

MODULE 1

MODULE -1

ELECTROCHEMISTRY & ENERGY STORAGE SYSTEMS

Thermodynamic functions

A part of total energy of a system is converted into work and rest is unavailable. Any kind of work which is converted to useful work is called available energy. Energy which cannot be converted to useful work is called unavailable energy which is represented by energy function. Isothermally available energy of system is known as free energy (Gibbs free energy).

Entropy (S): Entropy is measure of systems thermal energy per unit temperature that is unavailable for doing work. Entropy is a measure of disorder or randomness in a system. Entropy increases with increase in randomness.

Enthalpy (H): The enthalpy of a system is defined as the total amount of heat present in the system and measured as a sum of its internal energy (E) and the product of pressure (P) and volume (V).

$$H = E + PV$$

Free Energy (Gibb's free energy) : It is the difference between total enthalpy of the system and the product of absolute temperature and entropy. It is denoted by symbol G.

$$G = H - TS$$

Where T is constant temperature and S is entropy. TS represent unavailable energy in a system and it cannot be converted into useful work. It is also the maximum amount of energy available to a system to perform useful work

Electrochemistry

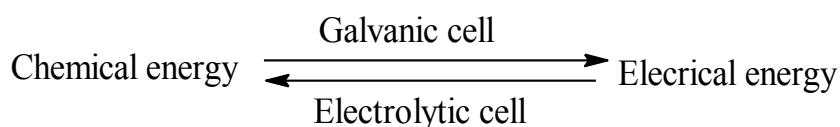
Electrochemistry is the branch of science, which deals with conversion of chemical energy into electrical energy and vice versa. An electric current is nothing but flow of electrons. Electrons flow from one point to another only when there is a potential difference between two points. In chemistry there are reactions which involve transfer of electrons from one species to another. These are redox reactions. *Electrochemistry* also deals with chemical reactions which take place at the interface of an electrode: usually a solid metal or a semiconductor and an ionic conductor, the electrolyte.

Electrochemical cells It is an arrangement of two electrodes in one or two electrolyte which converts chemical energy into electrical energy or electrical energy into chemical energy is called **electrochemical cell**. There are 2 types

1. The one which converts chemical energy into electrical energy is called Galvanic cell or voltaic cell. eg Daniel cell



2. The one which converts electrical energy into chemical energy is called Electrolytic cell.



Cell Potential: The cell potential, E_{cell} , is the measure of the potential difference between two half cells in an electrochemical cell. The cell potential is the difference between the electrode potentials of the anode and cathode which causes current to flow from higher potential to lower potential. E_{cell} depends upon nature of the electrodes, temperature and concentration of the electrolyte solutions. $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{Anode}}$

Single electrode potential: When a metal is in contact with a solution of its own ions, the potential developed at the interface between the metal and the solution is called *Single electrode potential*. It is denoted by E. Potential (E) varies with temperature and concentration of ions.

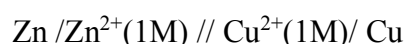
Standard electrode potential: It is the electrode potential developed when the electrode is in contact with a solution of unit molar concentration, at 298K, 1 atmospheric pressure, denoted by E°

CELL NOTATION AND CONVENTIONS: The conventions employed in the representation of electrochemical cell are as follows.

- Anode is written on the left hand side, while cathode is written on the right hand side.
- The electrode on the left (i.e. anode) is written by writing the metal or solid phase first and then the electrolyte. A vertical line or a semicolon separates the two. 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. Egs: Zn/ Zn^{2+} or Zn; ZnSO_4 (1M).

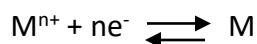
- The cathode of the cell (at which reduction takes place) is written on the right hand side. In this case, the electrolyte is represented first and the metal there after. A vertical line or a semicolon separates the two.
- E.g. $\text{Cu}^{2+} / \text{Cu}$ or $\text{Cu}^{2+}; \text{Cu}$ or Cu^{2+} (1M); Cu or $\text{CuSO}_4; \text{Cu}$
- Two vertical lines separating the two half- cells indicate a salt bridge. Concentration and state of chemical species are expressed as suffixes within the bracket. Thus applying the above considerations to Daniel cell, we may represent it as



Derivation of Nernst equation (Single electrode potential)

A quantitative relationship between electrode potential and concentration of the electrolyte species involved in an expression is known as Nernst equation.

