Contents

Chapter 1

Electrochemistry and Battery Chemistry

1.1 Electrochemistry

1.1.1 Introduction

Electrochemistry is the branch of chemistry which deals with the transformation of electrical energy into Chemical energy and vice-versa. It is the study of phenomena at electrode solution interfaces. Electrochemistry deals with the relationship between electrical, chemical phenomena and the laws of interaction of these phenomena. The branch of electrochemistry is of major technical importance.

The passage of electricity through a substance is called electrical conductance. Electrical conductance involves movement of electrons or ions. A substance which allows electric current to pass through it, is called a conductor.

Ex: all metals, fused salts, acids, alkalis.

The electrical conductors are of two types,

1. Metallic or Electronic conductors
2. Electrolytic conductors

1. Metallic or Electronic conductors:

Metallic conductors conduct electricity due to the movement of electrons from one end to another end. In a solid, the electrical conduction involves the free movement of electrons in the metallic lattice, without any movement of the lattice atom; this type of conduction is called metallic conduction. In metallic conductors, the electricity is carried by the electrons, the atomic nuclei remaining stationary. These conductors are further sub classified in to three types.

i. Good conductors

ii. Semi-conductors

iii. Non-conductors or Insulators

i. Good conductors:

It is a substance, which conduct electricity fully and freely.

Ex: Metals like Cu, Al and Fe

ii. Semi-conductors:

A substance, which partially conducts electricity.

Ex: Silicon, Germanium.

iii. Non-conductors or Insulators:

It is a substance, which does not conduct electric current i.e., which does not allow the passage of current through it.

Ex: Wood

2. Electrolytic conductors:

It is a substance, which in aqueous solution of in molten state liberates ions and allows electric current to pass through. Electrolytic conductors are further sub classified in to three types depending upon the extent of dissociation at ordinary dilutions.

- **Strong electrolytes:** These are completely dissociated into ions at all concentrations.

  Ex: NaCl, HCl, NaOH, etc.

- **Weak electrolytes:** Weak electrolytes dissociate only to a small extent even at very high dilutions.

  Ex: CH_3COOH, NH_4OH, etc.

- **Non-electrolytes:** Non-electrolytes do not dissociate into ions even at low dilutions.

  Ex: Glucose, Sugar.

Table 1.1 Differences between Metallic and Electrolytic conductors

S.No.	Metallic conductors	Electrolytic conductors
1.	It involves the flow of electrons in a conductor.	It involves the movement of ions in a solution.
2.	It does not involve any transfer of matter.	It involves transfer of electrolyte in the forms of ions.
3.	Generally metallic conduction shows an increase in resistance as the temperature is raised.	But the resistance of an electrolytic solution decreases as the temperature is raised.
4.	No net chemical change takes place.	Chemical reaction takes place at the two electrodes.

1.1.2 Electrolytic Conductance

Electrolytic conductance is the flow of electricity through a conductor. Electrolytic conductance is due to the existence of free ions. Electrolytic solutions are made by dissolving certain salt. When a neutral electrolyte is dissolved in water, the molecules split, forming two different charged ions. The positively charged ions are the cations, and the negatively charged ions are known as the anions.

Types of Electrolytic Conductance

Conductance:-

Reciprocal of the resistance is known as conductance(C).

$$C = \frac{1}{R}$$

Units:- ohm^{-1}.

Specific conductivity or Specific conductance:-

Reciprocal of the specific resistance of an electrolyte solution is known as specific conductivity (or) specific conductance(κ).

$$\kappa = \frac{1}{\rho} = \frac{1}{AR}$$

Units:- ohm^{-1} cm^{-1}.

Equivalent conductivity (or) Equivalent conductance:-

The conductance of all the ions present in 1gm equivalent of the electrolyte in the solution at given dilution. If 1gm equivalent of electrolyte is contained in 'v' ml, then;

$$\lambda_{eq} = vX\kappa$$

If normality of electrolytic solution is N, then;

$$v = \left(\frac{1}{N}\right)L = \frac{1000}{N}ml$$

$$\lambda_{eq} = \frac{1000\kappa}{N}$$

Units:- ohm^{-1} cm^{2} eq^{-1}.

Molar conductivity (or) Molar conductance:-

The conductance of all the ions present in 1 mole of the electrolyte in the solution is known as molar conductivity (λ_m). If M is the molar conductance in mole/L, then;

$$\lambda_m = \frac{1000\kappa}{M}$$

Units:- ohm^{-1} cm^{2} mol^{-1}.

Factors affecting Electrolytic Conductance

The following are the factors affecting electrolytic conductance:

1. ***The nature of the electrolyte:*** The nature of the electrolyte affects the electrolytic conductance. For example, a strong electrolyte will have a higher electrolytic conductance than a weak electrolyte.
2. ***The concentration of the electrolyte:*** The concentration of the electrolyte also affects the electrolytic conductance. A higher concentration of electrolyte will result in a higher electrolytic conductance.
3. ***The temperature of the electrolyte:*** The temperature of the electrolyte also affects the electrolytic conductance. A higher temperature will result in a higher electrolytic conductance.
4. ***The size of the electrolyte:*** The size of the electrolyte also affects the electrolytic conductance. A smaller size will result in a higher electrolytic conductance.

1.1.3 Redox Reactions

"Those reactions in which both oxidation and reduction reactions takes place are known as ***redox reactions***".

Oxidation:

Oxidation is a process which involves loss of electrons by a substance.

$$Zn(S) \longrightarrow Zn^{+2}(aq) + 2e^- \qquad \text{(oxidation)}$$

Reduction:

Reduction is a process which involves gain of electrons by a substance.

$$Cu^{+2}(aq) + 2e^- \longrightarrow Cu(S) \qquad \text{(reduction)}$$

It is quite apparent that if a substance loses electrons, some other substance must be involved in the reaction to accept these electrons. On the other hand, if a substance accepts electrons, some other substance must be involved in the reaction to supply these electrons. In other words, oxidation and reduction must always go side-by side. Thus if we place Zn metal in a solution of $CuSO_4$, immediate preparation of Cu takes place.

$$\begin{aligned} Zn(S) + CuSO_4(aq) &\longrightarrow ZnSO_4(aq) + Cu(S) \\ Zn(S) + Cu^{+2}(aq) &\longrightarrow Zn^{+2}(aq) + Cu(S) \end{aligned}$$

In this change, the Zn atom is oxidized to Zn ion (Zn^{+2}), since it loses electrons, while the copper ion (Cu^{+2}) is reduced to copper atom, since it gains electrons.

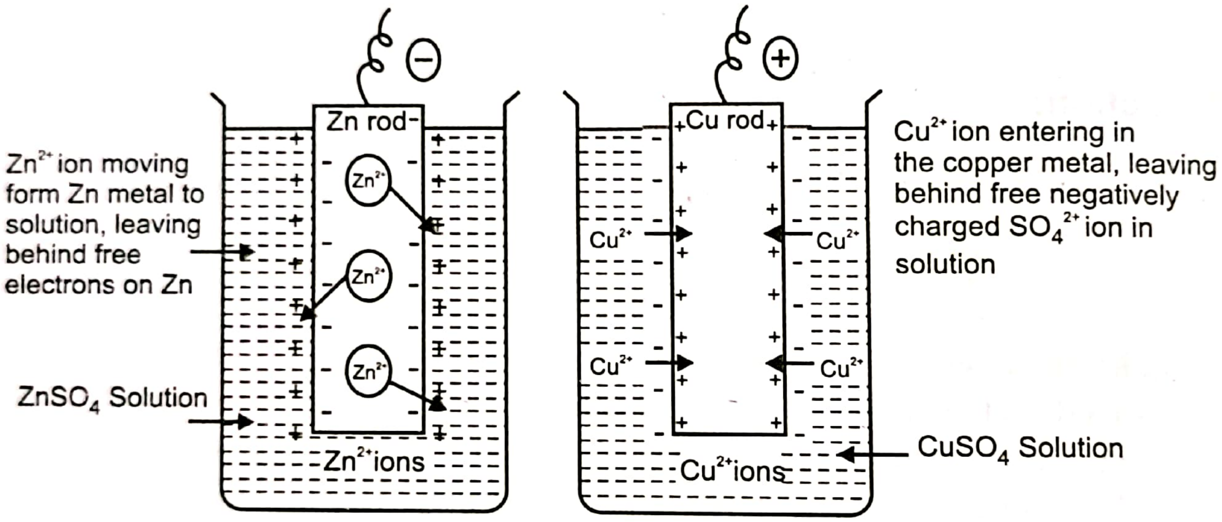
$$\begin{array}{lrcll} \text{i)} & Zn(S) & \longrightarrow & Zn^{+2}(aq) + 2e^- & \text{(oxidation)} \\ \text{ii)} & Cu^{+2}(aq) + 2e^- & \longrightarrow & Cu(S) & \text{(reduction)} \\ \hline & Zn(S) + Cu^{+2}(aq) & \longrightarrow & Zn^{+2}(aq) + Cu(S) & \text{(redox)} \end{array}$$

The overall reaction obtained by adding the i) & ii) is called ***redox*** or ***oxidation-reduction reaction***.

