CHAPTER-3

ELECTROCHEMICAL POWER SOURCES

Electrochemistry: Galvanic cell- Electrochemical cell representation - EMF series and its significance. Batteries: Terminology- Lead-acid accumulator- Nickel-Cadmium batteries, Lithium batteries: Li/$SOCl_2$ cell - Li/I_2 cell- Lithium ion batteries. Fuel cells: Hydrogen-oxygen fuel cell, Solid oxide fuel cell (SOFC)

3.1 INTRODUCTION

Batteries and fuel cells are energy storage and energy generating devices capable of converting the stored chemical energy to electric energy. These devices utilize controlled redox chemical reactions while other reactions like corrosion, polarization, adsorption are kinetically suppressed. The selection of a desired redox reaction involves careful choice of chemical components along with morphology and structure. In recent years, these areas have gained paramount importance in powering various technological devices like emergency lighting, motor ignition, cell phones, computer, i-pods, tablet, cam-corder and so on. Apart from electronic devices, there has been a surge of interest to develop vehicles that are either fully electrically driven or partially powered as in hybrid cars in order to focus into greener and less energy-intensive transportation. The dominance of electric and hybrid cars have been witnessed in recent Olympics held at London in 2012, where 240 electric and hybrid cars of BMW mini E series were used as a part of the fleet. The present generation of hybrid cars uses a combination of internal combustion engine and nickel-metal hydride battery as in Toyota Prius E and lithium-ion batteries in Fiat 500E series to be commissioned in 2013. The electric, hybrid cars and trucks are also used widely in land and water surveillance for military operations. The future hybrid cars have been focused on the combination of lithium batteries and fuel cells.

Fuel cells provide an uninterrupted power supply by utilizing a continuous supply of fuel. The fuel cell came into existence in the middle of the 19th century mainly for space exploration. The resurgence of fuel cell systems and materials in the last decade led to the growth and development of energy efficient systems for transportation and high energy density power sources for portable electronic devices.

3.2 BATTERY

A battery is a device which converts chemical energy of the active materials directly to electrical energy by means of electrochemical oxidation-reduction reaction commonly referred as redox reactions. The spontaneous redox reactions proceed with negative free energy change resulting the battery to perform work. These reactions occur at specified sites in the battery, at the anode and cathode. The electrons generated during the red-ox reaction flows through the external circuit between the anode and cathode. The electroactive species and the products formed in the reactions are usually solids. A battery consists of large number of electrochemical cells which are connected either in series or parallel connections in order to achieve desired voltage and current.

3.3 ELECTROCHEMICAL CELL

An electrochemical cell is a basic unit of battery in which a red-ox reaction is utilized to provide a direct source of electric energy. The components of an electrochemical cell consists of an assembly of electrodes (anode and cathode), electrolyte, separator and container.

Anode or negative electrode: It is an oxidation electrode or fuel electrode which releases the electrons to the external circuit.

Cathode or positive electrode: It is a reducing electrode or oxidant electrode which accepts electrons from the external circuit.

Electrolyte: It is an ionic conductor which acts a medium for transfer of charge as ions inside the cell between the anode and cathode. Solvents like water, aqueous solution of acids and alkalis, dissolved salts and organic solvents are widely employed to impart ionic conductivity.

Separator: It is a non-conductive material used to prevent short circuiting of the electrodes.

Container: It is a case to hold the components of the battery/cell, made up of corrosion resistant materials like polypropylene for acid batteries and stainless steel for alkaline batteries.

3.3.1. Galvanic Cell:

It consists of a zinc rod partially immersed in 1M zinc sulphate ($ZnSO_4$) solution and a copper rod partially immersed in 1M copper sulphate ($CuSO_4$) solution. The two solutions are connected by a salt bridge, which is an inverted U-tube filled with saturated KCl or NH_4NO_3 in agar-agar gel as shown in Fig 3.1. The salt bridge provides electrical contact between two compartments. It helps to maintain electrical neutrality by allowing the migration of ions. The electrodes are connected where electron flows from zinc to copper as the zinc is oxidised and copper is reduced.

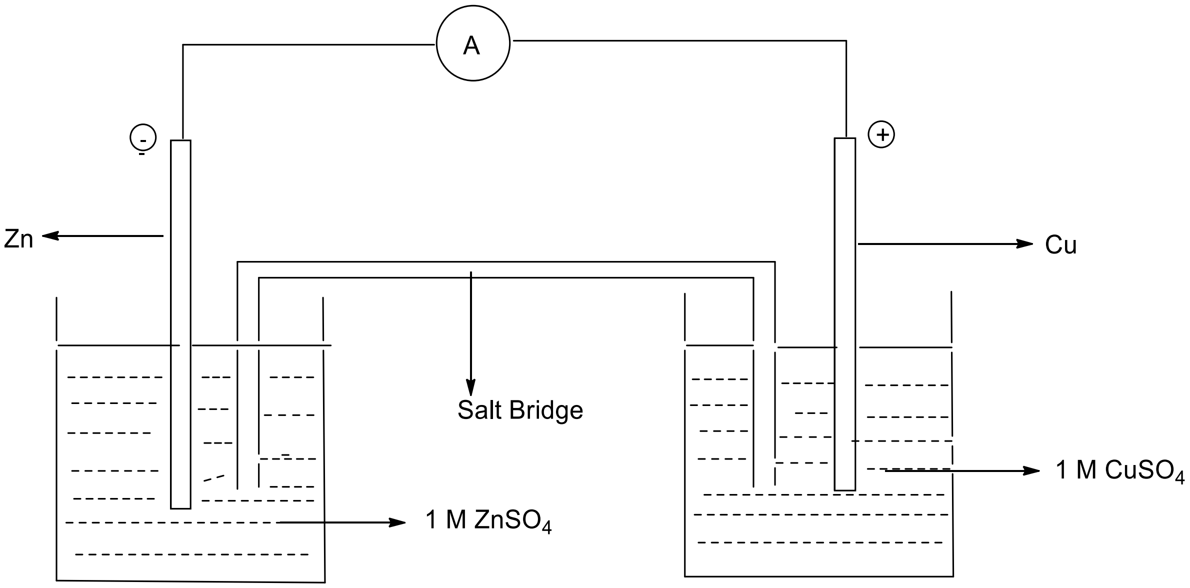


Fig 3.1 Galvanic Cell

3.3.2. Daniel Cell:

It consists of zinc rod dipped in $ZnSO_4$ and copper rod in $CuSO_4$ solution. The two solutions are separated by a porous pot. The two solution seep through the pot and contact with each other. It acts as a salt bridge. The electrode reactions in Daniel cell are as follows,

