Unit-I
ELECTROCHEMICAL CELLS

An electrochemical cell is a device which converts chemical energy into electrical energy or electrical energy into chemical energy. Thus, there can be two types of electrochemical cells.

(i) Electrolytic cells are devices which converts electrical energy into chemical energy.

(ii) Galvanic cells (or voltaic cells) are devices which convert chemical energy into electrical energy. e.g. Daniel cell (Fig.1): The Daniel cell consists of two containers, one of is with a zinc rod dipped in zinc sulphate solution and other is with a copper rod dipped in copper sulphate solution. The solutions of two containers are connected by a salt bridge. The salt bridge is a U-tube, filled with either a jelly containing KCl or NH_4NO_3, or saturated solution of KCl or NH_4NO_3 and both the ends of U-tube plugged with a porous material. The zinc and copper rods (electrodes) are connected externally through an ammeter or voltmeter by using a wire, the following changes are observed:

- Zinc starts to dissolve.
- Copper gets deposited on copper rod.
- The voltmeter indicates the flow of electrons from zinc to copper rod.
- The zinc sulphate solution becomes richer with Zn^{2+} ions.
- The copper sulphate solution becomes more dilute with respect to Cu^{2+} ions.

Anode (oxidation): $\quad Zn \rightarrow Zn^{2+} + 2e^-$

Cathode (reduction): $\quad Cu^{2+} + 2e^- \rightarrow Cu$

Cell reaction: $\quad Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$
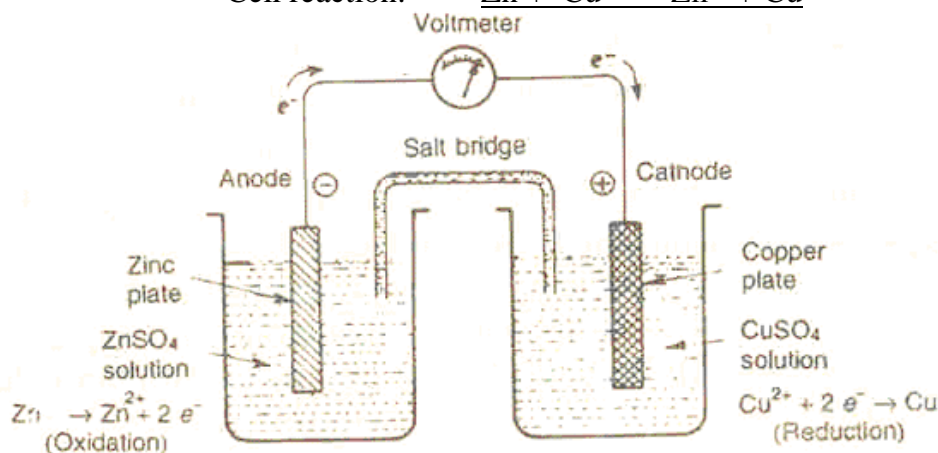

Fig.1. Daniel cell.

The flow of electrons from zinc electrode to copper electrode. Hence the flow of conventional current is from copper to zinc electrode.

Cell notation and convention:

By convention, the electrode at which oxidation occurs is **anode** and the electrode where reduction occurs is **cathode.** Thus in the above cell zinc electrode acts as anode and copper electrode acts as cathode. In a galvanic cell anode is **negative** and cathode is **positive.** The reason, to this is that oxidation is accompanied by the liberation of electrons which are given up to that electrode, which thereby acquires a negative charge. Reduction, on the other hand, is accompanied by the absorption of electrons by the reactant in the solution from the electrode, which thereby acquires a positive charge.

According to present conventions, a galvanic cell is represented by keeping view the following points:

(1) Anode is written on the left-hand side; while cathode is written on the right-hand side.

(2) The electrode on the left (i.e., anode) is written by writing the metal (or solid phase) first and then the electrolyte. Two are separated by a vertical line or a semicolon. The electrolyte may be represented by the formula of the whole compound or by ionic species. Additional information regarding the concentration may also be mentioned in bracket.

$$Eg., \quad Zn \mid Zn^{2+} \text{ or } Zn ; Zn^{2+} \text{ or } Zn \mid ZnSO_4(1M)$$
$$Pt, H_2 \text{ (1 atm.)} \mid H^+(1M).$$
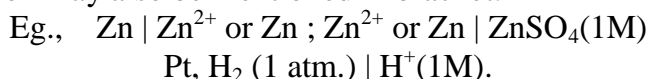
(3) The cathode of the cell (at which reduction takes place) is written on the right-hand side. In this case, the electrolyte is represented first and the metal (or solid phase) thereafter. The two are separated by a vertical line or a semicolon.

$$E.g., Cu^{2+} \mid Cu \text{ or } Cu^{2+}; Cu \text{ or } Cu^{2+}(1M) \mid Cu \text{ or } CuSO_4(1M) ; Cu$$
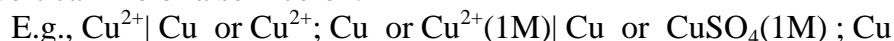
(4) A salt bridge is indicated by two vertical lines, separating the two half cells. Thus applying above considerations to Daniel cell, we may represent as:

$$Zn \mid Zn^{2+} (1M) \parallel Cu^{2+}(1M) \mid Cu$$
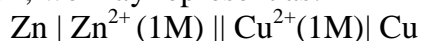
Electromotive force of the cell (EMF): The difference in potential which causes a current to flow from an electrode of higher potential to that of lower potential is called the electromotive force (emf). The cell potential is represented by the $E_{cell.}$

$$E_{cell} = E_{RHS} - E_{LHS}$$
$$E_{cell} = E_{cathode} - E_{anode}$$

Standard emf of the cell is defined as the emf of the galvanic cell when the reactants and products of the cell reaction are at unit concentration or unit activity, at 298K and 1 atmosphere pressure. $\quad E^0_{cell} = E^0_{RHS} - E^0_{LHS}$

Function of salt bridge:

In a galvanic cell, if the salt bridge is not used, then the two solutions should be either in contact with each other or separated by a porous membrane. In either case, positive and negative ions of the electrolytes will migrate across the junction in opposite directions as there is increase of positive and negative charges at anode and cathode respectively. Inside the cell the current is carried by ions, negative ions from cathode to anode and positive ions from anode to cathode. Because of the difference in the migration velocities of these ions, accumulation of charges across the junction occurs. This gives rise to the formation of an electrical double layer developing a potential called **liquid junction potential** across the junction. In such situations, the emf of the cell includes liquid junction potential also.

The use of salt bridge, however, avoids the liquid junction potential and provides the contact between the two solutions. It consists of saturated solution of a salt such as KCl or NH_4NO_3, whose ions have almost same migration velocities. The positive and negative ions of the salt in the salt bridge migrate with equal speed into cathode and anode compartments respectively, thereby avoiding liquid junction potential. During the cell reaction, either Cl^- diffuse from the salt bridge into the zinc half-cell or Zn^{2+} ions diffuse into the salt bridge to keep the zinc-half cell electrically neutral. At the same time, the copper half-cell is kept electrically neutral by the diffusion of either the positive (K^+) ions from the salt bridge to the copper cell or diffusion of SO_4^{2-} ions from the copper cell into the salt bridge. Without the salt bridge no electrical current would be produced by the galvanic cell since electrolytic contact must be maintained for the cell to function.

Single electrode potential (Reduction potential):

      Electrode potential is defined as the potential developed on the electrode at the interface when it is in contact with a solution of its own ions. It is denoted by E. All single electrode potentials represent reduction potentials which is the measure of the tendency of an electrode to undergo reduction.

Standard electrode potential (E^0):

      Standard electrode potential is the potential developed when the electrode (metal) is in contact with solution of unit concentration (1M) at 298K.

NERNST EQUATION

      Nernst equation is a thermodynamic equation which relates the change in free energy and cell potential with concentration, M^{n+}. The decrease in free energy ($-\Delta G$) represents maximum amount of work that can be obtained from a chemical reaction.

$$- \Delta G = W_{max} \dots\dots\dots\dots\dots (1)$$

      The work performed by an electrochemical cell depends on (i) number of coulombs that flow and (ii) the energy available per coulomb.

$$\text{Work = number of coulombs} \times \text{energy available / coulomb.}$$

      The number of coulombs that flow is equal to the product of number of moles of electrons that are involved in the cell reaction and faraday (F).

$$\text{Number of coulombs = nF.}$$

      Energy available per coulomb is the emf of the cell E, since volt is equal to energy per coulomb. When the emf is maximum, work derived from the cell is also maximum. The maximum is the cell potential E_{cell}. Thus W_{max} for an electrochemical cell (expressed in joule) is given by the equation.

$$W_{max} = n \times F \times E \dots\dots\dots\dots(2).$$
      (mole of e^-) (C mol^{-1}) (JC^{-1})
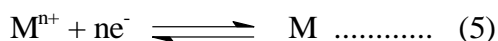
      Equating (1) and (2),

$$\Delta G = - nFE \dots\dots\dots\dots\dots (3).$$

      Under standard conditions, i.e., when the concentrations of all species is unity, the standard free energy ΔG^0 is given by the equation,

$$\Delta G^0 = - nFE^0 \dots\dots\dots\dots\dots (4).$$

Where E^0 is a constant called the standard reduction (electrode) potential.

      For a reaction,

$$M^{n+} + ne^- \rightleftharpoons M \dots\dots\dots (5)$$

The equilibrium constant K_c is related to change in free energy by the thermodynamic equation,

$$\Delta G = \Delta G^0 + RT \ln K_c \dots\dots\dots (6)$$

      Since $K_c = [M] / [M^{n+}]$,

$$\Delta G = \Delta G^0 + RT \ln [M] / [M^{n+}]\dots\dots\dots (7)$$

      Substituting from equations (3) and (4) for ΔG and ΔG^0

$$- nFE = - nFE^0 + RT \ln [M] / [M^{n+}]$$

      Dividing throughout by $- nF$

$$- nFE /- nF = - nFE^0 / - nF + (RT/- nF) \ln [M] / [M^{n+}]$$

$$E = E^0 - (RT/nF) \ln[M] / [M^{n+}]$$

$$\text{Or, } E = E^0 + \frac{RT}{nF} \ln [M^{n+}]\ldots\ldots\ldots\ldots \textbf{(8)}. \ \{\text{Since } [M] = 1\}$$

Equation (8) is mathematical representation for Nernst equation. E^0 is the electrode potential under standard conditions (for metal ion –metal electrodes, ion concentration is 1M and gas electrodes gas pressure is 1 atmosphere).

Substituting the values for R (8.3143 JK^{-1}mol^{-1}), F (96500 Cmol^{-1}) at 298K, and converting natural logarithm to base 10, the Nernst equation reduces to

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]\ldots\ldots\ldots\ldots \textbf{(9)}.$$

(i)   It may be seen from equation (9) that $E = E^0$ where $[M^{n+}]$ is unity.

(ii) If concentration of solution $[M^{n+}]$ is increased, the electrode potential increases and vice versa.

(iii) If temperature is increased, the electrode potential increases and vice versa.

Nernst equation for emf of cells: Nernst equation may also be used to calculate the emf of chemical cells

$E_{cell} = E^0{}_{cell} - (0.0591/n) \log [\text{products}] / [\text{reactants}]$

or, $E_{cell} = E^0{}_{cell} + (0.0591/n) \log [\text{reactants}] / [\text{products}]$

or, $E^0{}_{cell} + (0.0591/n)\log [\text{species at cathode}] / [\text{species at anode}]$

In Daniel cell, $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

$E_{Danielcell} = E^0{}_{Danielcell} + (0.0591/n) \log [Cu^{2+}] / [Zn^{2+}]$

Electrochemical series:

When elements are arranged in increasing order of (down-wards) of their standard electrode potentential, a series called electrochemical series (or emf series) is obtained. Such an arrangements of few elements is given in table 1

Table-1. Electrochemical seiries

M^{n+}/M	E^0 (V) at 298K
Li^+/Li	- 3.05 (Anode)
K^+/K	- 2.93
Ba^{2+}/Ba	- 2.90
Ca^{2+}/Ca	- 2.87
Na^+/Na	- 2.71
Mg^{2+}/Mg	- 2.37
Al^{3+}/Al	- 1.66
Zn^{2+}/Zn	- 0.76
Cr^{3+}/Cr	- 0.74
Fe^{2+}/Fe	- 0.44
Cd^{2+}/Cd	- 0.40
Ni^{2+}/Ni	- 0.23
Sn^{2+}/Sn	- 0.14
Pb^{2+}/Pb	- 0.13
H^+/H_2	0.00 (Reference)
Cu^{2+}/Cu	0.34
Ag^+/Ag	0.80
Hg^{2+}/Hg	0.85
Pt^{2+}/Pt	1.20
Au^{3+}/Au	1.38 (Cathodic)

Reference electrode: Any electrode of constant and reproducible potential, used to determine the potential of other electrode.
E.g.: Standard hydrogen electrode.

Measurement of single electrode potential: The potential of a given electrode is measured using standard hydrogen electrode (SHE) whose potential is arbitrarily taken as zero volt at all temperatures and is the reference point for all potential measurements.
Note: It is impossible to measure the absolute value of single electrode potential. It is because a single electrode constitutes only a half cell. A halfcell, not be lose or gain electrons by itself. The loss or gain of electrons can take place only in a complete circuit containing two half cells connected to each other. So, the electrode potential can only be measured by using some electrode as reference electrode.

Secondary reference electrodes: Because of the difficulties involved in the use of standard hydrogen electrode as reference electrode, some other electrodes constant electrode potential, referred to as secondary reference electrodes. Two such electrodes are (i) calomel electrode (ii) silver-silver electrode.