1.1.4 Electrode Potential

"The tendency of an electrode to lose or gain electrons, when it is in contact with its own ions is known as ***Electrode potential***."

A metal (M) consists of metal ions (M^{n+}), with the valency electrons that bind them together. Now, if a metal is in contact with a solution of its own salt, the positive ions in the metal come into equilibrium with those in the solution, leaving behind an equivalent number of electrons on the metal. Thus, the metal acquires a negative charge, since it is now left with excess number of electrons and a number of positive metallic ions are formed in solution .e.g. in case of Zn in $ZnSO_4$ solution (figure 1.1(a)). Conversely, if the positive metallic ions, from the solution, enter the metallic lattices, then metal acquires a positive charge, e.g.in case of Cu in $CuSO_4$ solution. figure 1.1(b).



(a) De-electronation (b) Electronation

Figure. 1.1 Electrode potential

Thus, following two chemical reactions takes place, when a metal is in contact with its salt solution.

1. Positive metallic ions passing into solution

$$M \longrightarrow M^{n+} + ne^- \qquad \text{(oxidation)}$$

When 'n' electrons are left behind on the metal, and it acquires a negative charge. The rate of this reaction depends on i) the nature of the metal ii) the temperature and iii) the concentration of metal ions in solution.

2. Positive ions depositing on the metal electrode

$$M^{n+} + ne^- \longrightarrow M \qquad \text{(reduction)}$$

When metal acquires a positive charge. The rate of this reaction depends on the above three factors.

When a metal is placed in the solution of its own salt, the chemical reaction 1) and 2) as the case may be, takes place and ultimately a dynamic equilibrium is established, because *−ve* or *+ve* 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 of layer of *+ve* ions in fig 1.1(a) or *−ve* ions in fig 1.1(b) is formed all around the metal. This layer is called ***Helm holtz 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 *+ve* ions from or to the metal.

At equilibrium, the potential difference between the metal and the solution becomes a constant value. The equilibrium, potential difference so established is called the "***Electrode potential***" of the metal. Thus,

- The measure of tendency of a metallic electrode to lose or gain of electrons, when it is in contact with a solution of its own salt of unit molar concentration at 25°C.
- Consequently, the tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidized and 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***".

It is quite obvious that the value of reduction potential is negative of its oxidation potential and vice versa. Thus if the oxidation potential of an electrode is $+X$ volts, then its reduction potential will have a value of $-X$ volt.

Importance of an electrode potential:

When elements are arranged in increasing order of their standard electrode potential in a series is called **electrochemical series**. The electrochemical series providing valuable information's.

1. **Relative ease of oxidation or reduction:-** A system with high reduction potential has a great tendency to undergo reduction, so we can easily interpret the behavior of different elements. For example, the standard reduction potential of F_2/F system is highest (i.e +2.87 volts), so F^- ions are very easily reduced to F_2 or conversely, F_2 is oxidised with great difficulty to F^- ions. On the other hand, standard reduction potential of

Li^+/Li system is least (i.e-3.05 volts), so Li^+ is reduced with great difficulty to Li or conversely, Li is very easily oxidised to Li^+.

2. **Replacement tendency:-** Higher value of reduction potential shows a great tendency to assume the reduced form, so knowledge of electrode potential gives an indication of relative replacement tendency. For example, we can know whether Cu will displace Zn from solution or vice-versa. We know that standard electrode potentials,

   $E_{Cu^{+2}/Cu} = 0.34$ volts and $E_{Zn^{+2}/Zn} = -0.76$ volt

   So, Cu^{+2} has a greater tendency to acquire Cu form than Zn^{+2} has for acquiring Zn form. In other words, zinc will displace copper from the solution of latter, or the reaction will occur in the direction.

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

3. **Predicting spontaneity of redox reactions:-** Spontaneity of a redox reaction can be predicted from the e.m.f (E) value of the complete cell reaction. Positive value of E of a cell reaction indicates that the reaction is spontaneous. It value of E is negative, the reaction is not feasible. In general, an element having lower reduction potential can displace another metal having higher reduction potential from its salt solution spontaneously.
4. **Calculation of Equilibrium constant:-** The standard electrode potential

$$E^0 = \frac{RT}{nF} lnK_{eq} = \frac{2.303RT}{nF} \log K_{eq}$$

$$\log K_{eq} = \frac{nFXE^0}{2.303RT} = \frac{nE^0}{0.0592V} \quad (\text{at } 25^\circ C)$$

So from the value of standard electrode potential (E^0) for a cell reaction, its equilibrium constant (K_{eq}) can be calculated.

1.1.5 Single Electrode Potential

The metal rod dipped in the aqueous solution of its salt or a gaseous non-metal in contact with a solution containing its anion in the form of salt (or acid or alkali) functions as single electrode. The metal electrodes like Zn electrode $Zn/Zn^{+2}(aq)$, copper electrode $Cu^{+2}(aq)/Cu$ etc and non-metal electrodes like Hydrogen electrode, $H^+(aq)/H_2(g), Pt$, Chlorine electrode, $Pt; Cl_2(g)/Cl^-(aq), Pt$ etc.

These single electrodes, exhibit its characteristic electrode potential. This potential is called "***single electrode potential***". (E). The value of this potential depends on the chemical identity of the metal or non metal, the concentration of the concerned ion in the aqueous solution and temperature.

"The potential exhibited by a single electrode at unit concentration of the concerned metal ion or non-metal ion solution at 25°C is called ***"standard single electrode potential*"** (E^0)

1.1.6 Electrochemical Cells (or) Galvanic Cells

"The devices in which redox reaction is utilized to get electrical energy from chemical energy are called ***Electrochemical cells***".

(or)

"The devices are used to convert the chemical energy produced in a redox reaction into electrical energy are known as an ***Electrochemical cells***".

An Electrochemical cell is also commonly referred to as voltaic or galvanic cell. The Electrode where oxidation occurs is called Anode, while the electrode where reduction occurs is called cathode.

Ex: Daniel cell

Daniel cell

The practical application of an electrochemical or galvanic cell is Daniel cell. It consists of Zn electrode, dipping in $ZnSO_4$ solution (where oxidation takes place) and a copper electrode, dipping in $CuSO_4$ solution (where reaction takes place). In other words, each electrode may be regarded as a half- cell. The two solutions are separated by a salt bridge the two solutions can seep through the salt bridge, and so come in contact with each other automatically.

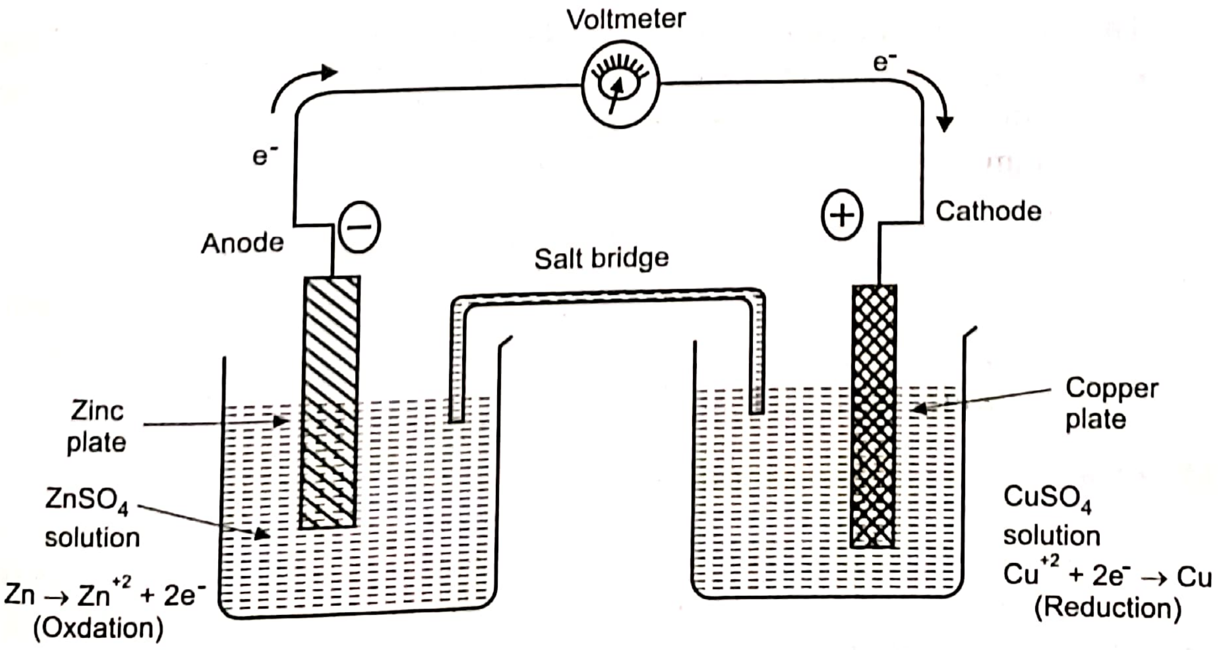


Figure. 1.2 Daniel cell

The electrode reactions in Daniel cell are

At Anode : $Zn \rightarrow Zn^{+2} + 2e^-$
At Cathode : $Cu^{+2} + 2e^- \rightarrow Cu$