Consider the following reversible electrode reaction



The decrease in free energy ($-\Delta G$) for any reversible process is equal to the maximum amount of work (W_{max}) that can be obtained from a chemical reaction.

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

In case of an electrochemical cell, W_{max} = Electrical energy generated by the cell.

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

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

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

Energy available per coulomb is the emf of the cell E . When the emf is maximum, the work derived from the cell is also maximum. The maximum is the cell potential E_{cell} . Thus W_{max} for an electrochemical cell is given by the equation

$$W_{\text{max}} = n \times F \times E \dots\dots\dots (2)$$

From equation (1) and (2)

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

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

$$-\Delta G^\circ = nFE^\circ \quad \dots\dots\dots (4)$$

Where E° is the standard electrode reduction potential.

The decrease in the free energy, $-\Delta G$, accompanying the process is given by the well-known thermodynamic equation (Vant'Hoff's equation).

$-\Delta G = -\Delta G^\circ - RT \ln K$, Where K is the ratio of the activities of the products to that of reactants. Substituting the values of K , we have

$$-\Delta G = -\Delta G^\circ - RT \ln \frac{[M]}{[M^{n+}]}$$

from eqn (3) &(4) for ΔG and ΔG°

$$\text{i.e., } nFE = nFE^\circ - RT \ln \frac{[M]}{[M^{n+}]}$$

Dividing throughout by nF

$$\text{i.e., } E = E^\circ - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$\text{i.e., } E = E^\circ + \frac{RT}{nF} \ln [M^{n+}] \quad \text{Since, } [M] = 1$$

$$\text{i.e., } E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}] \quad \text{————— (5) is the Nernst equation.}$$

Where E = electrode potential

T = temperature in Kelvin unit 298k

F = Faraday 96,500 C

n = number of electrons involved

E° = standard electrode potential

R = gas constant 8.314J/K/mo

CEC

Substituting the values for R and F at 298K Nernst equation reduces to

$$E = E^{\circ} + \frac{0.0591}{n} \log[M^{n+}] \quad \text{at 298K} \quad \text{--- (6)}$$

Note:

Applying Nernst equation for a cell reaction, $aA + bB \rightleftharpoons cC + dD$

$$\text{Or, } E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{n} \log \frac{[A]^a [B]^b}{[C]^c [D]^d} \quad \text{at 298K} \quad \text{--- (7)}$$

OR

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{2.303RT}{nF} \log \frac{[M^{n+}] \text{ at Cathode}}{[M^{n+}] \text{ at Anode}}$$

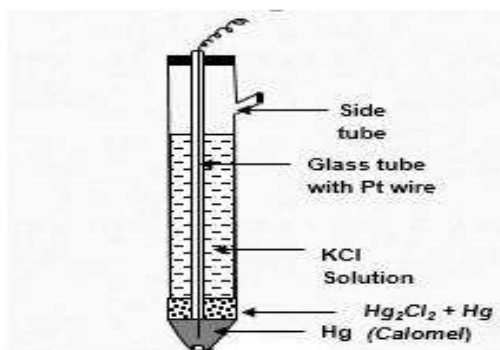
Reference electrodes:

Reference electrodes are the electrodes with reference to which electrode potential of any other electrode can be measured. E.g. Standard Hydrogen electrode (SHE) is a primary reference electrode. Its electrode potential is taken zero at all temperatures. Calomel electrode is a Secondary reference electrode (SRE).

