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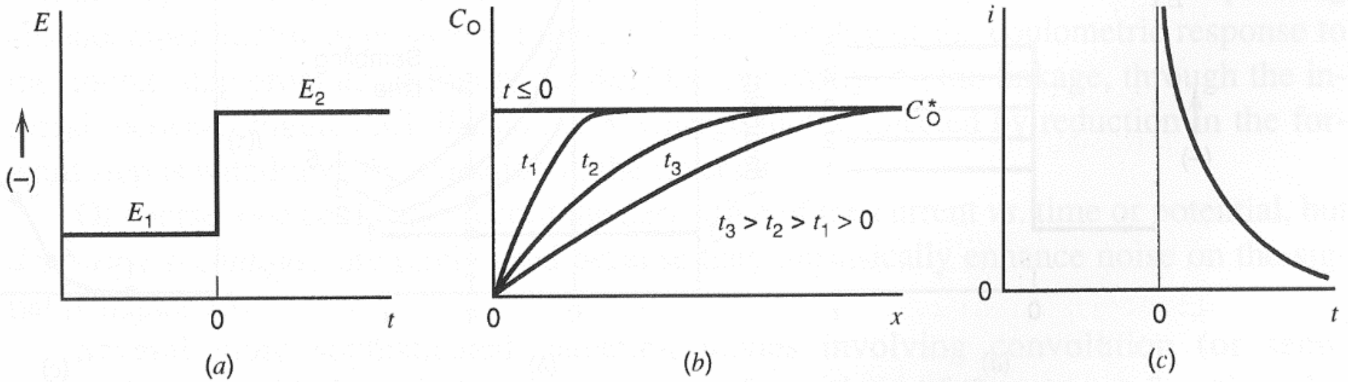

Figure 5.1.2 (*a*) Waveform for a step experiment in which species O is electroinactive at E_1, but is reduced at a diffusion-limited rate at E_2. (*b*) Concentration profiles for various times into the experiment. (*c*) Current flow *vs*. time.

Cottrell equation (a planar electrode in unstirred solution)

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

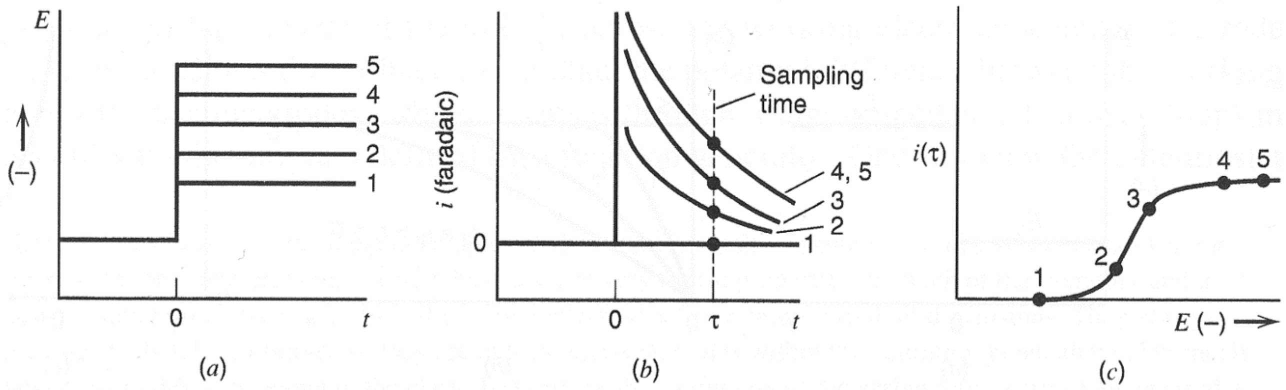

Figure 5.1.3 Sampled-current voltammetry. (*a*) Step waveforms applied in a series of experiments. (*b*) Current-time curves observed in response to the steps. (*c*) Sampled-current voltammogram.

