

## Basic Electrochemistry

Although those aspects of fluid dynamics given in the previous chapter are useful in outlining the patterns of flow likely to occur in ECM, clearly an understanding of the process also demands some knowledge of basic electrochemistry.

Relevant information can be derived from studies of the structure and properties of electrolytes, since these media largely determine the rates and types of reactions in ECM. Upon that framework can be built an appreciation of the interactions which arise when a single metal is placed in an electrolyte, and of those other equilibrium phenomena associated with an electrochemical cell consisting of two metals dipped in an electrolyte and externally connected.

Studies of these so-called reversible processes certainly provide a guide to the likelihood of certain reactions occurring in practice. But in ECM the only anode reaction which is wanted is metal dissolution, and that is achieved by an externally applied potential difference between the two electrodes. The process is now said to be irreversible, and the electrodes *polarised*. With an irreversible process are closely associated overpotentials, which are a measure of its departure from reversibility. Investigations of overpotentials in ECM require some of those aspects of fluid dynamics which were given in Chapter 2.

### 3.1 Basic assumptions and definitions

#### (a) Electrolyte conductivity

In the first chapter, the idea of the specific conductivity of the electrolyte was introduced. The magnitude of the conductivity is

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determined by the types and numbers of the ions present in the electrolyte. The different ions may also carry different quantities of electric charge. It is useful, therefore, to compare the conductivities of different electrolytes by reference to concentration, a quantity which can be applied to all electrolytes. Concentrations are often calculated from either the weight of the solute per unit weight (w/w), or weight per unit volume (w/v), of solution, or the volume of the solute per unit volume (v/v) of solution.

Of these measures of concentrations, a commonly used quantity is that of gram-molecules, or moles, of solute per litre of solution. (A gram-molecule is the molecular weight in grams.) Thus a one-molar (1M) solution is one which contains one gram-molecule of solute per litre of solution; a 2M solution contains two gram-molecules, etc. For example, a 1M NaCl solution has 58.5 g of NaCl per litre, since the atomic weights of Na and Cl are 23 and 35.5 respectively. The gram-equivalent of solute per litre of solution is another useful measure of concentration. (A gram-equivalent is the equivalent weight in grams.) A solution with one gram-equivalent of solute per litre of solution is a one-normal (1N) solution. For example, a 1N H<sub>2</sub>SO<sub>4</sub> solution has 49 g of H<sub>2</sub>SO<sub>4</sub> per litre of solution, since the respective atomic weights are 1, 32, and 16.

Concentrations of electrolytes so expressed provide a common base for the comparison of the conductivities of different electrolytes. In particular, the molar conductivity,  $\Lambda_m$ , and equivalent conductivity,  $\Lambda_c$ , are useful:

$$\Lambda_m = \frac{\text{specific conductivity at concentration } C \text{ of solution}}{\text{concentration of solution in moles per ml of solution}}$$

$$\Lambda_c = \frac{\text{specific conductivity at concentration } C \text{ of solution}}{\text{concentration of solution in g-equivalents per ml of solution}}$$

To establish the relationship between the molar and equivalent conductivities, we introduce the electrochemical valency  $n_e$ .

Suppose that an electrolyte of general formula P<sub>x</sub>Q<sub>y</sub> is electrically neutral and that, on ionisation, each molecule forms xP<sup>z+</sup> cations and yQ<sup>z-</sup> anions. Then each g-molecule of P<sub>x</sub>Q<sub>y</sub> contains xz<sub>+</sub> (=yz<sub>-</sub>) g-equivalents. (The condition of electrical neutrality gives that xz<sub>+</sub> = yz<sub>-</sub> = n<sub>e</sub>; for instance, for NaCl, x = 1, z<sub>+</sub> = 1, y = 1, and z<sub>-</sub> = 1, so n<sub>e</sub> = 1; whilst with Na<sub>2</sub>SO<sub>4</sub>, x = 2, z<sub>+</sub> = 1, y = 1, z<sub>-</sub> = 2, so n<sub>e</sub> = 2.)

Thus, the molar conductivity  $\Lambda_m$  at concentration  $C$  g-molecules/l is

$$\Lambda_m = \frac{1000 \kappa_e}{C} \quad (3.1)$$

whilst the corresponding equivalent conductivity  $\Lambda_c$  is

$$\Lambda_c = \frac{1000 \kappa_e}{n_e C} \quad (3.2)$$

#### (b) Degree of dissociation

It has been assumed so far that if a substance dissolves in water, it dissociates completely into ions. This is not necessarily the case. It becomes useful, therefore, to define the 'degree of dissociation',  $\alpha$ , of an electrolyte, that is, the fraction of the solute which is dissociated into ions that are free to carry current at a given concentration. On the basis of this definition, a rough division of electrolytes can be made: 'strong' electrolytes, which become greatly dissociated for concentrations ranging from very low to high values ( $\alpha$  always about unity), and 'weak' electrolytes, for which  $\alpha$  tends to unity at very low, limiting concentrations, and reduces to about zero at high concentrations. (It is important to distinguish between 'dissociation' and 'ionisation'. The former term applies to ions which are free to carry current, whilst the latter refers to the total number of ions present and not to their ability to carry current. Electrostatic attraction between ions of opposite sign can lead to the temporary formation of ion-pairs which behave as non-ionised molecules and so are unable to carry current. Consequently, a wholly ionised electrolyte may not become completely dissociated.) Weak electrolytes, of which weak organic acids are typical examples, are seldom used in ECM except as additives to the main solution to improve the quality of machining. Strong electrolytes are used as the main electrolytes in ECM; a common example is NaCl solution.

The degree of dissociation of an electrolyte can be related to Kohlrausch's observation that, at very low concentrations of an electrolyte, each ion makes a definite contribution towards the equivalent conductivity of the electrolyte, irrespective of the nature of the other ion with which it is associated in the solution. Before this relationship is established, the notion of ionic mobility must be introduced.

#### (c) Ionic mobility

We have already seen that it is the motion of the ions which makes possible the passage of current through the electrolyte. The rate of ionic movement is termed the ionic 'mobility'. Since the current is equal to the quantity of electrical charge passed per second, and since the cations and anions carry this charge, the sum of the velocities of the anions and cations is directly proportional to the

Table 3.1 Absolute ionic mobilities

Cation	Hydrogen	Potassium	Sodium
Mobility (m/s) $\times 10^{-6}$	36.2	7.6	5.2
Anion	Hydroxyl	Sulphate	Chloride
Mobility (m/s) $\times 10^{-6}$	20.5	8.3	7.9
			7.4

current. From Ohm's law, the potential difference between the electrodes is also directly proportional to the sum of the ionic velocities. When the potential gradient is 1 V/cm, the ionic velocity is termed the 'absolute ionic mobility', the symbols  $u_+$  and  $u_-$  being used for the cations and anions respectively. Some typical absolute ionic mobilities at 25°C are given in Table 3.1.

#### (d) Transport numbers

Although the sum  $u_+ + u_-$  is proportional to the current, the amount carried by each ion is proportional to its own velocity. The fraction of the total current carried by each ion type is called the 'transport number':

$$t_+ = \frac{u_+}{u_+ + u_-} \quad (3.3a)$$

and

$$t_- = \frac{u_-}{u_+ + u_-} \quad (3.3b)$$

Here,  $t_+$  and  $t_-$  are the transport numbers of the cations and anions, respectively, in the electrolyte. Transport number values are affected

by temperature and ionic concentration and usually have a limiting value at very low concentrations.

Measurements of transport numbers often reveal that ions in solution have become attached to one or more water molecules, i.e. they have become hydrated. Those water molecules in the 'primary hydration sheath' close to the ion are usually tightly bound to the ion. The others in the 'secondary hydration sheath' are more easily removed.

*(e) Relationship between electrolyte conductivity and concentration*

Now consider an electrolyte  $P_xQ_y$  of concentration  $C$  g-mole/l, of electrochemical valency  $n_e$ , and of degree of dissociation  $\alpha$ . For a potential drop of 1 V across a cube of side 1 cm of the electrolyte, Ohm's law gives  $I = \kappa_e$  where  $I$  is the current flowing across the cube. The quantity of anions, or cations, present in the cube is  $\alpha n_e C / 1000$  g-equivalents. Each cation and anion g-equivalent contains  $N/z_+$  and  $N/z_-$  ions respectively, where  $N$  is Avogadro's number; as usual,  $z_+$  and  $z_-$  are the cationic and anionic valency. (Avogadro's number is the number of atoms in one gram-atom,  $6 \times 10^{23}$ .) Therefore, the number of cations and anions in the cube are  $\alpha n_e C N / 1000 z_+$  and  $\alpha n_e C N / 1000 z_-$  respectively. Now suppose that current  $I$  is passed for 1 s. This current causes the discharge at the electrodes of a number  $\alpha n_e C N u_+ / 1000 z_+$  of cations (occupying a volume  $u_+$ ), and of a number  $\alpha n_e C N u_- / 1000 z_-$  of anions (occupying a volume  $u_-$ ). The corresponding electric charges carried by the groups of ions are  $e \alpha n_e C N u_+ / 1000$  and  $e \alpha n_e C N u_- / 1000$ , where  $e$  is the electronic charge. Since the total rate of charge is  $I$ , we have

$$I = \frac{e \alpha n_e C N}{1000} (u_+ + u_-) = \kappa_e$$

From Equation (3.2)

$$\kappa_e = \frac{n_e C \Lambda_c}{1000}$$

and, since  $eN = F$ , Faraday's constant,

$$\Lambda_c = \alpha F (u_+ + u_-) \quad (3.4)$$

It is customary to denote the quantities  $Fu_+$  and  $Fu_-$  by  $\lambda_+$  and  $\lambda_-$  respectively, so that

$$\Lambda_c = \alpha(\lambda_+ + \lambda_-)$$

At very low concentration,  $\alpha = 1$ , then

$$\Lambda_0 = (\lambda_+)_0 + (\lambda_-)_0$$

where here the suffix 0 denotes values at very low concentration.

