

Electrochemistry is a branch of science, which studies the conversion of chemical energy into electrical energy and vice versa or It is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (a metal or semiconductor) and an ionic conductor (an electrolyte) and which involve electron transfer between the electrode and the electrolyte or species in solution. The interconversions of energies take place through redox reactions form the basis of electrochemical cells.

The terminology used in the electrochemical cell:

Anode- is the electrode at which oxidation occurs.

Cathode - is the electrode at which electrons are received from the outer circuit. It has a positive charge and is known as (+) in the cell diagrams.

Oxidation- is the loss of electrons or an increase in oxidation state by a molecule, atom or ion

Reduction - is the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion.

Oxidation occurs at the anode and reduction occurs at the cathode.

The half-cell reaction at the anode is oxidation, while the half-cell reaction at the cathode is reduction.

Q-What are Electrochemical cells: Explain different types of electrochemical cells

The device, which converts chemical energy into electrical energy or electrical energy into chemical energy.
There are two kinds of electrochemical cells, they are -

1. Galvanic cell or Voltaic cell: It is an electrochemical cell that produces electricity as a result of spontaneous redox reaction due to conversion of chemical energy into electrical energy. Ex: Daniel Cell.

2. Electrolytic cell: It is an electrochemical cell in which non-spontaneous reaction is driven by an external source of current is called an Electrolytic cell (conversion of electrical energy into chemical energy)

Ex: Electro plating cell

Q- Describe the construction and working of Galvanic cell or Voltaic cell

A galvanic cell consists of two electrodes dipped in two electrolyte solutions which are separated by a porous diaphragm or connected through a salt bridge. The Daniel cell is a typical example for the Galvanic cell (Fig. 1.1). This cell can be constructed by placing zinc rod in zinc sulphate solution and copper rod in copper sulfate solution. Electrical contact is provided between the two electrodes through salt bridge and externally connected by a wire through an ammeter or voltmeter. In this cell zinc rod is found to be negative (anode) and copper rod becomes positive (cathode). The electrons are sent out from the zinc rod to the copper rod, The potential arising for anode is due to oxidation and it is referred as oxidation potential ($E_{\text{Zn/Zn}^{2+}}$). Similarly, the potential arising at cathode (copper) is due to reduction potential ($E_{\text{Cu}^{2+}/\text{Cu}}$)

Daniel cell can be represented as:

→



Cell reactions: When the zinc and the copper electrodes are connected externally connected, the following reactions are take place.

At anode or negative electrode (left electrode): Zinc goes into the solution as Zn^{2+} ions by liberation of electrons

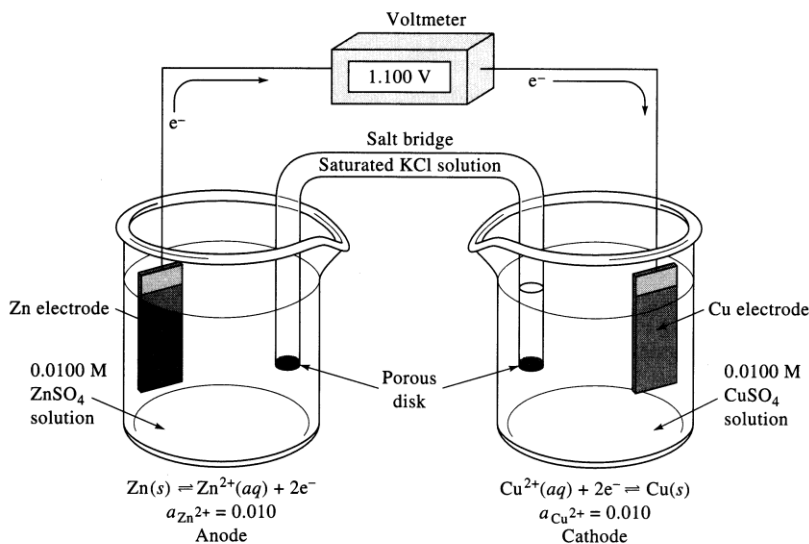
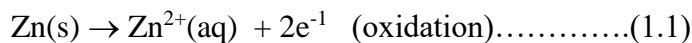
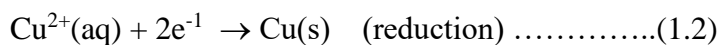
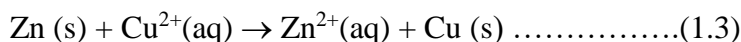


Fig. 1.1

At cathode or positive electrode (right electrode): Reduction of Cu^{2+} ions take place with deposition of metallic copper on copper by consuming electrons



Addition of equation (1.1) and (1.2) gives redox or net chemical cell reaction is



For the above cell the *emf* is found to be 1.1 V at 25°C. The reaction is found to proceed spontaneously from left to right ie., electrode on the left forces the electrons into the external circuit and electrode on the right withdraws them. Therefore, the *emf* of the cell is positive.

In Galvanic cell, *emf* can be expressed at the difference between two single electrode potential

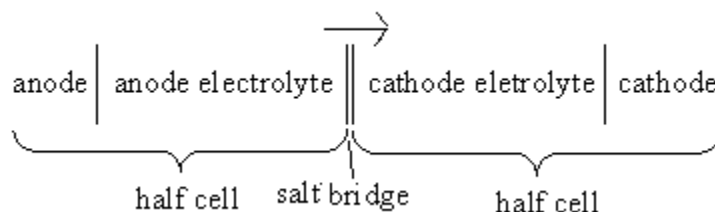
$$\text{The cell emf, } E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \dots\dots\dots(1.4)$$

When two electrodes are coupled to form a cell, the one with lower reduction potential value acts as anode and undergoes oxidation, the one with higher reduction potential value acts as the cathode and undergoes reduction. For example, in *Daniel cell* Zn-electrode has a lower reduction potential value; hence it behaves as an anode and undergoes oxidation. Whereas Cu-electrode has a higher reduction potential value, hence it

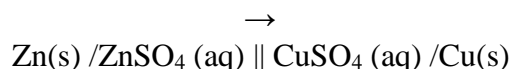
behaves as a cathode and undergoes reduction. In Zn-Hydrogen cell, Zn acts as an anode, Hydrogen electrode acts as a cathode. In Fe-Cu cell *Fe* -acts as an anode, *Cu*- electrode acts as a cathode.

Q - Write a note on cell notation or cell representation

In order to make it easier to describe a given electrochemical cell, a special symbolic notation has been adopted. If two electrodes are combined to form a cell, then the cell is represented by writing the electrode conventions side by side with the anode on the left and cathode on the right.



The half-cell in which oxidation occurs (anode) is always written on the left. The half-cell in which reduction occurs (cathode) is always written on the right. The vertical line indicates the phase boundary between the metal and solution. The two vertical lines represent the salt bridge. An arrow indicates the flow of electrons from anode to cathode (Spontaneous reaction). The electrolyte may be represented by the formula of the whole compound or by ionic species by its concentration in bracket. By placing an ammeter in the external circuit, we can measure the amount of electric charge that passes through the electrodes, and thus the number of moles of reactants that get transformed into products in the cell reaction. Based on the above guidelines *Daniel* cell can be represented as:



Q- What is a salt bridge? Explain its function

A Salt bridge is used to connect the oxidation and reduction half cells of a galvanic cell. Salt bridge is U-shaped glass tube filled with a relatively saturated inert electrolyte, usually potassium chloride or sodium chloride. Agar is used for jellification. The conductivity of the glass tube bridges depends on the concentration of the electrolyte solution. An increase in concentration below saturation increases the conductivity. Beyond saturated electrolyte content and narrow tube diameter are lower the conductivity.