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

The tendency of Zn to form Zn^{+2} is greater than the tendency Zn^{+2} to get deposited as Zn and hence, Zn metal acquires a negative charge. On the other hand, tendency of copper to go into solution is less than the tendency of Cu^{+2} to get deposited as Cu and hence, copper electrode becomes positively charged. The e.m.f of the cell is 1.1 volts.

Representation of a Galvanic cell

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

1. Anode is written on the left-hand side, while cathode is written on the right-hand side.
2. The electrode on the left (i.e Anode) is written by writing the metal (or solid phase) first and then the electrolyte. 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. Additional information regarding concentration may also be mentioned in bracket. These points will be made clear by following examples of representing anode half-cell as,

   Zn/Zn^{+2} or $Zn : Zn^{+2}$ or $Zn; ZnSO_4(1M); Pt, H_2$ (1atm); $H^+(1M)$
3. The cathode of the cell is written on the right-hand side. In this case, the electrolyte is represented first and the metal (or solid phase) thereafter. The two are separated by a vertical line or a semicolon. A few examples of representing cathode half- cell are cited below,

   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, applying above consideration to Daniel cell, we may represented as

   $Zn; Zn^{+2}(1M)//Cu^{+2}(1M); Cu$

EMF of an electrochemical cell

An electrochemical (or galvanic) cell is obtained by coupling two half-cells (or electrodes). For example, Daniel cell is obtained by coupling Zn half-cell and Cu half-cell, through a salt bridge.

$$Zn/ZnSO_4(aq)//CuSO_4(aq)/Cu$$

Mathematically, the e.m.f of an electrochemical cell is the algebric sum of the single electrode potential, provided proper signs are given according to the actual reaction taking place on the electrodes. Cell is generally written the negative electrode to the left. Based on this, the e.m.f of galvanic cell can readily be calculated from the reduction half-cell potentials, using the following relationship.

Where

$E_{cell} = E_{right} - E_{left}$

E_{cell} = E.M.F of the cell

E_{right} = reduction potential of right-hand side electrode

E_{left} = reduction potential of left -hand side electrode

It should be remember that a positive value of E_{cell} indicates that the cell reaction is feasible. If however, it comes out to be negative, the cell reaction is not feasible and in actual operation of the cell, the electrodes will have to be reversed in order to bring about cell reaction.

Nernst equation a cell reaction

$$Zn(s)/Zn^{+2}(aq)//Cu^{+2}(aq)/Cu(s)$$

Reaction is $Zn(s) + Cu^{+2}(aq) \longrightarrow Zn^{+2}(aq) + Cu(s)$

$$\therefore \quad E_{Cell} = E^0_{Cell} - \frac{2.303RT}{nF} \log Q \left[\therefore \quad Q = \frac{[Zn^{+2}]}{[Cu^{+2}]}\right]$$

At 298K or 25, the Nernst equation can be written as,

$$E_{Cell} = [E^0_{Cathode} - E^0_{anode}] - \frac{0.0592V}{n} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

$$= [E^0_{Cu^{+2}/Cu} - E^0_{Zn^{+2}/Zn}] + \frac{0.0592V}{n} \log \frac{[Cu^{+2}]}{[Zn^{+2}]}$$

1.1.7 Electrolytic Cell

An electrolytic cell can be defined as an electrochemical device that uses electrical energy to facilitate a non-spontaneous redox reaction. Electrolytic cells are electrochemical cells that can be used for the electrolysis of certain compounds. For example, water can be subjected to electrolysis (with the help of an electrolytic cell) to form gaseous oxygen and gaseous hydrogen. This is done by using the flow of electrons (into the reaction environment) to overcome the activation energy barrier of the non-spontaneous redox reaction.

The three primary components of electrolytic cells are:

- Cathode (which is negatively charged for electrolytic cells)
- Anode (which is positively charged for electrolytic cells)
- Electrolyte

The electrolyte provides the medium for the exchange of electrons between the cathode and the anode. Commonly used electrolytes in electrolytic cells include water (containing dissolved ions) and molten sodium chloride.

Diagram and Working of an Electrolytic Cell

Molten sodium chloride (NaCl) can be subjected to electrolysis with the help of an electrolytic cell, as illustrated below.

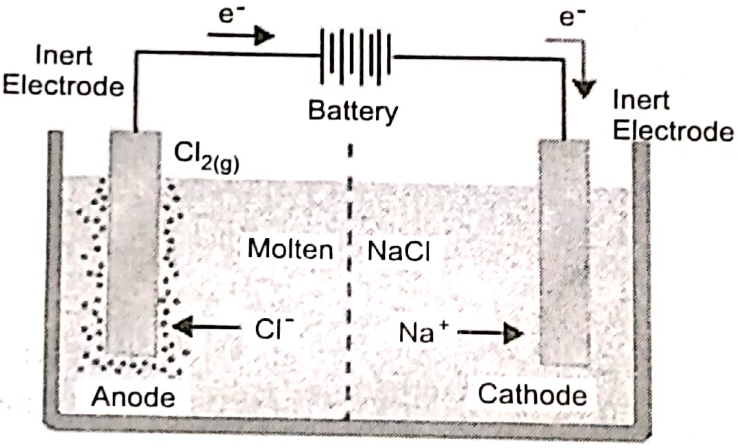


Figure. 1.3

Here, two inert electrodes are dipped into molten sodium chloride (which contains dissociated Na^+ cations and Cl^- anions). When an electric current is passed into the circuit, the cathode becomes rich in electrons and develops a negative charge. The positively charged sodium cations are now attracted towards the negatively charged cathode. This results in the formation of metallic sodium at the cathode.

Simultaneously, the chlorine atoms are attracted to the positively charged cathode. This results in the formation of chlorine gas (Cl_2) at the anode (which is accompanied by the liberation of 2 electrons, finishing the circuit). The associated chemical equations and the overall cell reaction are provided below.

- **Reaction at Cathode:** $[Na^+ + e^- \rightarrow Na]x2$
- **Reaction at Anode:** $2Cl^- \rightarrow Cl_2 + 2e^-$
- **Cell Reaction:** $2NaCl \rightarrow 2Na + Cl_2$

Thus, molten sodium chloride can be subjected to electrolysis in an electrolytic cell to generate metallic sodium and chlorine gas as the products.

Applications of Electrolytic Cells

- The primary application of electrolytic cells is for the production of oxygen gas and hydrogen gas from water.
- They are also used for the extraction of aluminium from bauxite.
- Another notable application of electrolytic cells is in electroplating, which is the process of forming a thin protective layer of a specific metal on the surface of another metal.
- The electrorefining of many non-ferrous metals is done with the help of electrolytic cells.
- Such electrochemical cells are also used in electrowinning processes.
- It can be noted that the industrial production of high-purity copper, high-purity zinc, and high-purity aluminium is almost always done through electrolytic cells.

1.1.8 Electrochemical Series

The electrochemical series is built up by arranging various redox equilibria in order of their standard electrode potentials (redox potentials). The most negative E values are placed at the top of the electrochemical series, and the most positive at the bottom.