These equations demonstrate that cations and anions contribute independently to the equivalent conductivity.

*(f) Onsager's equation*

Because of the electrical attraction between positive and negative ions, an ion may be regarded as being surrounded by a centrally symmetric ionic atmosphere whose total charge is equal and opposite to that of the central ion. When an electric field is applied, the ions are made to move. The central ion moves in one direction and during the finite time required by the atmosphere to readjust to the new conditions, the central ion is unsymmetrically positioned within the atmosphere, and the electrostatic attraction between it and its atmosphere reduces the motion of the central ion. In addition, the applied field makes the ionic atmosphere (carrying its customary molecules of water of hydration) move in the opposite direction to that of the central ion; as a result, the ion movement is retarded further by the dragging effect of the atmosphere.

On the basis of investigations of these phenomena by Debye and Hückel, Onsager put forward the following equation for a strong electrolyte which produces two univalent ions in solution (e.g. KCl or NaCl):

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{C} \quad (3.5)$$

where  $\Lambda_0$  is the limiting conductivity,  $A$  and  $B$  are constants for the given solvent and depend only on temperature, and  $C$  is the concentration of the solution in g-mole/l or g-equiv/l. The 'A' term describes the electrophoretic effect due to the dragging of the atmosphere, whilst the expression given by 'B' is caused by the asymmetrical positions of the central ion and atmosphere. The equation demonstrates that the equivalent conductivity decreases from the limiting value with increasing concentration.

For water at 25°C,  $A = 60.2$  and  $B = 0.229$ , so that for a strong aqueous electrolyte of type PQ, with both  $P^+$  and  $Q^-$  ions univalent, we have

$$\Lambda = \Lambda_0 - (60.2 + 0.229\Lambda_0)\sqrt{C}$$

that is,  $\Lambda$  decreases with the square root of  $C$ .

Onsager's equation is accurate for electrolyte concentrations up to about  $2 \times 10^{-3}$  g-equiv/l. The corresponding behaviour of  $\Lambda$  at higher concentrations has yet to be fully established, mainly owing to difficulties in the analysis of the ionic charge distribution in very concentrated solutions. Highly concentrated electrolytes are, of course, widely used in ECM. That the dependence of conductivity on concentration for such solutions is so complex is representative of the many problems encountered with the ECM process.

#### (g) Activity

Conditions of electrochemical equilibrium are really dependent not only on the concentrations of ions present in solution, but also upon the extent to which the ions react with each other and with the water molecules in the solution. Because of this overall dependence, concentration is not really a true indication of the ability of ions to determine the properties of an electrolyte. A more accurate description can be obtained on the replacement of the 'concentration' term by an 'activity',  $a$ , which takes into account the interactions between an ion and its surroundings. The relationship between the two can be conveniently expressed as

$$a = fC \quad (3.6)$$

where  $f$  is the activity coefficient. At very low concentrations, where there is negligible ionic interaction, the activity coefficient approaches unity. Since the amount of ionic interaction varies with concentration, some variation of activity coefficient with concentration can be expected. Table 3.2 shows the variation of  $f$  with concentration for NaCl electrolyte.

#### (h) pH values

Electrolytes can also be classified into acidic, neutral, or alkaline types. This classification is usually defined by the pH of the electrolyte, that is the negative logarithm of the hydrogen ion concentration,  $C_H$ , expressed in g-ion per litre:

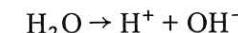
$$\text{pH} = -\log_{10} C_H \quad (3.7)$$

Note: the more formal definition of pH requires that the concentration term be replaced by activity. But measurement of activity is rendered difficult by experimental problems, and in practice concentration is the preferred term.

Table 3.2 Variation of mean activity coefficient with concentration of NaCl at 25°C

Concentration (g mole/litre water)	Mean activity, $f$
0·01	0·902
0·1	0·778
0·5	0·681
1·0	0·657
1·5	0·656
2·0	0·668
3·0	0·714
5·0	0·874

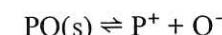
Consider next the dissociation of water:



The actual amount of dissociation of water is very small; in fact, pure water contains only  $10^{-7}$  g-ion of hydrogen per litre at 25°C, and the concentration of hydrogen ions is equal to that of hydroxyl ions. The water is said to be *neutral*; from the definition (3.7), its pH value is 7. This value of pH represents the neutral point in a scale whereby solutions can be classified by their degree of acidity. If the hydrogen ion concentration of a solution is greater than  $10^{-7}$ , the pH is less than 7 and the solution is *acidic*. If the solution has a pH of 7, it is *neutral*. When the hydrogen ion concentration is less than 7, the pH value exceeds 7, and the solution is *alkaline*. Later, the electrode reactions which occur in these types of electrolytes will be discussed. But at this stage it can be noted that neutral electrolytes (e.g. NaCl, NaNO<sub>3</sub>) are most commonly used in ECM, although for some applications, e.g. drilling, acid electrolytes are preferred.

#### (i) Solubility product

When a saturated solution of an electrolyte P<sub>x</sub>Q<sub>y</sub> is in contact with the solid solute, an equilibrium exists between the ions in the solution and the solid. For a simple electrolyte PQ ( $x = 1, y = 1$ ), the equilibrium may be represented by



The equilibrium constant,  $K$ , is given by

$$K = \frac{[a_{P^+}] \times [a_{Q^-}]}{[a_{PQ}]}$$

where the square brackets represent activities (or, alternatively, concentrations). If the activities of a pure liquid and a pure solid

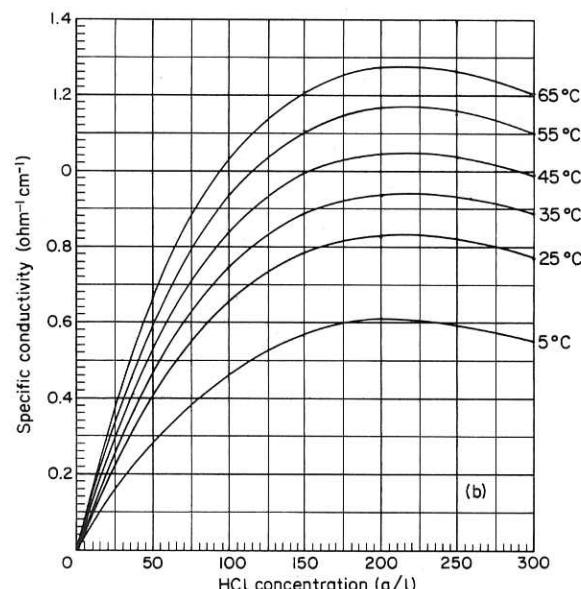
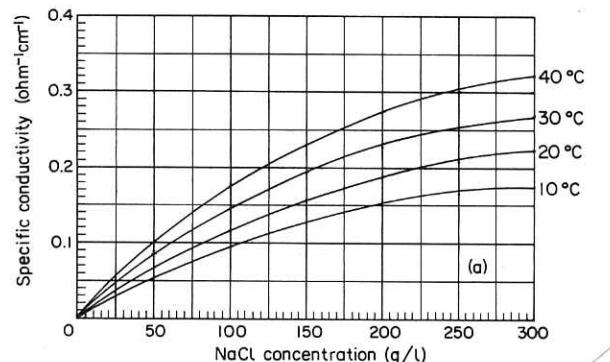


Fig. 3.1 Specific conductivity as a function of concentration and temperature for (a) NaCl and (b) HCl electrolytes

are taken to be unity, the above expression can be written

$$K_s = [a_{P^+}] \times [a_{Q^-}]$$

$K_s$  is known as the activity solubility product.

A significant observation from this result is that the product of the activities of the ions  $P^+$  and  $Q^-$  in a saturated solution of  $PQ$  must be constant for a given temperature. This condition holds irrespective of whether ions arise solely from the substance  $PQ$  or whether any contribution is made to their activities by the presence of other electrolytes in the solution.

### 3.2 Properties of ECM electrolytes

Based on the information given in the preceding section, several relevant general properties of electrolytes can be deduced. First, since the ionic mobility increases with temperature, the electrical conductivity of the electrolyte should have a similar temperature dependence (because of the relationship between conductivity and mobility, e.g. Equation (3.4).) Secondly, we expect some variation in conductivity with concentration, bearing in mind that concentrations of ECM electrolytes greatly exceed those for which the Debye-Hückel-Onsager theory is valid.

In Fig. 3.1(a) the variation of specific conductivity with concentration and temperature for NaCl solution is shown. Corresponding results for HCl solution are presented in Fig. 3.1(b). With the former electrolyte, the conductivity increases with temperature and with concentration up to the limit of solubility of the salt. With the HCl solution, the conductivity increases with concentration to a maximum value and then decreases. Data for a range of electrolytes, and for conditions encountered in ECM can be found elsewhere [1, 2].