Function of salt bridge:

- To avoid liquid junction potential.
- Bring about internal contact between the electrodes
- It keeps the solutions in two half-cells electrically neutral
- It connects the solutions of two half-cells and completes the cell circuit
- It prevents transference or diffusion of the solutions from one half-cell to the other

Q-Define the terms: electromotive force (*emf*) of the cell, standard electrode potential and single electrode potential (Reduction potential) or half-cell potential

Electromotive force (*emf*) of the cell: The difference in potential between the two electrodes of a galvanic cell which causes the flow of current from one electrode (higher potential) to the other (lower potential) as a result of a spontaneous redox reaction is called *emf* of the cell or the cell potential and it is denoted by E_{cell}

$$\text{The } emf \text{ of the cell, } E_{cell} = E_{cathode} - E_{anode} \quad \text{or} \quad E_{cell} = E_{right} - E_{left} \text{-----(1.5)}$$

Standard electrode potential: The potential that is developed when an element (metal or non-metal) is in equilibrium with a solution containing its own ions of unit concentration (1M) at 298 K is called standard electrode potential in case of the gas electrode the gas at 1 atm. pressure, it is denoted by E°_{cell} .

Single electrode potential (Reduction potential) or half-cell potential: *'The potential that is developed at the interface between the metal and the solution, when it is in contact with a solution of its ions'. Or 'it is a measure of the tendency of a given half-reaction to occur as reduction when it is in equilibrium with the other half cell'.* It is denoted by $E_{M^{n+}/M}$

For example, the reduction potential of zinc electrode is $E_{Zn^{2+}/Zn} = -0.76 \text{ V}$

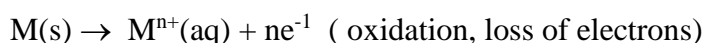
Oxidation potential of zinc electrode is $E_{Zn/Zn^{2+}} = 0.76 \text{ V}$

Q: Discuss the origin of single electrode potential.

Origin of electrode potential: *'The potential developed at the interface between the metal and the solution when it is in contact with a solution of its ions.* When an electrode is in contact with a solution of its ions, such as in a half-cell, a potential arises due to the interaction between the two phases i.e. metal ion – metal electrode.

If a metal M is dipped in a solution containing its ions M^{n+} , the following two reactions are possible.

- i. The metal shows the tendency to go into the solution as metal ions by losing electrons.



- ii. The metal ions in the solution shown to a tendency to get deposited as metal atoms.



Depending upon the nature of the metal, either the dissolution of the metal or the deposition of metal is faster in the beginning or the other one is slower. But after some time, the reaction will reach a state of equilibrium. $M^{n+}(aq) + ne^{-1} \leftrightarrow M(s)$

In this reaction, the number of metal atoms dissolving is equal to the number of atoms getting deposited.

If the dissolution is faster than the deposition reaction, at equilibrium, the net change is a few metal atoms have dissolved in the solution, liberating electrons [$M(s) \rightarrow M^{n+}(aq) + ne^{-1}$ (oxidation, loss of electrons)]. These electrons accumulate on the electrode surface. Making it negatively charged [**Fig. 1(a)**]. The negatively charged electrode surface attracts a layer of positively charged ions at the interface, developing an

electrical double layer called **Helmholtz Electric double layer (HDL)** across this double layer the potential develops and this potential is called single electrode potential.

Similarly, if the deposition reaction is faster than the dissolution, at equilibrium, the net change is the deposition of few metal ions as metal atoms by consuming electrons [$M^{n+}(aq) + ne^{-1} \rightarrow M(s)$ (reduction, gain of electrons)]. As a result, the electrode surface develops a layer of positive charge which attracts a layer of negatively charged ions at the interface [**Fig. 1 (b)**], again HDL is formed and develops single electrode potential. HDL is practically indistinguishable from the metal plane and may be visualized as parallel plane capacitor. *Therefore, the formation of an **electrode double layer** gives rise to potential difference across layer, this potential difference between the metal and the solution at the interface in the single electrode potential.*

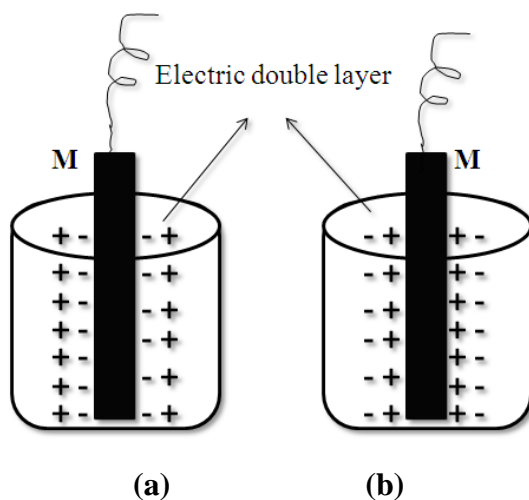


Fig. 1

Q- What is the importance of electrochemical series (electrode potential?)

When elements are arranged in increasing order of their standard electrode potential values form a series called electrochemical series, called electrochemical series. Standard electrode potential values of some elements are given in Table 1.1.

Table 1.1: Electrochemical Series

M^{n+}/M	$E^{\circ} (V)$	M^{n+}/M	$E^{\circ} (V)$	M^{n+}/M	$E^{\circ} (V)$
Li^{+}/Li	-3.05	Al^{3+}/Al	-1.66	H^{+}/H_2	0.0
K^{+}/K	-2.93	Zn^{+2}/Zn	-0.76	Cu^{+2}/Cu	0.34
Ba^{+2}/Ba	-2.90	Fe^{+2}/Fe	-0.44	Ag^{+}/Ag	0.80
Ca^{+2}/Ca	-2.87	Cd^{+2}/Cd	-0.40	Hg^{+2}/Hg	0.85
Na^{+}/Na	-2.71	Sn^{+2}/sn	-0.14	Pt^{+2}/Pt	1.20
Mg^{+2}/Mg	-2.37	Pb^{+2}/Pb	-0.13	Au^{+3}/Au	1.38

The electrochemical series gives the following valuable information.

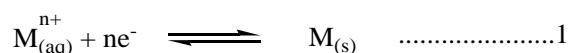
1. A negative value indicates oxidation tendency and a positive value indicates reduction tendency with respect to hydrogen.
2. The metal with lower electrode potential is more reactive and as the electrode potential increases, the reactivity decreases and the metal with higher electrode potentials are nobler.
3. Metals with lower electrode potentials have the tendency to replace metals with higher potential from their solutions.
4. Metals with negative electrode potentials can liberate hydrogen from acidic solutions.

Q- Derive Nernst equation for a single electrode (Thermodynamic concept of cell potential/electrode potential)

In 1889 WALTHER NERNST derived a thermodynamic equation, it relates the reduction potential of a half-cell (or the total voltage, i.e. the electromotive force, of the cell) at any point in time to the standard electrode potential (E°), temperature (T), concentration of metal ion (M^{n+}) in solution and reaction quotient of the underlying reactions and species used. It is named after the German physical chemist WALTHER NERNST (1864-1941) who first formulated it, He received the Nobel prize in 1920 “in recognition of his work in thermochemistry”. His contribution to chemical thermodynamics led to the well-known equation correlating chemical energy and the electric potential of a galvanic cell or battery.

