NRAO CHEMICAL LAB REPORT NO. 2

THEORY OF ELECTRODEPOSITED METALS

J. Lichtenberger

National Radio Astronomy Observatory
Charlottesville, Virginia

November 1975

ABSTRACT

A brief introduction to the theoretical analysis of applied electrodeposition is presented. The Nernst equation for electrochemical potenti is derived and deviations between observed and predicted reactions are considered.

The conceptual idea of electroplating is quite simple: one chooses the type of metal to be deposited, dissolves this metal in a suitable electrolyte, places the article to be coated in the solution, and passes electric current of the proper polarity through this set-up.

The underlying theory, as it turns out, is rather complex and has only recently been developed. Many aspects and observations are yet to be explained. The wide range of electrolytes presently available for depositing even one type of metal require separate analysis, since deposition mechanisms are often drastically different from one process to the next.

I. Thermodynamic Considerations

Electrodeposition requires that an ionic salt of the metal be used. This is necessary to provide mobility to the metal, since ionic salts are highly dissociated in aqueous solutions. This dissociation has been characterized by the Greek letter α, and is termed the <u>dissociation coefficient</u>. In dilute solutions of a metalic salt, the metal ions become positively charged (cations) and the acid residues become negatively charged (anions). As an example, if copper sulphate (formed when copper is dissolved in sulphuric acid) is dissolved in water, it dissociates according to the reaction:

$$CuSO_4 \rightleftharpoons Cu^{+2} + SO_4^{-2} \tag{1}$$

If 1/2 of the salt splits up in this way, the dissociation coefficient, α, equals 0.5. In general, for weak electrolytes the dissociation of a salt is inversely proportional to its concentration, derived as follows:

From the definition,

$$\alpha = C_A/C = C_B/C \tag{2}$$

where C = total concentration, C_A = anion concentration, C_B = cation concentration. Multiplying both sides of eq. 2 by C, one obtains

$$\alpha C = C_A = C_B$$

The total concentration C, is made up of the concentration of dissociated molecules αC, and the concentration of undissociated molecules C_{AB}, so that

$$C = C_{AB} + \alpha C \quad \text{or} \quad C_{AB} = C - \alpha C = C(1-\alpha) \tag{4}$$

In the case of the dissociation of a simple salt, eq. 1, the law of mass action gives the relationship between reactants and products:

$$(C_A \cdot C_B)/C_{AB} = K_c \tag{5}$$

where K_c is the dissociation constant. Substituting eq. 3 and eq. 4 into eq. 5:

$$(\alpha C \cdot \alpha C)/C(1-\alpha) = K_c \quad \text{or} \quad (\alpha^2 \cdot C)/1 - \alpha = K_c \tag{6}$$

This, the Ostwald dilution law, may be rearranged to

$$\alpha^2 C/K_c = 1 - \alpha \tag{7}$$

From eq. 7, we see that as the concentration C approaches 0, the term $\alpha^2 C/K_c \rightarrow 0$, and α must approach unity; thus dissociation is inversely proportional to concentration. In most electroplating baths, salts are completely dissociated, the above derivation applying only to weak electrolytes, such as boric acid and citric acid. Most strong acids and salts are strong electrolytes and dissociation is relatively independent of concentration. These behave as though weakly dissociated, despite the strong dissociation; this effect has been attributed to interionic electrostatic attraction. This necessitates defining a new concept, that of activity, as

$$a = f \cdot C \tag{8}$$

where f is termed the activity coefficient. This has a value <1 in all cases except at infinite dilution, and is on the order of 0.05 for 1 molar sulfate electrolytes commonly used in electroplating. In the copper bath used for electroforming, the $CuSO_4$ concentration is $\sim$68 g/l. At a concentration of 0.5M, the activity coefficient for copper sulfate is .062, so the effective concentration in the CuBath #1 process is only 4.2 g/l; i.e. the ions behave as if present at only 4.2 g/l without interionic attractions. This is important in the calculations involving the maximum permissible plating rates developed later.

