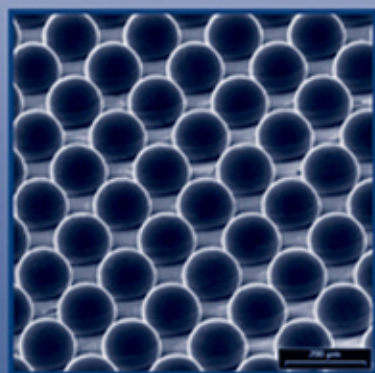
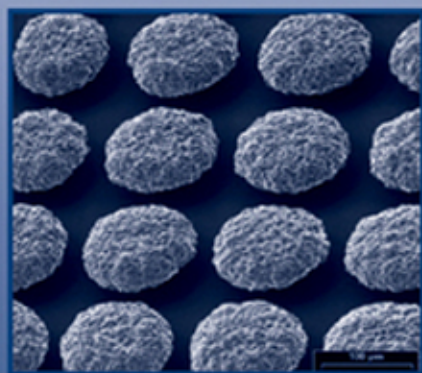


MODERN ELECTROPLATING

FIFTH EDITION



Edited by
MORDECHAY SCHLESINGER
MILAN PAUNOVIC

MODERN ELECTROPLATING

MODERN ELECTROPLATING

Fifth Edition

Edited by

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IBM T.J. Watson Research Center, Yorktown Heights, NY (Retired)



Sponsored by

THE ELECTROCHEMICAL SOCIETY, INC. *Pennington, New Jersey*



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Summary: "Electroplating is the coating of an electrically conductive object with a layer of metal using electrical current resulting in a thin, smooth, even coat of metal on the object. This text covers the methods and applications of electrochemical deposition of metals, alloys, semiconductors, and conductive polymers. It provides practical advice and some theoretical background to those entering the field of electrodeposition. Like previous editions, the fifth edition will be the first stop reference for the electroplating community. This fully updated edition includes significant advances in the field, from emerging electrodeposition techniques to electroplating in medical and data storage industries" – Provided by publisher.

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PREFACE

Ours is the information age. Consequently, the demand for high-performance, low-cost, and nonvolatile information storage systems is on a constant rise. There are a great variety of information storage systems, with varying degrees of development and commercialization. Those include, but are not limited to, magnetic tape drives, hard disc drives, magnetic floppy disc drives, magneto-optic (MO) disc drives, phase change optic disc drives, semiconductor flash memory, magnetic random-access memory (RAM), and holographic optical storage. Electrochemical deposition techniques are essential in the production of most of the above. This, among many others, is the *raison d'être* for the present (fifth) and the earlier (fourth) editions.

The fourth edition of *Modern Electroplating* appeared some 10 years ago. A great deal of progress has taken place in those years in the area of electrochemical plating and related fields. It is these developments that make this new edition both desirable and necessary. Those profound changes are reflected in the present edition in a number of different ways. Essentially, all chapters were rewritten, some by different authors, and/or updated. Unfortunately, two authors who contributed to the fourth edition (Drs. Rolf Wyle and Ned Mandich) have since passed on. Two chapters have been removed altogether and new ones are replacing them. The two new chapters are titled “Electrochemical Deposition Process for ULSI Interconnection Devices” by Osaka and Yoshino and “Electrochemical Synthesis of Metal Alloys for Magnetic Recording Systems” by Sugiyama, Yoshino, Hachisu, and Osaka. Four new chapters have been added:

“Applications to Magnetic Recording and Microelectronic Technologies” by Brankovic, Vasiljevic, and Dimitrov; “Microelectromechanical Systems” by Zangari; “Analysis of Electroplated Films Using Dual-Beam FIB/SEM and TEM Techniques” by Meng-Burany; and “Ionic Liquid Treatments for Enhanced Corrosion Resistance of Magnesium-Based Substrates” by Petro, Schlesinger, and Song. These and most other changes, including the publication of the new second edition in 2006 of *Fundamentals of Electrochemical Deposition*, reflect the present tendency of the applications of electroplating more and more in the arena of nanoelectronics in particular and nanotechnology in general as alluded to above. Typically, it may be observed that whereas the fourth edition is comprised of 26 chapters on about 800 pages, the present edition contains 30 chapters and is about the same number of substantially enlarged pages. In this edition as in the previous the chapters are self-contained in that those may be read in any order that the reader finds useful. Thanks are due to the over 30 contributors/authors who made this edition possible.

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PREFACE TO THE FOURTH EDITION

In planning this new edition of *Modern Electroplating*, we have realized from the start that it would be impossible to include in one volume both the fundamental aspects and the technology itself. For this reason we have decided to publish the recent developments in the science of deposition in a separate volume titled *Fundamentals of Electrochemical Deposition*. That volume was published in November 1998. Therefore, the present volume includes only a brief summary of fundamental technological advancements, and this is presented in the first, introductory chapter.

Since the last edition of *Modern Electroplating* in 1975, electrochemical deposition has evolved from an ill-defined area, as the Preface to the previous edition calls it, into an exact science. This development is, in the first place, seen as responsible for the ever-increasing number and widening types of applications of this branch of practical science and engineering.

The most significant developments in any field of science or technology in general, and in electrochemistry in particular, are made by those who possess a good understanding of the fundamental aspects of the discipline, which in this case is electrochemical deposition. We, the editors, found it necessary and highly desirable to seek and present to the reader a companion volume that, for all intents and purposes, makes essentially a completely new contribution and not just a revised version of the earlier editions. Thus, for the sake of illustration, the present edition includes a chapter devoted to the electrodeposition of semiconductors. Another deals with environmental issues. Last, but not least, in this connection, neither of the editors nor the vast majority of the contributors were associated with any of the earlier editions.

Technological areas in which the possession of technical knowledge of electroplating is found to be essential include all aspects of electronics; macro-, micro-, and nano-optics;

opto-electronics; and sensors of most types. In addition, a number of key industries, such as the automotive industry, employ methods of electroplating. This is so even when other methods such as evaporation and sputtering CVD (chemical vapor deposition) are an option. Electroplating is therefore often used for reasons of economy and/or convenience.

This volume is divided into 26 chapters. After a three-part introductory chapter by Paunovic, Schlesinger, and Weil come 13 chapters dealing with the electrodeposition of copper (Dini), nickel (DiBari), gold (Kohl), silver (Schlesinger), tin (Abys et al.), chromium (Snyder et al.), lead and alloys (Jordan), tin-lead alloys (Jordan), zinc and alloys (Winand), iron and alloys (Izaki), palladium and alloys (Abys et al.), nickel and cobalt alloys (DiBari), and semiconductors (T. E. Schlesinger). Closing this series of chapters is one on deposition on nonconductors (Schlesinger), and conductive polymers (Osaka et al.). Next come 6 chapters dealing with electroless deposition of copper (Paunovic), nickel (Schlesinger), cobalt (Osaka), palladium and platinum (Ohno), gold (Okinaka), and electroless alloys (Ohno). Finally, 4 chapters close the book, and these are on preparation for deposition (Dexter Snyder), manufacturing technologies (Turner), manufacturing control (Turner), and environmental considerations (Tomkiewicz).

In the preface to *Fundamentals of Electrochemical Deposition* we stated that it may be considered a lucky coincidence that this volume is published close to the time that copper interconnection technology is introduced in the microelectronic industry. This is still the case. There has been a truly revolutionary change from physical to electrochemical techniques in the production of microconductors on silicon, and developments in electrochemical deposition are bound to generate and maintain in the twenty-first century an increased interest and urgent need for up-to-date information regarding

the technology. The present volume together with the *Fundamentals* volume should be of great help in understanding these advancements.