In order to derive this equation, free energy concept is used

Consider the following reversible electrode reaction



The free decrease energy change ($-\Delta G$) in a spontaneous reaction is equal to the energy available to do work

$$(-\Delta G) = W_{\max} \text{ -----(2)}$$

The maximum work available from a reversible chemical process is equal to maximum amount of electrical energy that can be obtained, $W_{\max} = W_{\text{elec}}$ -----(3)

W_{elec} is the maximum amount electrical energy that can be obtained and it is equal to the product of number of coulomb and energy available per coulomb and it is given by

$$W_{\text{elec}} = nFE \text{ -----(4)}$$

The free energy changes due to transfer of 1 mole of ions across the double layer is related to the electrode potential (E)

$$\Delta G = -nFE \dots\dots\dots(5)$$

where n = the number of electrons involved in reaction; F = Faraday constant

The free energy change is also related to equilibrium constant (K). For a reversible reaction, the change in free energy (ΔG) are inter related as

$$\Delta G = \Delta G^0 + RT \ln K \text{ ----- (6)}$$

Where R = Gas constant

T = Absolute temperature

ΔG^0 = Standard free energy change ($\Delta G^0 = -nFE^0$)

From equation (5) and (6)

$$-nFE = \Delta G^0 + RT \ln K$$

$$-nFE = \Delta G^0 + RT \ln [\text{Product}] / [\text{Reactant}]$$

$$-nFE = \Delta G^0 + RT \ln [M] / [M^{n+}] \quad \text{since } K = [M] / [M^{n+}]$$

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

$$E = E^0 - RT/nF \ln [1] / [M^{n+}] \text{(7) since } [M] = 1$$

Equation (7) is basic Nernst equation. By substituting R (8.314 J K⁻¹ mol⁻¹) Faraday constant, F (965000 J V⁻¹ mol⁻¹) and absolute temperature, T (298 K) and converting ln to log₁₀, the above equation further reduced to

$$E = E^0 + 0.0591/n \log [M^{n+}] \text{ -----(8)}$$

The Nernst equation for a cell: The Nernst equation can also be applied for calculation of *emf* of a cell.

For Daniel cell: Zn(s) / ZnSO₄ (aq) || CuSO₄ (aq) / Cu(s)

$$E_{\text{cell}} = \{E^0_{\text{Cu}^{2+}/\text{Cu}} + 0.0591/n \log [\text{Cu}^{2+}]\} - \{E^0_{\text{Zn}^{2+}/\text{Zn}} + 0.0591/n \log [\text{Zn}^{2+}]\}$$

$$E_{\text{cell}} = [E^0_{\text{Cu}^{2+}/\text{Cu}} - E^0_{\text{Zn}^{2+}/\text{Zn}}] + 0.0591 \log [\text{Cu}^{2+}/\text{Zn}^{2+}]$$

$$E_{\text{cell}} = E^0_{\text{cell}} + 0.0591/2 \log [\text{Cu}^{2+}] / [\text{Zn}^{2+}] \text{ (9)}$$

In general-

$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log \frac{[\text{Concentration of ionic species in cathode half cell}]}{[\text{Concentration of ionic species in anode half cell}]}$$

Q- Discuss different types of Electrodes

Types of Electrodes: In electrochemical work, the various electrodes are used depending upon the purpose

1. Metal-metal ion electrode: This type of electrode consists of metal dipped in a solution containing its own ions. Ex: Zn/Zn²⁺, Cu/Cu²⁺

The electrode reaction can be written as $M^{n+}(\text{aq}) + ne^- \rightarrow M(\text{s})$

2. Metal – metal salt ion electrode (Metal – insoluble salt electrode): These electrodes consist of a metal in contact with a sparingly soluble salt of the same metal which is in contact with solution containing the anion of the salt. Ex: Calomel electrode (Hg/Hg₂Cl₂/KCl), Silver – Silver chloride electrode (Ag/AgCl/KCl) and Lead –lead sulphate electrode (Pb/PbSO₄/SO₄²⁻)

3. Gas electrode: Gas electrodes consist of a gas bubbling about an inert metal wire or foil, immersed in an

ionic solution of the gas molecule.

Ex: H_2 – gas electrode ($\text{Pt} / \text{H}_2 / \text{H}^+$)

Chlorine – gas electrode ($\text{Pt} / \text{Cl}_2 / \text{Cl}^-$)

4. Ion selective electrode (Membrane electrode): In this type of electrodes, a membrane is in contact with a solution, with which it can exchange ions.

Ex: Glass electrode (exchanges H^+ ions with the solution), various metal ions selective electrodes, which exchange metal ions with the solution.

Q- What are *Reference Electrodes*? Explain difference types of reference electrodes

Reference electrodes are those electrodes which have constant reduction potential and which are used to determine the electrode potential of another electrode

There are two types of reference electrodes. They are -

1. Primary reference electrode
2. Secondary reference electrode

1. Primary reference electrode: The primary reference electrode used for cell potential measurements. The best primary standard reference electrode is the *standard hydrogen electrode* (SHE), whose potential is taken as zero at all temperatures. However, it is not convenient for potential measurements. Because of that

- i. Construction and working is difficult on account of difficulties involved in maintaining concentration of H^+ ions at unity and in keeping the pressure of H_2 -gas uniformly at 1 atm.
- ii. The electrodes become inactive in the presence of impurity gases present in hydrogen.
- iii. It cannot be used in a solution containing strong oxidizing agents (salts of MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$).
- iv. In the presence of reducible ions or substances having positive electrodes, it cannot be used.

2. Secondary reference electrodes: Because of the difficulties involved in SHE as a reference electrode, some other electrodes of constant potential are used as reference electrodes and these electrodes are called secondary reference electrodes, important potential are employed secondary reference electrodes are (i) Calomel electrode (ii) Silver – silver chloride electrode.

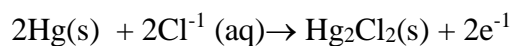
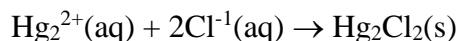
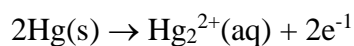
(i) **Calomel electrode:** Calomel electrode is a commonly used electrode containing mercury and sparingly soluble mercurous chloride along with potassium chloride solution.

Construction: It is a metal-metal insoluble salt electrode; it consists of a glass tube with a side tube. Mercury is placed at the bottom of the tube. A paste of mercurous chloride and mercury is placed over the pool of mercury. The remaining part of the tube is filled with KCl solution. Platinum wire is dipped into the mercury layer for electrical contact. The side tube filled with KCl solution functions as a salt bridge (Fig. 1.3).

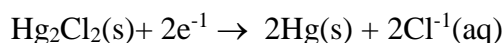
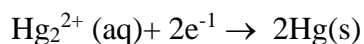
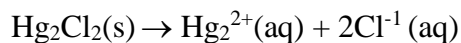
Notation of electrode: Calomel electrode can be represented as $\text{Hg(l)}/\text{Hg}_2\text{Cl}_2, \text{KCl(sat)}$

Electrode reactions: The calomel electrode can act as anode or cathode depending on the nature of the other electrode.

