ANALYTICAL ELECTROCHEMISTRY

Third Edition

Joseph Wang

WILEY-VCH

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

CONTENTS

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. The objective is to provide a sound understanding of the fundamentals of electrode reactions and the principles of electrochemical methods, and to demonstrate their potential for solving real-life analytical problems. The high performance, small size, and low cost of electrochemical devices has led to many important detection systems. Given the impressive progress in electroanalytical chemistry and its growing impact on analytical chemistry, this work offers also an up-to-date, easy-to-read presentation of more recent advances, including new methodologies, sensors, detectors, and microsystems. 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 very 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 discusses the study of electrode reactions and high-resolution surface characterization. Chapter 3 gives an overview of finite-current-controlled potential techniques. Chapter 4 describes the electrochemical instrumentation and electrode materials (including new and modified microelectrodes). Chapter 5 deals with the principles of potentiometric measurements and various classes of ion-selective electrodes, while Chapter 6 is devoted to the growing field of chemical sensors (including modern biosensors, gas sensors, microchip devices, and sensor arrays). Numerous up-to-date references, covering the latest literature, are given at the end of each chapter.

By discussing more recent advances, this book attempts to bridge the common gap between research literature and standard textbooks.

This third edition of *Analytical Electrochemistry* is extensively revised and updated, and reflects the rapid growth of electroanalytical chemistry since 1999. It contains a number of new topics, including DNA biosensors, impedance spectroscopy, detection for capillary electrophoresis, diamond electrodes, carbon-nanotube- and nanoparticle-based assays and devices, large-amplitude AC voltammetry, microfluidic ("lab on a chip") devices, or molecularly-imprinted polymeric sensors. Other topics, such as the principles of potentiometric measurements, spectroelectrochemistry, electrochemiluminescence, modified and microelectrodes, scanning electrochemical and atomic force microscopies, electrical communication between redox enzymes and electrodes, explosive detection, or enzyme and immunoelectrodes, have been greatly expanded. The entire text has been updated to cover the very latest (as of August 2005) developments in electroanalytical chemistry. Numerous new illustrations, worked-out examples and end-of-chapter problems have been added to this edition. Existing figures have been redrawn and improved. In the 5 years since the second edition I have received numerous suggestions, many of which have been incorporated in the second edition.

Finally, I wish to thank my wife, Ruth, and my daughter, Sharon, for their love and patience; Vairavan Subramanian and Daphne Hui for their technical assistance; the editorial and production staff of John Wiley & Sons, Inc. for their help and support; Professor Erno Pretsch (ETH, Zurich) for extremely useful suggestions; and the numerous electrochemists across the globe who led to the advances reported in this textbook. Thank you all!

JOSEPH WANG

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ABBREVIATIONS AND SYMBOLS

a	Activity
A	Area of electrode
Ab	Antibody
AC	Alternating current
AdSV	Adsorptive stripping voltammetry
AE	Auxiliary electrode
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
Ag	Antigen
ASV	Anodic stripping voltammetry
B	Adsorption coefficient
BDD	Boron-doped diamond
C	Concentration
C_{dl}	Differential capacitance
CE	Counter electrode
CME	Chemically modified electrode
CNT	Carbon nanotube
CSV	Cathodic stripping voltammetry
CV	Cyclic voltammetry
CWE	Coated-wire electrode
CZE	Capillary-zone electrophoresis
D	Diffusion coefficient
DME	Dropping mercury electrode
DNA	Deoxyribonucleic acid
DP	Differential pulse