The chapters were written by different authors and so differences in style and approach will be evident. We the editors have tried to smooth those differences without changing the basic message present in each chapter. We also intend this volume to be a useful reference for practitioners of deposition as well as for individuals who are about to enter this modern ever-evolving field of practical knowledge. For this reason each chapter is complete and may be read and consulted separately, and certainly the book can be read in any order.

Our thanks and heartfelt gratitude go to many members of the Electrochemical Society and in particular to those of the Electrodeposition Division. Our thanks also go to our respective families for their patience and understanding during the hectic long hours we spent in preparing this volume.

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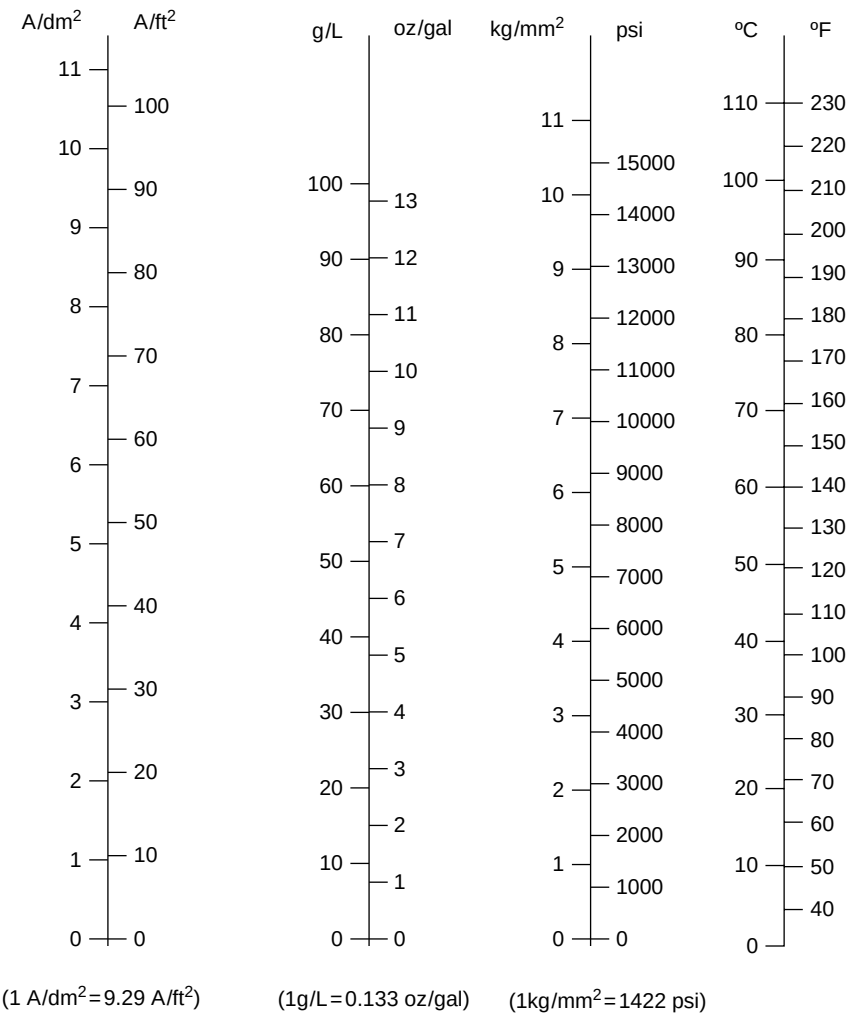
1 centimeter (cm) = 0.934 inch (in.)
 1 millimeter (mm) = 0.0394 inch (in.)
 1 micrometer (μm , micron) = 0.0394 mil = 39.37 microinch ($\mu\text{in.}$)
 1 square decimeter (dm^2) = 15.5 square inch (in.^2) = 0.1076 square foot (ft^2)
 1 square centimeter (cm^2) = 0.155 square inch (in.^2)
 1 square millimeter (mm^2) = 0.00155 square inch (in.^2)
 1 kilogram (kg) = 2.205 pound (lb)
 1 gram (g) = 0.0353 ounce (oz) avoirdupois = 0.0321 ounce Troy
 1 liter (L) = 0.264 gallon U.S. (gal) = 0.220 gallon British
 1 ampere per square decimeter (A/dm^2) = 9.29 ampere per square foot (A/ft^2)—see chart
 1 gram per liter (g/L) = 0.133 ounce per gallon. U.S. (oz/gal)—see chart
 1 kilogram per square millimeter (kg/mm^2) = 1.422 pounds per square inch $\text{lb}/\text{in.}^2$, psi—see chart;
 strictly, unit should be kilogram-force, or kgf/mm^2 ; in SI units, $1 \text{ kgf}/\text{mm}^2 = 9.806 \times 10^6$ newton/square meter (N/m^2) = 9.806 MN/ m^2 ; $1 \text{ N}/\text{m}^2 = 1$ Pa (pascal)

Approximate Conversion Factors for Mental Calculation (accurate to 10% or better)

To convert from	To	Do this
A/dm^2	A/ft^2	Multiply by 10
A/dm^2	$\text{A}/\text{in.}^2$	Divide by 15 (multiply by 2, divide by 30)
Celsius (Centigrade)*	Fahrenheit, F	Multiply by 9/5 (1.8) and add 32
g/L	oz/gal	Divide by 7.5 (multiply by 4, divide by 30)
kg/mm^2	$\text{lb}/\text{in.}^2$ (psi)	Multiply by 1500
mm	in.	Divide by 25 (multiply by 4, divide by 100)
micrometers (m)	mil	Divide by 25 (multiply by 4, divide by 100)

*Exact.

GRAPHICAL CONVERSIONS



THE ELECTROCHEMICAL SOCIETY SERIES

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Modern Electroplating, Fourth Edition

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Semiconductor Wafer Bonding: Science and Technology

Q.-Y. Tong and U. Göscle

Uhlig's Corrosion Handbook, Second Edition

Edited by R. Winston Revie



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FUNDAMENTAL CONSIDERATIONS

MILAN PAUNOVIC,¹ MORDECHAY SCHLESINGER,² AND DEXTER D. SNYDER³

1.1 INTRODUCTION

Already in the preparation of the fourth edition of *Modern Electroplating*, we realized that the first chapter in the third edition (1974) needed to be enlarged considerably in order to cover all the significant progress made since 1974. As the prospect of adding material to the chapter on fundamentals began to suggest an imbalance in the new edition, we chose to publish a separate volume titled *Fundamentals of Electrochemical Deposition* (*Fundamentals* in further text) that would treat the basic aspects of electrochemical deposition [1]. For this reason we provided in the fourth and now in the present fifth edition only a brief review of these fundamentals. The number of references in this chapter is also limited, and the reader is urged to consult the more extensive list of references given in both editions of *Fundamentals*.

This chapter is divided into three parts. Part A treats electrochemical aspects, part B treats physical aspects, and part C treats material science. For this presentation of the fundamentals our objective is to provide the basis for understanding only the electrochemical deposition processes treated in this volume. Information on a higher level is presented in the *Fundamentals* volume.

PART A ELECTROCHEMICAL ASPECTS

In Part A we discuss (1) electrode potential, (2) kinetics and mechanism of electrodeposition, (3) growth mechanism, and (4) electroless and displacement depositions. All four topics are presented in a concise manner that emphasizes the most important points. Most concepts are clarified by solutions of numerical examples. These examples are useful for this chapter and for the chapters that follow.

1.2 ELECTRODE POTENTIAL

When a metal M is immersed in an aqueous solution containing ions of that metal, M^{z+} (e.g., salt MA), there will be an exchange of metal ions M^{z+} between two phases, the metal and the solution. Some M^{z+} ions from the crystal lattice enter the solution, and some ions from the solution enter the crystal lattice. Initially one of these reactions may occur

¹ Milan Paunovic, Part A.