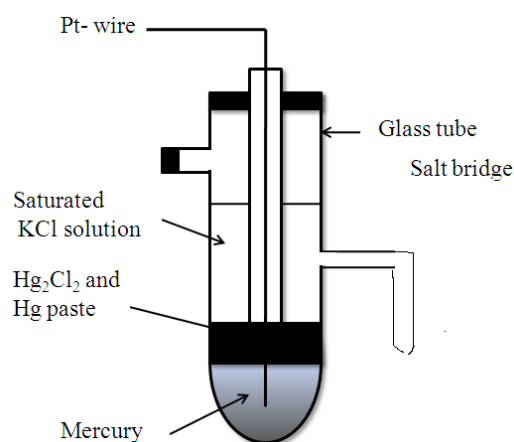
As Anode: when it acts as anode, the electrode reaction is



As Cathode: When it acts as cathode, the electrode reaction is:



The net reversible reaction is: $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^{-1} \rightleftharpoons 2\text{Hg(s)} + 2\text{Cl}^{-1}$



Or

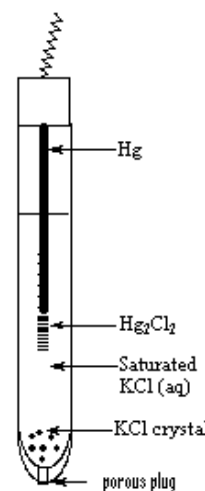


Fig. 1.3

Reduction electrode potential E for a given KCl solution is given by the equation

$$E = E^0 - 0.0591/n \log K$$

$$E = E^0 - 0.0591/n \log \frac{[\text{Hg}]^2[\text{Cl}^{-1}]^2}{[\text{Hg}_2\text{Cl}_2]}$$

$$E = E^0 - 0.0591/2 \log [\text{Cl}^{-1}]^2 \quad \text{since } [\text{Hg}] = [\text{Hg}_2\text{Cl}_2] = 1$$

Since the electrode is reversible with respect to chloride ion, the electrode potential depends on the concentration of KCl solution. The potential of the calomel electrode is found to depend on the concentration of KCl solution used in the half cell.

Concentration of the KCl solution

E_{calomel} at 298K

0.1 N

0.3334 V

1.0 N

0.2810 V

Saturated

0.2422 V

Advantages of calomel electrode:

1. It is very simple to construct.
2. Potential is reproducible and stable
3. Electrode potential doesn't vary with temperature

Applications:

- (i) Commonly used as reference electrode in all potentiometric determinations
- (ii) Used as a secondary reference electrode in the measurement of single electrode potential
- (iii) It is useful as a reference electrode in measurement of corrosion rate
- (iv) Used as reference electrode in measurement of pH of solution

Q - Discuss determination of single electrode potential using secondary reference electrode (SCE)

Principle: It is impossible to measure the absolute value of a single electrode potential experimentally. Only the difference in electrode potential between any two electrodes can be measured as *emf* of the cell formed by the combination of the electrodes. Hence electrode potential value is assigned for different electrodes with respect to the standard hydrogen electrode $[H^+ (1M) / Pt, H_2 (1atm)]$ whose potential is arbitrarily taken as zero at all temperatures. The single electrode potential of an unknown can also be determined by using secondary reference electrodes like calomel or Ag-AgCl electrode.

Determination of Single electrode potential using calomel electrode:

The potential of a given electrode is measured using saturated calomel electrode (SCE) whose potential is accurately known. The electrode whose potential to be determined is coupled with calomel electrode as shown in fig. The *emf* of the cell is determined using an electronic voltmeter (Fig.1.5), Ex: In determination of electrode potential of Zinc, Zn electrode is coupled with a saturated calomel electrode through salt bridge. The cell assembly can be represented as: $Zn / Zn^{2+} \parallel KCl (sat) / Hg_2Cl_2 / Hg$

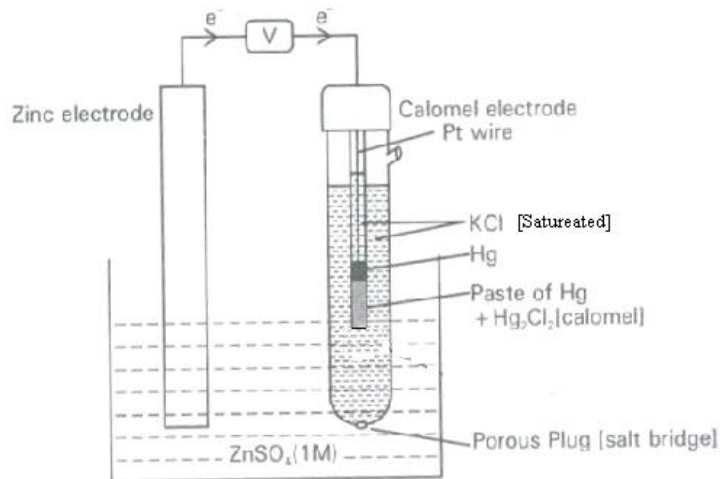


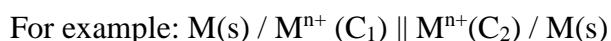
Fig. 1.5

$$\begin{aligned}
 \text{Calculation of } E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\
 &= E_{\text{SCE}} - E_{\text{Zn}^{2+}/\text{Zn}} \\
 &= 0.241 - E_{\text{Zn}^{2+}/\text{Zn}}
 \end{aligned}$$

$$\text{Therefore, } E_{\text{Zn}^{2+}/\text{Zn}} = 0.241 - E_{\text{cell}}$$

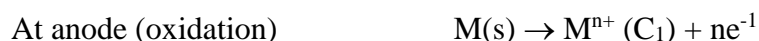
Q - What are concentration cells? Explain with suitable example

The electrode potential of a half cell dependent on the concentration of the electrolyte with which the electrode is in contact. In a concentration cell, two similar metal electrodes are in contact the solutions of its own ions at different concentrations, resulting in a difference in the electrode potential. So, *the concentration cell is a type of Galvanic cell, in which electrodes of the same metal are in contact with solutions of its own ions with different concentrations.* The *emf* arises due to the difference in concentrations of solutions.

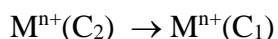


where C_1 and C_2 are molar concentration of M^{n+} ions in the two half cells respectively.

The concentration cell reaction is written as



Adding the two half-cell reaction (redox or net cell reaction or overall cell reaction)



The concentration of M^{n+} ions in the anode solution increases and that of the cathode solution decreases until both electrode solutions attain the equal concentration.

For example- copper concentration cell is illustrated as follows. $\text{Cu(s)} / \text{Cu}^{2+} (\text{C}_1) \parallel \text{Cu}^{2+}(\text{C}_2) / \text{Cu(s)}$

In concentration cells, two copper electrodes are immersed in copper sulfate solutions of concentrations C_1 and C_2 (Fig. 1.6). By convention, the left-hand electrode is the anode and the right-hand electrode is the cathode.

The following reactions are taking place in the copper concentration cell.