At anode (-ive electrode): Oxidation of zinc takes place

$$Zn_{(s)} \longrightarrow Zn^{2+} + 2e^-$$

At cathode (+ive electrode): Reduction of copper ions occurs,

$$Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$$

The net cell reaction is,

$$Zn_{(s)} + Cu^{2+} \longrightarrow Zn^{2+} + Cu_{(s)}.$$

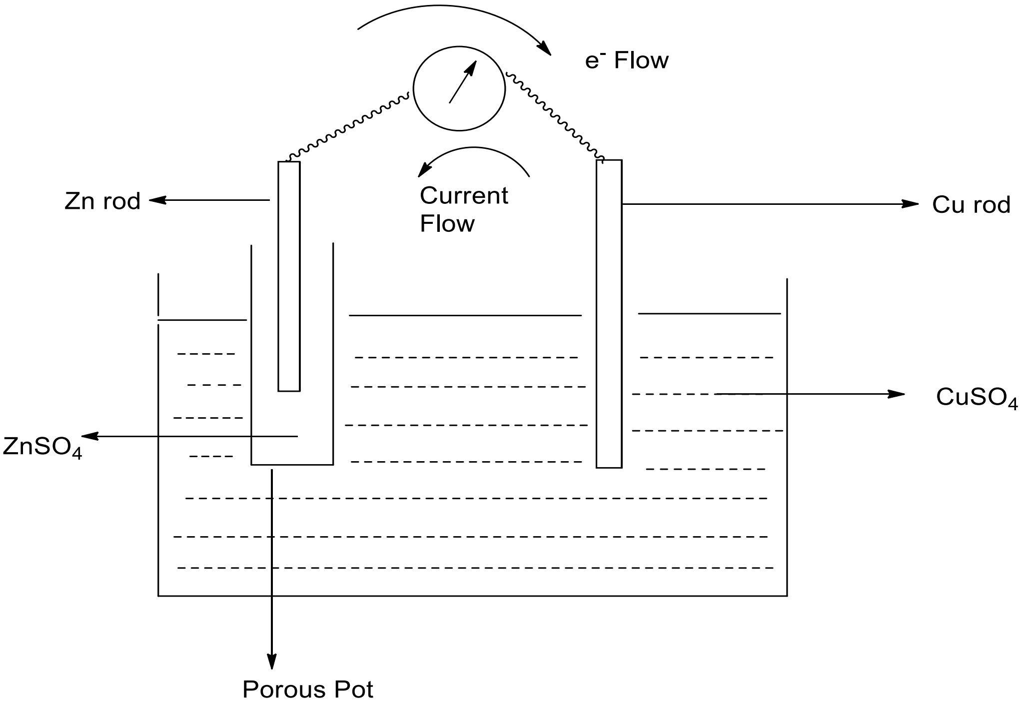


Fig 3.2 Daniel Cell

3.3 REPRESENTATION OF AN ELECTROCHEMICAL CELL

An electrochemical cell consists of two half cell namely anode and cathode separated by a salt bridge.

1. The anode half cell is written on the left side of the salt bridge while the cathode half cell is written on the right side of the salt bridge.

Anode || Cathode
↓ ↓ ↓
(LHS) (salt bridge) (RHS)

2. The anode half cell is represented by writing the metal first and the electrolyte. The two are separated either by a vertical line (/) or by a semicolon(;).

$$M/M^{n+} \text{ or } M;M^{n+}$$

3. The cathodic half cell is represented by writing the electrolyte first and then the metal. The two are separated either by a vertical line or by a semicolon.

$$M^{n+}/M \text{ or } M^{n+};M.$$

4. The electrolyte may be represented either by the whole formula or by its ionic species. The concentration of the electrolyte is represented in comma brackets ().
5. The salt bridge is indicated by two vertical lines (II) separating the half cell.

Thus, a Galvanic cell is represented by,

1. $Zn/ZnSO_4$ (1M) $\|$ $CuSO_4$ (1M)/ Cu
2. Zn/Zn^{2+}(1M) $\|$ Cu^{2+} (1M)/ Cu
3. $Zn;Zn^{2+}$(1M) $\|$ Cu^{2+} (1M);/ Cu
4. . $Zn;ZnSO_4$ (1M) $\|$ $CuSO_4$ (1M); Cu

3.4 ELECTROCHEMICAL SERIES

The arrangement of all the metals in the increasing order of their standard electrode potential is called an electrochemical series.

S.No	**Metal ion**	**Potential in volts**
1.	$Li^+ + e^- \rightarrow Li$	–3.05
2.	$K^+ + e^- \rightarrow K$	–2.93
3.	$Ca^{2+} + 2e^- \rightarrow Ca$	–2.90
4.	$Na^+ + e \rightarrow Na$	–2.71
5.	$Mg^{2+} + 2e \rightarrow Mg$	–2.37

6.	$Al^{3+} + 3e^{-} \rightarrow Al$	–1.66
7.	$Mn^{2+} + 2e^{-} \rightarrow Mn$	–1.19
8.	$Zn^{2+} + 2e^{-} \rightarrow Zn$	–0.76
9.	$Cr^{3+} + 2e^{-} \rightarrow Cr$	–0.74
10.	$Fe^{2+} + 2e^{-} \rightarrow Fe$	–0.44
11.	$Ni + 2e^{-} \rightarrow Ni$	–0.23
12.	$Sn^{2+} + 2e^{-} \rightarrow Sn$	–0.14
13.	$Pb^{2+} + 2e \rightarrow Pb$	–0.13
14.	$Fe^{3+} + 3e \rightarrow Ca$	–0.04
15.	$H^{+} + e^{-} \rightarrow \frac{1}{2} H$	0.00
16.	$Cu^{2+} + 2e^{-} \rightarrow Cu$	+0.34
17.	$Ag^{+} + e^{-} \rightarrow Ag$	+0.80
18.	$Pt^{4+} + 4e^{-} \rightarrow Pt$	+0.86
19.	$Au^{+} + e^{-} \rightarrow Au$	+1.69
20.	$1/2F_2 + e^{-} \rightarrow F^{-}$	+2.87

3.4.1 SIGNIFICANCE OF ELECTROCHEMICAL SERIES

1. Reactivity of metals

The activity of the metal depends on its tendency to lose electrons i.e., tendency to form cation. This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active. The chemical reactivity of metals decreases from top to bottom in the series. The metal higher in the series is more active than the metal lower in the series. For example,

(a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(b) Metals like Fe, Pb, Sn, Ni, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.

(c) Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water

2. Electropositive character of metals

The electropositive character also depends on the tendency to lose electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups

(**a) Strongly electropositive metals:** Metals having standard reduction potential near about – 2.0 volt or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.

(b) Moderately electropositive metals: Metals having values of reduction potentials between 0.0 and about – 2.0 volt are moderately electropositive Al, Zn, Fe, Ni, Co, etc., belong to this group.

(c) Weakly electropositive: The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. Cu, Hg, Ag, etc., belong to this group.

3. Displacement tendency of metals

To predict whether a given metal will displace another, from its salt solution: A metal higher in the series will displace the metal from its solution which is lower in the series, i.e., The metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential. A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

4. Calculation of standard emf of the cell

The standard emf of a cell can be calculated using the formula

$E^0_{cell} = E^0_{cathode} – E^0_{anode}$

5. Predicting the feasibility of the reaction

If the E^0_{cell} value is positive then the reaction is feasible and if it is negative the reaction is not feasible.