Sampled-current voltammetry (reversible reaction)

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

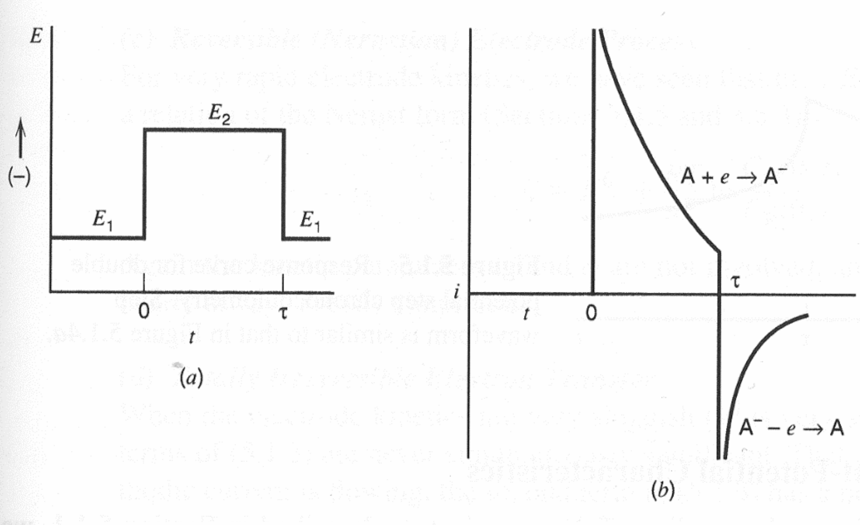

Figure 5.1.4
Double potential step
chronoamperometry.
(*a*) Typical waveform.
(*b*) Current response.

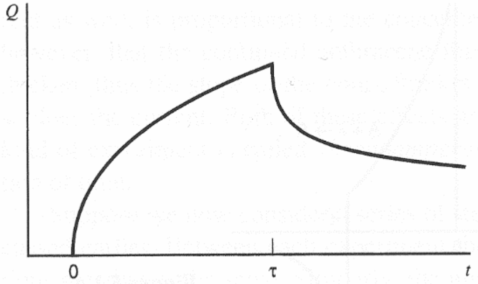

Figure 5.1.5 Response curve for double potential step chronocoulometry. Step waveform is similar to that in Figure 5.1.4*a*.

Chronocoulometry

Chronocoulometry, forward step:

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

Potential sweep method

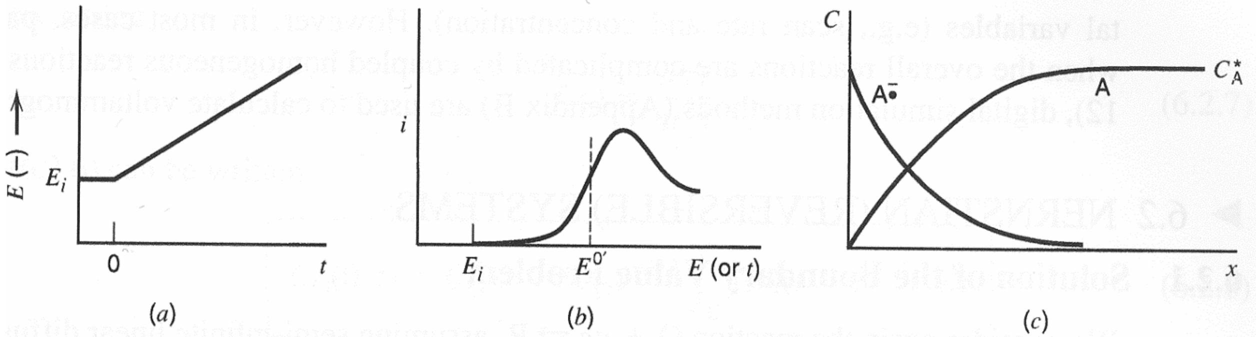

Figure 6.1.2 (*a*) Linear potential sweep or ramp starting at E_i. (*b*) Resulting *i-E* curve. (*c*) Concentration profiles of A and $A^{\bar{\bullet}}$ for potentials beyond the peak.

