

CHAPTER II

LITERATURE REVIEW



2.1 Theory of electrolysis

2.1.1 General Remarks.

If two pieces of metal sheet of a suitable metal, e.g. platinum, are immersed in an aqueous solution of a salt, an acid or base and if these are connected with the poles of a direct current source, a current flows through the solution at a certain minimum voltage. Reactions take place at the same time at the metal electrodes. Solutions which conduct electrical current are termed electrolytes, and the overall process which occurs at the electrodes is termed electrolysis. (9)

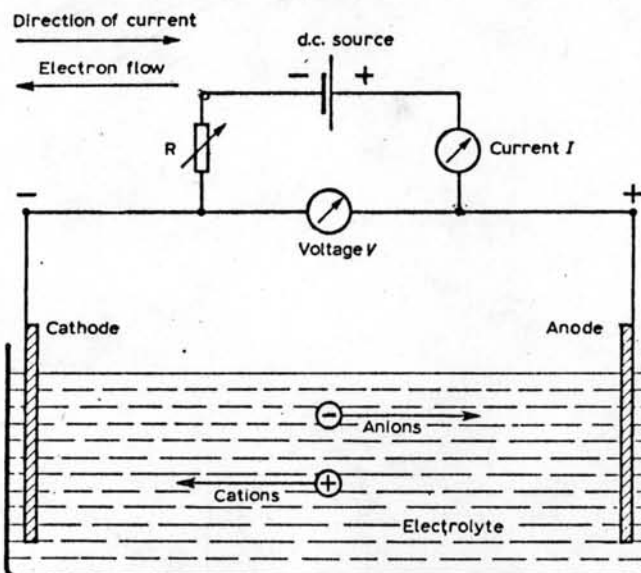


Figure 2.1 Electrolytic cell

Under the influence of the electrical current, the ions in the electrolyte migrate towards the electrodes. Thus, the passage of current entails transport of matter. The electrode connected with the negative pole of the direct current source is the cathode. The positively charged ions in the electrolyte, the cations, migrate towards the cathode. The electrode connected with the positive terminal of the direct current source is the anode, and the negatively charged ions, the anions, migrate towards the anode. (Figure 2.1) The electrode processes responsible for the passage of current from the electrode to the electrolyte and vice versa should be distinguished from the current conduction within the electrolyte. The processes in electrolysis should not be visualized as the ions delivering the charges transported by them to the electrodes, the anion at the anode and the cations at the cathode, thus giving rise to the electrode reactions. Electrolytic current conduction and the electrode processes responsible for the passage of current must be dealt with completely separately. The ions responsible for current transport in the electrolyte may or may not take part in the electrode reactions. The cations migrating to the cathode with the current are often not involved in cathode discharge or participate in it only to a slight extent. Even neutral molecules which do not migrate under the influence of the applied voltage may be decisive for the cathodic discharge processes. Finally, even anions which are transported to the anode by the current may also play a decisive role in the discharge processes.

The transport of ions with the current sometime plays no part at all in compensation of the charge in the electrolyte composition created round the electrodes by the electrode reactions. It may even increase the differences between the concentration at the electrodes and bulk composition of the electrolyte.

2.1.2 Ion migration and transport.

If a direct voltage is applied to the electrodes in an electrolyte a force acts on the ions and accelerates them towards the anode or cathode, depending on their charge. Because of friction with the ambient molecules and ions and the drag exerted by a water envelope around the ion, the accelerated motion is transformed after a brief acceleration into a steady motion termed the migration velocity of the ion. The migration velocity is defined as the constant velocity of an ion in cm/sec. at a field intensity of 1 v/cm. It is a characteristic constant for the particular ion involved. Its magnitude depends also on certain external conditions, such as pressure, temperature, nature of the solvent, and concentration. The migration velocities U_C of the cations and U_A of the anions are of the same order of magnitude, only those of the hydrogen and hydroxyl ions being considerably greater than those of the other ions (see table 2.1)

TABLE 2.1 MIGRATION VELOCITIES OF SOME ANIONS AND CATIONS AT
18°C IN AQUEOUS SOLUTION.

Cation	U_c cm/sec/v	Anion	U_A cm/sec/v
H^+	0.00315	OH^-	0.00167
Na^+	0.000367	Cl^-	0.000624
K^+	0.000606	NO_3^-	0.000581
Cu^{+2}	0.00029	SO_4^{2-}	0.000593
Ag^+	0.00049		
Fe^{+2}	0.00048		
Fe^{+3}	0.00046		

As long ago as 1853, J.W. Hittorf concluded on the basis of observed concentration changes during current passage that different ionic species have different migration velocities. If one of two oppositely charged ions migrates at higher velocity than the other, a greater impoverishment must occur at the electrode from which the faster ion migrates. Such concentration shifts in electrolyte were termed transport phenomena by Hittorf. These effects are possible without violation of the neutrality conditions in the electrolyte because more ions of one kind can be discharged at an electrode than are transported in electrolyte. The migration in electrical field represents only a preferred component of the motion, since owing to the thermal motion of the ions, both anion and cation species are always present in the vicinity of both electrodes.

The quantity of electricity transported by each ion species is proportional to velocity of the ions. Thus, of the cations having migration velocity U_C , the proportion

$$n_C = \frac{U_C}{U_C + U_A} \quad (2.1)$$

and of the anions having migration velocity U_A , the proportion

$$n_A = \frac{U_A}{U_C + U_A} \quad (2.2)$$

is transported. Hittorf termed these proportions the cation transport number n_C and the anion transport number n_A .

$$n_A + n_C = 1 \quad (2.3)$$

The relation always applies. If both ion species have the same velocity, i.e., if $U_A = U_C$, the transport numbers are $n_A = n_C = 0.5$. As table 2.2 shows, the transport numbers of the ions are in general close to 0.5. Only with acids and bases are extreme values found, which is accounted for by the particularly high migration velocities of the hydrogen and hydroxyl ions.

TABLE 2.2 TRANSPORT NUMBERS OF SOME CATIONS IN DILUTE AQUEOUS SOLUTION

Substance	Concentration	n_C
H ₂ SO ₄	0.02 N	0.823
NaOH	0.04 N	0.201
Na ₂ CO ₃	0.05 N	0.410
MgSO ₄	0.02 N	0.36

Substance	Concentration	n_c
NiSO_4	0.1 N	0.366
CuCL_2	0.05 N	0.405
CuSO_4	0.05 N	0.375
ZnSO_4	0.01 N	0.336
CdSO_4	0.008 N	0.387
AgNO_3	0.05 N	0.4648

2.1.3 Ohm's Law and Faraday's Law.

Electro - deposition is controlled by Ohm's Law and by Faraday's two law of electrolysis. ⁽¹⁰⁾

Ohm's Law express the relation between the three fundamental quantities, current, electromotive force, and resistance. The current I is directly proportional to the electromotive force E and inversely proportional to the resistance R , i.e.,

$$I = E/R \quad (2.4)$$

The unit of current is called the ampere, and was defined as that current which, flowing for one second, will cause the deposition of 1.11800 mg. of silver, or 0.33925 mg. of copper, from solution of their respective salts.

The unit of electrical resistance is the ohm. The international ohm is the resistance at 0°c of a column of mercury, of uniform cross - section, 106.300 cm. long and weighing 14.4521 g.

the cross - section area is very nearly 1 sq.mm.

The unit of electromotive force (emf.) is termed the volt, and is the difference of electrical potential required to maintain a current of 1 ampere through a system having a resistance of 1 ohm.

It must be remembered that because of the chemical and electrochemical reactions at the electrodes, changes take place which result in the appearance of an additional voltage E_{back} . This is in opposition to voltage applied to the electrolysis cell (E_{appl}). So that E_{appl} must exceed that of E_{back} and must also over-come the resistance of the solution to passage of current (i.e., the IR drop). The amount of current that flows is given by ohm's Law

$$E_{appl} - E_{back} = IR \quad (2.5)$$

Faraday's two laws of electrolysis state that.

(1) The amounts of substances liberated at the electrodes of a cell are directly proportional to the quantity of electricity which passes through the solution.

(2) The amounts of different substances which are deposited, or liberated, by the same quantity of electricity are proportional to their chemical equivalents.

The unit quantity of electricity is the coulomb, and is defined as the quantity of electricity passing when 1 amp. flows for 1 second. Each coulomb will deposit 1.1180 mg. of silver.