3.5 BATTERY TERMINOLOGY

Load: External device or component through which battery is discharged

Discharging: It is an electrochemical process which delivers current to an external circuit by redox reactions is known as discharging. When a cell is connected to an external load, electrons will flow from the anode to the cathode through the external load. The circuit is complete by the flow of anions and cations to the anode and cathode respectively. The discharging reaction in a battery is depicted in Fig 3.3

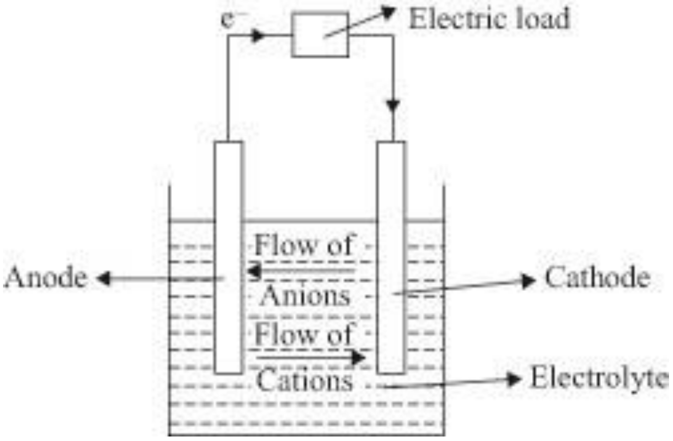


Fig 3.3 Discharging reactions in a battery

The discharge characteristics of a battery at constant load is illustrated in Fig 3.4. A flat discharge curve is highly desirable for a battery. In an ideal condition the cell potential remains steady with time until the capacity is fully exhausted and falls to a lower level as in lithium cells. In most other batteries, the voltage decreases gently with time as in alkaline cells or in two o rmore stages as in Lechlance cells.

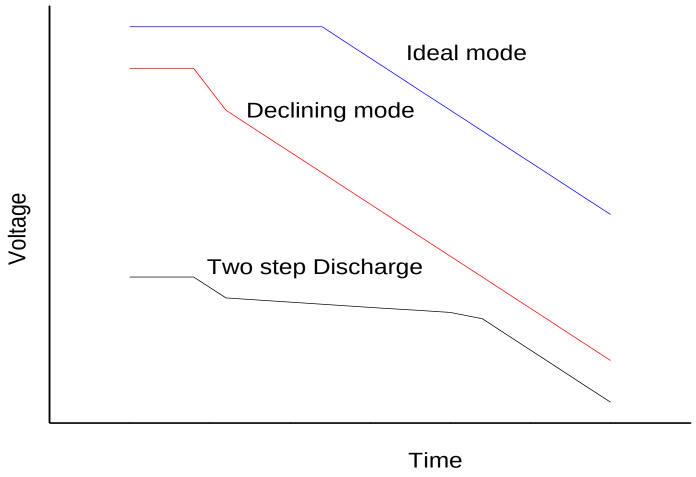


Fig. 3.4 Change of Voltage with time in different cells.

Charging: It is an electrolytic process by which constant current is supplied to the battery in order to regenerate electro-active materials is known as charging. During charging reactions, the positive electrode is connected to the positive terminal of the external DC power supply and the negative electrode to the negative terminal of the DC power supply. The flow of the current and ions are reversed which are shown in Fig 3.5

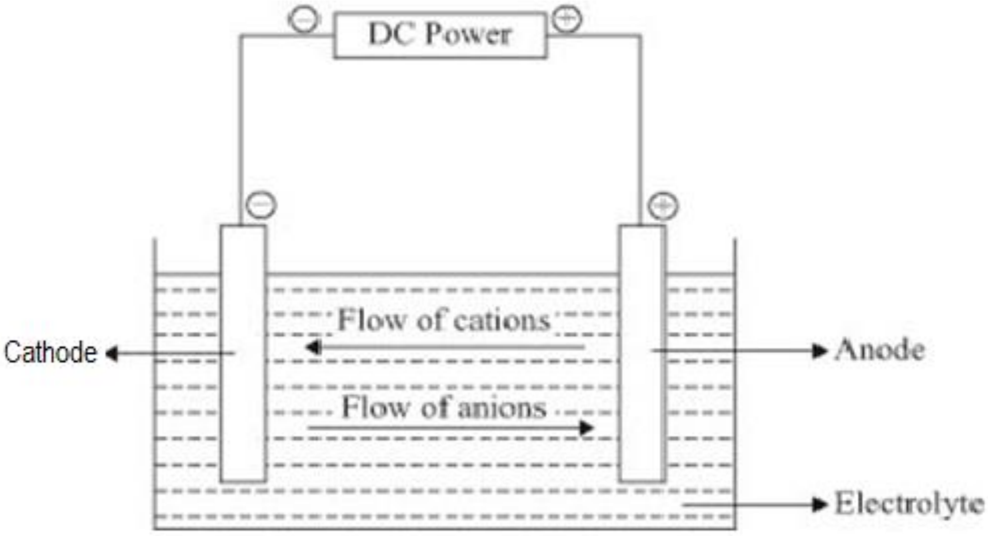


Fig 3.5 Charging reactions in a battery

Capacity: The amount of constant current (I) supplied by a battery for a definite time (t) period is known as capacity. It is expressed in ampere-hour, Ah. The capacity Q is given by

$$Q = I \text{ (in A)} \times t \text{ (in h)}$$

Cycle life: The number of times a battery can be charged and discharged before a failure occurs in the electro-active materials to generate current is known as cycle life.

Power (P): The product of cell voltage (V) and the constant current (I) is known as power and is expressed in watt,W.

$$P = V \times I.$$

Power Density (PD) : The amount of power produced by unit kilogram weight of a battery is known as power density. It is expressed in watt/Kg, W/Kg.

Energy Density (ED): The amount of energy (power) obtained for an hour by unit kilogram weight of a battery (w) is known as energy density. It is expressed in watt hour/kg, Wh/kg.

$$E = (P \times t) / w$$

Open circuit voltage (OCV): The cell voltage of a fully charged battery is known as open circuit voltage.

Closed circuit voltage (CCV): The cell voltage of a completely discharged battery, is known as closed circuit voltage.

Internal Resistance: It is the resistance offered by the components of a battery. It also refers to impedance in the electrical circuit. The internal resistance is defined as the ratio of difference between OCV and CCV to the load. The cell voltage versus current yields a straight line and the slope of the line gives internal resistance of the battery.

Shelf life: The life time of a battery is known as shelf life. A battery must possess a long shelf life and does not discharge on storage.

3.5 CLASSIFICATION OF BATTERIES

Batteries are classified depending on their capability of charging as

1. **Primary Battery:** These are non-rechargeable cells in which the cell reaction are not reversible and electro-active materials consumed in the discharging reactions cannot be regenerated by passing electric current . Eg. Leclanche cell, Zn- HgO cell.
2. **Secondary Battery:** These are chargeable batteries in which the cell reaction are reversed and electro-active materials consumed during discharging reactions are regenerated by passing electric current. Eg. Lead-Acid Battery, Nickel- Cadmium Battery.
3. **Reserve Battery /Fuel cell:** These are primary cell in which electro-active materials are supplied continuously either in gaseous or liquid or solid form to produce electric current is known as fuel cell. Eg. Hydrogen - Oxygen fuel cell.