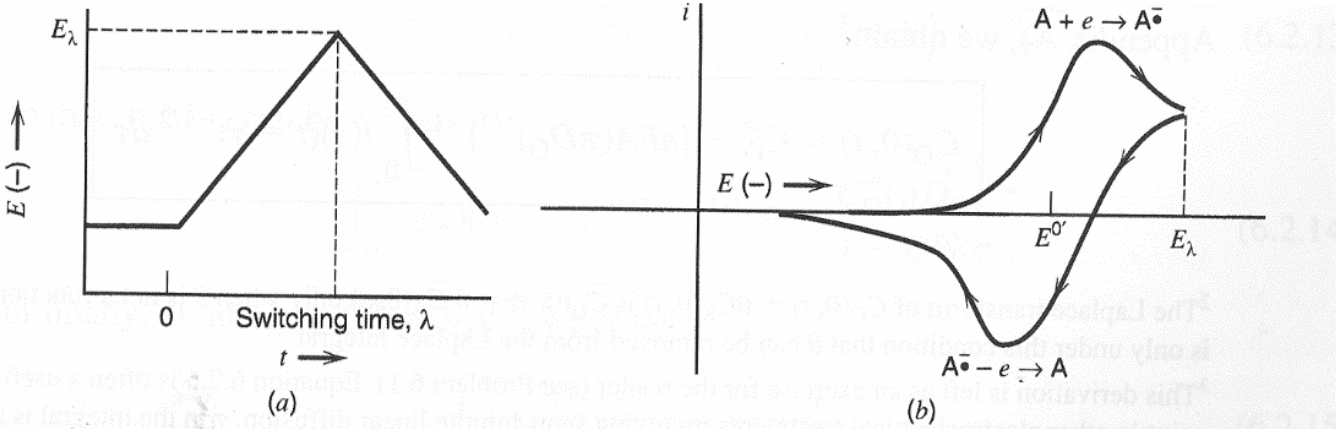

Figure 6.1.3 (*a*) Cyclic potential sweep. (*b*) Resulting cyclic voltammogram.

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Linear sweep voltammetry

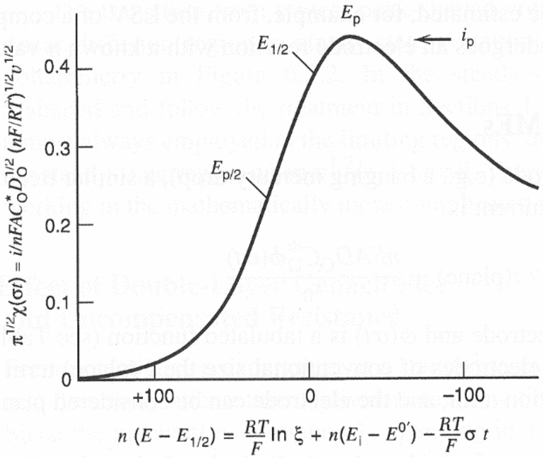


Figure 6.2.1 Linear potential sweep voltammogram in terms of dimensionless current function. Values on the potential axis are for 25°C

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

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

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

Controlled-current techniques “galvanostat”

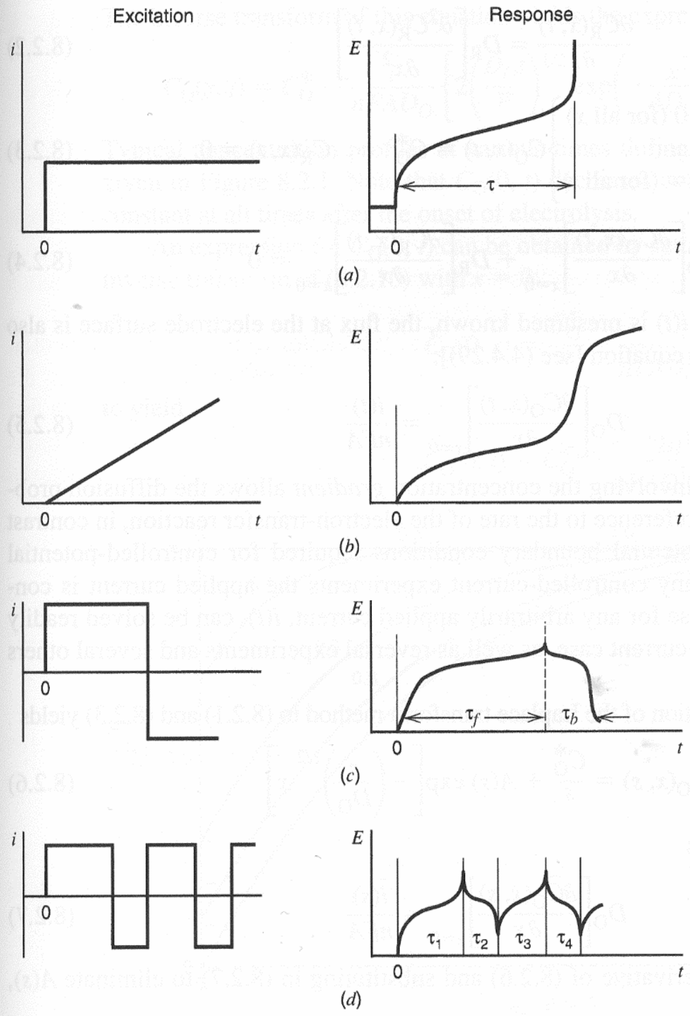
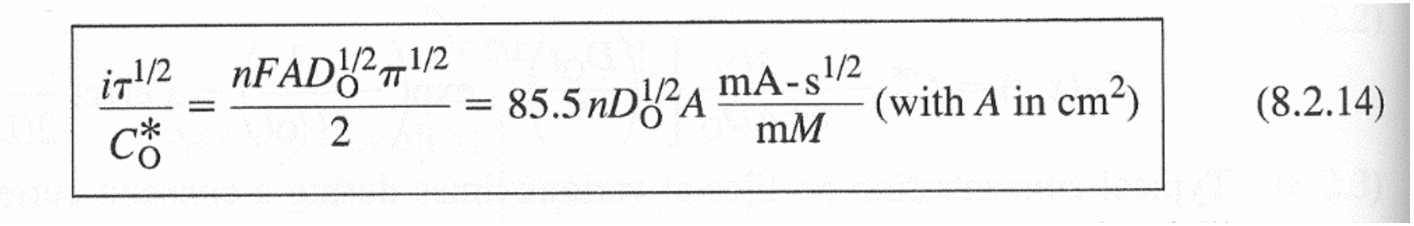