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³ Dexter D. Snyder, Part C.

faster than the other. Let us assume that conditions are such that more M^{z+} ions leave than enter the crystal lattice. In this case there is an excess of electrons on the metal and the metal acquires negative charge, q_M^- (charge on the metal per unit area). In response to the charging of the metal side of the interphase, there is also a rearrangement of charges on the solution side of the interphase. The negative charge on the metal attracts positively charged M^{z+} ions from the solution and repels negatively charged A^{z-} ions. The result of this is an excess of positive M^{z+} ions in the solution in the vicinity of the metal interphase. Thus, in this case, the solution side of the interphase acquires opposite and equal charge, q_s^+ (the charge per unit area on the solution side of the interphase). This positive charge at the solution side of the interphase slows down the rate of M^{z+} ions leaving the crystal lattice (due to repulsion) and accelerates the rate of ions entering the crystal lattice. After a certain period of time a dynamic equilibrium between the metal M and its ions in the solution will result:



where z is the number of electrons involved in the reaction. Reaction from left to right consumes electrons and is called reduction. Reaction from right to left liberates electrons and is called oxidation. At the dynamic equilibrium the same number of M^{z+} ions enter, $\vec{n}$, and the same number of M^{z+} ions leave the crystal lattice, $\bar{n}$, (see Fig. 1.1):

$$\vec{n} = \bar{n} \quad (1.1b)$$

The interphase region is neutral at equilibrium:

$$q_M = -q_s \quad (1.1c)$$

The result of the charging of the interphase is the potential difference, $\Delta\phi(M, S)$, between the potentials of the metal,

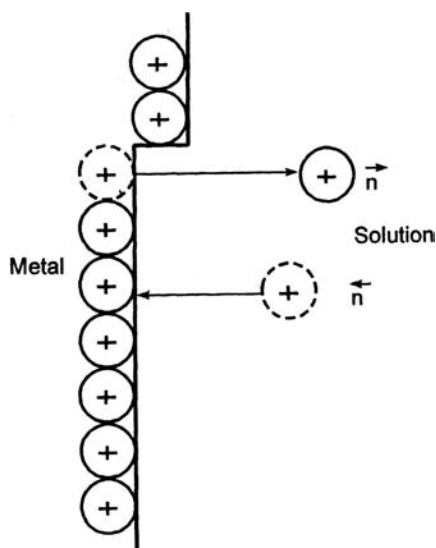


FIGURE 1.1 Formation of metal-solution interphase; equilibrium state: $\vec{n} = \bar{n}$.

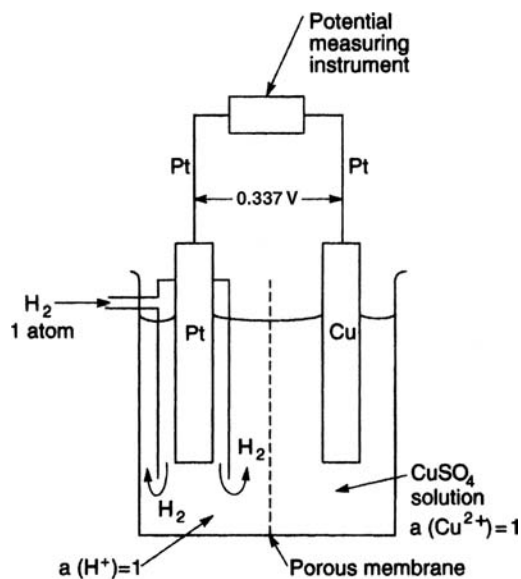


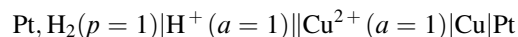
FIGURE 1.2 Relative standard electrode potential E^0 of a Cu/Cu^{2+} electrode.

ϕ_M , and the solution, ϕ_S :

$$\Delta\phi(M, S) = \phi_M - \phi_S \quad (1.2)$$

In order to measure the potential difference of an interphase, one must connect it to another one and thus form an electrochemical cell. The potential difference across this electrochemical cell can be measured.

For example, consider the cell shown in Figure 2.2. This cell may be schematically represented in the following way:



where the left-hand electrode is the normal hydrogen reference electrode; a stands for activity and p for the pressure of H_2 . When $p = 1$ atm and the activity of H^+ ions is 1, the hydrogen electrode is called the standard hydrogen electrode (SHE) and its potential is zero by convention. The measured value of the potential difference of this cell is $+0.337$ V at 25°C . This measured cell potential difference, $+0.337$ V, is called the relative standard electrode potential of Cu and is denoted E^0 . The standard electrode potential of other electrodes is obtained in a similar way, by forming a cell consisting of the SHE and the electrode under investigation. Standard electrode potentials at 25°C are listed in Table 1.1.

The potential E of the M^{z+}/M electrode is a function of the activity [see Eq. (1.5)] of metal ions in the solution according to the Nernst equation,

$$E = E^0 + \frac{RT}{zF} \ln a(M^{z+}) \quad (1.3)$$

TABLE 1.1 Standard Electrode Potentials

Metal/Metal Ion Couple	Electrode Reaction	Standard Value (V)
Au/Au ⁺	Au ⁺ + e ⇌ Au	1.692
Au/Au ³⁺	Au ³⁺ + 3e ⇌ Au	1.498
Pd/Pd ²⁺	Pd ²⁺ + 2e ⇌ Pd	0.951
Cu/Cu ⁺	Cu ⁺ + e ⇌ Cu	0.521
Cu/Cu ²⁺	Cu ²⁺ + 2e ⇌ Cu	0.3419
Fe/Fe ³⁺	Fe ³⁺ + 3e ⇌ Fe	-0.037
Pb/Pb ²⁺	Pb ²⁺ + 2e ⇌ Pb	-0.1262
Ni/Ni ²⁺	Ni ²⁺ + 2e ⇌ Ni	-0.257
Co/Co ²⁺	Co ²⁺ + 2e ⇌ Co	-0.28
Fe/Fe ²⁺	Fe ²⁺ + 2e ⇌ Fe	-0.447
Zn/Zn ²⁺	Zn ²⁺ + 2e ⇌ Zn	-0.7618
Al/Al ³⁺	Al ³⁺ + 3e ⇌ Al	-1.662
Na/Na ⁺	Na ⁺ + e ⇌ Na	-2.71

Source: G. Millazzo and S. Caroli, *Tables of Standard Electrode Potentials*, Wiley, New York, 1978.

or converting the natural logarithm into the decimal logarithm yields

$$E = E^0 + 2.303 \frac{RT}{zF} \ln a(M^{z+}) \quad (1.4)$$

where R , T , z , and F are the gas constant, absolute temperature, number of electrons involved in reaction (1.1a), and Faraday's constant (96,500 C), respectively. The activity of the ion, $a(M^{z+})$, is defined by

$$a(M^{z+}) = \gamma c(M^{z+}) \quad (1.5)$$

where $c(M^{z+})$ is the concentration of M^{z+} in moles per liter and $\gamma(M^{z+})$ is the activity coefficient of M^{z+} ; when the concentration of a solution is low, such as 0.001 M or lower, the activity may be replaced by concentration in moles per liter.

The activity coefficient γ is a dimensionless quantity which depends on the concentration of all ions present in the solution (ionic strength). The individual activity coefficients of the specific ionic species cannot be measured experimentally, but it can be calculated. The experimentally measurable quantity is the mean total ionic activity $\gamma_{\pm}$:

$$\gamma_{\pm} = \sqrt{\gamma_+ \gamma_-} \quad (1.6)$$

which is the geometric mean (the square root of the product) of the activity coefficients of the individual ionic species [2].

