

## **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**

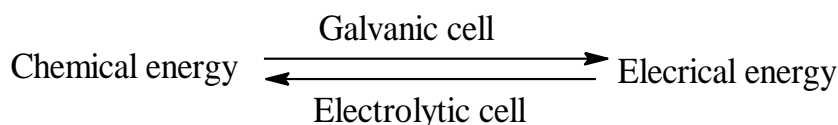
*Electrochemistry* is the branch of science, which deals with conversion of chemical energy into electrical energy and vice versa. An electric current is nothing but flow of electrons. Electrons flow from one point to another only when there is a potential difference between two points. In chemistry 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.



**EMF (Electromotive Force):**  $E_{cell}$ , is the measure of the potential difference between two half cells in an electrochemical cell. It 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.  $E_{cell} = E_{cathode} - E_{Anode}$

**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.

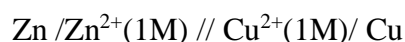
**Standard electrode potential:** It is the electrode potential developed when the electrode is in contact with a solution of unit molar concentration, at 298K, 1 atmospheric pressure, denoted by  $E^\circ$

**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/  $\text{Zn}^{2+}$  or Zn;  $\text{ZnSO}_4$  (1M).

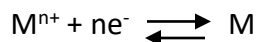
- The cathode of the cell (at which reduction takes place) is written on the right-hand side. In this case, the electrolyte is represented first and the metal there after. A vertical line or a semicolon separates the two.
- E.g.,  $\text{Cu}^{2+} / \text{Cu}$  or  $\text{Cu}^{2+}; \text{Cu}$  or  $\text{Cu}^{2+}$  (1M);  $\text{Cu}$  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 ( $W_{\text{max}}$ ) that can be obtained from a chemical reaction.

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

In case of an electrochemical cell,  $W_{\text{max}}$  = 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  $E_{\text{cell}}$ . Thus  $W_{\text{max}}$  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  $\Delta G^\circ$  is given by the equation,

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

Where  $E^\circ$  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  $\Delta G$  and  $\Delta G^\circ$

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

Dividing throughout by  $nF$

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

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

$$\text{i.e., } E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}]$$

— (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

$E^\circ$  = standard electrode potential

$R$  = gas constant 8.314J/K/mol

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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

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

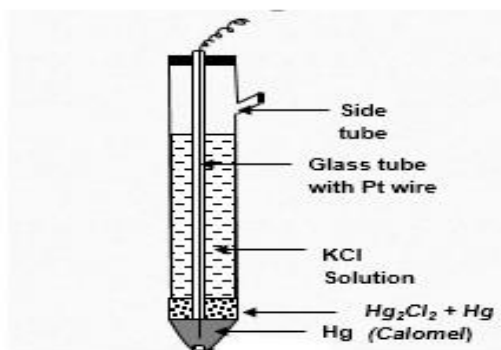
**Reference electrodes:**

*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)**

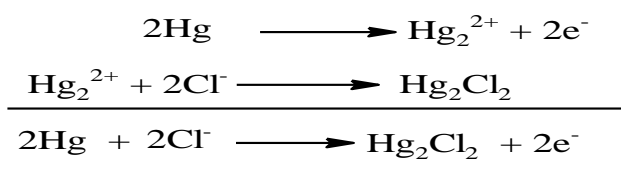
**Construction:**

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 **Hg / Hg<sub>2</sub>Cl<sub>2</sub> (s) / Cl<sup>-</sup>**

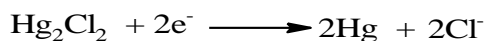


Working:

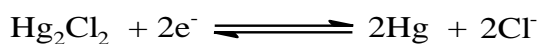
Calomel electrode can act as anode or cathode depending on the nature of other electrode of the cell. If it acts as anode, the reaction is



If it acts as cathode, the reaction is



The net reversible reaction is,



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

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

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

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

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

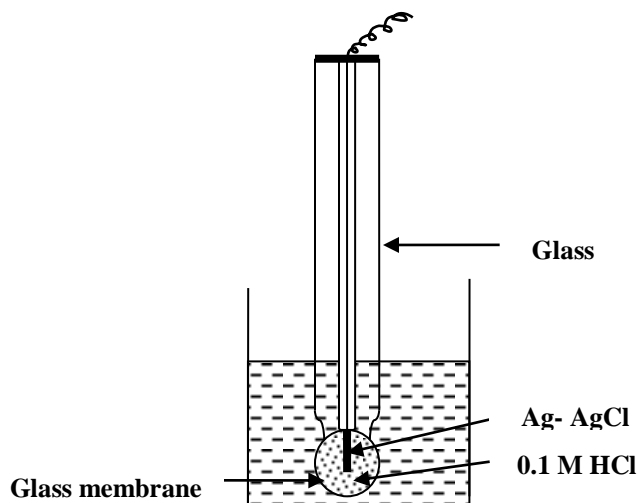
Uses:

- 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)**

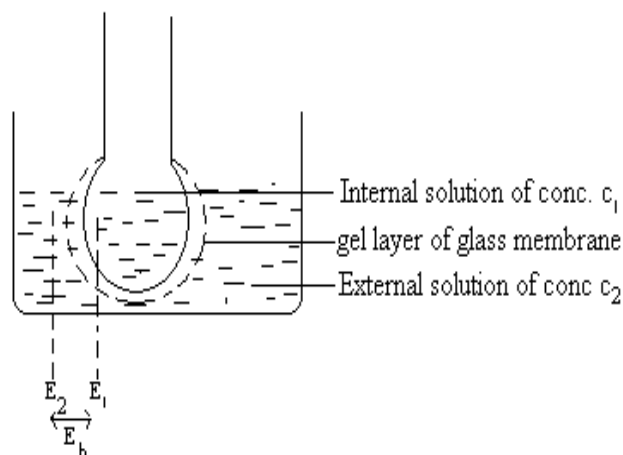
A glass electrode consists of a long glass tube with a thin walled bulb at one end. The Glass is made of silicate glass containing  $SiO_2$ ,  $Na_2O$ ,  $CaO$  of high electrical conductance & low melting point. The bulb contains 0.1M HCl & Silver - silver chloride electrode (Internal reference electrode)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



$$E_b = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

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 another 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.



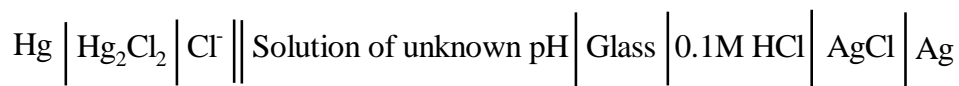
**Applications of Glass Electrode: -**

- It is used in pH measurements.
- Analysis of food and cosmetics.

**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

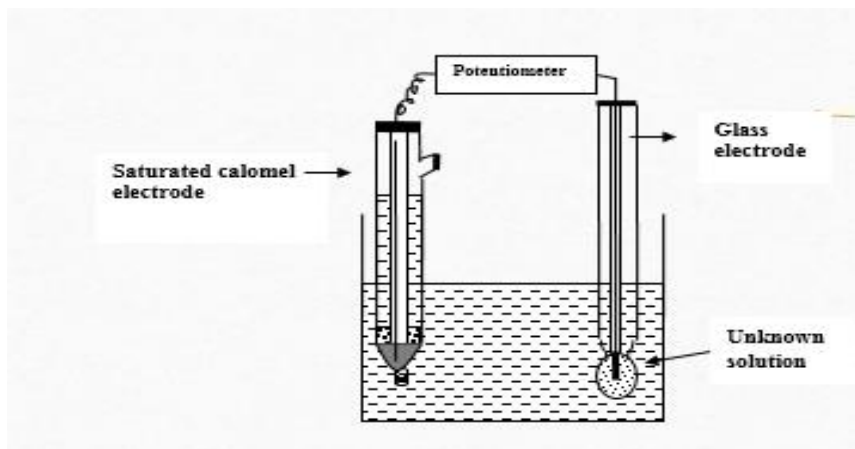
$$E_{\text{cell}} = E_{\text{C}} - E_{\text{A}} \quad \text{ie} \quad E_{\text{G}} - E_{\text{Cal}}$$

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

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

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

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



## **QUESTION BANK**

- 1. What is 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. Drive an expression of determination of pH of the solution using glass electrode*

## **Energy storage systems:**

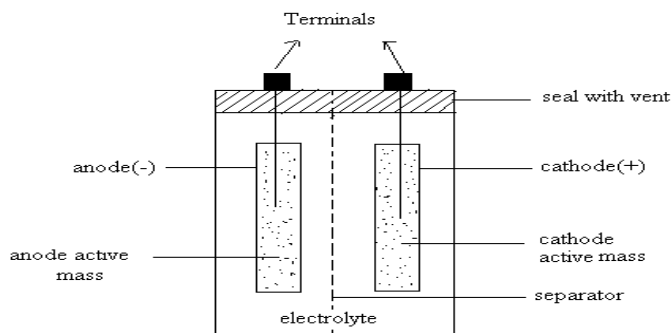
### **Introduction**

*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 lighting 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.

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-V<sub>2</sub>O<sub>5</sub>.