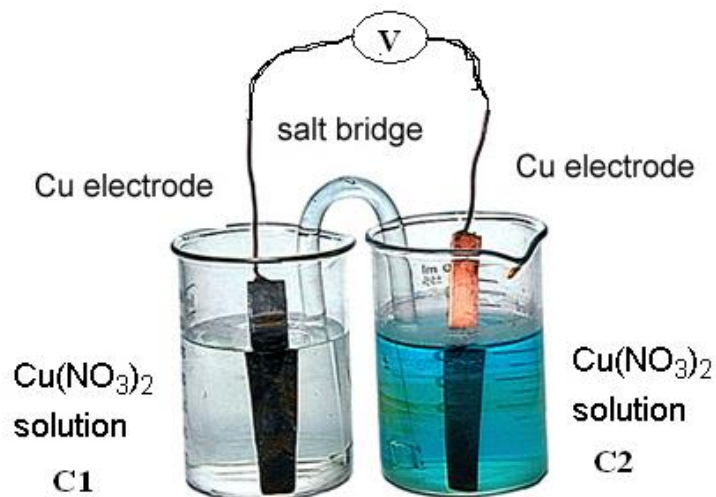


Fig. 1.6

The emf of the concentration cell can be represented as

$$E_{\text{cell}} = \{E^0 + 0.0591/n \log [C_2]\} - \{E^0 + 0.0591/n \log [C_1]\}$$

$$E_{\text{cell}} = 0.0591/n \log [C_2] / [C_1] \text{ at } 298 \text{ K, where } C_2 > C_1$$

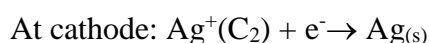
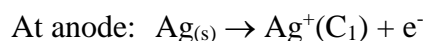
It may be noted that the term E^0 does not appear in the equation since it gets cancelled

From the above equation, we can conclude the followings

1. When two solutions are at the same concentration $\log [C_2] / [C_1] = 0$ and hence no electricity flows.
2. When $C_2 > C_1$ or $[C_2] / [C_1] > 1$, $\log [C_2] / [C_1]$ is positive. So that E is positive. Thus the direction of spontaneous reaction is from the more concentration solution C_2 to less concentration solution C_1 .
3. Higher the ratio of $[C_2] / [C_1]$, higher is the value of cell potential. For ex: If the ratio of $[C_2] / [C_1]$ increases from 0.001 M to 0.01 M (i.e 10 times) the voltage doubles and if the ratio increases 100 times, the voltage becomes three times.
4. When $C_2 < C_1$, $\log [C_2] / [C_1]$ is negative, so that E is negative. Thus the cell reaction is non-spontaneous.

Q-Derivation of Nernst equation for concentration cell (for Example –Ag concentration cell)

- Two silver rods are dipped in silver nitrate solutions of concentrations C_1 and C_2 respectively,
- The cell may be represented as: $\text{Ag}_{(s)} | \text{AgNO}_3 (C_1) || \text{AgNO}_3 (C_2) | \text{Ag}_{(s)}$. Where $C_2 > C_1$.
- The electrode reactions are:



- The EMF of the above cell is: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cell}} = E_{\text{Ag}}^0 + \frac{2.303RT}{nF} \log [\text{Ag}^+]_{\text{cathode}} - E_{\text{Ag}}^0 - \frac{2.303RT}{nF} \log [\text{Ag}^+]_{\text{anode}}$$

$$E_{cell} = \frac{2.303RT}{nF} \log(C_2) - \frac{2.303RT}{nF} \log(C_1)$$

$$E_{cell} = \frac{2.303RT}{nF} \log\left(\frac{C_2}{C_1}\right) \quad (\text{or}) \quad E_{cell} = \frac{0.0591}{n} \log\left(\frac{C_2}{C_1}\right); \text{ at } 298 \text{ K}$$

Where $C_2 > C_1$

Note – E^0 does not appear in Nernst equation of a concentration cell because it gets cancelled.

REVIEW QUESTIONS

- 1) Define the term single electrode potential. Describe the origin of single electrode potential.
- 2) What is single electrode potential? Derive Nernst equation for single electrode potential
- 3) What are ion selective electrodes? Explain determination of pH of a solution using a glass electrode.
- 4) Explain the terms with examples (i) galvanic cell (ii) half cell.
- 5) What are reactions that occur at the electrodes of a galvanic cell? Explain by taking Daniel cell as an example.
- 6) What are galvanic cells, electrolytic cells?
- 7) How potential of an electrode measured using a calomel electrode?
- 8) Why the anode of a galvanic cell is negative and cathode is positive? Write different electrode reactions occur at the electrodes.
- 9) Explain the method of determination of pH of a given solution using glass.
- 10) Describe the construction of calomel electrode. Mention the advantages of this reference electrode.
- 11) What are ion selective electrodes. Give example?
- 12) Describe the role of salt bridge in the Denial cell.
- 13) Discuss the construction of a calomel electrode with relevant chemical reactions. What are the advantages?
- 14) What are concentration cells? Derive an expression for the e.m.f. of a concentration
- 15) Justify the following statements
 - (i) In a galvanic cell anode is –ve and cathode is +ve.
 - (ii) The *emf* of a cell is always positive.
 - (iii) A salt bridge is used in the construction of a Galvanic cell
 - (iv) Ordinary volt meter are not used in the voltage measurement of Galvanic cell.
 - (v) In a concentration cell, no electricity flow when the concentration of metal ion is same in both the half cell.
- 16) A cell is constructed by coupling Zn-electrode dipped in 0.5 M ZnSO_4 and Ni-electrode dipped in

0.05 M NiSO_4 . Write the cell representation and cell reactions. Calculate *emf* of the cell. Given:

standard reduction potentials of Zn and Ni are -0.76 and -0.25 V respectively.

17). Calculate the voltage generated in the following cell $\text{Fe}/\text{Fe}^{2+} \parallel \text{Mn}^{2+}/\text{Mn}$. When iron rod is immersed in 1.0 M FeSO_4 solution and Mn rod is immersed in 0.1M MnSO_4 solution. Given E^0 for Fe^{2+}/Fe is -0.4V and Mn^{2+}/Mn is -1.18V.

18) What is *single electrode potential*? Calculate the *emf* of the Cell $\text{Fe}/\text{Fe}^{2+}(0.01) \parallel \text{Ag}^+(0.1)/\text{Ag}$ at 298 K, if standard reduction electrode potentials of Fe and Ag electrodes are -0.44 and 0.8 V respectively.

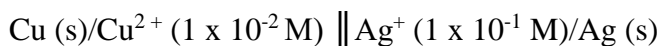
19). A cell is formed by placing two copper electrodes immersed separately in cupric sulphate solutions of which one is 100 times more concentrated than the other. Write the cell reactions and calculate the potential at 298 K.

20) A concentration cell was constructed by immersing two silver electrodes in 0.05 M and 0.1 M AgNO_3 solution. Write cell representation, cell reactions and calculate the *emf* of the concentration cell.

21) What is standard electrode potential? The spontaneous galvanic cell -

$\text{Tin}/\text{Tin ion (0.024 M)} \parallel \text{Tin ion (0.64 M)}/\text{Tin}$ develops an *emf* of 0.0126 V at 25 °C. Calculate the valency of tin.

22) Write the electrode reactions and calculate the *emf* of the following cell at 298K Given $E^0_{\text{cell}} = 1.3$ V.



23) What are concentration cells? Calculate the *emf* of the following cell at 298K $\text{Ag(s)}/\text{Ag}^+ (0.01\text{M}) \parallel \text{Ag}^+ (0.1\text{M})/\text{Ag(s)}$

24). A cell uses Zn^{2+}/Zn and Ag^+/Ag electrodes. Write the cell representation, half cell reactions and net cell reaction. Calculate the *emf* of the cell. Given $E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76$ V; $E^0_{\text{Ag}^+/\text{Ag}} = 0.8$ V.

25). Calculate the *emf* of a cadmium-copper cell in which Cd is in contact with 0.002 M CdSO_4 and Cu in contact with 0.02M CuSO_4 solution. The $E^0_{\text{cell}} = 0.74$ V at 298K.

Q - What is battery? Explain the basic components.

Battery: Battery is a device consisting of two or more galvanic cells, connected in series or parallel, they can store chemical energy in the form of active material and on-demand convert into electrical energy through spontaneous electrochemical redox reactions.