The weight of an element liberated by the passage of 1 coulomb of electricity (or 1 amp. for 1 second) is called electrochemical equivalent of the element. The equivalent weight of silver is 107.880, hence $107.880/0.0011180$, i.e., 96,493 coulomb will be required to liberate 1 g-equivalent of silver. The value generally employed is 96,500 coulomb, and this is termed a Faraday (F). The second law of electrolysis may be stated in the form that 1 faraday of electricity will liberate 1 g-equivalent of any substance at each electrode. (See Table 2.3)

TABLE 2.3 ELECTROCHEMICAL EQUIVALENTS OF THE ELEMENTS

Metal	Atomic weight	Valency	mg/ coulomb	g/Ah
Ag	107.880	1	1.11793	4.02454
Au	196.967	1	2.04145	7.35075
		3	0.68048	2.45025
Co	58.94	2	0.30539	1.09931
Ni	58.71	2	0.30420	1.09534
Cu	63.54	2	0.32922	1.18545
Fe	55.847	2	0.28938	1.04198
Zn	65.38	2	0.33876	1.21952

The weight corresponding to one equivalent of substance being electrolysed is its gram atomic weight or its gram molecular weight divided by the number of electrons involved in the electrode reaction. The weight W of substance produced or consumed in an

electrolysis involving Q coulombs is therefore given by the expression

$$W = \frac{W_m \cdot Q}{96,493 n} \quad (2.6)$$

Where W_m is the gram atomic weight or the gram molecular weight of the substance being electrolysed, and n is the number of electrons involved in the electrode reaction. If W_o is the origin weight of the substance in electrolyte and x is the remain portion.

$$x = W_o - \frac{W_m \cdot Q}{96,493 n} \quad (2.7)$$

Dividing Equation (2.7) by the volume of electrolyte, V , which is given constant, one obtains the expression in term of concentration.

$$\frac{x}{v} = \frac{W_o}{v} - \frac{W_m \cdot Q}{v \cdot 96,493 n} \quad (2.8)$$

$$\text{or, } C = C_o - \frac{W_m \cdot Q}{v \cdot 96,493 n} \quad (2.9)$$

Where C is concentration of the electrolyte at any time, C_o is the initial concentration.

There are two distinctly different electrolysis techniques available. Electrolysis under constant current and electrolysis under controlled potential.

(1) Electrolysis under constant current. In this method, the substance to be deposited is electrolysed with constant current until the reaction is completed (as detected by either a visual

indicator in the solution, potentiometric, spectrophotometric or Atomic Absorbtion) and the circuit is then opened. The total quantity of electricity passed is derived from the product : current (amperes) x Time (seconds). An accurate electric stop-clock may be used or, more conveniently, a low inertia integrating motor-counter unit. For the case of constant current, one has

$$Q = I \times t \quad (2.10)$$

Substituting Q in Equation (2.9), We have

$$C = C_0 - \frac{Wm.I}{V \ 96,493 \ n} \times t \quad (2.11)$$

This mean that, the concentration of the electrolyte varies linearly with time with C_0 as interception an slope being equal to $-\frac{Wm.I}{V \ 96,493 \ n}$ (see Figure 2.2)

(2) Electrolysis under controlled potential. In this method, the substance being deposited reacts with approach 100 percent current efficiency at working electrode, the potential of which is controlled. The completion of reaction is indicated by the current decreasing to practically zero. The quantity of electricity Q (coulomb) passed for a total time t is given by

$$Q = \int_0^t I_t dt \quad (2.12)$$

The current generally decreases exponentially with time according to the equation

$$I_t = I_0 10^{-kt} \quad (2.13)$$

Where I_0 = the initial current
 I_t = the current at time t
 k = a constant

It can be shown (Lingane) that $k = 25.8 DA/\delta V$, where D is the diffusion coefficient of the reducible substance (cm^2/sec). A is the electrode area (cm^2). δ is the thickness of the diffusion layer (cm), and V is the total Volume (ml) of the solution of concentration C . A typical time-current curve is shown in Figure 2.3

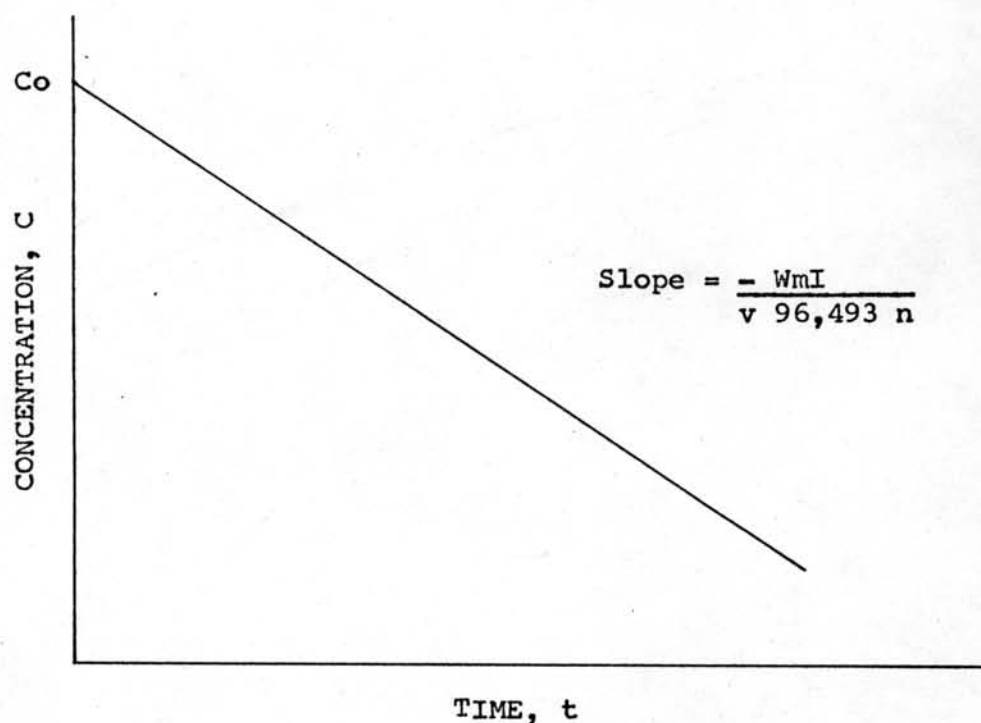


Figure 2.2. Concentration-time curve under constant current.

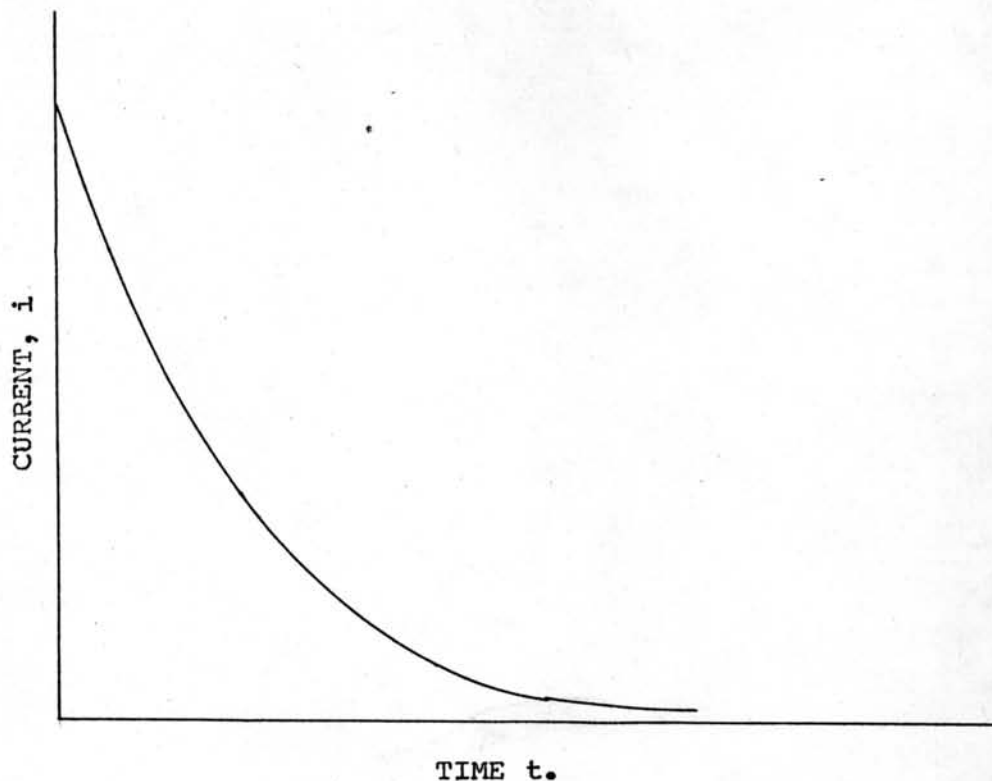


Figure 2.3 A typical time-current curve under controlled potential.