3.6 DIFFERENT TYPES OF BATTERY ARRANGEMENT

In a battery, individual electrochemical cells are connected either in series or parallel to obtain the desired voltage and current. In a series arrangement, the positive electrode of each cell is connected to the negative electrode of the adjacent cell as shown in Fig 3.6. The total emf or voltage of the battery is the sum of the separate voltages. The total current drawn from the series of cells is same as the current drawn from individual cell. In a battery, if six cells each with an emf of 2 volts are connected in series will provide an output of 12 volt.

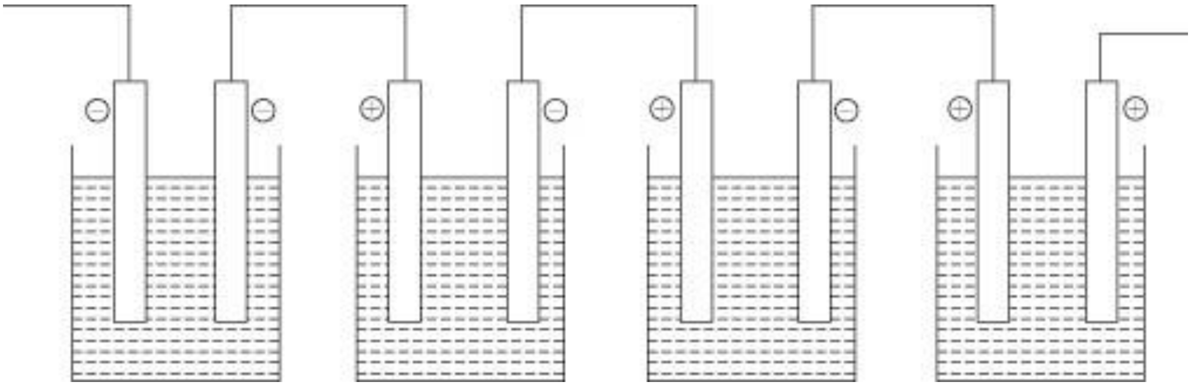


Fig 3.6 Series arrangement of cells in a battery

In a parallel arrangement, the positive electrodes of the individual cells are connected together and so as the negative electrodes as represented in the Fig 3.7. The battery voltage is same as that of individual cell and the total current is the sum of the current supplied by the individual cells.

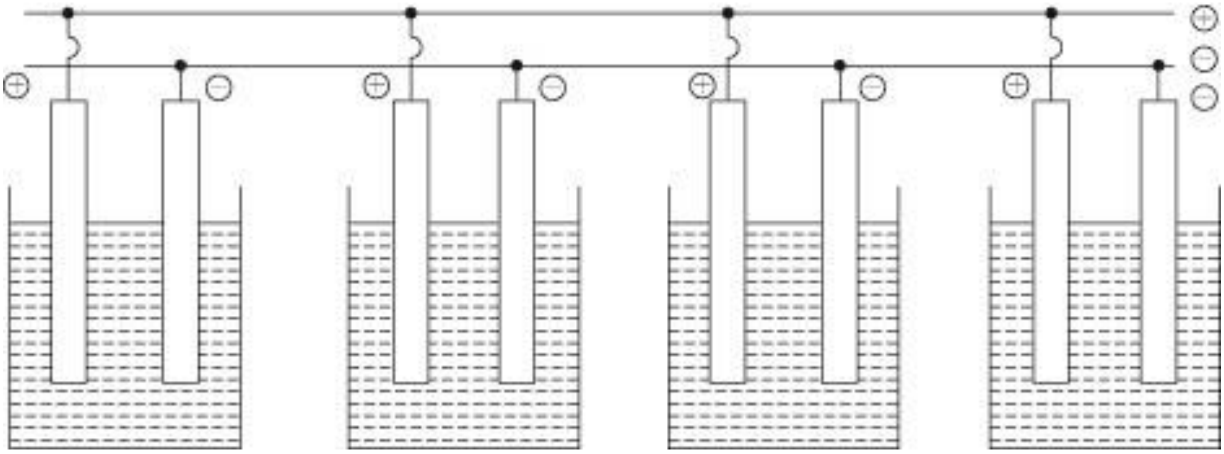


Fig 3.7 Parallel arrangement of cells in a battery

3.7 SECONDARY BATTERIES

3.7.1 Lead-Acid Battery:

Lead acid battery was the first practical storage battery invented by Gaston Plante in France, 1859. It is employed for the SLI (Starting-Lighting-Ignition) system for automobiles and farm vehicles. The name refers to the chemical nature of the electrode (lead) and the electrolyte (acid) in which the electrodes are immersed. A lead-acid storage battery is shown in the Fig 3.8 The anode in lead-acid battery is lead-antimony (Pb-Sb) grid coated with spongy lead while the cathode is a paste of lead dioxide,PbO2 pressed into a grid of Pb-Sb. A number of lead plates and lead dioxide plates are fitted alternatively and are connected in parallel. The plates are separated from each other by insulators like wood or rubber or glass fibre or a polymer. The cells are immersed in 21.4% dil. sulphuric acid (H_2SO_4), corresponds to a specific gravity of1.26 to 1.28 at 25°C. The entire combination of cells, separator and the electrolyte are held in polypropylene container. The emf of a lead acid cell is close to 2.1V in a fully charged state. The energy density for lead acid battery is roughly 44Wh/kg. In the discharged state, the emf of the cell is 1.78V. The battery is represented as,

$$Pb, PbSO_4 / H_2SO_4\ (21.4\%) / PbSO_4, PbO_2$$

Discharging Reactions:

When the storage cell operates as a voltaic cell (i.e for delivering electric current) it is said to be discharging. The lead electrode loses two electrons to form lead ions (Pb^{2+}) which combine with sulphate ions (SO_4^{2-}) to form lead sulphate ($PbSO_4$) at the anode. The electrons released from the anode flows to the cathode where lead dioxide (PbO_2) undergoes reduction from +4 to +2 oxidation state. The lead ions combines with SO_4^{2-} ions to from $PbSO_4$.

At anode, oxidation of lead occurs as follows,

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

The lead ions reacts with SO_4^{2-} ions to form $PbSO_4$

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

The overall anodic reaction is,

$$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$$

At cathode, PbO_2 where the Pb^{+4} oxidation state gets reduced to Pb^{+2} ions in the presence of acid.

