ELECTROCHEMISTRY

Introduction, Single electrode potential, Origin of single electrode potential theory, Nernst equation to calculate the electrode potential, Numerical problems. Electrochemical cells - galvanic cell and electrolytic cell, representation of galvanic cell, Construction and working of galvanic cell, Liquid junction potential, Functions of salt bridge, EMF of cell, Determination of EMF of cell by Poggendroff's method using Standard cell, Construction, working, application and limitations of calomel electrode, Numerical problems. Construction, working, applications, advantages and limitations of glass electrode, Numerical problems. Classification of Batteries – Introduction, primary and secondary with examples; construction, working and applications of lead acid battery. Construction, working and applications of Ni-Cd and Li-ion batteries, advantages and disadvantages. Fuel Cells – Introduction, construction and working of AFC & PEMFC, advantages and disadvantages. Metal finishing – Electroplating – polarization, over voltage, decomposition potential including determination of decomposition potential. Characteristics of good deposit, Factors influencing the nature of the deposit, Methods of cleaning the metal surface. Electroplating of Cu & Cr & electroless plating of Cu.

1 INTRODUCTION

Electrochemistry deals with the behavior of electrolytes in solution and interconversion of chemical and electrical energies; that is, the study of chemical changes due to the flow of an electric current and production of electric current due to chemical reaction. Electrolysis, electrometallurgy and electroplating use electrical energy to drive chemical reactions, while chemical energy is transformed into electricity in galvanic cells, batteries and fuel cells. Substances such as metals and alloys conduct electricity under the influence of an applied electric potential through a flow of electrons and hence are known as electronic conductors. The flow of electricity in electronic conductors does not cause any physical or chemical change in the conductor. On the other hand electrolyte solutions and molten salts conduct electricity through the migration of ions and are known as electrolytic conductors or electrolytes. When direct current is passed through an electrolyte solution, decomposition and changes occur in the composition of the electrolyte. The practical importance of electrochemistry includes electroplating, electroextraction of metals, electrorefining of metals, and electro-production of certain compounds.

1.1 ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes or metallic conductors, in contact with an electrolyte, an ionic conductor. An electrode and its electrolyte comprise an electrode compartment. The two electrodes may share the same compartment. If the electrolytes are different, the two compartments may be joined by a salt bridge, which is a tube containing a concentrated electrolyte solution in agar jelly that completes the electrical circuits and enables the cell to function. So an electrochemical cell can be defined as a single arrangement of two electrodes in one or two electrolytes which converts chemical energy into electrical energy or electrical energy into chemical energy. Electrochemical cells can be classified into two types:
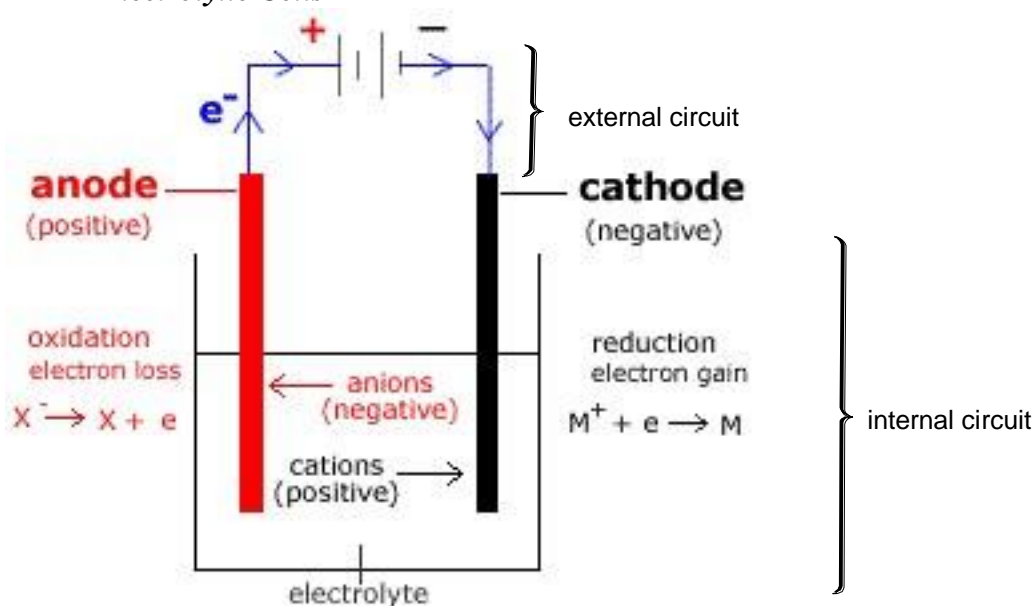
- *Galvanic Cells*
- *Electrolytic Cells*

Fig.1.1. A schematic diagram of Electrochemical Cell

1.1.1 Galvanic Cells

A galvanic cell is an electrochemical cell that produces electricity as a result of the spontaneous redox reaction occurring inside it. Galvanic cell generally consists of two electrodes dipped in two electrolyte solutions which are separated by a porous diaphragm or connected through a salt bridge. It is a single arrangement of two electrodes in one or two electrolytes which converts stored up chemical energy in the form of electroactive materials (anode & cathode active materials) directly into electrical energy. The negatively charged electrons flow from anode to cathode and are attracted to the positive cathode through the external circuit.

Anode vs. Cathode:
Anode ;

- the electrode at which oxidation occurs
- is where electrons are produced
- is what anions migrate towards
- has a –ve sign.

Cathode ;

- the electrode at which reduction occurs
- is where electrons are consumed
- is what cations migrate towards
- has a –ve sign

A typical galvanic cell can be illustrated by Daniel cell (Fig. 1.1.1)

Oxidation   at   Zn   reduction at Cu

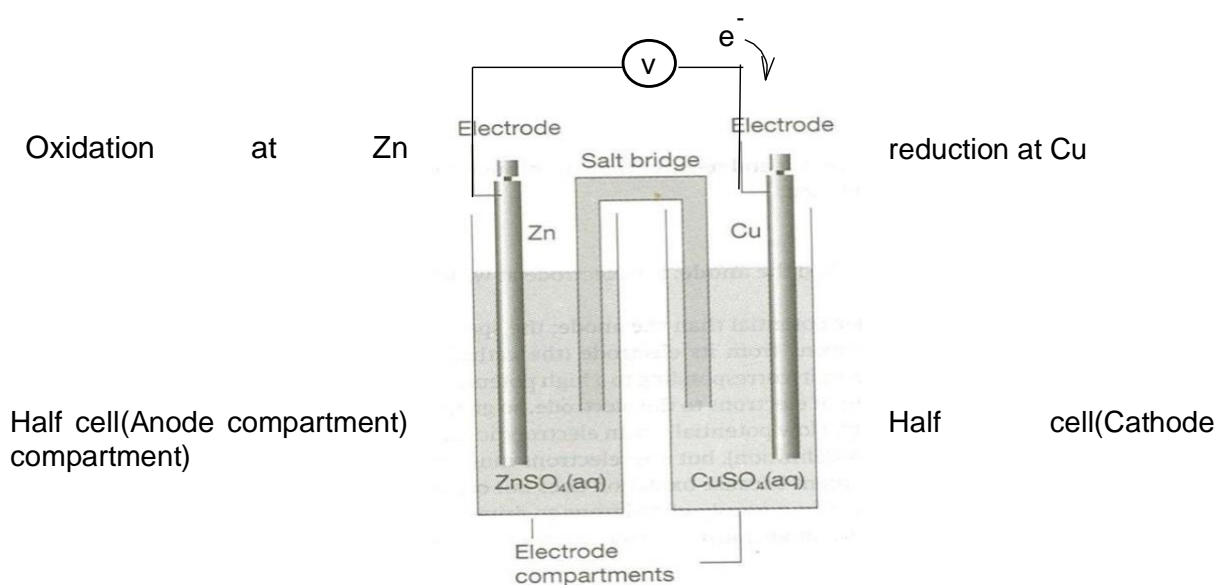Half cell(Anode compartment) compartment)   Half   cell(Cathode

Fig.1.1.1. A schematic diagram of Daniel cell

A Daniel cell consists of two compartments, one of which contains zinc rod dipped in zinc sulphate solution and the other with a copper rod dipped in a copper sulphate solution. The two electrolytes are connected by a salt bridge. When the zinc and copper rod electrodes are connected externally through a voltmeter by using a wire, the following oxidation-reduction reactions taking place at the electrodes. At the zinc electrode, zinc goes into the solution as Zn^{2+} ions, liberating two electrons. In the process zinc undergoes oxidation liberating two electrons. The positive ion flows from the salt bridge to the cathode and the zinc electrode becomes lighter.

- $Zn\,(s) \quad \rightarrow Zn^{2+}\,(aq) + 2e\text{-} \quad \text{--------------------------}(1).$
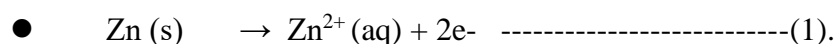
At the copper electrode reduction of Cu^{2+} ions takes place with the deposition of metallic copper on the copper rod, by consuming two electrons. The negative ions flow from salt

bridge to anode and copper electrode becomes heavier. The ionic conduction in the solution is coupled to the electronic conduction in the electrodes.

- $Cu^{2+}(aq) + 2e- \rightarrow Cu(s)$ --------------------------- (2)
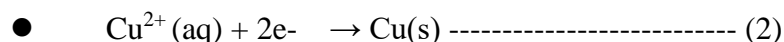
Each of these reactions is known as half cell reaction. The reaction (1) in which loss of electrons takes place is called oxidation half reaction; while the reaction 2, in which gain of electrons takes place, is called reduction half reaction. The net reaction is obtained by adding reactions 1 and 2. i.e. $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ is called redox or oxidation – reduction reaction. When the circuit is closed, the electrons flow from zinc to copper through the external wire to feed the Cu^{2+} ions in the process of discharging copper and thus electrical energy or current is produced which may be used for the purpose of external work.

As in the case of Daniel cell, by the combination of any two different electrodes materials one can construct a galvanic cell. The electrode with a greater tendency to go into the solution by liberating electrons acts as an anode, & the other one with more tendency to undergo reduction acts as a cathode. In a galvanic cell anode is negative and the cathode is positive. The reason to this nomenclature 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 absorption of electrons by reactant in solution from the electrode, which thereby acquires a positive charge. Hence the flow of electrons is from the negative electrode to positive electrode and the direction of flow of positive electricity, which is known as conventional current, is from the cathode to anode.

1.1.2 Electrolytic cells

An electrolytic cell is an electro –chemical cell in which a non- spontaneous reaction is driven by an external source of current although the cathode is still the site of reduction, it is now the negative electrode whereas the anode, the site of oxidation is positive.

The electrolytic cell (Fig.1.1.2) find wide applications in the purification of metals & also in electro deposition of a metal on to the surface of another metal, alloy or any conductor in general, by the process of electrolysis.
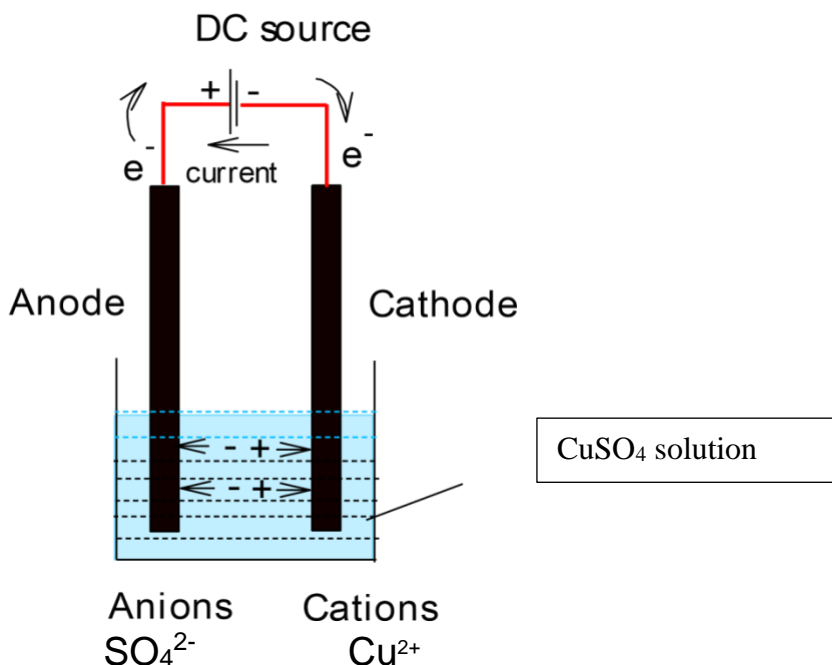
Fig.1.1.2 Schematic diagram of an electrolytic cell

Electrolysis involves the conversion of electrical energy into chemical energy i.e. chemical changes are brought about by the expense of electrical energy. Since electrolysis is a non spontaneous process, the minimum energy required to carry out such a process is equal to the free energy increase accompanying the change, & this is equal but opposite in sign to the free energy decrease accompanying the reverse spontaneous process. This is true when electrolysis is carried out reversibly. However, in irreversible conditions, the potential to be applied for electrolysis is higher than the reversible emf of the cell.

1.1.3 Representation of a galvanic cell

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

1. The anode is written on the left hand side and the cathode is written on the right hand side of cell representation.

2. The anode is written by writing the metal (or solid phase) first and then the electrolyte along with the concentration in the bracket. The 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.

   Anode representation
   Metal/ Metal ion (concentration) i.e. M/M^{n+} (c)
   $Zn\,|\,Zn^{2+}$ or Zn; Zn^{2+} or Zn $|$ $ZnSO_4$ (1M) or   Zn; $ZnSO_4$ (1M)

3. The cathode of the cell is represented by metal ion first and then the metal (or solid phase) thereafter. The two are separated by a vertical line or a semicolon.

   Cathode representation:

5

M^{n+} (c) / M i.e. Metal ion (concentration) / Metal

e.g. Cu^{2+} │ Cu or Cu^{2+}; Cu or Cu^{2+} (1M); Cu or $CuSO_4$ (1M)/Cu

4. A salt bridge is indicated by two vertical lines, separating the two half-cells. Thus the Daniel cell, may be represented as:

Zn │ $ZnSO_4$ (1M)‖ $CuSO_4$(1M)/Cu

Cu(s) / Cu^{2+} (aq) ‖Ag^+(aq) / Ag (s)

Comparisons of Galvanic and Electrolytic cells

Galvanic Cell	Electrolytic Cell
Cell reaction is spontaneous Converts chemical energy to electrical energy Anode is negative and cathode is positive Usually have two electrodes and two electrolytes Used as a potable source of electrical energy in cars, flashlights and calculators Example. Daniel cell	Cell reaction is non-spontaneous Converts electrical energy into chemical energy Anode is positive and cathode is negative Single electrolyte and two electrodes Used for electrolysis apparatus like electroplating and electrorefining Example. Electroplating of nickel

1.1.4 LIQUID JUNCTION POTENTIAL

The potential set up at the junction of the two electrolytes because of the difference in the speeds of the cations in one direction and anions in the other i.e. potential at the junction of the two electrolytes because of unequal migration of ions across the boundary between the two solutions is called the liquid junction potential, E_j. In a Daniel cell, if the concentrations of $ZnSO_4$ (aq) and $CuSO_4$ (aq) are equal SO_4^{2-} ions do not diffuse across the junction and the charge cannot flow around the circuit. But Cu^{2+} ions diffuse into $ZnSO_4$ (aq) and Zn^{2+} ions diffuse into $CuSO_4$ (aq) because Cu^{2+} ions are slightly more mobile than Zn^{2+} ions. This produces a small excess positive charge on the $ZnSO_4$ (aq) side of the junction and equal negative charge on the $CuSO_4$ (aq) side. The liquid junction potential is the difference between the electric potential developed in the two solutions across their interface

i.e. $E_j = \emptyset^{soln, R} - \emptyset^{soln,L}$ where $\emptyset^{soln. R}$ is the electric potential of the electrolyte solution on the right hand side half – cell in the cell scheme. $\emptyset^{soln. L}$ is the electric potential of the

electrolyte solution on the left hand side half-cell. Generally, LJPs are of the order of a few millivolts.