When the activity of M^{z+} in the solution is equal to 1, $a(M^{z+}) = 1$, then by Eqs. (1.3) and (1.4), since $\ln 1 = 0$,

$$E = E^0 \quad (1.7)$$

where E^0 is the relative standard electrode potential of the M^{z+}/M electrode. The quantity RT/F has the dimension of

voltage and at 298 K (25°C) has the value of 0.0257 V and 2.303 (RT/F) = 0.0592 V. With these values Eq. (1.4) reads

$$E = E^0 + \frac{0.0592}{z} \log a(M^{z+}) \quad (1.8)$$

The use of Eq. (1.8) is illustrated in Examples 1.1 and 1.2.

Example 1.1 Calculate the reversible electrode potential of a Cu electrode immersed in a CuSO₄ aqueous solution with concentrations 1.0, 0.1, 0.01, and 0.001 mol L⁻¹ at 25°C. The standard electrode potential for a Cu/Cu²⁺ electrode is 0.337 V. Use concentrations in Eq. (1.8) instead of activities in an approximate calculation.

From Eq. (1.8), for $z = 2$, $E^0 = 0.337$, and the concentration 1.0 mol L⁻¹ solution, we obtain $E = 0.337 + (0.0592/2) \log 1 = 0.337$ V, since $\log 1 = 0$. For the 0.1 mol L⁻¹ solution, we obtain $E = 0.337 + (0.0592/2) \log 0.1 = 0.37$ V, since $\log 0.1$ is -1 . Using the same procedure for 0.01 and 0.001 mol L⁻¹ solutions, we find that $E = 0.278$ and 0.248 V, respectively.

Example 1.2 Now calculate the reversible electrode potential of a Cu electrode for the conditions given in the Example 1.1, but use activities in Eq. (1.8) instead of concentrations. The mean activity coefficients of the above solutions, 1.0, 0.1, 0.01, and 0.001 are 0.043, 0.158, 0.387, and 0.700, respectively. Activities of these solutions are calculated using Eq. (1.5). For the 1.0 mol L⁻¹ solution and $\gamma = 0.043$, we find that the activity of this solution is $a_{1.00} = \gamma c(\text{Cu}^{2+}) = 0.043 \times 1 = 0.043$. Activities for solutions 0.1, 0.01, and 0.001 mol L⁻¹ are 1.58×10^{-2} , 3.87×10^{-3} , and 7.00×10^{-4} , respectively.

Using Eq. (1.8) for the 1.00 mol L⁻¹ solution, the reversible electrode potential at 25°C is $E = 0.337 + (0.0592/2) \log 0.043 = 0.337 - 0.0400 = 0.297$ V. For 0.1, 0.01, and 0.001 mol L⁻¹ solutions, the reversible electrode potentials at 25°C are 0.284, 0.266, and 0.244 V, respectively.

Hence Examples 1.1 and 1.2 illustrate that the effect of considering the activity coefficient in calculating electrode potential values is not substantial, and its effect decreases with a decrease in concentration, as seen in column 5 Table 1.2.

TABLE 1.2 Reversible Electrode Potential E of a Cu Electrode Immersed in a CuSO₄ Aqueous Solution

CuSO ₄ Concentration, c (mol L ⁻¹)	E , V Calculated Using c	Activity, a	E , V Calculated Using a	ΔE , V
1.0	0.337	4.3×10^{-2}	0.297	0.040
0.1	0.307	1.58×10^{-2}	0.284	0.023
0.01	0.278	3.87×10^{-3}	0.266	0.012
0.001	0.248	7.00×10^{-4}	0.244	0.004

Note: See Example 1.2.

The difference ΔE in Table 1.2 is due to ion-ion interactions in the solution (1.1). The ion-ion interactions include interactions of the hydrated Cu^{2+} ions with one another and with SO_4^{2-} anions. In using concentration in Eq. (1.8) instead of activity, one thus neglects the ion-ion interactions.

In deposition of alloys it is frequently necessary to complex metal ions, as will be shown in Part B of this chapter. In this case the concentration or activity of metal ions in solution and the reversible electrode potential are calculated using the stability constant of the complex.

1.3 KINETICS AND MECHANISM OF ELECTRODEPOSITION

1.3.1 Relationship between Current and Potential

When an electrode is made a part of an electrochemical cell through which current is flowing, its potential will differ from the equilibrium potential. If the equilibrium potential of the electrode (potential in the absence of current) is E and the potential of the same electrode as a result of current flowing is $E(I)$, then the difference η between these two potentials,

$$\eta = E(I) - E \quad (1.9)$$

is called *overpotential*.

An example of an electrochemical cell of industrial importance is shown in Figure 1.3. This figure shows how the potential $E(I)$ of a copper cathode in the electrodeposition of copper can be measured using the three-electrode cell. The potential $E(I)$ of a Cu cathode, the test electrode, is measured versus a reference electrode (e.g., saturated calomel electrode), a Lugin capillary, and a high-input-impedance device (voltmeter) so that a negligible current is drawn through the reference electrode.

For large negative values of overpotentials ($\eta \geq 100$ mV) the current density i ($i = I/S$, where S is the surface area of the

electrode) increases exponentially with the overpotential η according to the equation

$$i = -i_0 e^{-\alpha z f \eta} \quad (1.10)$$

and for large positive values of overpotential (anodic processes) according to the equation

$$i = -i_0 e^{(1-\alpha) z f \eta} \quad (1.11)$$

where i_0 is the exchange current density ($i_0 = i$ when $\eta = 0$), α the transfer coefficient, F the Faraday constant, R the gas constant, T the absolute temperature, and

$$f = \frac{F}{RT} \quad (1.12)$$

From Eqs. (1.10) and (1.11) it follows that, for $\eta = 0$, $i = i_0$. Thus, when an electrode is at equilibrium, there is a constant exchange of charge carriers (electrons or ions) across the metal-solution interphase (Eq. 1.1b).

At 25°C,

$$f = \frac{96487 \text{ C mol}^{-1}}{8.3144 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 38.94 \text{ V} \quad (1.13)$$

since the Faraday constant $F = 96,487.0 \text{ C mol}^{-1}$, the gas constant $R = 8.3144 \text{ J mol}^{-1} \text{ deg K}^{-1}$, and joules = volts $\times$ coulombs. These exponential relationships show that even small changes in η produce large changes in the current density, as seen from Figure 1.4. Taking the logarithm of Eqs. (1.10) and (1.11) and solving the resulting equations for η , one obtains the Tafel equation:

$$\eta = a \pm b \log|i| \quad (1.14)$$

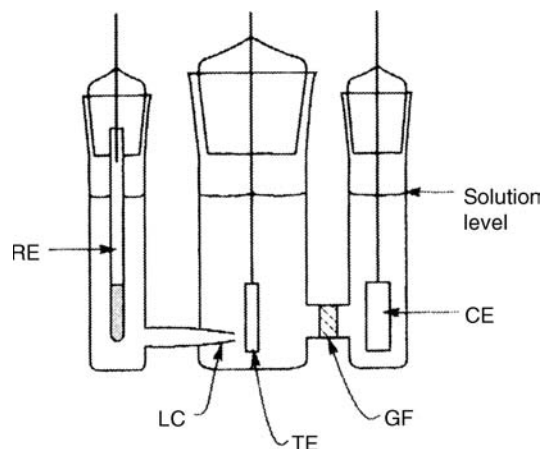


FIGURE 1.3 Three-component, three-electrode electrochemical cell: RE, reference electrode; LC, Lugin capillary; TE, test electrode; GF, glass frit; CE, counterelectrode.