CALOMEL ELECTRODE (SRE)

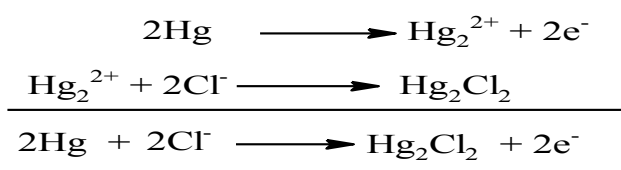
Construction:

It is a metal-metal salt ion electrode. Calomel electrode consists of a glass tube in which liquid mercury is placed at the bottom. It is covered by a paste of mercurous chloride (calomel) with mercury. A solution of KCl is introduced above the paste, through the side tube. A platinum wire sealed into a glass tube is dipped into mercury and used to provide the external electrical contact. Depending on the concentration of KCl used, the potential varies. The Calomel electrode is represented as $\text{Hg} / \text{Hg}_2\text{Cl}_2 (\text{s}) / \text{Cl}^-$

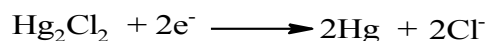


Working:

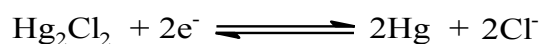
Calomel electrode can act as anode or cathode depending on the nature of other electrode of the cell. If it acts as anode, the reaction is



If it acts as cathode, the reaction is



The net reversible reaction is,



Electrode potential, $E = E^\circ - \frac{2.303RT}{nF} \log [\text{Cl}^-]^2$

i.e., $E = E^\circ - \frac{2.303RT}{2F} 2 \log [\text{Cl}^-]$

i.e., $E = E^\circ - \frac{2.303RT}{F} \log [\text{Cl}^-]$

i.e., $E = E^\circ - 0.0591 \log [\text{Cl}^-] \text{ at } 298\text{K}$

At 298K, for 0.1N KCl, $E = 0.334V$ and saturated KCl, $E = 0.2422V$

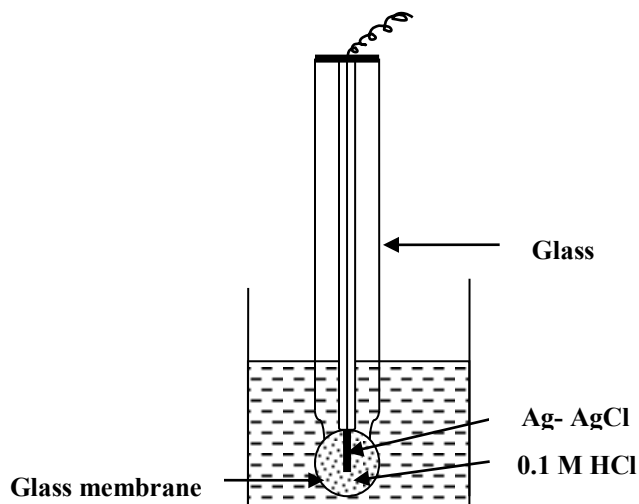
Uses:

- It is used as reference electrode in pH measurement.
- It is used as a secondary reference electrode for measuring single electrode potential.

Ion-selective electrode: *Ion selective electrodes are the electrodes that can interact more selectively with a particular ion in a mixture of ions neglecting the other ions. The potential developed by an ion-selective electrode depends only on the concentration of species or ions of interest. For e.g. Glass electrode is H^+ ion selective.*

Construction & working of glass electrode (Ion selective electrode)

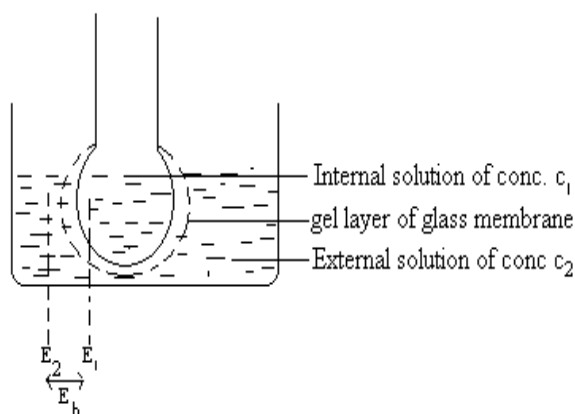
A glass electrode consists of a long glass tube with a thin walled bulb at one end. The Glass is made of silicate glass containing SiO_2 , Na_2O , CaO of high electrical conductance & low melting point. The bulb contains 0.1M HCl & Silver - silver chloride electrode (Internal reference electrode) is immersed into the solution & connected by a platinum wire for external contact. The electrode is represented as $Ag / AgCl_{(s)} / 0.1M HCl / glass$.