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

The lead ions reacts with SO_4^{2-} ions to form $PbSO_4$

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

The overall cathodic reaction is,

$$PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H^+{}_{(aq)} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$

The net cell reaction during discharge is the combination of overall anodic and cathodic reaction which is,

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4\,(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

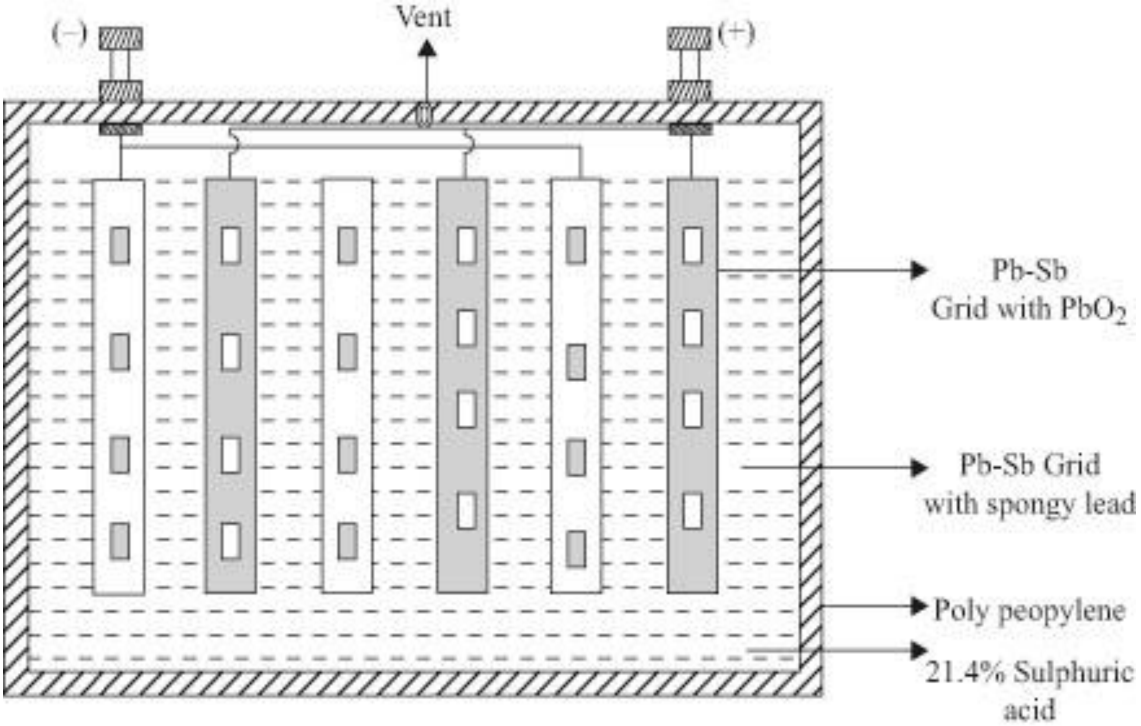


Fig 3.8 Lead acid storage battery

During the discharge, both the electrodes are converted to $PbSO_4$ and the specific gravity of acid decreases due to the formation of water. The emf of each cell is 2.0 volts at 21.4% H_2SO_4 at 25°C. Lead cell used in automobiles, is a combination of 6 such cells in series to form a 12 V battery.

Charging reactions:

When both anode and cathode electrodes become covered with $PbSO_4$, the cell stops to function as a voltaic cell. In order to recharge the battery, an external current (> 2V) is supplied through battery by connecting the positive plate electrode to positive terminal of the external battery and negative plate electrode to negative terminal of the external battery. At this stage, the system behaves as an electrolytic cell.

At anode/positive plate, $Pb^{+2}SO_4$ oxidizes to $Pb^{+4}O_2$ with the liberation of electrons. The reaction is

$$PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H^+{}_{(aq)} + 2e^-$$

At cathode/negative plate, $Pb^{+2}SO_4$ accepts the electrons and reduces to Pb^0. The reaction is,

$$PbSO_{4(s)} + 2e^- \longrightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$$

The net cell reaction during charging is

$$2PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4\,(aq)}$$

During the process, the electrodes are restored to the original state (i.e Pb at the negative plate and PbO_2 at the positive plate of the battery). At the same time the concentration of acid increases.

Note:

During the operation of Lead acid battery in automobiles two aspects are encountered

1. The degree of discharging reaction can be checked by measuring the density of the fluid (electrolyte) with a hydrometer. During the discharging reactions, the density of the electrolyte decreases since it is consumed and forms water. The density of fully charged battery is > $1.2 g/cm^3$.
2. An apparent break down in the battery is experienced in cold climatic conditions. It has been found by experiments that there is a decrease in voltage for every drop in temperature. As temperature decreases there is an increase in the viscosity of the electrolyte. Increased viscosity together with decrease in temperature leads to decrease in the power output of the battery. Hence the battery becomes apparently “dead” at cold temperatures and is warmed to room temperature for its normal functioning.

Applications:

1. Lead–acid batteries are used in automobile SLI batteries.
2. Lead acid batteries are used in large backup power supplies for telephone and computer centers, hospitals, grid energy storage, and off-grid household electric power systems.

3. Large lead–acid batteries are used to power the electric motors in diesel-electric submarines and are used on nuclear submarines as well.

3.7.2 Nickel Cadmium Battery:

The nickel–cadmium battery (NiCd battery or NiCad battery) is a type of rechargeable battery using nickel oxyhydroxide and metallic cadmium as electrodes. The acronym *Ni-Cd* is derived from the chemical symbols of nickel (Ni) and cadmium (Cd). The abbreviation *NiCad* is a registered trademark of SAFT Corporation although the brand name is commonly used in all Ni-Cd batteries. The battery is manufactured in the discharged state. The battery consists of spongy cadmium as negative plate. The positive plate consists of nickel oxide and hydroxide with flakes of graphite or metallic nickel to increase the conductivity. An addition of 2% $Ba(OH)_2$ is added to increase the shelf-life of the electrodes. The electrodes are immersed in an electrolyte of 6M KOH with little LiOH. The addition of LiOH provides an increased capacity for the battery. In the fully charged state, the emf of the cell is 1.34 to 1.40V and the energy density is 50 Wh/kg. The conventional representation of the cell is

$$Cd, Cd(OH)_2/KOH\ (6M)/Ni\ (OH)_2, Ni(OH)_3$$

Discharging Reactions:

When the battery delivers electric current to the external circuit it is said to be discharging.

Cadmium at the anode forms Cd^{+2} ions which interact with hydroxide ions to form insoluble cadmium hydroxide $Cd(OH)_2$. Nickel hydroxide in +3 oxidation state at the cathode is reduced to +2 oxidation state to give $Ni(OH)_2$.

At anode, Cadmium undergoes oxidation with the loss of electrons to form cadmium ions (Cd^{2+}).

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

The cadmium ions reacts with hydroxyl ions to form cadmium hydroxide $Cd(OH)_2$.

$$Cd^{2+} + 2OH^- \longrightarrow Cd(OH)_2$$

The overall anodic reaction is as follows,

$$Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$$

At cathode, $Ni(OH)_3$ undergoes reduction to form $Ni(OH)_2$.

$$2Ni(OH)_3 + 2e^- \longrightarrow 2Ni(OH)_2 + 2OH^-$$

The net discharging reaction is

$$Cd + 2Ni(OH)_3 \longrightarrow Cd(OH)_2 + 2Ni(OH)_2$$

Charging Reactions:

When the anode and the cathode are covered with $Cd(OH)_2$ and $Ni(OH)_2$, the cell stops delivering current to the circuit. In order to restore the electro-active materials, the battery is charged by passing electric current in the reverse direction.

At anode/positive plate, $Ni(OH)_2$ undergoes oxidation to form $Ni(OH)_3$

$$2Ni(OH)_2 + 2OH^- \longrightarrow 2Ni(OH)_3 + 2e^-$$

At cathode/negative plate, $Cd(OH)_2$ undergoes reduction to form Cd.

$$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$$

The net charging reaction is

$$Cd(OH)_2 + 2Ni(OH)_2 \longrightarrow Cd + 2Ni(OH)_3$$

3.7.2.1Types of Nickel Cadmium batteries:

Ni-Cd batteries are manufactured in two basic types 1)pocket-plate cells and 2) sintered plate cells. Pocket-plate designs are ideal for emergency power supply and in train lighting, switch gear and engine starting. These cells have long shelf-life (>20 years) without any maintenance. Sintered plate designs are suited for military applications and have high discharge rate at low temperatures.