The current decreases more or less exponentially to almost zero. In many cases an appreciable "back-ground current" is observed with the supporting electrolyte alone, and in such instances the current finally decays to the back ground current rather than to zero. As the electrolysis proceeds, the cathode tend to become more negative with respect to the reference electrode, and it is necessary to adjust the rheostat so as to restore the cathode to the desired potential. The ammeter reading decreases throughout the electrolysis and generally attains a low constant value signalling the completion of the determination. Frequent adjustment and constant attention are demanded by this procedure if the cathode potential is to be kept constant to ± 0.05 volt or better.

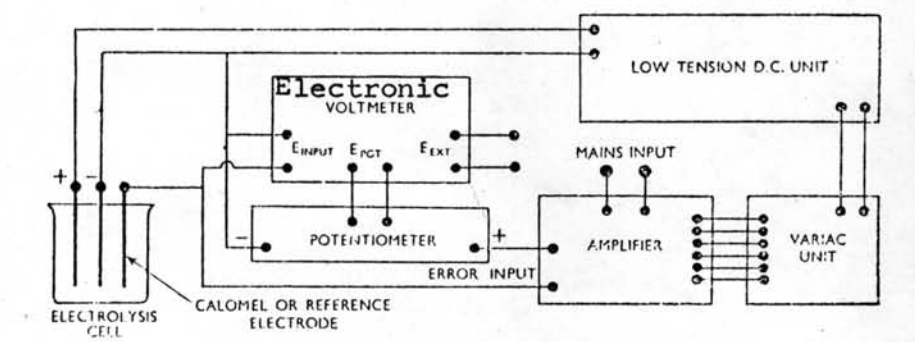


Figure 2.4 Potentiostats.

For these reasons manually controlled electrolyses have not found wide application in electrolysis. The development of instruments, known as "potentiostats" which automatically maintain the potential of an electrode constant to $\pm 5 - 10$ millivolts at any predetermined value are however relatively expensive. Schematic diagram of this process is shown in Figure 2.4

2.1.4 Current density and current efficiency

Current density.

Calculation in electrodeposition technology are usually based on the current density which is defined as the current per unit area of electrode surface. It is generally expressed in amperes per square decimeter (amp/dm^2) or per square cm.

(1 sq.dm. = 100 sq.cm.)

Current efficiency.

By measuring the amount of a particular substance that is deposited and comparing this with the theoretical quantity (calculated by Faraday's laws), the actual current efficiency may be obtain.

$$\eta = \frac{G_M, \text{ expt}}{G_M, \text{ theor}} \times 100 \quad (2.14)$$

where G_M is the weight of the deposited metal, in gram

2.1.5 Decomposition potential.

It is defined as the minimum external voltage that must be applied in order to bring about continuous electrolysis. It is experimentally shown that the decomposition voltage of an electrolyte varies with the nature of the electrodes employed for the electrolysis and is in many instances, higher than that computed from the difference of the reversible electrode potentials. The excess voltage over the calculated back e.m.f. is termed the "overvoltage"

To calculate the reversible electrode potential,

A reversible oxidation-reduction system may be written in the form (oxidant = Substance in oxidised state, reductant = substance in reduced state



The electrode potential which is established when an inert or unattackable electrode is immersed in a solution containing both

oxidant and reductant is given by the expression

$$E_T = E^\circ + \frac{RT}{nF} \ln \frac{a_{\text{ox}}}{a_{\text{Red}}} \quad (2.15)$$

Where E_T is the observed potential of the redox electrode at temperature T relative to the standard or normal hydrogen electrode taken as zero, E° is the standard potential (reduction), n the number of electrons gained by the oxidant in being converted into the reductant, and a_{ox} and a_{Red} are the activities of the oxidant and reductant respectively.

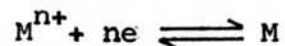
Since activities are often difficult to determine directly, they may be replaced by concentrations. The error thereby introduced is usually of no great importance. The equation therefore becomes

$$E_T = E^\circ + \frac{RT}{nF} \ln \frac{C_{\text{ox}}}{C_{\text{Red}}} \quad (2.16)$$

Substituting the known values of R and F , and changing from natural to common logarithms (by multiplying by 2.3026), we have for a temperature of 25°C ($T = 298^\circ$)

$$E_{25^\circ} = E^\circ + \frac{0.0591}{n} \log \frac{(\text{ox})}{(\text{Red})} \quad (2.17)$$

When a metal is immersed in a solution containing its own ions. A potential difference is established between the metal and the solution. The potential difference E for an electrode reaction



is given by the expression

$$E = E_o + \frac{0.0591}{n} \log C_{Mn+} \quad (2.18)$$

This is a form of the Nernst equation. In general, it may be stated that the theoretical back emf. is given by

$$E_{back} = E_{cathode} - E_{anode} \quad (2.19)$$

where $E_{cathode}$ and E_{anode} are calculated by eq. (2.18)

Because overvoltage may occur at the cathode as well as at the anode. The decomposition voltage E_D is therefore

$$E_D = E_{cathode} + E_{o.c.} - (E_{anode} + E_{o.a.}) \quad (2.20)$$

where $E_{o.c.}$ and $E_{o.a.}$ are the overvoltages at the cathode and anode respectively

The overvoltage at the anode or cathode is a function of the following variables.

- (1) The nature and the physical state of the metal employed for the electrodes.
- (2) The physical state of the substance deposited. If it is a metal, the overvoltage is usually small, if it is gas, the overvoltage is relatively great.
- (3) The current density employed. For current densities up to 0.01 amp/cm^2 (1 Asd), the increase in overvoltage is very rapid, above this figure the increase in over-voltage continues, but less rapidly.

(4) The change in concentration, or the concentration gradient, existing in the immediate vicinity of electrodes, as this increases the overvoltage rises. The concentration gradient depends upon the current density, the temperature, and the rate of stirring of the solution.

(5) The overpotential decreases, often very considerably, with increasing temperature.

The Decomposition potential of a substance can be determined in practice. For example, If a small voltage of, say, 0.5 volt is applied to two smooth platinum electrodes immersed in a solution of M-sulphuric acid, then an ammeter placed in the circuit will at first show that an appreciable current is flowing. Its strength, as shown by ammeter, decreases rapidly, and after a short time becomes virtually equal to zero. If the applied voltage is gradually increased, there is a slight increase in the current until, when the applied voltage reaches a certain value, the current suddenly

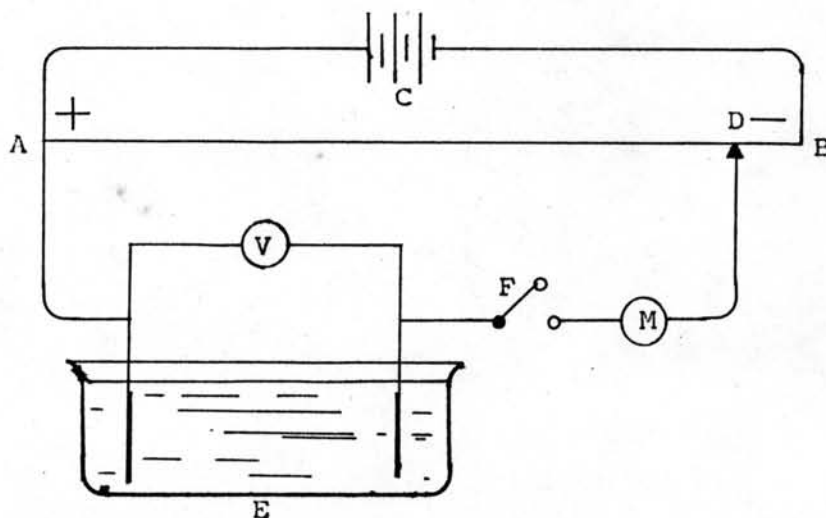


Figure 2.5 Apparatus for determination of decomposition voltage

increases with increase in the e.m.f. The experiment may be carried out by means of the apparatus shown diagrammatically in Figure 2.5. D.C. power supply C is connected across a uniform variable resistance AB, along which a contact maker D can be moved. The fall of potential between A and D can thus be varied gradually. Two smooth platinum electrodes are immersed in 1 M. sulphuric acid in the cell E. V is a suitable voltmeter placed between the two electrodes of the cell, M is a milliammeter and F is a switch. The applied voltage is slowly increased by moving D towards B, and the readings of the voltmeter and ammeter noted after allowing a short time for the values to become steady. Upon plotting the current against the applied voltage, a curve similar to that shown in Figure 2.6 is obtained, voltage at point which the current suddenly increases is termed the decomposition potential.