### 3.3 Equilibrium electrode potentials

#### 3.3.1 Electrical double layer

When a metal is placed in an electrolyte solution, an equilibrium potential difference usually becomes established between the metal and solution. This potential difference arises from the transfer into solution of metal ions and the simultaneous discharge of ions from the solution. Equilibrium is reached when the electrons left in the

metal contribute to the formation of a layer of ions whose charge is equal and opposite to that of the cations in solution at the interface. The positive charges in the solution and negative charges in the metal form the *electrical double layer*. Although the structure

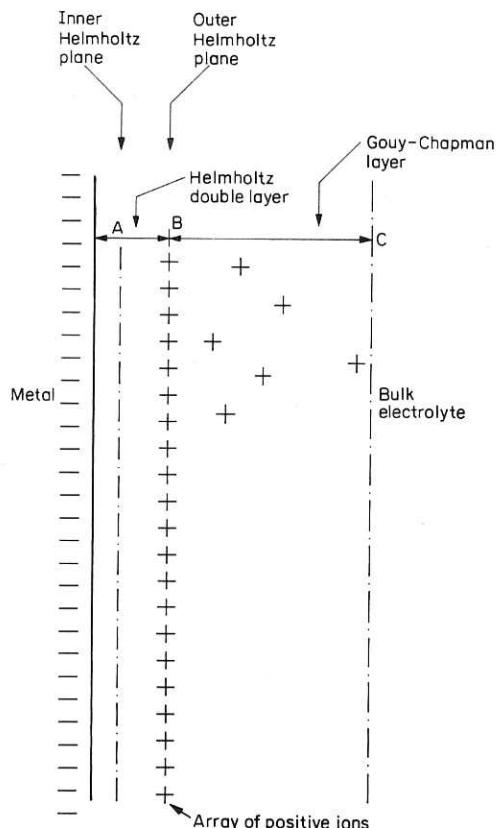


Fig. 3.2 The electrical double layer

of the double layer is complicated, the simple representation in Fig. 3.2 highlights several characteristic regions. Over the inner Helmholtz plane A, which lies very close to the metal, unsolvated charges which do not have molecules of water attached to them may be adsorbed. Beyond A is the outer Helmholtz plane, B, along which lies an array of the positive charges. Extending further into the solution is the Gouy-Chapman layer, C, which is more diffuse and mobile. Over that layer the potential drop is non-linear. The bulk electrolyte with its usual properties is situated outside the

Gouy-Chapman layer. The Helmholtz double layer has a minimum thickness of about  $2 \times 10^{-7}$  mm. The approximate thickness of the Gouy-Chapman layer is  $10^{-3}$  mm. The transfer of ions clearly will cease when the energy required for an ion to dissolve is less than the work necessary to pass it across the double layer. The reverse case also holds for the formation of a double layer owing to the deposition of ions on the metal.

### 3.3.2 Nernst equation

It will be of use to derive an expression for the equilibrium potential difference between the metal and its ion in solution [3].

Suppose that the atoms of the metal can be dissociated into metal ions and free electrons:



At the metal surface, ions are held by lattice forces, and they require an activation energy  $W_1$  to pass the metal-solution interface into solution. In the solution, ions are held by forces of hydration; they need an activation energy  $W_2$  to cross the interface in the opposite direction. From Maxwell's energy distribution law for the reacting particles, it can be shown that the number of particles,  $n$ , which have sufficient energy to cross the interface can be related to the total number of particles,  $n_t$ , by an expression of the form  $n = n_t \exp(-W/kT)$ . The respective rates of crossing from metal to solution, and vice versa, can then be deduced:

$$R_1 = K_1 \exp(-W_1/kT)$$

$$R_2 = CK_2 \exp(-W_2/kT)$$

$K_1$  and  $K_2$  are characteristic constants for the metal and solution which are independent of concentration,  $C$  is the free metal ion concentration in solution,  $T$  is the temperature, and  $k$  is Boltzmann's constant.

If  $R_1$  is greater than  $R_2$ , ions will dissolve at a rate greater than that at which they deposit, and vice versa if  $R_1$  is less than  $R_2$ . For either condition, an electrical double layer is established. A change in electrical potential difference takes place across the double layer, so that the energy required by an ion to pass from metal into solution is reduced to  $(W_1 - zeE_1)$ , and the energy required by an ion to cross from solution to metal is increased to  $(W_2 + zeE_2)$ . Here,  $E_1$  is the potential drop associated with the reduction of the energy

barrier at the metal side of the interface, and  $E_2$  is the corresponding potential drop on the solution side.

The rates at which ions cross in both directions now are

$$R'_1 = K_1 \exp[-(W_1 - zeE_1)/kT] \quad (3.8)$$

$$R'_2 = CK_2 \exp[-(W_2 + zeE_2)/kT] \quad (3.9)$$

In equilibrium,  $R'_1 = R'_2$ . Thus,

$$E = E_1 + E_2 = \frac{W_1 - W_2}{ze} + \frac{kT}{ze} \ln\left(\frac{CK_2}{K_1}\right)$$

Since  $RT/zF = kT/ze$ , and putting

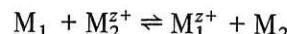
$$E_0 = \frac{W_1 - W_2}{ze} + \frac{kT}{ze} \ln\left(\frac{K_2}{K_1}\right)$$

we obtain the Nernst equation:

$$E = E_0 + \frac{RT}{zF} \ln C \quad (3.10)$$

$R$  is the Gas Constant and  $E_0$  is the normal electrode potential. (More correctly, of course, the concentration term in the Nernst equation should be replaced by the activity  $a$ .) Alternative derivations of the Nernst equation are available elsewhere [4].

For a more general cell reaction at reversible equilibrium, we have



The general expression for this reaction, corresponding to the Nernst equation, is written

$$E = E_0 + \frac{RT}{zF} \ln \frac{[a(M_1^{z+})][a(M_2)]}{[a(M_1)][a(M_2^{z+})]} \quad (3.11)$$

### Example

When  $C$  is 1 g-ion/litre,  $E = E_0$ , and the departure of  $C$  from this value causes a change in potential:

$$(E - E_0) = \frac{RT}{zF} \ln C$$

$$= 2.303 \frac{RT}{zF} \log_{10} C$$

When  $T = 298$  K ( $= 25^\circ\text{C}$ ),  $2.303RT/F = 0.059$  V. For  $z = 1$ , and an increase in  $C$  to 10 g-ion/litre,  $(E - E_0) = 59$  mV, whilst for  $z = 2$ , the same change in  $C$  gives  $(E - E_0) = 29.5$  mV.

### 3.3.3 Free energy of reaction

The equilibrium rates of ion movement,  $R'_1$  and  $R'_2$ , can also be represented by the *exchange current density*,  $J_0$ . This current density is usually of the order of  $10^{-1}$  to  $10^{-5}$  A/cm<sup>2</sup>. It can be expressed as

$$J_0 = \Omega_1 \exp(-\Delta G_1/RT) - \Omega_2 \exp(-\Delta G_2/RT) \quad (3.12)$$

where  $\Omega_1$  and  $\Omega_2$  are characteristic parameters for the dissolution and deposition reactions,  $R$  is the Gas Constant, and  $T$  is the temperature.  $\Delta G_1$  and  $\Delta G_2$  indicate the respective minimum free energies which atoms must possess to ionise to the solution and which ions must have to discharge from the solution. As shown in Fig. 3.3, the difference in the free energies  $\Delta G_1$  and  $\Delta G_2$  is  $\Delta G$ , the free energy change for the reaction.  $\Delta G$  is related directly to the reversible electrode potential,  $E$ , by

$$\Delta G = -zEF \quad (3.13)$$

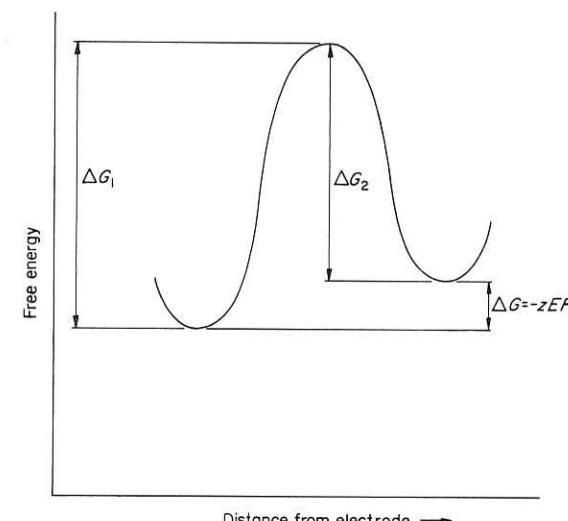


Fig. 3.3 Free energy-distance diagram for equilibrium conditions

### 3.3.4 Standard electrode potentials

Consider now two metals  $M_1$  and  $M_2$  placed in an electrolyte which contains their ions and which are externally linked at the junction  $M_1/M_2$ . Current is assumed to flow round the completed circuit in the direction of electron flow shown in Fig. 3.4. The potential drop in the circuit due to extraneous factors (e.g. ohmic drop in the bulk of the solution and along the electrodes' lengths) is assumed to be negligible. In the metal  $M_1$  electrons move towards the  $M_1$ /electrolyte interface as the  $M_1$  ions discharge from the metal into the solution. At the metal  $M_2$ , an equivalent quantity of  $M_2$  ions discharge on it causing electrons to flow away from the  $M_2$ /electrolyte interface round the circuit. At the junction  $M_1/M_2$ , the electrons must transfer from  $M_2$  to  $M_1$ . The energy required for this transfer is usually obtained from the *thermionic work function*  $\psi$ . Thus if the energy required to transfer the electron from the metal into free space is  $\psi_1$  and if  $\psi_2$  electron-volts are released by the transfer of an electron from free space into  $M_2$ , the transfer of an electron from  $M_1$  to  $M_2$  is identified with an energy change of  $(\psi_1 - \psi_2)$  electron-volts. (Note: an electron-volt is the change in energy of an electron passing through a potential drop of 1 volt.) This number of electron-volts  $(\psi_1 - \psi_2)$  is usually referred to as the potential difference at the junction of  $M_1$  and  $M_2$ , or contact potential of  $M_1$  and  $M_2$ .