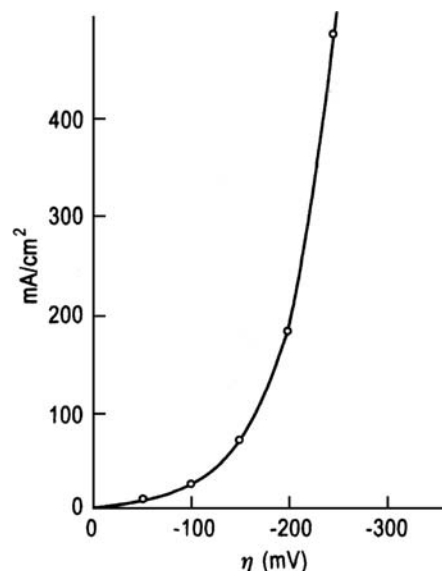


FIGURE 1.4 Exponential relationship between current density and overpotential for electrodeposition of copper from an aqueous solution of 0.15 N CuSO_4 and 1.0 N H_2SO_4 .

where a and b are constants and $|i|$ is the absolute value of the current density. The $\pm$ sign holds for anodic and cathodic processes, respectively. The theoretical value of the constant a for the cathodic process (a_c), is

$$a_c = \frac{2.303RT}{\alpha zF} \log i_0 \quad (1.15)$$

and that of b_c is

$$b_c = \frac{2.303RT}{\alpha zF} \quad (1.16)$$

The use of Eqs. (1.10) and (1.14) is illustrated in Examples 1.3 and 1.4.

Example 1.3 Mattsson and Bockris [3] studied the electrodeposition of copper from the aqueous solution $0.15 N$ CuSO_4 and $1.0 N$ H_2SO_4 and determined that the exchange current density for this process is 3.7 mA cm^{-2} ($3.7 \times 10^{-3} \text{ A cm}^{-2}$). Using Eq. (1.10), we calculate the cathodic current densities i as a function of overpotential value of -50 , -100 , -150 , -200 , and -250 mV. For α we take the most frequent value, $\alpha = 0.5$, and for temperature, 25°C . Next we plot $i = f(\eta)$.

Using Eq. (1.10), we see that i (in A cm^{-2}) for $\eta = -50$ mV (-0.050 V) is

$$i = -i_0 e^{-\alpha f \eta} = (-3.7 \times 10^{-3}) e^{0.9737} = -9.80 \times 10^{-3} \text{ A cm}^{-2}$$

since we have $-\alpha f \eta = -0.5 \times 38.94 \times (-0.050) = 0.9737$ and $e = 2.7183$. For $\eta = -100$ mV (-0.100 V),

$$i = -i_0 e^{-\alpha f \eta} = (-3.7 \times 10^{-3}) e^{1.947} = -25.9 \times 10^{-3} \text{ A cm}^{-2}$$

since we now have $-\alpha f \eta = -0.5 \times 38.94 \times (-0.100) = 1.947$.

In the same way we find i for the other η values. These are shown in Table 1.3.

The calculated values of η are used to plot the $i = f(\eta)$ function corresponding to this example Fig. 1.4. It again illustrates that even small increases in η result in large changes in the current density i .

TABLE 1.3 Current and Overpotential for Electrodeposition of Copper from Acid Copper Sulfate Solution

Overpotential $-\eta$ (mV)	Current Density, i (mA cm^{-2})	$\log i$
50	9.80	0.991
100	25.9	1.41
150	68.7	1.84
200	182	2.26

Note: See Example 1.3.

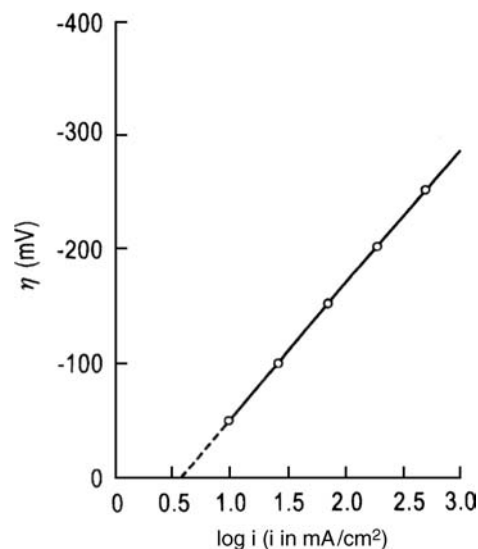


FIGURE 1.5 Tafel plot, $\eta = f(\log i)$, for electrodeposition of copper from the aqueous solution of $0.15 N$ CuSO_4 and $1.0 N$ H_2SO_4 .

Example 1.4 Using the calculated values of i for the given values of η from Table 1.3 plot the corresponding Tafel equation, $\eta = f(\log i)$.

The solution is given in Figure 1.5. It shows that for large values of η ($\eta \geq 100$ mV) the function $\eta = f(\log i)$ is a straight line. The experimentally determined cathodic and anodic Tafel lines for electrodeposition of copper in acid copper sulfate solution are shown in Figure 1.6. The figure shows that the transfer coefficients for the anodic and cathodic processes are different and that the extrapolated value of i at $\eta = 0$ gives the exchange current density. The transfer coefficient α_c for the cathodic process (deposition of Cu^{2+}) is obtained from the slope $d\eta/d(\log i)$ of the cathodic Tafel line. That for the anodic process, α_a , is obtained from the slope of the Tafel line for the anodic process.

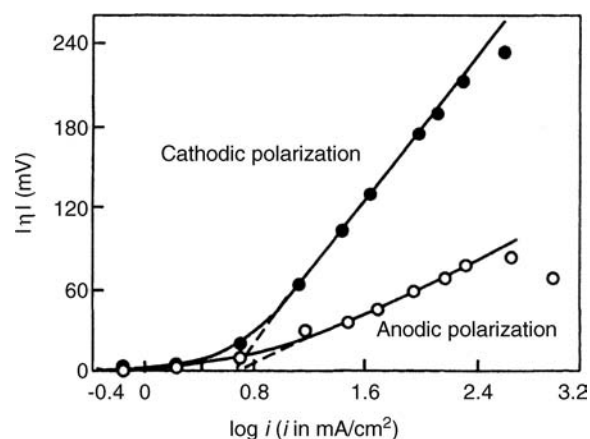


FIGURE 1.6 Current-potential relationship for the electrodeposition of copper from an acid CuSO_4 solution. (From J. O'M. Bockris, in *Transactions of the Symposium on Electrode Processes*, E. Yeager, Ed., Wiley, New York, 1961, with permission from the Electrochemical Society.)

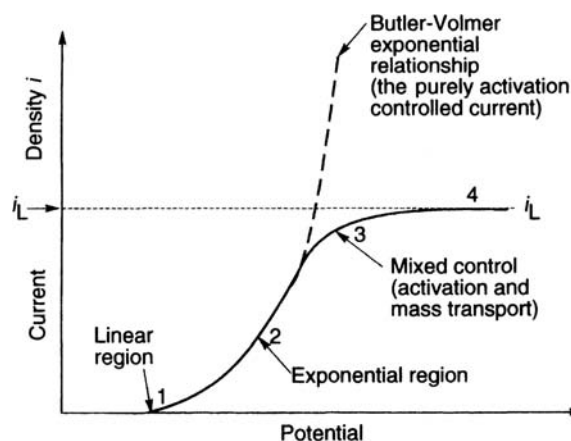


FIGURE 1.7 Four regions in the general current–overpotential relationship: 1, linear; 2, exponential; 3, mixed control; 4, limiting current density region.

1.3.2 Influence of Mass Transport on Electrode Kinetics

The current–potential relationship defined by Eqs. (1.10, 1.11) and (1.14) is valid for the case where the charge transfer, Eq. (1.1), is the slow process (rate-determining step). This relationship has a limit where the rate of deposition reaction is limited by transport of M^{z+} ions. A general current–potential relationship is shown in Figure 1.7. The limiting, or maximum, current density is given by [4]

$$i_L = \frac{nFD}{\delta} c_b \quad (1.17)$$

where D is the diffusion coefficient of the depositing species M^{z+} , c_b is the bulk concentration of M^{z+} ions in the solution, δ is the diffusion layer thickness, n the number of electrons involved in the reaction, and F the Faraday constant. The diffusion layer thickness δ is defined by the Nernst diffusion layer model illustrated in Figure 1.8. This model assumes that the concentration of M^{z+} ions has a bulk concentration c_b up to a distance δ from the electrode surface and then falls off linearly to $c_x = 0$ at the electrode surface. In this model it is assumed that the liquid layer of thickness δ is practically stationary (quiescent). At a distance greater than δ from the surface, the concentration of the reactant M^{z+} is assumed to be equal to that in the bulk. At these distances, $x > \delta$, stirring is efficient. Ions M^{z+} must diffuse through the diffusion layer to reach the electrode surface.