The electrochemical series

$Li^{+}_{(aq)} + e^{-} \rightleftharpoons Li_{s}$	-3.03
$K^{+}_{(aq)} + e^{-} \rightleftharpoons K_{(s)}$	-2.92
$Ca^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Ca_{(s)}$	-2.87
$Na^{+}_{(aq)} + e^{-} \rightleftharpoons Na_{(s)}$	-2.71
$Mg^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Mg_{(s)}$	-2.37
$Al^{3+}_{(aq)} + 3e^{-} \rightleftharpoons Al_{(s)}$	-1.66
$Zn^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Zn_{(s)}$	-0.76
$Fe^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Fe_{(s)}$	-0.44
$Pb^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Pb_{(s)}$	-0.13
$2H^{+}_{(aq)} + 2e^{-} \rightleftharpoons H_{2(g)}$	0
$Cu^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Cu_{(s)}$	+0.34
$Ag^{+}_{(aq)} + e^{-} \rightleftharpoons Ag_{(s)}$	+0.80
$Au^{3+}_{(aq)} + 3e^{-} \rightleftharpoons Au_{(s)}$	+1.50

Importance of Electrochemical Series

1. The metal which is higher in electrochemical series acts as reducing agent (or) anode and undergoes corrosion first.
2. Metals above hydrogen are called active metals, which can displace hydrogen from dilute acids or water.

   Eg:- $Zn + 2HCl \rightarrow ZnCl_2 + H_2$
3. The metals below hydrogen are less reactive. They do not liberate H_2 from dilute acids and water.
4. The metal with higher negative potential displaces a metal with lower negative potential or positive potential (i.e., all metals below it in the series) from the salt solution of the metal.

   Eg:- Zn displaces all metals underneath it in the electrochemical series.

   $Zn + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu$
5. The reactivity (or) reducing character decreases from top to bottom of electrochemical series. So, Li is the strongest reducing agent and fluorine is the strongest oxidizing agent.

Application of Electrochemical Series

1. Oxidizing and Reducing Strengths: Electrochemical series helps us to identify a good oxidizing agent or reducing agent.
2. Used for Calculation of Standard emf (E^0) of Electrochemical Cell.
3. Useful for Predicting the Feasibility of Redox Reaction.
4. Useful for Predicting the Product of Electrolysis

Differences between Electrochemical series and Galvanic series

S.No	Electrochemical series	Galvanic series
1	It is based on the electrode potential values measured in standard condition.	It is based on the corrosion potential in sea water.
2	Standard electrode potential is a constant value.	Corrosion potential varies from environment to environment.
3	Metals and non-metals are included but not alloys.	Metals and alloys are included
4	It indicates the relative oxidizing/ reducing tendency.	It indicates the relative corrosion tendency.
5	The position of the metal or non-metal is fixed.	The position of the metal or alloy varies with the environment.

1.1.9 Nernst Equation

The Nernst Equation is

$$E = E^0 + \frac{0.0592}{n}\log[M^{n+}] \text{ (OR) } E = E^0 + \frac{2.303RT}{nF}\log[M^{n+}]$$

$E-$ Electrode potential

$R-$ Gas constant

E^0- Standard electrode potential

$T-$ Temperature

$n-$ Number of valency electrons

$F-$ Faraday (96,500 coulombs)

Derivation of Nernst equation

Consider a general reversible reaction

$$M^{n+}(aq) + ne^- \rightleftharpoons M(S)$$

Now for a reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are inter-related as

$$\Delta G = RT lnK + RT ln\frac{[\text{product}]}{[\text{reactant}]}$$

$$\Delta G = \Delta G^0 + RT ln\frac{[\text{product}]}{[\text{reactant}]} \tag{1}$$

Where ΔG^0 is known as the standard free energy change (i.e., the change in free energy, when the concentrations of the reactants and the products are unity each).The above equation, is known popularly as Van't Hoff reaction isotherm.

In a reversible reaction, the electrical energy is produced at the expanse of the free energy decrease, i.e

$$-\Delta G = nEF \text{ and } \Delta G^0 = -nE^0F$$

Substitute $\Delta G \& \Delta G^0$ values in equation (1)

$$-nEF = -nE^0F + RT ln\frac{[M]}{[M^{n+}]}$$

$$-nEF = -nE^0F + RT ln\frac{1}{[M^{n+}]}$$

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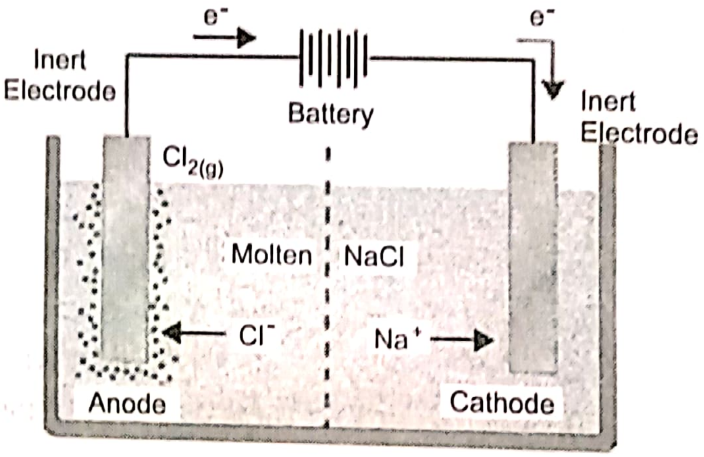

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Importance of Electrochemical Series

1. The metal which is higher in electrochemical series acts as reducing agent (or) anode and undergoes corrosion first.
2. Metals above hydrogen are called active metals, which can displace hydrogen from dilute acids or water.

   Eg:- $Zn + 2HCl \rightarrow ZnCl_2 + H_2$
3. The metals below hydrogen are less reactive. They do not liberate H_2 from dilute acids and water.
4. The metal with higher negative potential displaces a metal with lower negative potential or positive potential (i.e., all metals below it in the series) from the salt solution of the metal.

   Eg:- Zn displaces all metals underneath it in the electrochemical series.

   $Zn + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu$
5. The reactivity (or) reducing character decreases from top to bottom of electrochemical series. So, Li is the strongest reducing agent and fluorine is the strongest oxidizing agent.

Application of Electrochemical Series

1. Oxidizing and Reducing Strengths: Electrochemical series helps us to identify a good oxidizing agent or reducing agent.
2. Used for Calculation of Standard emf (E^0) of Electrochemical Cell.
3. Useful for Predicting the Feasibility of Redox Reaction.
4. Useful for Predicting the Product of Electrolysis

Differences between Electrochemical series and Galvanic series

S.No	Electrochemical series	Galvanic series
1	It is based on the electrode potential values measured in standard condition.	It is based on the corrosion potential in sea water.
2	Standard electrode potential is a constant value.	Corrosion potential varies from environment to environment.
3	Metals and non-metals are included but not alloys.	Metals and alloys are included
4	It indicates the relative oxidizing/ reducing tendency.	It indicates the relative corrosion tendency.
5	The position of the metal or non-metal is fixed.	The position of the metal or alloy varies with the environment.

1.1.9 Nernst Equation

The Nernst Equation is

$$E = E^0 + \frac{0.0592}{n}\log[M^{n+}] \text{ (OR) } E = E^0 + \frac{2.303RT}{nF}\log[M^{n+}]$$

$E-$ Electrode potential

$R-$ Gas constant

E^0- Standard electrode potential

$T-$ Temperature

$n-$ Number of valency electrons

$F-$ Faraday (96,500 coulombs)

Derivation of Nernst equation

Consider a general reversible reaction

$$M^{n+}(aq) + ne^- \rightleftharpoons M(S)$$

Now for a reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are inter-related as

$$\Delta G = RTlnK + RTln\frac{[\text{product}]}{[\text{reactant}]}$$

$$\Delta G = \Delta G^0 + RTln\frac{[\text{product}]}{[\text{reactant}]} \qquad (1)$$

Where ΔG^0 is known as the standard free energy change (i.e., the change in free energy, when the concentrations of the reactants and the products are unity each).The above equation, is known popularly as Van't Hoff reaction isotherm.