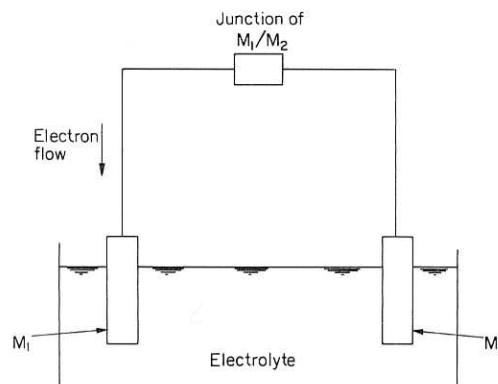


Fig. 3.4 Metals  $M_1$  and  $M_2$  in an electrolyte containing their ions

It is convenient to have a standard electrode whose reversible potential is made arbitrarily zero and against which the potentials of other electrodes can be measured. The *hydrogen electrode* is an

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accepted standard: it comprises a rod of platinum covered with platinum black saturated with hydrogen gas at atmospheric pressure. Electrode potentials based on this zero are said to refer to the *hydrogen scale*. However, in experimental work, it is often more

Table 3.3 Standard electrode potentials with reference to the hydrogen electrode at 25°C.

Electrode	Reaction	Volts
Lithium	Li → Li <sup>+</sup>	-2.96
Potassium	K → K <sup>+</sup>	-2.92
Sodium	Na → Na <sup>+</sup>	-2.72
Magnesium	Mg → Mg <sup>++</sup>	-2.38
Aluminium	Al → Al <sup>+++</sup>	-1.67
Zinc	Zn → Zn <sup>++</sup>	-0.76
Iron	Fe → Fe <sup>++</sup>	-0.44
Tin	Sn → Sn <sup>+++</sup>	-0.34
Nickel	Ni → Ni <sup>++</sup>	-0.25
Lead	Pb → Pb <sup>++</sup>	-0.12
Hydrogen	H → H <sup>+</sup>	0
Saturated calomel		+0.24
Copper	Cu → Cu <sup>++</sup>	+0.34
Silver	Ag → Ag <sup>+</sup>	+0.80
Oxygen	2H <sub>2</sub> O → O <sub>2</sub> + 4H <sup>+</sup>	+1.23
Chlorine	2Cl → Cl <sup>++</sup>	+1.36
Gold	Au → Au <sup>+++</sup>	+1.50

convenient to use another standard electrode. The calomel electrode is a common example. It consists of a pool of mercury covered with calomel (mercurous chloride) and immersed in a solution of potassium chloride which acts as the electrolyte. A platinum wire allows electrical contact with the mercury. The electrode potential depends mainly on the concentration of the potassium chloride; for example, at saturation its potential on the hydrogen scale is about 0.24 V at 25°C. In Table 3.3 is given a range of standard electrode potentials, referred to the hydrogen scale.

Metals at the top of the table are active or *base*, whilst those at the foot are inactive or *noble*. Thus, in a cell with two dissimilar metals immersed in the same solution, the metal which is higher in this series will tend to dissolve. The electromotive force (e.m.f.) of the cell is the difference of the standard potentials.

A common example of such an electrode system is the Daniell cell (Fig. 3.5). This cell consists of a zinc electrode dipped in dilute sulphuric acid, and a copper electrode in copper sulphate solution contained within a porous pot through which ions can pass from one

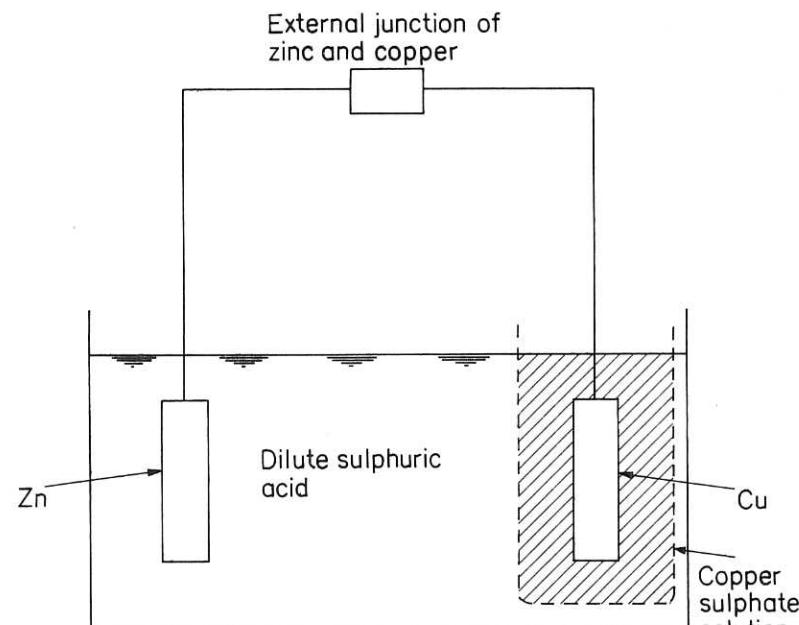
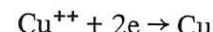


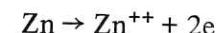
Fig. 3.5 Daniell cell

solution to the other. From Table 3.3, the e.m.f. of the cell is 1.1 V, the difference in the standard potentials between the copper and zinc. At the external junction, electrons move from the zinc to the copper. They thus lower the electron energy levels in the zinc, but since they have a negative charge they raise the positive ion levels in the zinc. Thus, zinc ions will tend to pass into solution. On the other hand, the positive ion levels in the copper will be lowered and copper ions will be deposited on that electrode. At both metal junctions the metal ion moves towards the lower energy state and the energy made available drives current round the circuit. Clearly, the contact potential difference is an important factor in determining the direction of current flow.

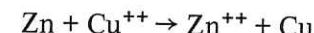
Thus at the copper electrode



and at the zinc electrode



so that the overall cell reaction is



Note, however, that if a potential difference, greater than the e.m.f. of the cell, is applied in the opposite direction, the current will flow, and the above reactions will take place, in that opposite direction. In ECM, the anode and cathode are usually made of different metals. For instance, suppose that a copper cathode is to be used for the machining of an iron anode. From Table 3.3 we note that the e.m.f. of the cell is 0.78 V, and that the preferred direction for current flow should lead to dissolution of the iron. Nevertheless, since the e.m.f. is so low, the rate of dissolution will be small. The use of an externally applied potential difference across the cell will lead to a greater metal removal rate, and depending upon the direction in which this potential difference is applied, either the iron or the copper will be machined.

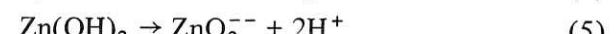
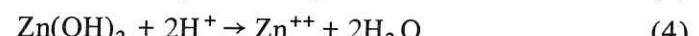
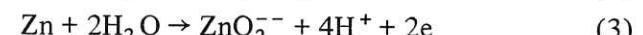
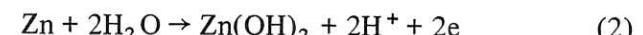
### 3.3.5 Pourbaix diagrams

The electrode potential,  $E$ , has been related to the Gibbs free energy,  $\Delta G$ , by the equation

$$\Delta G = -zEF \quad (3.13)$$

Now, if a metal is made anodic in an aqueous solution, and if several possible reactions are available, the most likely thermodynamic reaction is that for which the decrease in free energy is greatest. This fact can be explained further by reference to a particular case.

For example, possible reactions for zinc in water are



The equilibria (1)–(3) are electrochemical. Reactions (4) and (5) are chemical equilibria. Reaction (1) does not involve hydrogen ions, whilst reactions (2) and (3) involve both hydrogen ions and electrons. The equilibria (4) and (5) are independent of electrons.

We have also seen that, by means of the Nernst equation, the electrode potential at which these reactions occur can be expressed in terms of concentrations, or activities, of the different species involved. For instance, for reaction (2),

$$E = E_0\{\text{Zn}/\text{Zn}(\text{OH})_2\} + \frac{RT}{2F} \ln \frac{[\text{Zn}(\text{OH})_2]}{[\text{H}_2\text{O}]^2} [\text{Zn}]^2$$

The term  $E_0\{\text{Zn}/\text{Zn}(\text{OH})_2\}$  is the normal potential corresponding to reaction (2). As before, the square brackets represent activities. The activities of solid phases and of water present in large excess are usually assumed to be unity, so that we can write the above equation as

$$E = E_0\{\text{Zn}/\text{Zn}(\text{OH})_2\} - \frac{2.303RT}{F} \text{ pH}$$

where  $\text{pH} = -\log[\text{H}^+]$ . Similar expressions can be derived for the other reactions (1), (3), (4), and (5).

If a value is also chosen for the concentration of the metal ion in solution which corresponds to the condition of no dissolution, (e.g.  $10^{-6}$  mole/l), the linear relationship between the potential and pH can be represented on a ‘Pourbaix diagram’.

Since the first of the above five equilibria is independent of pH, the equilibrium potential will be the same for all pH values at which

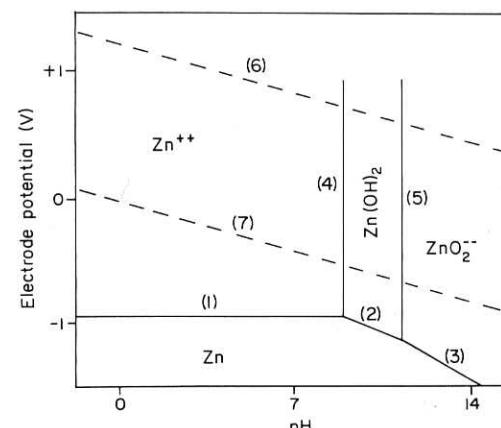


Fig. 3.6 Pourbaix diagram for zinc in water

the reaction is possible. This reaction equilibrium is represented by a horizontal straight line on the Pourbaix diagram for zinc (Fig. 3.6). The equilibria (2) and (3) are dependent on both pH and potential, and are represented by sloping lines. The fourth and fifth equilibria yield vertical lines in Fig. 3.6, since they depend only on pH, and thus the equilibria are the same whatever the potential.

