Yuliy D. Gamburg · Giovanni Zangari

Theory and Practice of Metal Electrodeposition

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Preface

The book reflects in a concise form the modern state of both theoretical and applied aspects of metal electrodeposition. The theoretical part concerns the electrochemistry of metals and includes a discussion of electrochemical thermodynamics and kinetics, the structure at the metal/electrolyte interface, nucleation, growth and morphology of metals and alloys, and current distribution. The applied part contains general information on the applications of metallic coatings, their selection, electrochemical basics and technology of deposition of selected metals and alloys, including individual peculiarities, properties and structure of coatings, testing and characterization. The book includes, where possible at an elementary level, a quantitative discussion of phenomena of relevance, providing formulas for the calculation of important quantities. Additionally, it contains information on surface leveling, hydrogenation, inclusion of impurities, physical properties of deposits, that is rarely available in textbooks on electrodeposition. The section on electrodeposition technology includes the most important processes and chemistries; information on any definite material system is provided using a unified scheme, namely: properties of the coating, advantages and disadvantages, solution chemistries and methods of preparation, peculiarities, anodes, and additives.

The essential concepts in theoretical electrochemistry necessary for the investigation of metal deposition processes is provided here, including data that are commonly absent in specialized academic courses. These topics are important for the reader aiming to achieve a thorough understanding of the latest scientific publications in this field. Information on different aspects of the process of electrolytic crystallization is gathered here from a large body of publications and is considered from a unified point of view.

The book is suitable for professional electrochemists, advanced undergraduate and postgraduate students and also for electrodeposition specialists with a physical, technical or chemical education. It can also be useful for engineers and specialists engaged in research on new electrodeposition technologies related to metallic layers, crystals and other metallic objects.

One of the authors (Yu. Gamburg) is hugely grateful to his colleagues from the Laboratory of the surface layers structure (A. N. Frumkin Institute, Russian Academy of Sciences) and particularly indebted to Maria R. Ehrenburg who translated the chapters 10 and 11 written originally in Russian.

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7 Potential Distribution in the Electrolyte and Current Distribution on the Electrode Surface 143

List of Symbols

A	atomic weight
A	different constants
A	the more electropositive metal
a	thermodynamic activity
a	first Tafel coefficient
a	attraction constant in Frumkin equation
B	the more electronegative metal
B	adsorption constant
b	second Tafel coefficient
C	electric capacitance (per unit area)
C, c	concentration
CE	current (cathodic) efficiency
D	grain size
D	diffusion coefficient
d	density
d	distance
E	Young's modulus
E	potential
E^0	standard potential
E_{eq}	equilibrium potential
e	electron
e	electronic charge
F	Faraday constant
f	F/RT
f	frequency
f	different functions
G	Gibbs energy
g	gravity factor
$\boldsymbol{g}$	number of atoms in the cluster
h	height, thickness
H	hardness
H	root-mean-square roughness

I	electric current
i	current density
i_0	exchange current density
i_d	diffusion current density
i_lim	limiting current density
IS	internal stress
J	flux
K, k	different constants
$\mathbf{K}$	electrochemical equivalent of the metal
K_m	mass transfer coefficient
k_r	roughness coefficient
$\mathrm{k_B}$	Bolzmann constant
L	ligand
l	length, distance
M	metal
M	molar mass
M^{z+}	ion of metal
m	mass
N	number of species
$\mathrm{N_A}$	Avogadro number
n	net amount of transferred electrons
P	leveling power of the electrolyte
Q	net charge passed through the circuit
q	electric charge
q_m	electric charge at the metal surface
R	molar gas constant
R	Ohmic resistance
$\mathrm{R_c}$	contact resistance
R	radius
r	distance along the radius
ω	angular rotation rate
RDE	rotating disc electrode
S	area
SAS	surface active substance
T	absolute temperature
TP	throwing power
t	time
U	voltage (between cathode and anode)
V	volume
v	volume per one species
V_m	molar volume of the metal
W	Wagner number
w	velocity (of a flux)
x	distance
y	distance

z	electric charge of the species in electron units
Z	number of clusters
α	transfer coefficient
β	polarizability $\partial\eta/\partial i$
γ	interface energy
Γ	adsorption
Γ_{∞}	limiting adsorption
δ	thickness of the reaction layer
δ_{N}	Nernst diffusion layer
$\delta_{\text{пр}}$	Prandtl layer
ε	relative permittivity
ε	roughness amplitude
η	overpotential
η_c	cathodic overpotential
η_a	anodic overpotential
θ	coverage
κ	conductivity
l	distance of propagation
λ_D	Debye length
μ	chemical potential
$\mathrm{\mu}$	electrochemical potential
v_i	stoichiometric coefficients
v	viscosity (kinematic)
ρ	volume charge density
ρ	resistivity
σ	surface tension (specific surface energy)
σ	stress
σ_{B}	breaking stress
τ	duration of the process
Φ	electric potential
Φ	form factor
φ	Galvani potential
ω	angular rotation rate (RDE)
ω	frequency
ω	fraction (mass, molar)