If a thin walled glass bulb containing an acid is dipped in a solution(analyte), a potential is developed across the glass membrane. The potential difference E_b at the interface is referred to boundary potential, given by, $E_b = E_2 - E_1$

E_1 = Potential of inner membrane

E_2 = Potential of outer membrane



$$E_b = \frac{2.303RT}{nF} \log \frac{C_2}{C_1} \quad \text{Or} \quad \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Since the concentration C_1 of solution inside the glass bulb is constant

$$E_b = 0.0591 \log C_2 + L,$$

Where $L = -0.0591 \log C_1$, Here $n=1$ for H^+ ion at 298K

Since $C_2 = [H^+]$, the equation is represented as

$$E_b = L + 0.0591 \log [H^+]$$

$$E_b = L - 0.0591 \text{pH} \quad , \quad \text{Since } \text{pH} = -\log [H^+]$$

The Potential of glass electrode (E_G) is sum of three potentials

- Boundary potential (E_b)
- Potential of Ag/AgCl electrode
- Asymmetry potential (E_{asy})

Asymmetric potential is the potential that exists across the glass membrane even when the concentration of external solution is equal to internal solution ($C_1 = C_2$). This potential arises due to some difference in thickness of the inner and outer surface or curvature of the glass membrane. It varies with time and from one electrode to other electrode.

Therefore, Glass Electrode potential $E_G = E_b + E_{Ag/AgCl} + E_{asy}$

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

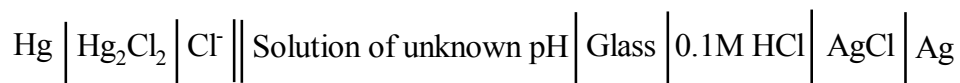
$$E_G = L^1 - 0.0591 \text{pH} \quad \text{where } L^1 = L + E_{Ag/AgCl} + E_{asy}$$

The above equation for potential of glass electrode is used to measure the pH of a solution.

DETERMINATION OF A p^H OF A SOLUTION USING A GLASS ELECTRODE

To determine the pH of a given solution, glass electrode is immersed in the unknown solution whose pH of which is to be determined. It is combined with a reference electrode like calomel electrode.

The cell is represented as



The emf of the cell formed is determined Potentiometrically by

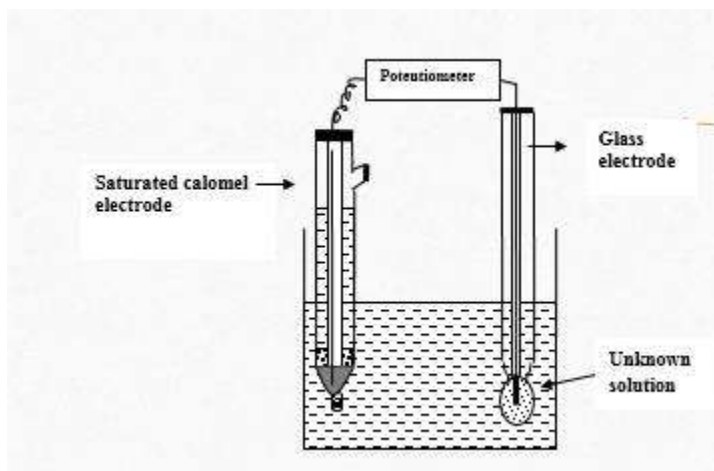
$$E_{\text{cell}} = E_{\text{C}} - E_{\text{A}} \quad \text{ie} \quad E_{\text{G}} - E_{\text{Cal}}$$