A fundamental relationship in electrochemical theory is represented by the Nernst equation which relates the electric potential developed on an electrode placed in a salt solution to the activity of the ionic species involved in reactions with this electrode. It is derived by noting that free energy ΔF, is produced in an electrochemical reaction and may produce external electrical work under suitable conditions. This free energy results from a change in activity of the reacting ions from a to a_o in a manner as follows:

$$\Delta F = RT \cdot \ln (a_o/a) \qquad R = \text{gas constant} \qquad (9)$$

T = absolute temperature

ΔA, or external work is given by the equation:

$$\Delta A = -z\,FE_h, \qquad z = \text{valency of ion(s)} \qquad (10)$$

F = Faraday constant

E_h = Electrode potential

The work is given a negative sign to indicate that energy is being expended. Eqs. 9 and 10 may then be combined, producing

$$RT \ln a_o/a = -zFE_h \text{ which rearranges to} \qquad (11)$$

$$E_h = -RT/zF \cdot \ln a_o/a = -RT/zF \cdot \ln a_o + RT/zF \cdot \ln a$$

at constant temperature and final concentration, the term $-RT/zF \cdot \ln a_o$ is a constant, $E_{h,n}$ producing

$$E_h = E_{h,n} + RT/zF \cdot \ln a \qquad (13)$$

Substituting numerical values for R (1.98 cal/mole deg) and F (23,060 cal/volt) with T = 298°K, we obtain

$$E_h = E_{h,n} + .0591/z \cdot \ln a \text{ (volts)} \tag{14}$$

which is the standard form of the Nernst equation. If the activity of the potential determining ions is one, Eq. 14 reduces to $E_h = E_{h,n}$. This potential, $E_{h,n}$, is termed the standard potential, and gives the voltage to be expected when an electrode is placed in a solution of unimolar ion activity. When this potential is determined for many reactions and referenced to the arbitrary value:

$$H_2 \lessgtr 2H^+, \; E_{h,n} = 0.00 \text{ volts} \tag{15}$$

The resulting values may be arranged to yield the familiar electromotive series:

TABLE I[1]

REACTION	$E_{h,n}$	REACTION	$E_{h,n}$
$Au \rightarrow Au^+$	+1.7 (volts)	$Fe \rightarrow Fe^{+3}$	-.036 (volts)
$Au \rightarrow Au^{+3}$	+1.4	$Ni \rightarrow Ni^{+2}$	-.23
$AG \rightarrow Ag^+$	+.799	$Fe \rightarrow Fe^{+2}$	-.44
$Cu \rightarrow Cu^+$	+.52	$CR \rightarrow CR^{+3}$	-.71
$Cu \rightarrow Cu^{+2}$	+.34	$Zn \rightarrow Zn^{+2}$	-.763
$H_2 \rightarrow 2H^+$	0.00	$Al \rightarrow Al^{+3}$	-1.66

Such a list may be used to provide clues to the performance of electrodeposits as corrosion-resistant coatings. A coating of zinc, for example, would protect iron from corrosion, since the zinc would preferentially dissolve. The series indicates the relative ease with which metals tend to form ions. Thus, if a copper wire is immersed into a solution of gold ions, it begins to dissolve; simultaneously, gold ions are reduced at the surface of the wire and form an immersion coating of gold on the wire. Any metal with a more negative potential will similarly displace another metal occurring at a less negative potential in the chart. This is important in electroplating; for example, iron cannot be successfully plated with copper from an acid sulfate bath without a preliminary "strike" coating from a cyanide copper bath, in which the electromotive series does not apply in the usual sense. This is due in part to the fact that in complex cyanide baths, the copper is present in the anionic residue of the salt, the dissociation being

$$K_2Cu(CN)_3 \rightarrow 2K^+ + Cu(CN)_3^{-2} \tag{16}$$

and very few, if any, free cations of copper (Cu^+ or Cu^{+2}) are available for the immersion displacement reaction.

II. Kinetic Effects

The Nernst equation, while being useful in predicting corrosion behavior and displacement reactions, is limited in that it deals only with thermodynamic properties and phenomena. Kinetic and catalytic effects often override those reactions predicted by eq. 14, producing much greater polarizations than expected during electrochemical reactions. These include hydrogen overvoltage, diffusion polarization, reaction inhibition, and resistance polarization.