(i) Calomel electrode (mercury-mercurous electrode):
Construction: Mercury is placed at the bottom of glass tube. A paste of calomel (Hg_2Cl_2) and mercury is placed over the pool of mercury. The remaining part of the tube is filled either a saturated or standard (normal or decinormal) solution of potassium chloride. A platinum wire is fused in a glass tube is dipped into mercury is used for electrical contact. A salt bridge is used to couple with other half-cells (Fig. 2a).
The calomel electrode is represented as
$Hg \mid Hg_2Cl_2$ (s) $\mid$ KCl (saturated or standard) or Hg, Hg_2Cl_2 (s) , KCl (saturated or standard).
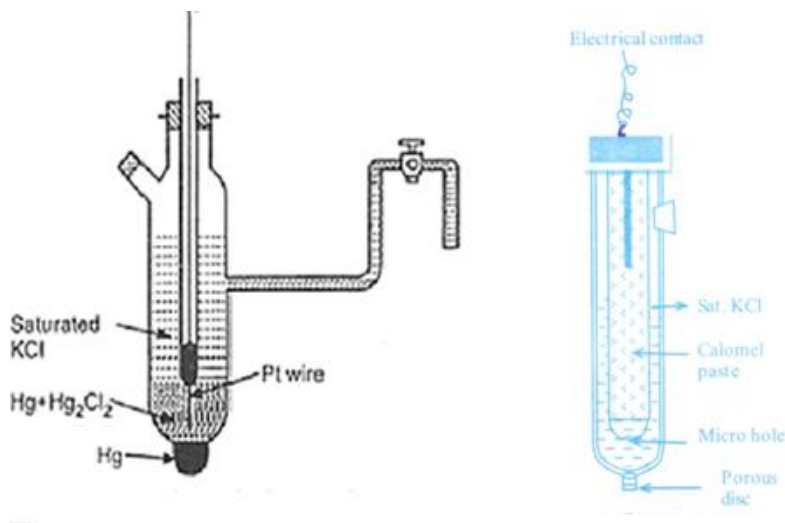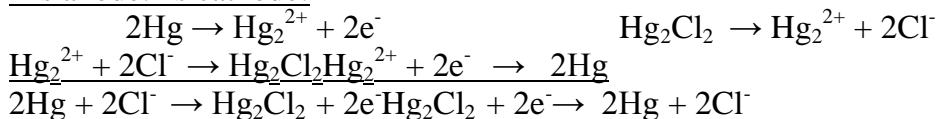

Fig.2. Calomel electrode

Working: Calomel electrode can act as anode or cathode depending on the nature of the other electrode of the cell.

The electrode reactions are represented as follows.
As anode:As cathode:

$$2Hg \rightarrow Hg_2^{2+} + 2e^- \qquad\qquad Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2Cl^-$$

$$Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2 Hg_2^{2+} + 2e^- \rightarrow 2Hg$$

$$2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^- Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$$

The net reversible electrode reaction is

$$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^- \qquad\qquad 1/2\ Hg_2Cl_2 + e^- \rightleftharpoons Hg(l) + Cl^-$$

or

Electrode potential $E = E^0 - \dfrac{2.303RT}{F} \log [Cl^-]$

At 298K, $E_{cal} = E^0{}_{cal} - 0.0591 \log [Cl^-]$

Since the calomel electrode is reversible with respect to chloride ion its electrode potential depends on the concentration of KCl solution.

At 298K, the electrode potentials as follows:

KCl concentration	0.1N	1N	Saturated
Electrode potential (V)	0.334	0.281	0.2422

Advantages of calomel electrode (a secondary reference electrode):
     i)   It is very simple in construction.
     ii) The potential is reproducible and stable over a long period.
     iii) Its electrode potential will not vary with temperature.
Hence, it is commonly used as secondary reference electrode for potential measurements.

Determination of single electrode potential using calomel electrode: The test electrode (e.g., Zn^{2+}/Zn) is coupled with a saturated calomel electrode (Fig.3).

The cell, so formed, may be represented as
            Zn(s) | ZnSO$_4$(1M) || KCl (Saturated solution) | Hg$_2$Cl$_2$ (s) | Hg(*l*)
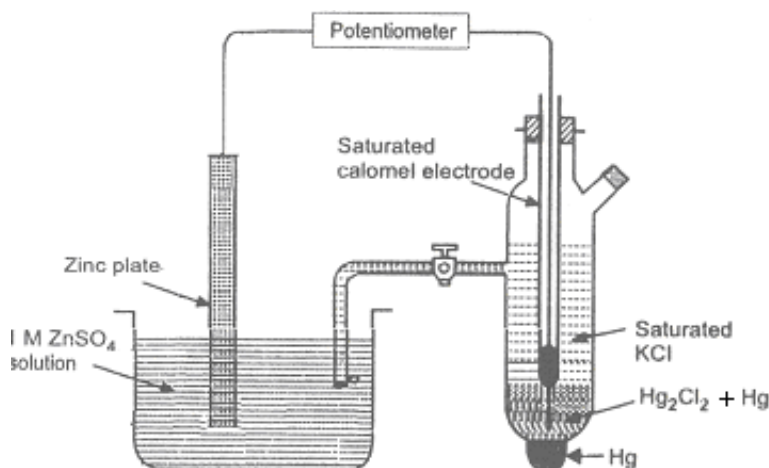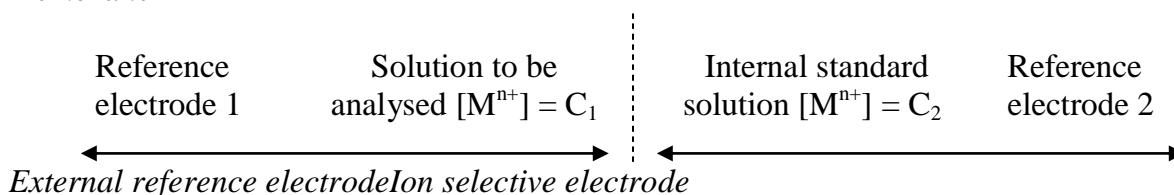

Fig.3. Determination of electrode potentialof zinc electrode using calomel electrode as reference electrode.

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The calomel electrode is written on the right as reduction takes place at this electrode

The emf of this cell measured potentiometrically.

$$\text{Then } E_{cell} = E_{cathode} - E_{anode}$$
$$= E_{cal} - E_{Zn^{2+}/Zn}$$
$$= 0.2422 - E_{Zn^{2+}/Zn}$$
$$\text{i.e., } \mathbf{E_{Zn^{2+}/Zn} = 0.2422 - E_{cell}}$$

Ion-selective electrodes: Ion-selective electrode is the one which selectively responds to a specific ion in a mixture and potential developed at the electrode is a function of concentration of that ion in the solution. The electrode generally consists of a membrane which is capable of exchanging the specific ions with the solution with which it is in contact. Therefore these electrodes are also referred to as membrane electrodes

Membrane

Reference electrode 1	Solution to be analysed $[M^{n+}] = C_1$	Internal standard solution $[M^{n+}] = C_2$	Reference electrode 2

External reference electrodeIon selective electrode

There are three types of membranes (Fig. 4):

(1) Glass membrane (e.g., glass electrode).

(2) Solid state membranes

(i) For fluoride (F^-) ions- lanthanum trifluiride crystal doped with europium difluoride.

(ii) For chloride (Cl^-) ions – pressed pellet of $Ag_2S + AgCl$. The electrode has a Teflon body and crystal is held in position with epoxy resin.

(3) Liquid state membranes:

(i) For certain alkali and alkaline earth cations-neutral monocyclic crown ethers and phosphatediester.

(ii) For anions-iron phenanthrolic complexes. Liquid state membrane is usuallyobtained by absorbing the active molecules on an inert porous support such as porous polymer.
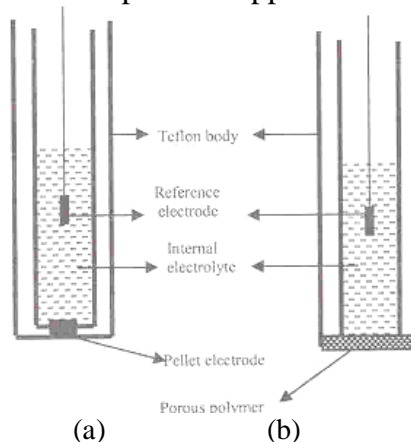

Teflon body

Reference electrode

Internal electrolyte

Pellet electrode

Porous polymer

(a)   (b)

Fig.4. Ion selective electrodes with different types of membranes (a) solid state (b) liquid membrane on a porous polymer.

Applications: Ion selective electrodes are used in determining
   (i)   The concentration of a number of cations such as H^+, Li^+, Na^+, K^+, Ag^+, NH_4^+, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ca^{2+} and hardness $[Ca^{2+} + Mg^{2+}]$;
   (ii)   The concentration of anions such as F^-, NO_3^-, CN^-, S^{2-} and halide ions;
   (iii)   The pH of a solution using glass electrode (H^+ ion-selective electrode) and
   (iv)   The concentration of gas using gas sensing electrodes. For example, an electrode which measures the level of CO_2 in blood samples makes use of glass electrode in contact with a very thin CO_2 permeable silicone rubber membrane soaked in a dilute solution of sodium bicarbonate.

Glass electrode:
Construction: A glass electrode (Fig.5.) consists of a long glass tube with a thin walled glass bulb at one end. Special glass (Corning glass containing 22% Na_2O, 6% CaO and 72% SiO_2) of low melting point and high electrical conductance is used for the purpose. This glass can specifically sense hydrogen ions up to a pH of about 9. The bulb contains 0.1 M HCl and a Ag/AgCl electrode (as internal reference electrode) is immersed into the solution and connected by a platinum wire for electrical contact. The electrode is represented as,
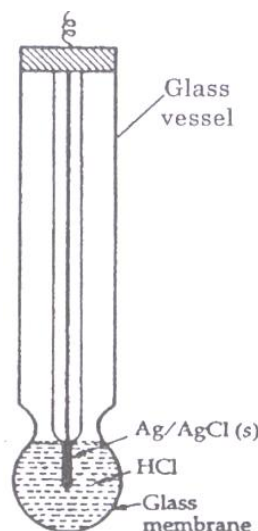Ag | AgCl (s) | HCl (0.1M) | glass.

Fig.5. Glass electrode

Electrodepotential of glass electrode (E_g):
Principle: If a thin walled glass bulb containing an acid is immersed in another solution, the membrane undergoes an ion exchange reaction; Na^+ ions on the glass are exchanged for H^+ ions. The potential is developed across the glass membrane (Fig.6).

$$H^+ + Na^+Gl^- \rightleftharpoons Na^+ + H^+Gl^-$$
solution membrane   solution membrane
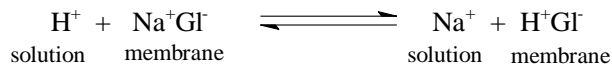
The potential difference, E_b at the interface also referred to as the boundary potential is the result of difference in potential (E_2-E_1) developed across the gel layer of glass membrane between the two liquids.
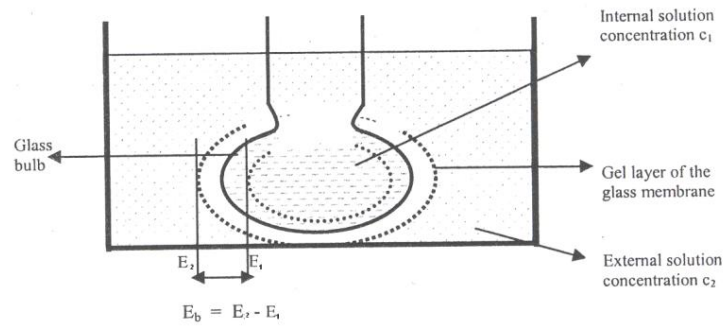
Fig.6. Glass membrane

E_b can be related to the difference in the hydrogen ion concentration of the two solutions by the relation, $E_b = E_2 - E_1 = \dfrac{RT}{nF} (\ln C_2 - \ln C_1)$ ......(1)

Where C_1 is the concentration of H^+ ions of acid solution inside the glass bulb and C_2 is the concentration of the acid solution into which the glass bulb is dipped.

$$E_b = -\dfrac{RT}{nF} \ln C_1 + \dfrac{RT}{nF} \ln C_2 \quad ......(2)$$

If the concentration C_1 of the solution inside the glass bulb is constant, then the first term on the R.H.S. of equation (2) is constant. Therefore

$$E_b = \text{constant} + \dfrac{RT}{nF} \ln C_2$$

Substituting the value of R and F at 298K

$$E_b = L + 0.0591 \log C_2 \quad ....(3)$$

Where L is a constant which depends primarily on the pH of the solution taken in the bulb and glass electrode assembly. Since $C_2 = [H^+]$ of the solution, Equation (3) written as,

$$E_b = L - 0.0591 \text{ pH} \quad ....(4)$$

The boundary potential established is mainly responsible for the glass electrode potential E_g and is given by

$$E_g = E_b + E_{Ag/AgCl} \quad ....(5)$$

From equation (1), $E_b = 0$ when $C_1 = C_2$. But in practice, it has been observed that even when $C_1 = C_2$, a small potential is developed. This is called asymmetric potential (E_{asy}). Hence, Equation (5) can be written as

$E_g = E_b + E_{Ag/AgCl} + E_{asy}$

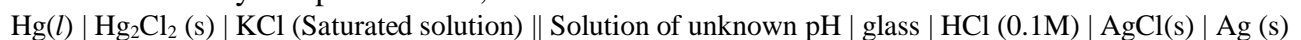$$E_g = L - 0.0591 \text{ pH} + E_{Ag/AgCl} + E_{asy}$$

$$\mathbf{E_g = E_g{}^0 - 0.0591 \text{ pH}}.............(6)$$

Where $\mathbf{E_g{}^0}$ is a constant equal to $L + E_{Ag/AgCl} + E_{asy}$

Determination of pH using glass electrode:
The glass electrode is immersed in the solution, the pH of which is to be determined. It is combined with a reference electrode such as a calomel electrode through a salt bridge (Fig.7).
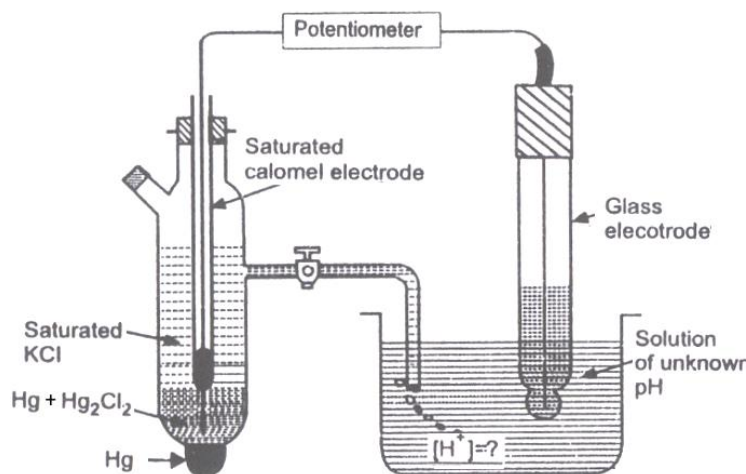The cell assembly is represented as,
Hg(l) | Hg$_2$Cl$_2$ (s) | KCl (Saturated solution) || Solution of unknown pH | glass | HCl (0.1M) | AgCl(s) | Ag (s)

Fig.7. Determination of pH using glass electrode

The emf of the above cell, E_{cell} is measured using an electronic voltmeter with a null type potentiometer circuit (or a pH meter) (An ordinary potentiometer with a low resistance of the galvanometer is not used because of high internal resistance of the glass electrode). E_{cell} measured is the difference between the calomel electrode (E_{cal}) and E_g.

$$E_{cell} = E_g - E_{cal}$$

$$= [E_g^0 - 0.0591 \, pH] - E_{cal}$$

Therefore, $\mathbf{pH = \dfrac{E_g^0 - E_{cal} - E_{cell}}{0.0591}}$

Advantages of glass electrode:
   (i)   Glass electrode can be employed in the presence of strong oxidizing or reducing substances and metal ions.
   (ii)   It is not poisoned easily.
   (iii) Accurate results are obtained between pH range 1-9. However, by using special glass electrodes, pH 1-13 can be measured.
   (iv)   It is simple to operated, can be used in portable instruments and therefore extensively used in chemical, industrial, agricultural and biological laboratories.