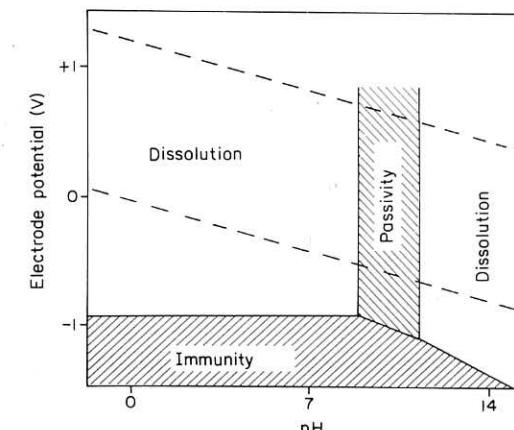
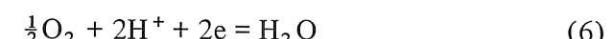


Fig. 3.7 Regions of dissolution, passivity, and immunity for zinc

When the pH of the solution is less than 7, zinc will dissolve at suitable potentials to form freely soluble  $\text{Zn}^{2+}$ . The complex zincate ions  $\text{ZnO}_2^-$  are also forms of zinc in solution, so that the domains in Fig. 3.6 thus marked represent areas where the corrosion of zinc is thermodynamically possible. In solutions where the pH is between 8 and 11, the main product of the anodic reaction is zinc hydroxide. This compound is only slightly soluble in water, and can therefore represent a solid precipitate which may form a protective film on the metal surface. This domain is designated *passivity* because passivation by such a film is thermodynamically possible. The region marked ‘Zn’ at the foot of the diagram represents solid metal which is thermodynamically stable. That is, dissolution of the zinc is not possible. In this way, the regions of dissolution, passivity, and immunity from dissolution shown in Fig. 3.7 are constructed.

In Fig. 3.6, two other lines are of interest. One is associated with the reaction



The other line represents



For potentials greater than those on the line representing (6), water evolves oxygen from an immersed electrode. At potentials less than those given by the slope representing (7), hydrogen is evolved at electrodes dipped in water. The domain between these two lines defines the region of stability of water.

Conditions of pH and potential which lead to passivation are encountered with many metals. For instance, the Pourbaix diagram for titanium (Fig. 3.8) indicates that this metal passivates owing to a surface film of  $\text{TiO}_2$ . In the same way, oxide formation over a wide range of pH-potential values causes chromium to passivate.

Although potential-pH diagrams have been compiled for all the elements, the information is restricted to reactions between the metal, its oxides, hydroxides, and water [5].

The presence of various anions in ECM electrolytes modifies, and undoubtedly complicates, any simple Pourbaix diagram. Nevertheless, useful information can be obtained. In the case of titanium mentioned above, the indication from the Pourbaix diagram that

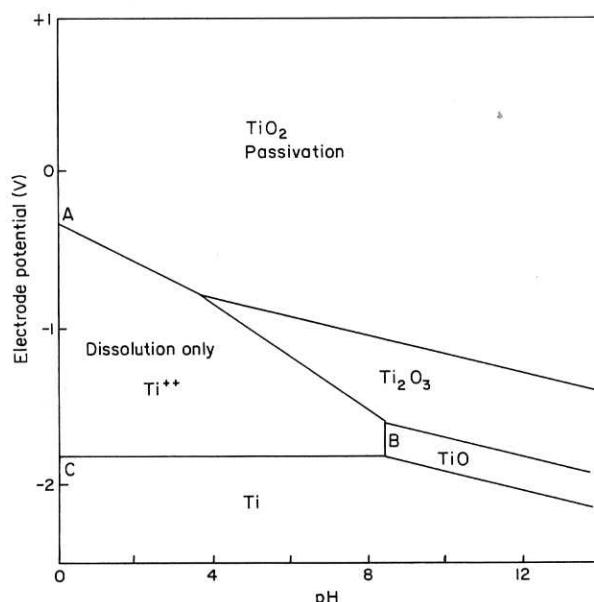


Fig. 3.8 Pourbaix diagram for titanium at 25°C

passivation is likely due to a surface film means that appropriate action can be taken by the addition to the electrolyte of a complexing agent which will dissolve the oxide film.

Even less information is available about the application of Pourbaix diagrams to alloys. Again, though, some deductions from the behaviour of elements can be made. The passivating nature of chromium is known to contribute substantially to the passivity of stainless steel, because of its large chromium content. In like fashion, behaviour about titanium alloys can be established from that of titanium metal.

The anodic processes considered so far in this section refer, of course, only to conditions of thermodynamic equilibrium. The non-equilibrium processes at work in ECM can be understood from the kinetics of dissolution.

### 3.4 Irreversible electrode reactions

In ECM, we have observed that metal dissolution is achieved by the deliberate application of an external potential difference which gives rise to a corresponding current flow. It will be shown below that, the greater the current flow, the greater is the difference in potential between the equilibrium value and the *working* value. The electrode reaction is now said to be *irreversible*, and the difference between the equilibrium and working values of the potentials is known as the *overpotential*. It is commonly accepted that, in most electrochemical reactions, there are three specific types of overpotential: activation, concentration, and resistance. Each type is now discussed.

#### 3.4.1 Activation overpotential

Suppose a potential difference is now applied across the cell to cause anodic dissolution. The anode electrode must then ionise at a greater rate than that of discharge of its ions. The electrode potential is accordingly altered from its equilibrium value by an amount  $\eta_a$ , the *activation overpotential*, and the energy-distance diagram of Fig. 3.3. The free energy required for dissolution is now reduced from  $\Delta G_1$  to  $(\Delta G_1 - z\alpha\eta_a F)$ , and the energy for discharge is increased from  $\Delta G_2$  to  $[\Delta G_2 + z(1-\alpha)\eta_a F]$  where  $\alpha$  is that fraction of overpotential associated with dissolution.

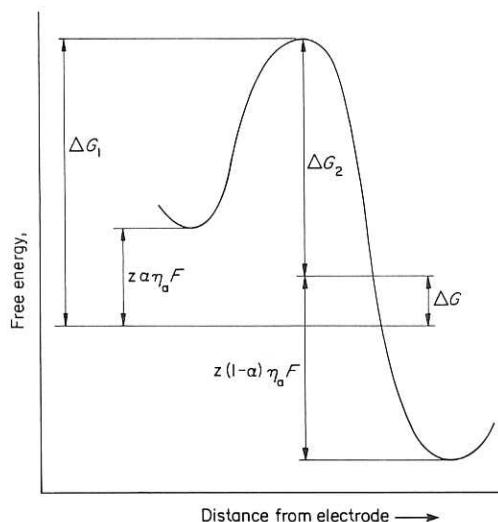


Fig. 3.9 Free energy-distance diagram for irreversible conditions of anodic dissolution

Under these conditions, the current density  $J$  related to the dissolution becomes

$$\begin{aligned} J &= \Omega_1 \exp\left[-\frac{(\Delta G_1 - z\alpha\eta_a F)}{RT}\right] - \Omega_2 \exp\left[-\frac{(\Delta G_2 + z(1-\alpha)\eta_a F)}{RT}\right] \\ &= J_0 \left[ \exp\left(\frac{z\alpha\eta_a F}{RT}\right) - \exp\left(\frac{z(1-\alpha)\eta_a F}{RT}\right) \right] \end{aligned} \quad (3.14)$$

### 3.4.2 The Tafel equation

It will be readily appreciated that ECM is a highly irreversible process, so that the rate of reaction in the direction opposed by the overpotential is negligible. Numerically, this means that  $\eta_a$  probably exceeds 0.05 V and that the second term on the right-hand side of Equation (3.14) may be ignored. The equation then becomes

$$\begin{aligned} \eta_a &= \left(\frac{2.303RT}{z\alpha F}\right) \log J/J_0 \\ &= a + b \log J \end{aligned} \quad (3.15)$$

where

$$a = -\frac{2.303RT}{z\alpha F} \log J_0; \quad b = \frac{2.303RT}{z\alpha F}$$

Table 3.4 Overpotential values for hydrogen evolution in 1N H<sub>2</sub>SO<sub>4</sub> (current density 10<sup>-2</sup> A/cm<sup>2</sup>) (after Evans [7])

Cathode material	Overpotential (V)
Pt, bright	0.07
Fe	0.56
Ni	0.74
Cu	0.58

are the Tafel constants. A similar expression can be derived for the cathodic reaction.

At this stage it is worth stressing the extreme nature of the electrode processes at work in ECM. The large currents involved and steep concentration gradients (see below) in the immediate vicinity of the metal-solution interface may induce a more complex form for the activation overpotential.

Tafel overpotentials have been studied mainly in connection with hydrogen evolution at the cathode although some information has been collected on anodic phenomena [6]. Values are found to depend on a number of factors including the condition and material of the electrode. Some data [7] for overpotentials for hydrogen evolution from 1N H<sub>2</sub>SO<sub>4</sub> are available in Table 3.4. Further values for the Tafel constants are presented in Table 3.5.