DPV	Differential pulse voltammetry
E	Potential (V)
ΔE	Pulse amplitude
E°	Standard electrode potential
$E_{1/2}$	Half-wave potential
E_p	Peak potential
E_pzc	Potential of zero charge
EC	Electrode process involving electrochemical followed by chemical steps
ECL	Electrochemiluminescence
EQCM	Electrochemical quartz crystal microbalance
ESCA	Electron spectroscopy for chemical analysis
EXAFS	X-ray adsorption fine structure
F	Faraday constant
FET	Field effect transistor
FIA	Flow injection analysis
f_i	Activity coefficient
f_0	Base resonant frequency
FTIR	Fourier transform infrared
$\Delta G\ddagger$	Free energy of activation
HMDE	Hanging mercury drop electrode
i	Electric current
i_c	Charging current
i_t	Tunneling current
IHP	Inner Helmholz plane
IRS	Internal reflectance spectroscopy
ISE	Ion-selective electrode
ISFET	Ion-selective field effect transistor
J	Flux
k_{ij}^{pot}	Potentiometric selectivity coefficient
k°	Standard rate constant
K_m	(1) Michaelis Menten constant; (2) mass transport coefficient
LB	Langmuir–Blodgett
LCEC	Liquid chromatography/electrochemistry
LEED	Low-energy electron diffraction
m	Mercury flow rate (in polarography)
Δm	Mass charge (in EQCM)
MFE	Mercury film electrode
μTAS	Micro–total analytical system
MIP	Molecularly imprinted polymer
MLR	Multiple linear regression
MWCNT	Multiwall carbon nanotube
N	Collection efficiency
n	Number of electrons transferred
NP	Normal pulse

O	The oxidized species
OHP	Outer Helmholz plane
OTE	Optically transparent electrode
PAD	Pulsed amperometric detection
PCR	Principal-component regression
PLS	Partial least squares
PSA	Potentiometric stripping analysis
PVC	Poly(vinyl chloride)
q	Charge
QCM	Quartz crystal microbalance
R	(1) Resistance; (2) gas constant
R_p	Electron transfer resistance
R_s	Ohmic resistance of the electrolyte solution
RDE	Rotating disk electrode
Re	Reynolds number
RE	Reference electrode
RRDE	Rotating ring–disk electrode
RVC	Reticulated vitreous carbon
S	(1) Barrier width (in STM); (2) substrate
SAM	Self-assembled monolayer
SECM	Scanning electrochemical microscopy
SEM	Scanning electron microscopy
SERS	Surface enhanced Raman scattering
SPM	Scanning probe microscopy
STM	Scanning tunneling microscopy
SW	Square wave
SWCNT	Single-wall carbon nanotube
SWV	Square-wave voltammetry
T	Temperature
t	Time
t_m	Transition time (in PSA)
U	Flow rate
UHV	Ultrahigh vacuum
v	Potential scan rate
V_Hg	Volume of mercury electrode
$\mathrm{W}_{\square}$	Peak width (at half-height)
WE	Working electrode
WJD	Wall-jet detector
XPS	X-ray photoelectron spectroscopy

α	Transfer coefficient
Γ	Surface coverage
γ	Surface tension
δ	Thickness of the diffusion layer
δ_H	Thickness of the hydrodynamic boundary layer

ε	Dielectric constant
η	Overvoltage
μ	Ionic strength
ν	Kinematic viscosity
ω	Angular velocity

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, or 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, or biomedical analysis. Advances since the mid-1980s, including the development of ultramicroelectrodes, the design of tailored interfaces and molecular monolayers, 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 or of high-resolution scanning probe microscopies, and the microfabrication of molecular devices or efficient flow detectors, have led to a substantial increase in the popularity of electroanalysis and to its expansion into new phases and environments. 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

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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 (i.e., 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 5), 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 deal with the study of charge transfer processes at the electrode–solution interface, and are based on dynamic (non-zero-current) situations. Here, the electrode potential is being used to derive 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, that is, that can be made to reduce or oxidize. Knowledge of the reactivity of functional group 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 ranging from 10^{-13} to 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.

TABLE 1.1 Properties of Controlled-Potential Techniques[a]

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

[a] All acronyms used here are included in the "Abbreviations and Symbols" list following the Preface.

