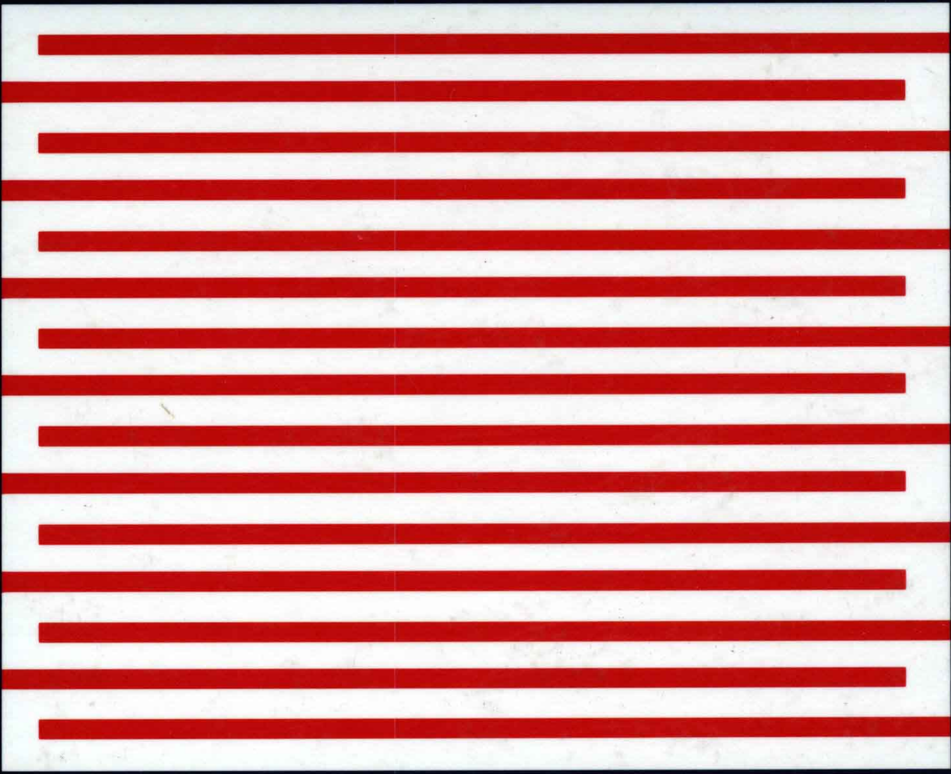
ANALYTICAL ELECTROCHEMISTRY

Joseph Wang



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Dedicated to the memory of my parents,
Elka and Moshe Wang

Preface

The goal of this textbook is to cover the full scope of modern electroanalytical techniques and devices. The main emphasis is on electroanalysis, rather than physical electrochemistry. Given the impressive progress in electroanalytical chemistry, and its growing impact on analytical chemistry, this work offers an up-to-date, easy-to-read presentation of recent advances including new methodologies, sensors and detectors. The book is suitable for a graduate-level course in electroanalytical chemistry or as a supplement to a high-level undergraduate course in instrumental analysis. It should also be useful to those considering the use of electroanalysis in their laboratories.

The material is presented in six roughly equal chapters. The first chapter is devoted to fundamental aspects of electrode reactions and the structure of the interfacial region. Chapter 2 gives an overview of finite-current controlled-potential techniques. Chapter 3 describes the electrochemical instrumentation and electrode materials (including new modified electrodes and microelectrodes). Chapter 4 deals with the principles of potentiometric measurements and various classes of ion-selective electrodes. Chapter 5 is devoted to the growing field of chemical sensors (including modern biosensors, gas sensors, solid-state devices, and sensor arrays), while Chapter 6 discusses the study of electrode reactions and high-resolution surface characterization. I have tried to provide numerous references to review literature at the end of each chapter. By discussing the latest advances, it is hoped to bridge the common gap between recent research literature and standard textbooks.