$$= L^1 - 0.0591\text{pH} - E_{\text{cal}}$$

$$\text{Or, } \text{pH} = \frac{L^1 - E_{\text{Cal}} - E_{\text{cell}}}{0.0591}$$

$$\text{Or, } \text{pH} = \frac{k - E_{\text{cell}}}{0.0591}$$

$$\text{where, } k = L^1 - E_{\text{Cal}}$$



Advantages: -

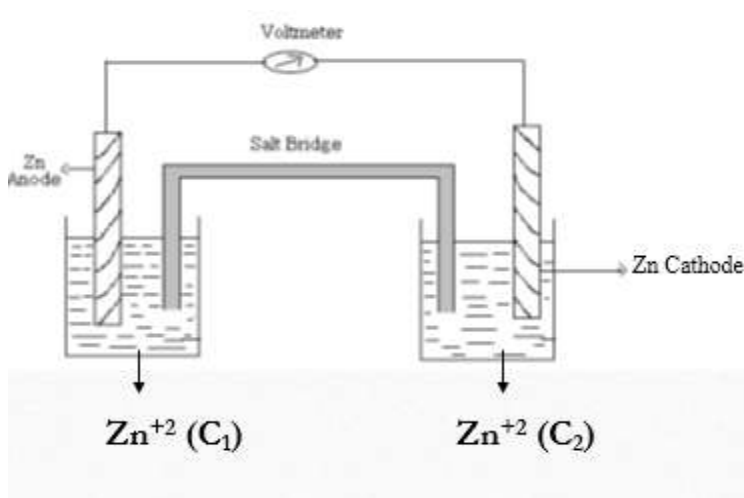
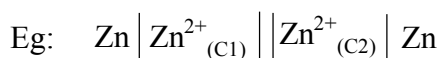
- It can be used in oxidizing and reducing environments.
- By using special glass electrodes pH range 1–14 can be measured.
- Electrode does not get poisoned.

Limitations: -

- It does not function properly in alcohol and some organic solvents.
- The bulb is too fragile, so the glass electrode has to be used with utmost care.
- Due to high resistance of glass it is necessary to use special & sensitive potentiometers.
- Frequent calibrations needed with special type of buffer solution.

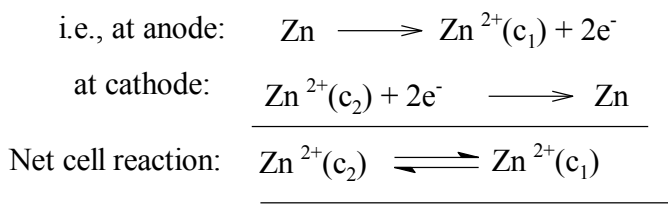
Galvanic cells are classified into three types namely primary, secondary and concentration cells.

Electrolyte Concentration cells: *Galvanic cells in which both the anode and the cathode are made up of the same element in contact with the solutions of the same electrolyte, emf arises due to difference in concentration are referred to as **concentration cells**.* It is a type of galvanic cell, consists of two identical electrodes in contact with its salt solution of different concentration. The electrode with lesser concentration of metal ions behaves as anode and with higher concentration of metal ions acts as cathode.



Where C_1 and C_2 are the concentrations of Zn^{2+} ions in two half cells. By convention, left hand electrode is taken as anode and right hand electrode is taken as cathode.

Therefore, electrode reactions are,



Therefore, cell potential, $E_{\text{cell}} = E_{\text{C}} - E_{\text{A}}$

$$\begin{aligned}
 E_{\text{cell}} &= E^{\circ} + \frac{0.0591}{n} \log C_2 - \left[E^{\circ} + \frac{0.0591}{n} \log C_1 \right] \\
 \text{i.e., } E_{\text{cell}} &= \frac{0.0591}{n} \log \frac{C_2}{C_1}, \text{ at } 25^{\circ}\text{C}
 \end{aligned}$$

Where, E° is the standard electrode potential.

Note:

When $C_2 = C_1$, the concentration cell does not generate electrical energy. E_{cell} is positive if $C_2 > C_1$. Higher the ratio of C_2 / C_1 , greater is the cell potential.