Limitations of glass electrode:
   (i)   In strongly acidic solutions of pH<1, the salt effect due to anions is observed.
   (ii)   It can be used upto a pH of 13 but being sensitive to Na^+ ions above a pH of 9, the linear relationship between glass electrode altered. So an alkaline error is introduced beyond a pH of 9, which should be taken into consideration.
   (iii) It does not function properly in some organic solvents like pure alcohol.

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BATTERY TECNOLOGY

Battery is a device consisting of two or more galvanic cells connected in series or parallel or both, that can store chemical energy in the form of active materials and on demand convert it into electrical energy through electrochemical redox reaction. Batteries can thus generate power and can act as portable sources of electrical energy.

Introduction:

The basic electrochemical unit in a battery is a galvanic cell. The components of such a cell are shown schematically in Fig. 1. In common usage, the term battery is often applied to a single cell.
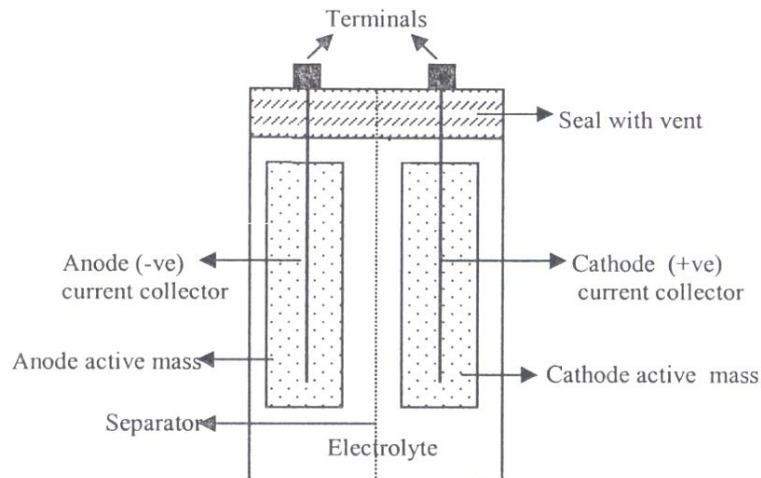

Fig.1. Principal Components of a battery

The principal components of a battery are:

1. *The anode or negative electrode*- it gives out electrons to the external circuit by undergoing oxidation during electrochemical reaction.
2. *The cathode or positive electrode*-it accepts electrons from the external circuit and reduction of active species occurs.
3. *The electrolyte-an ionic conductor*: The electrolyte (active mass in the anode and cathode compartments) is commonly a solution (or a slurry) of an acid, alkali or salt having high ionic conductivity. Solid electrolytes with appreciable ionic conductivity at the operating temperature of the cell are also used.
4. *The separator*- The material that electronically isolates the anode and the cathode in a battery to prevent internal short circuiting is referred to as a separator. It is permeable to the electrolyte so as to maintain the desired ionic conductivity. Thus the main function is to transport ions from anode compartment to the cathode compartment and vice versa. Fibrous forms of regenerated cellulose, vinyl polymers and polyolefins, cellophane and nafion membranes are commonly used as separators.

The battery components are selected based on the following properties.
Anode material: (i) ease of oxidation (low reduction potential) (ii) capacity to deliver high coulombic output (iii) good conductivity (iv) high stability and (v) ease of fabrication. The anodes are usually low cost materials. Zinc is predominantly used as anode since it has the properties mentioned above. Lithium, the lightest metal is also used as an anode in the modern batteries.

Cathode material: (i) capacity to facilitate reduction of active species in the medium (ii) resistance to electrolyte.

Electrolyte: (i) good ionic conductivity but poor electrical conductivity to prevent internal short circuit (ii) resistance to the electrode materials (iii) safety during handling.

Separator: (i) permeability for passage of ions from anode to cathode compartment and vice versa during discharging and charging (ii) capacity to prevent mixing of active masses in the two components (iii) high ionic conductivity but electronically insulating (iv) high strength flexibility (v) resistant to the active materials.

The cell is designed such that the electrodes are surrounded by the active mass; the electrodes are electrically separated by a suitable separator so as to prevent internal short-circuiting. The cells are built in many shapes and configurations-cylindrical, button, flat plates and prismatic. The cell components are designed according to the desired cell shape of the cell. The cells are sealed by different methods to prevent leakage and drying out.

Battery characteristics:

The suitability of a battery system for a particular application is decided based on certain performance characteristics of the battery or the cells constituting the battery system. Some of the important characteristics are briefly discussed below;

(i) Voltage: The voltage available from a battery depends upon the emf of the cells which constitute the battery system. The emf of the cell depends upon the free energy change in the overall cell reaction. As given by Nernst equation,

$$E_{cell} = E^o{}_{cell} - \frac{2.303RT}{nF} \log Q,$$

where $E^o{}_{cell} = E^o{}_{cathode} - E^o{}_{anode}$ and Q is the reaction quotient for the cell reaction at any stage of the reaction, which is the ratio of the molar concentration of the reaction product molecules to that of the reactants.

As it is evident from the above equation, emf of the cell and also the voltage available from the battery depend on standard electrode potential difference between the cathode and the anode, temperature and the extent of the cell reaction.

(a) If the difference in the standard electrode potential is more, higher is the emf of the cell.

(b) As the temperature increases the emf of the cell decreases.

(c) As the value of Q increases, i.e., when current is drawn from the cell and the reaction proceeds, the emf of the cell decreases marginally.

(d) Also, high cell potential is possible when the cell is with low resistance, i.e., with a high conductivity electrolyte.

(ii) Current: Current is a measure of the rate at which the battery is discharging. High current can be delivered without excessive voltage penalty if there is rapid electron transfer reaction.

(iii) Capacity: Capacity is the charge or amount of electricity that may be obtained from the battery and is given in ampere hours (Ah). Capacity depends on size of the battery and is determined by the Faraday relation,

$$C = \frac{wnF}{M}$$

Where C is the capacity in Ah, w is the mass of active material and M is its molar mass. The amount of the active materials actually consumed during discharge determines the capacity of the

battery. The capacity is also dependent on the discharge conditions. It is measured by finding, for a fixed current discharge (i amperes), the time t taken for the battery to reach a minimum voltage, E^{min}_{cell}, when the cell is said to be dead. A plot of V against t at a fixed current discharge is shown in fig.2. The variation of the battery voltage during discharge is shown by the flatness of the curve. The length of the flat portion of the curve is a measure of the capacity of the battery; longer the flat portion of the curve better is the capacity. Such a characteristic is one of the primary requirements of a battery.
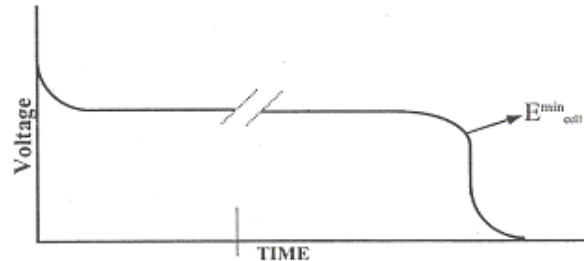

Fig.2. Battery voltage against time at constant current discharge

(iv) Energy density: The ratio of the energy available from a cell or a battery to its weight (or volume) is referred to as energy density. It is expressed as

$$\text{Energy density} = \frac{i\, t^1 E^{ave}_{cell}}{W}$$

where t^1 is the time taken at the fixed current i to reach an average voltage, E^{ave}_{cell}. Energy density is determined by determining the capacity and recording the average voltage (voltage averaged during the discharge) and the total weight (or volume) of the battery. It depends on the cell voltage. Requirement for batteries include a continuous energy density above a certain value or a very high energy density for a short period.

(v) Electricity storage density: Electricity storage density is a measure of the charge per unit weight stored in the battery, i.e., it is the capacity per unit weight. The weight indicates the weight of the complete battery and includes those of electrolyte, current collectors, terminals, the case and other subsidiary elements. A high storage density indicates a good battery design (minimum weight of all subsidiary elements) and also appropriate selection of electrode reactions. For instance, use of lithium (lightest metal) as anode would give 1F of charge for just 7 g of Li.

(vi) Power density: The ratio of the power available from a battery to its weight (W/kg) or volume (W/L) is called power density. A continuous power density above a certain value and a very high power density for a short period are the requirements of a battery. During discharge, power density decreases.

(vii) Energy efficiency: The energy efficiency for storage batteries is given by

% Energy efficiency = Energy released on discharge × 100 /energy required for charging.

Batteries should have high energy efficiency. Energy efficiency depends on the rate of charge and discharge. It also depends on the current efficiency of the electrode processes, the over potentials during discharge and charge reactions and on the internal resistance.

(viii) Cycle life: The number of charge/discharge cycles that can be achieved, in secondary batteries, before failure occurs is referred to as cycle life. The discharge/charge cycle thus cycle thus depends on the chemical composition, morphological changes and distribution of active

materials in the cell. The common reasons for a battery to fail to achieve a high cycle life include (i) corrosion at contact points, (ii) shedding of the active material from the plates, (iii) shorting between the electrodes due to irregular crystal growth and changes in morphology.

(ix) Shelf life: The duration of storage under specified conditions at the end of which a cell or battery retains the ability to give specified performance is called the shelf life. Long shelf life of batteries is likely when there is no self discharge. Self discharge occurs when there is reaction between the anode and cathode active material or corrosion of current collectors.

Classification of batteries:
Batteries are classified as (i) primary (irreversible) batteries, (ii) secondary (reversible) batteries and (iii) reserve batteries.

(a) *Primary batteries*: In primary batteries, the cell reactions is not completely reversible and hence are also referred to as irreversible batteries. These are not rechargeable and once discharged have no further electrical use. Examples of primary batteries are Zn-MnO_2 battery and Li-MnO_2 battery.

(b) *Secondary batteries*: Secondary batteries are rechargeable. The cell reactions are reversible and hence these are also referred to as storage or reversible batteries. After discharge, secondary batteries can be recharged electrically to their original condition by passing current through them in the direction opposite to that of discharge current. Lead storage battery and nickel-cadmium battery are examples of secondary batteries.

(c) *Reserve batteries*: Reserve batteries are batteries which may be stored in an inactive state and made ready for use by activating them prior to the application. The activation involves adding electrolyte or any other cell component. One of the components is isolated and stored separately and fitted (or added) just before it is needed. Electrolyte is the component that is usually isolated and hence the battery has long-term storage capacity. These batteries are highly active component materials for low temperature performance. They designed to meet extremely long and environmentally severe storage requirements. *Uses:* To deliver high power for relatively short period of time after activation in applications such as radiosonds (air borne instruments to send meteorological information back to earth by radio), missiles, trajectory, mid-ocean disasters and crisis in space.
Examples: Mg water activated batteries (Mg-$AgCl$ and Mg-$CuCl$); Zn-Ag_2O batteries.
Advantages: (i) Unlimited shelf life when properly packed. (ii) High reliability of performance. (iii) Variety of design options.

Lithium-ionbattery (Fig.3)

Li-ion battery has a four layer structure. The **anode** (negative electrode) is made of lithium, intercalated (included between the layers) in graphite (C_6), has a current collector of thin copper foil. The **cathode** (positive electrode) is made up from lithium liberating compounds such as Lithium cobalt oxide (or Lithium manganese oxide or Lithium Nickel-oxide), has a current collector of thin aluminium foil. An **electrolyte** is made with lithium-salt ($LiPF_6$, $LiBF_4$, or $LiClO_4$) and organic solvents (ethylene carbonate or dimethyl carbonate). The electrolyte provides conductivity medium for lithium ions to move between the electrodes. A **separator** is a fine porous polymer film such polyethylene or polypropylene.
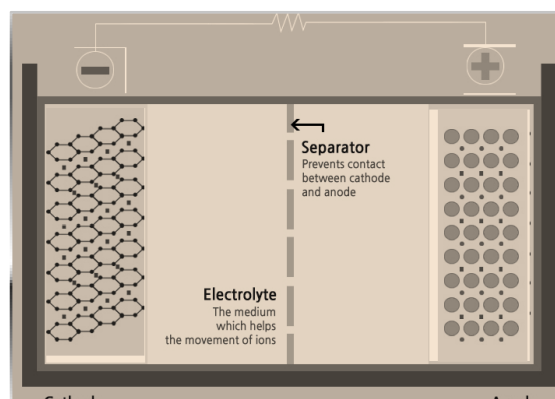
Fig. 3. Li-ion battery

Working: **During discharge** Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal structure of cathode. At the same time electrons travel through external circuit from negative to positive terminals powering external device to balance the reaction.