At the values of the limiting (maximum) current density the species M^{z+} are reduced as soon as they reach the electrode. At these conditions the concentration of the reactant M^{z+} at the electrode is nil, and the rate of deposition reaction is controlled by the rate of transport of the reactant M^{z+} to the electrode. If an external current greater than the limiting current i_L is forced through the electrode, the double

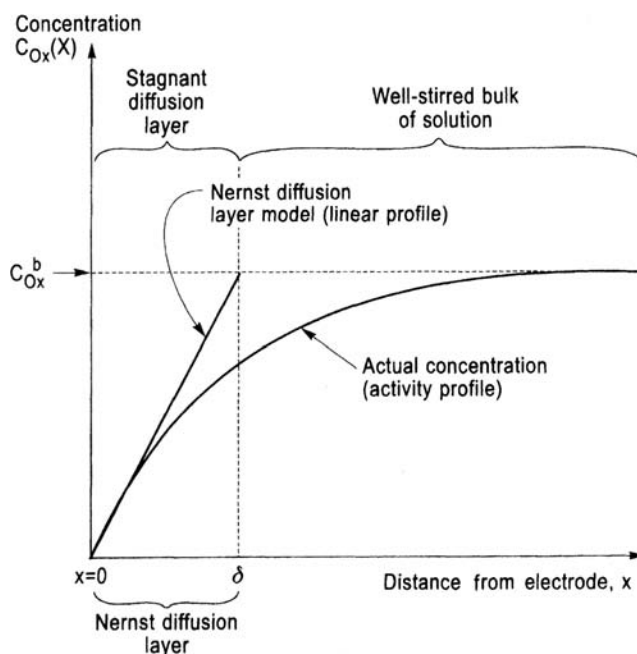


FIGURE 1.8 Variation of the concentration of the reactant during non-steady-state electrolysis; c_{Ox}^b is the concentration in the bulk; $c_{Ox}(x)$ is the concentration at the surface.

layer is further charged, and the potential of the electrode will change until some other process, other than reduction of M^{z+} , can occur. It will be shown later that the limiting current density is of great practical importance in metal deposition since the type and quality of metal deposits depend on the relative values of the deposition current and the limiting current. One extreme example is shown in Figure 1.9.

Example 1.5 Calculate the diffusion limiting current density i_L for the deposition of a metal ion M^{2+} at a cathode in a quiescent (unstirred) solution assuming the diffusion

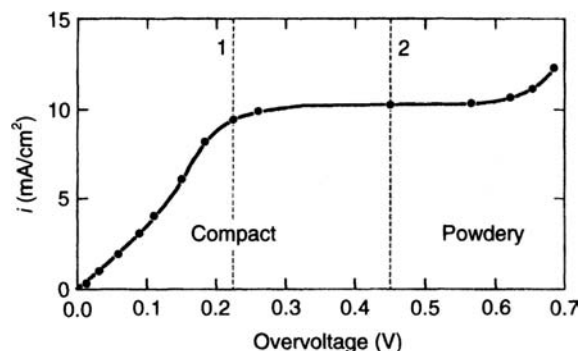


FIGURE 1.9 Overpotential characteristic of transition from compact to powdery deposit in electrodeposition of Cu from CuSO_4 (0.1 M) + H_2SO_4 (0.5 M) solution. (From N. Ibl, in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 2, C. W. Tobias, Ed., Wiley, New York, 1962, with permission from Wiley.)

layer thickness δ is 0.05 cm. The concentration of M^{2+} ions in the bulk (c_b) is $10^{-2} \text{ mol L}^{-1}$ ($10^{-5} \text{ mol cm}^{-3}$) and the diffusion coefficient D of M^{2+} , in the unstirred solution, is $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Using Eq. (1.17), we calculate that the limiting diffusion current density for this case is

$$\begin{aligned} i_L &= \frac{nFD}{\delta} c_b = \frac{2 \times 96487 \times 2 \times 10^{-5} \times 10^{-5}}{0.05} \\ &= 7.72 \times 10^{-4} \text{ A cm}^{-2} = 0.72 \text{ mA cm}^{-2} \end{aligned}$$

In the same way we find that, for $c_b = 10^{-1} \text{ mol L}^{-1}$ ($10^{-4} \text{ mol cm}^{-3}$), $i_L = 7.20 \text{ mA cm}^{-2}$.

In the stirred electrolyte solution the diffusion layer thickness δ and the limiting current density i_L depend on the nature of stirring.

For a rotating electrode the diffusion layer thickness depends on the angular speed of rotation ω according to

$$\delta = \frac{1.61 D^{1/6} \nu^{1/6}}{\sqrt{\omega}} \quad (1.18)$$

and the limiting current density depends on ω according to

$$i_L = \frac{0.62 n F a D^{2/3} c}{\nu^{1/6}} \sqrt{\omega} \quad (1.19)$$

where D is the diffusion coefficient, ν the kinematic viscosity (the coefficient of viscosity/density of the liquid), ω the rotation angular speed (in radians per second), c the concentration of the solution, and a the disc surface area [4]. We use these equations in the next two examples.

Example 1.6 Determine the diffusion layer thickness for a rotating electrode at 60, 240, and 360 rpm. For kinematic viscosity ν use $10^{-2} \text{ cm}^2 \text{ s}^{-1}$ and for the diffusion coefficient D use $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

For the above given values for ν and D , Eq. (1.18) becomes

$$\delta = \frac{1.61 \times 10^{-2}}{\sqrt{\omega}} = \frac{1.61 \times 10^{-2}}{\sqrt{2\pi N}}$$

In the above equation the rotation speed ω in radians per second is replaced by $\omega = 2\pi N$, where N is the number of rotations per second, rps.

Applying the above equation for $N = 1$ rps (60 rpm), one gets $\delta = 64 \mu\text{m}$. For $N = 4$ rps (240 rpm), $\delta = 32 \mu\text{m}$, and for $N = 6$ rps (360 rpm), $\delta = 26 \mu\text{m}$.

Example 1.7 Calculate the limiting current density i_L for the deposition of a metal ion M^{2+} at a rotating disc cathode with a surface area $a = 1 \text{ cm}^2$ and the rotating speed 300 rpm (5 rps) using Eq. (1.19) assuming that the concentration of

M^{2+} is $10^{-5} \text{ mol cm}^{-3}$ ($10^{-2} \text{ mol L}^{-1}$). The diffusion coefficient D of M^{2+} is $2 \times 10^{-5} \text{ cm}^2$, $\nu = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$.

Substitution of the above given values for a , D , and ν into Eq. (1.19) yields

$$i_L = (1.91 \times 10^2) c \sqrt{\omega}$$

For $c = 10^{-2} \text{ mol L}^{-1} = 10^{-5} \text{ mol cm}^{-3}$ and $\omega = 2\pi N = 31.41$

$$i_L = 1.07 \times 10^{-2} \text{ A cm}^{-2} = 10.7 \text{ mA cm}^{-2}$$

This value should be compared with the i_L value for a quiescent (unstirred) solution in Example 1.5.