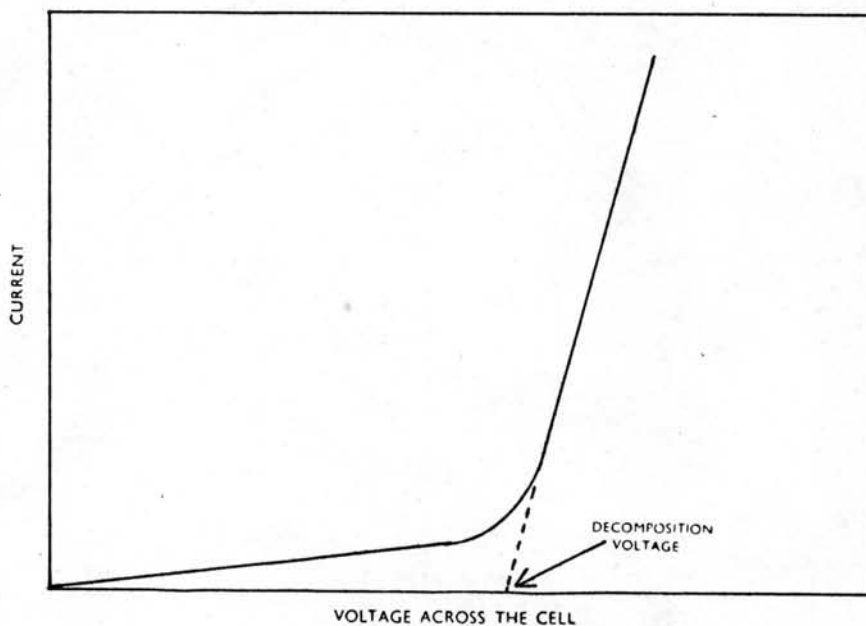


Figure 2.6 Curve showing decomposition voltage

The decomposition potential obtained by extrapolation has, strictly, no exact meaning, but it does serve to indicate the approximate minimal value of the applied voltage which must be exceeded in order to carry out an electrolysis fast enough to be of value in practice. For a reversible cell reaction, with the electrodes initially in equilibrium with the solution, the decomposition potential does pass exact meaning because it is equal to the reversible e.m.f. of the cell. The small current observed before the decomposition voltage is reached termed the residual current.

Strictly speaking, the voltage across the cell, measured by the voltmeter V , is greater than the decomposition potential by the quantity IR , where I is the current flowing in amperes and R is the resistance in ohms. However, since I is very small and R is not very large, the quantity IR may be neglected, and the voltage measured on V taken as the decomposition potential.

TABLE 2.4 DECOMPOSITION VOLTAGES OF N-SOLUTIONS BETWEEN SMOOTH PLATINUM ELECTRODES

Substance	Decomposition voltage	Substance	Decomposition voltage
AgNO_3	0.70	CH_3COOH	1.57
CuSO_4	1.49	HNO_3	1.69
$\text{Pb}(\text{NO}_3)_2$	1.52	H_2SO_4	1.67
CoCl_2	1.78	NH_4OH	1.74
ZnBr_2	1.80	KOH	1.67
NiCl_2	1.85	NaOH	1.69

2.1.6 Completeness of deposition.

The voltage applied E_{app} to an electrolytic cell must overcome the decomposition potential E_D or back e.m.f., as well as the ohmic resistance of the solution, i.e., E_{app} must be equal to or greater than $E_D + IR$. It has been shown that

$$E_{app} \gg E_{cathode} + E_{o.c.} - (E_{anode} + E_{o.a.}) + IR \quad (2.21)$$

Overvoltage at the cathode makes the effective cathode potential more negative than the equilibrium value, whilst overvoltage at the anode causes the effective anode potential to be more positive. Let us consider the variations in e.m.f. at the cathode during the deposition of metal in an electrolysis. Let the ionic concentration at the commencement of the estimation be C_i . For n valent metal, the cathode potential at 25°C will be (see eq.2.18)

$$E_{cathode} = E_{Mn+}^{\circ} + \frac{0.0591}{n} \log C_i$$

If the ionic concentration is reduced to one-ten-thousandth of its original value, the new cathode potential will be

$$\begin{aligned} E_{cathode}' &= E_{Mn+}^{\circ} + \frac{0.0591}{n} \log C_i \times 10^{-4} \\ &= E_{Mn+}^{\circ} + \frac{0.0591}{n} \log C_i - 4 \times \frac{0.0591}{n} \\ &= \text{Potential at commencement of deposition} - \\ &\quad 4 \times \frac{0.0591}{n} \end{aligned}$$

This is independent of the value of C_i , and hence whenever the ionic concentration is reduced to one-ten-thousandth of its initial value, the potential is altered by $4 \times \frac{0.0591}{n}$. For a univalent ion,

the change is $= 4 \times 0.0591/1 = 0.236$ volt, and for bivalent ion it is $4 \times 0.0591/2 = 0.118$ volt. Otherwise expressed, the decomposition potential increases as the deposition of the metal proceeds.

When a constant current is passed through a solution of electrolytes, the electrochemical process with the most positive reduction potential will occur first at the cathode, followed by the next most positive electrochemical process, etc. Thus metal ions with positive reduction potentials may be separated, without external control of the cathode potential, from metal ions having negative reduction potentials. It will be clear from what has been stated that the initial deposition potentials of two metals must differ by at least 0.25 volt for a virtually quantitative separation to be theoretically possible. For most practical purposes, the difference in potential should be at least 0.4 volt. When, however, the standard potentials of the two metals differ only slightly, the electro - separation is more difficult. The obvious method is to alter the electrode potential of one of the metal in some way. This is most simply achieved by decreasing the ionic concentration of the ion being discharged by incorporating it in complex ion of small instability constant. The deposition potential of the metal forming a complex ion is thus raised. Furthermore, the overvoltage at the small ionic concentration is also usually increased.

The ideal deposit should be adherent, dense, and smooth in this form it is readily washed without loss. Flaky, spongy,

powdery, or granular deposits adhere only loosely to the electrode, and for this and other reasons should be avoided. As a rule, more satisfactory deposits are obtained when the metal is deposited from a solution in which it is present as complex ions rather than as simple ions.

In practice two methods of electrolysis are utilised. In the first method stationary electrodes are used and the solution is not stirred, small current densities must of necessity be applied in order to secure a coherent deposit, and the procedure is a slow one (Slow electrolysis). In the second method, which is superseding the first, the solution is rapidly stirred (Rapid electrolysis). Various devices are employed for stirring. An independent mechanical stirrer may be used, but it is more usual to have a rotating electrode. A very much higher current density may then be applied without seriously affecting the purity or the physical character of deposit. The stirring results in a liberal supply of metal ions always being present near the cathode, and consequently the current is principally used in the deposition of the metal. A considerable saving of time is thus effected, and this accounts for the popularity of the method.

2.2 Rotating Electrodes.

It has already been known that stirring of the electrolyte during electrolysis reduces considerably the time required for deposition. A method often employed to accomplish stirring is to rotate the inner electrode.⁽¹⁰⁾ The inner electrode should be placed

concentrically with the outer electrode so that the electrical field is as uniform as possible. Next sections will consider the analysis of a simple electrochemical system, namely, two concentric cylindrical electrodes with an electrolytic solution in the annulus between the two, ⁽¹¹⁾ as shown in Figure 2.7

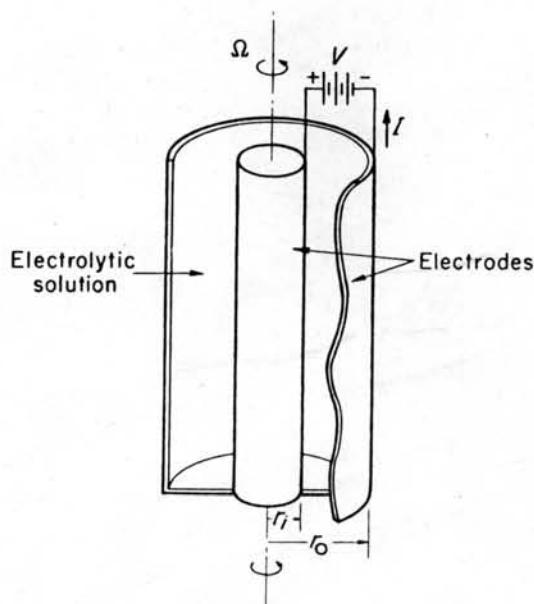


Figure 2.7 System of cylindrical electrodes, the inner of which can rotate.