At the anode: $Li_xC \rightarrow C + xLi^+ + x\ e^-$

At the cathode: $Li_{1-x}\ CoO_2 + x\ Li^+ + x\ e^- \rightarrow LiCoO_2$

Overall reaction: $Li_xC + Li_{1-x}CoO_2 \rightarrow C + LiCoO_2$

During charging: Lithium in cathode electrode material is ionized and moves from cathode to anode and gets inserted into the anode. Electrons are pumped by the charger from the cathode to the anode terminals.

It gives an overall voltage of 4 V, more than twice that of a standard alkaline battery. This gives much **better energy density than** other rechargeable batteries

Applications: They are used to operate laptop computers, mobile phones, telecommunication equipments, portable radios and TVs, pagers and aerospace applications.

Special properties of Li metal that make it advantageous to used an electrode material:
i) Light weight, (ii) low electrode potential (-3.05V), (iii) Highly reactive and (iv) high electrical conductivity.

FUEL CELLS

Fuel cells are defined as galvanic cells in which chemical energy of a fuel is directly converted into electrical energy by means of redox reactions involving fuels and oxidants.

Like any other electrochemical cell, the fuel cell has two electrodes and an electrolyte. However, the fuel and the oxidizing agents are continuously and separately supplied to the two electrodes of the cell, at which they undergo reactions. These cells are capable of supplying current as long as they are supplied with reactants.

A fuel cell essentially consists of the following arrangement:

Fuel / electrode/ electrolyte /electrode / oxidant

At anode, fuel undergoes oxidation: Fuel $\rightarrow$ Oxidation product + ne^-

At the cathode, the oxidant gets reduced: Oxidant + $ne^- \rightarrow$ Reduction products.

The electrons liberated from the oxidation process at the anode can perform useful work when they pass through the external circuit to the cathode.

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Difference between a fuel cell and a battery:

	Fuel cell	Battery
1.	Fuel cells need constant supply of reactants and the products are removed constantly.	Batteries are not be supplied with reactants constantly.
2.	They do not store chemical energy	They store chemical energy
3.	They are more efficient and not rechargeable	Some are rechargeable.

Advantages of fuel cells:
  (i)   High efficiency of energy conversion process (75%).
  (ii) They are eco-friendly as the products of the overall reactions are not toxic and hence pose no pollution problems.
  (i)   They can produce direct currents for long periods at a low cost.

Methanol-Oxygen fuel cell:

Methanol is one of the most electroactive organic fuels in the low temperature range. It is mainly because, (i) It has low carbon content. (ii) It possesses a readily oxidisable OH group and (iii) It has high solubility in aqueous electrolytes.

A typical methanol-oxygen fuel cell is shown in Fig. 4.

Methanol containing some sulphuric acid (3.7M) is circulated through the anode chamber. Pure oxygen is passes through the cathode chamber and sulphuric acid (which is electrolyte), is placed in the central compartment. Both the electrodes are made of platinum. A membrane is inserted adjacent to the cathode on the inner side to minimize diffusion of methanol into the cathode thereby reducing the concentration of methanol near the cathode. In the absence of a membrane, methanol diffuses through the electrolyte into the cathode and undergoes oxidation.
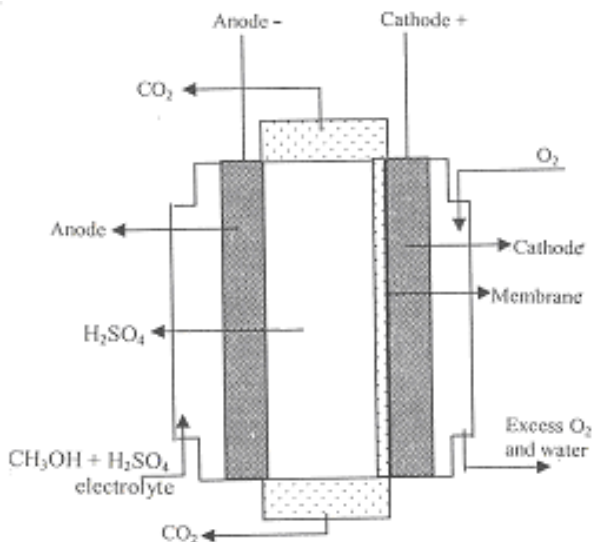

Fig.4. Methanol-oxygen fuel cell

Electrode reactions:

At anode: $\quad\quad\quad\quad\quad\quad CH_3OH \ (l) + H_2O \ (l) \ \rightarrow \ CO_2(g) + 6H^+(aq) + 6e^-$

At cathode: $\quad\quad\quad\quad 3/2O_2(g) + 6H^+(aq) + 6e^- \rightarrow 3H_2O \ (l).$

Overall reaction: CH_3OH (l) + $3/2O_2(g) \rightarrow CO_2(g) + 2H_2O$ (l).

The emf the cell is 1.20V at 25^0C. Anadvantage of the use of an acid electrolyte is that the CO_2, a product of the reaction can be removed easily. The use of alkali as electrolyte presents problems. The CO_2 produced is absorbed by the electrolyte and the electrolyte gradually converted into carbonate. This decreases the efficiency because of the increasing concentration polarization at the electrode surface and decreasing the conductivity of the electrolyte.
Applications: It is used in military applications and in large scale power production.

FLOW BATTERY

A flow battery is an electrochemical device that converts the chemical energy in the electro-active materials directly to electrical energy, similar to a conventional battery and fuel cells. A flow battery is an electrical storage device that is a cross between a conventional battery and a fuel cell. The electro-active materials in a flow battery, however, are stored mostly externally in an electrolyte and are introducedinto the device only during operation.Liquid electrolyte of metallic salts is pumped through a core that consists of a positive and negative electrode, separated by a membrane. The ion exchange that occurs between the cathode and anode generates electricity.

The fundamental difference between conventional batteries and flow cells is that energy is stored as the **electrode material** in conventional batteries but as the **electrolyte** in flow cells.

One of the biggest **advantages** of flow batteries is that they can be almost instantly recharged by replacing the **electrolyte**liquid, while simultaneously recovering the spent material for re-energization.

Different classes of flow cells (batteries) have been developed, including vanadium redox, hybrid membraneless and organic.

Vanadium redox flow battery:
The vanadium redox flow batteryconsists of an electrolyte comprised of vanadium and sulfuric acid flows over nonreactive carbon or carbon-filled polymer electrodes.The structure of vanadium redox flow batteries are schematically shown in fig. 5. During discharging, reduction occurs at the cathode and oxidation occurs at the anode. While these redox reactions occur, proton ions diffuse across the membrane and electrons transfer through an external circuit

Electrode reactions:
Negative electrode: $V^{2+} \leftrightarrow V^{3+} + e^-$
Positive electrode: $VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O$
Overall reaction:$V^{2+} + VO_2^+ + 2H^+ \leftrightarrow V^{3+} + VO^{2+} + H_2O$
The standard cell voltage for the all-vanadium redox flow batteries is 1.26 V.
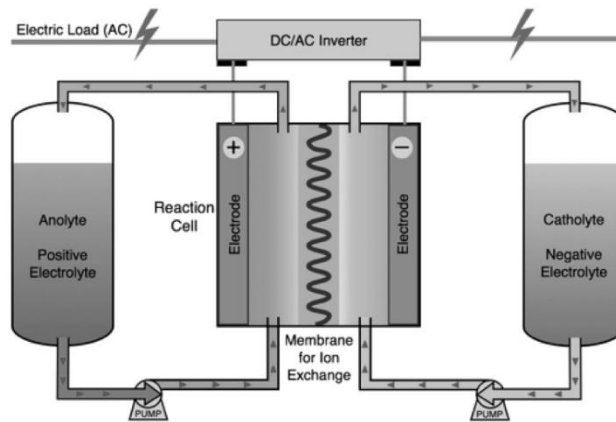
Fig. 5. Vanadium redox flow battery

Applications:

(i) Load balancing – where the battery is connected to an electrical grid to store excess electrical power during off-peak hours and release electrical power during peak demand periods.

(ii) Storing energy from renewable sources such as wind or solar for discharge during periods of peak demand.

(iii) UPS, where the battery is used if the main power fails to provide an uninterrupted supply.

(iv) Power conversion – because all cells share the same electrolyte/s. Therefore, the electrolyte/s may be charged using a given number of cells and discharged with a different number.

(v) Electric vehicles – Because flow batteries can be rapidly "recharged" by replacing the electrolyte, they can be used for applications where the vehicle needs to take on energy as fast as a combustion engined vehicle.

(vi) Stand-alone power system – An example of this is in cellphone base stations where no grid power is available. The battery can be used alongside solar or wind power sources to compensate for their fluctuating power levels and alongside a generator to make the most efficient use of it to save fuel.

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CORROSION SCIENCE

Introduction: Most of metals (except noble metals such as Au, Pt etc.) exist in combined forms as their oxides, carbonates, hydroxy carbonates, sulphides, chlorides and silicates etc. The extraction of metals from their ores is an endothermic process, energy being supplied in the form of heat or electrical energy. Consequently are relatively at higher energy state compared to their ores, and they have a natural tendency to revert back to their combined state. Therefore when metals are put into use in various forms, they combine with constituents of the environment and get converted into their compounds. Thus corrosion of metals can be considered as extractive metallurgy in reverse.
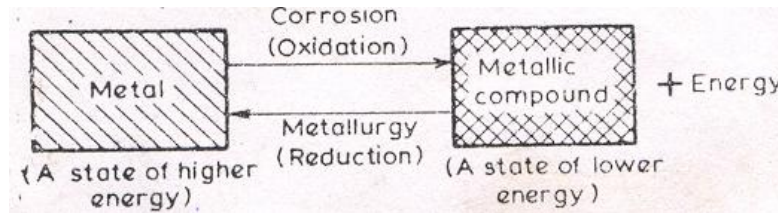

Fig.1.Corrosion and oxidation processes.

Definition: "Any process of destruction (or deterioration) and consequent loss of a solid metallic material, through an unwanted chemical or electrochemical attack by its environment, starting at its surface." is called corrosion.

Eg: (i) Rusting of iron, when exposed atmospheric conditions, a layer of reddish scale and powder of oxide is (F_3O_4) is formed and iron becomes weak.

(ii) Formation of green film of basic carbonates ($CuCO_3 + Cu(OH)_2$) on the surface of cupper, when exposed to moist-air containing carbon dioxide.

Corrosion may occur either in a dry environment or in an aqueous medium.

(i) **Dry or direct chemical corrosion:** Dry corrosion involves the direct attack of metals by dry gases mainly through chemical reactions. An important dry corrosion process is the attack of air or oxygen on the metal to form an oxide layer over the surface.

(ii) **Wet or electrochemical corrosion:** Wet corrosion, which is more common, involves reactions in aqueous medium. The conducting surface of the metal undergoes an electrochemical reaction with moisture and oxygen present in the atmosphere. This process can be explained on the basis of electrochemical theory of corrosion.

Electrochemical theory of corrosion (taking Fe as example):

When a metal, such as iron, is exposed to the environment, according to electrochemical theory the following electrochemical changes occur gradually.

(a) Formation of a large number of minute galvanic cells (anodic and cathodic areas).

(b) Corrosion (oxidation) takes place at the **anodic area** and electrons are liberated.

$$M \rightarrow M^{n+} + ne^-$$

Eg. When iron undergoes corrosion, $Fe \rightarrow Fe^{2+} + 2e^-$

(c) The electrons released at the anodic area are taken up by the cathodic area constituting corrosion current. Consumption of electrons with either by (i) evolution of hydrogen or (ii) absorption of oxygen depending on the nature of corrosive environment.

(i) Evolution of hydrogen takes place in the absence of oxygen.

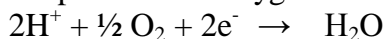(a) In acidic medium and in the absence of oxygen, the cathodic reaction is,

$$2H^+ + 2e^- \rightarrow H_2\uparrow$$
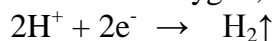
(b) In neutral or alkaline medium and in the absence of oxygen, hydroxide ions are formed with simultaneous liberation of hydrogen

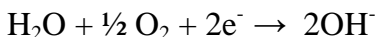$$2H_2O + 2e^- \rightarrow 2OH^- + H_2\uparrow$$
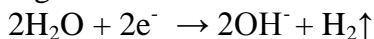
(ii) Absorption of oxygen takes place in the presence of oxygen

a) In acidic medium and in the presence of oxygen

$$2H^+ + ½ O_2 + 2e^- \rightarrow H_2O$$

(b) In neutral or alkaline medium and in the presence of oxygen, hydroxide ions are formed by the following reaction

$$H_2O + ½ O_2 + 2e^- \rightarrow 2OH^-$$

Corrosion of iron produces Fe^{2+} ions and OH^- ions at the anode and cathode sites respectively. These ions diffuse towards each other. Since smaller Fe^{2+} ions diffuse more rapidly than OH^- ions, their combination occurs more commonly near the cathodic region to produce insoluble $Fe(OH)_2$.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$
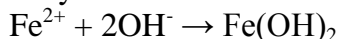
In an oxidizing environment, it is oxidized to ferric oxide and the yellow rust is hydrated ferric oxide (corrosion product).

$$2Fe(OH)_2 + ½ O_2 + H_2O \rightarrow Fe_2O_3.3H_2O.$$

In the presence of limited oxygen, ferrous hydroxide is converted into magnetic oxide of iron (F_3O_4) and is known as black rust (corrosion product).

$$3Fe(OH)_2 + ½ O_2 \rightarrow Fe_3O_4.3H_2O.$$
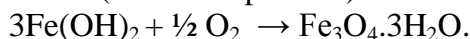
Types of corrosion:

(a) Differential metal corrosion (Galvanic corrosion):

When two dissimilar metals are in contact with each other in a corrosive conducting medium, the metal with lower electrode potential or more active metal (higher in electrochemical series) acts as anode and with higher electrode potential (lower in electrochemical series) acts as cathode. The potential difference between two metals is the cause or driving force for corrosion. The anodic metal undergoes corrosion and the cathodic metal generally un attacked.