Figure 8.1.2 Different types of controlled-current techniques. (*a*) Constant-current chronopotentiometry. (*b*) Chronopotentiometry with linearly increasing current. (*c*) Current reversal chronopotentiometry. (*d*) Cyclic chronopotentiometry.

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 8)

Sand equation (constant-current electrolysis)



$$\boxed{\frac{i\tau^{1/2}}{C_{\mathrm{O}}^{*}} = \frac{nFAD_{\mathrm{O}}^{1/2}\pi^{1/2}}{2} = 85.5\,nD_{\mathrm{O}}^{1/2}A\,\frac{\mathrm{mA\text{-}s}^{1/2}}{\mathrm{m}M}\ (\text{with } A \text{ in cm}^2)} \qquad (8.2.14)$$

Hydrodynamic methods

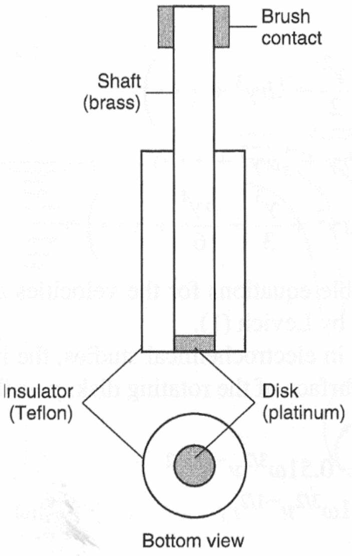
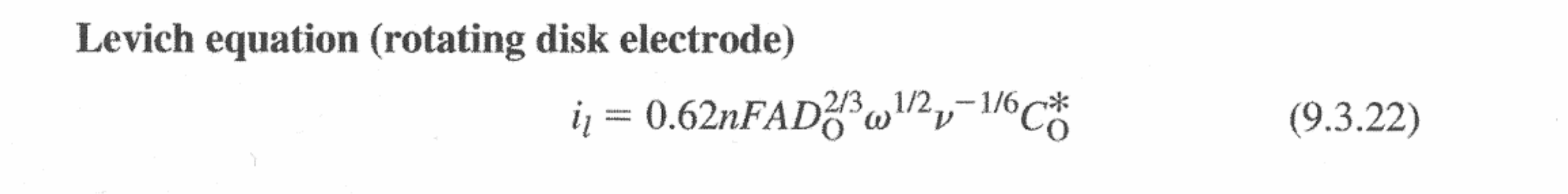


Figure 9.3.1 Rotating disk electrode.

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)

