ELECTROCHEMISTRY

BATTERIES

BATTERIES (PART - I):-

A battery is an arrangement of electrochemical cells used as an energy source. The basis of an electrochemical cell is an oxidation-reduction reaction.

A useful battery should also fulfil the following requirements

1) It should be light and compact so that it can be easily transported.

2) It should have reasonably long life both when it is being used and when it is not used.

3) The voltage of the battery should not vary appreciably during its use.

TYPES OF COMMERCIAL CELLS

There are mainly two types of commercial cells:

- 1) Primary batteries or cells
- 2) Secondary batteries or cells

Primary batteries or cells

In these cells, the electrode reactions cannot be reversed by an external electric energy source. In these cells, reactions occur only once and after use they become dead. Therefore, they are not chargeable.

Some common examples are dry cell, mercury cell.

Secondary batteries or cells

In the secondary cells, the reactions can be reversed by an external electric energy source. Therefore, these cells can be recharged by passing electric current and used again and again. These are also called storage cells.

Examples of secondary cells are lead storage battery and nickel-cadmium storage cell.

BATTERIES (PART - II): -

1) Primary Cells

1) Dry cells



These are used in torches, toys, flash lights, calculators, tape recorders and many other devices.

Construction of Dry Cell

- a) It consists of a zinc cylinder. This is filled with a moist paste of NH₄Cl and little of ZnCl₂.
- b) The zinc cylinder acts as a anode. The cathode is a graphite (carbon) rod.
- c) The carbon rod is surrounded by a black paste of manganese dioxide (MnO₂) and carbon powder.
- d) During use, the zinc case gets consumed and, in the end, it will develop holes which are responsible for leakages. The leak proof cells or dry cells have an iron or steel sheet covering the zinc.

Working of Dry Cell

Zinc loses electrons and Zn^{2+} ions dissolve in the electrolyte. The electrons pass around the external circuit and are taken up at cathode. This causes discharge of NH_{4^+} ions from the electrolyte.

Chemistry

The reactions taking place at the electrodes are:

Anode

 $Zn \longrightarrow Zn^{2+} + 2e^{-}$

Cathode

 $NH_{4^{+}}(aq) + MnO_{2}(s) + 2e^{-} - - -> MnO(OH) + NH_{3}$

 $Zn + 2NH_{4^+}(aq) + 2MnO_2(s) - -->Zn^{2_+} + 2MnO(OH) + 2NH_3$

In the cathode reaction, manganese is reduced from +4 Oxidation state to +3 oxidation state. Ammonia is not liberated as a gas but it Combines with some of the Zn^{2+} ions produced from the anode to form Complexion having the formula $[Zn(NH_3)_2]^{2+}$

It gives voltage of approximately 1.2 to 1.5 V. This dry cell does not have an indefinite life because NH₄Cl being acidic corrodes the zinc Container even when not in use.

2) Mercury cell

A new type of cell which has found use in small electrical circuits such as hearing aids, Watches and cameras is the mercury cell.

It consists of a zinc anode and a mercury (II) oxide cathode. The electrolyte is a paste of KOH and ZnO.

The reactions occurring in the cell are as follows:

Anode:

 $Zn(Hg) + 20H^{-} \rightarrow ZnO(s) + H_2O + 2e^{-}$

Cathode:

 $HgO(s) + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

 $Zn + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

(Amalgam)

It has the advantage that its potential remains almost constant throughout its life. The voltage of mercury cell is approximately 1.35 V.

2) Secondary Cells

There are some cells which can be recharged. These are called accumulators or storage cells. These can be recharged and used again and again as a source of electric current.

Lead Storage Cell



Each battery consists of a number of voltaic cells connected in series. Three to six such cells are generally combined to get 6-to-12-volt battery.

- a) The anode is a grid of lead packed with finely divided spongy lead and the cathode is a grid of lead packed with PbO₂.
- b) The electrolyte is aqueous solution of sulphuric acid.
- c) At the anode, lead is oxidised to Pb^{2+} ions and insoluble $PbSO_4$, is formed. At the cathode PbO_2 , is reduced to Pb^{2+} ions and $PbSO_4$ is formed.

The following reactions take place in the lead storage cell:

At anode

The lead loses two electrons and is oxidised to Pb²⁺ ions.

 $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^{-}$

Chemistry

During the working of the cell $PbSO_4$ is formed at each electrode and sulphuric acid is used up. As a result, the concentration of H_2SO4 decreases and the density of the solution also decreases.

Recharging the Battery

The cell can be charged by passing electric current of a suitable voltage in the opposite direction. The electrode reaction gets reversed. As a result, the flow of electrons gets reversed and lead is deposited on anode and PbO_2 on the cathode. The density of sulphuric acid also increases.

The reaction may be Written as

 $2PbSO_4(s)+2H_2O \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4$

When it is used to start the engine of the automobile, it acts as a voltaic cell and produces electric energy. During recharging, it acts as an electrolytic cell.

Nickel Cadmium Storage Cell

This is also a rechargeable cell. It has longer life than the lead storage cell but more expensive than lead storage battery. However, it has some advantages because it is smaller and lighter. It can be used in portable and cordless appliances.

1) It consists of a cadmium anode and a metal grid containing NiO_2 acting as a cathode.

2) The electrolyte in this cell is KOH.

The reactions taking place during discharge and charge are:

Anode:

 $Cd(s)+20H^{-} \Leftrightarrow CdO(s)+H_2O(l)+2e^{-}$

Cathode:

 $2Ni(OH_3)(s) + 2e^- \Leftrightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

 $Cd(s) + 2Ni(OH_3)(s) \Leftrightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

The reaction products generally remain sticking to the electrodes and can be reconverted by recharging the cell. The charging process is similar to lead storage battery.

It produces a potential of about 1.4 V.