Ex: Dry batteries, Lead acid batteries, Ni - Cd batteries.

The batteries can generate electrical power and can act as a portable source of electrical energy.

General Applications of Batteries: these are used in calculators, digital watches, pacemakers for heart, hearing aids, portable computers, emergency lighting, electroplating, military and space applications. The portability of electronic equipment in the form of handsets has been made possible by batteries.

Basic components of the battery: The basic components of the battery are (Fig. 1.7):

1. Anode/ anodic active materials (M_A)
2. Cathode/ Cathodic active materials (M_c^{n+})
3. Electrolyte
4. Separator

1. Anode /Anodic active materials: Anode or anodic active materials (M_A) is oxidized during the electrochemical reaction and liberates electrons to the external circuit.



To become effective anode/ anodic material should have:

- (i) Efficiency as a reducing agent must be good
- (ii) It must deliver high columbic output (very low reduction potential)
- (iii) It should have good conductivity and stability
- (iv) Fabrication must be easy and low cost.

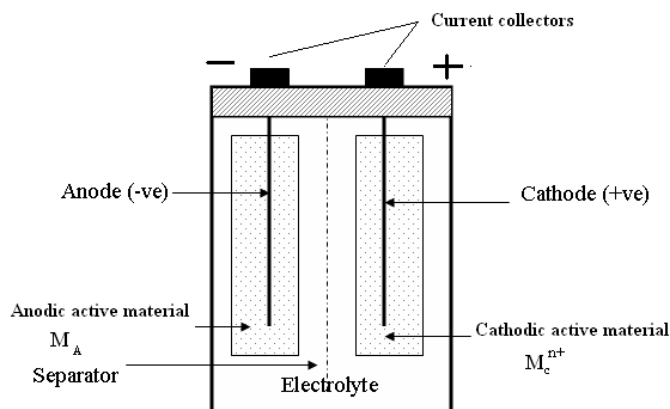
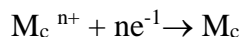


Fig. 1.7

2. Cathode/ Cathodic active materials: The cathode or cathodic active material (M_c^{n+}) is reduced during electrochemical reaction which accepts electron from the external circuit.



To become effective cathode / cathodic material should have:

- (i) Efficiency as an oxidizing agent must be good
- (ii) It must deliver high columbic output (very high reduction potential)
- (iii) It should have good conductivity and stability
- (iv) Fabrication must be easy and low cost.
- (v) stable in contact with electrolyte

3. Electrolyte: It provides medium for transfer of ions inside the battery between anode and cathode. Electrolyte is usually a liquid such as H_2O and other solvent in which acids, alkalis or salts are dissolved. Some batteries may use solid electrolytes, which are ionic conductors used must have good ionic conductivity.

4. Separator: The separator which electronically isolate anodes and cathodes in a battery to prevent internal short circuiting. They are permeable to the electrolyte so as to maintain desired ionic conductivity.

Q - Explain the operation mechanism of a secondary battery.

The operation of a secondary battery involves discharge and recharge reactions.

a. Discharge reactions:

During the discharge (Fig 1.8A) the anode of a battery undergoes oxidation reaction and the electrons produce flow from anode to the cathode through external circuit. At the cathode electrons are accepted and the cathode material gets reduced. The anion and cation moves towards anode and cathode respectively as shown in figure.

The anodic and cathodic and discharge reactions can be represented as follows.

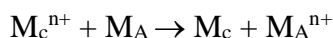
At anode, oxidation reaction takes place by the loss of electrons



At cathode, reduction takes place by gain of electrons



The overall discharge reaction is represented as shown

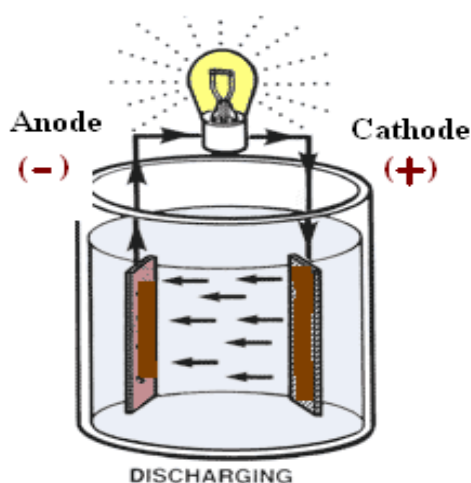
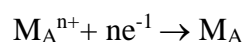


b. Recharge reaction:

During recharge (Fig 1.8B) of a battery the current flow is reverse and therefore oxidation occurs at positive electrode

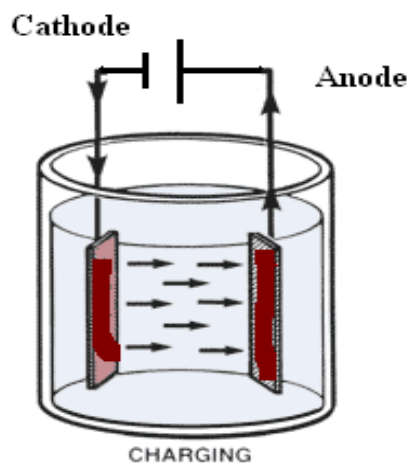
(becomes anode) and reduction occurs at negative electrode (becomes cathode). The recharge reactions are represented as:

At negative electrode (cathode) reduction takes place by gain of electrons.



Chemical Energy
↓
Electrical Energy
Galvanic cell

Fig. 1.8A



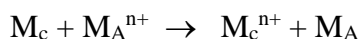
Electrical Energy
↓
Chemical Energy
Electrolytic cell

Fig. 1.8B

At positive electrode (anode), oxidation takes place by loss of electrons.



The overall recharge reaction is represented as shown



Q Discuss the classification of batteries with examples

Classification of batteries: The batteries are mainly classified into two types, they are:

- 1. Primary batteries:** These supply electric current from the active chemicals used. Continuous supply of electric current occurs as long as active materials are present in it. Once the chemicals are exhausted, the battery has to be discarded because it cannot be recharged. Ex: Dry cell ($Zn - MnO_2$) battery, $Li - MnO_2$ battery.
- 2. Secondary batteries or Storage batteries or Accumulators:** These are rechargeable by passing external electric current. These batteries behave like a galvanic cell during discharge and act as an electrolytic cell during recharging. These batteries are also named as reversible batteries. Ex: Lead storage battery, Ni-Cd battery, Ni-MH, Zn-air.
- 3. Reserve Batteries:** The batteries which may be in an inactive state and made ready for use by activating are referred to as reserve batteries. In the reserve batteries, one of the principal components (electrolyte) is isolated from the rest of the components, prior to the application, the battery is activated. When one of the key components of the battery is isolated from the rest of the battery components, a chemical reaction (secondary

reactions) between cell components is prevented and the battery is capable of long term storage period or longer shelf life. Example: Magnesium batteries activated by water, Zn-Ag₂O, Mg-H₂O, Li-V₂O₅

The advantages of reserve batteries are long shelf life, high-performance reliability and a variety of design options.

Applications: These batteries are used to deliver high power for relatively short periods of time, hence these are used in the communication system, missiles, weapon systems, rocket propulsion, etc.

Q-Explain the Battery Characteristics.