Mechanism: *At anode*, $M \rightarrow M^{n+} + ne^-$ (Less noble metal)

At cathode, In acidic medium the corrosion occurs by the hydrogen evolution process; while in neutral or slightly alkaline medium, oxygen absorption occurs.

$$(a) \quad 2H^+ + 2e^- \rightarrow H_2\uparrow$$
$$(b) \ H_2O + ½ O_2 + 2e^- \rightarrow 2OH^-$$
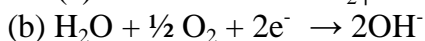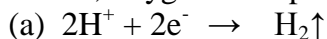
Thus, it is evident that the corrosion occurs at the anodic metal; while the cathodic part is protected from the attack.

Examples: (i) Steel screws in brass marine hardware (ii) Lead-antimony solder around copper wire (iii) Steel pipe connected to copper plumbing.

Galvanic series: In the electrochemical series (reduction electrode potential arranged down in an increasing order), metal high in the series is more anodic and undergoes corrosion faster than the metal below it. For example, Li corrodes faster than Mg; Zn corrodes faster than Fe; Fe corrodes faster than Sn; Cu corrodes faster than Ag and so on. However, some exceptions to this generalization are known. For example, Ti (above Ag in the electrochemical series) is less reactive than Ag. In Zn-Al couple, Zn (below Al in the electrochemical series) is corroded; while Al acts as cathodic and is protected. These observations, exactly opposite to that predicted by the emf series, are due to the fact that metals like Ti and Al develop, strongly adhering oxide layers on their surfaces, thereby making their effective electrode potential more positive (or less negative).

From the above, it is clear that electrochemical series does not account for the corrosion of all metals and alloys. Consequently, more practical series, called *galvanic series* have been prepared by studying the corrosion of metals and alloys in a given environment like sea-water. *An arrangement of metals and alloys in the increasing order of their corrosion resistance in the given environment is referred to as galvanic series (Table-1).*

Table-1. *Galvanic series*

1.	Mg	**Active** (or anodic)
2.	Mg alloys	
3.	Zn	
4.	Al	
5.	Cd	
6.	Al alloys	
7.	Mild steel	
8.	Cast iron	
9.	High Ni cast iron	
10.	Pb-Sn solder	
11.	Pb	
12.	Sn	
13.	Iconel	
14.	Ni-Mo-Fe alloys	
15.	Brasses	
16.	Monel (7=Ni, 30= Cu, rest=iron)	
17.	Siver solder	
18.	Cu	
19.	Ni	
20.	Cr stainless steel	
21.	18-8 Stainless steel	
22.	18-8 Mo Stainless steel	
23.	Ag	
24.	Ti	
25.	Graphite	
26.	Au	
27.	Pt	Noble (or cathodic)

(b) Differential aeration corrosion: Differential aeration corrosion occurs when a metal surface is exposed to differential air concentrations or oxygen concentrations. The part of the metal exposed to higher oxygen concentration acts as cathodic region and part of the metal exposed lower oxygen concentration acts as anodic region. Consequently, poorly oxygenated region undergoes corrosion.

At the anode (less O_2 concentration), $M \rightarrow M^{n+} + ne$

At the cathode (more O_2 concentration), $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

Definition: Corrosion of metals arising as a result of the formation of an oxygen concentration cell due to the uneven supply of air on the metal surface is known as differential aeration corrosion.

(i) Waterline corrosion: Waterline corrosion is a case of differential aeration corrosion, more prevalent in cases such as ocean going ships, water storage steel tanks, etc., in which a portion of the metal is always under water.

The waterline corrosion takes place due to the formation of differential oxygen concentration cells. The part of the metal below the water line is exposed only to dissolved

oxygen while the part above the water is exposed to higher oxygen concentration of the atmosphere. Thus, part of the metal below the water acts as anode and undergoes corrosion and part above the waterline is free from corrosion. A distinct brown line is formed just below the water line due to the deposition of rust.
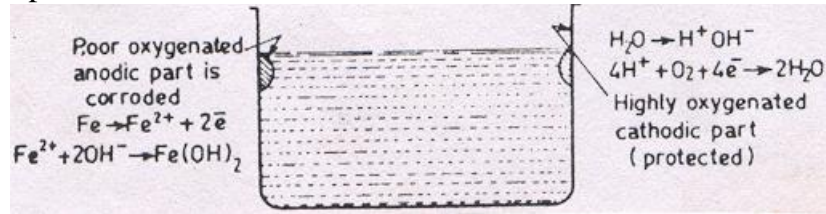

Fig. 2. Water line corrosion

(ii)Pitting corrosion: The pitting corrosion is generally initiated by the deposition of sand, scale, water drop, dust etc. or due to the break down of the protective film. The metal below the deposit is exposed to lower oxygen concentration, acts as anode and undergoes corrosion. The metal surrounding the deposit acts as cathode since it is exposed to higher concentration of oxygen. Because of small anodic area and large cathodic area, accelerated corrosion takes place below the deposit. Once corrosion product is formed, it further provides the condition for differential aeration below the corrosion product and surrounding metal parts. The pit grows and ultimately may case failure of the metal.
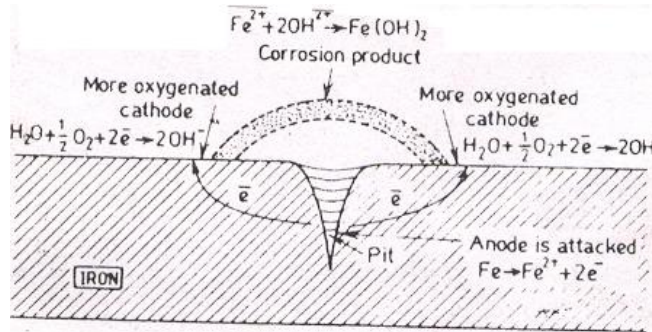

Fig.3. Pitting corrosion at the surface of iron.

Differential aeration corrosion is also observed in
   1) Less aerated areas in a machinery;
   2) Cracks which are not well aerated in metals;
   3) Points of contact which are less aerated in a wire screen;
   4) Bottom of an oil tank or bend of an oil pipe where water is trapped. Oil readily dissolves the oxygen in water creating differential oxygen concentration.

(c) Stress Corrosion: Stress corrosion is the combined effect of static tensile stresses and the corrosive environment on a metal. The corrosive agents are highly specific and selective such are: (a) caustic alkalis and strong nitrate solution for mild steel; (b) traces of ammonia for brass; (c) acid chloride solution for stainless steel.

Stress may result from mechanical operations such as poor design, riveting, cold working, welding, bending, pressing and quenching. In a corrosive environment, the stressed portion behaves anodically with respect to the unstressed portion and undergoes corrosion. At the stressed portion, the atoms are somewhat displayed creating an anodic zone of higher electrode potential. The stress produces strains resulting in localized zones of increased energy. These become so chemically-active that they are attacked even by a mild corrosive environment, resulting in the

formation of a crack, which grows and propagates in a plant (perpendicular to the operating stress), until failure occurs or it may stop, after progressing a finite distance.
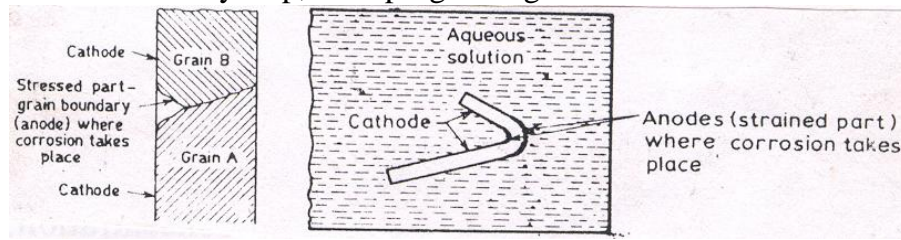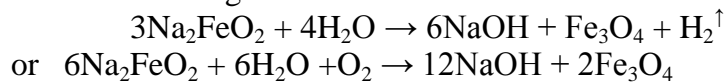

Fig.4. Stress corrosion

Caustic embrittlement: It is a very dangerous form of stress corrosion, occurring in mild steel exposed to alkaline solutions at high temperatures and stresses. The failure is often associated with steam-boilers and heat-transfer equipments in which water of high alkalinity attacks the mild steel plates, particularly at the crevices near rivets. Boiler-water, usually contains a certain proportion of sodium carbonate, added for water softening purposes. In high-pressure boilers, this breaks up to give sodium hydroxide and carbon dioxide, and boiler water become alkaline.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2\uparrow$$
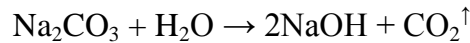
This very dilute alkaline boiler-water (in boiler) flows into minute hair-cracks and crevices (by capillary action), where water evaporates and the caustic soda concentration build up. This concentrated alkali dissolves iron as sodium ferroate (hypoferrite) in crevices, cracks, where the metal is stressed and the concentration of alkali is much higher than that in the body of the liquid. The sodium ferroate (Na_2FeO_2) decomposes, a short distance away from its point of formation, according to either of the following reactions:

$$3Na_2FeO_2 + 4H_2O \rightarrow 6NaOH + Fe_3O_4 + H_2\uparrow$$
$$or \quad 6Na_2FeO_2 + 6H_2O + O_2 \rightarrow 12NaOH + 2Fe_3O_4$$

Sodium hydroxide is regenerated and magnetite (Fe_3O_4) is precipitated, thereby enhancing further dissolution of iron.

Caustic embrittlement can be explained by considering the following electrochemical cell:

$$^+Iron \mid Concentrated\ NaOH \mid dilute\ NaOH \mid Iron^-$$

The iron surrounded by the dilute NaOH (main body) is the cathodic side; while the iron in contact with rather concentrated caustic soda (e.g, crevices, hair-cracks, rivets) is the anodic portion, undergoing corrosion and is thus dissolved.

Caustic embrittlement can be prevented by the addition of compounds such as sodium sulphate, tannin, phosphates, etc., which block the cracks or crevices, thereby preventing the infiltration of alkali.

Factors affecting rate of corrosion:
The rate and extent of corrosion, depends the following factors:
1. Related to nature of the metal: **(a) Electrode potential:** When two different metals exposed to the atmosphere are in contact with each other (galvanic corrosion), the potential difference between the anodic and the cathodic areas control the corrosion rate. Such a potential difference is referred to as the open circuit potential difference. Larger the difference in open circuit potential, higher is the rate of corrosion. For instance, the potential difference between iron and copper is 0.78V which is more than that between iron and tin (0.3V). Therefore, iron corrodes faster when in contact with copper than that with tin. Thus, farther the positions of the metals in the galvanic series, greater is the intensity of corrosion on the anodic metal. On this account, the use of

dissimilar metals should be avoided wherever possible. For example, bolt and nut or screw and washer should made of the same metal (or alloy) to avoid galvanic corrosion.

(b) Relative areas of the anodic and cathodic parts: When two dissimilar metals are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of cathodic part and the anodic part. Corrosion is more rapid and severe, and highly localized, if the anodic area is small and cathodic area is large (e.g., a small steel pipe fitted in a large copper tank), because the current density at smaller anodic area is much greater, and the demand for electrons (by large cathodic areas) can be met by smaller anodic areas by undergoing corrosion more briskly.

Tin, for instance, is cathodic to iron as seen from its position in electrochemical series. If during plating of tin on iron, some areas are not covered or some pin holes are left, there results a small anode and large cathode (Fig.5a). An intense localized corrosion occurs at the exposed small anodic surface. On the other hand, zinc plating on iron gives an anodic coating to iron since zinc is above Fe in the electrochemical series. Even if zinc plating peels off at some points intense corrosion of iron would not occur. This is because of formation of large anodic and small cathodic areas (Fig.5b).
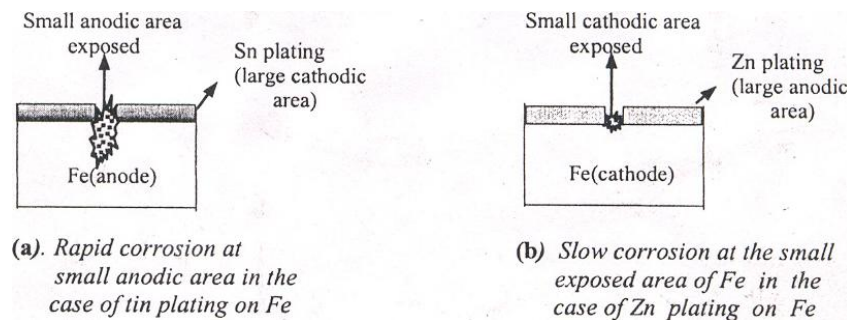

Fig. 5 Corrosion rate of iron at anodic and cathodic areas.

(c) Nature of corrosion product and tendency to form protective film: The corrosion product formed on the surface of the metal may or may not act as a protective film. If the corrosion product deposited is insoluble, stable, uniform and nonporous, it acts as a protective film preventing further corrosion of metal. A thin, invisible, impervious, continuous film formed on the surface acts as a barrier between the fresh metal and corrosion environment. On the other hand if the corrosion product is soluble, unstable, non uniform and porous, the fresh metal surface is continuously exposed to the corrosion environment and corrosion of the metal surface takes place continuously.

In oxidizing environments, metals like aluminium, chromium, titanium, etc., are highly passive as their oxides as corrosion products form protective films on the metal surface, preventing further corrosion. Metals such as iron, zinc, magnesium etc., do not form any protective film and are highly susceptible for continuous corrosion, when exposed to oxidizing environments.

(d) Hydrogen overvoltage: Metal with low hydrogen overvoltage on its surface is more susceptible for corrosion, when cathodic reaction is hydrogen evolution type. With low hydrogen overvoltage, hydrogen gas is liberated easily and thus the cathodic reaction rate is faster. This will make the anodic reaction also faster, thereby promoting overall corrosion reaction. When the hydrogen overvoltage on the metal surface is high, cathodic reaction is slower and the corrosion of the metal also becomes slower.