The current densities for which these results have been obtained are much lower than those used in ECM. However, an investigation has been reported [8] in which hydrogen overpotentials at current densities up to 10<sup>2</sup> A/cm<sup>2</sup> have been measured, other effects such

Table 3.5 Values of the Tafel constants  $a$  and  $b$ , at 20°C (after Evans [7])

Cathode material	Electrolyte solution	$a$ (V)	$b$ (V)
Fe	1N HCl	0.70	0.125
	2N NaOH	0.76	0.112
Ni	0.11N NaOH	0.64	0.100
Cu	1N H <sub>2</sub> SO <sub>4</sub>	0.80	0.115

as heating and concentration overpotentials, having been made negligible by high solution velocities (above 20 m/s). In particular from those results, for a nickel cathode in 1N HCl, the Tafel relationship was found to hold only for current densities up to  $1 \text{ A/cm}^2$ . Above that value the overpotential increased substantially with current density (e.g. about 1 V at  $10 \text{ A/cm}^2$ ). The need for information relevant to ECM has led to studies of anode potentials in high-rate anodic dissolution of copper [9]. Tafel behaviour was observed up to  $39 \text{ A/cm}^2$  for copper dissolved in  $1\text{M H}_2\text{SO}_4 + 0.1\text{M CuSO}_4$  solution, the maximum electrolyte flow-rate being 10 m/s.

The accuracy of the results is also discussed in that work; the two main factors which influence accuracy are the *IR* drop in the solution and effects due to the double layer. It is also relevant to mention some observations by Mao [10]. He reports that no hydrogen is formed at a brass cathode during ECM of mild steel in 2 to 4.5M NaNO<sub>3</sub> at current densities ranging from 12 to  $47 \text{ A/cm}^2$ . But Mao did find that a small amount of hydrogen is generated at a platinum electrode in the same electrolyte because of the comparatively small hydrogen overpotential on platinum. This characteristic low overpotential is the reason for the wide use of platinised platinum electrodes in studies of hydrogen evolution.

#### *Example*

A useful estimate of the value of Tafel overpotential for ECM conditions can be obtained from Equation (3.15). For typical values,  $RT/zF = 1/40 \text{ V}$ ,  $\alpha \approx \frac{1}{2}$ ,  $J_0 \approx 10^{-5} \text{ A/cm}^2$ ,  $J = 10^2 \text{ A/cm}^2$ , the Tafel constants  $a$  and  $b$  are calculated to be 0.58 V and 0.12 V respectively, and  $\eta_a$  is found to be 0.82 V. This is a significant amount in comparison with a typical applied potential difference of 10 V.

#### *3.4.3 Concentration overpotential*

As dissolution proceeds in ECM, the movement of ions is controlled by three processes:

- (i) migration, i.e. movement under the influence of the electric field;
- (ii) convection, i.e. bodily movement of the electrolyte solution; in ECM this is mainly effected by forced agitation of the electrolyte;
- (iii) diffusion, i.e. movement due to ion concentration gradients in the solution.

In studies of these processes, the concept of the diffusion layer is very useful. Thus, consider the anodic dissolution reaction. When the rate of metal dissolution is greater than the rate at which the metal ions can diffuse away from an electrode, a condition is reached in which an ionic concentration gradient exists over a thin layer of electrolyte adjacent to the electrode. This layer is called the 'diffusion layer'. A change in the electrode potential from the reversible value occurs due to this concentration gradient, and the numerical difference between the reversible and new value is said to be the *concentration overpotential*,  $\eta_{\text{conc}}$ . We shall now estimate the magnitude of  $\eta_{\text{conc}}$  [11].

Usually the outer edge of the diffusion layer is assumed to be plane and parallel to the electrode surface. Its thickness is designated by  $\delta$ . Next, consider a volume element within the diffusion layer, and the net rate of flow of particles entering and leaving it. The number of particles per second passing through the surface  $S$  surrounding the volume  $V$  is  $-\oint j \, dS$ , where  $j$  is the number flux (i.e. the number of particles per second passing through unit area of the surface). Suppose that  $c$  is the concentration, i.e. the number of particles per unit volume of solution for each ion. (Later,  $c$  will be related to  $C$ , the bulk concentration of the electrolyte.) Then if  $\partial c / \partial t$  is the change in the number of particles per unit volume per second, the change in the number of particles in the volume  $V$  is  $\int (\partial c / \partial t) \, dV$ . Hence

$$\int \frac{\partial c}{\partial t} \, dV = - \oint j \, dS$$

Using the Gauss theorem, we deduce that

$$\int \frac{\partial c}{\partial t} \, dV = - \int \operatorname{div} j \, dV$$

or

$$\frac{\partial c}{\partial t} + \operatorname{div} j = 0 \quad (3.16)$$

The number flux  $j$  receives contributions from the diffusion flux ( $= -D \operatorname{grad} c$ ) due to the concentration gradient, the migration flux ( $= z e E_\delta u c$ ) due to the electric field, and the convection flux ( $= c U$ ) due to the movement of the ions by the solution flow.  $D$  is the diffusion coefficient; although it is dependent upon concentration and temperature, it is assumed constant here.  $E_\delta$  is the electric field

strength across the diffusion layer,  $u$  the ionic mobility,  $e$  the electronic charge, and  $U$  the local solution velocity. We then have

$$\frac{\partial c}{\partial t} = -\operatorname{div}(-D \operatorname{grad} c + zeE_\delta uc + cU)$$

Since  $D$  is constant,  $\operatorname{div}(D \operatorname{grad} c) = D \operatorname{div} \operatorname{grad} c$ . Also,  $\operatorname{div}(cU) = (U \operatorname{grad})c + c \operatorname{div} U$ . The electrolyte solution being assumed to be incompressible,  $\operatorname{div} U = 0$ . Finally, we consider that the thickness of the diffusion layer is very small compared with the gap width, so that transport of ions by convection within it can be neglected. Then we can assume that  $U = 0$ . (Note, however, that the solution velocity is relevant in the determination of the thickness of the diffusion layer.) The position of each volume element of the solution is now specified by its distance  $y$  from the electrode surface. If the number of ion types is restricted to metal, positive and negative electrolyte ions (assuming that the electrolyte is a simple typical one like NaCl), and if the respective subscripts m, +, and - are used, Equation (3.16) becomes, for each type

$$\begin{aligned}\frac{\partial c_m}{\partial t} + \frac{\partial}{\partial y} \left( -D_m \frac{\partial c_m}{\partial y} + z_m e E_\delta u_m c_m \right) &= 0 \\ \frac{\partial c_+}{\partial t} + \frac{\partial}{\partial y} \left( -D_+ \frac{\partial c_+}{\partial y} + z_+ e E_\delta u_+ c_+ \right) &= 0 \\ \frac{\partial c_-}{\partial t} + \frac{\partial}{\partial y} \left( -D_- \frac{\partial c_-}{\partial y} - z_- e E_\delta u_- c_- \right) &= 0\end{aligned}\quad (3.17)$$

Einstein's relation between diffusion coefficient  $D$  and mobility  $u$  for each ion type is also useful:

$$D = ukT \quad (3.18)$$

In the steady-state, time-independence of the concentrations and integration of Equation (3.17) give

$$\frac{-dc_m}{dy} + \frac{z_m e E_\delta c_m}{kT} = A \quad (3.19)$$

$$\frac{-dc_+}{dy} + \frac{z_+ e E_\delta c_+}{kT} = 0 \quad (3.20)$$

$$\frac{-dc_-}{dy} - \frac{z_- e E_\delta c_-}{kT} = 0 \quad (3.21)$$

where  $A$  is the constant of integration which is to be determined. If electrical neutrality within the diffusion layer is assumed, then

$$z_m c_m + z_+ c_+ - z_- c_- = 0 \quad (3.22)$$

For simplicity, suppose that

$$z_m = z_+ = z_- = 1$$

Equation (3.22) becomes

$$c_m + c_+ = c_- = \frac{1}{2}c, \text{ say} \quad (3.23)$$

Addition of the three equations (3.19), (3.20), and (3.21) and the use of Equation (3.23) yield, on integration,

$$c = -Ay + B \quad (3.24)$$

where  $B$  is a constant. At  $y = 0$ , let  $c = c_0$ , and at  $y = \delta$  let  $c = c_\delta$ . Then

$$A = \frac{c_0 - c_\delta}{\delta}$$

The current density across the diffusion layer is now given by

$$\begin{aligned}J &= e D_m A \\ &= e D_m \left( \frac{c_0 - c_\delta}{\delta} \right)\end{aligned}\quad (3.25)$$

Now, since  $E_\delta = -d\phi/dy$  in the layer, from Equations (3.21) and (3.23),

$$d\phi = \frac{kT}{e} \frac{dc}{c}$$

which, on integration, gives

$$\eta_{\text{conc}} = \frac{kT}{e} \ln \frac{c_\delta}{c_0} \quad (3.26)$$

Substituting from Equation (3.25) for  $c_0$ , we obtain

$$\eta_{\text{conc}} = -\frac{kT}{e} \ln \left( 1 + \frac{\delta J}{e D_m c_\delta} \right) \quad (3.27)$$

The electrolyte is assumed to be sufficiently agitated so that  $c_\delta$  takes the value of the bulk concentration of the electrolyte,  $C$ . The thickness of  $\delta$  also depends on the electrolyte flow conditions. (In this section a subscript m has had to be used to distinguish the properties

of the metal ions from those of the other (electrolyte) ions. The symbol used elsewhere for, say, metal ion valency,  $z+$  is identical with  $z_m$ .

### 3.4.4 Thickness of the diffusion layer

In the determination of  $\delta$ , three flow conditions for the electrolyte need consideration.

For unstirred electrolytes,  $\delta$  is usually found to be about  $10^{-2}$  mm. (For instance, Higgins [12] calculates that  $\delta$  is  $2.8 \times 10^{-2}$  mm for nickel dissolving at  $2.54 \text{ A/cm}^2$  in 1N HCl.)

Several methods have been put forward from which the thickness of  $\delta$  for flowing conditions can be estimated.