Finally, I wish to thank my wife, Ruth, and my daughter, Sharon, for their love and patience; the editorial and production staff of VCH Publishers for their help and support; Dr. Clark Kelly for many useful suggestions; Mrs. Rowena

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Joseph Wang
Las Cruces, NM
July, 1994

Contents

CHAPTER

1

Fundamental Concepts

1.1 Why Electroanalysis?

Electroanalytical techniques are concerned with the interplay between electricity and chemistry, namely the measurements of electrical quantities, such as current, potential, and charge, and their relationship to chemical parameters. Such use of electrical measurements for analytical purposes has found a vast range of applications, including environmental monitoring, industrial quality control, and biomedical analysis. Advances over the past 15 years, including the development of ultramicroelectrodes, the design of tailored interfaces, the coupling of biological components and electrochemical transducers, the synthesis of ionophores and receptors containing cavities of molecular size, the development of ultratrace voltammetric techniques and of high-resolution scanning probe microscopies, and the fabrication of molecular devices and efficient flow detectors, have led to a substantial increase in the popularity of electroanalysis, and to its expansion into new phases. Indeed, electrochemical probes are receiving a major share of the attention in the development of chemical sensors.

In contrast to many chemical measurements, which involve homogeneous bulk solutions, electrochemical processes take place at the electrode-solution interface. The distinction between various electroanalytical techniques reflects the type of electrical signal used for the quantitation. The two principal types of electroanalytical measurements are potentiometric and potentiostatic. Both types require at least two electrodes (conductors) and a contacting sample (electrolyte) solution, which constitute the electrochemical cell. The electrode surface is thus a junction between an ionic conductor and an electronic conductor. One of the two electrodes responds to the target analyte(s) and is thus termed the indicator (or working) electrode. The second one, termed the reference electrode, is of constant potential (that is, independent of the properties of the solution). Electrochemical cells can be classified as electrolytic (when they consume electricity from an external source) or galvanic (if they are used to produce electrical energy).

Potentiometry (discussed in Chapter 4), which is of great practical importance, is a static (zero current) technique in which the information about the sample composition is obtained from measurement of the potential established across a membrane. Different types of membrane materials, possessing different ion recognition processes, have been developed to impart high selectivity. The resulting potentiometric probes have thus been widely used for several decades for direct monitoring of ionic species such as protons or calcium, fluoride, and potassium ions in complex samples.

Controlled-potential (potentiostatic) techniques are based on dynamic (no zero current) situations. Here, the electrode potential is used to drive an electron-transfer reaction, and the resultant current is measured. The role of the potential is analogous to that of the wavelength in optical measurements. Such a controllable parameter can be viewed as "electron pressure," which forces the chemical species to gain or lose an electron (reduction or oxidation, respectively). Accordingly, the resulting current reflects the rate at which electrons move across the electrode-solution interface. Potentiostatic techniques can thus measure any chemical species that is electroactive, i.e., that can be made to reduce or oxidize. Knowledge of the reactivity of functional groups in a given compound can be used to predict its electroactivity. Nonelectroactive compounds may also be detected in connection with indirect or derivatization procedures.

The advantages of controlled-potential techniques include high sensitivity, selectivity toward electroactive species, a wide linear range, portable and low-cost instrumentation, speciation capability, and a wide range of electrodes that allow assays of unusual environments. Several properties of these techniques are summarized in Table 1.1. Extremely low (nanomolar) detection limits can be achieved with very small (5–20 μL) sample volumes, thus allowing the determination of analyte amounts of 10^{-13}–10^{-15} mol on a routine basis. Improved selectivity may be achieved via the coupling of controlled-potential schemes with chromatographic or optical procedures.

This chapter attempts to give an overview of electrode processes, together with discussion of electron-transfer kinetics, mass transport, and the electrode/solution interface.

1.2 Faradaic Processes

The objective of controlled-potential electroanalytical experiments is to obtain a current response which is related to the concentration of the target analyte.

Table 1.1 Properties of Controlled-Potential Techniques

Technique*	Working Electrode†	Detection Limit, *M*	Speed (*time per cycle*), min	Response Shape
DC polarography	DME	10^{-5}	3	Wave
NP polarography	DME	5×10^{-7}	3	Wave
DP polarography	DME	10^{-8}	3	Peak
DP voltammetry	Solid	5×10^{-7}	3	Peak
SW polarography	DME	10^{-8}	0.1	Peak
AC polarography	DME	5×10^{-7}	1	Peak
Chronoamperometry	Stationary	10^{-5}	0.1	Transient
Cyclic voltammetry	Stationary	10^{-5}	0.1–2	Peak
Stripping voltammetry	HMDE, MFE	10^{-10}	3–6	Peak
Adsorptive stripping voltammetry	HMDE	10^{-10}	2–5	Peak
Adsorptive stripping voltammetry	Solid	10^{-9}	4–5	Peak
Adsorptive-catalytic stripping voltammetry	HMDE	10^{-12}	2–5	Peak

*DC = direct current; NP = normal pulse; DP = differential pulse; SW = square wave; AC = alternating current.

