

Fundamentals of Electrodeposition

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Introduction

Electrodeposition is an extensive and complicated subject. This discussion is confined to the energetics and kinetics of metal deposition from aqueous solutions. The formation of anodic films and the morphology of deposits is briefly mentioned. The elucidation of the atomic mechanisms has made significant progress in the past decade; it is the object here to review the present status. The cited works represent the more available literature and may be consulted for details, particularly the more recent reviews (1,2).

Energetics

The energy of the reaction between a metal and an electrolyte is the difference between the cohesive energy of the metal and the solvation energy of the metal ions. The former is the sum of the mutual potential energy of the valence electrons and the ions, that of the valence electrons, that of the ions and the kinetic energy of the electrons and the ions. The last may be neglected. The cohesive energy per atom may be expressed as

$$E_c = \frac{1}{2}U_{i,i} + \frac{1}{2}U_{e,e} + U_{i,e} + \frac{3}{5}\epsilon_F \quad (1)$$

The mutual potential energy between the electrons and the ions may, on the average, be divided into half for the electrons and half for the ions. We may then express the cohesive energy of the metal in terms of an ionic work function, α_+ , and the electronic work function, α_e , as follows:

$$\alpha_+ = \frac{1}{2}U_{i,e} + \frac{1}{2}U_{i,i} - \frac{2}{5}\epsilon_F$$

$$\alpha_e = \frac{1}{2}U_{i,e} + \frac{1}{2}U_{e,e} + \epsilon_F$$

and

$$\alpha_+ = E_c - \alpha_e = S + I - \alpha_e$$

where S and I are the sublimation energy and ionization energy per atom, respectively.

The energy of solvation, W_+ , is the energy change for solvating a gaseous ion. These quantities and the relevant potential energy curves are shown in fig. 1.

The standard free energy change for a metal ion to leave the lattice and go into solution is approximately

$$\Delta G_{\text{chem}}^{\circ} \approx \alpha_+ - W_+$$

An electrical potential difference, $(\phi_M - \phi_S)$, develops across the interface so that the total free energy change for the transition of ions from metal to solution is the sum of the chemical free energy change, $\Delta G_{\text{chem}}^{\circ}$, and the electrical

free energy change, $ZF[\phi_M - \phi_S]$. At equilibrium the total free energy change is zero and $\Delta G_{\text{chem}} = -\Delta G_{\text{elec}}$. At equilibrium the exchange rates of the ions are equal - the exchange current density, i_0 .

The ΔG_{elec} may be varied by an external circuit, disturbing the equilibrium and causing either a net deposition or net dissolution. The change in ΔG_{elec} from the equilibrium value is $ZF\eta$, where η is the overvoltage.

The energy α_+ and S must have the values appropriate to an internal ion. Since ions come from the surface during the reaction, we must look for the representative ion or atom on the surface.

Crystal Structure

The various surface sites are shown in fig. 2. The binding energy of an atom or ion varies according to its lattice position. The kink atom or kink site (K.S.) on the close packed planes is the representative one. The energy to remove this atom is equal to the average energy per atom, provided the ratio of surface atoms to bulk atoms is very small. At equilibrium the electrochemical potential of this ion is equal to that of an ion in solution. When the crystal is built up by the addition of ions, the ion is incorporated into this site, the "repeatable step." Ions "at ledges" or adsorbed on planar sites have higher potential energies. To form a new surface layer without the presence of steps requires an "excess energy" - nucleation energy. The new cluster of atoms requires a critical radius, r_c , in order to become a nucleus and grow. The value of r_c varies inversely with η , where η is analogous to a supersaturation.

The free energy increase required for the formation of a nucleus with height d is

$$\Delta G_c = \frac{\pi d V \sigma}{Z \eta}$$

where V is the atomic volume and σ is the surface energy of the edge. Vermilyea has estimated that an η of about 0.1 v would be required for most metals for a significant rate of growth with nucleation. This agreed with his findings for deposition of Cu on Cu whiskers which were bound by atomically flat surfaces (3,4).