Chapter 1
Introduction to Electrodeposition: Basic Terms and Fundamental Concepts

1.1 Electrodeposition of Metals

Electrodeposition refers to a film growth process which consists in the formation of a metallic coating onto a base material occurring through the electrochemical reduction of metal ions from an electrolyte. The corresponding technology is often known as *electroplating*. Besides the production of metallic coatings, electrochemical metal reduction is also used for the extraction of metals starting from their ores (*electrometallurgy*) or for the reproduction of molds to form objects directly in their final shape (*electroforming*). In most cases, the metallic deposit thus obtained is crystalline; this process can therefore be called also electrocrystallization; this term was introduced by the Russian chemist V. Kistiakovski in the early twentieth century.

The electrolyte is an ionic conductor, where chemical species containing the metal of interest are dissolved into a suitable solvent or brought to the liquid state to form a molten salt. The solvent is most often water, but recently various organic compounds and other ionic liquids are being used for selected electroplating processes. This book will be concerned exclusively with electrodeposition from aqueous solutions.

The electrodeposition process consists essentially in the immersion of the object to be coated in a vessel containing the electrolyte and a counter electrode, followed by the connection of the two electrodes to an external power supply to make current flow possible. The object to be coated is connected to the negative terminal of the power supply, in such a way that the metal ions are reduced to metal atoms, which eventually form the deposit on the surface.

This chapter introduces the terms and concepts utilized in the description of the electrochemical process for metal reduction. Additionally, it includes an introductory discussion of the various concepts that will be rigorously developed in successive chapters of the book.

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1.2 Examples of Electrocrystallization

The process of formation of a metallic coating may occur through various mechanisms and can proceed through a variety of precursors. Some representative examples of electrodeposition include the following:

1. Electrodeposition of a zinc coating onto a low carbon steel sheet for corrosion protection; this process may occur for example through the following reaction:

$$Na_2ZnO_2 + H_2O + 2e \rightarrow Zn_{met} + 2Na^+ + 4OH^- \tag{1.1}$$

The Zn-containing salt is dissolved in water to form an aqueous solution and the electrons for the reaction are provided by the external power supply.

2. Copper powder production through copper electrodeposition from dilute acidified solutions of copper sulfate:

$$CuSO_4 + 2e \rightarrow Cu_{met} + SO_4{}^{2-} \tag{1.2}$$

Also in this case, the Cu salt is first dissolved in an aqueous solution.

3. Electroforming of nickel by means of electrodeposition of nickel metal from a neutral solution based on nickel sulfamate

$$Ni(NH_2SO_3)_2 + 2e \rightarrow Ni_{met} + 2NH_2SO_3{}^- \tag{1.3}$$

4. Formation of metallic lead at the anode of a lead acid battery during charging:

$$PbSO_4 + H^+ + 2e \rightarrow Pb^0 + HSO_4{}^- \tag{1.4}$$

All electrodeposition processes have in common the transfer of one or more electrons through the electrode/solution interface, resulting in the formation of a metallic phase Me_{met}.

Metal deposition processes are and have been utilized for practical purposes in a wide variety of technical fields, ranging from metallurgy and heavy engineering industries to (more recently) microelectronics and nanotechnology. Examples of these applications include the following: gold and gold alloy deposition for electrical contacts in electronic circuits, Cu deposition for microelectronic interconnects, Ni–Fe alloys for magnetic recording heads, or the production of high purity metals. Currently, the most intensively developing branches of electrodeposition are associated with information and energy technologies, as well as microelectronics, sensors and microsystems in general. The list of materials and structures that are being produced in commercial processes or at the development stage is also very long and will be discussed in successive chapters. Suffice here to say that the length scales of commercially synthesized materials covers many orders of magnitude, going from the hundreds of meter of tin-coated strips to the 20–100 nm width of copper interconnects.

1.3 Electrode Processes. Faraday's Law

A general reaction for the process of metal formation is the following:

$$\left(M_xL_y\right)^z + nxe \rightarrow xM^0 + yL \tag{1.5}$$

L is a molecule, an ion, or radical (e.g. H_2O or CN^-) tightly bound to the metal ion M and thus forming a *complex* species $(M_xL_y)^z$ which takes part in the charge transfer process. This intermediate compound is usually named the *electroactive species.*

In Eq. (1.5) n is the net amount of electrons transferred in the overall process per deposited metal atom; this is always a positive quantity. z is the electric charge of the electroactive species in electron units; z can be both negative or positive, and may also be zero. For instance, the charge of the $[Ag(CN)_3]^{2-}$ ion is equal to −2. The electric charges of M and L are not shown in Eq. (1.5) but in the following they may sometimes explicitly indicated.

The simplest case of metal ion discharge is that of the simple (hydrated) metal ion, where $n=z$. The reaction in this case is written:

$$M^{z+} \cdot xH_2O + ze \rightarrow M^0 + xH_2O. \tag{1.6}$$

where the dot indicates an electrostatic interaction. In general however $n \neq z$, and n should not be confused with z.