One analysis [13] has been based on the equations for convective diffusion (3.17) which, as noted, describe the transport of dissolved particles in terms of the concentration gradients and the components of the solution velocity. There is great similarity between these equations and the Navier-Stokes equations. They can be reduced, therefore, to describe the behaviour of the solution over the diffusion layer in the same way that Prandtl's boundary layer equations have been derived. By an order of magnitude analysis, similar to that used in Chapter 2 to obtain an estimate of the boundary layer thickness,  $\delta$  can be deduced to be given by

$$\delta = \delta_0 \left( \frac{D}{\nu} \right)^{1/3} \quad (3.28)$$

where  $\delta_0$  is the hydrodynamic, laminar boundary layer thickness,  $D$  is the diffusion coefficient and  $\nu$  the kinematic viscosity of the solution.

Since  $D \approx 10^{-5} \text{ cm}^2/\text{s}$ ,  $\nu \approx 1 \text{ mm}^2/\text{s}$ ,  $\delta$  is about one tenth of the thickness of  $\delta_0$ . This result can be related to the expression derived in Chapter 2 for  $\delta_0$ :

$$\delta_0 = 5 \left( \frac{\nu x}{U} \right)^{1/2}$$

where  $U$  is the mainstream velocity.

Note that the thickness of the diffusion layer increases in the downstream direction, and decreases with increasing velocity. This theory has been utilised [14] to obtain an expression for the average thickness of the diffusion layer  $\bar{\delta}$  over an electrode length  $L$ :

$$(\bar{\delta})^{-1} = \left( \frac{2}{3} \right) \left( \frac{\nu}{D} \right)^{1/3} \left( \frac{U}{\nu L} \right)^{1/2} \quad (3.29)$$

(As pointed out in Chapter 2, in this work a numerical coefficient of three, rather than the more usual five, is used in the Prandtl expression for the laminar boundary layer thickness.) In a related experimental study, in which  $L = 2 \text{ mm}$ ,  $h = 0.1 \text{ mm}$ ,  $U \approx 9 \text{ m/s}$  (calculated from volume flow-rate at inlet), the average diffusion layer thickness was found to be about  $1.5 \times 10^{-3}$  mm. The theoretical comparison from Equation (3.29) gives  $2.2 \times 10^{-3}$  mm, with the assumed values  $D = 10^{-5} \text{ cm}^2/\text{s}$  and  $\nu = 1 \text{ mm}^2/\text{s}$ .

In turbulent flow the hydrodynamic viscous sub-layer has its analogous diffusion sub-layer. The thicknesses of these layers have been related by the expression

$$\delta = \left( \frac{D_m \delta_1^3}{\gamma u_f} \right)^{1/4} \quad (3.30)$$

where  $\delta_1$  is the thickness of the viscous sub-layer,  $u_f$  is the friction velocity, and  $\gamma$  is a dimensionless constant, found experimentally to be approximately unity.

From the previous chapter, Equation (2.42) gives

$$\delta_1 \approx \frac{5\nu}{u_f}$$

so that on substitution into Equation (3.30)

$$\delta = \delta_1 \left( \frac{D_m}{5\nu} \right)^{1/4} \quad (3.31)$$

It was also shown in Chapter 2 that  $\delta_1$  can be obtained from the solution of the equation

$$\delta_1 = \frac{5\nu C_1}{U} \ln \left( \frac{\delta_1}{2h} \right)$$

where  $C_1 \approx -2.5$ . From this equation and Equation (3.31),  $\delta$  can be calculated.

### Example

From experimental results [15], in which  $h = 0.43 \text{ mm}$ ,  $U = 9.2 \text{ m/s}$ , with  $\nu = 1 \text{ mm}^2/\text{s}$  and  $D_m = 10^{-5} \text{ cm}^2/\text{s}$  (assumed),  $\delta_1$  is calculated to be  $6.6 \times 10^{-3}$  mm. From Equation (3.31) the corresponding thickness of the diffusion layer thickness  $\delta$  is  $7.9 \times 10^{-4}$  mm.

An alternative method for estimating the average diffusion layer thickness is available [16, 17]. Here  $\delta$  is related to the average Nusselt number, Nu, by

$$\delta = \frac{d_h}{\text{Nu}} \quad (3.32)$$

where  $d_h$  is the hydraulic diameter for the flow channel. For fully developed velocity profiles, and at short distances from the leading edge of the electrode, experimental mass transfer rates are described by the relation

$$\text{Nu} = 0.28 \text{ Re}^{0.58} \text{ Sc}^{1/3} \left( \frac{d_h}{L} \right)^{1/3} \quad (3.33)$$

where Nu is defined by

$$\text{Nu} = \frac{J_1 d_h}{z F C_b D} \quad (3.34)$$

Here  $J_1$  is the limiting current density,  $z$  is the number of electrons transferred per mole,  $F$  is Faraday's constant,  $C_b$  is the bulk concentration of the reacting species. Re is the Reynolds number, and Sc ( $= \nu/D$ ) is the Schmidt number,  $\nu$  and  $D$  being the viscosity and diffusion coefficient respectively.

Relation (3.33) applies if the condition

$$\frac{0.2L \text{ Re}^{7/8}}{d_h} < 10^3 \quad (3.35)$$

is satisfied.

If

$$\frac{0.2L \text{ Re}^{7/8}}{d_h} \gg 10^3 \quad (3.36)$$

the mass transfer rates are given by

$$\text{Nu} = 0.022 \text{ Re}^{7/8} \text{ Sc}^{1/4} \quad (3.37)$$

(Note: expression (3.37) is derived [16] with the aid of a friction factor which is made equal to  $0.079/\text{Re}^{1/4}$ ).

For laminar flow, the equivalent expression for fully developed velocity profiles is

$$\text{Nu} = 1.85 \left( \text{Re} \text{ Sc} \frac{d_h}{L} \right)^{1/3} \quad (3.38)$$

Substitution of typical values  $\nu = 1 \text{ mm}^2/\text{s}$ ,  $D = 10^{-5} \text{ cm}^2/\text{s}$ ,  $h = 0.5 \text{ mm}$  ( $d_h = 2h$ ) into these formulae has shown that over the mass transfer entry region,  $\delta$  is about  $4 \times 10^{-3}$  to  $8 \times 10^{-4} \text{ mm}$  for velocities ranging from 1 to 25 m/s respectively [16].

### Example

The magnitude of the concentration overpotential  $\eta_{\text{conc}}$  can now be estimated from Equation (3.27), the appropriate values of  $\delta$  for the different flow conditions being obtained from the relevant formulae above.

Suppose  $J = 40 \text{ A/cm}^2$ ,  $c_\delta = 1.7 \text{ N}$ ,  $kT/e = 1/40 \text{ V}$ ,  $D_m \simeq 10^{-5} \text{ cm}^2/\text{s}$ ,  $\nu \simeq 1 \text{ mm}^2/\text{s}$ ,  $\delta \simeq 1.5 \times 10^{-3} \text{ mm}$  (laminar flow), and  $\delta \simeq 7.9 \times 10^{-4} \text{ mm}$  (turbulent flow).  $|\eta_{\text{conc}}|$  is calculated to be 0.027 V and 0.038 V respectively for the smaller and larger values of  $\delta$ . Both values for the overpotential are considerably less than a typical applied potential difference of 10 V. It can be inferred that, under the usual conditions of electrolyte flow in ECM, concentration polarisation is negligible.

Fitz-Gerald and McGeough [18] have also postulated that convection in the diffusion layer may cause considerable variation in the diffusion currents along the electrode, thus causing a supplementary overpotential effect which is dependent on the electrolyte velocity. They have called this possible effect the 'convection overpotential'.

In their analysis, the transport equations for the metal and electrolyte ions are modified to include a term for convection of ions within the diffusion layer. The presence of this term leads to expressions for the concentration gradient which are dependent on the electrolyte flow velocity:

$$\frac{\partial c}{\partial y} \propto x^{-(1-s)/3}$$

where  $s = -\frac{1}{2}$  for laminar flow and  $s = 0$  for turbulent flow. The current density at the anode, of course, has a similar dependence; therefore,

$$J \propto x^{-1/2}$$

for laminar flow, and

$$J \propto x^{-1/3}$$

for turbulent flow.

**Example**

For turbulent flow and for an electrode of length 80 mm, say, in the absence of other effects, the current density at  $x = 80$  mm is one-half of that at  $x = 10$  mm.

Only steady-state conditions have been considered in the analyses in this section. For electrode processes under diffusion control the transition time required for equilibrium to be reached has been shown [19] to be estimable from the expression

$$Jt^{1/2} = \text{constant}$$

For electrodeposition processes,  $t \approx 0.1$  to 1 s. For ECM,  $t$  will probably be less than  $10^{-4}$  s. For conditions in which a limiting concentration of reaction products is obtained at the electrode, passivation (see below) might occur in a shorter time.

In relation to this section, it is interesting finally to note that an experimental technique has been developed for analysing the properties of the anode diffusion layer, including its thickness, for conditions akin to those met in ECM [20].

**3.4.5 Resistance overpotential,  $\eta_r$** 

Resistance overpotential is generally regarded as the potential drop across a thin layer of electrolyte or film layer (e.g. an oxide film) on the electrode surface. Its magnitude depends principally on the current flowing in the cell and on the nature and conductivity of the electrolyte. For a small volume element of the electrolyte, the resistance is inversely proportional to the concentration, and by Ohm's law, the current at which  $\eta_r$  becomes appreciable is proportional to the electrolyte concentration.

There is clearly a connection between the resistance and activation overpotentials. In practical cases, the presence of the former is usually noticed by the need to increase the voltage required to maintain the reaction.

The principal differences between  $\eta_a$  and  $\eta_r$  are in their different variations with current density and in their rates of build-up and decay;  $\eta_r$  forms or decays almost instantaneously while  $\eta_a$  forms and decays quickly but measurably.