In a reversible reaction, the electrical energy is produced at the expanse of the free energy decrease, i.e

$$-\Delta G = nEF \text{ and } \Delta G^0 = -nE^0F$$

Substitute $\Delta G \& \Delta G^0$ values in equation (1)

$$-nEF = -nE^0F + RTln\frac{[M]}{[M^{n+}]}$$

$$-nEF = -nE^0F + RTln\frac{1}{[M^{n+}]}$$

[Since concentration of metal $[M] = 1$]

$$-nEF = -nE^0F - RTln[M^{n+}]$$

$$E = E^0 + \frac{RT}{nF}ln[M^{n+}]$$

$$E = E^0 + \frac{2.303RT}{nF}\log[M^{n+}]$$

This is known as Nernst equation of electrode potential at 25°C.

$$\frac{2.303RT}{nF} = \frac{0.0592}{n}$$

$$\therefore\ E = E^0 + \frac{0.0592}{n}\log[M^{n+}]$$

1.1.10 Types of Electrodes

Reference Electrodes:

The electrode of standard potential, with which we can compare the potentials of an other electrodes, is called a reference electrode. The best reference electrode used is "**standard hydrogen electrode**", whose electrode potential at all temperatures is taken as zero. Important reference electrodes are:

- Calomel Electrode
- Quinhydrone Electrode
- Glass Electrode

Calomel Electrode:

It is the most commonly used mercury - mercurous chloride electrode. The potential of the calomel electrode, on the hydrogen scale, has been found to vary with the concentration of the potassium chloride solution used. The potential of this electrode is equal to the e.m.f. of the cell.

Construction: It consists of tube in the bottom of which is a layer of mercury, over which is placed a paste of $Hg + Hg_2Cl_2$. The remaining portion of cell is filled with a solution of normal or decinormal or saturated solution of KCl. A platinum wire dipping into the mercury layer is used for making electrical contact. The side-tube is used for electrode is formulated as:

$$KCl(sat.)|Hg_2Cl_2(s)|Hg(l)$$

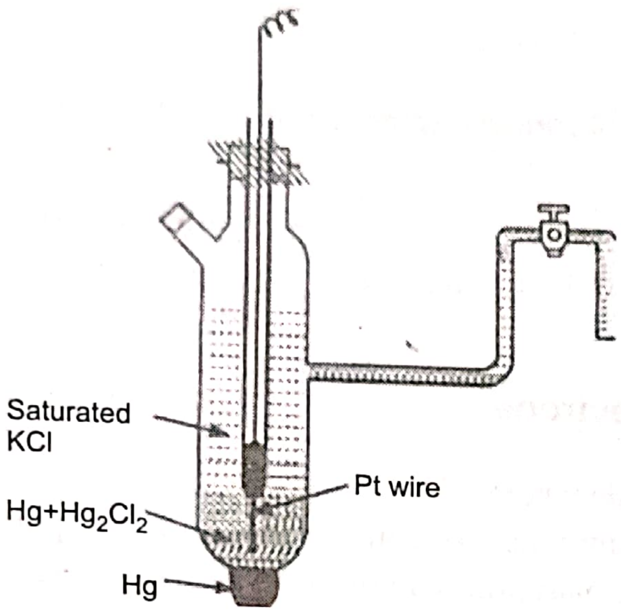


Figure. 1.4 Saturated Calomel Electrode

The calomel electrode can acts as anode or cathode depending on the nature of the other electrode of the cell.

The net cell reversible electrode reactions,

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$$

$$E = E^0 - \frac{2.303RT}{nF}\log[Cl^-]^2$$

$$E = E^0 - \frac{2.303RT}{F}\log[Cl^-], \text{ where } n = 2$$

$$E = E^0 - 0.0591\log[Cl^-] \text{ at } 298K$$

Therefore electrode potential of calomel electrode is depending upon the concentration of KCl. The electrode is reversible with chloride ions.

The electrode can be coupled with hydrogen electrode containing solution of unknown pH.

The potential of the calomel electrode depends upon the concentration of KCl solution used. Following table gives the values of std. oxidation potentials for different concentrations of KCl solution used. (measured at 298K).

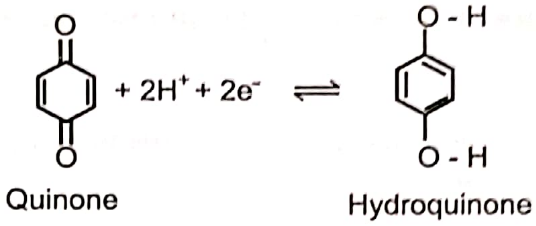
Concentration of KCl	Saturated KCl	1M KCl	0.1M KCl
$E^0[v]$	0.241	0.281	0.334

Applications

1. It is used as secondary reference electrode in the measurement of sing electrode.
2. It is used as reference electrode in all potentiometer determinations and measure pH of the given solution.

Quinhydrone Electrode

It is a redox electrode where oxidation and reduction happens on organic substra quinone and hydroquinone. An equimolar solution of quinone and hydroquinor is used here and the platinum wire of the calomel elctrode is attached to it.



$$C_6H_4O_2 + 2H^+ + 2e^- \rightleftarrows C_6H_4(OH)_2$$

Quinone (Q) Hydroquinone (QH_2)

$$Q + 2H^+ + 2e^- \rightarrow H_2Q$$

The Nernst equation for this half cell reaction will be like $Q+2H^+ +2e^- \rightarrow H_2$

$$E_{Q|H_2Q} = E^0_{Q|H_2Q} - \frac{0.0591}{2} \log \frac{[H_2Q]}{[Q][H^+]^2}$$

$$E_{Q|H_2Q} = E^0_{Q|H_2Q} - \frac{0.591}{2} \log \frac{1}{[H^+]^2}$$

$$E_{Q|H_2Q} = E^0_{Q|H_2Q} + \frac{0.591}{2} \log [H^+]^2$$

$$E_{Q|H_2Q} = E^0_{Q|H_2Q} + 0.0591 \log [H^+]$$

$$E_{Q|H_2Q} = E^0_{Q|H_2Q} - 0.0591\, pH$$

$$pH = \frac{E^0_{Q|H_2Q} - E_{Q|H_2Q}}{0.0591}$$

Thus pH can be determined by using quinhydron electrode.

Construction

Quinhydrone electrode can very easily be set up by adding a pinch of quinhydrone powder (a sparingly soluble solid) to the experimental solution with stirring, until the solution is saturated and a slight excess of its remains undissolved. The indicator electrode usually of bright platinum is inserted it. For determining the pH values, this half-cell is combined with any other reference electrode, usually saturated calomel electrode and the EMF of cell so formed is determined potentiometrically. The cell may be represented as

$$Pt/H_2Q,Q,H^+\ \text{(unknown)}\ //\ \text{KCl(sat)},Hg_2Cl_2(s)/Hg^+$$

$$E_{\text{Cell}} = E_{\text{Calomel}} - E_{\text{Quinhydrone}}$$

$$E_{\text{Cell}} = 0.2422V - (0.6994V - 0.0591V\,pH)$$

$$pH = \frac{0.6994V - 0.2422V + E_{\text{cell}}}{0.0591V}$$

Advantages and limitations of Quinhydrone

1. The electrode is very easy to set up.
2. The pH values obtained are very accurate.
3. Very small quantities of the solution are sufficient for themeasurement. The electrode cannot be used for more alkaline (pH $\geq$ 8.5) solutions and the solutions which react with quinhydrone or quinone. (E.g.: Fe^{2+}, MnO_2).

Glass Electrode

When two solutions of different pH values are separated by a thin glass membrane, there develops a difference of potential between the two surfaces of the membrane. The potential difference developed is proportional to the difference in pH value. The glass membrane functions as an ion-exchange resin, and an equilibrium is set up between the Na^+ ions of glass and H^+ ions in solution. For a particular type of glass, the potential difference varies with the H^+ ion concentration, and is given by the expression

$$\begin{aligned} E_G &= E_G^0 - \frac{2.303RT}{F}\log[H^+] \\ &= E_G^0 - 0.0592\log[H^+] \\ &= E_G^0 + 0.0592V\ pH \end{aligned}$$