Equation (1.5) shows that n electrons, i.e. a charge of ne, need to be transferred for the deposition of one atom of the metal. Consequently, the formation of one mole of the metal requires $N_A ne = nF$ coulombs of electricity (N_A is the Avogadro number $N_A = 6.022 \times 10^{23}$ mol^{-1}; $F = N_A e$ is the Faraday constant $F = 96485$ C mol^{-1}). This relationship is referred to as Faraday's Law:

$$m = QA/nF \tag{1.7}$$

where m is the deposited metal mass (grams), Q the net charge passed through the circuit (coulombs), and A the atomic weight of the metal. At constant current $Q = I\tau$, otherwise $Q = \int I d\tau$ (I is the current, τ is the duration of electrolysis).

This equation is extremely important and widely used in practice to calculate the amount of metal deposited during electrolysis, to determine the duration of electrolysis necessary to achieve a predetermined thickness, the time of charge/discharge of a battery, etc.

The electrochemical process (1.5) occurs at the interface between metal and solution; in this respect the structure and properties of this interface, as shown in successive chapters, will greatly influence the process. Faraday's Law however does not reflect said dependence, as it only relates m to Q.

1.4 Current Density

When applied to coatings, Eq. (1.7) is often used in a different form, as the dependence of deposit thickness h upon the duration of electrolysis τ and the applied current I. Taking into account that $h = m/Sd$ (S is the surface area, d is the density) and $Q = I\tau$, we obtain after rearranging

$$h = (I/S)\, A\tau/dnF, \tag{1.8}$$

or

$$h = (V_m/nF)\,(I/S)\,\tau. \tag{1.9}$$

In the last equation $V_m = A/d$ is the molar volume of the metal. This equation highlights the importance of the *current density* (*CD*) $i = I/S$.

Current density, usually expressed in amperes per square meter A m^{-2}, governs the rate of the deposition process, usually measured in mol/cm^2 s, or in microns per hour. The current density is the most practical measure for the rate of any electrochemical process since its value is readily determined from an ammeter reading and the knowledge of the electrode area S.

The factor $\mathbf{K}_v = V_m/nF$ is the volume *electrochemical equivalent* of the metal; it can be expressed, for instance, in cm^3/C. Sometimes it is more convenient to use the mass equivalent $\mathbf{K}_m = \mathbf{K}_v d$, which can be expressed in g/Ah. For electrodeposited coatings the one-dimensional equivalent of $\mathbf{K}_v$, i.e. $\mathbf{K}_l$ (μm/(Ah/dm^2)) is particularly convenient, since it immediately gives the thickness of a deposit in microns:

$$h = \boldsymbol{K}_l i \tau \tag{1.10}$$

if i is expressed in A/dm^2, and τ in hours.

The electrochemical equivalents of some metals $\mathbf{K}_v$, $\mathbf{K}_m$ and $\mathbf{K}_l$ are listed in Table 1.1. For alloy deposition one can use the equivalent calculated for alloys $K_{m(alloy)}$ which is given by

$$\mathbf{K}_{m(alloy)} = 1/\left(\omega_1/\mathbf{K}_1 + \omega_2/\mathbf{K}_2 + \omega_3/\mathbf{K}_3 + \ldots + \omega_n/\mathbf{K}_n\right). \tag{1.11}$$

In this equation ω_i and $\mathbf{K}_\mathrm{i}$ are respectively the mass fractions and mass equivalents of the elements in the alloy. To obtain the electrochemical equivalent for the alloy in linear form it is necessary to know the alloy density. This can be found experimentally or it can be estimated approximately, for example for a two-component alloy, by

$$d_{(alloy)} \approx d_1 d_2/\left(d_1\omega_1 + d_2\omega_2\right). \tag{1.12}$$

In order to rigorously define current density it is necessary to precisely determine the *surface area S*. In fact, real surfaces are ideally smooth only in the case of liquid metals (for example mercury or an amalgam) or in monocrystalline smooth electrodes. Only in this case the geometric surface area S_g coincides with the real one S_t. In real surfaces, any roughness results in an increased true surface as compared with S_g. The ratio $k_r = S_t/S_g$ is defined as the *roughness coefficient*. For polished or high quality electrodeposited surfaces k approximates 2–3. If $k_r > 1$ a "real current density" i_r. $i_r = i_{app}/k_r$ should be used, where i_{app} is the apparent CD, calculated for the geometrical area.

Current density is usually assumed to be uniform across the surface. However, any real surface has heterogeneous properties, and electrochemical processes at solid electrodes start first at high energy sites, called active centers or growth sites. As a consequence the current density is initially highly non-uniform and its distribution tends to change during film growth; in particular, both changes in k_r changes as well as distribution and overall area of active sites should be considered.