Energy storage systems:

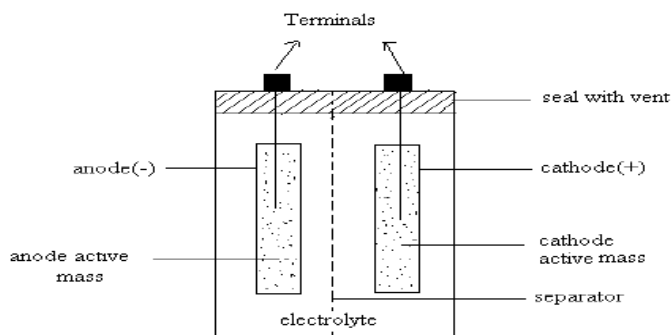
Introduction

Battery is a device consisting of two or more galvanic cells connected in series or parallel or both, which convert chemical energy into electrical energy through electrochemical redox reaction.

Batteries are used in calculators, watches, computers, car engines, standby power supplies, emergency lightning in hospitals, electroplating industrial tractions and military and space applications. The size of the batteries ranges from a fraction of a cubic centimeter to several cubic decimeters.

Basic concepts

The basic electrochemical unit in a battery is a galvanic cell. The components of such cell are shown in the fig.



Principal components of battery

The principal components of a battery are as follows.

1. *The anode or negative electrode* – it gives electrons to the external circuit by undergoing oxidation during electrochemical reaction.
2. *The cathode or positive electrode* – it accepts electrons from the external circuit and reduction of the active species occurs.
3. *The electrolyte* – an ionic conductor. The electrolyte is commonly a solution of an acid, alkali or salt having high ionic conductivity
4. *The separator* – It separates the anode and cathode compartments in a battery to prevent internal short-circuit. It allows transport of ions from anode to cathode and vice versa. Eg. Cellulose, Polypropylene.

Classification of batteries

i) Primary battery or primary cells: In primary the cell reaction is not reversible. These are not rechargeable and once discharged have no further electrical use and battery becomes dead. Eg. Dry Cell.

ii) Secondary batteries: Secondary batteries are rechargeable. The cell reactions are reversible and these are also known as reversible batteries. After discharge secondary batteries can be recharged electrically to their original condition by passing current through them in the direction opposite to that discharge current. Eg: Lead acid battery, Ni-MH battery

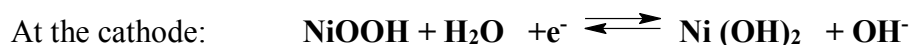
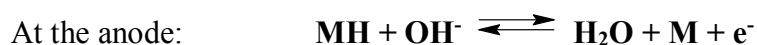
iii) Reserve batteries: In these batteries, a key component is separated from the rest of the battery prior to activation. Usually the electrolyte is the component that is isolated. The

activation involves adding electrolyte and hence the battery has long term storage capacity. In this condition, chemical deterioration or self- discharge is essentially eliminated. Eg: Li-V₂O₅.

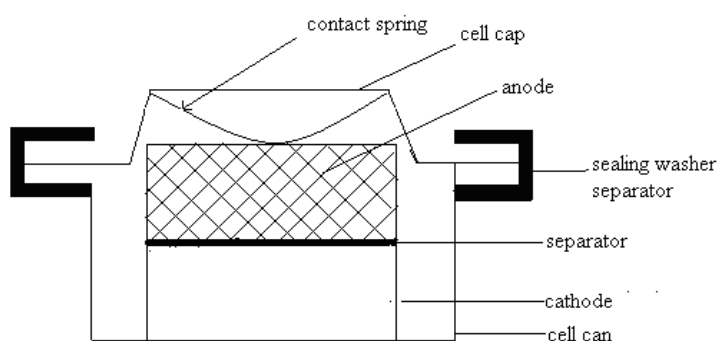
Nickel-metal hydride batteries (Ni-MH Battery)

The active material for the anode is a metal hydride such as VH₂, ZrH₂ and TiH₂ with a hydrogen storage metal alloy such as TiNi. The active material for the cathode is nickel oxyhydroxide (NiOOH). Electrodes are made up of porous nickel foil on which the active materials are coated. The electrolyte is an aqueous solution of KOH and polypropylene is used as the separator. The anode and the cathode are stacked alternately in a stainless steel container and connected in series to get the desired voltage.