The increased polarization over that predicted by the Nernst equation is termed over-voltage ΔE_h, given by:

$$\Delta E_h = E_{h,obs} - E_{h,n} \tag{17}$$

where $E_{h,obs}$ is the experimentally determined electrode voltage. The kinetics of all electrode-solution reactions can be described by characterizing two phenomena; (1) the reacting ions must pass through an electrode-solution interface; (2) the ions must be transported towards or away from this phase boundary. The increased voltage is thus due to an inhibiting effect occurring in the phase boundary, or in the transport mechanism.

The chemical reactions occurring at an electrode may be viewed as a dynamic equilibrium, where ions are constantly being exchanged between the solid phase (electrode) and the liquid phase (electrolyte). With no externally applied voltage, ions are being reduced at the electrode at the same rate as other ions are dissolving from the electrode. These ionic interactions constitute a charge flow, producing a voltage characteristic of the reaction. This voltage is due to the presence of an electrical double layer, made up of positive and negative charges at the electrode surface, which requires that ions possess a certain minimum energy to pass. This is called activation polarization and is analogous to the concept of activation energy in more familiar reactions such as production of water from hydrogen and oxygen. Part of this excess polarization is due to the presence of a "hydration sphere" of water molecules which surrounds a metal ion in solution. These water molecules must be removed before an ion can be incorporated into a metalic bond of the electrode, thus requiring excess energy.

The flow of ions between phases in an electrochemical reaction produces an electrical current, called the exchange current of the reaction. For metals such as copper and zinc, the exchange current is on the order of 10^{-2} mamp/cm^2, while for nickel and iron, it is $\sim 10^{-6}$ mamp/cm^2. This compares to the rates with which these metals coordinate in other chemical reactions involving exchange of ligands. This exchange current reflects the solubility of a metal in a given electrolyte.

The total activation polarization is predicted by the Tafel equation, written for cathodic deposition as:

$$\eta_{act} = a - b \log i \tag{18}$$

a and b are coefficients dependent on the reaction mechanism. This is a reduced form of the general equation:[2]

$$\eta_{act} = RT/\beta zF \ln (i/i_o) \tag{19}$$

where i = net current density
i_o = exchange current density
β = symmetry factor for the reaction

From Eq. 19, it is seen that activation polarization is dependent on the exchange current and β, usually ~ 0.5, which accounts for the hydration envelope of water molecules.

Other inhibitory effects occur simultaneously during electrolysis. Concentration polarization develops as electrodeposition proceeds due to the depletion of ions in the double layer because ions can only be supplied from the solution bulk at a finite rate. It is given by the equation[3]:

$$\eta_{conc} = RT/nF \ln (C_E/C_O) \tag{20}$$

C_E = concentration of ion next to electrode
C_O = bulk concentration of the ion
n = number of electrons involved in the discharge

At the cathode, $C_E < C_O$ and η_{conc} is negative; at the anode, the reverse situation exists. The concentration gradient occurring due to this effect has been measured as far away as .015 inch from the electrode. A third effect is the resistance polarization arising from the ohmic resistance of a plating cell, given by

$$\eta_\Omega = i\ R_{bath} \qquad (21)$$

Often, an insulating film is also present on an electrode as well.

The total polarization is a combination of these individual overvoltages and represents the voltage needed to maintain a steady current during electrodeposition. After the initial plating, both anode and cathode are usually the same metal and the polarization becomes the total cell potential. Initially the anode and cathode may be different metals, requiring an additional voltage predicted by the Nernst equation.

In order for cations to reach an electrode for deposition, some process must account for their mobility. The process of mass transport has been subdivided into three categories. An ion under the influence of an applied electric field will move toward the cathode if positively charged and toward the anode if negatively charged. Due to frictional effects within the electrolyte, the initial acceleration due to the applied voltage is transformed into a steady motion termed the <u>migration velocity</u>. Typical values are given in Table II below:[4]

TABLE II (18°C)

Cation	u_c cm/sec/volt	Anion	u_c cm/sec/volt
H^+	.00315	OH^-	.00167
Na^+	.000367	Cl^-	.000624
K^+	.000606	SO_4^{-2}	.000593
Cu^{+2}	.00029		
Fe^{+2}	.00048		
Fe^{+3}	.00046		

These values are very small compared to deposition rates usually encountered. This migration can account for only a fraction of the ions being deposited at a cathode. Convection refers to mechanical motion of ions relative to the electrode. Close to the electrode surface, convection is negligible, due to frictional forces acting to retard motion. The greatest portion of ions are supplied to the electrode by diffusion due to the concentration gradient existing in the solution. A useful concept developed is the diffusion layer, which describes the area of electrolyte in the vicinity of an electrode. The boundary between this and the bulk of the electrolyte is not sharp; its thickness has been arbitrarily set as the region in which the concentration of a reacting ion differs by more than 1% from the bulk electrolyte. As agitation is increased, the diffusion layer decreases, being ∿.2mm (.007 inch) in still electrolytes and .015mm on a rotating disk at 1200 rpm.