1.1.5 SALT BRIDGE

The contribution of the liquid junction to the potential can be reduced (to about 1 to 2 mV) by joining the electrolyte compartments through a salt bridge containing salts such as KCl, KNO_3, and NH_4NO_3 whose ions have the same migration velocities. Then the ions move with equal speed to anode and cathode compartments minimizing the junctions potentials almost zero. A salt bridge is used to connect electrolytically, the two electrolyte solutions of a galvanic cell, as shown in the Fig. 1.1.5.
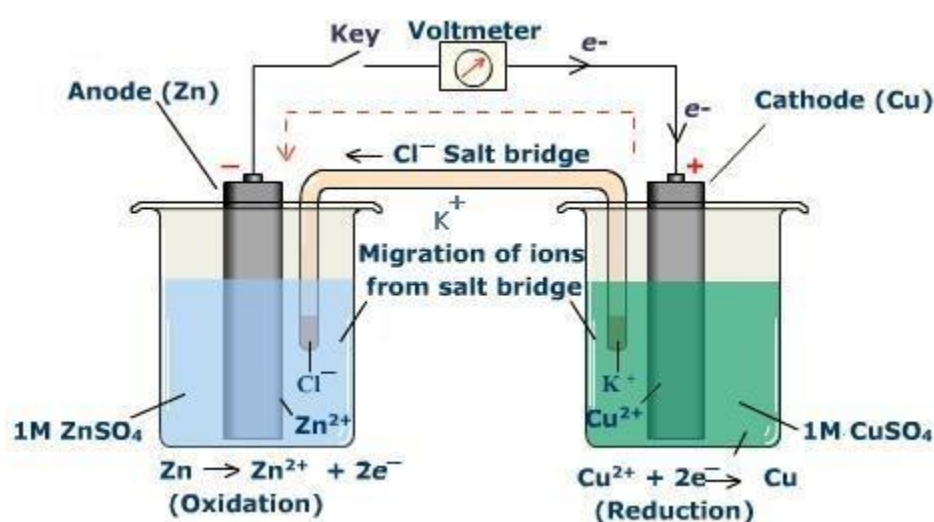

Fig.1.1.5 Daniel Cell indicating the function of a salt bridge

The salt bridge consists of a 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 minimizing liquid junction potential.

The salt bridge is prepared by dissolving 5g agar in 100 mL aqueous solution of KCl containing 35 g of KCl and filling in a U-tube. On cooling, the agar forms a jell with KCl solution in it. A salt bridge has the following functions:

1. It provides electrical contact between the two electrolyte solutions of a cell i.e., it physically separates the two electrolytes but completes the electrical circuit by altering ions causing charge to move from half-cell to the other.
2. It minimizes liquid junction potential in galvanic cells containing two electrolyte solutions in contact. i.e., it reduces the LJP to a minimum by nearly equal diffusion rates of cations and anions.

7

3. It maintains the electrical neutrality of the two half cells i.e., it prevents any net charge accumulates in the two electrolytes.

1.1.6 ELECTROMOTIVE FORCE OF THE CELL

Electricity cannot flow from one electrode to another unless there is a potential difference between the two points. The difference of potential, which causes a current to flow from the electrode at higher potential to an electrode at lower potential is called the "electromotive force"(e.m.f.) of the cell "or the "cell potential" and is expressed in volts V. The emf of a cell is denoted by E_{cell} .Mathematically,

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

The driving force that pushes the negatively charged electrons away from the anode and pulls them towards the cathode is known as emf. The E_{Cell} depends on the nature of the electrodes composition, (combination of electrodes, strong tendency to lose or gain electrons produces large cell potential) temperature ($E \propto T$) and concentration of the electrolyte solutions. To facilitate comparison of different galvanic cells, their standard emf, denoted by E^0_{cell} is used. Standard emf of a cell is defined as the emf of a cell when the reactants & products of the cell reaction are at a unit concentration or unit activity, at 298 K and at 1 atmospheric pressure including pure solids and liquids.

The emf of a cell represents the driving force of a cell reaction. As represented by the thermodynamic relation,

$\Delta G = -nFE$

Where ΔG is the free energy change accompanying a cell reaction, n is the number of electron transfer during the cell reaction, and F is the Faraday constant, $F = eN_A$, the magnitude of the charge per mole of electrons. Hence the above equation is the key connection between the electrical measurements on the one hand and thermodynamic properties on the other.

The cell reaction is spontaneous or feasible when ΔG is negative. ΔG can be negative only if the emf of the cell is positive, because, the other two factors, n & F are always positive. Thus emf of a galvanic cell is always positive. The positive emf value indicates the spontaneity of cell reaction in the given direction. When the cell potential is large, a given number of electrons traveling between the electrodes can do a large amount of electrical work. When the cell potential is small, the same number of electrons can do only a small amount of work. A cell in which the overall reaction is at equilibrium can do no work, and then the cell potential is zero.

1.1.7 Measurement of emf of a cell

The emf cannot be measured accurately by connecting directly a voltmeter between the two electrodes, because during such a measurement, a part of the cell current is drawn to deflect the needle as part of the emf is used to overcome the internal resistance of the cell. Consequently, such a measurement would indicate a potential difference less than the actual emf of the cell. For precise emf measurements potentiometers are used, which require extremely small current at the balance point.

The potentiometric measurement of emf of a cell works based on Poggendorff's compensation method. In this method, emf of a test cell is opposed by the impressed emf from an external source of emf, and the measurement is made when there is no net flow of current in the circuit. The basic principle is that the emf of the cell to be measured is exactly balanced by an equal and opposite known emf so that no current flows in the circuit (null point) A schematic diagram of the potentiometer is shown in Fig.1.1.7
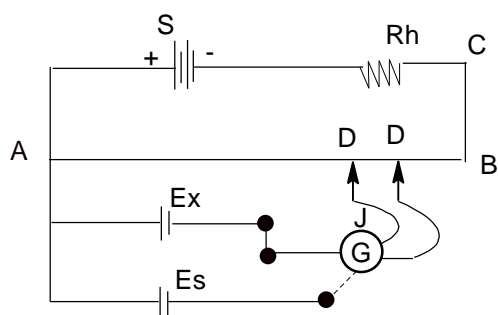

Fig.1.1.7. Potentiometric arrangement for the measurement of EMF of a galvanic cell.1.1.5

AB- Potentiometric wire
S- Storage battery
E_S- Standard cell
Ex- unknown cell
G- Galvanometer
J- Sliding contact.
Rh – adjustable resistance

The two terminals of a storage battery(S) which has a constant and higher emf than the test cell, is connected to two ends of a long uniform wire AB of high resistance. The positive terminal of the test cell is connected to the end A, to which the positive terminal of S is connected & the negative terminal is connected to a sliding contact J through a galvanometer (G). The sliding contact is moved along the wire AB until the null point is reached, which is indicated by no current flow in the galvanometer. The position of a null point is noted & the distance AD is measured. The emf of the unknown cell E_x is proportional to the length AD.

- E_x α AD

9

Then the test cell Ex is replaced by a standard cell Es, whose emf, is known the position of the sliding contact is readjusted by moving it over AB, as before, till null point D^1 is reached .The length AD^1 is measured. The emf of the standard cell E_s is proportional to the length AD^1.

- $E_s \, \alpha \, AD^1$
- $\dfrac{E_x}{E_s} = \dfrac{AD}{AD^1}$
- $E_x = \dfrac{AD}{AD^I} \; x \; E_s$

Thus the emf of the test cell is calculated by substituting the emf of the standard cell in the above equation.

1.1.8 Standard cell requirements:

1. Its emf should remain constant for a longer period of time.
2. It should be capable of providing highly reproducible emf.
3. The temperature coefficient of emf should be negligibility small i.e $(\delta E/ \delta T)= 0$
4. The cell reaction should be reversible.
5. It should not be subjected to permanent damage due to the passage of current.
6. A standard cell is one which has a constant and reproducible known emf with a negligible variation of emf with temperature e.g. Weston standard cell or Weston cadmium cell.

1.2 Energetic of cell reactions:
1.2.1 The relation between E and ∆G:
A cell in which the overall reaction has not reached chemical equilibrium can do electrical work as the reaction drives electrons through an external circuit. The work that a given transfer of electrons can accomplish depends on the cell potential.

The maximum electrical work as per thermodynamics, chemical reaction can do is given by the value ∆G for the reaction.

W_e, max = ∆G----------------- 1

Where, W_e is electrical work. It follows that, to draw thermodynamic conclusions from measurements of the work a cell can do, we must ensure that the cell is operating reversibly. Only then it is producing maximum work and only then we can relate electrical work to ∆G.

Both these conditions are achieved by measuring the cell potential when it is balanced by an exactly opposing source of potential so that the cell reaction occurs reversibly, the composition is constant, and no current flows.

The net electrical energy and the emf of the cell produced in a cell is the product of the quantity of electricity that passes through the cell and the emf of the cell.

W_e = QE Joules. -------(2)

Q is the quantity of electrical charge in coulombs produced by the reaction and E is the emf of the cell in volts.

Charge on 1 mol (6.02 x 10^{23}) electrons is F coulombs, where F is Faraday constant. When n electrons take part in the cell reaction, n mols of electrons are involved per mol of a reactant of the reaction. Hence charge on n mol of electrons = nF coulombs. This is the charge, Q in coulombs produced by the reaction. For 1 mole of electrons transferred in the cell reactions, the quantity of electricity = 1F

If n moles of electrons are transferred in the cell reactions, the quantity of electricity = n F

Therefore electrical energy= nFE, ----------(3)

In a large number of reactions, electrical energy produced is not equal to chemical energy.

Electrical energy produced = decrease in free energy for cell reaction i.e. $- \Delta G = nFE$ or

ΔG = -nFE Joules-------(4)

If we know emf E, ΔG can be calculated. The larger the value of cell potential the further the reaction is equilibrium.

1.2.2 Relation between E and ΔH
Enthalpy Change   *$\Delta H = nF[T(\delta E/\delta T)_P –E]$* --------(5)
If we know emf and temperature coefficient of emf, ΔH can be calculated..

1.2.3 Relation between E and ΔS :
    $\Delta S = nF(\delta E/\delta T)_P$ ------------------(6)

1.2.4   Numerical Problems
1.   Emf of Weston Cadmium cell is 1.0183 V at 293 K and 1.0l81 V at 298 K. Calculate ΔG, ΔH and ΔS of the cell reaction at 298 K.
Solution:- ΔG: ΔG = - n FE n = 2 for the cell reaction;

F = 96,500 C   E= 1.0181 V at 298 K

ΔG = -2 x 96,500 x 1.0181 J = -196.5 KJ

ΔH: ΔH = nF [T ($\delta E /\delta T)_P$ – E]
$(\delta E/\delta T)p$ = 1.0181 – 1.0183 / 298-293 = -0.0002 / 5
          = - $0.00004 VK^{-1}$

T = 298 K

ΔH = 2 x 96,500 { [298 x (-0.00004)] – 1.0181}
            = -198. 8 KJ

ΔS: ΔS = nF($\delta E / \delta T)_P$
= 2 x 96,500 x (0-00004) = $-7.72 JK^{-1}$

2.   The emf of the cell Cd|$CdCl_2$. 2.5 H_2O (saturated) || AgCl(s)| Ag is 0.6753V and 0.6915 V at 298 K and 273 K respectively. Calculate ΔG, ΔH and ΔS of the cell reaction at 298 K.

Solution. Here n = 2, E = 0.6753 V at 298 K and 0.6915 at 273 K.

$\therefore$ $(\delta E/\delta T)p$ = (0.6753-0.6915) V/ (298-273) K = - 0.00065 V/K

Now at 298 K, ΔH = nF [T $(\delta E /\delta T)_P$ – E]

$\qquad\qquad\qquad$ = 2 mol x 96,500 C mol^{-1} { [298 K x (- 0.00065 V/K)] – 0.6753 V }

$\qquad$ = -167. 7 KJ

ΔG at 298 K ; ΔG = - n FE = -2 x 96,500 x 0.6753 = -130.33 KJ

ΔS = nF$(\delta E / \delta T)_P$

$\qquad$ = 2 x 96,500 x (0-00065) = -125.45 J.K^{-1}

1.3 SINGLE ELECTRODE POTENTIAL

The potential of the single electrode is the difference of potential between a metal and the solution of its salt. i.e the tendency of an electrode to lose or gain electrons when in contact with its own ions in the solution. In a cell, the electrode with lower electrode potential has less tendency to undergo reduction and acts as an anode. The electrode with higher electrode potential has a higher tendency to undergo reduction and acts as a cathode.

Example: In case of Zn in ZnSO$_4$ solution acquires a negative charge (Fig. 1.3a).

$M(s) \rightarrow M^{n+} + ne^-(aq)$ $\qquad$ (1) Dissolution reaction and conversely, the metal shows the tendency to go into the solution as metal ion by losing electrons (Fig. 1.3b).

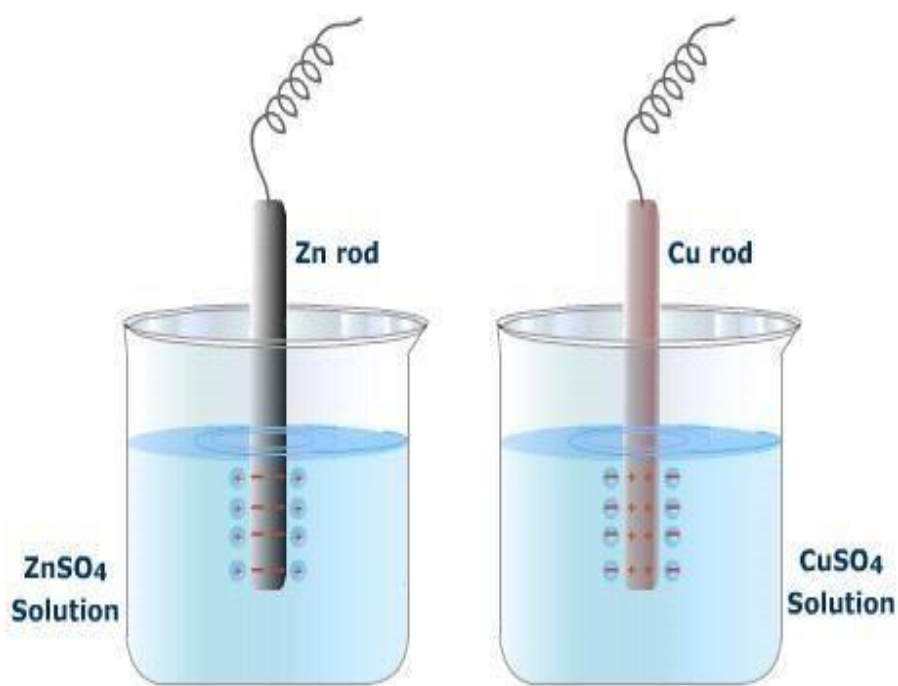$M^{n+}(aq) + ne^-(aq) \rightarrow M(s)$ $\qquad$ (2) Deposition reaction

Fig.1.3a. Zinc ions move into solution leaving behind electrons making it electron rich	Fig.1.3b.Copper ions get deposited as copper leaving behind free negatively charged sulfate ions in solution makes the electrode electron poor

The rate of this reaction depends on,

(i) the nature of the metal

(ii) the temperature

(iii) the concentration of metal ions in solution.

When a metal is placed in the solution of its own salt, the chemical reaction (1) or (2), takes place depending on whether the dissolution reactions are faster than deposition or vice versa. A dynamic equilibrium is established, because negative or positive charge developed on the metal attracts the positively or negatively charged free ions in the solution. Due to this attraction, the positive or negative ions remain quite close to the metal. Thus, a short layer of positive ions or negative ions as in the figure is formed at the junction of the electrode and the solution. This layer is called a Helmholtz electrical double layer. A difference of potential is consequently, set up between the metal and the solution. This potential difference will persist as long as the charge is allowed to remain on the metal; and this will prevent any further passing of the positive ions from or to the metal. At equilibrium the potential difference between the metal & solution becomes a constant value. The equilibrium potential difference so established is called the "electrode potential" of the metal. Thus, the electrode potential of a metal is the measure of the tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 298K. Consequently, the tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidized & this tendency, is called oxidation potential. Similarly, the tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced and this tendency is known as reduction potential. By concentration, electrode potential refers to reduction potential.