Analogous to growth from the vapor, low values of η suffice for electrocrystallization in many cases. Following the ideas of Burton, et al (5), it is assumed that growth occurs at the steps of screw dislocation (see fig. 3). A critical radius of curvature is required for the steps at a given η , as in the case of nucleation. This leads to a ledge spacing, ℓ , which varies inversely with η .

Kinetics and Deposition Path

Advances in knowledge on mechanisms of crystal growth from the vapor have furnished the background for developments in electrodeposition (5,6). The latter is more complicated, and specific effects of solvation and field strengths must be taken into consideration. As previously indicated, the mechanism must provide for the ultimate incorporation of the ion into the K.S. when reaction proceeds near to equilibrium conditions - very low η .

Two alternate paths must be considered: Path I - direct deposition of an ion from the solution to the K.S.; Path II - transfer of the ion from solution to an adsite with subsequent surface diffusion to the K.S. In the latter case either transfer to adsite or surface diffusion may be the rate-determining step (r.d.s.).

Conway, et al (7) calculated the potential energy profiles for the two paths. Their necessarily qualitative results indicate that at low η Path II is energetically more feasible. Mott, et al (8), Vermilyea (3), and Fleischmann, et al (2) have suggested the conditions for either Path I or II to be predominant.

The basic consideration is the mean diffusion distance of an adion, which is determined by its residence time on the surface and the activation energy for surface diffusion. When the jump time on the surface, τ_D , is greater than the jump time to the solution, τ , Path I will dominate. When $\tau_D < \tau$, Path II will be significant. $\tau_D \cong a^2/D$ where "a" is the distance between the two adsites and D is the surface diffusion constant.

$$\tau = 1 / \frac{i_0}{C_0} \exp \left[\frac{\beta Z F}{RT} \eta \right]$$

where C_0 is the adion concentration at equilibrium and β the anodic transfer coefficient. η is considered a negative quantity for cathodic polarization. Mott, et al (8) suggest that, if N is the concentration of K.S., surface diffusion will be slow and rate controlling when $Na^2\tau/\tau_D < 1$; and that transfer will be rate controlling when the ratio is greater than one. Since τ increases as $|\eta|$ increases, surface diffusion control would be expected at lower values of η with a shift to transfer control as η increases.

The net current density at a point x distant from the growth site at a time t is given by

$$i(x,t) = i_0 \left[\exp \left(\frac{-\alpha Z F}{RT} \eta \right) - \frac{C(x,t)}{C_0} \exp \left(\frac{(1-\alpha) Z F}{RT} \eta \right) \right]$$

and

$$\frac{\partial [C(x,t)]}{\partial t} = \frac{i(x,t)}{Z F} + D \frac{\partial^2 [C(x,t)]}{\partial x^2}$$

where C is the adion concentration. In the steady state C(x) becomes constant and adions diffuse from x to growth sites at the same rate as they transfer from solution to adsites at x.

Damjanovic and Bockris (4) have treated the steady state conditions assuming $C = C_0$ at the growth site and a random distribution of dislocations, N/cm^2 . The model is shown in fig. 5. Some results of their calculations are given in fig. 6. The ratio

$$ND/i_0 \exp \left(\frac{\beta Z F}{RT} \eta \right)$$

is equivalent to the Mott ratio. As ND increases for a given η , the rate control shifts to transfer and a more uniform current density. For a given ND an increase in η produces the same effect. These authors appear to maintain that even when $i_x/i_{x_0} \sim 1.0$, deposition is to an adsite, and not directly to K.S.

The conditions for Path I have been developed by Vermilyea (3), Fleischmann, et al (2), and Hurlen (9). Expressions for i have been determined by considering hemicylindrical diffusion from the solution to ledges and hemispherical diffusion to the K.S. The stirring-independent limiting current predicated by the treatment for certain conditions has not been observed on metals with high i_0 .