1.3.3 Faraday's Law

Faraday's law states that the amount of electrochemical reaction that occurs at an electrode is proportional to the quantity of electric charge Q passed through an electrochemical cell. Thus, if the weight of a product of electrolysis is w , then Faraday's law states that

$$w = ZQ \quad (1.20)$$

where Z is the *electrochemical equivalent*, the constant of proportionality. Since Q is the product of the current I in amperes and the elapsed time t in seconds,

$$Q = It \quad (1.21)$$

$$w = ZIt \quad (1.22)$$

According to Faraday's law the production of one gram equivalent of a product at the electrode, W_{eq} , in a cell requires 96,487 C. The constant 96,487 is termed the *Faraday constant* F . The coulomb (C) is the quantity of electricity transported by the flow of one ampere for one second.

The Faraday constant represents one mole of electrons and its value can be calculated from

$$F = N_A e \quad (1.23)$$

where N_A is Avogadro's number (6.0225×10^{23} molecules mol^{-1}) and e is the charge of a single electron ($1.6021 \times 10^{-19} \text{ C}$):

$$F = (6.0225 \times 10^{23})(1.6021 \times 10^{-19}) = 96,487 \text{ C mol}^{-1} \quad (1.24)$$

One equivalent, w_{eq} , is that fraction of a molar (atomic) unit of reaction that corresponds to the transfer of one electron. For example, w_{eq} for silver is the gram atomic

weight of silver, since the reduction of Ag^+ requires one electron. The deposition of copper from a Cu^{2+} salt involves two electrons, and the w_{eq} for Cu is (gram atomic weight of Cu)/2. In general,

$$w_{\text{eq}} = \frac{A_{\text{wt}}}{n} \quad (1.25)$$

where A_{wt} is the atomic weight of metal deposited on the cathode and n the number of electrons involved in the deposition reaction.

From Eqs. (1.20) and (1.22) it follows that when $Q = 1 \text{ C}$, or $Q = 1 \text{ A s}$, then

$$w_{Q=1} = Z \quad (1.26)$$

Thus the electrochemical equivalent of a metal M, $Z(\text{M})$, is the weight in grams produced, or consumed, by one coulomb (one ampere second). The combination of Eqs. (1.20) and (1.26) yields

$$w = w_{Q=1} Q \quad (1.27)$$

The value of Z , or $w_{Q=1}$, can be evaluated in the following way. Since 96,487 C is required for the deposition of an equivalent of a metal, w_{eq} , from Eq. (1.20) it follows that

$$w_{\text{eq}} = 96,487 Z \quad (1.28)$$

and

$$Z = w_{Q=1} = \frac{w_{\text{eq}}}{96,487} = \frac{w_{\text{eq}}}{F} \quad (1.29)$$

Since $w_{\text{eq}} = A_{\text{wt}}/n$ [Eq. (1.25)],

$$Z = \frac{A_{\text{wt}}}{nF} \quad (1.30)$$

Finally, from Eqs. (1.20) and (1.30)

$$w = ZQ = \frac{A_{\text{wt}}}{nF} Q \quad (1.31)$$

Example 1.8 Determine the electrochemical equivalent of Cu for the case of electrodeposition of Cu from Cu^{2+} solutions. The atomic weight of Cu is 63.55.

From Eq. (1.29),

$$Z(\text{Cu}^{2+}) = \frac{A_{\text{wt}}\text{Cu}}{nF} = \frac{63.55}{2 \times 96,487} = 3.293 \times 10^{-4} \text{ gC}^{-1}$$

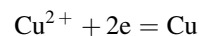
Example 1.9 A current of 300 mA was passed for 20 min through an electrochemical cell containing copper electrodes

in H_2SO_4 acidified CuSO_4 aqueous solution. Calculate the amount of copper deposited at the cathode. The gram atomic weight of Cu is 63.55.

In order to calculate w using Eq. (1.31), we find first the number of coulombs Q , the quantity of electricity passed during the electrolysis,

$$Q = It = 0.300 \text{ A} \times 1200 \text{ s} = 360 \text{ As} = 360 \text{ C}$$

The number of electrons n involved in the Cu deposition reaction



is 2. Substituting these values into Eq. (1.31), we get the amount of Cu deposited at the electrode,

$$w = \frac{63.55 \times 360}{2 \times 96,487} = 0.118 \text{ g}$$

Alternatively, using the value of the electrochemical equivalent for Cu, $Z(\text{Cu}^{2+}) = 3.293 \times 10^{-4} \text{ g C}^{-1}$, and Eq. (1.31), we get

$$w = ZQ = 3.293 \times 10^{-4} \times 0.300 \times 1200 = 0.118 \text{ g}$$

1.3.4 Current Efficiency

When two or more reactions occur simultaneously at an electrode, the number of coulombs of electricity passed corresponds to the sum of the number of equivalents of each reaction. For example, during deposition of Cu from a solution of cupric nitrate in dilute nitric acid, three cathodic reactions occur: the deposition of Cu (the reduction of cupric ions) and the reduction of both nitrate and hydrogen ions.

The current efficiency CE of the j th process, namely of any one of the simultaneous reactions, is defined as the number of coulombs required for that reaction, Q_j , divided by the total number of coulombs passed, Q_{total} :

$$\text{CE} = \frac{Q_j}{Q_{\text{total}}} \quad (1.32)$$

An alternative equation defining current efficiency is

$$\text{CE} = \frac{w_j}{w_{\text{total}}} \quad (1.33)$$

where w_j is the weight of metal j actually deposited and w_{total} is that which would have been deposited if all the current had been used for depositing metal j .

Thus, in general, at a current efficiency under 100%, the remainder of the current is used in side processes, such as the reduction of hydrogen and nitrate ions in the example above.

Example 1.10 When a current of 3 A flows for 8 min through a cell composed of two Pt electrodes in a solution of $\text{Cu}(\text{NO}_3)_2$ in dilute HNO_3 acid, 0.36 g of Cu is deposited on the cathode. Calculate the current efficiency for the deposition of copper.

The number of coulombs required for deposition of 0.36 g of Cu is obtained from Eq. (1.31):

$$Q_j = \frac{wn \times 96,487}{A_{\text{wt}}} = \frac{0.36 \times 2 \times 96,487}{63.55} = 1093$$

$$Q_{\text{total}} = It = 3 \times 480 = 1440$$

and

$$\text{CE} = \frac{Q_j}{Q_{\text{total}}} = \frac{1093}{1440} = 0.759 \text{ or CE} = 75.9\%$$

1.3.5 Deposit Thickness

The deposit thickness may be evaluated by considering the volume of the deposit. Since the volume of the deposit V is the product of the plated surface area a and the thickness (height) h , it follows that $h = V/a$. The volume of the deposit is related to the weight of the deposit w and the density of the deposit d by the relationship defining the density, $d = w/V$. Thus

$$h = \frac{V}{a} = \frac{w}{ad} \quad (1.34)$$

In the case where it is necessary to calculate the time t (in seconds) required to obtain the desired deposit thickness h at a given current density, we introduce Faraday's law [Eq. (1.31)], into Eq. (1.34) and obtain

$$h = \frac{w}{ad} = \frac{ZQ}{ad} = \frac{ZIt}{ad} \text{ cm} \quad (1.35)$$

$$t = \frac{had}{ZI} \text{ s} \quad (1.36)$$

Example 1.11 The weight of a Co deposit is 0.00208 g on a substrate with surface area of 7.5 cm^2 . What is the thickness of the Co deposit. Remember that the density of Co is 8.71 g cm^{-3} .

Using Eq. (1.34), we have that

$$h = \frac{0.00208}{7.5 \times 8.71} = 3.184 \times 10^{-5} \text{ cm} = 3184 \text{ \AA}$$

Example 1.12 Determine the time required to obtain a Cu deposit of thickness $1 \text{ }\mu\text{m}$ (10^{-4} cm) when electrodeposition

is done at 4 and 6 A. The surface area a of the substrate is 314 cm^2 .