†HMDE = hanging mercury drop electrode; MFE = mercury film electrode; DME = dropping mercury electrode.

This objective is accomplished by monitoring the transfer of electron(s) during the redox process of the analyte:

$$\mathrm{O} + ne^- \rightleftarrows \mathrm{R} \tag{1.1}$$

where O and R are the oxidized and reduced forms, respectively, of the redox couple. Such reaction will occur in a potential region that makes the electron transfer thermodynamically or kinetically favorable. For systems controlled by the laws of thermodynamics, the potential of the electrode can be used to establish the concentration of the electroactive species at the surface [$C_O(0,t)$ and $C_R(0,t)$] according to the Nernst equation:

$$E = E^\circ + \frac{2.3RT}{nF} \log \frac{C_O(0, t)}{C_R(0, t)} \tag{1.2}$$

where E° is the standard potential for the redox reaction. R is the universal gas constant (8.314 $\mathrm{JK^{-1}mol^{-1}}$), T the Kelvin temperature, n is the number of electrons transferred in the reaction, and F is the Faraday constant (96,487 coulombs). On the negative side of E°, the oxidized form thus tends to be reduced, and the forward reaction (i.e., reduction) is more favorable. The current resulting from a change in oxidation state of the electroactive species is termed the *faradaic current* because it obeys Faraday's law (i.e., the reaction of 1 mole of substance involves a change of $n \times 96{,}487$ coulombs). The faradaic current is a direct measure of the rate of the redox reaction. The resulting current-potential plot, known as the *voltammogram*, is a display of current signal (vertical axis) vs. the applied potential (horizontal axis). The exact shape and magnitude of the response are governed by the processes involved in the electrode reaction. The total current is the summation of the faradaic currents for the sample and blank solutions, as well as the nonfaradaic charging background current (discussed in Section 1.3).

The pathway of the electrode reaction can be quite complicated, and takes place in a sequence that involves several steps. Simple reactions involve only mass transport of the electroactive species to the electrode surface, the electron transfer across the interface, and the transport of the product back to the bulk solution. More complex reactions include additional chemical and surface processes which precede or follow the actual electron transfer. The net rate of the reaction, and hence the measured current, may be limited either by mass transport of the reactant or by the rate of electron transfer. The more sluggish process will be the rate-determining step. Whether a given reaction is controlled by the mass transport or electron transfer is usually determined by the type of compound being measured and by various experimental conditions (electrode material, media, operating potential, mode of mass transport, timescale, etc.). When the overall reaction is controlled solely by the rate at which the electroactive species reach the surface (i.e., a facile electron transfer), the current is said to be mass transport limited. Such reactions are called nernstian or reversible, because they obey thermodynamic relationships.

1.2.1 Mass-Transport-Controlled Reactions

Mass transport occurs by three different modes:

- *diffusion*—the spontaneous movement under the influence of concentration gradient, i.e., from regions of high concentrations to regions of lower ones, aimed at minimizing concentration differences.
- *convection*—transport to the electrode by a gross physical movement; such fluid flow occurs by stirring or flowing the solution and by rotating or vibrating the electrode (i.e., forced convection) or because of density gradients (i.e., natural convection);
- *migration*—movement of charged particles along an electrical field (i.e., the charge is carried through the solution by ions according to their transference number). These modes of mass transport are illustrated in Figure 1.1.

The flux (J) is a common measure of the rate of mass transport at a fixed point. It is defined as the number of molecules penetrating a unit area of an imaginary plane in a unit of time, and has the units of mol cm^{-2} s^{-1}. The flux to the electrode is described mathematically by a differential equation, known