Table 1.1 Electrochemical equivalents of some metals

Metal	K_v, cm^3/A-h	K_m, g/A-h	K_l, μm/(A-h/dm^2)
Ag	0.3837	4.025	38.37
Au(I)	0.380	7.35	38.0
Au(III)	0.127	2.45	12.7
Bi	0.1590	1.560	15.9
Cd	0.2424	2.097	24.24
Co	0.1243	1.099	12.43
Cr	0.0449	0.323	4.49
Cu(I)	0.2652	2.371	26.52
Cu(II)	0.1326	1.186	13.26
Fe(II)	0.1324	1.042	13.24
Fe(III)	0.0883	0.695	8.83
In	0.1956	1.428	19.56
Mn	0.1374	1.025	13.74
Mo	0.0670	0.597	6.70
Ni	0.1229	1.095	12.29
Pb	0.3409	3.866	34.09
Pd	0.1651	1.985	16.51
Pt	0.1696	3.640	16.96
Re	0.0472	0.993	4.72
Rh	0.1032	1.280	10.32
Ru	0.1017	1.257	10.17
Sb	0.1359	0.909	13.59
Sn	0.3033	2.214	30.33
W	0.0587	1.143	5.87
Zn	0.1711	1.220	17.11

1.5 Electrodes and Electrode Potential

The term "*electrode*" has various connotations in electrochemistry. First, the electrode is the region at which the electrochemical process of interest is occurring; depending on the current direction or the nature of the reaction, it can be the cathode (where a reduction occurs) or the anode (where oxidation occurs); in some cases an electrode can comprise both cathodic and anodic areas. Second, the electrode in a purely electrochemical sense is the half-cell element as a whole, i.e. the combination of the solid electrode and the electrolyte region in contact with the electrode, where a predetermined reaction is occurring. In some cases the reaction forms a new phase and the term "electrode" refers to a particular sequence of phases together with their interfaces. An example of electrode is the reference electrode where the equilibrium between Ag and AgCl takes place; this electrode is schematically indicated by the series of phases Ag|AgCl|KCl present at the interface.

Electrode potential is another physical variable, along with current density, controlling the electrode process. The potential φ of the electrode is the potential drop between the solution and the bulk of the metal, otherwise called the Galvani poten-

Table 1.2 Potentials of the reference electrodes

Electrode	Symbol	Potential at 298 K, mV	Temperature coef., mV/K
1 *M* calomel	$Pt\|Hg\|Hg_2Cl_2\|1\ M\ KCl$	+283	−0.24
Satur. calomel	$Pt\|Hg\|Hg_2Cl_2\|satur.\ KCl$	+244	−0.65
Silver chloride	$Ag\|AgCl\|HCl$	+222	−0.65
Mercury sulfate	$Pt\|Hg\|Hg_2SO_4\|a(SO_4^{2-})=1$	+615	−0.82
Cadmium oxide	$Cd\|CdO, a(OH^-)=1$	+13	

tial difference. This quantity cannot be measured experimentally since the solution potential cannot be defined operationally without introducing an additional metal/electrolyte interface, and therefore cannot be used as a reference point. For this reason in actual practice it is conventional to measure the electrode potential with reference to some other electrode having a constant, reproducible and stable potential. Various *reference electrodes* of this kind exist; the Standard Hydrogen Electrode (SHE) uses the equilibrium between H^+ and hydrogen gas to generate this potential, and is most often used as a standard. Its potential at any temperature is defined equal to zero. Electrode potential expressed relative to SHE is symbolized by the letter E.

SHE is too inconvenient to be practical; in the laboratory practice therefore one can use other reference electrodes (calomel or silver/silver chloride electrode), using other reactions to generate the potential; their potentials at different temperatures are listed in Table 1.2.

The concepts connected with electrode potentials (the problem of absolute potential drop, the rigorous definition of Volta and Galvani potentials, etc.) are of great importance in electrochemistry but are beyond the scope of the present book; pertinent information is available elsewhere [1].

Current density and electrode potential of any given electrode reaction at steady state are related to each other through a one-to-one correspondence; however, actual conditions at an electrode where a growth process is occurring are rarely stationary. For this reason a *potentiostatic process* (at $E=\text{const}$) occurs with the current density changing over time; similarly, a *galvanostatic process* ($i=\text{const}$) is usually accompanied by variations in E. Possible reasons for these changes include the following: (a) the surface state (roughness, morphology) evolves with time, and (b) composition of the solution adjacent to the electrode (concentration of chemical species, pH) can change during the process. In the initial stages of electrolysis these changes can be significant.