1.3.1 Measurement of electrode potential

It is impossible to determine the absolute half cell potential We can only measure the difference in potential between two electrodes potentiometrically, by combining them to form a complete cell. All voltage measuring devices determine differences in potential. If one knob of voltameter is connected to a test electrode, another one will make contact with the solution in the electrode compartment via another conductor. This second contact involves solid/ solution interface and acts as a record half cell. The redox reaction must take place if the

charge is to flow and potential is to be measured. A potential is associated with this second reaction and absolute half cell potential is not obtained. What we measure ultimetaly is the difference between the half cell potential of test electrode and a half cell made up of the second contact and the solution. Therefore, absolute electrode potentials cannot be measured. We can only determine the relative value of electrode potential, if we can fix arbitrarily the potential of any one electrode. For this purpose, the potential of a standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE) (i.e., a platinum electrode in contact with 1 M H^+ ion concentration and hydrogen gas at 1 atmospheric pressure is constantly bubbled through it) has been arbitrarily fixed as zero and the numerical values of electrode potentials of different electrodes are relative values w.r.t SHE. Therefore, single electrode potentials of electrodes are referred to as potentials on the hydrogen scale.

Sign of electrode potential: When an electrode is coupled with a SHE, if reduction occurs then EP is given a +ve sign e.g Copper electrode + SHE

- $Cu^{2+} + 2e^- \rightarrow Cu(s)$ reduction at copper electrode (cathode)
- $H_2(g) \rightarrow 2H^+ + 2e^-$ oxidation at hydrogen elecrode (anode) $\rightarrow E^0 = 0.34$ volt

A +ve sign on the EP value indicates that the half cell acts as cathode and acepts electrons from the hydrogen electrode.

Similarlly, when an electrode is coupled with SHE, if oxidation occurs then EP is given a -ve sign e.g . Zinc electrode + SHE

- $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation at Zinc elecrode)
- $2H^+(aq) + 2e^- \rightarrow H_2(g)$ (reduction at Hydrogen elecrode) $\rightarrow E^0 = -0.76$ volt

A –ve sign on the electrode potential value indicates that the half cell acts as an anode by releaseing electrons to the hydrogen electrode.

1.3.2 Standard electrode potential:

Standard electrode potential is the electrode potential when the electrode is in contact with a solution of unit concentration at 298 K involving pure solids and liquids. If the electrode involves a gas, then the gas is at 1 atmospheric pressure. It is denoted by E^o. When elements are arranged in increasing order (downwards) of their standard electrode potential, a series called electrochemical series is obtained. In a cell, the electrode with lower electrode potential has less tendency to undergo reduction and it acts as anode similarly electrode with higher electrode potential has higher tendency to undergo reduction and acts as cathode.

Reducing agents	Stable ions	Electrode half reaction E^0 volts
Lithium	Li^+	-3.03
Potassium	K^+	-2.92

Aluminium	Al^{3+}	-1.66
Zinc	Zn^{2+}	-0.76
Iron	Fe^{3+}	-0.44
Lead	Pb^{2+}	-0.13
H_2	$2H^+$	0
Copper	Cu^{2+}	0.34
Silver	Ag^+	0.80
Gold	Au^{3+}	1.52

Fig. 1.3.2. Selected standard electrode potentials

1.3.3 Nernst equation

Nernst equation is an expression of a quantitative relationship between electrode potential/cell potential and concentration of the electrolyte species in an electro-chemical reaction. i.e. mathematical expression that relates the potential of an electrode to the concentrations of those species in solution that are responsible for the potential. Consider a general redox reaction: $M^{n+}(aq) + ne^- \rightleftharpoons M(s)$

$E = E^o + 2.303RT/nF \quad \log [M^{n+}]$

E= Electrode potential at some moment in time

E^0= Standard electrode potential

R= Universal gas constant (joules per mol K)

T= Temperature in Kelvin scale F= Faraday constant (96,500 Coulumbs)

n = Number of electrons transferred in the half reaction/ cell reactions

$[M^{n+}]$= Concentration of metal ion at that moment in time (moles per litre).

At 298 K, when the values of R.T and F are substituted, the equation reduces to,

$E = E^o + (0.0592/n) \quad \log [M^{n+}]$

This expression is known as the Nernst equation for electrode potential at 298 K. From these equations, it is clear that,

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

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

The Nernst equation can also be applied for the calculation of emf of a cell. Consider the cell reaction aA+ bB $\rightleftharpoons$ cC +dD

The Nernst equation for the emf of the cell is

15

$E_{cell} = E^o_{cell} - 2.303RT/nF \ \log [C]^c [D]^d /[A]^a [B]^b$

At 298 K,

$E_{cell} = E^o_{cell} - (0.0591/n) \ \log [C]^c [D]^d /[A]^a [B]^b$

Where n is the number of electrons transferred during the cell reaction and E^o_{cell} is the standard emf of the cell.

1.3.3.1 Significance of the Nernst equation

1. It can be used to calculate the potential of a cell that operates under non-standard conditions. The Nernst equation tells us that a half-cell potential will change by 59 millivolts per 10-fold change in the concentration of a substance involved in one-electron oxidation or reduction; for two electron processes, the variation will be 28 millivolts per ten fold concentration change. Thus for the dissolution of metallic copper

$$Cu(s) \rightarrow Cu^{2+} + 2e–$$

the potential $E = (– 0.337) – .0295 \log [Cu^{2+}]$ becomes more positive (the reaction has a greater tendency to take place) as the cupric ion concentration decreases.

2. It can be used to measure the equilibrium constant for a reaction. At equilibrium the overall cell potential for the reaction is zero. i.e. E=0

Nernst equation,

$0 = E^o - RT/nF \ lnK_c$

$K_c = e^{nFE^° / RT}$

1.4 Calomel electrode

The calomel electrode (Fig.1.4.1), a mercury mercurous chloride electrode develops + 0.242 V at 289 K when the KCl solution is saturated. It has been found that the potential of the calomel electrode, on the hydrogen scale varies with the concentration of the potassium chloride solution used. The concentration of KCl solution used is either decinormal, normal or saturated. Correspondingly, the electrode is known as decinormal, normal or saturated calomel electrode respectively.

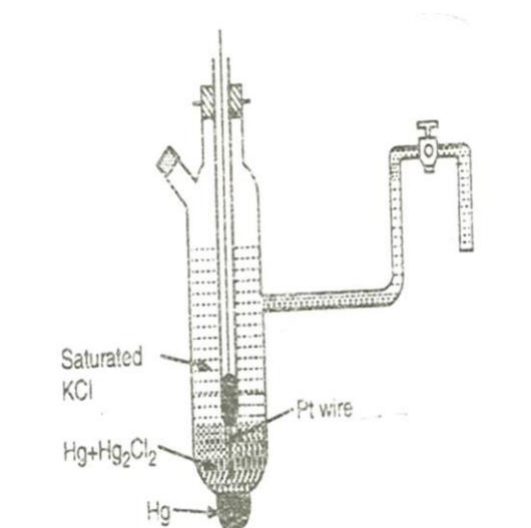### 1.4.1 Construction & Working:

Fig.1.4.1 Schematic diagram of calomel electrode.

It consists of a tube, in the bottom of which is a layer of mercury, over which is placed a paste of mercury and mercury chloride. The remaining portion of the cell is filled with a solution of normal or decinormal or saturated solution of KCl. A platinum wire sealed at its end fixed into the main tube dipping into the mercury layer is used for making electrical contact. The electrode can be represented as $Hg_{(l)} / Hg_2Cl_2$ (sat'd) $/ KCl^-$ (sat'd/ xM)

The calomel electrode can act as anode or cathode depending on the nature of other electrode of the cell. When it acts anode, the electrode reaction is

- $\cdot$ $2Hg (l) \rightarrow Hg_2^{2+} (aq) + 2e^-$

- $Hg_2^{2+}(aq) + 2Cl^- (aq) \rightarrow Hg_2Cl_2$

- $2Hg(l) + 2Cl^- (aq) \rightarrow Hg_2Cl_2 (s) + 2e^-$
  When it acts as cathode, the electrode reaction is,
- $Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$
- $Hg_2Cl_2 (s) \rightarrow Hg_2^{2+} (aq) + 2Cl^-$
  _____
- $Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg (l) + 2 Cl^-(aq)$

The net reversible electrode reaction is,

$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2 Hg (l) + 2 Cl^-(aq)$
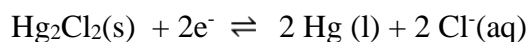
Electrode potential is given by

$E = E^o - \dfrac{2.303\ RT}{2F}\ \log [Cl^-]^2$

17

$= E^o - 0.0591 \log [Cl^-]$ at 298 K

1.4.2 Uses:

Since the electrode potential is a constant it can be used as a secondary reference electrode to replace the inconvenient SHE for potential measurements.

i) To determine the electrode potential of the unknown electrode

For example: The test electrode, $Zn_{(s)} / Zn^{2+}{}_{(aq)}$ is coupled with a saturated calomel electrode.

$Zn(s) / Zn^{2+} (aq) \mid\mid Cl^- $ (saturated soln) $/Hg_2Cl_{2(s)} / Hg (l)$

The emf of the so formed cell is determined experimentally by potentiometric method.

Then

$E_{cell} = E_{cathode} - E_{anode} \qquad = 0.2444 - E_{zn}$

$\qquad E_{zn} = 0.2444 - E_{cell}$

ii) To determine the pH of a solution cell: $Hg(l) / Hg_2Cl_2 (s) // H^+ /pt, H_2 (g)$

$\qquad E_{cell} = E_{cathode} - E_{anode}$

$\qquad\qquad = 0.242 - (- 0.0592 \text{ pH})$

$\qquad pH = E_{cell} - 0.242/0.0592$

1.4.3 Advantages

> ➢ It is very simple to construct.
> ➢ It can be used for a long time without much attention.
> ➢ Electrode potential is stable over a long period (reproducibly).
> ➢ It hashes the low temperature coefficient of emf.
> ➢ It is less prone to contamination because the mercury/ mercurous chloride interface is protected inside a tube not in direct contact with the electrolyte.

1.4.4 Disadvantages

> ➢ Calomel electrodes should not be used above 50°C because the mercurous chloride breaks down, yielding unstable readings. This is important if substantial temperature changes occur during measurement.
> ➢ Calomel electrode should be used with proper precaution as mercury compounds are toxic.

1.5   Ion Selective Electrode.

The electrode which is sensitive to a specific ion present in an electrolyte whose potential depends upon the activity of a specific ion in the electrolyte is called an ion selective electrode. The magnitude of the potential of this electrode is an indicator of the activity of the specific ion in the electrolyte. Example for this type of electrode is glass electrode.

1.5.1 Glass electrode: Construction

Glass   Membrane

Electrical contact

Protective sleeve

Ag/AgCl
Ag/AgCl wire

HCl, 0.1 mol dm^{-3}(Referrence solution of dilute HCl)

Thin walled glass membrane

Solution of unknown pH

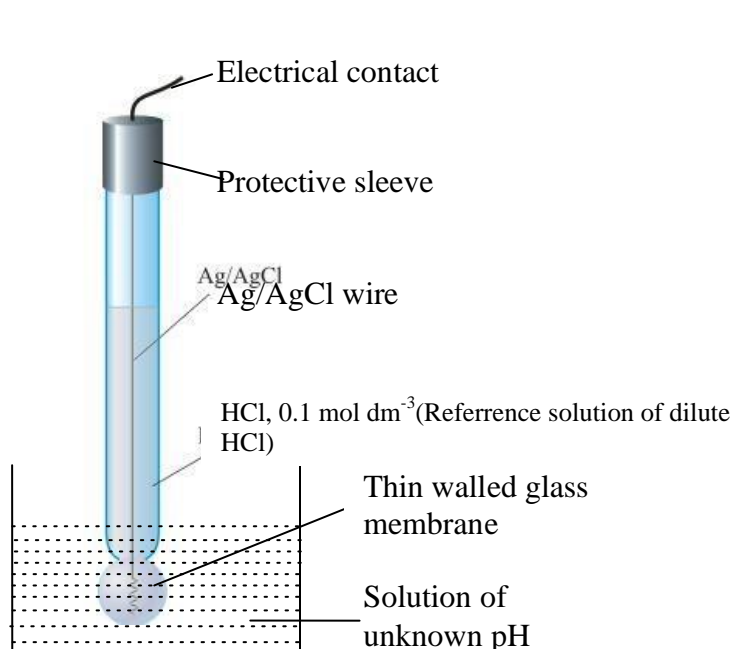Outer

Inner

E1   E2

1

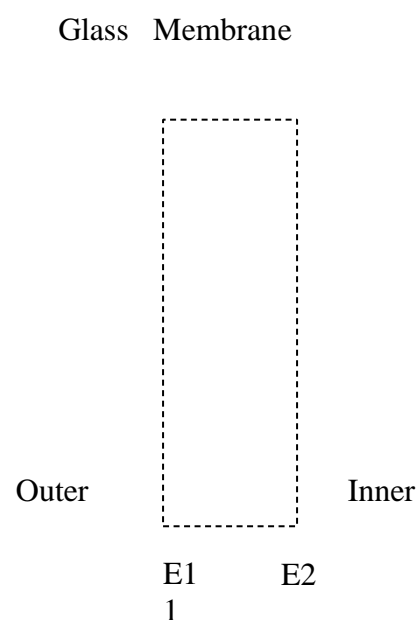Fig.1.5.1a. Schematic diagram of the Glass electrode

Fig. 1.5.2b. Line sketch of a glass membrane showing outer analyte solution and internal reference solution.

The electrode consists of a thin glass membrane, typically about 0.03 to 0.1 mm thick, sealed onto one end of a heavy–walled glass tube. A special variety of glass (corning 0l5 glass with approximate composition 20 % Na_2O, 6 % CaO & 72 % SiO_2) is used which has a low melting point and high electrical resistance. The glass bulb is filled with a solution of

constant pH (0.1 M HCl). A small volume of saturated silver chloride is contained in the tube. A silver wire in this solution forms a silver/silver chloride reference electrode which is connected to one of the terminals of a potential measuring device. The internal reference electrode is a part of the glass electrode and it is not the pH sensing element. Only the potential that occurs between the outer surface of the glass bulb and the test solution responds to pH changes.

1.5.2 Working: A silicate glass used for membranes consists of an infinite 3D- network of SiO_4^{4-} groups in which each silicon is bonded to four oxygen and each oxygen is shared by two silicons. There are sufficient cations to balance the negative charge of the silicate groups within the interstices of this structure. Singly charged cations such as sodium and lithium are mobile in the lattice and are responsible for electrical conduction within the membrane. The glass is a partially hydrated aluminosilicate containing sodium or calcium ions. The hydration of a pH sensitive glass membrane involves an ion-exchange reaction between singly charged cations in the interstices of the glass lattice and protons from the solution. The process involves univalent cations exclusively because divalent cations are too strongly held within the silicate structure to exchange with ions in the solution and hence immobile. The ion-exchange reaction can be written as

- H^+ $+$ Na^+ $\rightleftharpoons$ Na^+ $+$ H^+
  Solution   glass   solution   glass
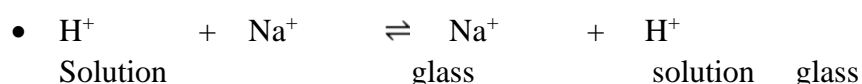
The Na^+ ions on the glass membrane are exchanged for H^+ ions in the solution. The potential of the electrode is controlled by the difference between the hydrogen ion concentration inside and outside the thin glass membrane. Since the H^+ ion concentration inside the electrode is constant, the electrode's potential varies only with the concentration of H^+ in the solution outside. Thus the potential arises from the difference in positions of ion-exchange equilibrium on each of the two surfaces. The surface exposed to the solution having the higher H^+ concentration becomes positive with respect to the other surface. This charge difference or potential serves as the analytical parameter when the pH of the solution on one side of the membrane is held constant. Evidently the selectivity of glass electrodes is related both to the ability of the various monovalent cations to penetrate into the glass membrane and to the degree of attraction of the cations to the negative sites within the glass.