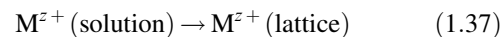
From Eq. (1.36), for $I = 4 \text{ A}$,

$$t = \frac{had}{ZI} = \frac{10^{-4} \times 314 \times 8.93}{3.29 \times 10^{-4} \times 4} = 213 \text{ s} = 3 \text{ min}, 33 \text{ s}$$

for $I = 6 \text{ A}$, in the same way, one obtains that $t = 142 \text{ s} = 2 \text{ min}, 22 \text{ s}$.

1.3.6 Atomistic Aspects of Electrodeposition

In the electrodeposition of metals, generally a metal ion M^{z+} is transferred from the solution into the ionic metal lattice. A simplified atomistic representation of this process is



This reaction is accompanied by the transfer of z electrons from an external electron source (e.g., power supply) to the electron gas in the metal M.

Before discussing the individual atomistic processes that make up the overall electrodeposition process, [Eq. (1.37)], it is necessary to consider the basic characteristics of the bulk and the surface structures of metals [1]. A metal may be considered to be a fixed lattice of positive ions permeated by a gas of free electrons. Positive ions are the atomic cores, while the negative charges are the valence electrons. For example, the copper atom has a configuration (electronic structure) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ (the superscripts indicate the number of electrons in the orbit configuration) with a single valence electron (4s). The atomic core of Cu^+ has the set of configurations given above less the one valence electron $4s^1$. The free electrons form what is known as the *electron gas* in the metal, and they move nearly freely through the volume of the metal. Each metal atom thus contributes its single valence electron to the electron gas in the metal. Interactions between the free electrons and the metal ions are largely responsible for the metallic bond.

Surfaces may be divided into ideal and real. Ideal surfaces exhibit no surface lattice defects (vacancies, impurities, grain boundaries, dislocations, etc.). Real surfaces have a variety of defects. For example, the density of metal surface atoms is about 10^{15} cm^{-2} , while the density of dislocations is of the order of 10^8 cm^{-2} . The structure of real surfaces differs from those of ideal surfaces by surface roughness. While an ideal surface is atomically smooth, a real surface may have defects, steps, kinks, vacancies, and clusters of adatoms (Fig. 1.10).

The atomic processes that make up the electrodeposition process [Eq. (1.37)] can be viewed considering the structure of the initial, $\text{M}^{z+}(\text{solution})$, and the final state, $\text{M}^{z+}(\text{lattice})$. Since metal ions in an aqueous solution are hydrated, the structure of the initial state in Eq. (1.37) should be

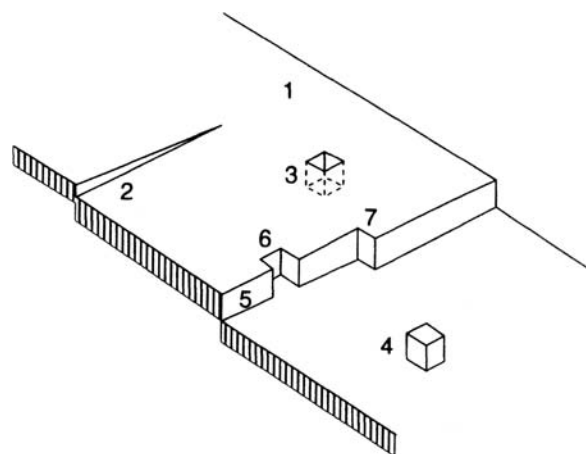
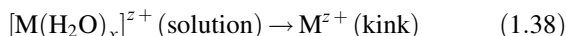


FIGURE 1.10 Some simple defects found on a low-index crystal face: 1, perfect flat face, terrace; 2, an emerging screw dislocation; 3, a vacancy in the terrace; 4, an adatom on the terrace; 5, a monatomic step in the surface, a ledge; 6, a vacancy in the ledge; 7, a kink, a step in the ledge.

represented by $[M(H_2O)_x]^{z+}$. The structure of the final state is an M adion (adatom; adsorbed ion, atom) at a kink site (Fig. 1.11), since it is generally assumed that atoms (ions) are attached to a crystal via a kink site [1]. Thus the final step of the overall reaction [Eq. (1.37)] is the incorporation of the M^{z+} adion into the kink site. Because of surface inhomogeneity, the transition from the initial state $[M(H_2O)_x]^{z+}$ (solution) to the final state M^{z+} (kink),



may proceed via either of the two mechanisms: (1) step-edge site ion transfer or (2) terrace site ion transfer.

Step-Edge Ion-Transfer Mechanism The step-edge site ion transfer, or direct transfer mechanism, is illustrated in Figure 1.12. As the figure shows, this mechanism ion transfer from the solution takes place on a kink site of a step edge or on any other site on the step edge. In both cases the result of

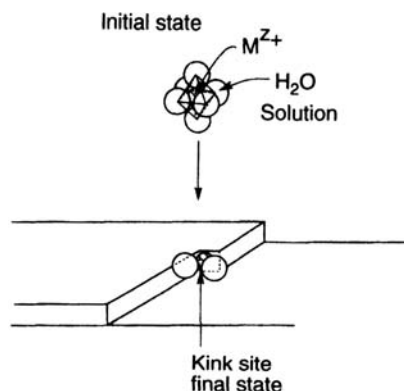


FIGURE 1.11 Initial and final states in metal deposition.

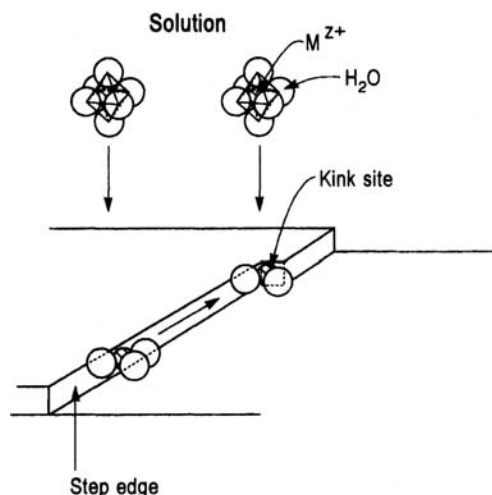


FIGURE 1.12 Step-edge ion-transfer mechanism.

the ion transfer is an M adion in the metal crystal lattice. In the first case of a direct transfer to the kink site, the M adion is in the half-crystal position, where it is bonded to the crystal lattice with one-half of the bonding energy of the bulk ion. Thus the M adion belongs to the bulk crystal. However, it still has some water of hydration (Fig. 1.12). In the second case of a direct transfer to the step-edge site other than a kink, the transferred metal ion diffuses along the step edge until it finds a kink site (Fig. 1.12). Thus, in a step-edge site transfer mechanism, there are two possible paths: direct transfer to a kink site and the step-edge diffusion path.

Terrace Ion-Transfer Mechanism In the terrace site transfer mechanism a metal ion is transferred from the solution to the flat face of the terrace region (Fig. 1.13). At this position the metal ion is in the adion (adsorbedlike) state having most of the water of hydration. It is weakly bound to the crystal lattice. From this position it diffuses on the surface, seeking a position of lower energy. The final position is a kink site.

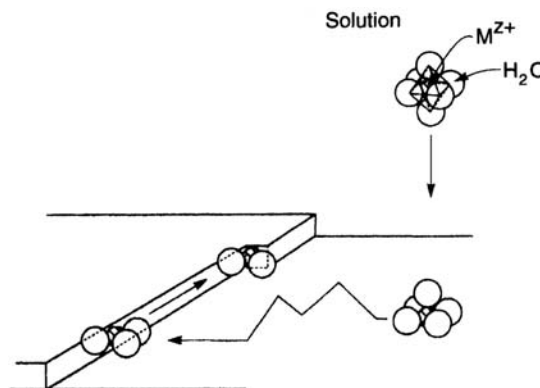


FIGURE 1.13 Ion transfer to a terrace site, surface diffusion, and incorporation at kink site.