1.2 FARADAIC PROCESSES

The objective of controlled-potential electroanalytical experiments is to obtain a current response that is related to the concentration of the target analyte. Such an objective is accomplished by monitoring the transfer of electron(s) during the redox process of the analyte:

$$\mathrm{O} + n\mathrm{e}^- \rightleftharpoons \mathrm{R} \tag{1.1}$$

where O and R are the oxidized and reduced forms, respectively, of the redox couple. Such a 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 [$C_\mathrm{O}(0,t)$ and $C_\mathrm{R}(0,t)$] according to the Nernst equation

$$E = E^\circ + \frac{2.3RT}{nF}\log\frac{C_\mathrm{O}(0,t)}{C_\mathrm{R}(0,t)} \tag{1.2}$$

where E° is the standard potential for the redox reaction, R is the universal gas constant ($8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$), T is the Kelvin temperature, n is the number of electrons transferred in the reaction, and F is the Faraday constant [96,487 C (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 mol of substance involves a change of $n \times 96{,}487\,\mathrm{C}$). 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 (ordinate)] versus the excitation potential [horizontal axis (abscissa)]. The exact shape and magnitude of the voltammetric response is 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. The rate of such reactions is determined by the slowest step in the sequence. Simple reactions involve only mass transport of the electroactive species to the electrode surface, electron transfer across the interface, and transport of the product back to the bulk solution. More complex reactions include additional chemical and surface processes that either precede or follow the actual electron transfer. The net rate of the reaction, and hence the measured current, may be limited by either mass transport of the reactant or the rate of electron transfer. The more sluggish process will be the rate-determining step. Whether a given reaction is controlled by 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, time scale, etc.). For a given system, the rate-determining step may thus depend on the potential range under investigation. 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. Several important techniques (discussed in Chapter 4) rely on such mass-transport-limited conditions.

1.2.1 Mass-Transport-Controlled Reactions

Mass transport occurs by three different modes:

- *Diffusion*—the spontaneous movement under the influence of concentration gradient, 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; the major driving force for convection is an external mechanical energy associated with stirring or flowing the solution or rotating or vibrating the

electrode (i.e., forced convection). Convection can also occur naturally as a result of density gradients.

- *Migration*—movement of charged particles along an electrical field (i.e., where 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*), a common measure of the rate of mass transport at a fixed point, is defined as the number of molecules penetrating a unit area of an imaginary plane in a unit of time and is expressed in units of $\mathrm{mol\,cm^{-2}\,s^{-1}}$. The flux to the electrode is described mathematically by a differential equation, known as the *Nernst–Planck equation*, given here for one dimension

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

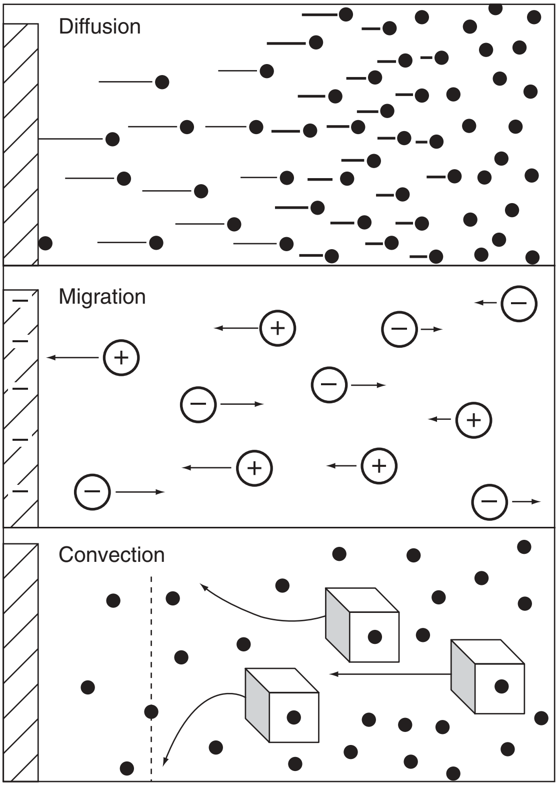

Figure 1.1 The three modes of mass transport. (Reproduced with permission from Ref. 1.)