The suitability of any battery for a particular application is based on certain characteristic properties. Some of the important characteristics of the battery are

1. Voltage
2. Capacity
3. Energy density
4. Energy efficiency
5. Power density
6. Cycle life
7. Shelf life

1. Voltage: In general, high voltage is desired from any battery. The voltage of any battery depends on the emf of the cells which constitute the battery system. The emf of the cell depends on the free energy in the overall cell reactions as given by the Nernst equation.

$$E_{\text{cell}} = E_{\text{cell}}^0 - 2.303 RT/nF \log 1/Q \text{ -----(i)}$$

$$\text{Or } E_{\text{cell}} = E_{\text{cell}}^0 + 2.303 RT/nF \log Q$$

Where Q = Reaction quotient

From the above equation, emf of the cell or the voltage available from the battery is dependent on the following factors (i) standard electrode potential difference between the cathode and anode, (ii) temperature (iii) the concentration ratio given by reaction quotient (Q) (iv) resistance of the battery

(i) Standard electrode potential difference between the cathode and anode: The emf or voltage of a battery *largely depends* on E_{cell}^0 and it is given by $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$, as the difference in electrode potential increases the emf also increases for given value of Q at a constant temperature. In other words, the emf of a cell is larger if the electrodes used in a cell are further apart in the emf series.

(ii) As temperature increases the battery voltage increases due to an increase in the diffusion of ions

(iii) Reaction quotient 'Q'- As 'Q' value increases the emf of the cell increases marginally. This is because as M_c^{n+} increases 'Q' increases. In other words, the voltage of a battery increases when the concentration of reducible species present in the cell increases.

(iv) Resistance of the battery - high voltage is possible when the cell is with low resistance. Or the

conductivity of the electrolyte should be high.

2. Capacity: The total number of ampere hour (Ah) or watt hour (Wh) that can be withdrawn from a fully charged battery under specific conditions of discharge is termed as capacity of the battery. The capacity depends on the size of the battery and is given by Faraday's equation.

$$C = WnF / M$$

Where W = weight of the active material

C = capacity

M = molar mass of the active material

F = Faraday constant

The amount of active material actually consumed during discharge determines practical capacity of each electrode and hence the capacity of the battery.

The capacity of a battery is evaluated experimentally by plotting the voltage versus time, the area under the curve is the capacity. More area more is the capacity (**Fig. 1.9**)

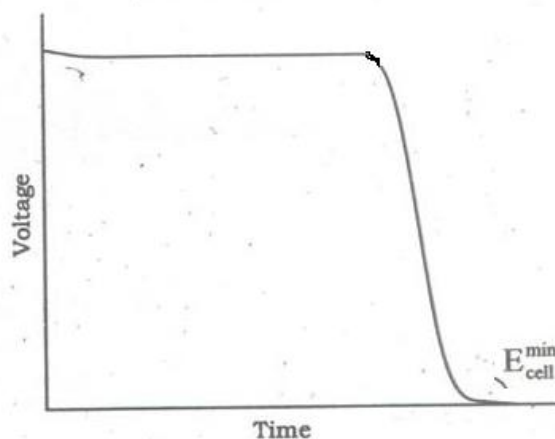


Fig. 1.9

3. Energy density: It is a measure of how much energy can be extracted from a battery per unit weight or volume of a battery. The ratio energy available from a battery to its volume or weight is called as energy density and is represented as

The ratio energy available from a battery to its volume or weight is called as energy density and is represented as

$$\text{Energy density} = i \times t \times E_{\text{average cell}} / W$$

Where t is the time to reach average voltage $E_{\text{average cell}}$

The energy density is measured by determining the capacity and recording average voltage during the discharge and total weight (W) of a battery.

4. Energy efficiency: The energy efficiency in % is given by the equation

$$\% \text{ Energy efficiency} = \frac{\text{Energy released during discharge}}{\text{Energy required during charge}} \times 100$$

Energy efficiency depends on: 1. current efficiency of the electrode process, 2. the potential encountered in both discharge and the charge reactions 3. the battery resistance and 4. rate of recharging and discharging.

5. Power density: The ratio of the power available from a battery to its weight (W / Kg) or its volume (W / V) is called power density. The power density will increase during discharge and while recharge it will decrease.

6. Cycle life: The number of discharge or discharging cycles that be done on a secondary battery before the complete failure of the battery is called cycle life. The discharge per recharge cycle depends on the correct chemical composition, morphology, and proper distribution of active material in the battery.

The common reasons for the failure of a battery are 1. Corrosion of current collectors 2. Shedding of the active material from the plates 3. Shorting between the electrodes due to irregular crystal growth (dendrites) and changes in morphology.

7. Shelf life: The duration of storage under specific conditions at the end of which the battery still retaining the ability to give specific performance is called shelf life or the period of time can be stored without significant deterioration. Shelf life for most of the storage must be good. Good shelf life for a battery is possible when there is no shelf discharge or corrosion on the correct collectors.

All charged batteries will slowly lose their charge over time, even if they are not connected (through the moisture in the air or the slight conductivity of the housing. The rate at which a battery loses power in this way is called the shelf-discharge rate. This rate can be from a few percent per day till 5% to 10% per year.

Q: What are modern batteries? Explain the construction, reactions and applications of Ni-MH₂ battery

Many commercial batteries are not able to meet performance requirement of many applications. The batteries with high energy density, long storage life, maintenance free, low cost, higher safety level with capability to meet the performance requirements of many applications are *called modern batteries*.

The important modern batteries are: (i) Nickel – metal hydride batteries (ii) Lithium – MnO₂ batteries (iii) Metal – air batteries (Ex: Al – air battery).

(i) Ni-MH₂ battery: It is a sealed battery similar to Ni-Cd battery and is assembly used in electrical vehicles and is more environmentally friendly than Ni-Cd battery. Nickel metal hydride (metal hydride is a binary compound formed by the union of hydrogen and other elements) batteries are similar to Ni-Cd battery, but are less toxic and offer higher capacities. Ni-MH₂ batteries have a high self-discharge rate and are relatively expensive to purchase.

In nickel – metal hydride battery, the active material for the cathode is mixture of $\text{Ni}(\text{OH})_2$ and oxy hydroxide (NiOOH). The active material for the anode is a metal hydride such as VH_2 , ZrH_4 and TiH_2 (metal hydride is a binary compound formed by the union of hydrogen and other elements). An aqueous solution of KOH (6 M or 30%) act as the electrolyte and poly propylene is used as insulator separator for anode and cathode (**Fig. 1.10**).

The battery can be represented as $\text{MH}_2 / \text{KOH (6M)} / \text{Ni}(\text{OH})_2, \text{NiO}(\text{OH})$

The metal alloy is capable of undergoing a reversible reaction as the battery is charged or discharged.