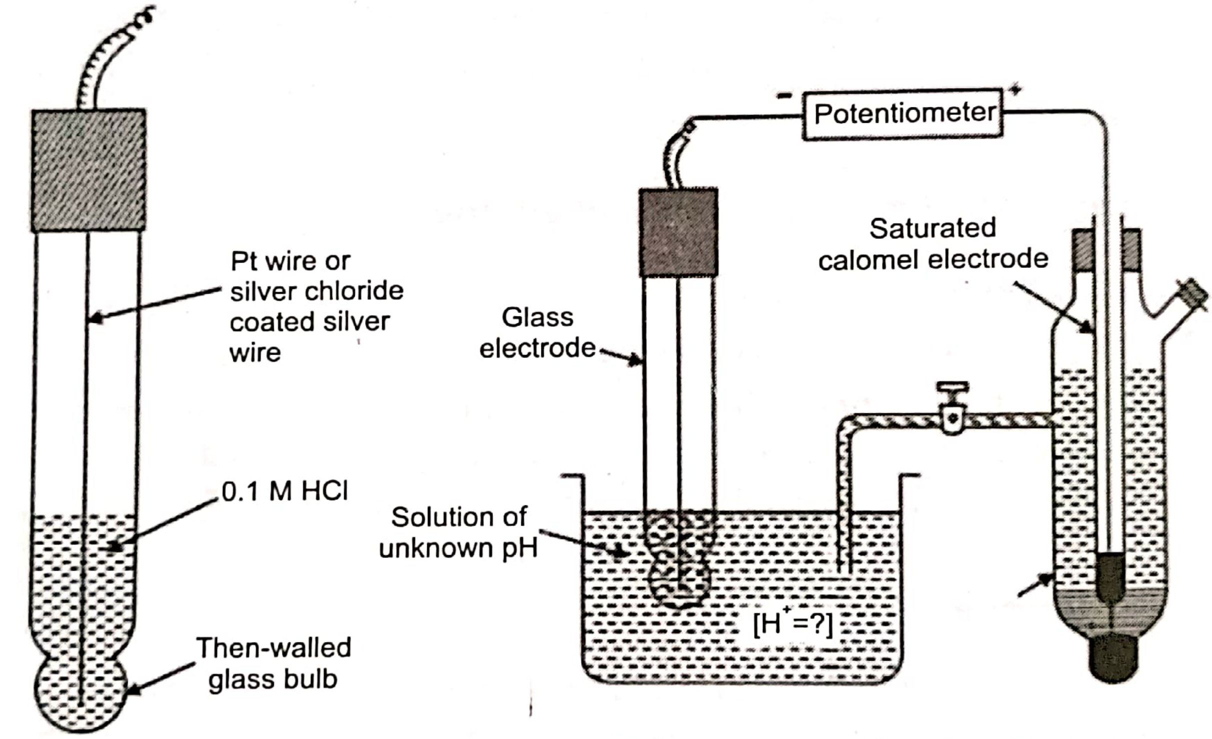
Over a range of pH of the rest-solution from 0 to 10.

Construction

A glass electrode consists of thin walled glass bulb containing $AgCl^-$ coated Ag electrode or simply a Pt electrode in 0.1 M HCl. The glass electrode may be shown schematically as

$$-Ag|AgCl(S), HCl(0.1M)||\text{glass or } Pt, (0.1M)HCl|\text{glass}^-$$

HCl in the bulb furnishes a constant H^+ ion concentration. Thus; it is an Ag-AgCl electrode, reversible with respect to chloride ions.



Glass Electrode

Determination of pH by Glass Electrode.

Figure. 1.5

Glass electrode is used as the "Internal reference electrode" for determining the PH of solutions, especially coloured solutions containing oxidizing or reducing agents. Usually, Calomel electrode is used as the second electrode. In order to determine the pH of a solution, the glass electrode is placed in the solution under-rest and this half-cell is coupled with saturated calomel electrode. The E.m.f of the cell is measured. Since the resistance is very high, so special electron tube voltammeters are used to measure the E.m.f of the above cell. The E.m.f of the complete cell is given by

$$E_{cell} = E_{calomel} - E_{glass} = E_C - E_G^0 - 0.0592\,pH$$

$$pH = \frac{E_C - E_G^0 - E_{Cell}}{0.0592}$$

Advantages of glass electrode

1. It is simple and can easily be used.
2. Equilibrium is rapidly achieved.
3. The results are accurate.
4. It is easily poisoned.

Limitations of glass electrode

1. Glass electrode can be used in solutions with pH range 0-10, because electrodes are composed of special glass that can be used up to pH 12.
2. The resistance is extremely high in the order of 10 to 100 million ohms, which cannot be measured by ordinary potentiometers and special electronic potentiometers have to be used.

1.2 Battery Chemistry

1.2.1 Batteries (or) Cells

"A device that stores chemical energy for later release as electricity is known as ***Battery***."

(or)

An electrochemical cell or often, several electrochemical cells connected in series that can be used as source of direct electric current at a constant voltage.

Batteries or cells can be divided into three types

1. Primary cells
2. Secondary cells
3. Fuel cells

Primary Cells

Those cells in which the cell reaction is not reversible are known as Primary cells. Thus, when the reactants have for the most part been converted to products, no more electricity is produced and the battery or cell becomes "dead".

Ex: *Zn* - Carbon battery or Dry cell (or) Laclache cell

Zn-Carbon battery (or) Dry cell (or) Laclanche cell

A cell without fluid component is perhaps the most familiar of all batteries. The anode of the cell is zinc (or container) containing an electrolyte consisting of $NH_4Cl, ZnCl_2$ and MnO_2 to which starch is added to make it thick paste-like so that it is less likely to leak. A carbon (graphite) rod serves as the cathode, which is immersed in the electrolyte in the centre as the cell.

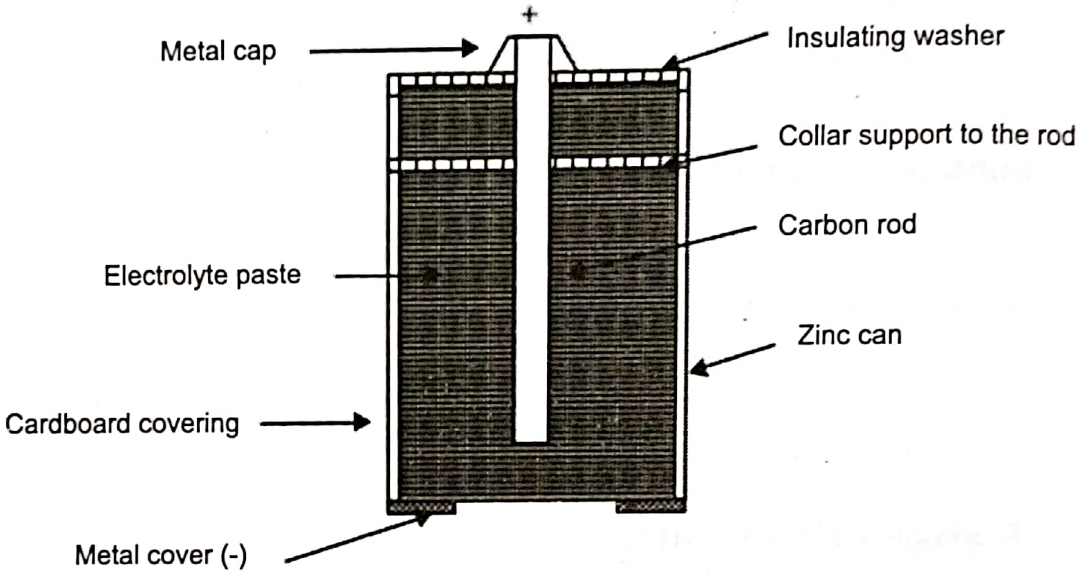


Figure. 1.6

The anode (oxidation) half-cell reaction is

Oxidation: $Zn(s) \longrightarrow Zn^{+2}(aq) + 2e^-$ (at anode)

The cathode reaction is quite complex. Essentially, it involves the reaction of MnO_2 to a series of compounds having Mn in $+3$ oxidation state. For example, Mn_2O_3.

Reduction: $2MnO_2(s) + H_2O + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$ (at cathode)

However an acid-base reaction between OH^- and NH_4^+ (derived from NH_4Cl) evolves $NH_3(g)$, which disrupts the current flow.

$$2NH_4Cl(aq) + 2OH^-(aq) \longrightarrow 2NH_3(g) + 2H_2O + 2Cl^-$$

This is prevented by a reaction of $NH_3(g)$ with Zn^{+2} (from $ZnCl_2$) to form the complex ion $[Zn(NH_3)_2]Cl_2$. Hence, the reaction at two electrodes are,

$$Zn^{+2} + 2NH_3 + 2Cl^- \rightarrow [Zn(NH_3)_2]Cl_2$$

Anode: $Zn(s) \rightarrow Zn^{+2}(aq) + 2e^-$

Cathode: $2MnO_2(s) + 2NH_4Cl + Zn^{+2} + 2e^- \longrightarrow Mn_2O_3 + [Zn(NH_3)_2]Cl_2 + H_2O$

Overall reaction: $Zn(s) + 2MnO_2 + 2NH_4Cl \longrightarrow Mn_2O_3 + [Zn(NH_2)_2]Cl_2 + H_2O$

The dry cell is a primary cell, since various reactions involved cannot be reversed by passing electricity back through the cell. Dry cell is cheap to make, and gives a voltage of about 1.5V. But it has two significant disadvantages.

- When current is drawn rapidly from it, products build up on the electrodes there by causing drop in voltage.
- Since the electrolytic medium is acidic, so zinc metal dissolves slowly, thereby the cell run down slowly, even if it is not in use.