### Li-ion Battery

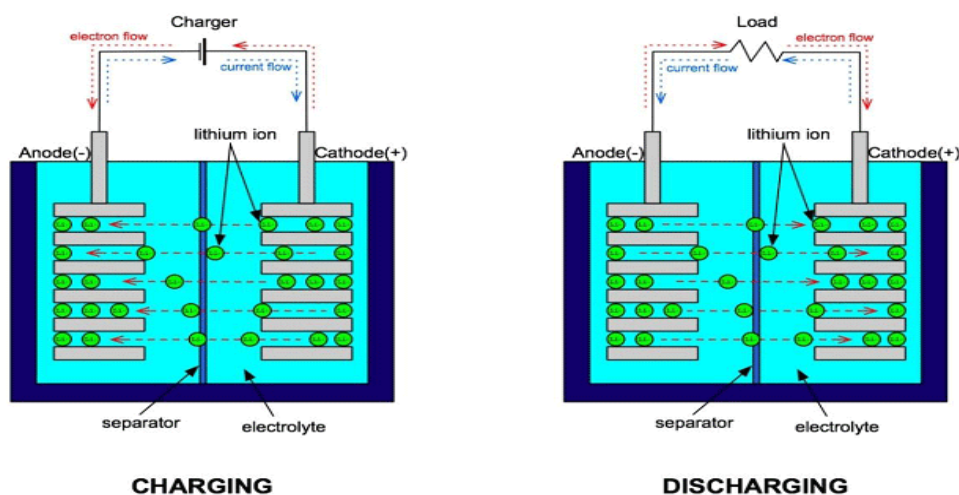
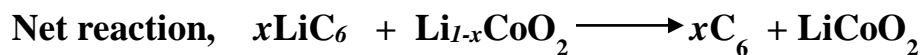
**Anode** - Lithium intercalated in graphite having thin copper foil as current collector

**Cathode** – Lithium Cobalt Oxide (Li<sub>1-x</sub>CoO<sub>2</sub>) layer having aluminum foil as current collector.

**Electrolyte** – Lithium salt in organic electrolyte such as LiPF<sub>6</sub> dissolved in binary organic solvent mixture such as ethylene carbonate – dimethyl carbonate.

**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 Li<sub>1-x</sub>CoO<sub>2</sub> oxidizes from Co<sup>3+</sup> to Co<sup>4+</sup> during charge and reduced from Co<sup>4+</sup> to Co<sup>3+</sup> during discharge.



### APPLICATIONS:

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

### ADVANTAGES :

- Lithium-ion batteries contain relatively low levels of toxic heavy metals found in other types of batteries, such as lead-acid and nickel-cadmium (Ni -Cd) batteries.
- Lightweight and compact.
- High energy density
- Low maintenance
- Low self-discharge rate
- Lithium-Ion batteries are fairly maintenance free.
- Lithium-ion batteries are much more efficient at low temperatures.
- Fast & Efficient Charging

### **RECYCLING OF Li-ion BATTERY:**

Lithium-ion (Li-ion) batteries are used in many products such as small and large appliances, electric vehicles and electrical energy storage systems. If not properly managed at the end of their useful life, they can cause harm to human health or the environment. Li-ion batteries, should therefore be recycled at certified battery electronics recyclers that accept batteries rather than being discarded in the trash or put in municipal recycling bins. The materials recovered from batteries could be used to make new batteries, lowering manufacturing costs. Currently, those materials account for more than half of a battery's cost. In addition to economic benefits, recycling will reduce the quantity of material going into landfills. Cobalt, nickel, manganese, and other metals found in batteries can readily leak from the casing of batteries and contaminate soil and groundwater, threatening ecosystems and human health. There are three methods to recycle the batteries such as pyrometallurgy, hydrometallurgy and direct recycling method.

Direct recycling involves first complete discharging the battery and next dismantling or shredding the cells by physical processes which recover metals without causing chemical changes in structure. Aluminium and copper foils can be recovered in this process. Leaching can be done with hydrochloric or sulfuric acid to dissolve the ions out of a solid like the cathode, producing a mixture of ionic species in solution. These can be recovered by precipitation. In this method metals like Copper, Cobalt Nickel Iron and lithium are recovered. The metals can be reused to prepare new cathodic material.

The method is very cost effective and involves low temperature energy process.

### **Na-ion Battery - Introduction**

The sodium-ion battery (NIB) is a type of rechargeable battery analogous to the lithium-ion battery but uses sodium ions ( $\text{Na}^+$ ) as the charge carriers. Its working principle and cell construction are almost identical with those of the commercially widespread lithium-ion battery types, but sodium compounds are used instead of lithium compounds. Sodium-ion battery cells consist of a cathode based on a sodium containing material, an anode (not necessarily a sodium-based material) and a liquid electrolyte containing dissociated sodium salts in polar protic or aprotic solvents. During charging, sodium ions are extracted from the cathode and inserted into the anode while the electrons travel through the external circuit; during discharging, the reverse process occurs. where the sodium ions are extracted from the anode and re-inserted in the cathode with the electrons travelling through the external circuit doing useful work.

The largest advantage of sodium-ion batteries is the high natural abundance of sodium. Compared to lithium-ion batteries, current sodium-ion batteries have somewhat higher cost, better safety characteristics. Challenges to adoption include low energy density and a limited number of charge-discharge cycles. Sodium-ion batteries offer better performance and can

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operate at a wider temperature range. They work much more efficiently in cold environments, compared to lithium-ion batteries.

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## **QUESTION BANK**

- 1.Explain primary, secondary and reserve batteries with example.*
- 2.Describe construction, working and uses of Li - ion battery.*
- 3. Write a note on recycling of Lithium- ion batteries.*

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