1.5.3 Electrode Potential of GE

The overall potential of the glass electrode has three components; 1) The boundary potential E_b, which varies with the pH of the analyte solution. It is made up of two potentials, E_1 & E_2 which develop at the two surface of the glass membrane i.e. the potential developed at the inner glass surface & the potential developed at the outer glass surface.

$$E_b = E_1 - E_2 \text{_____ (1)}$$

Where E_b is the boundary potential

E_1 = potential developed at the interface between the exterior of the glass and the analyte solution

E_2 = Potential developed at the interface between the internal solution and the interior of the glass. The boundary potential is related to the concentration of hydrogen ion in each of the solution by the Nernst-like equation.

$$E_b = E_1 - E_2 = 0.0592 \log C_1 / C_2 \text{_____ (2)}$$

Where C_1 = concentration of the analyte solution

C_2 = concentration of the internal solution

For a glass pH electrode the hydrogen ion concentration of the internal solution is held constant.

So eqn. (2) becomes

$$E_b = K + 0.0592 \log C_1 \text{_____(3)} \quad \text{(Recall pH= -log [H}^+])$$

$$E_b = K - 0.0592 \log \text{pH where K= -.0592 log } C_2$$

The boundary potential is then a measure of

1) the hydrogen ion concentration of the external solution.

2) The potential of the internal Ag/AgCl reference electrode. $E_{Ag/AgCl}$.

3) A small unpredictable contribution called the asymmetry potential, E_{asym}.

The sources of the asymmetry potential include the following.

i) Differing conditions of strain in the two glass surfaces during manufacture

ii) Mechanical abrasion on the on the outer surface during use

iii) Chemical etching of the outer surface during use.

The asymmetry potential changes slowly with time. The glass electrode potential can be written in the equation form as

$$E_G = E_b + E_{Ag/AgCl} + E_{asym} \text{_____ (4)}$$

Substitution of eqn – (3) for E_b, gives

$E_G = K + 0.0592 \log C_1 + E_{Ag/AgCl} + E_{asym}$

$\quad = K - 0.0592 \log pH + E_{Ag/AgCl} + E_{asym} \underline{\quad}(5)$

$E_G = E^o_G - 0.0592\ pH \underline{\hspace{5cm}}(6)$

where $E^o_G = K + E_{Ag/AgCl} + E_{asym.}$ a combination of three constant terms = constant To measure the hydrogen ion concentration of the test solution, the glass electrode (indicator electrode) must be combined with an external reference electrode, which is required for all kinds of ion-selective electrode determinations.

1.5.4 Applications: Determination of pH:

The glass electrode has an emf that changes with hydrogen ion concentration, i.e the glass electrode is the most important indicator electrode for hydrogen ion. It is used for the measurement of pH under many conditions and normally calomel electrode is used as reference electrode to complete the cell (Fig.1.4.4)
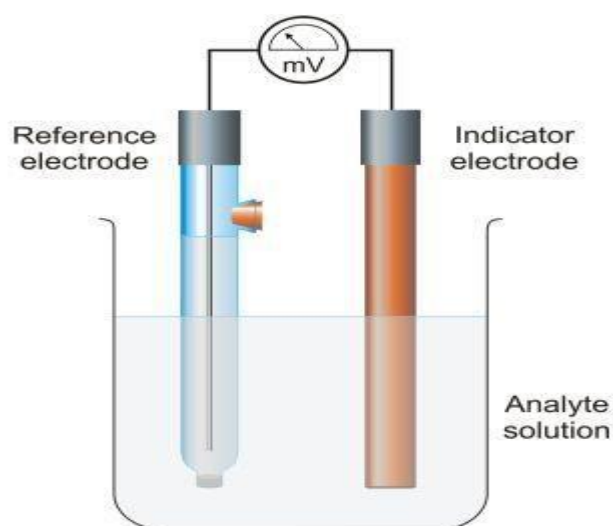
Cell: SCE / Test solution / GE

Fig.1.4.4.   Set up of indicator electrode and reference electrode for the measurement of pH.

$E_{cell} = E_{glass} - E_{calomel}$ where E_{glass} = the E.P. of the glass electrode.

$\quad\quad E_{calomel}$ = the E.P. of the SCE

$E_{cell} = E^o_G - 0.0592\ pH - 0.2444$

The E^o_G value of a glass electrode can be determined by dipping the glass electrode in a solution of known pH. Typical fields are the clinical & food analysis, environmental monitoring (industrial waste acidity of rain) and process control (fermentation, boiler water, galvanization & precipitation)

1.5.5 Advantages:

➢ It can be used without interference in solutions containing strong oxidants, strong reductants, proteins, viscous fluids and gases as the glass is chemically robust.

➢ The glass electrode gives accurate results in the pH range 2 – 10. With some special glass (by incorporation of Al_2O_3 or B_2O_3) measurements can be extended to pH values up to 12.

➢ It is immune to poisoning and is simple, robust and easy to operate.

➢ The equilibrium is reached quickly & the response is rapid.

➢ It can be used for very small quantities of the solutions. Small electrodes can be used for pH measurement in one drop of solution in a tooth cavity or in the sweat of the skin (micro determinations using microelectrodes)

➢ The glass electrode is much more convenient to handle than the inconvenient hydrogen gas electrode.

➢ Glass electrodes which are selective for Li^+, Na^+, Cs^+, Ag^+ and NH_4^+ ions are commercially available and these special electrodes are useful for measuring the above ions.

1.5.6.   Disadvantages:

➢ The bulb of this electrode is very fragile and has to be used with great care. The sensitive tip is easily scratched and ruined.

➢ The alkaline error arises when a glass electrode is employed to measure the pH of solutions having pH values in the 10-12 range or greater. In the presence of alkali ions, the glass surface becomes responsive to both hydrogen and alkali ions. Hence the measured pH values are low and thus the glass pH electrode gives erroneous results in highly alkaline solutions.

➢ The acid error results in highly acidic solutions (pH less than zero) Measured pH values are high.

➢ Dehydration of the working surface may cause erratic electrode performance. It is crucial that the pH electrode be sufficiently hydrated before being used. When not in use, the electrode should be stored in an aqueous solution because once it is dehydrated; several hours are required to rehydrate it fully.

➢ As the glass membrane has a very high electrical resistance (50 to 500 MΩ), the ordinary potentiometer cannot be used for measurement of the potential of the glass

electrode. Thus special electronic potentiometers are used which require practically no current for their operation.

> Standardization has to be carried out frequently because asymmetry potential changes gradually with time. It is better to determine E^o_G for a glass electrode before use.

> The commercial version is moderately expensive.

> To some extent, the constant E^o_G is a function of the area of glass in contact with the acid analyte. For this reason, no two glass electrodes will have the same value of E^o_G. Note that E^o_G depends on a particular glass electrode used & it is not a universal constant.

1.6 BATTERY   TECHNOLOGY

1.6.1 Introduction

Can you imagine a world without batteries? The clock on your wall requires a battery for it to work. The watch on your wrist goes on a battery. The motor vehicle needs a battery for it to start and take you to your destination. Battery is the backbone of UPS to run your computer without interruption. After a days work, if you pick-up the remote control of the television, it is again the battery that helps you to change channels of the T.V. Cameras, laptop computers, cellular phones, key chain laser, heart pacemaker and children toys – they all require batteries.

Batteries are used for so many different purposes and different applications require batteries with different properties. The battery required to start a car must be capable of delivering a large electrical current for a short period of time. The battery that powers a cardiac pacemaker must be small, rugged, leak proof, compact and capable of delivering a steady current for an extended period of time. In UPS systems, longer and consistent backup is needed. Batteries for hearing aids must be above all tiny. Batteries for torpedoes and submarines must be stable during storage and give high power for short times & certainly rechargeable. For a lap-top computer, a battery in the form of a flexible sheet distributed

around the case is much preferred. Batteries remain an enormous industry with a turnover of billions of pounds worldwide.

1.6.2 Classification of commercial cells

Primary Cells: They are galvanic cells which produce electricity from chemicals that are sealed into it when it is made. This type of cells cannot be recharged as the cell reaction cannot be reversed efficiently by recharging. Once the cell reaction has reached equilibrium the cell must be discarded. No more electricity is generated and we say the battery is 'dead'. These are also known as 'throw – away' batteries or irreversible batteries.

Eg: Dry cell, Lithium copper sulfide cell

Secondary cells: A secondary cell is rechargeable by passing current through it. In the charging process, an external source of electricity reverses the spontaneous cell reaction and restores a non- equilibrium mixture of reactants. After charging, the cell can be used for supplying current when required, as the reaction sinks toward equilibrium again. Thus as the secondary cell can be used through a large number of cycles of discharging and charging. Such cells are also known as rechargeable cells, storage cells, or accumulators.

Eg. Lead-acid batteries, Nickel-cadmium cell, Lithium- ion battery

1.6.2.1 Requirements of Primary Battery:

- Compact, lightweight and must be fabricated from easily available raw materials.

- Economic and have benign environmental properties

- Should have a high energy density, longer shelf life

- Provide constant voltage and should have a long discharge period

1.6.2.2 Requirements of Secondary Battery

- Long shelf-life in both charged & discharged conditions

- Longer cycle life and design life

- High power to weight ratio

- Short time for a recharge.

- High voltage & high energy density

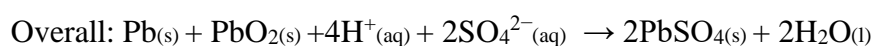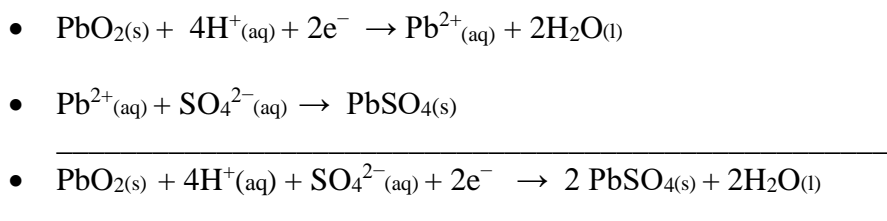**1.6.2.3 Differences between Primary and Secondary batteries**

Primary Batteries	Secondary Batteries
1.Cell reaction is irreversible	Cell reaction is reversible
2. They must be discarded after its active elements have been consumed	They may be recharged a number of times from an external d.c. source during its useful life
3. Have a relatively short shelf life	Have a very long shelf life
4. Function only as galvanic cells	Function as galvanic cells during discharge as & as electrolytic cells during the charging process.
5. They cannot be used as energy storage devices	They can be used as energy storage devices (e.g. solar/ thermal energy converted to electrical energy)
6. They cannot be recharged	They can be recharged.
e.g. Dry cell, Li-MnO$_2$ battery	e.g.Lead acid battery, Ni-cd battery

1.6.3 Lead Storage Battery (Lead Accumulator or Car Battery or The acid battery)

Construction: The electrodes are lead grids to maximize its surface area. The anode grid is filled with finely divided spongy lead (Pb) and the cathode grid is packed with lead dioxide (PbO$_2$). Both electrodes are submerged in a sulfuric acid solution (H$_2$SO$_4$) having a specific gravity of about 1.25 that acts as the electrolyte. Anode and cathode grids are separated by insulators like strips of wood, rubber or glass fiber. In car batteries, six cells are connected in series (anode to cathode) to produce a 12–volt battery. The battery is encased in a plastic container or hard vulcanized rubber vessel. The cell doesn't need to have a separate anode and cathode compartments because the oxidizing and reducing agents are both solids (PbO$_2$ & Pb) that are kept from coming in contact by the presence of insulating spacers between the grids. Both anode and cathode are immersed in a common electrolyte (i.e. cell without liquid
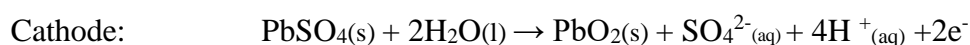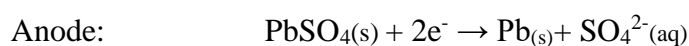
junction). This is an example of a 'wet cell', because the electrolyte is an aqueous solution of sulphuric acid. The lead acid battery is very widely manufactured – 300 million units are made each year.

At the cathode:

- $PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)}$

- $Pb^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \rightarrow PbSO_{4(s)}$

  _____

- $PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{2-}_{(aq)} + 2e^- \rightarrow 2\ PbSO_{4(s)} + 2H_2O_{(l)}$

  _____

Overall: $Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO_4^{2-}_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

Explanation: At the anode, lead atoms lose two electrons (e⁻) and become positively charged lead ions (Pb^{2+}). The lead ions combine with the sulfate ions (SO_4^{2-}) in the sulfuric acid solution to produce lead sulfate ($PbSO_4$). At the cathode, lead dioxide gains electrons, releasing oxygen, which attaches to hydrogen ions (H+) to produce water (H_2O (l) and lead ions. The lead ions react with sulfate ions to produce lead sulfate. As this reaction progresses, the flow of electrons creates an electric current. Lead sulfate adheres on each electrode and water increases. The concentration of sulfuric acid decreases and the amount of lead and lead dioxide decrease. When the reactants are depleted, the battery stops producing electricity. The reaction can be reversed by recharging the battery & the $PbSO_4$ formed during discharge remains adhered on each electrode and is available at the site during recharging. The nominal voltage of each cell is about 2.1 V. The lead storage battery is designed to operate reversibly, so that it can be used for the storage of electrical energy. They are called storage batteries because their essential function is to store electrical energy. It is used to store energy in chemical form.

Reactions during Charging:

Anode: $PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}_{(aq)}$

Cathode: $PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow PbO_{2(s)} + SO_4^{2-}_{(aq)} + 4H^+_{(aq)} + 2e^-$

Net reaction: $2PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4$

Recharging is possible because $PbSO_4$ formed during discharge adheres to the electrodes. By attaching an external power source to a battery (>2 volts), a current runs through the poles in the opposite direction from normal discharge. This changes the lead sulfate and water back into the original reactants, lead dioxide and sulfuric acid, i.e. the electrodes return to their former composition and the sulfuric acid is regenerated. Charging, therefore, produces a gradual increase in the sulfuric acid concentration. Since the level of charge on a storage battery is related to sulfuric acid concentration, the specific gravity of the H_2SO_4 solution is a measure of the operational condition of a battery. A charged battery at room temperature with its electrolyte at normal concentration supplies a potential difference of 2.1 to 2.2 V. The complete reaction cycle of a lead acid storage battery is as follows.

$$Pb_{(s)} + PbO_2 + 2 H_2SO_{4(aq)} \underset{Ch}{\overset{Disch}{\rightleftarrows}} 2 PbSO_{4(s)} + 2 H_2O_{(l)}$$
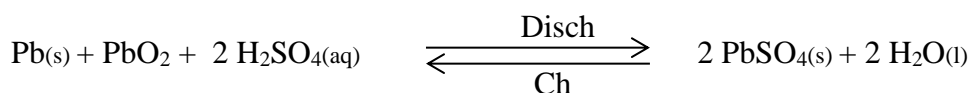
In an automobile, the energy necessary for recharging the battery is provided by the generator driven by the engine. As the external source forces electrons from one electrode to another, the $PbSO_4$ is converted to Pb at one electrode & to PbO_2 at the other.

Overcharging:

Electrolysis of water: The net reaction can be summarized by the equation.