where D is the diffusion coefficient (cm^2/s); $[\partial C(x,t)]/\partial x$ 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 between 10^{-5} and 10^{-6} cm^2/s. The current (i) is directly proportional to the flux and the surface area (A):

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

As indicated by Eq. (1.3), the situation is quite complex when the three modes of mass transport occur simultaneously. This complication makes it difficult to relate the current to the analyte concentration. The situation can be greatly simplified by suppressing the electromigration through the addition of excess inert salt. This addition of a high concentration of the supporting electrolyte (compared to the concentration of electroactive ions) helps reduce the electrical field by increasing the solution conductivity. Convection effects can be eliminated by using a quiescent solution. In the absence of migration and convection effects, movement of the electroactive species is limited by diffusion. The reaction occurring at the surface of the electrode generates a concentration gradient adjacent to the surface, which in turn gives rise to a diffusional flux. 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 Eqs. (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 equations above, 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, specifically, 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), Fick's second law is expressed as

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

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 requires application of a (Laplace transformation) mathematical method. The Laplace transformation is of great value for such application, as it enables the conversion of the problem into a domain where a simpler mathematical manipulation is possible. Details of using the Laplace transformation are beyond the scope of this text, and can be found in Ref. 2. The establishment of proper initial and boundary conditions (which depend on the specific experiment) is also essential for this treatment. The current–concentration–time relationships resulting from such treatment are described below for several relevant experiments.

1.2.1.1 Potential-Step Experiment Let us see, for example, what happens in a potential-step experiment involving the reduction of O to R, a potential value corresponding to complete reduction of O, a quiescent solution, and a planar electrode embedded in a planar insulator. (Only O is initially present in solution.) The current–time relationship during such an experiment can be understood from the resulting concentration–time profiles. Since the surface concentration of O is zero at the new potential, a concentration gradient is established near the surface. The region within which the solution is depleted of O is known as the *diffusion layer*, and its thickness is given by δ. The concentration gradient is steep at first, and the diffusion layer is thin (see Fig. 1.2 for t_1). As time goes by, the diffusion layer expands (to δ_2 and δ_3 at t_2 and t_3), and hence the concentration gradient decreases.

Initial and boundary conditions in such an experiment include $C_O(x,0) = C_O(\mathrm{b})$ [i.e., at $t = 0$, the concentration is uniform throughout the system and equal to the bulk concentration, $C_O(b)$], $C_O(0,t) = 0$ for $t > 0$ (i.e., at later times the surface concentration is zero); and $C_O(x,0) \rightarrow C_O(\mathrm{b})$ as $x \rightarrow \infty$ (i.e., the concentration increases as the distance from the electrode increases). Solution to Fick's laws (for linear diffusion, i.e., a planar electrode) for these conditions results in a time-dependent concentration profile:

$$C_O(x,t) = C_O(\mathrm{b})\left\{1 - \mathrm{erf}\left[x/(4D_O t)^{1/2}\right]\right\} \tag{1.9}$$

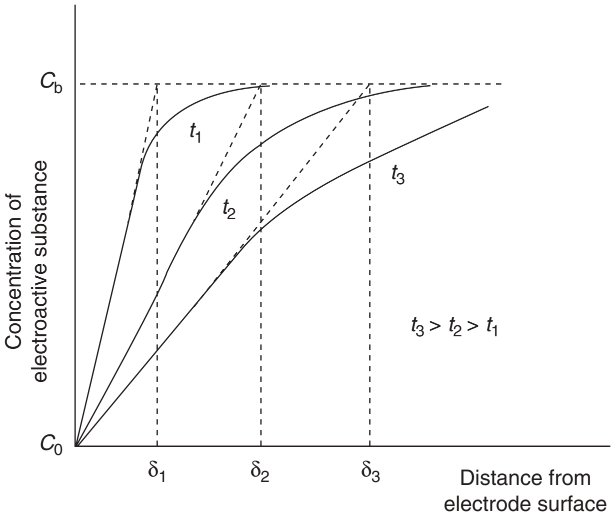

Figure 1.2 Concentration profiles for different times after the start of a potential-step experiment.