2.2.1 Electrolytic conduction.

In the solution, cupric sulfate will dissociate into charged cupric ions Cu^{++} and sulfate ions $\text{SO}_4^{=}$, which are driven through the solution by the electric field; the cupric ions are driven toward the negative electrode, and the sulfate ions toward the positive electrode. The velocity of migration of an ion is proportional to the charge on the ion and the electric field, the negative of the gradient of electric potential.

$$V_i = - Z_i U_i F \frac{dE}{dr} \quad (2.22)$$

Here E is the potential; r is the radial distance from the axis, Z_i is the charge number of ion; and F is Faraday's constant, equal to 96,487 C/equiv. Thus $Z_i F$ is the charge per gram ion. The proportionality factor U_i is called the mobility of the ion and has units of $\text{cm}^2\text{-mole/J-sec}$.

The current density i is the sum of the currents carried by the two kinds of ions and has the units of A/cm^2 . It is obtained by multiplying the ionic velocities by the concentrations and the charges and adding

$$i = Z_+ C_+ F V_+ + Z_- C_- F V_- \quad (2.23)$$

In this case $Z_+ = 1$, $Z_- = -1$ and the ionic concentrations C_+ or C_- can be identified with the stoichiometric concentration of silver nitrate.

Equations (2.22) and (2.23) can be combined to yield

$$i = Z_+ C_+ F (V_+ - V_-) = - Z_+ C_+ F^2 (Z_+ U_+ - Z_- U_-) \frac{dE}{dr} \quad (2.24)$$

The coefficient in this relationship between the current density and the gradient of the potential is a transport property of the solution known as the conductivity K with units of $\text{ohm}^{-1}\text{cm}^{-1}$

$$K = Z_+ C_+ F^2 (Z_+ U_+ - Z_- U_-) \quad (2.25)$$

Consequently, equation (2.24) can be written as Ohm's law

$$i = - K \frac{dE}{dr} \quad (2.26)$$

This relationship is valid only if the concentration is uniform, as we shall see presently. The total current I passing from one electrode to the other is obtained by multiplying the current density by the area at a section in the solution

$$I = 2\pi rHi = 2\pi rHK \frac{dE}{dr} \quad (2.27)$$

Where H is the depth of solution. Since I is a constant independent of position, this equation can be integrated to yield the potential distribution.

$$E(r) - E(r_i) = - \frac{I}{2\pi HK} \ln \frac{r}{r_i} \quad (2.28)$$

Where r_i is the radius of the inner electrode. Correspondingly, the relationship between the current I and the potential difference V applied between the electrodes is

$$V = E(r_i) - E(r_o) = \frac{I}{2\pi HK} \ln \frac{r_o}{r_i} = IR \quad (2.29)$$

Where we can identify the resistance of this system as

$$R = \frac{\ln \frac{r_o}{r_i}}{2\pi HK} \quad (2.30)$$

This analysis illustrates the application of Ohm's law and conservation of current in a cylindrical annulus where the area available for the passage of current varies with radial position. The potential distribution is sketched in Figure 2.8 which show that the electric field becomes greater near the inner electrode.

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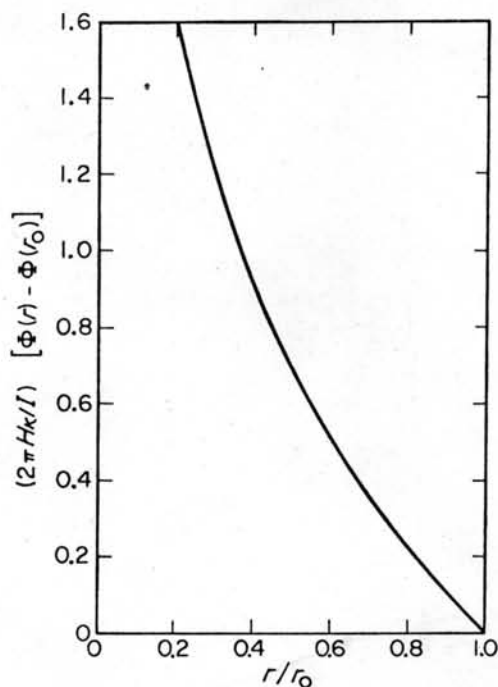


Figure 2.8 Distribution of potential applied to cylindrical electrodes.

2.2.2 Fluid flow.

Flow patterns of the electrolytic solution produced in the rotating-electrode system are quite important in determining the behavior of electrochemical systems, since they provide a mechanical mixing that helps to reduce concentration variation and contributes materially to the transport of reactants to electrode surfaces. These flow patterns are sufficiently complicated to warrant discussion.

Very low rotation speeds lead to simple flow of the fluid in concentric circles as shown in Figure 2.9. Such a flow is not of much practical interest because the fluid velocity is perpendicular to the direction of mass transfer. The flow simply carries the

material in circles and does not lead to any enhancement of the rate of mass transfer.

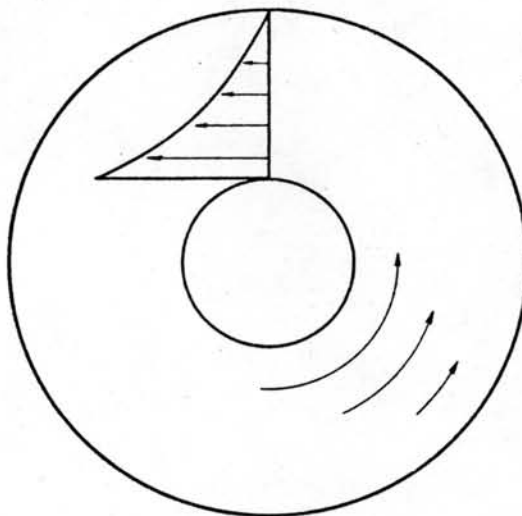


Figure 2.9 Velocity distribution for concentric streamlines between rotating cylinders.

This simple flow pattern becomes unstable at higher rotation speeds, particularly if the inner electrode rotates, as we shall suppose here. The flow then has a cellular motion superimposed upon the flow around the inner cylinder. These so-called Taylor vortices are shown in Figure 2.10. Now there is a component of the velocity in the direction from one cylinder to the other, and rates of mass transfer can be enhanced. However, a deposit of metal made under these conditions will be irregular, corresponding to the cellular flow pattern.

At still higher rotation speeds, the flow becomes turbulent and is characterized by rapid and random fluctuations of velocity and pressure. These induce a fluctuating velocity component in direction from one cylinder to the other. Hence, the rate of mass

transfer can be enhanced considerably, in a uniform manner over surface of cylinder. At a solid surface, the fluid velocity is equal to that of the solid, since the fluid cannot flow through the surface and since frictional effects do not allow a discontinuity in the tangential velocity. For this reason, the velocity fluctuations die away as a solid surface is approached.

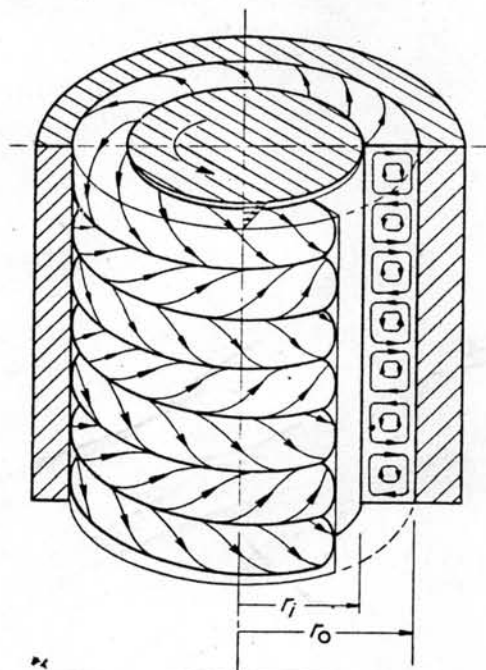


Figure 2.10 Sketch of Taylor vortices.

For the rotating cylinders, we thus encounter three flow regimes. The simple laminar flow with concentric streamlines requires the least torque to rotate the inner cylinder and leads to no particular enhancement of mass-transfer rates. The flow with Taylor vortices is still regular, laminar, and steady, but is much more complex to analyze. It requires a higher torque and contributes to mass-transfer rates. Turbulent flow provides effective stirring and requires the highest torques. Turbulent flow cannot be analyzed satisfactorily from fundamental principles.