Uses

1. Dry cell is used in flash- lights
2. Used in transistor radios
3. Used in calculators etc.

Secondary Cells

Secondary cells in which the cell reaction can be reversed by passing direct electric current in opposite direction. Thus, a secondary cell may be used through a large number of cycles of discharging and charging.

Lead-acid storage cell

A storage cell is one that can operate both as a voltaic cell and as an electrolytic cell. When operating as a voltaic cell, it supplies electrical energy and as a result eventually becomes “rundown”. It must then be recharged. When being recharged, the cell operates as an electrolytic cell. Thus, storage cell has the great advantage of its ability to work both ways, to receive electrical energy and also to supply it.

The common example of a storage cell is the lead -acid storage cell. One of its electrodes is made of lead. The other electrode is made of lead dioxide (PbO_2) or rather a paste of PbO_2 is pressed into a grid, made of lead. A number of lead plates ($-ve$ plates) are connected in parallel and a number of lead dioxide plates ($+ve$ plates) are also connected in parallel. The lead plates fit in-between the lead dioxide plates. Various plates are separated from the adjacent ones by insulators like strips of wood or rubber or glass fiber. The entire combination is then immersed in approximately 20 to 21% dil. H_2SO_4 corresponding to a density of 1.2 to 1.3.

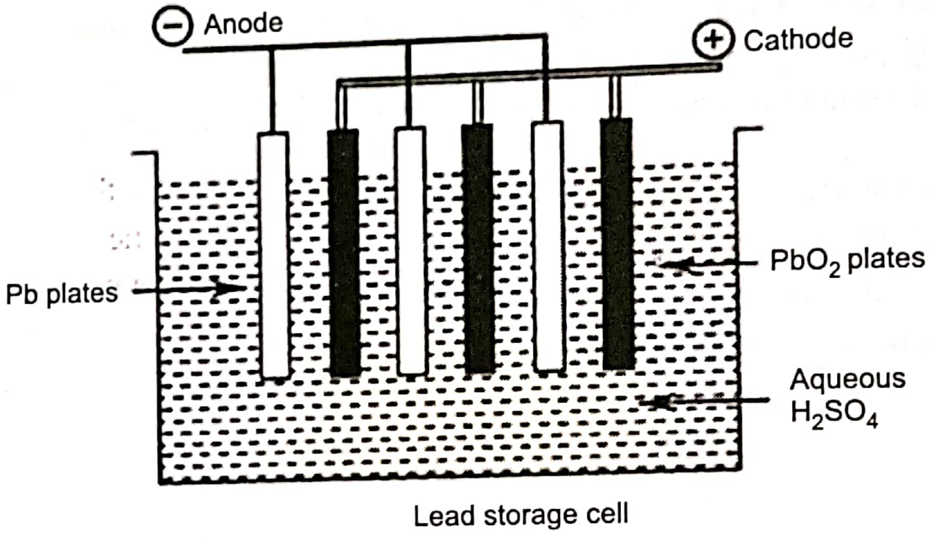


Figure. 1.7 Lead-Acid storage cell

Discharging

When a storage cell is operating as a voltaic cell, it is said to be discharging. The lead electrode loses electrons, which flow through the wire. In this reaction, oxidation of lead takes place at the anode.

$$Pb \longrightarrow Pb^{+2} + 2e^- \quad (at\ lead\ anode)$$

The Pb^{+2} ions then combine with sulphate (SO_4^{-2}) ions.

$$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4$$

The electrons released from the anode (lead plate) flows to the dioxide electrode. Here PbO_2 gains electrons to form Pb^{+2} ions. In other words, lead undergoes reduction at the cathode from oxidation state +4 to +2. The Pb^{+2} ions then combine with SO_4^{-2} ions.

$$PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{+2} + 2H_2O \quad \text{(at } PbO_2 \text{ cathode)}$$
$$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4$$

So the net reaction during use (or discharging) is,

$$Pb + PbO_2 + 4H^+ + 2SO_4^{-2} \longrightarrow 2PbSO_4 + 2H_2O + \text{Energy}$$

It may be noted that lead sulphate is precipitated at both the electrodes. The voltage of each cell is about 2.0 volts at a concentration of 21.4% H_2SO_4 at 25°C. Lead cell, commonly used in automobiles, is a combination of six such cells in series to form a battery with an e.m.f of 12 volts.

Charging

When both anode and cathode become covered with $PbSO_4$, the cell ceases to function as a voltaic cell. To re-charge a lead storage cell, the reactions taking place during discharging are reversed by passing an external e.m.f greater than 2 volts from a generator. The $+ve$ pole of the generator is attached to the $-ve$ pole the cell and the following reactions take place.

Reaction at the $-ve$ terminal (cathode)

$$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{-2}$$

Reaction at $+ve$ terminal (anode)

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{-2} + 2e^-$$

Hence, the net reaction during charging is

$$PbSO_4 + 2H_2O + \text{Energy} \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{-2}$$

During the process the charging, the electrodes of cell are restored to their original conditions (i.e Pb and PbO_2 respectively). It may also be noted that during discharging operation, the concentration of acid (H_2SO_4) decreases, while the concentration of acid increases during the charging operation.

Uses: Lead acid storage cells are used for many purposes such as to supply current for electrical vehicles, gas engine ignition, in telephone exchanges, railways, mines, laboratories, hospitals, broadcasting stations, automobiles, power stations and distribution works.

Notes

1. The lead storage cell is both a voltaic cell and an electrolytic cell. When electricity is being drawn from the cell to start the car, it acts as a voltage cell. The alternator forces electrical energy (generated by it due its motion) into the cell, thereby causing electrolysis reactions to take place that restore the original reactants of the cell.
2. The lead storage battery (of 12v) commonly used in automobiles consists of six identical cell joined together in series.

Lithium ion batteries

Lithium ion batteries are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

Anode: $LiCoO_2 \rightleftharpoons Li_{1-x}CoO_2 + xLi^+ + xe^-$

Cathode: $xLi^+ + xe^- + xC_6 \rightleftharpoons xLiC_6$

Overall: $LiCoO_2 + xC_6 \rightleftharpoons Li_{1-x}CoO_2 + xLiC_6$

With the coefficients representing moles, x is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