1) Pocket-plate cell:

The cells are manufactured in the discharged state with capacity ranging from 10 to 1200Ah. These cells have moderate energy density in the range of 15-25 Wh/kg. The active material for positive electrode consists of 80% nickel hydroxide, 2% cobalt hydroxide, 18% graphite and traces of barium compound. The graphite is present in powder or in flakes form in order to improve the conductivity while barium and cobalt compounds are used to increase the cycle life of the battery. The nickel hydroxide is prepared by treating nickel sulphate with sodium hydroxide. The precipitate, nickel hydroxide is filtered, dried, re-washed to ensure complete removal of sodium sulphate and finally re-dried. The active material for negative electrode consists of 78% cadmium hydroxide, 18% iron, 1% nickel and 3%graphite. It is prepared by dry mixing the iron, nickel, graphite and either cadmium hydroxide or cadmium oxide and reduce to ball-up morphology.

The manufacturing procedure for pocket-plate electrodes is shown in the Fig 3.9. The positive and negative electrodes of pocket-plate Ni-Cd batteries are made of same pocket-plate design to hold the active materials. The pocket-plates are built of flat pockets of thin perforated steel strips which holds the active materials. The perforation hole is between 15 to 30%. The steel strips are nickel plated to prevent iron poisoning. The active mass is pressed into briquettes and are placed into the preshaped strips as powder. The upper and lower strips are folded together by rollers. A large number of folded strips are interlocked with each other to form electrode sheets of different thickness. The negative plate is thinner than the positive plate. Plates of opposite polarity are intermeshed and electrically separated by insulating rods. The cell is assembled in steel or plastic case and filled with 6M KOH solution.

The advantages of pocket-plate are:

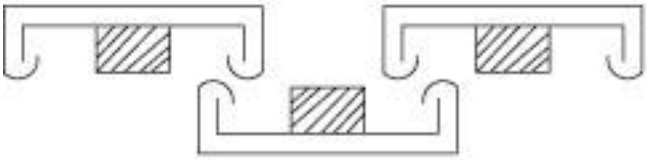
- Its ability to retain charge for longer time.
- To maintain steady voltage at all temperatures.
- Long cycle life.

(a) Two Perforated Ni coated steel strips

(b) Shape as Pocket

(c) Fill the lower strip with briquette of active material

(d) Upper dtrips are folded over and edges are bent to form inter-locking keys



(e) Electrode plates are formed by connecting with inter-locking keys

Fig 3.9 Schematic diagram for the manufacture of pocket plate NICAD battery

2) Sintered-plate:

Sintered-plates are available in various sizes from rectangular plates with capacity 1-1000Ah; cylindrical cells of 0.1-10Ah and button cells of 0.04 -1.75 Ah. The energy density of these cells is better than pocket-plate which is above 50 Wh/kg. The electrodes are manufactured from sintered nickel metal with thickness of 0.5 -1.0 mm, porosity around 80-85% and a surface area of 0.25-0.50m2/g. The sintered nickel electrode is prepared by decomposing nickel tetra carbonyl at 600 to 700°C to nickel powder. It is then moulded into rod shape by compression and heated below its melting point. The active materials are impregnated into the sintered metal in a series of steps. The sintered metal is dipped into a solution of nickel or cadmium ions and a vacuum is used to draw the solution into the pores. The sintered metal containing the solution is chemically treated to cause the ions to precipitate, nickel as hydroxide and cadmium as mixture of oxide and or hydroxide. The cycle is repeated several times to obtain high loading of the active materials. The cells are charged after assembly.

The advantages of sintered-plate are:

- Its ability to remain charge even for 6 months.
- High capacity is obtained at high currents.
- Long cycle life.

Applications:

- Ni-Cd batteries are used for portable electronics like camera, flash light and toys.
- Larger Ni-Cd batteries are used for aircraft starting batteries, electric vehicles and standby power generator.

3.8 LITHIUM BATTERIES

Lithium has dominated the development of high performance primary and secondary batteries during the last two decades. Lithium metal has been found attractive as an anodic material due to its light weight, high cell voltage, high electrochemical equivalents and good conductivity. Lithium batteries came into prominence in the early 1970s in selected military applications and their usage was limited due to their cell structures, formulations and safety considerations. Now a days, lithium primary cells and batteries have been designed in a variety of sizes and configurations with size ranging from less than 5mAh to 10,000Ah; configurations from small coin, cylindrical to large prismatic cells used for memory backup, portable applications and standby power in missiles.

Cells and batteries which use lithium anodes are called lithium cells and batteries irrespective of the cathode material. The uniqueness of lithium as anode can be attributed to

1. **High cell voltage:** Lithium cells/batteries have voltages up to 4V, depending on the cathode. The formal potential of Li^+/Li couple is highly negative, -3.01V with respect to SHE (Standard Hydrogen electrode) in combination with cathode materials produces high cell voltages which reduces the number of cells in a battery pack.

2. **High specific energy and energy density:** The energy output of a lithium battery is 200 Wh/Kg much higher than the conventional zinc-carbon battery due to its light weight. The density of lithium is 0.534 g/cm^3, half that of water.
3. **Wide range of temperature:** Most of the lithium batteries operate over a temperature range of 70°C to -40°C with some capable of performing at high temperature of 150°C and as low as -80°C.
4. **Good power density:** Lithium batteries are designed to deliver their energy output at high current.
5. **Flat discharge characteristics:** A flat discharge curve (constant voltage and resistance during discharge) at high current density is typical for many lithium batteries.
6. **Superior shelf life:** Lithium batteries can be stored for long periods even at elevated temperatures.
7. **Aprotic solvent:** Lithium reacts vigorously with water releasing hydrogen. The heat generated may ignite the hydrogen evolved and burns the lithium metal. Hence, lithium must be handled in dry state and used in non-aqueous media.

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$

Cathode materials:

Lithium cells/batteries use solid, liquid and gaseous materials as the cathode. The characteristics of the cathode are its compatibility with the electrolyte, conductive nature, low cost, non-toxic, non-flammable and easily available. In case of solid cathode materials, the conductive is improved by mixing with carbon or any other conductive material.

Electrolyte:

The reactivity of lithium in aqueous solutions necessitates the use of non-aqueous electrolytes for lithium batteries. The properties of the solvent are

1. It must be aprotic, have no reactive protons or hydrogen atoms in the molecule.
2. It must have low reactivity with lithium and the cathode.

3. It must be capable of forming an electrolyte of good ionic conductivity.
4. It must be liquid over a broad range of temperature.
5. It must possess low vapour pressure, non-toxic, non-flammable and stable in nature.

The organic solvent commonly used in lithium cells/batteries are acetonitrile, dimethyl sulphoxide (DMSO), dioxolane, propylene carbonate, γ- butyro lactones, tetrahydrofuran (THF) etc., Lithium salts like perchlorate ($LiClO_4$), bromide (LiBr), aluminum chloride ($LiAlCl_4$) are the electrolyte solutes used to provide ionic conductivity. The solutes are soluble in organic solvent and dissociate to form electrolyte solution. The solute forms stable electrolytic solution which does not react with the active electrode materials.