The flow between rotating cylinders is characterized by two dimensionless ratios : the ratio of the gap distance $r_o - r_i$ to the inner radius r_i , and the Reynolds number $Re = (r_o - r_i) r_i \Omega / \nu$, where Ω is the rotation speed (radian/sec) and ν is kinematic viscosity of the fluid (cm^2/sec). For small values of $(r_o - r_i)/r_i$, the simple laminar flow is stable for a Taylor number less than 1708.

$$Ta = Re^2 \frac{r_o - r_i}{r_i} = \frac{r_i \Omega^2 (r_o - r_i)^3}{\nu^2} \quad (2.31)$$

At higher values of the Taylor number, one encounters Taylor vortices or turbulent flow. For example, for $(r_o - r_i)/r_i = 0.19$, turbulent flow prevails for Reynolds numbers greater than 3960 or Taylor number greater than about 3×10^6 .

2.2.3 The diffusion layer

The flux N_i of a species i is equal to its velocity multiplied by its concentration, and represents the number of moles passing per unit time through a unit area oriented perpendicular to velocity. In dilute solutions, Equation (2.22) can be generalized to express the flux of an ionic species as

$$N_i = C_i v_i = - Z_i U_i F C_i \nabla E - D_i \nabla C_i + C_i v \quad (2.32)$$

This equation is written in vector notation, its component in the radial direction is

$$N_{ir} = - Z_i U_i F C_i \frac{\partial E}{\partial r} - D_i \frac{\partial C_i}{\partial r} + C_i v_r \quad (2.33)$$

The first term on the right represents transport by migration, just as in Equation (2.22), The second term represents transport by diffusion and is proportional to the gradient of concentration, the proportionality factor being called the ionic diffusion coefficient, with units of cm^2/sec . The last term represents transport by convection, with the fluid velocity V .

Figure 2.11 is sketch of concentration profile of cupric ions in the diffusion layer near the cathode. Both migration and diffusion will tend to drive cations toward the electrode, since the electric field is in this direction and the concentration decreases toward the electrode. Far from the electrode, convective transport dominates, and the concentration becomes uniform.

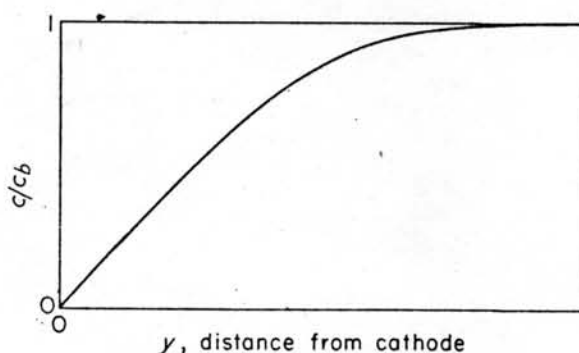


Figure 2.11 Concentration profile of cupric ions in the diffusion layer near the cathode. The scale of distance will depend on the rotation speed since the diffusion layer becomes thinner at high rates of stirring.

Figure 2.12 is a sketch of the concentration profile of cupric sulfate in the solution between the electrodes. Consider first the dashed curve which would apply when there is no radial component of velocity, for example, in slow, laminar flow with

concentric streamlines. In the steady state, there is no transport of sulfate ions, since only the cupric ions react at the electrodes. The sulfate ions are driven by migration toward the positive electrode, that is, toward the left in the figure. Since there is no net movement of these ions, this tendency for migration is exactly compensated by a tendency for diffusion toward the right, toward a region of lower concentration. Thus, the precise form of concentration profile is dictated by this requirement for a balance between diffusion and migration of sulfate ions.

The cupric ions, on the other hand, are driven toward the right by migration. The diffusion tendency is also toward the right, thus aiding migration and cupric ions can be said to carry all the current from the anode to the cathode.

The solid curve in Figure 2.12 indicates the effect of stirring the solution by rotation of the inner cylinder to create turbulent flow. The convective transport tends to eliminate concentration variations in the middle of annular space. However, turbulent fluctuations are damped near the solid electrodes, and in these region migration and diffusion again become the dominant modes of transport. The electrode reactions still lead to depletion of the solution near the cathode and enhancement of the concentration near the anode.

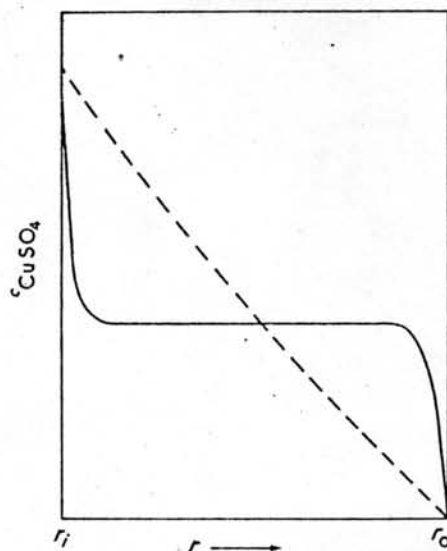


Figure 2.12 Concentration profile in the annular space between the electrodes. The dashed curve refers to the absence of a radial component of velocity. The solid curve refer to the presence of a turbulent flow regime.

For high rates of stirring, we are led to the concept that concentration variations are confined to thin boundary layers near the electrodes. This concept has important consequences in simplifying the quantitative treatment of transport in electrochemical systems. As the rotation speed is increased, these diffusion layers become thinner.

2.3 Factors Effecting Metal Deposition in Electrolytic Processes.

2.3.1 Current Distribution

This factor is utilized to the arrangement of the anodes and cathode for uniform thickness deposition which improve mechanical handling. Since electric current is not distributed

evenly throughout, a plating tank, but is concentrated along paths of least electrical resistance.⁽¹²⁾ Therefore, the electrical conductivity of plating solution, the arrangement of the anodes and cathodes, and the complexity of shape of the electrode all influence the current flow and current density at local areas. Thus, large current density variations from one area to another are encountered corners, edges, fins, ribs and other protuberances acquire more than an equal share of the deposited metal because they are high current density regions. The variations in electroplate thickness are shown exaggeratedly in Figure 2.13 for selected simple shapes and poorly positioned anodes. Better thickness uniformity over the surface of these representative shapes can be obtained if the anodes are positioned as shown in Figure 2.14.

2.3.2 Temperature.

Increases of temperature ordinarily increase the conductivity of the solution, increased rate of stirring and rate of diffusion, and changed overvoltage effects. Stirring by heat or by mechanical means makes possible the use of a high current density and therefore a rapid deposition.⁽¹⁰⁾ Lowered resistivity of the electrolyte with increased temperature causes lessened current concentration at

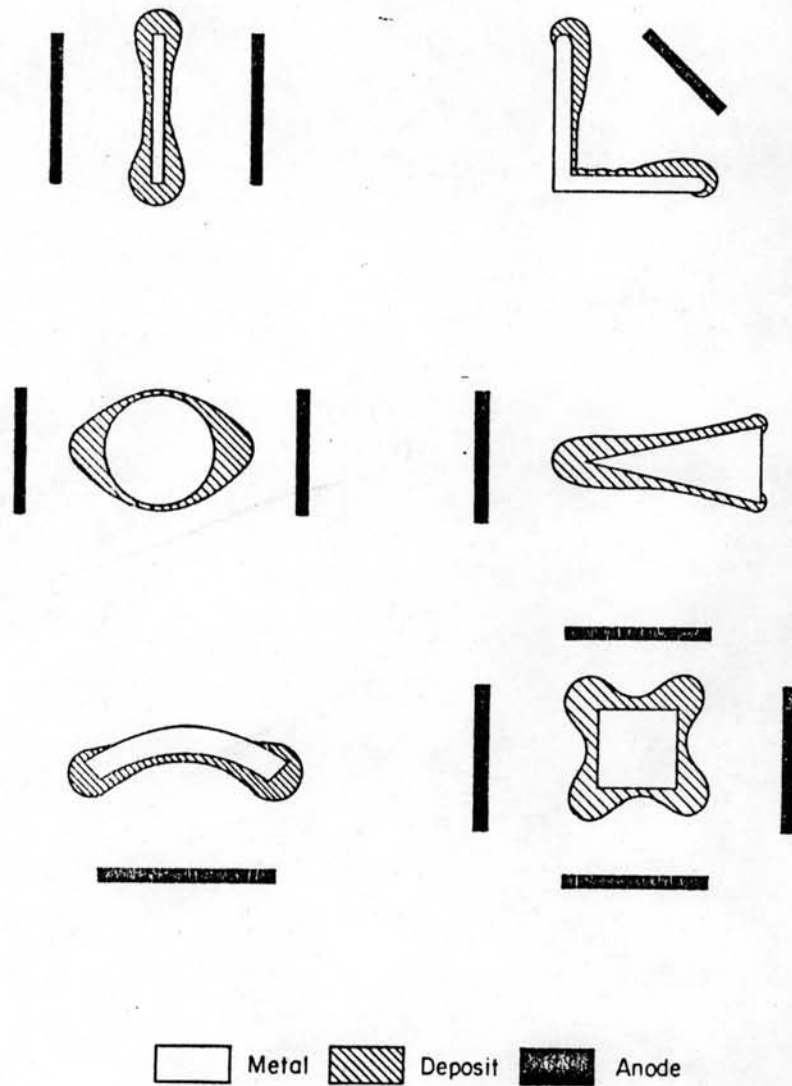


Figure 2.13 Variations in electroplate thickness over various shapes.