2. *Related to nature of environment:* (a) pH of the medium: In general, higher the acidity of the environment (low pH) higher is the rate of corrosion. At pH greater than 10, corrosion of iron practically ceases due to the formation of a protective coating of hydroxides of iron. Between pH 10 and 3, presence of oxygen is essential for corrosion of iron. A case in point of this phenomenon is that ships submerged for hundreds of years remains almost unaffected. However if the pH is lower than 3, severe corrosion occurs even in the absence of air due to the continuous evolution of hydrogen at the cathodic region.

(b) Temperature: In general, as the temperature is increased, the corrosion is accelerated. Increase in temperature results in an increase in the conductance of the aqueous medium and hence an increase in the diffusion rate. As a consequence, corrosion progresses faster at higher temperatures. In some cases, rise in temperature decreases passivity, which again leads to an increase in the corrosion rate.

(c) Humidity of air: Humidity of air is the deciding factor in atmospheric corrosion. Critical humidity is defined as the relative humidity above which the atmospheric corrosion rate of metal increases sharply. The value of critical humidity depends on the physical characteristics of the metal as well as nature of the corrosion products. The reason why corrosion of a metal becomes faster in humid atmosphere is that gases (CO_2, O_2, etc.) and vapours, present in atmosphere furnish water to the electrolyte, essential for setting up an electro-chemical corrosion cell. Moreover, the oxide film on a metal surface, although a solid body, yet possesses the property of absorbing moisture.

(d) Presence of impurities in atmosphere: Atmosphere, in the vicinity of industrial areas, contains corrosive gases like CO_2, H_2S, SO_2, and fumes of HCl, H_2SO_4, etc. In presence of these gases, the acidity of the liquid, adjacent to the metal surfaces, increases. This consequently, results in an increase of corrosion current, flowing in the local electro-chemical cells on the exposed metal surfaces. Similarly, in the marine atmosphere, the presence of sodium and other chlorides (of sea water) leads to increased conductivity of the liquid layer in contact with the metal surface, thereby corrosion is speeded up.

Corrosion control:

(a) Protective coatings:

(1) Inorganic coatings: Inorganic coatings are generally chemical conversion coatings. A surface layer of the metal is converted into a compound, by chemical or electrochemical reactions, which forms a barrier between the underlying metal surface and corrosion environment. Such coatings are particularly used an excellent base for paints, laquers oils and enamels.

(i) Anodizing (Anodized coating): Anodized coating is generally produced on non-ferrous metals like Al, Zn, Mg and their alloys by anodic oxidation process, in which the base metal is made as anode. It is carried out by passing a moderate direct current through a bath in which the metal or alloy is suspended from anode. The bath usually contains sulphuric acid, chromic acid, phosphoric acid, oxalic acid or boric acid.

Aluminium coatings are formed by electrolysis in a suitable acid electrolyte (sulphuric, chromic, oxalic or phosphoric acid) at moderate temperature ($35\text{-}40^0C$) and moderate current densities (10-20 $mAcm^{-2}$). The coating forms as a result of progressive oxidation, starting at the aluminum surface. An oxide film, initially very thin, grows from the metal surface outwards and increases in thickness as oxidation continuous at aluminium anode. The outer part of the oxide film formed is very porous and considerably softer than the layer directly adjoining the metal surface. The minute exposed pores can be made more corrosion-resistant by the process of

sealing, which consists of exposing film to boiling water. This treatment porous alumina at the surface of coating into its monohydrate ($Al_2O_3.H_2O$), which occupies more volume, there-by the pores are sealed. Anodized articles are used as soap boxes, tiffin carriers, window frames, etc.

(ii) Phosphating (Phosphate coating): Phosphate coating is obtained generally on steel surface by converting the surface metal atoms into their phosphates by chemical or electrochemical reactions. Chemical phosphating includes dipping and spraying and electrochemical phosphating includes cathodic and anodic phosphating. The phosphating bath contains three essential components:

(1) Free phosphoric acid. (2) A primary metal phosphate like Fe, Mn and Zn phosphates and (3) An accelerator such as nitrates, nitrites, chlorates, H_2O_2 etc.

The pH is usually within the range 1.8 and 3.2. Lower pH are favoured for immersion deposits while spray processes often employ a high pH. The reactions include dissolution of metal as ions, forming a phosphate with the bath solution which subsequently gets deposited on the surface of the metal.

Originally phosphate coating was applied only on iron and steel. But now it has been extended to Zn, Al and their alloys.

The most important application of phosphate coating is as an under layer for paint finishers. Phosphating is a standard pretreatment before painting of automotive bodies and steel sheet fabrications such as refrigerators and washing machines. Phosphating is widely applied for the protection of metal parts which cannot be painted or plated, such as nuts, bolts, the moving parts of machinery; etc.

(2) Metal coatings: Deposition of a protective metal over the surface of a base metal is called metal coating. Metal coatings are applied by electrodeposition, flame spraying, calding, hot dipping, diffusion coating and vapor deposition.

(i) Anodic metal coating: Anodic coatings are produced by coating a base metal with more active metals which are anodic to the base metal. For example, iron is coated with anodic and more active metals such as Zn and Mg. The one of the important characteristics of anodic coating is that, even if the coating is ruptured, the base metal does not undergoes corrosion. The exposed surface of the metal is cathodic with respect to the coating metal and the coating metal preferentially undergoes corrosion. The protection is ensured as long as the anodic coating metal is still present on the surface. Therefore, anodic coating is also known as sacrificial coating. Galvanization is a familiar example for anodic coating and is extensively used to protect iron and steel objects.

Galvanizing (Galvanization) is a process of coating a base metal surface with zinc metal. Galvanization is carried out by hot dipping method. The galvanization process involves the following steps.

1. The metal surface is first washed with organic solvents to remove oil and grease deposits.
2. Rust and other deposits are removed by washing with dilute sulphuric acid (pickiling).
3. Finally the article is washed with water and air dried.
4. The article is then dipped in a bath of molten zinc, maintained at 425-430^{0}C and covered with a flux of ammonium chloride to prevent the oxidation of molten zinc.
5. The superfluous (excess) zinc on the surface is removed by passing through a pair of hot rollers, which wipes out excess of zinc coating and produces a thin coating.

Uses: It is most widely used for protection of iron from atmospheric corrosion in the form of roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc. It may be pointed here that

zinc gets dissolved in dilute acids, to form highly toxic (or poisonous) compounds. Hence, galvanized utensils cannot be used for preparation and storing foodstuffs, especially acidic ones.

(ii) Cathodic metal coating: Cathodic coatings are produced by coating a base metal with a more noble metal which is cathodic. The metals such as Cu, Ni, Sn, Ag are commonly used as cathodic coatings on steel. These coating metals are less reactive than the base metal and are less susceptible for corrosion. The cathodic coating provides protection only when it is undamaged, continuous and non porous. When the coating is discontinuous, an intense localized corrosion occurs due to the setting up of a galvanic cell that consists of a large cathodic area and small anodic area.

   Tinning is a process of coating a base metal with tin. Tinning of iron or steel is carried out by hot dipping method and the process involves the following steps.
1. The metal surface is first washed with organic solvents to remove oil and grease deposits.
2. Rust and other deposits are removed by washing with dilute sulphuric acid (pickling).
3. Finally the article is washed with water and air dried.
4. The clean and dry sheet is passed through molten zinc chloride flux. The flux helps in molten metal to adhere on the metal surface.
5. It is then passed through a tank that contains molten tin, maintained at $219\text{-}310^0C$.
6. Finally passed through a series of rollers immersed in palm oil. The rollers wipe out excess tin deposit and produce a continuous, thin coating of tin on the sheet. The oil prevents the oxidation of the tin coated surface.

Uses: Because of non-toxic nature of tin, tinning is widely used for coating steel, Cu, and brass sheets, used for manufacturing containers of storing foodstuffs, ghee, oils, kerosene and packing food materials. Tinned-copper sheets are employed for making cooking utensils and refrigeration equipments.

(c) Cathodic protection: Cathodic protection is method of protecting a metal or alloy from corrosion by converting it completely into cathodic and no part of it is allowed to act as anode. The corrosion of metal takes place at anodic region whereas at the cathodic region metal is unaffected. Therefore corrosion can be prevented by eliminating the anodic sites and converting entire metal into cathodic area.

   Cathodic protection can be achieved by the following methods: (i) Sacrificial anode method (ii) Impressed current method.

(i) Sacrificial anode method: In this protection method, the metallic structure (to be protected) is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly; while the parent structure (cathodic) is protected. The more active so-employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys. Important applications of sacrificial anodic method include protection of buried pipelines, underground cables, marine structures, ship-hulls, water-tanks. Piers, etc. (Fig.6).
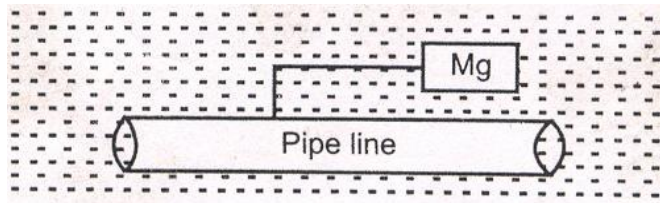
Fig.6. Cathodic protection by sacrificial anode method.

(ii) Impressed current method: In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. Usually, the impressed current is derived from a direct current source (like battery or rectifier on a.c. line) with an insoluble anode (like graphite, high silicon iron, scrap iron stainless steel or platinum). Usually, a sufficient d.c. current is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium), and connected to the metallic structure to be protected (Fig.7). This type of cathodic protection has been applied to open-box coolers, water-tanks, buried or water pipes, condensers, transmission line towers etc.
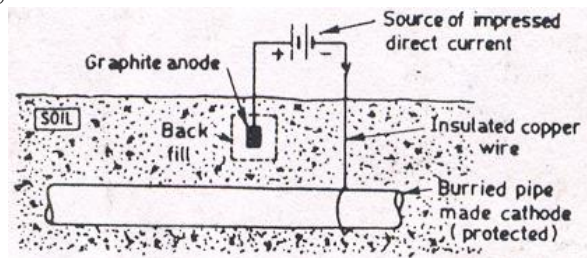

Fig.7. Impressed current method

METAL FINISHING

Metal finishing and its technological importance:
Definition: The term metal finishing applies to all surface processes carried out in order to change surface properties by deposition of layer of another metal or a polymer or by the formation of an oxide film.
The important metal finishing techniques are
- (i)   Electroplating of metals, alloys and composites.
- (ii)   Electrolessplating of metals, alloys and composites.
- (iii)   Immersion plating of metals (involves chemical displacement of metals).
- (iv)   Chemical conversion coatings based on metal compounds (involves the deposition of inorganic coatings such as oxides, chromates, phosphates and their mixtures. E.g., anodizing, phosphating, chromating).
- (v)   Electrophoretic painting which involves painting on electrically charged conducting surface such as motor car body.

Essentials of metal finishing:
The fundamental principles governing metal finishing are (i) polarization (ii) decomposition voltage and (iii) over voltage.
Polarization: Polarization is an electrode phenomenon. The electrode potential in a cell is determined by the Nernst equation:

$$E = E^0 + \frac{0.0591}{n}\log [M^{n+}]$$

where E^0 is the standard electrode potential and $[M^{n+}]$ is the concentration of the metal ion surrounding the electrode surface at equilibrium. When electric current is passed, the metal ion concentration in the vicinity of the electrode surface decreases, due to the reduction of some of the metal ions to metal atoms.

$$M^{n+} + ne^- \rightarrow M$$
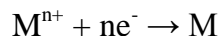
Consequently, there is a change in the value of electrode potential. However, the equilibrium is re-established as the ions from the bulk of the solution diffuse towards the electrode, due to existence of concentration gradient between the bulk of the solution and around the electrode surface. If the diffusion is slow, the electrode potential changes and in such a situation the electrode is said to get polarized.
Definition: Polarization is defined as a process where there is a variation of electrode potential due to inadequate supply of species from the bulk of the solution to the electrode.
 Polarization leads to accumulation of charge on electrode. Thus, polarized galvanic cells develop smaller potential than theoretically predicted. Polarized electrolytic cells lead to the use of a potential more negative than required in order to maintain a given current. Electrode polarization depends on several factors.
- (i)   *Size of the electrode*: Large surface area of the electrode decreases the polarization effects.
- (ii) *Nature of electrode surface:* Smooth surface of the electrode possesses higher polarization effects than rough surfaces. For example, polarization effects on platinum black electrode (black platinum covered with a layer of platinum particles) is much less than that on smooth platinum electrode.
- (iii) *Concentration of electrolyte:* Low concentration of electrolyte decreases the polarization effects.

(iv) *Temperature:* Polarization effects are minimized by increasing the temperature, since rate of ions increases.

(v) *Stirring of electrolytic solution:* Stirring help in minimizing the polarization effects.

(vi) *Use of depolarizer:* Use of strong oxidizing agents (e.g., chromic acid, nitric acid) as depolarizer help in converting evolved hydrogen into water. In this way, hydrogen in not permitted to be adsorbed on the electrode, thereby polarization effects are reduced.

Decomposition potential (decomposition voltage):

When electrolysis is carried out, the products of electrolysis accumulate around the electrodes. This causes change in concentration around the electrodes and an opposing emf (called back emf) is produced. For example, when a voltage is applied between two platinum electrodes dipping in dilute sulphuric acid solution, at once the electrolysis of water starts evolving hydrogen and oxygen. But electrolysis stops very soon, because of back emf (produced by the adsorption of evolved gases on the two electrodes) is greater than the applied voltage. Now if we increase the applied voltage slowly, the electrolysis proceeds smoothly, when the applied voltage just exceeds the back emf. Thus, decomposition potential is equal to back emf.

Definition: The minimum potential which must be applied between the two electrodes immersed in the given electrolytic solution in order to bring about continuous electrolytic decomposition is called decomposition potential.