whose derivative with respect to *x* gives the concentration gradient at the surface

$$\frac{\partial C}{\partial x} = C_O(b) \big/ (\pi D_O t)^{1/2} \tag{1.10}$$

when substituted into Eq. (1.6) leads to the well-known *Cottrell equation*:

$$i(t) = nFAD_O C_O(b) \big/ (\pi D_O t)^{1/2} \tag{1.11}$$

Thus, the current decreases in proportion to the square root of time, with $(\pi D_O t)^{1/2}$ corresponding to the diffusion-layer thickness.

Solving Eq. (1.8) (using Laplace transform techniques) will yield the time evolution of the current of a spherical electrode:

$$i(t) = nFAD_O C_O(b) \big/ (\pi D_O t)^{1/2} + nFAD_O C_O \big/ r \tag{1.12}$$

The current response of a spherical electrode following a potential step thus contains both time-dependent and time-independent terms—reflecting the planar and spherical diffusional fields, respectively (Fig. 1.3)—becoming time independent at long timescales. As expected from Eq. (1.12), the change from one regime to another is strongly dependent on the radius of the electrode.

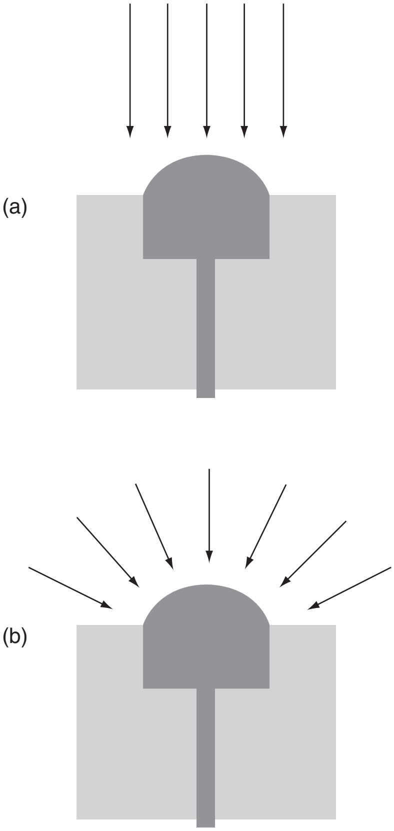

Figure 1.3 Planar (a) and spherical (b) diffusional fields at spherical electrodes.

The unique mass transport properties of ultramicroelectrodes (discussed in Section 4.5.4) are attributed to shrinkage of the electrode radius.

1.2.1.2 Potential-Sweep Experiments Let us move to a voltammetric experiment involving a linear potential scan, the reduction of O to R and a quiescent solution. The slope of the concentration gradient is given by $(C_O(\mathrm{b},t) - C_O(0,t))/\delta$, where $C_O(\mathrm{b},t)$ and $C_O(0,t)$ are the bulk and surface concentrations of O. The change in the slope, and hence the resulting current, are due to changes of both $C_O(0,t)$ and δ. First, as the potential is scanned negatively, and approaches the standard potential (E°) of the couple, the surface concentration rapidly decreases in accordance with the Nernst equation [Eq. (1.2)]. For example, at a potential equal to E° the concentration ratio is unity $[C_O(0,t)/C_R(0,t) = 1]$. For a potential 59 mV more negative than E°, $C_R(0,t)$ is present at 10-fold excess $[C_O(0,t)/C_R(0,t)] = \frac{1}{10}(n = 1)$. The decrease in $C_O(0,t)$ is coupled with an increase in the diffusion-layer thickness, which dominates the