$2H_2O_{(l)} +$ electrical energy $\rightarrow$ $2H_{2(g)} + O_{2(g)}$

No gases will be liberated on charging as long as lead ions are present in solution. If the electrolysis is permitted to proceed further, hydrogen gas is formed at the cathode and oxygen gas is evolved at the anode. The hydrogen ions are discharged at the cathode through the reaction

$2H^+(aq) + 2e^- \rightarrow H_2(g)$
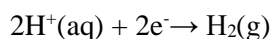
Sulphate ions are resistant to oxidation and are not discharged at the cathode. Water is oxidized at the anode in preference to SO_4^{2-}

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
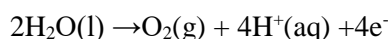
Consequences: (i) Excessive charging may reduce the acid level and may damage the exposed electrode grids (ii) In extreme cases, there will be dangerous high-pressure build-up that can lead to a serious risk of explosion. In more normal circumstances, the older version of the battery needs to be 'topped up' from time to time.

Recent years have seen the introduction of "maintenance – free batteries" without a gas – release vent. Here the gassing is controlled by careful choice of the composition of the lead alloys used i.e. by using a Pb-Ca (0.1 %) as the anode which inhibits the electrolysis of water.

Alternatively, some modern batteries contain a catalyst (e.g. a mixture of 98% ceria (cerium oxide) & 2% platinum) that combines the hydrogen and oxygen produced during discharge back into the water. Thus the battery retains its potency and requires no maintenance. Such batteries are sealed as there is no need to add water and this sealing prevents leakage of cell materials.

*Applications***:** The many battery designs available for a wide variety of uses can be classified into three main categories. (a) Automotive (b) Industrial & (c) Consumer batteries.

The automotive type is used in cars and trucks, to provide a short burst of power for starting the engine. It is incorporated as an essential accessory into the starting circuit of internal combustion engines for starting, lighting & ignition (SLI). Units normally have nominal voltages of 12 V for LMVS and 24 V for HGVS. It is still playing a major role in transportation, powering literally millions of ICES in automobiles. The industrial batteries are used for heavy–duty applications such as motive and standby power. This class of batteries is used to operate electric trucks, submarines and mine locomotives. They also provide power

for the air conditioning and lighting systems. It is used in the stationary back–up power applications such as telecommunication systems, to ensure that, for example, the telephone network will continue to operate even in the event of a mains power failure. Such batteries are kept in hospital operating theaters, railway signal centres and other places where a power failure might be disastrous and is used to supply electrical power during emergencies.The consumer batteries are used in aemergency lighting systems, security and alarm systems, public address systems, power tools, UPS in computers, and small engine starting including electronic vehicles.

Advantages:

- A lead storage battery is highly efficient. The voltage efficiency of the cell is defined as follows.

- Voltage efficiency = <u>average voltage during discharge</u>
    - average voltage during charge
- The voltage efficiency of the lead – acid cell is about 80 %.

- The near reversibility is a consequence of the faster rate of the chemical reactions in the cell i.e. anode oxidizes easily and cathode reduces easily leading to an overall reaction with a high negative free energy change.

- A lead – acid battery provides a good service for several years. The number of recharges possible range from 300 to 1500, depending on the battery's design and conditions. The sealed lead-acid batteries can withstand up to 2000 – recharging. Time required for recharging is relatively low i.e about 2-8 hours.

- The battery has low internal self – discharge.

- A typical car battery provides a voltage of 12 V. This is not a large voltage, but the battery can provide a large current. E.g. over 10 A, without being destroyed.

Disadvantages:

- If left unused in partially charged condition, it can be ruined in a short time by nucleation and the growth of relatively large $PbSO_4$ crystals, which are not easily reduced or oxidized by the charging current. This disaster is known as 'sulfation'.

- The lead acid battery has low energy storage to weight ratio i.e. its chief disadvantages is its great weight.(energy density $\sim$ 35 wh / kg)

- The cell potential decreases with a decrease in concentration of sulfuric acid. During the discharge process sulfuric acid is consumed and water is produced. So the solution of sulfuric acid in the cell becomes less concentrated. The state of charge of the cell can be judged by the concentration of sulfuric acid in the liquid and this is usually done with a simple device to measure the density of the liquid. The density of a healthy, fully charged battery is $\geq$ 1.25 g/mL.

- The battery is not efficient at a lower temperature. Foe a battery to function properly, the electrolyte must be fully conducting. There will be an increase in the viscosity of the electrolyte due to a decrease in the temperature. This leads to a decrease in the cell potential.

- Overcharging may damage the exposed electrodes and may also lead to an explosion in extreme cases. Sulfuric acid is highly corrosive liquid. In the event of an explosion, the electrolyte is sprayed on to the individual who is working on the battery. Therefore, safety goggles must be worn when working with these batteries.

- Lead is toxic and hence environmental & health problems arise due to careless disposal by consumers.

- The corrosion of the lead grid at the lead dioxide electrode is one of the primary causes of lead acid battery failure.

1.6.4 Nickel-Cadmium Cell

Construction: NiCad cell consists of a nickel wire gauze electrode grids. The anode grid consists of spongy cadmium metal and the cathode grid contains the nicked (III) compound NiO(OH). The electrolyte is a concentrated solution of KOH. It is the electrolyte of choice because of its compatibility with the various electrodes, good conductivity and low freezing point temperature (about -30° C). Anode and cathode are separated by a very thin separator. The contents are encased as a sealed unit in a steel case.
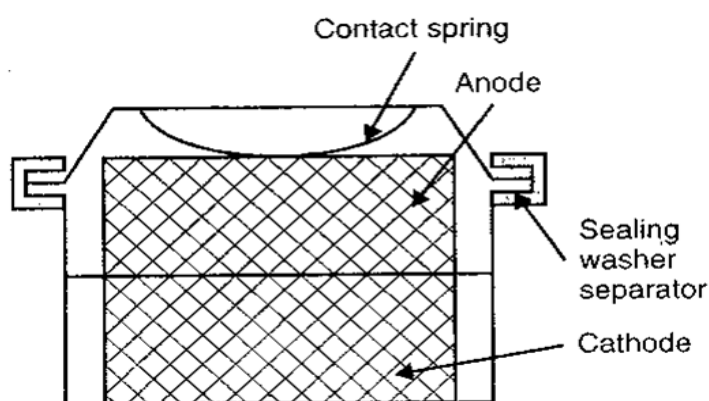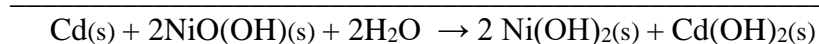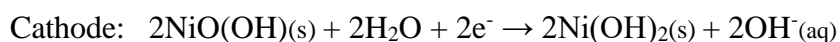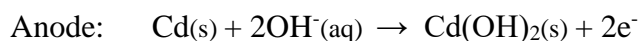

Figure 1.6.4 Schematic representation of NiCad cell

Working:

Discharging reactions

Anode: $Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^-$

Cathode: $2NiO(OH)_{(s)} + 2H_2O + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)}$

$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O \rightarrow 2\,Ni(OH)_{2(s)} + Cd(OH)_{2(s)}$

Charging reactions:

Anode: $Cd(OH)_{2(s)} + 2e^- \rightarrow Cd_{(s)} + 2OH^-_{(aq)}$

Cathode: $2\,Ni(OH)_{2(s)} + 2OH^-_{(aq)} \rightarrow 2\,NiO(OH)_{(s)} + 2H_2O + 2e^-$

Overall reaction: $2\,Ni(OH)_{2(s)} + Cd(OH)_{2(s)} \rightarrow 2\,NiO(OH)_{(s)} + Cd_{(s)} + 2H_2O_{(l)}$
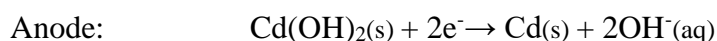
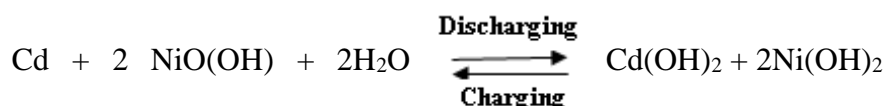**Explanation:** At anode cadmium metal undergoes oxidation from 0 to +2, leaving behind two electrons for every atom oxidized, as the cell discharges. At cathode nickel is reduced from the +3 oxidation state (in nickel oxide hydroxide) to +2 (in nickel hydroxide). Note that

OH⁻ is not used up as the cell is discharged. Therefore, there is no voltage drop through most of the useful life of the battery as it discharges. The net reaction can take place until the active materials are exhausted, during charging process, the cadmium hydroxide is re-converted into cadmium and the nickelous hydroxide is reconverted to nickeloxide hydroxide. The overall chemical reaction of the Ni-Cd system may be represented as

$$Cd \ + \ 2 \ NiO(OH) \ + \ 2H_2O \quad \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} \quad Cd(OH)_2 + 2Ni(OH)_2$$

The cell must be recharged by applying the correct dc charging voltage.

Applications: Nicad cells are available in standard sizes (AA, D, C,F etc.) for use in flash lights, photoflash units and portable electronic equipment such as radios, micro tape recorders, calculators, cordless phones, electronic shavers, drills & garden tools. It is also used in emergency lighting systems, alarm systems, personal audio equipment (walkman type cassette players), kitchen appliances and other battery powered small tools, toys & games.

Advantages:

➢ Ni-cad batteries can be recharged many times because the solid products of the electrode reactions adhere to the surface of the electrodes. Normally this battery can withstand up to 3000 – recharging (longer cycle life)

➢ They maintain nearly constant voltage level throughout their discharge. Note that there is no change change in the electrolyte composition during the operation.

➢ It can be left unused for long periods of time at any state of charge without any appreciable damage (i.e. long shelf life).

➢ It can be encased as a sealed unit like the dry cell because gassing will not occur during nominal discharging or recharging.

- They possess a longer design life. It can be extended upto 30 years or more if maintained.

- They exhibit good performance ability at low temperatures.

- They can be used to produce large instantaneous currents as high as 1000-8000 A for one second.

Disadvantages:

- It poses an environmental pollution hazard due to careless disposal by consumers and produces health problems (decreases range from asthma to cancer) due to higher toxicity of metallic cadmium than lead.

- Cadmium is a heavy metal and its use increases the weight of batteries, particularly in larger versions. The energy density is approximately 40 Wh/kg.

- Cost of cadmium metal and hence the cost of construction of NiCad batteries is high. The overall capital cost of these batteries is roughly then higher than that of lead storage batteries.

- The KOH electrolyte used is a corrosive hazardous chemical. It is a poison and if ingested attacks the throat and stomach linings. Eye contact can result in serve burns and blindness. Protective clothing and face shields or goggles should be worn while performing maintenance work.

1.6.5 Lithium ion cells

Lithium metal cannot be used safely in secondary batteries. Hence, various lithium compounds have been made, which are used in rechargeable batteries, commonly known as Lithium –Ion Cells. In these type of batteries, a lithiated metal oxide such as $LiCoO_2$, LiV_2O_5, $LiMn_2O_4$ etc is inserted into the cathode which consists of a layered graphite crystal. The electrolyte is normally $LiPF_6$, but $LiBF_4$ can also be used as $LiPF_6$ is not corrosion resistant.

Construction:

The anode is a lithium-carbide type intercalate (Li_xC_6). The cathode is a transition metal oxide MO_2 of variable oxidation state (MnO_2, CoO_2, NiO_2) which can intercalate lithium usually cobalt dioxide, CoO_2 is used. The electrolyte is usually inert polar dry ether or carbonate (diethyl carbonate or propylene carbonate), in which a conductivity salt such as $LiPF_6$ or $LiBF_4$ is dissolved.
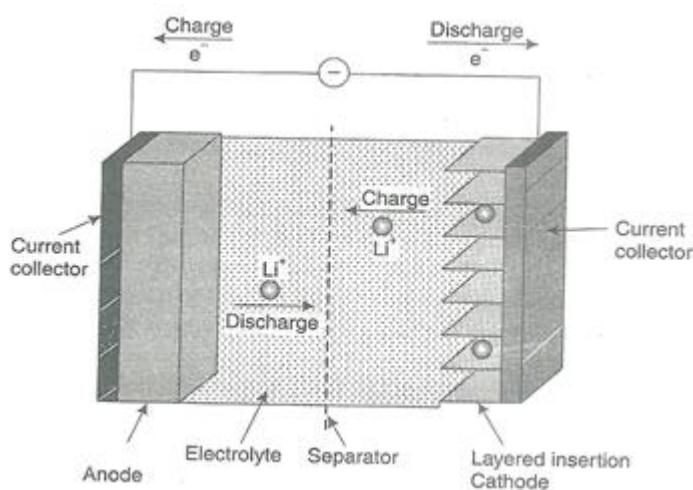

Figure 1.6.5 Schematic diagram of Rechargeable lithium ion battery
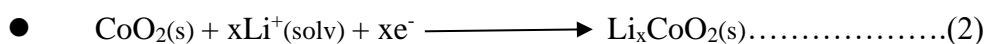
Working: Graphite has a layered structure and its electrochemically reduced in an aprotic organic electrolyte containing lithium salts and lithium in interclated (or doped) between the layers of graphite to form Lithium-Graphite interclated compound (GIC). Li-GIC undergoes oxidation leaving an electron.
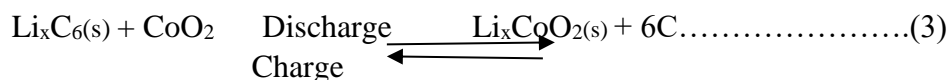
At anode:

- $Li_xC_6 \longrightarrow xLi^+_{(solv)} + 6C_{(s)} + xe^-$ ....(1)

When a negative electrode is discharged, lithium is deinterclated (undoped) from lithiated graphite and lithium ions dissolve into the elctrolyte. The lithium content in the $LiCoO_2$ electrode reversibly changes during charge and discharge as indicated in the following equation:

At cathode:

35

- $CoO_2(s) + xLi^+(solv) + xe^- \longrightarrow Li_xCoO_2(s)$……………….(2)

Net cell reaction:

$Li_xC_6(s) + CoO_2$ — Discharge / Charge $\rightleftharpoons Li_xCoO_2(s) + 6C$…………………(3)

***Explanation*s:** It is called as a lithium ion battery to emphasise that it contains no lithium metal. Both the electrodes are intercalation compounds. The electrode on the left serves as the anode when the cell discharges. It is a special intercalation compound consisting of a graphite host into which lithium ions have been electrochemically inserted between the carbon atom layers. The lithiated graphite is written as Li_xC_6. During the discharge, the lithium ions are extracted by the half-reaction (1). The electrode that serves as cathode during discharge is normally cobalt dioxide. The reduction half reaction is cathode during discharge is normally cobalt dioxide. The reduction half reaction shown in eq.(2), where cobalt undergoes reduction from IV to III oxidation state. The overall reaction is shown in eq.(3). During discharge the Li^+ ions spontaneously migrate from the lithium graphite anode to the CoO_2 cathode enablingcurrent to flow through the external circuit. When charged, cobalt ions are oxidized and lithium ions migrate into the graphite, when discharging the battery delivers energy to the external load and when charging it recieves energy from a d.c. power source. The electrode that acts as an anode, during discharging becomes a cathode when its charging.

Applications:

- Lithium-ion batteries are most commonly used in applications where one or more of the advantages (size, weight or energy) outweigh the additional cost, such as mobile telephones and mobile computing devices.

- Lithium-ion-polymer batteries are used when the battery design matters in a particular application as different designs are possible (Cylindrical, jelly-roll design, flat rectangular).

- It is used in current-generation laptops, cellular phones, video-recorders.

- It is also used in portable CD players, televisions and implantable medical devices.

Advantages:

➢ Lithium-ion batteries were designed to overcome the safety problems associated with the highly reactive properties of Lithium metal.

➢ Long cycle life (400-1200 cycles).

➢ They are smaller, lighter and provide greater energy density than either nickel-cadmium or nickel-metal-hydride batteries

➢ They can be operated in a wide temperature range and can be recharged before they are fully charged.

➢ Typically designed to be recharged in the device rather than in an external charger.

➢ The average voltage of a Li-ion battery is equivalent to three Ni-Cd cells.