Along with stationary processes, dynamically changing conditions at the electrode are rather common, particularly for the investigation of electrode phenomena; most utilized are potentiodynamic procedures. These processes are usually carried out at predetermined linear sweep rate of the potential, e.g., $E=E_0+a\tau$, where a may range from 10^{-4} to 10^6 V/s, typically 10 mV/s. At very slow sweep rate, the electrochemical process under study is quasi-stationary and it is often indistinguishable from a stationary one. At very fast sweep rates the concentrations of species near the electrode cannot follow the potential change due to the limited reaction rates and

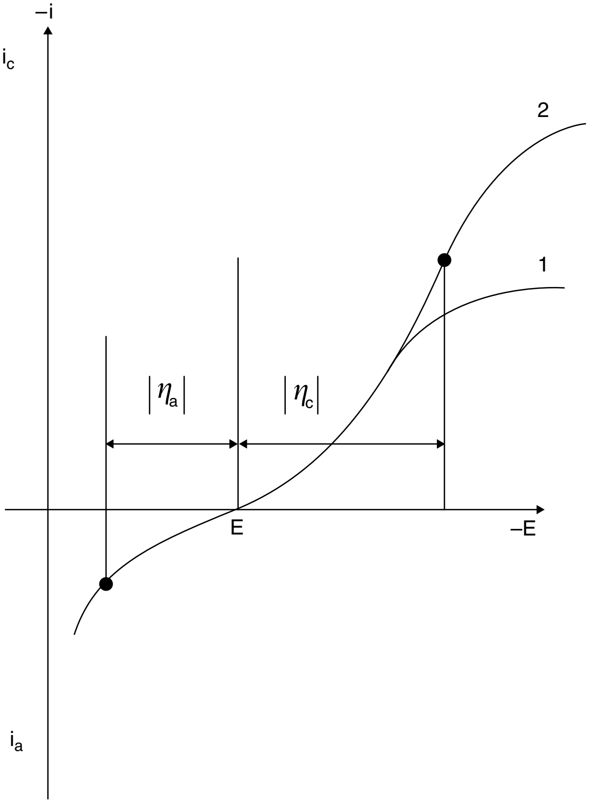


Fig. 1.1 Current–potential characteristics for a metal deposition process without agitation (*1*) and with electrolyte stirring (*2*). At high overvoltages (more negative potentials) the region of limiting current density i_{lim} is approached; i_{lim} increases by stirring. The equilibrium potential is E; cathodic η_c and anodic η_a overpotentials are also shown

the quantities of interest are often time-dependent. In general, various scan rates are necessary for the different methods used in electrode studies.

Modern studies in this field are made with experimental instruments especially built for electrochemical investigations, among which electronic potentiostats/galvanostats have a significant role and considerable capabilities. Detailed descriptions of these instruments can be found elsewhere [2]. The typical dependence of current density upon E for an electrodeposition process is shown in Fig. 1.1. This curve corresponds to copper deposition from an acidic sulfate solution. The details of the curve are discussed in the following section.

1.6 Equilibrium Potential and Overpotential

The electrode potential at which the current density i is zero assumes particular importance. If this potential corresponds to the thermodynamic equilibrium of a well defined electrode process this potential value is defined as the *equilibrium potential* of this process E_{eq}. This potential is directly determined by the thermodynamic activity of the electroactive species in solution and is described by the Nernst equation, which in the simplest case of an equilibrium between a metal ion and a metallic electrode takes the form

$$E_{eq} = E_0 + (RT/nF)\ ln\,(a_M z+) = E_0 + (1/nf)\ ln\,(a_M z+). \tag{1.13}$$

In this equation $f = F/RT = 11604/T$ (V^{-1}); $R = 8.3145$ J/mol K (gas constant), and T is the absolute temperature. E_0 is called the standard potential for this process, observed under standard conditions (unit activity for all the species involved, T=298 K, and atmospheric pressure).

It is important to realize that the thermodynamic equilibrium corresponds to the condition where the observed *overall* rate for the process of interest is zero; however, this equilibrium is achieved by the balance of two partial reactions occurring in opposite directions. This very important idea was firstly stated by Ershler and Shlygin [3] where the term "*exchange current density*" i_0 was introduced to quantify the rate of these two partial processes at equilibrium. In other words, the equilibrium is a dynamic process that can occur slow or fast, depending on the characteristics of the process involved. Typically, the exchange current will be large when the energy barrier for the transformation of interest is low.

A more general form of the Nernst equation can be written for a generic electrochemical reaction:

$$\Sigma v_{ox} A_{ox} + ne \leftrightarrow \Sigma v_{red} A_{red} \tag{1.14}$$

where the v_i denote stoichiometric coefficients; the corresponding Nernst equation can be written as

$$E_{eq} = E_0 + (RT/nF)\,ln\left(\Pi a_{\mathrm{OX}}{}^{\nu(\mathrm{OX})} / \Pi a_{\mathrm{red}}{}^{\nu(\mathrm{red})}\right). \tag{1.15}$$

Very often in practice, especially for diluted solutions, the thermodynamic activities a_i are substituted by the molar concentrations c_i. It should be recalled that the activity of a pure solid phase is equal to unity; this is the reason for the absence of the corresponding term in Eq. (1.13).