Lithium anode:

The mechanism for the discharge of lithium anode is the oxidation of lithium to lithium ion with the release of an electron.

$$Li \longrightarrow Li^+ + e^-$$

The electron moves through the external circuit to the cathode where it reduces the cathodic material. At the same time, Li^+ ion which is small in size and mobile in both solid/liquid state electrolytes reaches the cathode to form lithium compound.

3.8.1 Lithium Primary cells

Classification of Lithium primary cells

Lithium primary cells are classified based on the nature of the cathode material and the electrolyte.

Based on the nature of the cathode

Lithium primary cells are categorized as 1) Lithium soluble cathode cells and 2) lithium solid cathode cells

1) Lithium soluble cathode cells

Cells which utilize liquid or gaseous cathode materials that dissolves in the electrolyte or the electrolyte solvent. These cells operate by the formation of passive layer on the lithium anode resulting from the reaction between lithium and cathodic materials. They are usually fabricated in cylindrical configuration for low rate energy density and spirally wound structure for high rate designs.

Eg: Lithium- sulphur dioxide cells; Lithium- thionyl chloride cells; Lithium- sulphuryl chloride.

2) Lithium solid cathode

Lithium cells which utilize solid materials as the cathode. These cells have the advantage of not being pressurized and do not have high rate capacity as the soluble cathode. They are usually fabricated in button, flat and cylindrical shapes used for memory backup, watches, calculators and portable electronic equipments.

Eg: Lithium-Manganese dioxide; Lithium-Vanadium pentoxide; Lithium- iron sulphide; Lithium- cupuric oxide.

Based on the nature of the electrolyte

They are categorized as lithium solid electrolyte cells.

Lithium solid electrolyte

Lithium cells which use solid materials as the electrolyte. These cells have extremely long storage life (>20 years) and are capable of discharging at a low rate in µA range. They are used in cardiac pacemakers and in memory backup.

Eg: Lithium- iodine cell; Lithium-lead iodide; Lithium-lead sulphide.

3.8.1.1 Lithium-Thionyl chloride cell (Li/$SOCl_2$)

Lithium- thionyl chloride cells are fabricated in various size and design from wafer, coin cells and cylindrical cells to large prismatic cells. Fig 3.10 represents the cylindrical Li/$SOCl_2$. The construction of the cell consists of lithium foil as an anode which is lined in the inner walls of a stainless steel or nickel plated steel can. The cathode is a highly porous cylindrical carbon, made of Teflon-bonded acetylene black. The cathode occupies most of the cell volume and incorporates a current collector, metal cylinder in case of larger cells and a pin in smaller cells. The anode and cathode are separated by a non-woven glass fiber. The electrolyte consists of non-aqueous solvent of lithium aluminium chloride ($LiAlCl_4$) in $SOCl_2$ solution.

These cells have the highest cell voltage of 3.6V and energy density of 350-400Wh/kg. The low rate cells are used as memory backup and large prismatic cells find its application in military operations as an emergency backup power source. They are also used in medical devices such as neuro-simulator, drug delivery system etc.,

Discharging reactions:

$Li/SOCl_2$ cell consists of lithium anode, a porous carbon cathode and a non-aqueous $SOCl_2$: $LiAlCl_4$ electrolyte. Other electrolyte salts like lithium gallium chloride ($LiGaCl_4$) can also be used. The $SOCl_2$ is both the electrolyte solvent and the active cathode material. When the porous carbon is placed in the electrolyte solvent, $SOCl_2$ gets absorbed preferentially onto the pores of the carbon. The discharging reactions are,

At anode, lithium oxidizes to lithium ion with the liberation of electron,

$$4Li \longrightarrow 4\,Li^+ + 4e^-$$

The electron moves in the external circuit from anode to cathode.

At cathode, $SOCl_2$ accepts the electrons and undergoes the following reduction reaction,

$$2SOCl_2 + 4e^- \longrightarrow S + SO_2 + 4Cl^-$$

The overall reaction is

$$4Li + 2SOCl_2 \longrightarrow 4LiCl + S + SO_2$$

The cell is represented as $Li/\ LiAlCl_4, SOCl_2/SOCl_2,C$

The reaction involves two electrons per thionyl chloride molecule. The S and SO_2 are initially soluble in the excess of thionyl chloride electrolyte. During the discharge, there is a moderate build up of pressure due to the generation of SO_2. The LiCl formed precipitates within the porous carbon black cathode. Sulfur may also precipitate in the cathode at the end of the discharge which limits the cells capacity. The lithium anode is protected by forming a protective LiCl film on the anode as soon as it contacts with the electrolyte. This passivating film contributes to excellent shelf life and causes a voltage delay at the start of the discharge especially after long standing even at elevated temperatures. To overcome the voltage delay, special anode treatments and electrolyte additives are used along with Li foil.

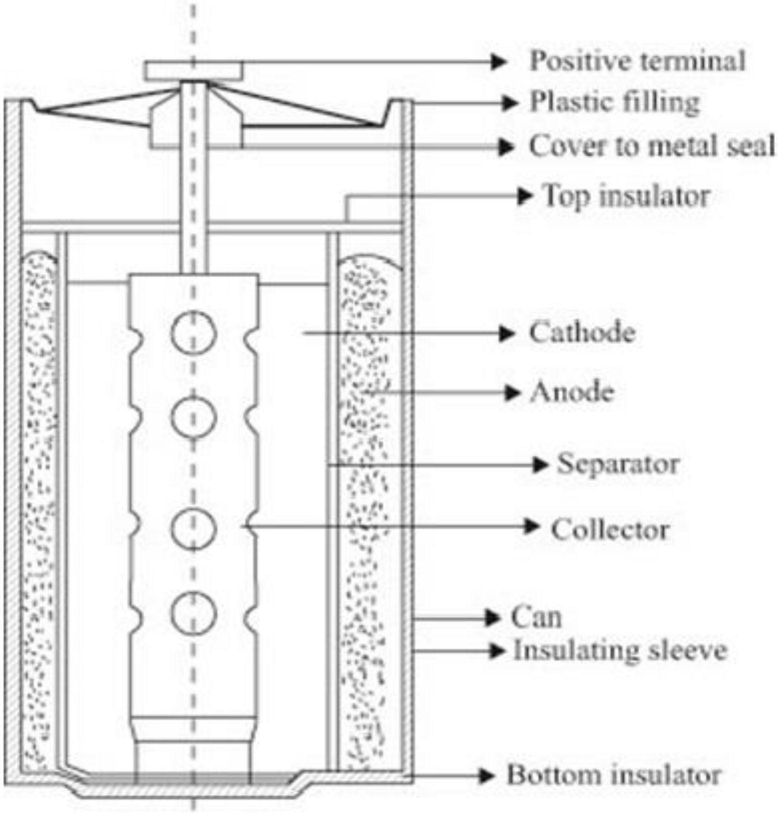


Fig 3.10 Cross-section of Lithium - thionyl chloride cell

3.8.1.2 Lithium Manganese dioxide (Li/MnO_2)

Lithium Manganese dioxide battery is most widely used primary battery available in various configurations such as coin, bobbin, spirally-wound, cylindrical and in prismatic designs. The cross-section of a typical coin-type Li/MnO_2 cell is shown in the Fig 3.11. The cathode, MnO_2 pellet is placed on the front side of the lithium anode disk. The anode and cathode are separated by a non-woven poly-propylene impregnated with lithium perchlorate in propylene carbonate and 1,2-dimethoxy ethane electrolyte. The cell is crimped-sealed with the can serving as the positive terminal and the cap as the negative terminal. The cell has high cell voltage of 3.3 to 3.5 V and specific energy as high as 230 Wh/kg. These batteries are employed as a long-term memory backup, safety and security devices, cameras and in military electronics as Emergency Positioning Indicating Radio Beacons (EPIRBS) and pipeline -test vehicles.