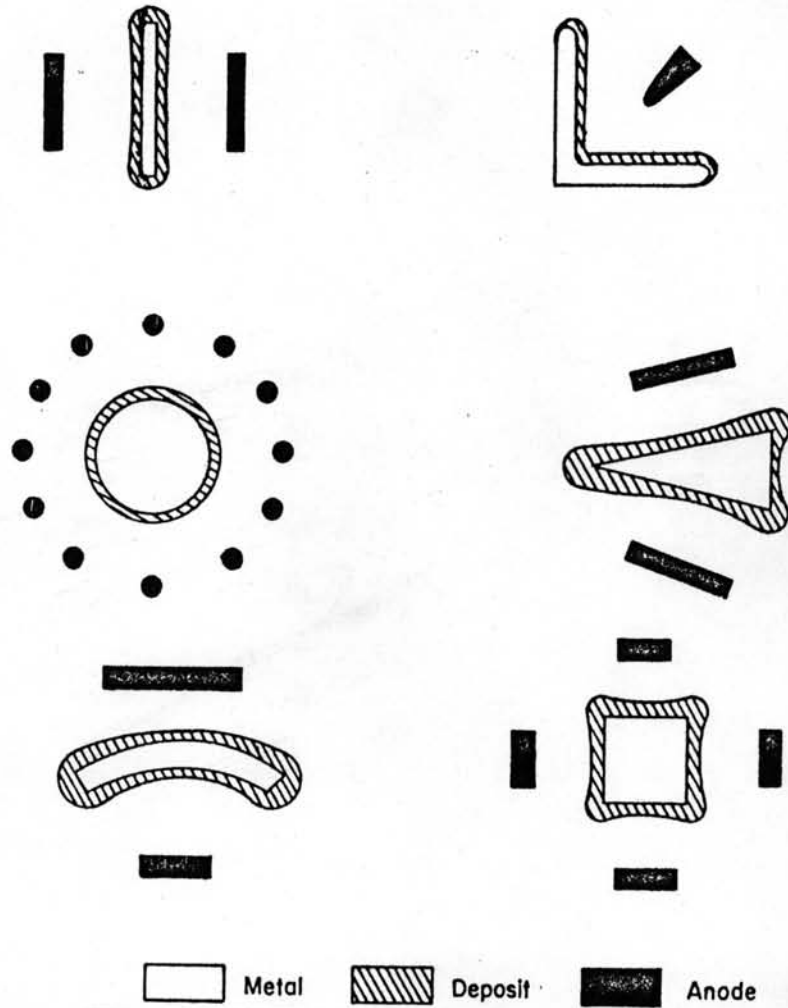


Figure 2.14 Effect of anode size and position on the thickness variations on electroplate.

protruding points on the cathode, so that irregularities develop less rapidly than at lower temperatures. ⁽⁸⁾ Temperature increase promotes hydrogen evolution and the precipitation of contaminating salts. Both these factor deleteriously effect the character of the deposit.

2.3.3 pH.

The pH of an electrolyte from which metal is deposited markedly affects both the character and appearance of the deposit as well as the current efficiency. In some industrial processes such as nickel, buffers such as boric acid are added to maintain the pH at desired point. In nickel plating different operating conditions are necessary if the process be carried on near the neutral point or at low pH under conditions of relatively greater acidity. In iron deposition the acidity of the bath may be such that there will be chemical dissolution of the deposit whose rate may exceed that of electrolytic deposition. In a some what analogous manner the pH of the bath may be so high i.e., so alkaline, that similar dissolution effects are encountered under poor operating conditions. In electrowinning operations, as the electrolyte is depleted of metal, the pH increase so that deposition occurs over a wide range of conditions. Decrease in pH, i.e., increase in acidity, favorably affects the conductivity and increase the deposition polarization. The precipitation of basic salts is prevented, but hydrogen evolution is favored.

2.3.4 Current Density.

Increasing the current density of the cell, in that the current per unit of area of electrode surface is intensified, augments the capacity or output of products and decreases capital cost, floor space per unit of product, and interest charges on material in operation. Upward changes in current density cause cell voltages and contact losses to rise, while energy efficiencies are lowered. In most electroplating operations, the range of current density is limited, in that the physical character of the deposit is the controlling factor.

For any given process, the most desirable current density results from a balance of many factors, such as power cost, operating charges, value of material in process, and energy consumption per unit of product. In materials as valuable as gold undergoing refining, high current densities are employed even though they be less efficient, to speed the product through the operation and minimize high interest charges.

2.3.5 Conductivity.

In many baths additions of salts, acids, or bases are made to lower the resistance of the electrolyte. The potential drop through the electrolyte itself is lowered for the same current density. It is not possible to change the conductivity of a solution without changing some other properties such as the metal ion concentration. The addition of H_2SO_4 to a $CuSO_4$ solution increases the conductivity, but the common ion effect decreases

the Cu^{++} ion concentration. In as much as the increase in conductivity produced by the H_2SO_4 is many times greater than the decrease in metal ion concentration, the assumption is made that better performance is due to the lowered resistance.

2.3.6 Metal Ion Concentration.

The metal ion concentration in an electrolyte is affected by the molal concentration of the salts, their ionization, the temperature, the presence or absence of common ions or of bath constituents with which complex ions are formed. Additions of common ions produce only a relatively slight change in metal concentrations, particularly in concentrated solutions, as the result of the limited solubilities of the salts which might be added. Formation of stable complex ions markedly reduces the metal ion concentration. Very low molal concentrations yield powdery deposits even at low current density.

Of the complex ions, these of the double cyanides are favored for the plating of metals such as silver, copper, cadmium, zinc, and brass. Metal ion concentration is low as the result of secondary ionization, while the primary ions serve as a reservoir from which a small but constant supply of material available for crystal growth is furnished.

2.3.7 Addition Agents.

A wide range of colloidal or reducible substances has been added to electrolytes to improve the quality of the deposit.

Crystal size is decreased when there are present at the cathode surface substances which are adsorbed by the deposited metal. A wide range of high-molecular-weight organic products has been found to give smoother and finer - grained deposits in particular cases. Substances which increase the weight of the cathode deposit, i.e., are adsorbed, tend to reduce the size of the crystals in the deposit, where as substances which do not vary the crystal size cause no increase in the weight of the deposit for the same amount of current.

Mettallic ion additions affect the character of deposits. They are often referred to as brighteners, an example of which is the addition of nickel, cobalt, or copper salts to cadmium electrolytes. Addition agents such as glue in copper and lead refining.

2.4 Design Consideration of an Electrolytic system.

An electrolytic facility comprises four distinct component groups : cell feed preparation equipment, electrolytic cells, electrical power supplies, and product recovery equipment. The technology and costs for cell feed preparation and product recovery are well established and need not be considered, Instead, attention is given to the electrochemical cells and associated power equipment.

The basic design goal of any process is to obtain a large amount of product (high yield) of high quality for a minimum input of energy and investment. To maximize the performance of a cell

for a given reaction, these three basic parameters affecting process economics must be optimized : electrical current efficiency, cell voltage, and current density.⁽¹³⁾

Electrical current efficiency is defined as the fraction of current passed that is effective in producing the required product. It depends on a large number of factors such as mass transport, pH. of electrolyte, and the kinetics of competing processes.⁽¹⁴⁾ If overall cell voltage is kept to a minimum, power costs may be reduced significantly for an electrochemical facility. The total cell voltage is made up of the following components : the cell's reversible potential, the electrodes' overvoltages, and the voltage drop due to the sum of ohmic losses throughout the cell. Typically the voltage components decrease when the operating temperature increases. The final parameter is current density. For any given surface area requirement, an increase in current density will reduce the number of cells needed, thereby reducing capital costs. From another perspective, the productivity of a given number of cells will become greater as the current density is increased. However, a value of current density is reached beyond which the system becomes mass transfer limited. This limit depends on such factors as the nature of electrode surfaces, temperature, and fluid velocity.⁽¹³⁾ Also, the point at which unwanted side reactions occur must be considered as a limiting element.