Electrode reactions during discharging and charging are given below.



Uses: ▶ Used in electric vehicles, computers and cellular phones etc.



Li-ion Battery

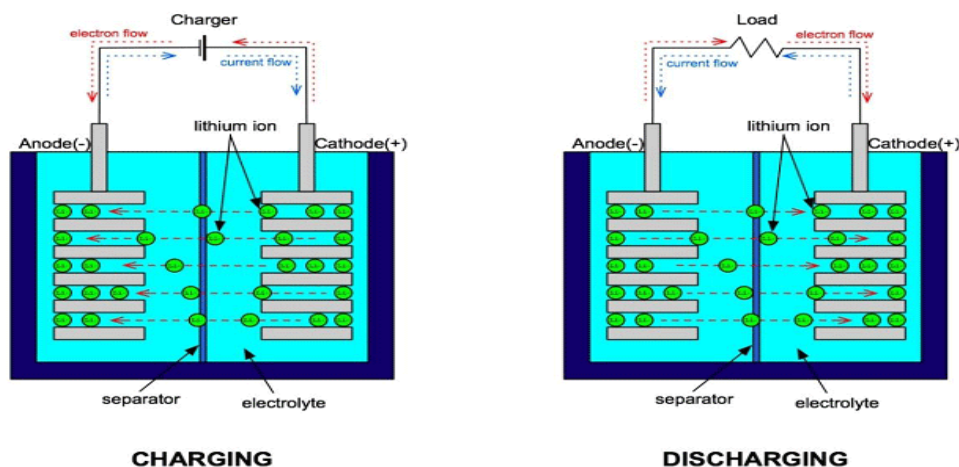
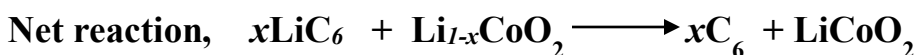
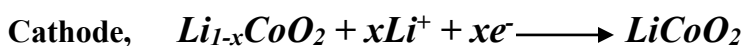
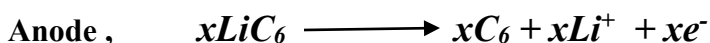
Anode - Lithium intercalated in graphite as anode

Cathode – Lithium Cobalt Oxide (Li_{1-x}CoO₂)

Electrolyte – Lithium salt in organic electrolyte such as LiPF₆ dissolved in binary organic solvent mixture such as ethylene carbonate – dimethyl carbonate.

The Separator – Polypropylene.

The electrolyte provides a conductive medium for lithium ions to move between the electrodes. During discharge, Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal lattice of the cathode. Here lithium ions become embedded in the porous electrode material in a process known as intercalation. During Charging lithium in cathode electrode material is ionized and moves from cathode to anode and gets inserted into the anode. The transition metal cobalt (Co), in $\text{Li}_{1-x}\text{CoO}_2$ oxidizes from Co^{3+} to Co^{4+} during charge, and reduced from Co^{4+} to Co^{3+} during discharge.



APPLICATIONS:

- These are used in cell phones, laptops, electrical vehicles and aerospace applications.

1. *What are ion selective electrodes? Discuss construction and working of glass electrode.*
2. *What are reference electrodes? Explain construction and working of calomel electrode.*
3. *What is single electrode potential? Derive Nernst equation for single electrode potential of electrode.*
4. *What are concentration cells? Derive expression for EMF of concentration cell?*
5. *Derive an expression of determination of pH of the solution using glass electrode*
6. *Explain primary, secondary and reserve batteries with example.*
7. *Explain construction and working of Ni-MH battery.*
8. *Describe construction, working and uses of Li - ion battery.*

PSK