The experimental approach to determine mechanisms have used transient behavior. The technique involves the application of current or potential pulses of very short duration ~ milliseconds. The object is to deposit less than a monolayer without changing the existing surface structure. The use of the time dependent terms obtained from the above equations allows the determination of C_0 , i_0 and v_0 , where ZFv_0 is the "diffusion current" on the surface at equilibrium. The parameters obtained also make it possible to determine the slow step of Path II. (1,2,3,10)

Ag has been studied extensively. The results indicate that $i_0 \sim 30-100$ mA/cm^2 , $C_0 \sim 10^{-9}$ moles/ cm^2 and that surface diffusion is the r.d.s. up to about $\eta = 50$ Mv. The adion appears to have about 30-50% of its charge in solution (1,2,10).

Bockris, et al (11) studied liquid and solid gallium and showed that surface diffusion is rate controlling on the solid up to about $\eta \approx 50-100$ Mv; but that transfer was the r.d.s. on the liquid, as expected. On the other hand, Gerischer (10) found transfer rate control on both liquid and solid Hg.

The case for Cu is not so clear cut. Results indicated "mixed" control by both surface diffusion and transfer at low η , with transfer control at higher η . The kinetic parameters show that transfer involves the consecutive reactions, reduction to Cu^+ in the solution and transfer of Cu^+ (10,12).

Lorenz (13) showed that surface diffusion is the r.d.s. on Zn at low η .

Bockris, et al (14) found that Fe has the transfer step as rate controlling and that the reaction is catalyzed by OH^- . Anions affect the rate where $\text{ClO}_4^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{Ac}^- > \text{NO}_3^-$.

Fleischmann, et al (15) deposited a single layer of Ni, one unit cell high, on Hg from thiocyanate solutions. Indications are that deposition is via Path II and that the rates of surface diffusion and transfer are comparable.

Generally the experimental results agree with the theoretical developments and support Path II as the predominant path for the metals with relatively high i_0 . The field is ripe for further experimental work and closer scrutiny of the theories, however.

Crystal Growth

Theories and many experimental observations on crystal growth are present in the literature (1,2,5,6,16,19). Growth proceeds by flow of steps and kinks on the surface. Macrosteps - visible ones - occur by "bunching" - a clustering of the smaller atomic steps. The morphology of a deposit is very dependent on the presence of adsorbed impurities, current density, and type of electrolyte. Without presence of impurities and at low η , existing steps will spread; their curvature depends upon η . The higher η , the greater the curvature. Formation of multilayers is primarily by rotation of screw-dislocation steps. In the presence of impurities and/or at higher η , new layers nucleate. Growth habits consist of many types; e.g., layers, spirals, blocks, pyramids, and ridges. The spirals are visual evidence of the screw-dislocation mechanism. Pyramids probably develop from spiral growth. Figures 7 and 8 show layer and spiral growth on copper.

Anodic Films

When the metallic ions can form an insoluble compound with a constituent of the solution (e.g., OH^- , S^{2-} , Cl^-), the solid compound may form on the surface - usually during anodic dissolution. If the film is continuous, metallic ions and/or

the negative ions migrate through the film as it grows. This is assumed to be the case for many oxide films such as passive films and capacitor films. The ionic transport through the film is usually the r.d.s. Non-continuous films nucleate on or near the surface. Their growth may be by ionic transport through the film or by deposition of the ions from solution and along the surface. The mechanisms of electrocrystallization of these films is basically similar to those of the metal deposits (20).

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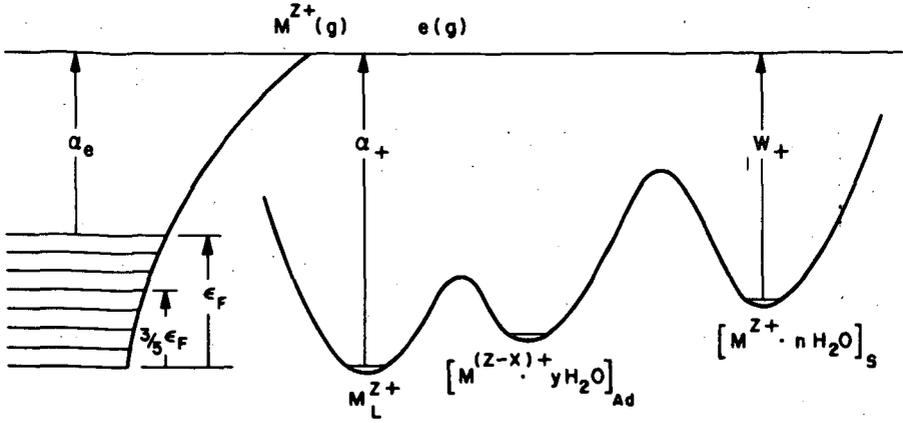