The decomposition voltage can be determined using an electrolytic cell shown in Fig.1. The cell consists of two platinum electrodes immersed in the electrolyte. The voltage is varied by moving the contact maker D along the wire AB and the current passing through the cell is measured using an ammeter. If a dilute solution of an acid or base is taken in the cell, at low voltages no reaction is found to occur and there is a very slight increase in the current. On increasing the voltage slightly above 1.7V, a sudden evolution of H_2 and O_2 at the electrodes is noticed. This is accompanied by an abrupt increase in the current. The applied voltage of 1.7V is the decomposition voltage for dilute acids and bases.
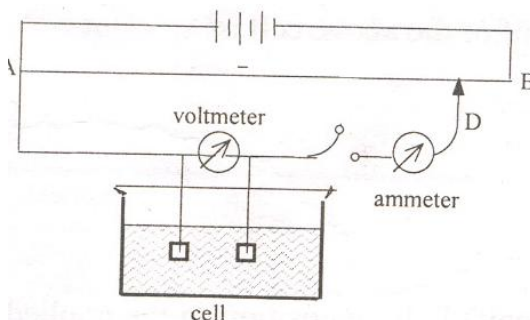

Fig. 1 Electrolytic cell

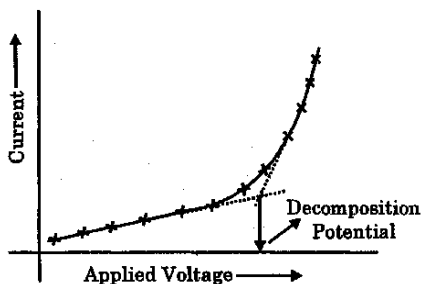When current is plotted against voltage, a curve of the type shown in Fig.2 is obtained.

Fig. 2 Curve showing decomposition potential

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It is clear from the figure that the increase in current in proportion to the voltage occurs only after a certain potential (decomposition potential). If voltage is increased further current also increases. Below the decomposition potential the increase in current only marginal indicating that no electrolysis is taking place.

$$E_d = E_{cathode} - E_{anode}$$

The decomposition voltage of an electrolyte is of the same magnitude as the emf set up by the cell resulting from electrolysis.

Significance of decomposition potential: Decomposition potential plays a very important role in*(a) Electroplating:* The minimum potential required for electroplating of a metal under a given set of bath conditions is known by decomposition potential.

(b) Separation of metals: A solution containing copper and zinc ions can be separated by electrolysis. Since the decomposition potential of copper is low (1.2V), so at this voltage, only copper is deposited. When all copper is deposited, zinc ions get deposited latter at a higher decomposition potential (2.55V).

(c) *Refining of metals:* A particular metals can made to get deposited on cathode by applying a potential equal to its decomposition potential (electrolytic refining).

Over voltage (over potential):
Normally, electrolysis takes place continuously when the applied voltage is slightly more than the decomposition potential. However, in few cases, it is observed that electrolysis does not occur, until and unless a potential higher than the theoretical decomposition potential is applied. For example, the theoretical decomposition potential value for the electrolysis of dilute H_2SO_4 solution with Pt electrode is 1.30V, but actual decomposition takes place at a potential value of 1.70V. Therefore oxygen over voltage on Pt = 0.4V. This is known as over voltage and is represented by η.

Definition: Over voltage is defined as the excess voltage that has to be applied above the theoretical decomposition potential to start electrolysis.

η = Experimental decomposition potential – Theoretical decomposition potential.

Therefore, the decomposition potential E_d for such systems over potential observed as given as

$E_d = E_{cathode} - E_{anode} + η$

For evolution of hydrogen gas, this potential difference is called hydrogen over voltage. Hydrogen overvoltage is a measure of the liberation of hydrogen gas from the electrode surface. A lower hydrogen overvoltage indicates a quick release of hydrogen gas.Table.1 gives the hydrogen over voltage of few metals.
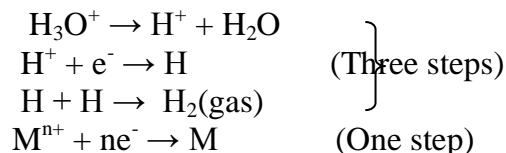
Table-1. Hydrogen over voltage (current density = $0.01 Am^{-2}$)

Electrode	Pt (black)	Pt (smooth)	Cu	Bi	Sn	Cd	Zn	Pb	Hg
η, V	0.01	0.09	0.14	0.19	0.39	0.40	0.50	0.64	0.80

Factors affecting the over voltage values:
(i) Nature and physical state of metals employed as electrodes: Rough electrodes (like platinized platinum) possesses lower overvoltage than smooth electrodes (like smooth platinum). This is because platinized platinum possesses much larger surface area than the smooth platinum. On the other hand, soft electrodes (Hg) possess much higher over voltages.

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(ii) *Nature of the substance deposited*: In general, metals have low overvoltage than that of hydrogen. This is because the liberation of H_2 gas on electrode surface takes place in three steps; while, the deposition of metals over electrode surface takes place in one step only.

$$H_3O^+ \rightarrow H^+ + H_2O$$
$$H^+ + e^- \rightarrow H \qquad \text{(Three steps)}$$
$$H + H \rightarrow H_2(gas)$$
$$M^{n+} + ne^- \rightarrow M \qquad \text{(One step)}$$

(iii) Current density (current per unit area of the electrode surface): Over voltage increases with increase in current density.

(iv) Temperature: Over voltage decreases with increase in temperature.

(v) Rate of stirring of the electrolyte: Stirring results in reduction of concentration gradient existing in immediate vicinity of electrode. Overvoltage increase with increase of concentration gradient. Thus, stirring reduces overvoltage.

Significance: The concept of overvoltage is used in the electrolysis for deposition of metals. For example, according to electrode potential (E^0) values, metals with higher electrode potentials than hydrogen will be preferentially deposited before H_2 set free. In the cases of metals with lesser E^0 values (zinc, cadmium etc.) than hydrogen we expect the liberation of H_2 in preference to metals. But in many such cases, the metal gets deposited rather than H_2 due to the hydrogen over voltage.

ELECTROPLATING:

Definition: Electroplating is the deposition of metal, by electrolysis, over the surface of a substrate; the latter may be another metal, polymer, ceramic or a composite. Alloy or metal-polymer or metal-composite deposition is also carried out by electroplating.

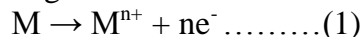The following types of electrodeposition are in practice.

(i) Single metals: the most important are Sn, Cu, Ni, Cr, Zn, Cr, Pb, Ag, Au and Pt.

(ii) Alloys: including Cu-Zn, Cu-Sn, Pb-Sn, Sn-Ni, Ni-Co, Ni-Cr and Ni-Fe.

(ii) Composites: metals containing dispersed solids such as PTFE (Teflon), Al_2O_3 WC, diamond, SiC, Cr_3C_2 and graphite.

Principles of electrodeposition: The electrodeposition is carried out by electrolyzing a suitable salt solution of the metal being plated. The substrate is the cathode and the anode is usually the pure metal. On electrolysis, the anode dissolves into the electrolytic bath and the metal ions from the bath solution are deposited as metal over the cathode. The reactions taking place for an electrolyte MA are given below:
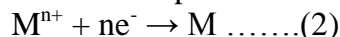
The electrolyte (MA) ionizes in aqueous solution

$$MA (aq) \rightleftharpoons M^{n+}(aq) + A^{n-}(aq)$$
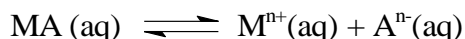
At anode, the electrode dissolves giving raise to metal ions
$$M \rightarrow M^{n+} + ne^- \ldots\ldots\ldots(1)$$
At cathode, the metal ions get reduced and are deposited as metal atoms
$$M^{n+} + ne^- \rightarrow M \ldots\ldots(2)$$
In an ideal situation the conditions of electrolysis are controlled in such a way that the current efficiency of the reactions (1) and (2) are equal so that the concentration of M^{n+} remains the same in the electrolyte. In some cases where an inert anode is used, the main anode reaction is oxygen evolution and hence metal ions are added in the form of metal salt to the electrolyte to maintain the concentration.

$$H_2O \rightarrow \frac{1}{2} O_2\uparrow + 2H^+ + 2e^-$$
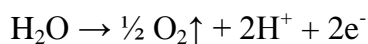
In acid conditions H_2 may get liberated at the cathode as a side reaction

$$H^+ + e^- \rightarrow \frac{1}{2} H_2$$
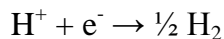
It is necessary to have a highly conducting electrolytic solution and current density ($mA\ cm^{-2}$) is adjusted so as to get a good deposit.

Mechanism of electrodeposition: Deposition of metal is similar to crystal growth since metals have well defined crystal structures. Electrodepositon takes place in two distinct phases. In the first phase, formation of nuclei takes place covering the electrode with a few atomic layers of the metal. In the second phase, growth of the deposited resulting in the thickening of the layer into a macroscopic (1-10 μm thick) deposit takes place. Formation of nuclei requires a high overvoltage. However, nuclei once formed will grow quite rapidly at a relatively low overvoltage. The atoms (adatoms) that are formed during the plating process on the crystal plane quickly move and occupy favourable sites. The most favourable site is kink site where the atom can interact with three neighbours. Atoms also occupy less favourable sites such as edge site (two neighbours) or just remain as adatoms (one neighbour). The latter diffuse to more favourable sites of redissolve. The overall phase growth sequently takes place as follows:

   (a) Mass transport in solution by diffusion of ions to the electrode surface.
   (b) Electron transfer to form adatom and
   (c) Surface diffusion i.e., the diffusion of the adatoms across the surface into the most favourable positions (kink sites).

A good electrodeposit is characterized by good adhesion, fine-grained texture, uniformity in thickness, good covering power and brightness. Such a deposit is seen if well formed spirals, blocks and layers are allowed to form on the surface.

A poor deposit has macroscale features such as steps, ridges and polycrystalline block growth resulting in a deposit which is coarsely crystalline, nonuniform and dull in appearance.Itis characterized by an outward growth often resulting in a deposit with powdery (burnt) texture. During plating operation, the factors are so adjusted that steps (b) and (c) predominate.

Effect of plating variables on the nature of electrodeposit:
(1) Current density of deposition: The current density (c.d) of deposition is defined as the current per unit area generally expressed in milliamperes per square centimeter (mA /cm^2) of the electrode surface. As the applied voltage is increased the current density rises till it reaches a limiting value.

At low current densities, surface diffusion is fast compared with electron transfer and the adatoms finds the most favourable position (kink sites) resulting in a well formed deposit. As the current density is increased, surface diffusion is slowed down compared to the electron transfer and the adatoms may not reach the most favourable positions. Further, at high potentials, number of nuclei formed may also increase. These may lead to a less ordered deposit with macroscale features.

At very high current densities (below limiting current region) mass transport predominates in solution resulting in a bad deposit with rough and powdery texture which is poorly adherent to surface.

At very high current densities above the limiting current, hydrogen evolution on the surface predominates causing a fast depletion of H^+ ions in the vicinity of the cathode. This results in

dispersed powders containing oxides and hydroxides of the metal. In practice, *optimum current density* for a particular deposition is actually determined and used so as to get a good deposit.

(2) Plating bath: The bath contains the solution used for plating. It is normally a mixture of metal ion solution, other electrolytes, complexing agents and various organic additives added to improve the nature of the deposit.

(a) Metal ion concentration and electrolytes: Normally, metal ion concentration (either as simple or complex ion) is moderate (about 1-3 mole/dm^3). By employing still higher metal-ion concentration, the mass transfer process decreases, thereby badly affecting the quality of the deposit. Moderate metal ion concentration, however, yields very adherent coating films. For getting thick deposit of metal, somewhat higher metal ion concentration is used.

Electrolytes are also added in high concentrations to increase the conductivity of the plating bath. Electrolytes do not participate in the electrode reactions but only increase the conductivity of the plating and sometimes exert buffer action and control the variation of pH.

(b) Complexing agents: The metal ion is converted into a complex ion by the addition of suitable complexing agents so as to get a fine-grained and more adherent deposits than that obtained from simple ion solutions. Complex ions are used
(i) To prevent the chemical reaction between the cathode metal and plating ions (e.g., in plating Cu on Fe or steel, copper ion is complexed to prevent the reaction $Cu^{2+} + Fe \rightarrow Cu + Fe^{2+}$).
(ii) To make the potential of the plating ion more negative so that the plating takes place at lower potential.
(iii) To prevent the passivation of anodes so that anodes dissolves easily and thus increase the current efficiency (e.g., Chloride ions in low concentration is used in many baths).
(iv) To improving the throwing power of the plating bath.
The most frequently used complexing agents are cyanides, hydroxides and sulphamates. Cu. Ag, Au, Zn and Cd are plated as smooth deposits and with maximum efficiency in the presence of cyanide ions.

(c) Organic additives: Certain organic compounds added to the plating baths have a remarkable influence on the nature of the electrodeposit. They modify the *structure, morphology and properties of the electrodeposit*. These include brighteners, levelers, structure modifiers and wetting agents.
(i) Brighteners: For a deposit to be bright, the light falling on the surface should be reflected and not scattered. This happens when the grain size of the deposit is lower than the wavelength of the incident light. Brighteners are added to produce microscopically fine deposits. These plate over the metallic surface and probably function by encouraging the plating to the substrate surface and inhibiting the plating perpendicular to the surface. Examples: Aromatic sulphones or sulphonates and molecules containing C≡N, N=C=S, C=O groups (e.g., thiourea and coumarin).
(ii) Levellers: Plating takes place rapidly on certain regions such as on dislocations where the diffusion of ions is faster resulting in a deposit of uneven thickness. Levellers help to produce a level deposit by getting adsorbed at regions where rapid deposition takes place. Thus adsorbed additives reduce the rate of electron transfer at such places. Many brighteners also act as levelers. Example: Sodium allyl sulphonate is used as a leveler for nickel deposition.
(iii) Structure modifiers (Stress relievers): Structure modifiers modify the structure of the deposit in such a way as to alter the deposit properties. For example, all electrodeposits are associated

with internal stress (due to lattice misfit) and may give away to impact if the stress levels are too high. Sometimes this results in microcracking of the deposit. Example: Saccharin.