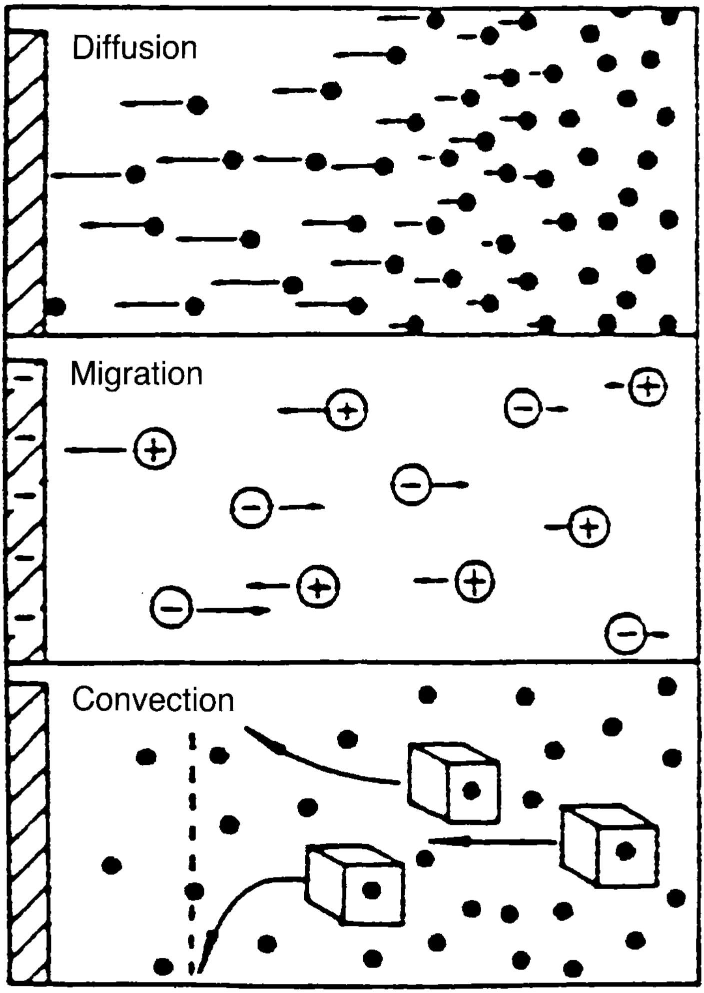

Figure 1.1 The three modes of mass transport. [Reproduced with permission (1).]

as the Nernst–Planck equation, given here for one dimension:

$$J(x, t) = -D\frac{\partial C(x, t)}{\partial x} - \frac{zFDC}{RT}\frac{\partial \phi(x, t)}{\partial x} + C(x, t)V(x, t) \tag{1.3}$$

where D is the diffusion coefficient (cm^2 s^{-1}), $\partial C(x, t)/\partial x$ is the concentration gradient (at distance x and time t), $\partial \phi(x, t)/\partial x$ is the potential gradient, z and C are the charge and concentration, respectively, of the electroactive species, and $V(x, t)$ is the hydrodynamic velocity (in the x direction). In aqueous media, D usually ranges beween 10^{-5} and 10^{-6} cm^2 s^{-1}. The current (i) is directly proportional to the flux:

$$i = -nFAJ \tag{1.4}$$

where A is the electrode area.

As indicated by equation (1.3), the situation is quite complex when the three modes of mass transport occur simultaneously. Such complication makes it difficult to relate the current to the analyte concentration. The situation can be greatly simplified by suppressing the electromigration or convection, through the addition of excess inert salt or use of a quiescent solution, respectively. Under these conditions, the movement of the electroactive species is limited by diffusion. Equations governing diffusion processes are thus relevant to many electroanalytical procedures.

According to Fick's first law, the rate of diffusion (i.e., the flux) is directly proportional to the slope of the concentration gradient:

$$J(x, t) = -D\frac{\partial C(x, t)}{\partial x} \tag{1.5}$$

Combination of equations (1.4) and (1.5) yields a general expression for the current response:

$$i = nFAD\frac{\partial C(x, t)}{\partial x} \tag{1.6}$$

Hence, the current (at any time) is proportional to the concentration gradient of the electroactive species. As indicated by the above equations, the diffusional flux is time dependent. Such dependence is described by Fick's second law (for linear diffusion):

$$\frac{\partial C(x, t)}{\partial t} = D\frac{\partial^2 C(x, t)}{\partial x^2} \tag{1.7}$$

This equation reflects the rate of change with time of the concentration between parallel planes at points x and $(x + dx)$ (which is equal to the difference in flux at the two planes). Fick's second law is valid for the conditions assumed, namely planes parallel to one another and perpendicular to the direction of diffusion, i.e., conditions of linear diffusion. In contrast, for the case of diffusion toward a spherical electrode (where the lines of flux are not parallel but are perpendicular to segments of the sphere), the Fick's second law has the form of

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right] \tag{1.8}$$

where r is the distance from the center of the electrode. Overall, Fick's laws describe the flux and the concentration of the electroactive species as functions of position and time. The solution of these partial differential equations usually