Disadvantages:

➢ Poor charge retention.

➢ The self discharge rate is about 10% per month.

➢ It prices are high compared to other types of cells commonly used.

1.7 Fuel cells

A fuel cell is a galvanic cell of a special type in which chemical energy contained in a fuel – oxidant system is converted directly into electrical energy in a continuous electrochemical process. It is an energy conversion device or electricity producer. The fuel cell has two electrodes and an electrolyte like a primary cell. The reactants (i.e. fuel + oxidant) are constantly supplied from outside and the products are removed at the same rate as they are formed.

Cell: Fuel/ electrode/electrolyte/electrode/oxidant.

Anode: Fuel + oxygen -----------$>$Oxidation products+ ne-

Cathode: Oxidant + ne$^-$ ----------$>$Reduction products

A fuel cell consists of fuel, electrodes, electrolyte, & oxidant. Fuel undergoes oxidation at the anode and oxidant gets reduced at the cathode. The cell can produce current as long as the reactants are supplied. Most fuel cells produce low voltages, commonly less than one volt, So a number of them are connected in series in "fuel batteries."
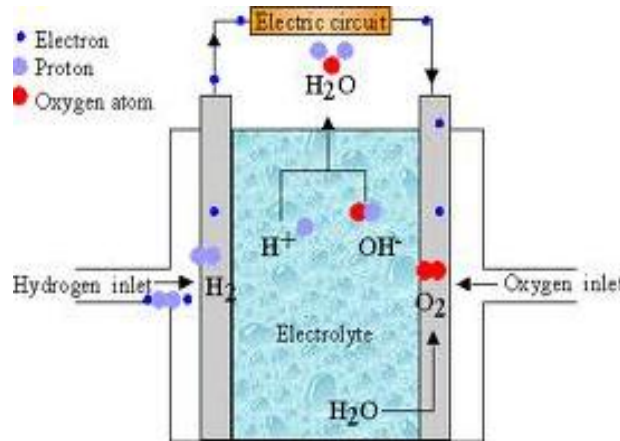

Figure 1.7 Fuel cell

Eg:- H_2-O_2 fuel cell, CH_3OH-O_2 fuel cell, Solid-oxide fuel cell, Molten carbonate fuel cell

1.7.1 Advantages of fuel cells

- High fuel to electricity conversion efficiency of 70-75 % while a thermal power plant converts 35-40% chemical energy of coal into electrical energy.

- Fuel cell products do not cause pollution problems such as noise pollution, chemical pollution and thermal pollution normally associated with conversional power plants.

- Fuel cell power plants can be located near the point of use electricity such as on an urban location,rather than at a remote place. So transmission and distribution lose (~30%) could be avoided.

- A fuel cell will produce a steady electric current as long as fresh reactants are available.

1.7.2 Classification of fuel cells

S. No.	Fuel cell type	Electrolyte used

38

1	Polymer electrolyte	Polymer membrane
2	Direct methanol	Polymer membrane
3.	Alkaline	Potassium hydroxide
4.	Phosphoric acid	Phosphoric acid
5.	Molten carbonate	Lithium/potassium carbonate
6.	Solid oxide	Yittria stabilized zirconia

1.7.3 Alkaline fuel cell (AFC)

The hydrogen gas is continuously supplied at the anode and pure oxygen gas is continuously supplied at the cathode form an external reservoir. The cell operates at about 80 $^{\circ}$C and the normal voltage is 1.10 V. At the anode, hydrogen is oxidized to the H$^+$ ions, which are neutralized by the OH$^-$ ions of the electrolyte, forming water and electrons are released. At the cathode, oxygen and water take electrons to form hydroxide ions. The overall reaction is equivalent to the combustion of hydrogen. The only product discharge by the cell is water vapor that escapes through the exhaust point. Note that the gases H$_2$ and O$_2$ diffuse into the electrode pores and so does the electrolyte solution.
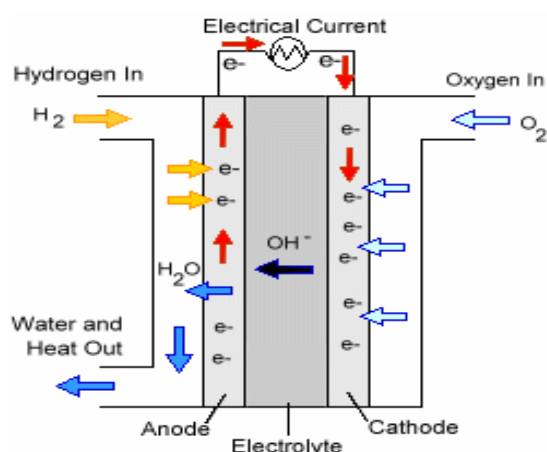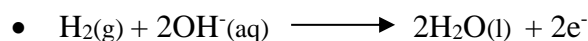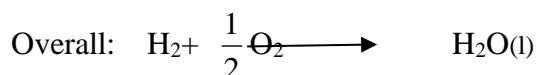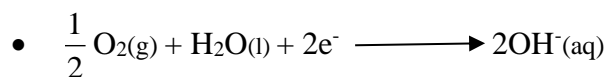

Figure 1.7.3 AFC

Working:

 At Anode:

- $H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$

  At Cathode:

- $\dfrac{1}{2} O_2(g) + H_2O(l) + 2e^- \longrightarrow 2OH^-(aq)$

  Overall: $H_2 + \dfrac{1}{2} O_2 \longrightarrow H_2O(l)$

Advantages: Desirable attributes of the AFC include its excellent performance on hydrogen (H_2) and oxygen (O_2) compared to other candidate fuel cells due to its active O_2 electrode kinetics and its flexibility to use a wide range of electro-catalysts.

Disadvantages:

- The sensitivity of the electrolyte to CO_2 requires the use of highly pure oxidant and fuel.

- As a consequence, the use of a reformer would require a highly effective CO and CO_2 removal system.

- If ambient air is used as the oxidant, the CO_2 in the air must be removed. While this is technically not challenging, it has a significant impact on the size and cost of the system.

Applications: AFC is widely used in US space programs to produce electrical energy and water onboard spacecraft.

1.7.4 Direct Methanol fuel cell (DMFC)

Construction: Both electrodes are made up of porous nickel plates impregnated with finally-divided platinum. Methyl alcohol is used as the fuel which is circulated through the anode chamber. Pure oxygen / air acts as an oxidant and it is passed through the cathode chamber. Concentrated phosphoric acid, used as electrolyte is placed in the central compartment. The cell operates at 150-200 °C. At lower temperatures, phosphoric acid is a poor ionic conductor. At ~200 °C, phosphoric acid polymerizes to pyrophsphoric acid which has higher ionic

conductivity. A membrane is inserted adjacent to the cathode on the electrolyte side to minimize the diffusion of methanol into the cathode. In the absence of a membrane, diffusion of the dissolved methanol through the electrolyte to cathode takes place and chemical oxidation of methanol occur forming formaldehyde ($CH_3OH \rightarrow HCHO$). The emf of the cell is 1.20 V at 25 °C.
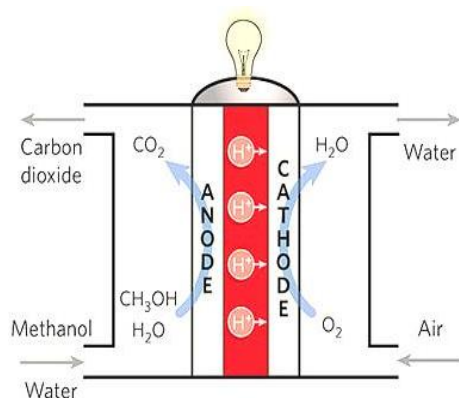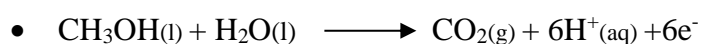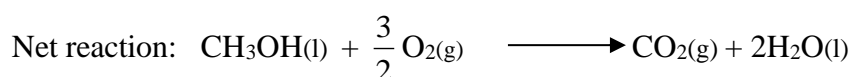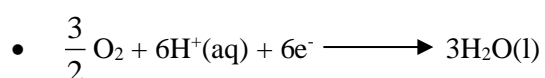

Figure 1.7.4 DEMFC

MeOH is one of the most electro active organic fuels in the low temperature range because (i) it has a low carbon content (ii) it possesses a readily oxidizable OH group and iii) it is miscible in all proportions in aqueous electrolytes.

Working:

At anode:

- $CH_3OH_{(l)} + H_2O_{(l)} \longrightarrow CO_{2(g)} + 6H^+_{(aq)} + 6e^-$

At cathode:

- $\dfrac{3}{2} O_2 + 6H^+_{(aq)} + 6e^- \longrightarrow 3H_2O_{(l)}$

Net reaction: $CH_3OH_{(l)} + \dfrac{3}{2} O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$

Explanation: At the anode methanol from the fuel gas steam is consumed, yielding electrons to the anode and producing hydrogen ions, which enter the electrolyte. At the cathode, oxygen combines with electrons (from the cathode) and hydrogen ions (from the electrolyte)

41

to produce water. Water is consumed at the anode and is produced at the cathode. Positive ions (H^+) are transported across the proton exchange membrane to the cathode where they react with oxygen to produce water. Electrons are transported via an external circuit from anode to cathode providing power to external devices.The products of the overall reaction water vapor and carbon dioxide, are removed constantly. The nominal emf of the cell is 1.20 V.

Applications: It is used in military applications and in large scale power production. It has been used to power television relay stations.

Advantages:

- MeOH can be easily transported stored & dispensed within the current fuel network because it is a liquid fuel.

- The fuel is very cheap and available in large quantities.

- The only products of combustion are CO_2 and H_2O which can be removed easily.

- There is no production of NO_x gases as the operating temperature is about 150 ^{o}C.

- Methanol is stable in contact with the acidic membrane.

Disadvantages:

- The anode reaction has poor electrode kinetics, particularly at lower temperatures.

- The reduction of oxygen at the cathode is also slow.

- The permeability of the current perfluorosulfonic acid membranes to methanol, allowing a considerable crossover of fuel. This leads to both degradation of performance, since a mixed potential develops at the cathode and to a deterioration of the use of fuel.

- Methanol is toxic to humans, causing blindness in low doses and death in larger amounts.So there are concerns about their proper handling.

**1.7.5 Proton exchange membrane fuel cell (PEMFC)**

Polymer electrolyte membrane fuel cells – also called proton exchange membrane fuel cells – deliver high power density and offer the advantages of low weight and volume, compared to other fuel cells. PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst. They need only hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids like some fuel cells. Polymer electrolyte membrane fuel cells operate at relatively low temperatures, around 80 ^{o}C (176 ^{o}F).

Low temperature operation allows them to start quickly (less warm-up time) and results in less wear on system components, resulting in better durability. However, it requires that a noble-metal catalyst (typically platinum) be used to separate the hydrogen's electrons and protons, adding to system cost. The platinum catalyst is also extremely sensitive to CO poisoning, making it necessary to employ an additional reaction to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds cost. Developers are currently exploring Pt/Ru catalysts that are more resistant to CO.

Role of Proton conducting membranes:

- The membrane function in two ways: It acts as the electrolyte which provides ionic communication between the anode and the cathode and also it serves as the separator for the two-reactant gases.

- Optimized proton and water transport properties of the membrane and proper water management are crucial for efficient fuel cell operation.

- Dehydration of the membrane reduces the proton conductivity and excess of water can lead to the flooding of the electrolyte. Both conditions result in poor performance.

- The absence of solution-phase electrolyte in PEF fuel cells, compared to alkaline and phosphoric acid fuel cells greatly reduces the complexity of the fuel and oxidant flow controls.

- Polymeric electrolyte is carbon dioxide tolerant.

- The most important breakthrough came with the development of perflourinated membrane by DuPont. From 1966, the membrane requirements were best met by nafion family of perfluorinated ionomer membranes. Lifetimes over 60,000 hrs have been achieved at 353 K. Their general formula is
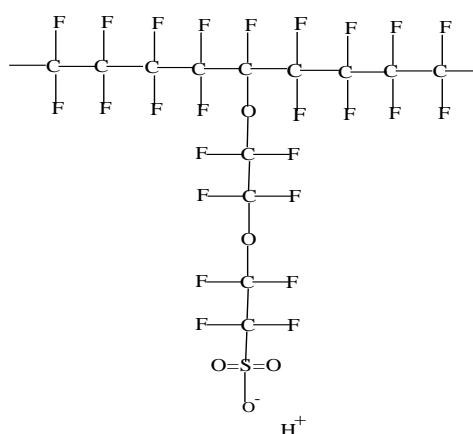
Construction:

Electrolyte:-Ion exchange polymeric membranes. This is an excellent insulator, but an excellent conductor of H^+ ions. The material used, consists of a fluorocarbon polymer backbone, similar to Teflon, to which sulphonic acid groups are fixed to the polymer and cannot leak out, but the protons of these groups are free to migrate through the membrane.

Electrodes:-Typical gas diffusion electrodes, made up of porous C impregnated with Pt catalyst. Noble metal treated carbon fiber paper/cloth which is directly bonded to the polymer membrane at an elevated temperature and pressure (The catalytic electrode/membrane configuration is referred to as membrane electrodes assemble, MEA).

Fuel:- Hydrogen

Oxidant:- Air

Catalyst:-Platinum

Interconnect:- Carbon or metal

Operating temperature:- 40 – 80 ℃.
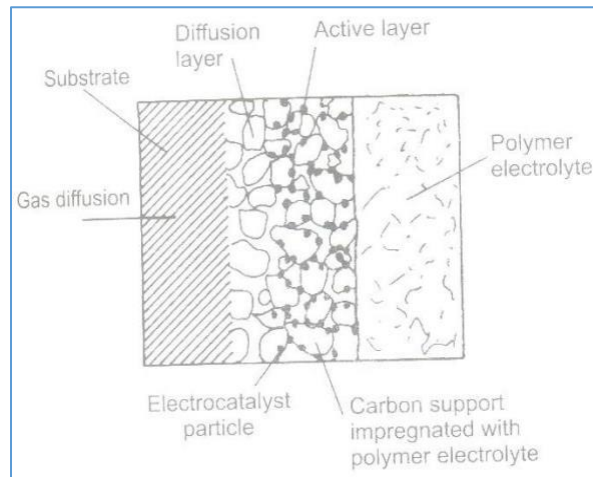
Charge-carrier:-H^+

Electrode:-

Fig.1.7.5.1 schematic of a typical PEMFC electrode, which displays three layers

(i) A Teflonized substrate (typically, carbon cloth)

(ii) A diffusion layer, generally formed by carbon particles of about 0.1 μm size with Teflon.

(iii) An active layer, where Pt catalyst grains are supported on carbon particles (Pt loading is usually 0.4 mg/cm^{2}or less) with or without Teflon.

Cell reactions and Function of PEMFC:

PEM fuel cells operate at around 80 ℃ and practical efficiency of 60 %. Power output is in the range of 5-200 KW. They are ideal for transportation and portable power. Additional advantages are their high response, small size and low cost. A polymer electrolyte membrane fuel cell is unusual in that its electrolyte consists of a layer of solid polymer which allows protons to be transmitted from one fact to the other. Porous carbon is used as the anode and cathode of the PEMFC, as shown in Fig. It basically requires H_2 and O_2 as its inputs, though the oxidant may also be ambient air, and these gases must be humidified. It operates at a low

temperature because of the limitations imposed by the thermal properties of the membrane itself. The operating temperatures are around 90°C and a Pt catalyst is used.
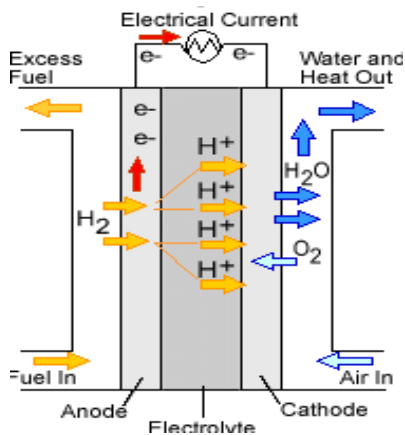

Fig.1.7.5.2 PEMFC

At anode:

- $H_2(g) \longrightarrow 2H^+(aq) + 2e^-$

At cathode

- $\frac{1}{2} O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O(l)$

Overall reaction: $\quad H_2(g) + \frac{1}{2} O(g) \longrightarrow H_2O(l)$
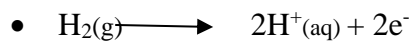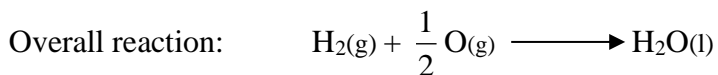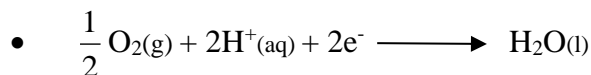
Applications:

- PEM fuel cells are used primarily for transportation applications and some stationary applications.
- Due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio, PEM fuel cells are particularly suitable for use in passenger vehicles, such as cars and buses.