(iv) Wetting agents: During the process of electroplating hydrogen gas is evolved on the cathode. Wetting agents are added to release the gas bubbles from the surface. They also improve the leveling and uniformity of the deposit and reduce the deposit brittleness. In the absence of wetting agents, the gas bubbles may get entrapped within the plated metal and try to escape after the plating process. This often makes the substrate metal itself brittle when subsequently heat treated (hydrogen embrittlement).Example: Sodium lauryl sulphate.

(3) pH: At low pH values, evolution of hydrogen occurs on the cathode resulting in a burnt deposit. In such cases pH has to be increased. On the other hand at higher pH values the electrode surface gets coated with insoluble hydroxides. Therefore the optimum pH range for the most of the plating processes is from 4 to 8, i.e., slightly acid or slightly alkaline. The desired pH in the plating process is maintained using buffers. Example: Borate buffer is used in nickel plating and citrate buffer in gold plating.

(4) Temperature: A good deposit is formed at slightly elevated temperatures because of the increase in the surface diffusion of ions. However, high temperatures may lead to hydrogen evolution on the cathode, corrosion of process equipment and sometimes decomposition of the organic additives. At moderate temperatures, surface diffusion is more than the hydrogen evolution and hence plating of many metals carried out between 35 and 60^0C.

(5) Throwing power of the plating bath: The ability of a plating bath to give a uniform and even deposit on the entire surface of the object is measured by its throwing power. This is of particular importance in objects which have complex shapes. For example, plating in holes and recesses of the objects takes place less uniformly than on even because the former points are at a lower over potential.If the distribution of the deposit is uniform, irrespective of the shape of the object, throwing power is said to be good.

Components of electroplating:

A description of a rectangular tank (vat) plating process as shown in Fig.3 is given below.
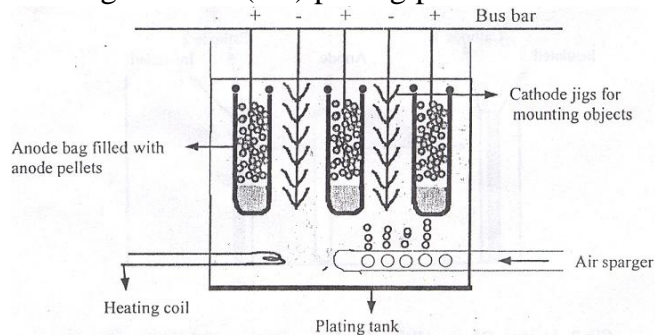

Fig.3. Electroplating process using a rectangular plating tank with jigs for mounting objects

(a) Plating tank: They are usually made of wood or steel with a suitable lining of ceramic or polymeric material on the inside which can provide thermal insulation.

(b) Heating equipment: Many electrodeposition processes operate at moderate temperatures. Heating of the plating bath solution may be done either by heating coils or by hot gases. To introduce convection in the electrolyte, air (if oxygen does not interfere) spargers are used.

35

(c) Plating bath solution: The plating bath must be highly conducting solution of the metal to be plated. Non-participating electrolytes are added to increase the conductivity and throwing power. Buffers are sometimes added to maintain the pH and additives to get bright and improved deposit. The level of the electrolyte in the tank must be sufficiently high to completely cover the cathode and sufficient area of the anode.

(d) Electrical equipment: For the plating operations a dc voltage of -8 to -12V operating at a current between 1 and 200 mA cm^{-2} is needed. Motor generators or dc rectifier units are used for the purpose. There must be provision to regulate the voltage and current. High overpotential is needed to produce nucleation in the initial stages. The current is maintained at the optimum level so as to get a good deposit.

(e) Filters: The plating bath solution must be regularly and thoroughly filtered to separate metal particles, and other solid impurities which otherwise may affect smooth deposition. This is done by using pumps and filters. The anode sludge may be retained by covering the anode with cotton bags.

(f) Electrodes-anode and cathode: The dc power is supplied to electrode baths or tanks by means of copper, brass or aluminium bus bars. These are positioned above the tank and run full length of the tank. The anodes and substrate (made the cathodes) are suspended from the bus bars. Anodes are usually made of the same as the metal ion to be plated. In some cases insoluble anodes are used (for example in chromium plating). The anode may be rods or plates or even pellets taken in a titanium mesh basket (for example in nickel plating). For small objects, jigs connected to the bus bars are used to hold the components. The electrodes are placed in such a way that a uniform current distribution is achieved. Auxiliary anodes may also be used to get a good throwing power.

Electroplating process:
The plating process is carried out by pretreating the object followed by electrolysis.

Pretreatment: All metallic surfaces (substrate surface) are associated with greasy materials or a thin film of metallic oxide as scale. The substrate surface should be made free from dirt, oil and grease. A typical procedure employed for this purpose is given below:

(i) Removal of organic impurities (greases): Organic solvents such as toluene, trichloroethylene and methylene chloride are used to remove organic matter and grease on the surface. Removal of these impurities is also effected by aqueous alkali treatment usually assisted by making the surface cathodic (30-80 mA cm^{-2}) at 60-80^{0}C. This increases the pH and catalyses the hydrolysis of fats. At the same time hydrogen liberated on the electrode removes the organic impurities.

(ii) Pickling, removal of scale and oxide films: The excess alkali is removed by immersion in 10% sulphuric acid. This also removes any oxide scale or rust on the surface. An effective removal of oxide scale on the surface is to pickle in sulphuric acid making the surface anodic (100 mA cm^{-2}).

(iii) Polishing: Mechanical or electropolishing is given to get a polished surface. Mechanical polishing involves grinding using silicon carbide abrasion wheels. This is followed by sand blasting and mechanical buffing to get a bright lustrous surface. Electropolishing involves the anodic dissolution of the metal.

(iv) Rinsing and drying: The object is finally rinsed with deionized water preferably in hot condition and dried before it is subjected to electroplating.
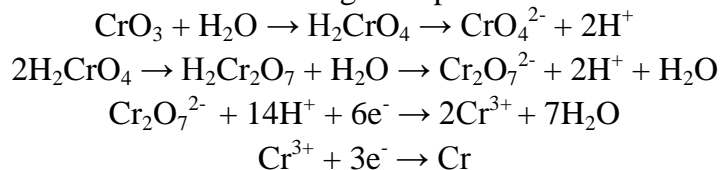
Electrolysis: After the pretreatment, the anode and the object are connected respectively to the positive and negative terminals of the bus bars (or jigs) and are placed in the electrolyte. The electrolyte is maintained at the desired temperature. The plating operation is conducted at the suitable voltage by maintaining the current density for the required time to get a smooth deposit of the metal on the cathode. In general, the thickness of the deposit ranges from 0.01 to 100 μm,

depending up on the application. The time required for electroplating varies from a few seconds to thirty minutes. The conditions under which electroplating of Chromium is given below.

Electroplating of Chromium:

	Chromic acid bath
Plating bath solution	Chromic acid (CrO_3) and H_2SO_4 in 100:1 proportion
Operating temperature	$45\text{-}60^0C$
Current density	$100\text{-}200$ mAcm^{-2}
Current efficiency	8-12%
Anode	Insoluble anodes- Pb-Sb or Pb-Sn coated with PbO_2 or stainless steel
Cathode	Object to be coated; pretreated
Applications	Decorative and corrosion resistant finish

The plating bath contains CrO_3 in which Cr is in +6 oxidation state. This is reduced +3 oxidation state by a series of complex reactions in the presence of SO_4^{2-}(catalyst) furnished byH_2SO_4. Cr^{3+} ions are reduced to elemental chromium which gets deposited on the substrate.

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \rightarrow CrO_4^{2-} + 2H^+$$
$$2H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_2O \rightarrow Cr_2O_7^{2-} + 2H^+ + H_2O$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
$$Cr^{3+} + 3e^- \rightarrow Cr$$

The amount of Cr^{3+}ions should be restricted in order to obtain good deposit. Insoluble anodes like Pb-Sb or Pb-Sn alloys covered with a layer of PbO_2 which oxidize Cr^{3+} to $Cr^{6+}$are used thus controlling the Cr^{3+}concentration.

$$2Cr^{3+} + 3\ O_2\ \rightarrow 2CrO_3 + 6e^-$$
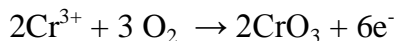
Chromium anodes are not used in Cr plating because (i) Chromium metal passivates strongly in acid sulphate medium.(ii) Chromium anode gives rise to Cr^{3+}ions on dissolution therefore in the presence of large concentration of Cr^{3+} ions, a black Cr deposit is obtained.

ELECTROLESS PLATING:

Definition: Electroless plating is the controlled deposition of a continuous film of a metal from its salt solution on to a catalytically active surface by a suitable reducing agent without using electrical energy.

The reducing agent brings about the reduction of the metallic ions to the metal which gets plated over a catalytic surface. The driving force in electroless plating is an autocatalytic redox reaction on a pretreated active surface.

$$\text{Metal ion + Reducing agent} \xrightarrow{\text{catalyst surface}} \text{Metal + Oxidized product}$$
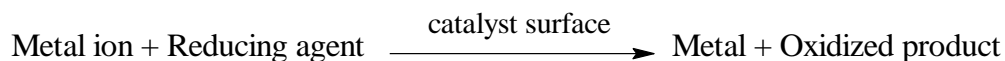
Electroless plating of Copper (on PCB):

Pretreatment and activation of the surface: The PCB is degreased and etched in acid. It is activated by dipping in stannous chloride solution containing HCl at 25^0C followed by dipping in palladium chloride. The surface is dried to get a layer of palladium.

Plating bath solution:
A solution of copper sulphate (12 g/dm^3);
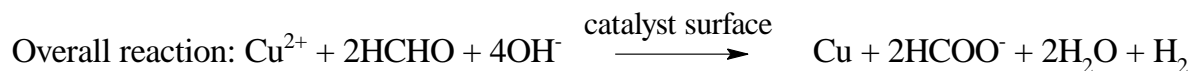Reducing agent- Formaldehyde (8 g/dm^3);
Buffer - Sodium hydroxide (15 g/dm^3) + rochelle salt (14 g/dm^3);
Complexing agent and exaltant – EDTA (20 g/dm^3);
pH – 11 ; Temperature – 25^0C.
Reactions: Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$
$\qquad$ Anode: $2HCHO + 4OH^- \rightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$

Overall reaction: $Cu^{2+} + 2HCHO + 4OH^- \xrightarrow{\text{catalyst surface}} Cu + 2HCOO^- + 2H_2O + H_2$

Rate of plating: 1 to 5 μm h^{-1}.

Applications: An important application of electroless copper plating is printed circuit boards (PCB). In double side and multilayer boards where plating-through-holes is required, electroless technique is the best since the holes cannot be electroplated

The technique used to manufacture printed circuit boards is the substrative method (Fig.5).The base object in PCB is a plastic material such as glass fibre reinforced plastic (GRP), epoxy or phenolic polymer over which a layer (5 to 100 μm) of copper is electroplated. Selected areas are then protected by a photo-resist or electroplated image and the rest of the copper is etched away to produce the circuit pattern or the track. Usually, double sided tracks are made in order to pack more number components in a small space. Finally, the connection between the two sides of PCB is made by drilling holes, followed by electroless copper through holes.

Copper coating

Plastic base

Copper coating

Cu is etched to
produce tracks

Through-holes
produced by
drilling

Activating and
electroless plating
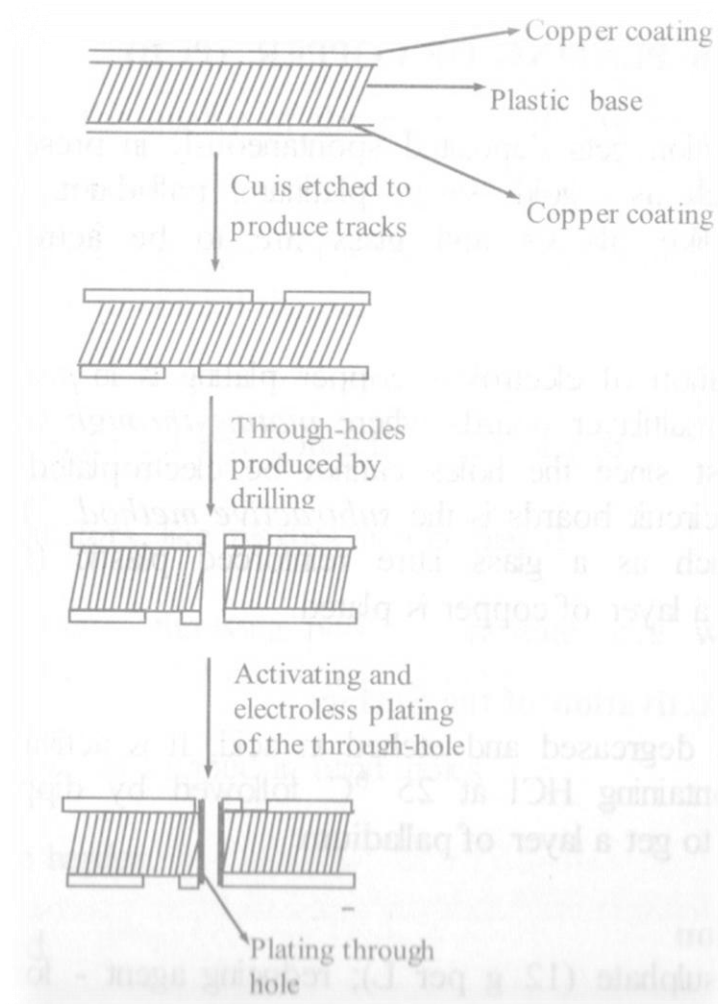of the through-hole

Plating through
hole

Fig.4. Steps in subtractive technique of plating-through in the manufacture of double sided PCB. Copper cladded tracks on each side of the plastic board are connected through-hole.

Advantages of electroless plating:
(i) Use of electrical power and electrical contacts are eliminated.
(ii) Semiconductros and insulators like plastics can also be plated.
(iii) Electroless baths have better throwing power. Intricate parts with irregular shapes, inside parts of tubes, recesses can be uniformly coated.
(iv) Hydrogen gas liberated is not trapped in blind holes.
(v) Electroless coating are harder than that produced by conventional electroplating.
(vi) No levelers are required.
(vii) Deposits have unique chemical, mechanical and magnetic properties.

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