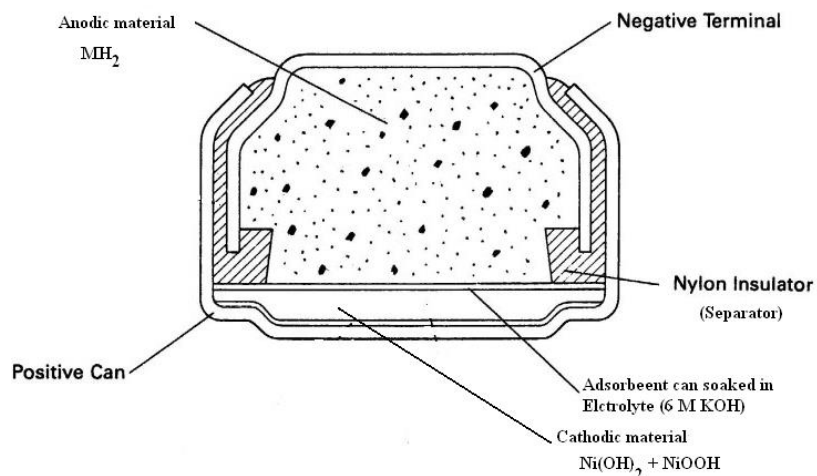
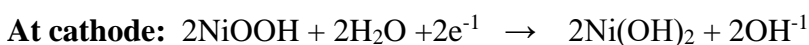
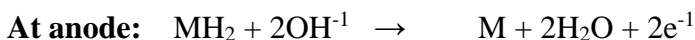


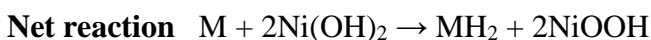
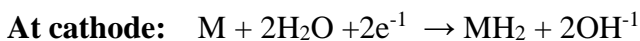
Fig. 1.10

Battery reactions:

Discharge reaction: Electrode reactions during discharge can be represented as shown



Recharge Reaction: Electrode reactions during recharge can be represented as shown



The open circuit potential of the cell ranges from 1.25 to 1.35 V.

Advantages: - 1. High capacity 2. Least environmental problems 3. Sealed construction, no maintenance required 4. Rapid recharge capacity 5. Long cycle life 6. Long shelf life 7. If it is used in automobiles, it can be used for 2 – 3 years with approximately 160000 Km without any maintenance.

Applications: 1. Used in hearing aids. 2. in electric vehicles 2. in consumer electronic devices such as cellular phones, computers, other portable applications.

Q- Why electrolyte used in Lithium batteries should be non-aqueous electrolyte:

Aqueous electrolytes cannot be used in Li-batteries because of high reactivity of Li with H_2O .

Q- What are Lithium battery: Explain construction and working of Li-ion battery

Lithium battery

- Lithium is the lightest of metals and it can float on water.
- The electrochemical properties of lithium are excellent and it is also a highly reactive material.
- These properties give Lithium the potential to achieve very high energy and power densities in high-density battery applications such as automotive and standby power.
- Lithium batteries are primary batteries in which lithium metal (or) lithium compound acts as a Anode. A lithium cell can produce voltage from 1.5 V to about 3 V based on the types of materials used.

There are two types of lithium-based batteries available.

1. Lithium batteries 2. Lithium-ion batteries

- ❖ In lithium primary batteries, a pure lithium metallic element is used as anode. These types of batteries are not rechargeable; hence these are primary batteries.
- ❖ In lithium-ion batteries, lithium compounds are used as anode. These batteries are known as re-chargeable batteries. Therefore, Lithium-ion batteries are considered as better than pure Lithium based batteries.

Lithium-ion battery (Li-ion Battery)

Principle - Li-ion batteries consist of lithium metal oxides LiO (Eg: Lithium Manganese-oxide (LiMn_2O_4) in the positive electrode (Cathode), where lithium ions can be stored, and carbon (LiC_6) in the negative electrode (Anode). The electrolyte used is lithium salts dissolved in organic carbonates. Lithium-ion batteries operate via the transfer of lithium ions in two phases. During charging, lithium ions pass from the positive to the negative electrode, while the opposite occurs during discharging. Li-ion batteries do not require temperature monitoring to ensure effective operation.

Construction

- Positive electrode is made with Lithium Manganese-oxide (LiMn_2O_4) and has a current collector made of thin aluminum foil – cathode.
- Negative electrode made with LiC_6 and has a current collector of thin copper foil–anode
- Separator is a fine porous polymer film.
- An electrolyte made with lithium salt in an organic solvent.

Working:

The most common lithium-ion cells have an anode containing carbon (LiC) and a cathode of LiMn_2O_4 (Fig 1.11). The electrolyte used is lithium salts dissolved in organic carbonates. The manganese and oxygen bond together to form layers of octahedral manganese oxide structures, separated by sheets of lithium. It's important that this structure allows the manganese ions to change their valence states between Mn^{3+} and

Mn^{4+} (gain and lose a negatively-charged electron) when charging and discharging.

Battery Notation: LiC/ lithium salt in an organic solvent/LiMn₂O₄

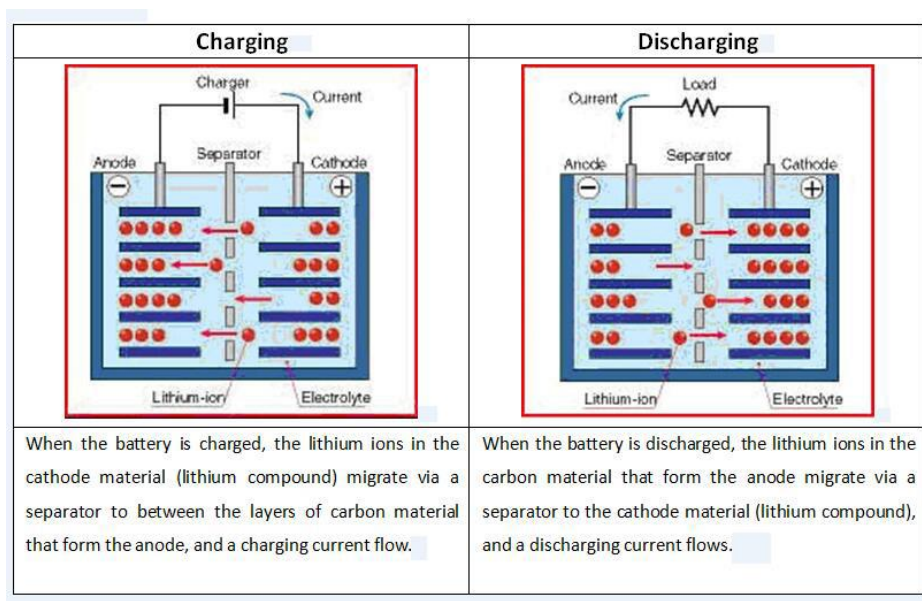
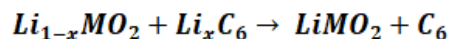
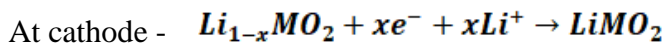
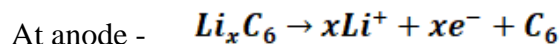


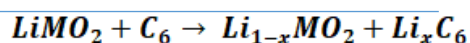
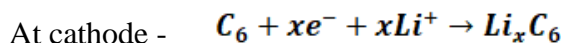
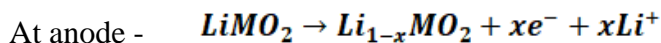
Fig. 1.11

Reactions:

During Discharge: (where M = Mn)



During Charging:



Advantages

- They have high energy density than other rechargeable batteries
- They are less weight
- They produce high voltage out about 4 V as compared with other batteries.
- They have improved safety, i.e., more resistance to overcharge
- No liquid electrolyte means they are immune from leaking.
- Fast charge and discharge rate

Disadvantage

- They are expensive

- They are not available in standard cell types.

Applications

- Lithium-ion batteries (Li-ion) have many desirable characteristics such as high efficiencies, a long cycle life, high energy density, and high power density (Table 2) [4]. These characteristics, along with their capability for fast discharge, have made them nearly ideal for portable electronics applications.
- The Li-ion batteries are used in cameras, calculators
- They are used in cardiac pacemakers and another implantable device
- They are used in telecommunication equipment, instruments, portable radios and TVs, pagers
- They are used to operate laptop computers and mobile phones and aerospace applications.