**3.4.6 Decomposition potential**

Generally, in ECM, the higher the applied potential difference the greater is the rate of metal dissolution at the anode (and hydrogen

evolution at the cathode). The characteristic shape of the curve of applied potential difference against current is shown in Fig. 3.10. For the low, initial values of potential difference the current is low

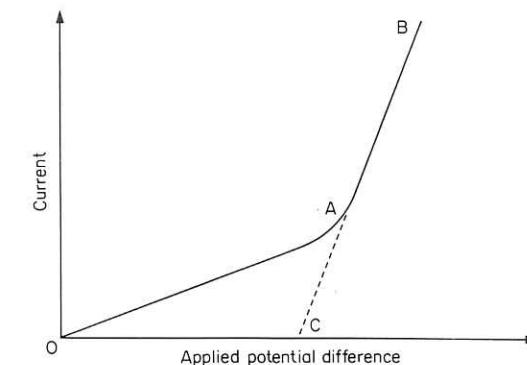


Fig. 3.10 Decomposition potential

(along OA) but near values of the potential difference corresponding to region A, the current rises sharply. If the potential difference is further increased, the cell current still increases appreciably (along AB). That part of the curve corresponding to A represents the onset of anodic dissolution and cathodic gas evolution of the process. If the section AB is extrapolated back to zero current, the value of the potential at that point C is known as the *decomposition potential*.

A typical example for ECM is the electrolysis involving the dissolution of iron in NaCl solution, discussed in Chapter 1. At the cathode, the molecular hydrogen will only be formed when the reversible hydrogen electrode potential is exceeded. Similarly, the dissolution of iron will only occur when its reversible electrode potential is exceeded. Thus, the potential difference between the electrodes which must be exceeded so that the overall cell reaction can take place is given by the difference between the reversible potentials for the hydrogen and iron. If the hydrogen electrode potential is taken as zero, then from Table 3.3 the minimum potential difference required for anodic dissolution is seen to be the same as the reversible potential for iron (0.44 V).

However, it has been observed that the actual potential difference in ECM is greater than this minimum potential difference, because of the irreversibility of the process (and the consequent presence of

overpotentials). Thus, to maintain a current  $I$  in the cell the applied potential difference  $V$  necessary is given by

$$V = (E_c - E_a) + \eta_a + \eta_{\text{conc}} + \eta_r + IR$$

where  $E_c$  and  $E_a$  are the reversible potentials at the cathode and anode respectively,  $\eta_a$ ,  $\eta_{\text{conc}}$ , and  $\eta_r$  are the overpotentials at both electrodes, as discussed above, and  $IR$  is the ohmic potential drop across the electrode gap,  $R$  being the resistance of the electrolyte.

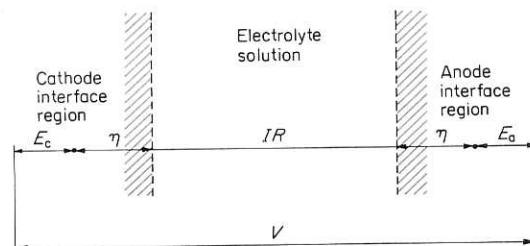


Fig. 3.11 Schematic potential distribution in an ECM cell

In Chapter 1 the  $IR$  drop was shown to be dependent on the cell conditions of current density, gap width, and electrolyte conductivity ( $IR \equiv Jh/\kappa_e$ ). In practice  $\eta_{\text{conc}}$  and  $\eta_r$  are often small compared with  $\eta_a$ , so that, in calculations, only the activation overpotentials at anode and cathode need consideration. Note, however, that an additional contribution is possible from the voltage drop across the leads. A very simple schematic representation of the potential distribution for an ECM cell is given in Fig. 3.11.

It is worth mentioning at this stage the possibility of anodic reactions other than, or in addition to, dissolution. In aqueous solutions, few metals dissolve without the generation of gas (e.g. oxygen) at sufficiently high potential differences. Since part of the current is now used in evolving the gas, a practical observation then is the decrease in the metal dissolution rate below the Faraday rate. Gas evolution is discussed more fully in the next section.

### 3.5 Polarisation curves

During anodic dissolution, a curve of anodic potential against current density can be obtained. The usefulness of such a polarisation curve will become clear, and will be discussed more fully, in Chapter 4. However, since its form relates to some of the anodic phenomena

discussed above, its main features are outlined here. A simple, characteristic polarisation curve is shown in Fig. 3.12. For anodic potentials in the range AB, the metal is said to be in the 'active' state, and dissolves by the removal of cations from the crystal planes.

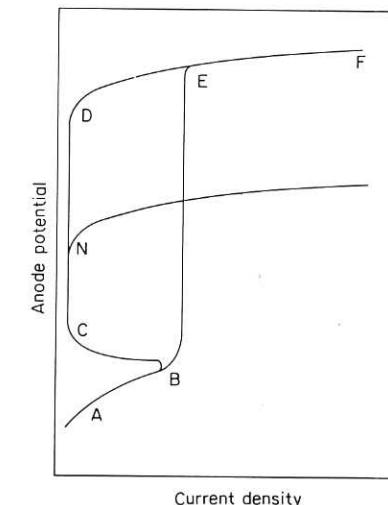


Fig. 3.12 Simple illustration of polarisation curve

Since the rates of dissolution depend on the geometry of the plane, the metal surface becomes etched. Under these conditions, Tafel's equation, derived earlier, applies to the current density–potential relationship.

When the anode potential becomes greater than B in Fig. 3.12, a solid oxide film may form on the anode, which causes the reaction rate to be reduced, for example, to the level CD. The metal is then said to have become 'passive'. The solid films associated with this condition are often similar to those already discussed in relation to the thermodynamics of equilibrium anodic processes. (In passing we note that the passivity of iron in concentrated  $\text{HNO}_3$  was first observed by Faraday.)

Alternatively, surface films may be formed on metals which are so conductive that the passage of a considerably greater amount of current becomes possible. This condition is shown as the region BE in Fig. 3.12. When the oxide films are present in this state, dissolution takes place in a random manner over the metal surface. (It is now controlled by the film and not by the geometry of the

crystal plane.) Since the atoms are removed in a random fashion, the metal surface becomes polished.

For oxide films with good electronic conductivity, and for appropriate conditions of potential, the oxidation of solution anions may take place in preference to, or in addition to, polishing or passivity. This reaction yields the evolution of gas; e.g. for hydroxyl ions, oxygen is formed:



This condition is represented by DF in Fig. 3.12.

A condition which is sometimes difficult to distinguish from gas evolution is transpassivity. This condition arises when cations of the oxide film are themselves oxidised to soluble higher-valency forms. Chromium is one metal which is known to exhibit this condition yielding chromates.

If a passive film is present on a metal and the metal is exposed to a solution containing an appropriate concentration of aggressive anions (e.g. chloride ions), those anions will penetrate into the film, causing a disruption of the film. (This condition is well known in corrosion studies.) The areas of penetration permit greater local current flow than elsewhere over the electrode where the film is unbroken. Such local current flow can lead to the formation of pitting on the electrode surface. Pitting is most likely to occur at weak points in the oxide film, e.g. at grain boundaries. The potential at which the oxide film is disrupted is the 'critical breakdown potential' and is dependent on the concentration of the aggressive ion. The effect of increasing chloride concentration on the potential which gives rise to pitting is given by D and N in Fig. 3.12. The increase in current after pitting is due to the exposure of the metal surface within the pits to the electrolyte.

Several final remarks must be made about polarisation curves. They are usually derived from experiments carried out at low or zero electrolyte velocities and low current densities. An increase in electrolyte velocity causes little change in the shape of the polarisation curve apart from increasing any limiting value of the current density. This is demonstrated in Fig. 3.13 for an electropolishing curve. This figure is also presented in an alternative form – with current density and potential axes interchanged – which is also popular in polarisation work. Little work has been done to study the anodic polarisation characteristics of the alloys used in ECM.

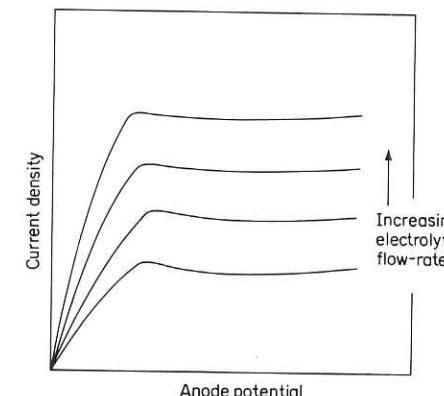


Fig. 3.13 Increase in limiting current density with electrolyte flow-rate

Nonetheless, a start has been made in reported studies of the behaviour of copper, zinc, and brass [21] and iron-chromium alloys [22].

### 3.6 Reactions at the electrodes

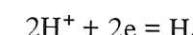
Common reactions which occur in ECM for different types of electrolytes are finally summarised.

#### (a) Acidic electrolytes (e.g. HCl)

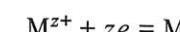
Anodic reaction: dissolution of the metal:



where  $\text{M}^{z+}$  is the metal ion of valency  $z$ , and  $e$  is the electron charge.  
Cathodic reaction: evolution of hydrogen:



Reduction of the positive metal ion is also possible, but is undesired.

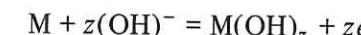


#### (b) Neutral electrolytes (e.g. NaCl)

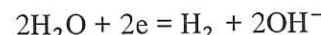
Anodic reaction: metal dissolution



or



Cathodic reaction: hydrogen generation

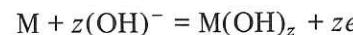


The metal ions from the anode and hydroxyl ions from the cathode usually react in the bulk of the electrolyte to form a metal hydroxide:

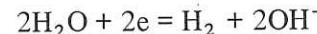


(c) *Alkaline electrolytes*

Anodic reaction: metal dissolution



Cathodic reaction: hydrogen generation



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