2.5 Properties of Silver

2.5.1 Physical properties.

Silver in its pure form is a soft, white, lustrous metal which is extremely malleable and ductile and is capable of taking a high polish. It has the highest thermal conductivity and the lowest electrical resistivity of any metal at normal temperature

Density = 10.49 g/cc. at 20°C (68°F)

Melting point = 960.50 °c

2.5.2 Chemical properties.

Silver is resistant to most common acids except nitric acid, in which it dissolves readily, and chromic acid with which it forms a dark red deposit of silver chromate, this reaction serving as a useful "spot" test for identifying the metal. On heating in clean air, the pure metal does not oxidise but because it has an affinity for sulphur, traces of sulphur compounds present in both industrial and rural air cause tarnishing. ⁽¹⁵⁾

Atomic weight = 107.880

electrochemical equivalent = 0.0011180 gm. per amp-sec.

The standard potential = + 0.7978 volt in normal ionic
solution at 25°C

2.6 Chemistry of Fixing and Electrolytic Recovery

2.6.1 Chemistry of Fixing

The latent image formed during exposure is developed in the photographic developer to produce the visible image. At this stage in processing, the emulsion still contains most of unexposed silver halides. The purpose of the fixing bath is to remove the unexposed silver halides from the emulsion and thereby make the image more permanent. (16)

A suitable fixing agent for silver halide emulsions should meet the following requirements : (1) it must dissolve the silver halides completely, (2) it must form salts with halides that are soluble in the fixing bath itself and are stable when diluted so that they will not decompose during washing, (3) it must not attack gelatin, and (4) it must not affect seriously the silver grains of the developed image. There are several compounds that will dissolve silver halides, but most of them do not meet all of the above requirements. Some of these are sodium sulfite, ammonia, potassium iodide, thiourea and the cyanides. Only the thiosulfates come sufficiently close to meeting all the requirements to be of interest in general photography. Sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, and ammonium thiosulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_3$ have proved to be most practical both chemically and economically.

After development of the photographic image, the undeveloped, insoluble silver halide is fixed by converting it to a soluble complex with a sodium or ammonium thiosulfate fixing bath. The reaction may be considered to be :



The resulting soluble complex diffuses out of the emulsion into the fixing bath. In addition to the original chemicals and the complex silver salts, there are probably several of these thiosulfate-silver complex existing in a used fixing bath and that their composition changes progressively as more of the silver halides are dissolved. (17)

In addition to the sodium or ammonium thiosulfate, called "hypo" in the photographic trade, practical fixing baths contain a number of other ingredients which perform various special functions.

Acid.

In order to avoid various possible troubles, the fixing bath must be able to neutralize any of the alkaline developer solution that might be carried in by the photographic material. To accomplish this, an acid must be added. However, when a strong acid is added to a hypo solution, the hypo is decomposed to form a fine suspension of sulfur in the bath. A film fixed in such a solution becomes opalescent on drying, because the "colloidal sulfur" as it is known, enters the emulsion structure during fixation and is not removed during washing. An opalescent negative cannot be printed satisfactory, or at best only with considerable difficulty. Fortunately, a weak acid, such as acetic acid, produces colloidal sulfur very slowly and can be used in the fixing solution with the addition of a preservative to prevent the formation of the sulfur.

Preservative.

The most commonly used preservative is sodium sulfite (Na_2SO_3) which, in solution, reacts with colloidal sulfur according to the equation



to form sodium thiosulfate. Actually, the chemistry involved is more complex than the equation indicates, but this is a satisfactory representation of the final result.

Hardener.

In order to prevent excessive swelling and softening of the emulsion during washing, with the consequent danger of mechanical injury, a hardening agent is generally used in the fixing bath. Potassium alum is the most widely used hardener for this purpose.

Buffer.

To be most useful in practice, a fixing bath should be able to withstand the addition of a considerable amount of developer with only a small change in pH, that is, the solution must be buffered and at the same time have a large reserve acidity. Therefore, acetic acid and sodium sulfite are used in sufficient quantity and in the correct relative amounts to satisfy these requirements, (see table 2.5) the addition of a hardener, such as potassium alum, also has a definite effect upon the buffering of the solution. Boric acid is used, in addition to acetic acid, to

improve the buffer action and antisludging characteristics.

Thus, the used fixing bath contains sodium sulfate, sodium halide sodium ferrocyanide (in color processing), gelatin and many other chemicals from previous solution.

Table 2.5 Kodak Fixing Bath F-5.

Sodium Thiosulfate	240.0	grams.
Sodium Sulfite	15.0	grams.
Acetic Acid, 28 %	48.0	C.C.
Boric Acid, crystals	7.5	grams.
Potassium Alum	15.0	grams.
Cold water to make	1.0	liter.

2.6.2 Chemistry of Electrolytic Recovery.

In the electrolytic recovery system, silver in the fixing bath is plated on the cathode of an electrolytic cell. The soluble silver complex Thiosulfate in a used fixing bath ionizes as follows.



Note that the silver is in the negatively charge ion, which is driven away from the negative cathode toward the positive anode. A small amount of free silver ion is yielded by the dissociation of the negative ion.



If this dissociation takes place in the vicinity of the cathode, the silver ion will be reduced and will deposit on the cathode as silver plate ⁽¹⁸⁾



Since the silver thiosulfate ions tend to migrate away from the cathode and yet should be in that vicinity when dissociation take place, that mean vigorously agitation is very necessary to keep a high concentration of the ions near the cathode. Also, the total silver concentration of the fixing bath must exceed a certain minimum for any specified current density. (18)

If the silver thiosulfate ion at the cathode fall below a certain minimum concentration, the thiosulfate ions will react at the cathode as follows :



The resulting sulfide ion will react with the silver ion as silver sulfide which is impurity for silver production. (19)



2.7 Quantity of Silver in Appropriate Processing Solution.

In considering the profitability of recovering silver from processing solutions, it is necessary to know how much silver is potentially available and the total volume of fixer that is handled between solution changes. Table 2.6 indicates the average amount of silver available in processing solution on 1,000 unit basis for black-and-white and color films, prints, and papers processed with typical processing equipment. The figures are based on the assumption that the fixing bath has been used to the point where it should be discarded.

Table 2.6 Quantity of Silver in Appropriate Processing
Solution*

Type	Size per unit	gram per 1,000 units processed
Aerial Films		
Color Negative Films	1 ft. x 9 1/2 inches	420 to 467
Color Positive Films	1 ft. x 9 1/2 inches	373 to 420
Color Print Films	1 ft. x 9 1/2 inches	249 to 280
B & W Negative Films	1 ft. x 9 1/2 inches	171 to 249
B & W Print Films	1 ft. x 9 1/2 inches	78 to 202
Radiography Films		
Medical X-Ray Films	14 x 17 - inch sheet	467 to 933
Industrial X-Ray Films	14 x 17 - inch sheet	1555 to 2488
Commercial and Professional Films and Papers		
Color Negative Films	8 x 10 inch sheet	373 to 420
Color Reversal Films	8 x 10 inch sheet	327 to 358
B & W Negative Films	8 x 10 inch sheet	140 to 187
Color Prints from Negatives	8 x 10 inch sheet	16 to 22
B & W Prints from Negatives	8 x 10 inch sheet	31 to 62
Photofinishing Films and Papers		
Color Negative Films	1-620 or 1-135/roll	327 to 358

Table 2.6 Quantity of Silver in Appropriate Processing
Solution* (continue)

Type	Size per unit	gram per 1,000 units processed
Color Reversal Films	1-620 or 1-135/roll	249 to 280
B & W Negative Films	1-620 or 1-135/roll	109 to 156
Color Prints from Negative	$3\frac{1}{2}$ x $3\frac{1}{2}$ inch print	6 to 9
B & W Prints	$3\frac{1}{2}$ x $3\frac{1}{2}$ inch print	3 to 6
Motion Picture Films		
Color Negative Films	1 ft. x 35 mm.	62 to 78
Color Print Films	1 ft. x 35 mm.	19 to 22
Color Reversal Films	1 ft. x 35 mm.	44 to 59
B & W Negative Films	1 ft. x 35 mm.	37 to 56
B & W Print Films	1 ft. x 35 mm.	25 to 31
Glass Plates		
B & W Photofabrication (LITH - Type)	1 square foot	187 to 280
B & W Photofabrication (Continuous Tone)	1 square foot	249 to 342

- * The data was listed from " Recovering Silver From
Photographic Materials" Eastman Kodak Company 1972,
page 6 - 7.