In order to deposit a metal at a finite rate it is necessary to shift the electrode potential in the cathodic (negative) direction from its equilibrium value. It follows that a negative potential shift speeds up reduction processes whereas a positive shift accelerates anodic reactions (oxidation). The value of this shift is called the *overpotential* (*overvoltage*) of this process and is usually indicated by the greek letter η:

$$\eta = E - E_{eq} \tag{1.16}$$

Defined in such a manner the overpotential has a well defined sign; according to another convention however the overpotential is defined as $\eta = \left|E - E_{eq}\right|$ and is always positive, and its actual effect is determined by whether it is cathodic (η_c) or anodic (η_a).

In practical metal deposition processes the overpotential may range from few mV to more than 2 V. Its value determines the rate of the process and to a large extent the structure and properties of the deposit. Upon application of relatively high η fine grained and dense coatings are obtained. The extent of adsorption at the electrode of surface-active components from the solution, which strongly influences the deposition process and the structure of the deposit, is also determined by the electrode potential during deposition, i.e. by the overpotential.

In the following chapters we will repeatedly direct our attention to the influence of overpotential and adsorption processes on the microstructure and morphology of the deposits. Here we only underline the interesting possibility of classifying the metals according to the value of η corresponding to ordinary current densities (10–100 mA/cm^2). The first group of metals includes those having high overpotential (of the order of hundreds of millivolts): Fe, Co, Ni, Cr, Mn, Pt. The second comprises the metals with intermediate η (Cu, Bi, Zn). The overpotentials characteristic for the third group (typically low-melting elements: Pb, Sb, Ag, Sn, Cd, Tl) are low (up to tens of millivolts). This classification is closely related to the exchange current densities measured for the reduction/oxidation of these elements: high values of i_0 correspond to low overpotential and vice-versa. Metals deposited at high overpotentials are usually much more fine-grained as compared to those of the second and third groups. It should however be noted that this classification is valid only when the metal ions in solution are not bound to form complexes; in this latter case in fact it is possible to sharply increase the value of η at a given current density and correspondingly change the characteristic film morphology.

At positive (anodic) overpotential the reverse process of anodic dissolution occurs. If the process of metal deposition is performed using a soluble anode from the same metal as the counter electrode then the voltage U between cathode and anode is equal to the sum $|\eta_c|+|\eta_a|$ plus the ohmic drop in the solution:

$$U = |\eta_c| + |\eta_a| + IR \tag{1.17}$$

Finally, it should be noted that it is not always necessary to apply a potential negative to the redox potential of the metal under study in order to achieve metal deposition; a metal can be deposited at potentials more positive than the equilibrium one, due to strong interactions with the substrate material. This phenomenon is referred to as *underpotential deposition* (upd, [4]). This phenomenon, very interesting both for electrodeposition and for electrocatalysis will be considered later.

1.7 Mixed Potential

The equilibrium potential is achieved only when the influence of other electrochemical processes occurring in parallel with the reaction of interest can be neglected. If this condition is not satisfied the zero current condition corresponding to a situation of macroscopic equilibrium is achieved at a different potential, often named the steady-state, rest or mixed potential E_r. For instance, if several direct and reverse electrode processes occur simultaneously, then in the absence of external power sources the potential assumes spontaneously the value at which the net current is zero. Under this condition, no single process is in equilibrium, and each one proceeds at a non-zero rate. Corrosion processes often occur under these conditions. The actual value of the mixed potential depends on the relevant reactions and on electrode surface conditions, for example roughness, the presence of adsorbed species and/or films produced by corrosion processes, etc.

1.8 Potential–Current Curves (Voltammograms)

The potential–current density (*E*–*i*) relationships for generic electrochemical reactions are also called voltammograms, *polarization curves*, or current–potential characteristics, and are of fundamental importance in electroplating. The theory of the functional dependence of *i* vs. *E* is presented in Chap. 3. These curves (see for example Fig. 1.1) can be derived experimentally or theoretically and show clearly the key features of various electrochemical processes. As a consequence, they are extensively used in general electrochemistry and particularly in investigations of metal deposition.

Potential–current density characteristics for two different processes occurring simultaneously at an electrode are shown in Fig. 1.2. Two electrochemical processes can occur in the electrodeposition of a pure metal from aqueous solutions when the applied cathodic potential is sufficient to induce the reaction of hydrogen evolution. Equilibrium potentials of the two processes are shown in the figure along with values of current densities ("*partial current densities*" and overall current den-

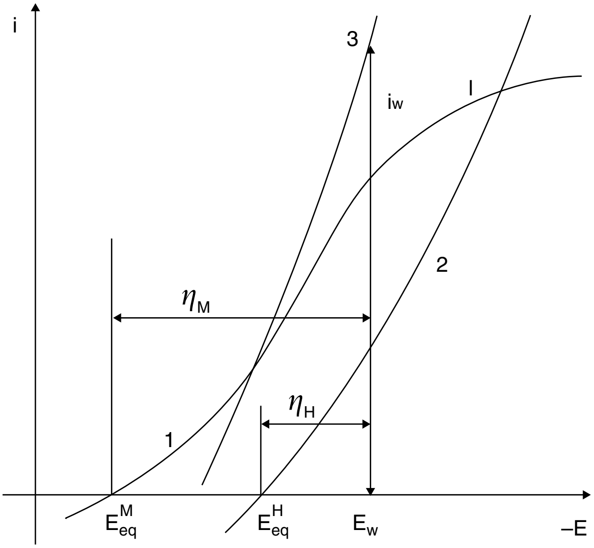


Fig. 1.2 Current–potential characteristics for simultaneous metal deposition (*1*) and hydrogen evolution (*2*). *1* and *2* are the partial current curves, and *3* represents the experimentally measured total current. Cathodic overpotentials η_1 and η_2 for both processes are shown along with equilibrium potentials and the working potential E_W