The total transport phenomenon is made up of the migration in an electric field and the diffusion through the diffusion layer. For one molar copper sulfate, the migration velocity is 5.9×10^{-4} cm/sec/volt at 25°C. In a typical setup, the anode-cathode distance may be 15 cms, and the applied voltage one volt, producing a potential gradient of .06 V/cm and a migration velocity of 3.5×10^{-5} cm/sec. A copper ion would travel 15 cms in ∿119 hrs. if no other transport process occurs. At 1 cm^2 of cathode, copper arrives at a rate of 3.5×10^{-5} cm/sec x 1 cm^3 corresponding to a current density of 33 mA/cm^2. In typical plating baths, the sulfuric acid reduces the mobility to ∿15% of its value in $CuSO_4$ alone, the rate becomes ∿5 mA/cm^2 ($0.5A/dm^2$). In CuBath #1, plating is performed at 3 A/dm^2, diffusion thus being the major transport mechanism.

Another reaction important in electroplating involves co-deposition of hydrogen at a cathode. This presents an undesirable process since the hydrogen deposition consumes part of the current supplied and may also diffuse into the metal lattice of the cathode. Fortunately, hydrogen is non-metalic and exhibts peculiar properties during electrolysis. The activation energy for the reaction

$$2H^+ + 2e^- \rightarrow H_2 \text{ (gas)}$$

is abnormally high on most surfaces. This is due to inhibition in the formation mechanism of H_2 molecules from H^+ cations, and is incompletely understood. The effect of this high activation energy is to reduce the potential at which hydrogen is deposited to more negative values from its equilibrium valve of 0.00 volts. Were it not for this high <u>overvoltage</u>, metals such as zinc, iron, or nickel could not be deposited from aqueous solutions. From the Nernst equation, at a pH of 3, hydrogen should be deposited on a cathode at a voltage of -0.177 volts, zinc at one molar activity is not deposited until a voltage of -0.76 volts is reached, unattainable in this case. The deposition mechanism for H_2 production on zinc is greatly inhibited, hydrogen being produced only at potentials more negative than -0.89 volts. If the electrode is made from platinum, which catalyses the hydrogen reaction, the expected results occur, i.e., no zinc is deposited. The order of increasing hydrogen overvoltage is related to the solubility of H_2 in metals, the lower overvoltages corresponding to high solubility and is found to be: Pd, Pt, Fe, Au, Ag, Ni, Cu, Zn, Sn, Pb, Hg[5].

The important electrochemical phenomena are all interelated, competing with each other to produce the results seen during electrodeposition. Diffusion control is usually the limiting reaction, and plays a critical role in engineering electrolytes which are designed to produce brilliant, levelling deposits. These effects will be discussed in Section III of this report.

REFERENCES

[1] E. Raub and K. Müller, "Fundamentals of Metal Deposition", Elsevier Publishing Co., N.Y., 1967, pp.35.

[2] Frederick A. Lowenheim, ed., "Modern Electroplating", 3rd ed., Wiley & Sons, Inc., N. Y., 1974, pp.16.

[3] Ibid, pp.17.

[4] E. Raub and K. Müller, "Fundamentals of Metal Deposition", Elsevier Publishing Co., N.Y., 1967, pp.21.

[5] Ibid, pp.83.

BIBLIOGRAPHY

1) Frederick A. Lowenheim, ed., "Modern Electroplating", 3rd ed., Wiley & Sons, N.Y., 1974.

2) E. Raub and K. Müller, "Fundamentals of Metal Deposition", Elsevier Publishing Co., N.Y., 1967.

3) Metals and Plastics Publications Inc., "Metal Finishing Guidebo Directory", 42nd ed., Westwood, N.J., 1974.