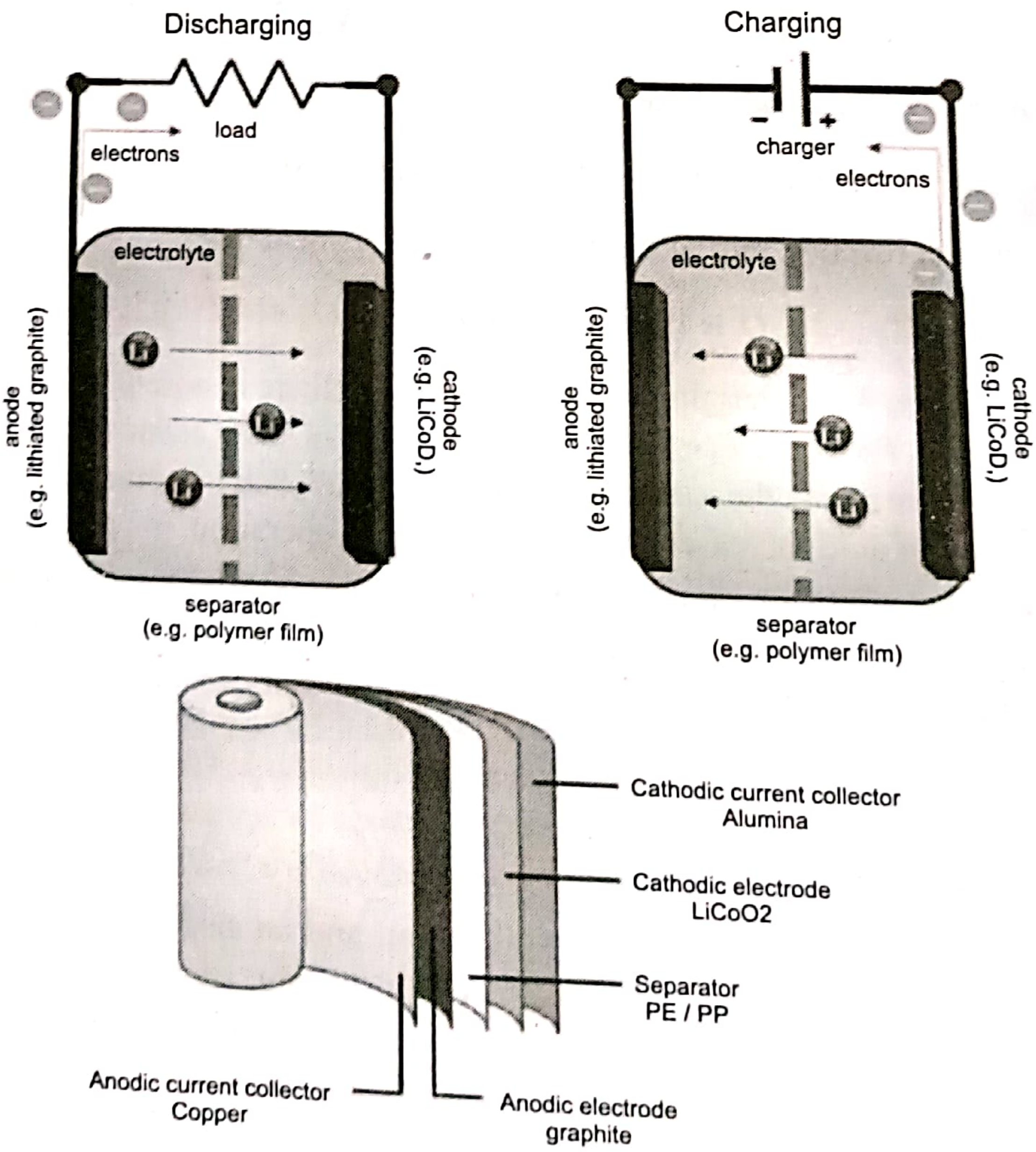


Figure. 1.8 · Lithium-ion Battery

Applications of Li-ion battery to electrical vehicles (EVs)

Electric vehicle (EVs) needs an energy storage system to power the vehicle propulsion system. At present, many batteries have been explored for the electric vehicles applications like Nickel-cadmium, Nickel-Metal Hydride, and Lead-acid but Li-ion battery is found more useful in the EVs application.

1. **Eco-friendly:** They have relatively low levels of toxic heavy metals such as Cd, Pb, Hg etc compared to other types of batteries such as Lead-acid and Ni-Cd batteries.
2. **Cell voltage:** Li-ion Battery has cell voltage of 3.7 V which is high compared to other batteries like Ni-MH(1.2 V).
3. **Light weight and compact:** Electrodes commonly used in Lithium ion batteries, Lithium and carbon, are light weight on their own and this makes them light weight and compact compared to other batteries.
4. **High energy density:** Li element has the ability to release and store large amounts of energy. This allows Li-ion batteries to pack high energy in small size. Because of high energy efficiency Li-ion batteries last much longer between charges than other rechargeable batteries - a parameter which is very important for electric car batteries. Performance at high temperatures is also good.
5. Low maintenance: Ni-Cd or Ni-MH batteries have "memory effect" or "lazy battery effect" which causes them to hold less charge. They should be maintained by completely discharging or recharging them. Li-ion batteries don?t suffer from memory effect and they give up their last bit of power. Hence maintenance is less.
6. **Low self-discharge rate:** Self discharge rate of Li-ion batteries increases about 5% within first 24 hrs after charging and then tapers off to 1-2% per month.
7. **More charge cycles:** Quality Li-ion batteries last about 1000 full charge cycles.

Flow Batteries

Fuel cells:

Fuel cell is an electrochemical cell which converts energy of a fuel directly into electricity through redox reaction.

When a fuel is burned, the electron exchange takes place only when the atoms of the oxidizing agent (oxygen or air) come in direct contact with the atoms of the substance being oxidized (the fuel).

In fuel cell, the electrons from the anode side of the cell cannot pass through the membrane to the positively charged cathode; they must travel around it via an electrical circuit to reach the other side of the cell. This movement of electrons is an electrical current.

The energy is released as heat. In a fuel cell, electric energy is obtained without combustion from oxygen and a gas that can be oxidized.

Hence, a fuel cell converts chemical energy of the fuel cells directly to electricity. The process in fuel cell is,

$$\text{Fuel} + \text{Oxygen} \longrightarrow \text{Oxidation products} + \text{Electricity}$$

Ex: - Hydrogen-Oxygen fuel cell, Methanol-oxygen fuel cell etc.

Methyl Alcohol - Oxygen Alkaline Fuel Cell

In this fuel cell, CH_3OH is used as fuel and O_2 as oxidant to generate electrical energy. The figure shows a typical $CH_3OH - O_2$ fuel cell.

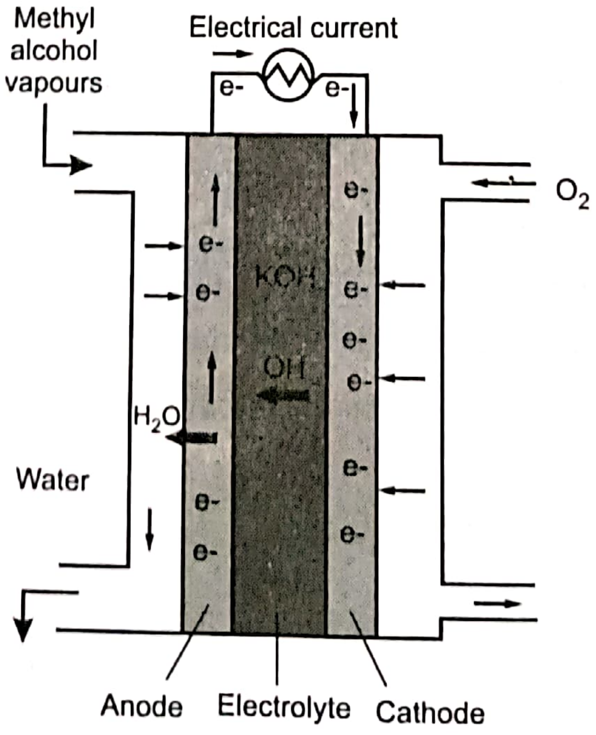


Figure. 1.9

The methyl alcohol - oxygen fuel cell has two electrodes. The anode consists of porous nickel electrode impregnated with Pt/Pd catalyst. Porous nickel electrode coated with silver catalyst constitutes a cathode of the cell. The electrolyte, KOH, is taken in between the two electrodes. CH_3OH and O_2 are sent continuously into their respective electrodes as shown in figure and the electrical energy is produced with the continuous replenishment of the fuel, CH_3OH at the anode.

In neutral medium the half cell reactions are:

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode: $3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

Cell reaction: $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$

whereas in alkaline conditions the half reactions are:

Anode: $CH_3OH + 6OH^- \rightarrow 5H_2O + 6e^- + CO_2$

Cathode: $3/2O_2 + 6e^- + 3H_2O \rightarrow 6OH^-$

Cell reaction: $CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$

Advantages of methyl alcohol - oxygen fuel cell

1. Methanol fuel cells are reasonably stable at all environmental conditions.
2. Easy to transport.
3. Do not require complex steam reforming operations.
4. These fuel cells are targeted to portable applications.
5. Because of high hydrogen concentration in methanol it is an excellent fuel.
6. Methanol poses less risk to aquatic plants, animals and human beings than gasoline.
7. Because methanol possess lower inflammability limit than gasoline it poses less fire risk than gasoline.
8. There is zero emission by the cells hence the fuel cells are eco friendly.

Applications of alcohol - oxygen fuel cells

The major application of methyl alcohol - oxygen fuel cells is a fuel for fuel cell motor vehicles like NECAR - 5 in Japan, USA etc.

Differences between Primary, Secondary & Fuel cells

S.No.	Primarycells	Secondarycells	Fuel cells
1	It only acts as galvanic or voltaic cell. i.e., produces electricity	It acts as galvanic or voltaic cell while discharging (produces electricity) and acts as electrolytic cell (consumes electricity)	It is a simple galvanic or voltaic cell. i.e., produces electricity
2	Cell reaction is not reversible.	Cell reaction is reversible.	Cell reaction is reversible.
3	Can't be recharged.	Can be recharged.	Energy can be withdrawn continuously.
4	Can be used as long as the active materials are present.	Can be used again and again by recharging.	Reactants should be replenished continuously. it does not store energy.
5	**Ex:** Leclanche cell or Dry cell, Lithium cell.	**Ex:** Lead storage battery, NiCd battery, Lithium ion cell.	**Ex:** $H_2 \& O_2$ Fuel cell.
6	**Uses:** In Pace makers watches, Transistors, radios ect.	**Uses:** In electronic equipments, automobile equipments, digital cameras, laptops, flash light.	**Uses:** Great use in space vehicles due to its light weight (product of this source is fresh water for astronauts) $CH_3OH \& O_2$ Fuel cell