sity) and overpotentials. We emphasize that hydrogen evolution is very important in electroplating as atomic hydrogen can be incorporated in the deposit and/or into the substrate and impact their properties. Only a small fraction of the hydrogen evolved is incorporated in the metal, while the most part evolves in gaseous form.

An experimental *E–i* relationship is obtained by successively imposing various values of the electrode potentials and measuring the corresponding values of current density; after a rapid switch of potential from one value to another a certain time (about 10–100 s) is needed to stabilize the current. In an alternative experimental set-up it is also possible to impose a set of current values and measure the corresponding potentials; the first method is called potentiostatic, the second galvanostatic. The two curves can be different, especially when processes of inhibition at the electrode surface occur, causing the appearance of maxima in the *i* vs. E curve. In addition, potentiodynamic and galvanodynamic measurements (including cyclic ones), where the potential or current change continuously with time, can be performed and are often used. The shape of dynamic *E–i* curves depends on the sweep rate; some electrochemical methods are based on this dependence.

The derivative of the potential with respect to current density $dE/di = d\eta/di$ (i.e. the slope of the *E–i* curve) is designated *polarizability*. This quantity is relevant in the analysis of the uniformity of current distribution throughout the electrode surface. As a rule, the higher the polarizability, the more uniform the current distribution is; as a consequence the thickness of the metal deposited becomes more uniform. The electrode for which $d\eta/di \to \infty$ is identified as an *ideally polarizable* electrode. This idealized electrode is important in the theory of current distribution. The electrode having $d\eta/di \to 0$ on the other hand is called non-polarizable. The values of polarizabilities for several plating processes are given in Table 1.3.

The overpotential of any process depends strongly on the deposition conditions: solution composition and pH, temperature, electrolyte stirring, etc. Two methods can be used to compare *i–E* characteristics obtained under different conditions. For example, consider curves 1 and 2 in Fig. 1.1, obtained experimentally for the same reaction with and without solution agitation. It can be said that at the same potential the current density CD for curve 2 is higher than for curve 1; it can also be said however that at the same CD the deposition potential in curve 2 is decreased; both

Table 1.3 Polarizabilities of several electrolytes (averaged values)

Metal	Type of the electrolyte	Polarizability, Ohm cm^2
Ag	Cyanide	20–24
Cd	Stannate	12–14
Cd	Sulfate	1.3–1.5
Cu	Sulfate	2.2–2.5
Cu	Cyanide	11–16
Cu	Pyrophosphate	10–15
Fe	Sulfate	1.7–2.0
Ni	Sulfate	4.0–4.5
Zn	Sulfate	1.5–1.8
Zn	Zincate	8–10

statements are equivalent. The decrease in CD (η increase) is described as an *inhibition* of the process, while the decrease of η (CD raise) is called *depolarization*.

1.9 Current Efficiency

In most practical processes the overall current (charge) is consumed in part for side processes occurring in parallel with metal deposition. In this case it is important to determine the relationship between the current densities of the two or more parallel processes occurring simultaneously at some predetermined potential.

Side reactions can be of various nature. As already noted, hydrogen evolution may occur as the result of water electrolysis:

$$2H_3O^+ + 2e = H_2 + 2H_2O \tag{1.18}$$

Besides, deposition (co-deposition) of another metal can take place:

$$M_2{}^{z+} + ze \rightarrow M_2{}^0 \tag{1.19}$$

Furthermore, partial reduction of metal ions is possible, for example:

$$Fe^{3+} + e \rightarrow Fe^{2+}, \tag{1.20}$$

and finally, the reduction of surface oxide layers can occur, such as

$$M_xO_y + 2yH_3O^+ + 2ye \rightarrow xM + 3yH_2O \tag{1.21}$$

along with some other reactions, some of which can be purely chemical in origin.

If the second process is the deposition of another metal, evaluation of the current density for the two processes is closely related with the composition of the depositing alloy, considering that the ratio of the molar concentrations of the two metals in the alloy is proportional to the corresponding current densities. When other side reactions proceed, the ratio between the partial current of the process of interest i_p and the overall current is called "*current efficiency*" CE:

$$CE = i_p/\Sigma_j i_j = Q_p/\Sigma_j Q_j. \tag{1.22}$$

The current efficiency is often expressed in percent.