Advantages:

The PEMFC has a solid electrolyte which provides excellent resistance to gas crossover.

The PEMFCs low operating temperature allows rapid start-up and, with the absence of corrosive cell

constituents, the use of the exotic materials required in other fuel cell types, both in stack construction.

PEMFCs are capable of high current densities of over 2 kW/I and 2 W/cm^2.

Disadvantages:

- The low and narrow operating temperature range makes thermal management difficult, especially at very high current densities, and makes it difficult to use the rejected heat for cogeneration.

- Optimized proton and water transport properties of the membrane and proper water management are crucial for efficient fuel cell operation. Dehydration of the membrane reduces the proton conductivity and excess water can lead to the flooding of the electrolyte. Both the conditions lead to poor performance.

- Perflourinated membranes have a high cost.

- PEMFCs are quite sensitive to poisoning by trace levels of contaminants including CO, sulfur species and ammonia.

1.7.6 Differences between the fuel cell and galvanic cell:

Fuel Cell	Galvanic Cell
1. They do not store chemical energy	They store chemical energy
2. Reactants are fed from outside the cell continuously	The reactants from an integral part of its construction.
3. Need expensive noble metal catalysts & an optimum to an operative for their efficient functioning.	These special conditions are not required
4. Do not get discharged and no need of charging	Get-discharged when stored – up energy is exhausted.
5. Such cells never become dead as long as fresh reactants are available	Limited life span in use
6. Useful for long-term electricity generation.	Useful as portable power services.
7.Reaction products must be continuously removed	No such problem
8. No pollutants are generated (significant environmental benefits)	Pollutants are generated after their useful life
9. Produce power from fuels	They cannot generate electricity from fuels
10. Significantly higher power densities	Lower power density

1.8 Metal finishing

1.8.1 Introduction

Metal objects such as car components, kitchen utensils, juice cans, window frames, railings and so on which we see in everyday life will have undergone a surface modification, referred to as finishing. It covers a wide range of processes carried out to modify the surface properties of a metal. The process involves deposition of a layer of another metal or a polymer, conversion of a surface layer of atoms into oxide film or any other inorganic compound film or any process which can finally improve the surface characteristics. Metal finishing is done by electroplating, electroless plating, grinding wheels and honing, lapping and burnishing tools to obtain a smooth surface of a component with desired characteristics. Metal finishing is a process of electro deposition of an adherent metallic film of uniform thickness on the surface of the substrate for the purpose of modifying its surface properties.

The metal finishing techniques were originally introduced in the industry for improving the physical appearance of the metal objects by imbibing a decorative appeal. Since then a wide range of technological developments in the field was taken place for imparting additional desirable surface properties to the material other than their intrinsic properties to enhance the utility of the metal. Some of them are

- Improving resistance to corrosion

- Enhancing resistance to chemical attack, abrasion and wear

- Imparting thermal resistance and resistance to impact

- Improving thermal and electrical properties

- Increasing hardness, thermal and optical reflectivity to the surface

- Making the surface resistant for moisture attack

1.8.2 Electroplating

The techniques of metal finishing include electroplating of metals and alloys and Electroless plating of a modified surface. Electroplating is the process by which coating metal is deposited on the base metal by passing a direct current through an electrolytic solution, containing the soluble salt of the coating metal. It is primarily used for depositing a layer of material to bestow a desired property (e.g., abrasion and wear resistance, corrosion protection and aesthetic qualities) to a surface that otherwise lacks that property and sometimes to build up thickness on undersized parts. The common metals used for coating purpose are Zn, Cu, Ni, Cr, Ag, Au and Pt.

1.8.3 Theory of electroplating

Electroplating is the process of coating a metal on a substrate made up of another metal, alloy or non-metal by the process of electrolysis. The process used in electroplating is called electrodeposition and the principle is electrolysis. The electroplating device is an electrolytic cell in which two electrodes (anode and cathode) are dipped in an electrolytic solution. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved meal salts as well as other ions that permit the flow of electricity. A rectifier supplies a direct current to the anode, oxidizing the metal atoms that compromise it and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they 'plate out' on to the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, ie the current flowing through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode. Other electroplating processes may use an inert anode such as lead or graphite. In these techniques, ions of the metal to be plated must be periodically

replenished to maintain proper coating metal ion concentration in the bath. The device used for electroplating is an electrolytic cell in the form of a tank having two electrodes immersed in the electrolyte solution. The schematic representation of various components of the electroplating unit is shown in Fig. 1.8.3.
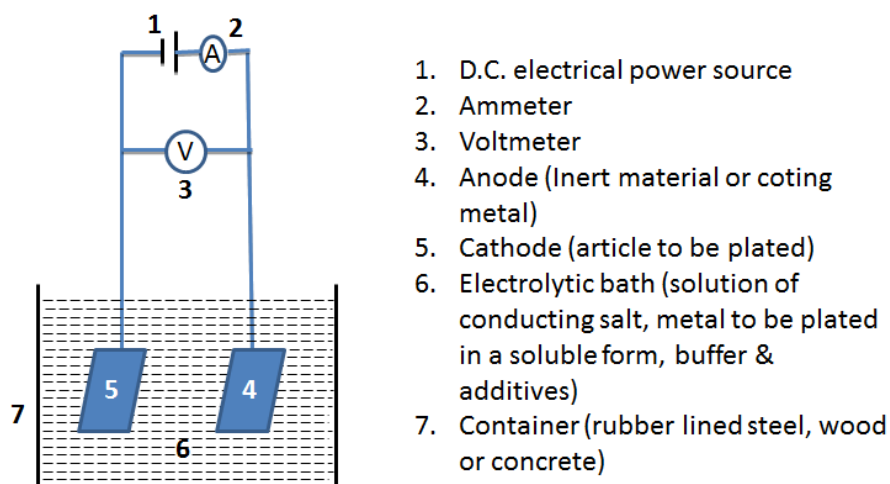

1. D.C. electrical power source
2. Ammeter
3. Voltmeter
4. Anode (Inert material or coting metal)
5. Cathode (article to be plated)
6. Electrolytic bath (solution of conducting salt, metal to be plated in a soluble form, buffer & additives)
7. Container (rubber lined steel, wood or concrete)

**Fig. 1.8.3** Schematic of the electroplating bath

Essential components include:

- An electroplating bath containing a conducting salt and the metal to be plated in a soluble form as well as a buffer and additives.

- The article to be plated - electronically conducting cathode.

- The electronically conducting anode, the coating metal itself, or an inert material of good electrical conductance like graphite.

- An inert vessel to contain the above mentioned materials made up of either rubber lined steel, concrete or wood.
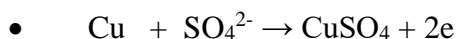
Suppose the anode is made of coating metal itself. During electrolysis, the concentration of the electrolytic bath remains unaltered, since the metal ions deposited from the bath are replenished continuously by the reaction of free anions with the anode metal. As an example, if the $CuSO_4$ solution is used as an electrolyte, it ionizes as

$$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$$
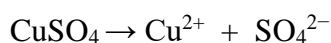
On passing current, Cu^{2+} ions go to the cathode and get deposited there.

- $Cu^{2+} + 2e^- \rightarrow Cu$
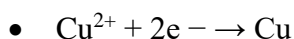
The free SO_4^{2-} ions migrate to the copper anode and dissolve an equivalent amount of copper to form sulfate.

- $Cu + SO_4^{2-} \rightarrow CuSO_4 + 2e$

Thus there is a continuous replenishment of electrolytic salt during electrolysis. If however, the anode is made of some inert material like graphite, then electrolytic salt is added continuously in order to maintain proper coating metal ion concentration in the bath. Moreover the process of electroplating goes on nonstop, since the anode is not consumed and its replacement is not required. The process involves the passage of current and electrolysis of conducting media. Three important factors governing the electroplating process include decomposition potential (E_D), polarization and overvoltage.

1.8.3.1 Decomposition Potential (E_D):

When an electric current is passed through the electrolyte solution the electrolysis starts and the products formed, gather around the electrodes. Concentration in the vicinity of the electrodes changes and a back emf sets in. e.g., in the electrolysis of water, if a small voltage (~ 0.75V) is applied between two platinum electrodes immersed in the 1M sulphuric acid solution, the electrolysis starts, proceeds to some extent and then decreases rapidly finally to stop. The reason for this observation is the initial passage of current causing release of a small amount of hydrogen and oxygen at the cathode and anode respectively. The gases are adsorbed at the surface of electrodes and the inactive platinum electrode is converted into active gas electrodes. This produces a back emf of the polarization current, which resists the emf of the battery or applied voltage. At potential below 1.7V the back emf counterbalance the effect of applied emf and the process of electrolysis is not sustained. If the applied voltage is slowly increased, there is a slight increase in the current until the applied voltage just

51

exceeds the back emf (1.7 V), the current suddenly increases appreciably at that point. Thus, the minimum external potential or voltage, at which the electrolysis current begins to increase appreciably and continuous electrolysis sets in is known as decomposition potential of the electrolyte. It is equal to back emf.

Measurement of decomposition potential (E_D):

The schematic diagram for the determination of decomposition potential is shown in Fig.1.8.4.1a The electrolytic cell consists of two platinum electrodes (E_1 and E_2) dipped in the electrolytic solution. The applied voltage (V) is measured at different resistance and the corresponding current is measured with the help of milliammeter (M).
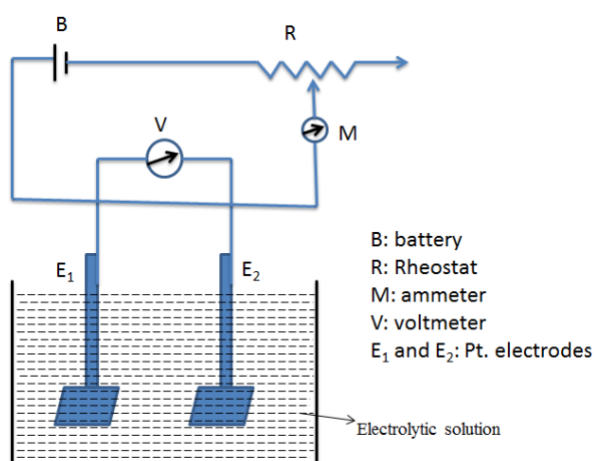

Fig. 1.8.3.1a Setup for measurement of decomposition potential

A series of readings for current passing through the electrolyte cell at corresponding applied voltage is recorded and a graph is plotted to measure the electrode potential. A graph between applied emf and the current density is shown in the following Fig.1.8.3.1b
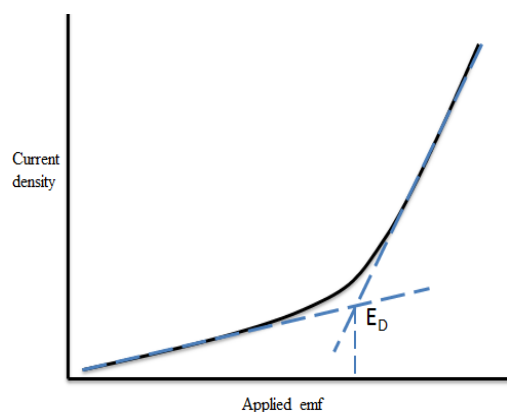

52

Fig. 1.8.3.1b A graph of external voltage applied vs current density

The linear portions of the graph are extended, until they intersect. Voltage corresponding to the point of intersection is the E_D of the electrolyte.

Factors influencing decomposition potential:

Decomposition potentials of different electrolytes are different. Even the E_D of an electrolyte is not a constant. It depends upon the following factors;

- Strength of the current flowing through the cell

- Chemical nature of the electrodes

- Physical nature of the electrodes

- Activity of the electrolyte

- Absolute temperature.

Use of decomposition potential values:

- Knowledge of E_D value enables the calculation of actual emf which is required for setting in continuous electrolytic processes, electroplating and electrorefining.

- It helps in predicting the sequence of discharge process to occur.

- Used in the separation of a mixture of metal ions from a solution by electrolysis.

1.8.3.2 Overvoltage

The decomposition potential of an electrolyte is approximately equal to the emf of the galvanic cell formed due to the discharge of products at the electrodes. The decomposition of an electrolyte is therefore expected to start as soon as applied potential reaches the value of reversible emf of the cell. This is true with respect to metal ions. But when products discharged at the electrodes are gases, then the actual decomposition potential is invariably much higher than its theoretical reversible electrode potential. The excess voltage is referred to as overvoltage (η) of the gas. It may occur at both the electrodes.

Overvoltage (η) is the difference between the actual applied emf to bring about continuous electrolysis and the theoretical emf needed for such electrolysis. For instance, the reversible potential of oxygen gas with smooth Pt electrode is 1.23 V. But actual gas evolution takes place at a potential of 1.68 V. The excess 0.45 V is the overvoltage of oxygen on smooth Pt surface. The following factors influence the overvoltage of an electrolyte;

- Nature of the electrode surface (or material)

- Current density and temperature

- Nature of the electrolyte

Overvoltage is believed to be a surface phenomenon at the electrodes. Of the many steps involved in gas evolution at electrodes, at least one is rather a slow process and requires energy. The extra energy is supplied by the applied voltage and this extra energy is related to overvoltage.

e.g., electrolysis of water

(i) $H^+_{(aq.)} + e^- \longrightarrow H$ (fast)

(ii) $H + H \longrightarrow H_2$ (slow)

The step (ii) being slow, consumes energy and accounts for overvoltage. Hydrogen overvoltage is the measure of the tendency of hydrogen to be liberated at the cathode. Higher the value of overvoltage more difficult is the liberation of hydrogen on that metal.

1.8.3.3 Polarization

Since the electrolysis is a non spontaneous process, the minimum energy required to carry out such a process is equal to the free energy increase accompanying the change. However, in irreversible conditions, the potential to be applied for electrolysis is higher than the reversible emf of the cell. A cell that requires excess voltage over the theoretical is said to be polarized and the phenomenon is referred to as polarization. Electrolytic processes occur at the electrodes of the cell. Polarization sets in the cell when the electrode processes become slow

and irreversible. Thus polarization in the cell is due to polarization at the electrodes. Magnitude of overpotential is directly proportional to the extent of polarization. The observed polarizations are of two types.

(a) Concentration polarization   (b) Kinetic polarization

Concentration polarization:

An electrochemical reaction occurs only at the surface of the two electrodes. Reactant concentration decreases in the electrolyte adjacent to the electrode surface. The reactant species are transported to the electrode surface by processes like diffusion, migration and convection from the bulk of the solution. When the rate of transport is insufficient to match the rate of electrode reaction, current flowing through the cell drops. A higher potential than the theoretical value is required to maintain the current at the necessary level.   This phenomenon is called concentration polarization. The steps involved in electrolytic processes are

(i)   Diffusion of reactant species towards the electrode and

(ii)   Diffusion of product away from the electrode, cause concentration polarization.

Concentration polarization can be eliminated or at least minimized by increasing the convection, by raising the temperature or mechanical agitation of the solution.