Fig. 1 Potential Energy Curves

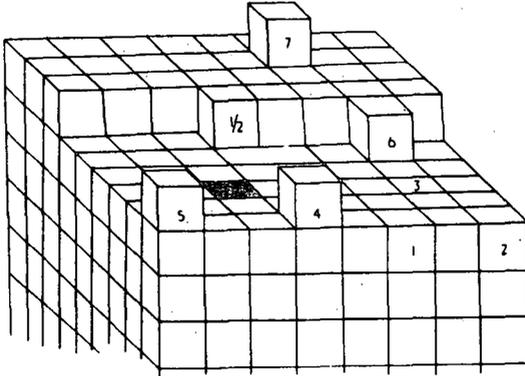


Fig. 2 Crystal Model
[From Knacke (16)]

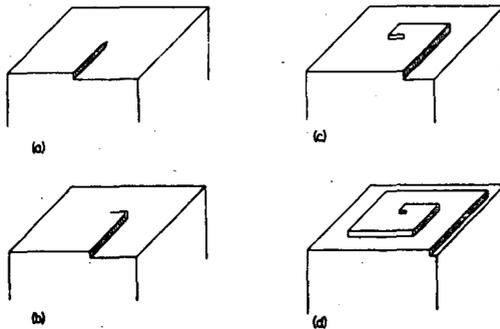


Fig. 3 Screw Dislocation
[From Gerischer(10)]

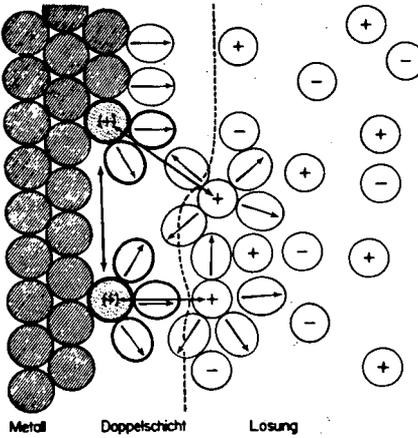


Fig. 4 Double Layer
[From Gerischer (10)]

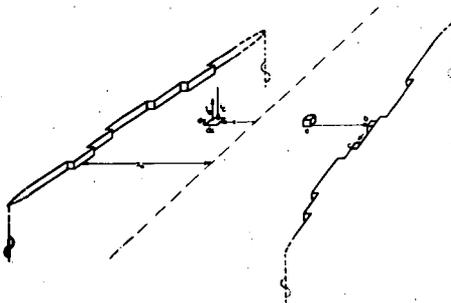


Fig. 5 Model For Deposition
[From Damjanovic(4)]

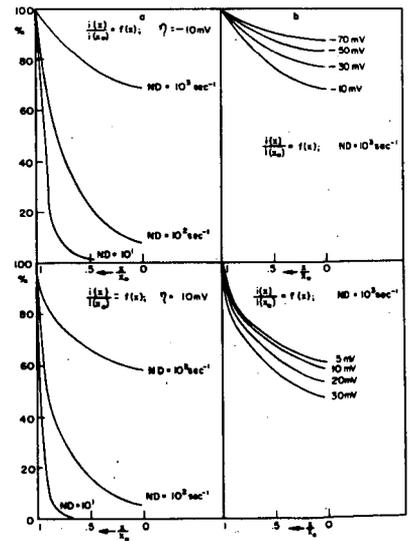


Fig. 6 Current Density vs. Distance
[From Damjanovic (4)]



Fig. 7 Layer Growth-Copper
[From Damjanovic (17)]



Fig. 8 Spiral Growth-Copper
[From Seiter (18)]