Practical determination of CE in electroplating processes is performed by both pre- and post-electrolysis weighing of the sample on an analytical balance in parallel with precise determination of the charge passed (by means of an electronic current integrator or by using an ammeter and a stop-watch). The current efficiency is equal to the ratio of the actual deposit mass Δm to its theoretical value calculated from Faraday's Law:

$$CE = \Delta m/(QA/nF). \tag{1.23}$$

Table 1.4 Cathodic efficiencies in some electrolytes

Metal	Type of the electrolyte	Average cathodic efficiency
Ag	Cyanide	0.98
Au	Citrate	0.60
Au	Phosphate	0.95
Cd	Cyanide	0.90
Cd	Sulf.-ammonia	0.90
Co	Sulfate	0.88
Cr	Chromate	0.18
Cu	Sulfate	1.00
Cu	Cyanide	0.75
Cu	Pyrohosphate	0.99
Fe	Chloride	0.90
Fe	Sulfate	0.92
Fe	Fluoroboric	0.95
Ni	Sulfate	0.96
Ni	Sulfamate	0.98
Pb	Fluoroboric	0.99
Pd	Amino-chloride	0.80
Re	Sulf.-ammonia	0.25
Rh	Sulfate	0.70
Sb	Citrate	0.94
Sn	Stannate	0.80
Sn	Pyrophosphate	0.90
Sn	Sulfate	0.95
Zn	Cyanide	0.80
Zn	Sulfate	0.97

When the CE value for a specific process is already known, one can input this value into the formula of Faraday's Law, to determine the actual deposit thickness

$$h = \mathrm{CE} \cdot K_l i \tau. \tag{1.24}$$

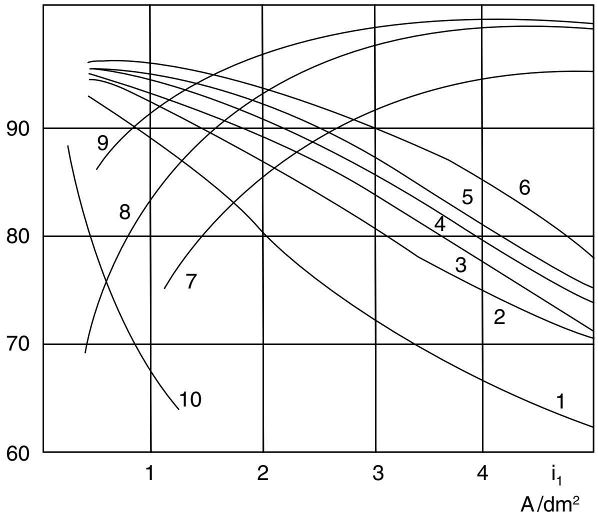
The values of CE can differ widely for different metal deposition processes of metal. CE depends on the metal, the solution type, temperature, current density, pH and so on. Commercial processes usually have relatively high CE; the tentative and averaged values for some processes are listed in Table 1.4.

The dependence of CE upon current density for several processes is depicted in Fig. 1.3; it can be noticed that CE may either rise or fall with current density.

1.10 The Various Steps Occurring in Electrode Processes. Fast and Slow Steps

The overall process of electrochemical metal deposition is complex and can be divided into sequential steps. Together with one (or more) charge transfer process(es), other steps such as chemical reactions, mass transfer and crystallization occur.

Fig. 1.3 The dependence of cathodic current efficiencies on current density for various metal deposition processes. *1* copper (cyanide solution), *2* cadmium (cyanide), *3* copper (pyrophosphate), *4* tin (stannate), *5* antimony (citrate), *6* zinc (cyanide), *7* iron (sulfate), *8* nickel (sulfate), *9* zinc (sulfate), *10* gold (citrate)



Chemical steps occurring near the electrode may involve ion dehydration or ligand dissociation.

Consumption of electroactive species at the electrode is balanced by mass transfer, which occurs by diffusion, convection and electric migration from the bulk of solution. Mass transfer of reducible species to the electrode is therefore the first step of the overall deposition process. Near the electrode the electroactive species may be dissociated from the ligand and/or dehydrated; in parallel, charge transfer occurs and the (partially) reduced metal atoms adsorbs at the growing surface. Finally, adsorbed ions or metal atoms (adions or adatoms) diffuse across the surface to active growth sites, where they are incorporated into the crystal lattice of the deposit, resulting in its growth. These steps are schematically shown in Fig. 1.4.

A generic multi-step process can be schematically represented as a chain of elementary reactions, as follows:

$$A \xrightarrow{1} B \xrightarrow{2} C \overset{3}{\leftrightarrow} D \xrightarrow{4} M \tag{1.25}$$

where A represents the initial state of the electrochemical system (the ion is located in the bulk of the solution, the electrons in the crystal lattice), and M is its final state, namely the metal atom in the crystal lattice. B etc. are intermediate states of

Fig. 1.4 The fundamental steps of electrodeposition at an electrode surface. *1* hydrated ions in the solution, *2* ions (atoms) at the surface while they diffuse to the surface steps, *3* kinks at the step (growth sites)