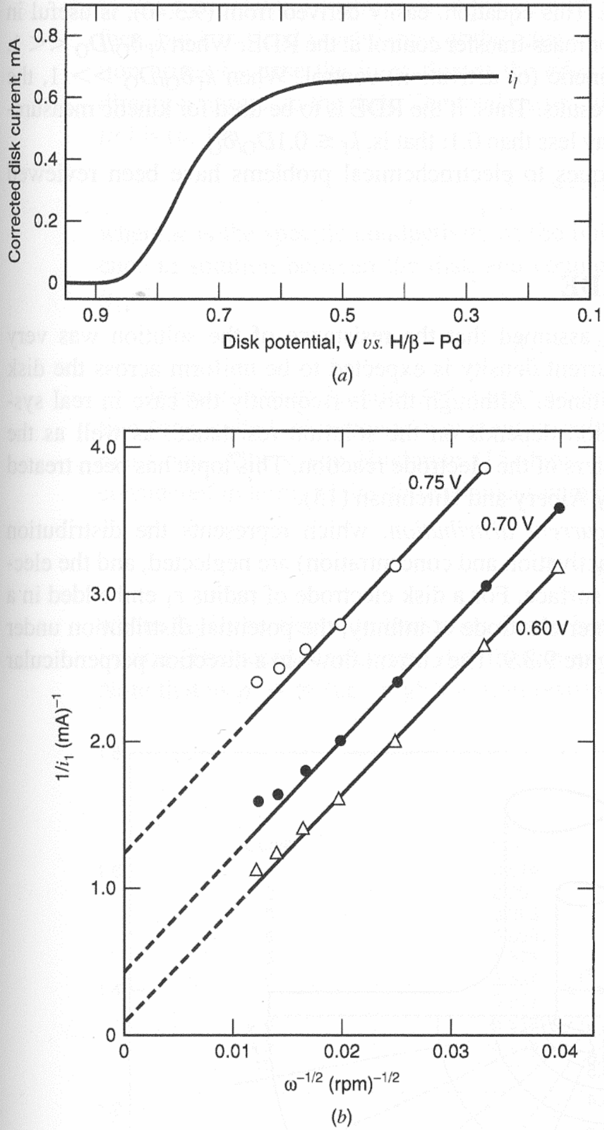


Figure 9.3.8 (*a*) i_D *vs.* E at 2500 rpm and (*b*) Koutecký–Levich plots for the reduction of O_2 to HO_2^- at a gold electrode in O_2-saturated (~1.0 m*M*) 0.1 *M* NaOH at an RDE (A = 0.196 cm^2). The potential was swept at 1 V/min. T = 26°C. (i_1 represents the corrected current attributable to O_2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

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

ac techniques & impedance

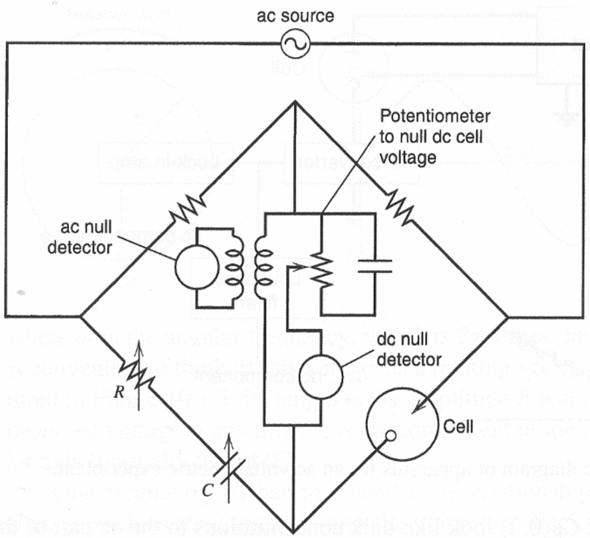


Figure 10.1.1 A bridge circuit for measurements of electrochemical impedance.

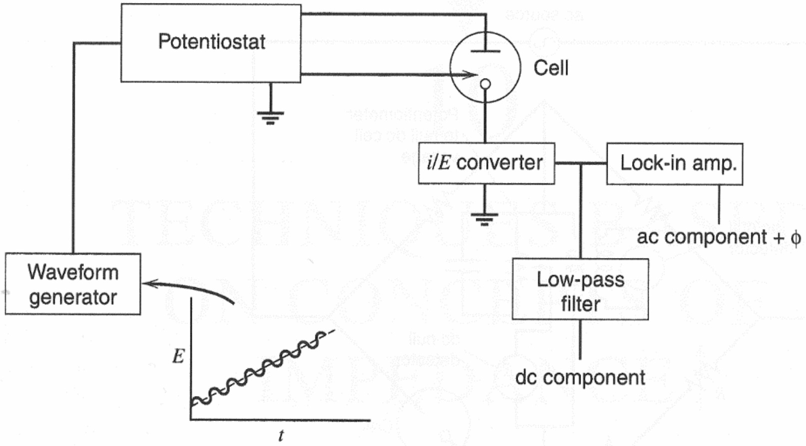


Figure 10.1.2 Schematic diagram of apparatus for an ac voltammetric experiment.

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001. (ch. 10)