Kinetic or Activation polarization:

Activation polarization is caused when steps

   i)   Adsorption of the reactant on the electrode

   ii)   Charge transfer across the metal-solution interface and

   iii)   Desorption of the product from the electrode become slow and need activation energy.

A higher potential than the theoretical value is to be applied to maintain current at the necessary level. It is not possible to eliminate or minimize kinetic polarization by any means.

Activation polarization is normally very low, when metal deposition or metal dissolution is the electrode process. When the electrode process is a gas (H_2 and O_2) evolution, kinetic or activation polarization is usually very high.

Factors influencing polarization:

- Size and nature of the electrode

- Nature of ions accumulated on electrodes

- Electrolytic concentration

- Temperature

- Conductivity of electrolytic solution

- Stirring of electrolytic solution

- Use of depolarizer

Importance of polarization effect:

An impervious or non-porous film, contributes to the increase of polarization at an electrode. Considerable polarization effect can also be seen where loosely adhering and even porous films are formed. Such films either formed naturally (during manufacturing) or artificially (by the application of special coatings or products of corrosion) are important in determining the rate of corrosion of a metal or an alloy and also for the protection form corrosion.

1.8.4 Applications of electroplating

- *Plating for aesthetic appearance*:

- *Plating for protection*

- *For electroforming*

- *Plating on non-metals*

1.8.5 Characteristics of a good deposit

- The deposit should be bright and lustrous

- The deposit should be continuous, uniform, non porous and adhesive

- It should be hard and ductile

- It should be of fine grained nature

1.8.6 Factors influencing the nature of the deposit

There are several factors which affect the nature of an electro deposit.

(a) Current density

Higher the current density, more the deposition rate but will enforce the poor adhesion and loose and brittle plating quality. There is the possibility of a burnt and spongy deposit. Whereas low current density takes extra time to finish the job and is uneconomical. Therefore, optimum moderate current densities should be applied.

(b) Metal ion concentration

As the electroplating involves the discharge of free metal ions, the concentration of free metal ions plays an important role. If the concentration of metal ion is low the crystal size will be smaller and a fine adherent film may be coated. Thus the ideal situation is low free metal ion concentration in a concentrated solution of a metal compound which can be attained by addition of a compound with a common ion or by the formation of complex compound and ions. e.g., when copper is deposited from an electroplating bath containing copper sulphate solution, sulphuric acid is added to increase the concentration of sulphate ion. The concentration of cupric ions is reduced due to common ion effect.

(c) Temperature:

Generally, the solution to be deposited is used at room temperature. However, warm baths are used for increasing solubility of electrolyte and current density. The size of the crystals increases with increasing temperature and renders lower adherence. But on the other hand

the solubility and metal dissociation increase at higher temperature leading to the higher conductance of the solution. Also, the mobility of ions increases at a higher temperature and decreases the viscosity of the electrolyte solution so that the cathode film is replenished at a faster rate. This increases the current density for a given voltage and reduces the tendency towards treeing. There are disadvantages also of using high temperatures. Since, the possibility of corrosion of equipment, decomposition of the organic addition agent and evolution of hydrogen gas at cathode would increase at a higher temperature. So the optimum range of temperature needs to be selected.

(d) pH of the electrolyte

The pH of the electrolyte solution should be properly maintained. The range of the pH varies for different types of the plating bath. If pH is more towards the acidic side the nature of the deposit will be affected adversely as the evolution of hydrogen gas is expected at cathode thereby forming a burnt deposit. If pH is more towards the basic side the plating is delayed, so uneven and thick deposit is obtained. Suitable buffers may be used for maintaining the appropriate pH.

(e) Presence of additives:

To obtain electroplate with desire qualities and specifications, additional substances called additives are added in small quantities to the electrolyte bath. These additives have the capacity to modify the structure, appearance and characteristics of the deposit. The different types of additives used are

(i) Complexing agents:

(ii) Brighteners:

(iii) Levellers:

(iv) Wetting agents:

(v) Structure modifiers:

(f) Throwing power of the plating bath

Throwing power is defined as the degree of uniformity of metal distribution or evenness of deposit thickness obtained on a cathode of irregular shape. If the distribution of the deposit is uniform throughout the surface of the article to be coated, the throwing power is considered good.

1.8.7 Methods of cleaning the metal surface

It is essential to clean the surface of base metal before the application of the electroplated coating. The common impurities found on the metal surface are grease, oil, oxide layer and other extraneous matters. The following methods are employed to clean the metal surfaces.

(iii)   *Physical (Solvent) cleaning:-* Physical cleaning is done with the help of solvents to make the surface free from oil, grease, superficial dirt, and buffing, polishing and fatty substances. The commonly used solvents such as chlorinated hydrocarbons, xylene, toluene, aqueous cleaning agents are used with or without electric current. Solvent cleaning is made more effective by vapour degreasing. An organic volatile solvent like trichloroethene is heated and vapours are passed over the metal surface to be cleaned. The vapours condense on the surface and condensed liquid dissolves and washes away the oil, grease and other organic matter from the surface. The emulsifying agents are also added to the solvent to remove organic impurities from the surface of the metal.

(ii) Chemical (Alkali) Cleaning: It is used to remove the minute residue of soil and grease and for removal of tarnish and oxide film. The commonly used alkali cleaners consist of a number of alkalies, soap, chelating agents like Na_2O_3, sodium phosphates, NaOH etc. Alkali cleaning is made more effective by passing current through a hot alkaline solution, with the article to be cleaned constituting the cathode. The evolution of H_2 at the cathode and O_2 at the anode, metal helps to dislodge the greasy substance. It is followed by thorough rinsing with

water and then immersing in a very dilute solution of acids to remove traces of alkali after cleaning is completed.

(iii) Mechanical Cleaning: Involves removal of the oxide layer (tarnish), loose rust and other inorganic deposits from the surface to obtain better appearance, protection and optimum effects. This is done by hand cleaning with bristle brush and some abrasives like sand papers, polishing tools (grinding with grinding stone), scratch rubbing with chisel, knife, scrapers, wire brush or a abrasive stone or paper and detergent.

(iv) Pickling: The oxides sometimes cannot be removed by simple alkali or mechanical cleaning. The extraneous fragments like heavy scales of oxides, scratches and strains can be removed from the surface by dissolving in the acid solution. The acid pickling involves the removal of such oxides; rust or tarnish by immersing the material (except Al) in acid like dil. HCl or dil.H_2SO_4 or dil. HNO_3. Pickling of Al is done in alkaline solution, whereas pickling of Cu, Ni or brass articles are accomplished in a solution of dil. HNO_3 or a mixture of dil. HNO_3 and dil. H_2SO_4. Pickling is usually followed by polishing and buffing.

(v) Electro polishing :- In this method, the metal to be cleaned is made anode in a suitable solution. During the process, a surface layer of the metal gets dissolved along with the impurities. It also helps to remove minor surface irregularities. The most commonly used baths for electro polishing contain sulphuric acid, phosphoric acid, chromic acid, nitric acid etc. After the process, the metal is thoroughly rinsed with water, dried and used for electroplating.

1.8.8 Electroplating of chromium

Chromium plating is a finishing treatment utilizing the electrodeposition of a thin layer of chromium on a metal object. This layer can be decorative or corrosion protective to the base surface. The process of chromium plating includes degreasing to remove heavy soiling, manual cleaning to remove all residual traces of dirt and surface contamination and various

pretreatments depending on the objectives of the coating. Different etching solutions such as hydrochloric, hydrofluoric, sulphuric acid and ferric chloride are used. Further, the treated base material is placed into the chrome plating bath for electroplating of desired thickness.

- Chromium coatings are generally thinner and have micro pores in it. As the thickness of the coating increases, cracks develop in the coatings. Hence, chromium coatings are always plated on nickel/copper undercoates. Ni gives protection and chromium gives a decorative finish.

- Chromium anodes are not used in electroplating of chromium on account of two difficulties. These electrodes become passive in acidic medium and they result in a black deposit.

- Chromium has higher electrode potential and can be easily coated on the iron to protect from rusting/corrosion

- The anode efficiency is nearly 100 % whereas cathode efficiency is at best around 20 %. It may be inferred that metal going into the solution is five times of the metal getting deposited, resulting in building up of excessive chromic acid concentration. This disturbs the ratio of Cr(III) to Cr(VI) and the conductivity of the bath and dull deposits called burnt deposits are obtained. To avoid this, inert material is used as anode and chromium electrolyte in the bath.

Table 1.8.8 Comparison of decorative and hard coating of chromium

	Decorative coating	Hard coating
Bath composition	Chromic acid (250 g) + H_2SO_4 (2.5 g) + Trivalent chromium (1g)	Chromic acid (250 g) + H_2SO_4 (2.5 g) + Trivalent chromium (1 g)
Operating Temperature	45 – 55 °C	45 – 55 °C
Anode	Insoluble anodes like Pb – Pb : 6% Sb - Pb--7%	Lead – lead : 6% Sb – Pb: 7% Sn

	Sn	
Cathode	Article to be coated	Article to be coated
Current density	145--430 A/ft^2	290--580 A/ft^2
Cathode efficiency	10 – 15	17 – 21
Applications	Decorative applications with corrosion resistance finish on cycles, automobiles, furniture, household fittings, aircraft, surgical and dental instruments.	Coating of industrial components like gauges, dies, cutting tools, piston rings and hydraulic rams.

1.8.9 Electroless plating

Electroless plating is a method of depositing a metal film on a substrate surface (conductor or non-conductor) from metal salt solution using a suitable reducing agent without using electrical energy. The reaction can be depicted as

Metal ions + Reducing agent $\longrightarrow$ Metal + Oxidized product
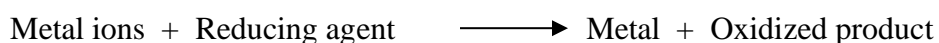
The method involves the deposition of metals such as Cu, Ag, Ni, Au or Pd on the surface of the base material by means of a reducing agent. Electroless plating results in a fine grained metal deposit that has similar finishing as that of traditional electrodeposit finishing. In industries, such process is used for plating on non-conductors like plastic, electroformed dies, hard memory disks, printed circuit boards (PCBs) or to obtain an extremely uniform plate. This technique is also used for the prevention of corrosion.

Process of electroless plating: The process of electroless plating involves the following steps:

(i) *Preparation of active surface*: This is the most important step and the surface is activated by any of the following ways.

  (a) etching – by acid treatment

(b) electroplating with a thin layer of metal or insulators like plastic surfaces followed by heat treatment

(c) Alternate treatment with $SnCl_2$ and $PdCl_2$ on the plastic surface

$$SnCl_2 + PdCl_2 \longrightarrow Pd + SnCl_4$$
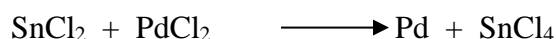
Pd is coated on plastic.

(ii) *Preparation of plating bath:*

(a) Metal to be coated in the form of chloride or sulphate solution

(b) Reducing agents like formaldehyde and sodium hypophosphate for reduction of metal ion to metal

(c) Complexing agents like EDTA, tartrates, citrates to form metal complexes to prevent excess deposition

(d) Stabilizers like thiourea, calcium ions too prevent decomposition of the bath and to impart stability to the solution

(e) Exaltants (accelerators) like succinates, glycinates and fluorides to increase the rate of plating

(f) Brighteners like thiosulphate to give a lustrous appearance

(g) Buffers like boric acid to maintain the pH

(iii) *Reduction step*: Active surface is dipped in the bath and deposition is carried out. The plating is carried out in a series of tanks where the object is immersed to plate the desired metal. The rate of deposition is controlled by the amount of reducing agent present and the type of chelating agent used. The deposition rate is normally $12.5 – 25$ µm, although, it has been done up to 650 µm in thickness.

Advantages of electroless plating

The following are main advantages of electroless plating

- More uniform coating on the surface of object whatever shape it may have. Even the objects having irregular shapes, holes, recesses, internal surfaces, valves or threaded parts get uniform deposit since it has better throwing power than electroplating.

- Electrical power and other accessories are not required.

- Coating is harder than regular plating and better wear resistance.

- Deposits have compatible wettability for oils, inherent lubricity and non-galling characteristics, unlike electrolytic nickel.

- Deposits are much superior to electroplated nickel and hard chrome, as they are less porous and provide better corrosion protection to steel substrates.

- Electroless plating of Ni on aluminum substrate enhances the solderability together with providing a non-magnetic under lay in magnetic components. The deposits are less porous and possess unique characteristic chemical, mechanical and magnetic properties.

- Additives or levelers are not required in the process nor the complex filtaration method requirement.

- It is a simple process, so requires simple equipment.

Disadvantages of electroless plating

The main disadvantages of the process are the following;

- Due to speedy chemical renewal, cost of waste treatment is high.

- The frequency of dumping electroless bath is high as it is sensitive to contamination

- Costs per unit weight of the deposited metal are more.

- It needs pure chemicals.

- Chemical reductants are more expensive than electricity.

- Metal salts and reductant used in electroless plating solutions are thermodynamically not stable.

64

- Impurities or dust or colloidal matter (even if present in trace amount) promote the decomposition of bath components.

1.8.9.1 Electroless plating of Copper

It is an auto-catalytic reaction used to deposit a coating of electroless copper on a substrate without the use of electrical energy. It is commonly used to plate plastic for decorative purposes and parts for engineering applications, particularly to render conductivity for electronic and printed circuit boards.
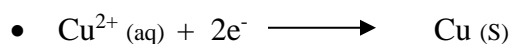
Reducing agents generally react with the plating bath, resulting in slow, deposition rates and poor deposit quality. It can be prevented by rejuvenating the bath at regular intervals. The bath solution undergoes spontaneous decomposition, resulting in an additional waste stream of copper and etching solution as copper built up on the tanks from the bath solution, must be stripped with an etchant such as sulphuric acid and hydrogen peroxide.

Electroless plating bath for copper includes;

- Coating solution : $CuSO_4$ soln

- Reducing agent : HCHO

- Buffer: NaOH & Rochelle salt

- Complexing agent: EDTA di sodium salt

- Optimum pH: 11

- Optimum temperature: 25 °C

The reactions involved at two electrodes are

At cathode:

- $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

At anode:

- $2HCHO + 4OH^-_{(aq.)} \longrightarrow 2HCOO^-_{(aq.)} + 2H_2O_{(l)} + H_2(g) + 2e^-$

Overall reaction:

$Cu^{2+}_{(aq.)} + 2HCHO + 4OH^-_{(aq.)} \longrightarrow 2HCOO^-_{(aq.)} + 2H_2O_{(l)} + H_{2(g)}$

Since Cu^{2+} ions and HCHO are consumed during the redox reaction, these are replenished periodically. The redox reaction involves consumption of hydroxyl ions and pH of the solution decreases as the reaction progresses. Hence addition of buffer is essential. Usual plating rate is 1-5 μmh^{-1}.

Applications of electroless plating:

- Electroless copper plating is widely used for metalizing printed circuit boards (PCBs)

- It is used as a base coating for subsequent conventional electroplating

- It is used for producing through hole connections and for decorative plating on plastics. When double sided PCBs are fabricated then holes are drilled for making electrical connections. These holes are plated by electroless plating.

1.8.10 Comparison of electroplating and electroless plating

Table 1.8.9 Comparison of electroplating and electroless plating

Property	Electroplating	Electroless plating
Driving force	Electric current	Autocatalytic redox reaction
Anode reaction		
Cathode	Article to be plated	Article to be plated with a catalytic surface
Anode	Separate anode	Article to be plated
Reducing agent	Electrons bring about	Chemical reagents bring about reduction reaction
Anode reactant	M or H_2O	R, the reducing agent in solution
Nature of deposit	Pure metal or alloy	Usually metal contaminated with species derived from the redox reaction
Thickness limit (μm)	1 - 100	1 – 100
Applicability	Applicable to conductors only	Can be used for conductors and non-conductors

Throwing power	Less throwing power; cannot be used for irregular shapes and intricate parts	More throwing power and can be used for irregular and uneven shaped objects