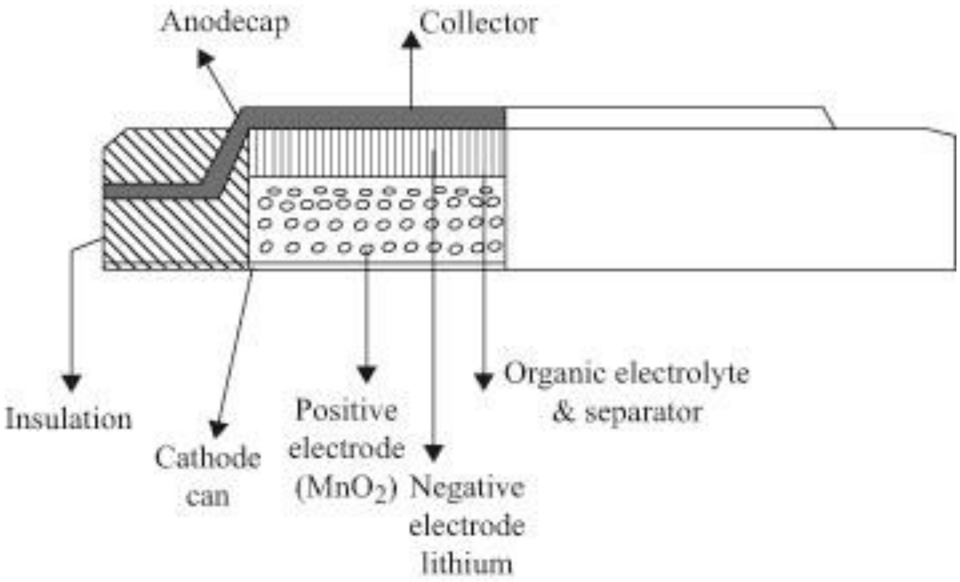


Fig 3.11 Cross-section of Lithium Manganese dioxide coin cell.

Discharging reactions:

Li/MnO_2 consists of lithium as active anodic material and preheated MnO_2 as cathode. The electrolyte is lithium perchlorate in mixed organic solvents of propylene carbonate and 1,2-dimethoxy ethane. The cell reactions are as follows

At anode, Lithium oxidizes to lithium ions with the liberation of electrons

$$xLi \longrightarrow xLi^+ + xe^-$$

The electrons moves to the external circuit from anode to cathode

At cathode, $Mn^{+4}O_2$ accepts the electrons and undergoes the following reaction,

$$Mn^{+4}O_2 + xLi^+ + xe^- \longrightarrow Li_xMn^{+3}O_2$$

The overall cell reaction is,

$$xLi + Mn^{+4}O_2 \longrightarrow Li_xMn^{+3}O_2$$

The cell is represented as,

$$Li/LiClO_4/\ MnO_2$$

The reaction involves one electron transfer per $Mn^{+4}O_2$. MnO_2, an intercalation compound is reduced from tetravalent state to trivalent state producing lithiated manganese dioxide

(Li_xMnO_2) as Li^+ ions enters into MnO_2 crystal lattice. The formation of Li_xMnO_2 at the end of the discharge reaction limits the cell capacity.

3.8.1.3 Lithium-Iodine (Li/I)

The only commercial inorganic solid electrolyte is lithium iodine cell. These cells are formed by contacting the iodine containing cathode directly with the lithium anode. The chemical reactions between the materials form a thin layer of LiI. The layer serves to separate the electro-active materials electronically and prevents failure making it suitable for high reliability. These cells have cell voltage of 2.6V and low energy density of 150-200Wh/kg. The button type Li-I cells are shown in the Fig 3.12. are made by pressing iodine cathode and lithium anode layers into a stainless steel cup. The cup is a positive current collector. A glass to metal feed -through brings the negative terminal to the exterior. The case is positive terminal and the negative connection is button at the end of the cell. The design is able to withstand shock, vibration, swelling, leaking and explosion in the battery.

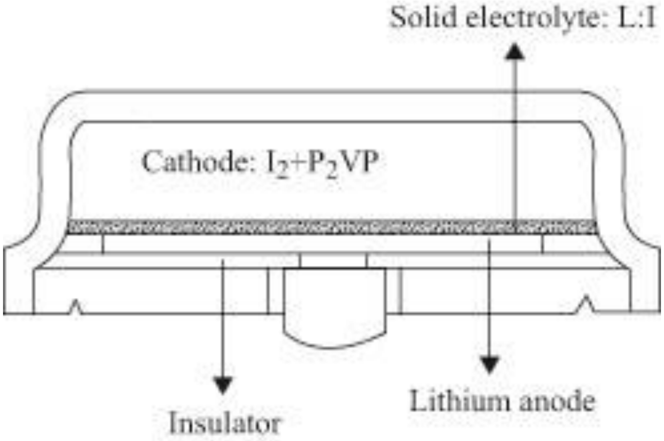


Fig 3.12 Cross-section of button type Li-I cell.

Discharging reactions:

Li/I cell consists of a lithium anode, the solid electrolyte LiI formed *in situ* as the discharge product. The cathode is a mixture of solid iodine and a saturated viscous liquid solution containing poly-2-vinyl pyridine and iodine. The Li/I battery is regarded as a quasi-solid state system because of the high viscosity of the polymer containing liquid phase and preponderance of solid iodine. The viscous liquid imparts plasticity to the cathodic material, making it to adapt volumetric changes during the cell discharge. The cell reactions are

At anode, lithium oxidizes to lithium ion with the liberation of electron,

$$2\mathrm{Li} \longrightarrow 2\,\mathrm{Li}^+ + 2e^-$$

The electron moves in the external circuit from anode to cathode.

At cathode, the iodine accepts the electrons and undergoes reduction reaction,

$$2\mathrm{Li}^+ + 2e^- + \mathrm{P2VP.nI_2} \longrightarrow 2\mathrm{LiI} + \mathrm{P2VP.(n-1)I_2}$$

The overall cell reaction is as follows,

$$2\mathrm{Li} + \mathrm{P2VP.nI_2} \longrightarrow 2\mathrm{LiI} + \mathrm{P2VP.\ (n-1)I_2}$$

The cell is represented as $\mathrm{Li/LiI/I_2}$ (P2VP)

Lithium and iodine are consumed during the discharging reactions and the product LiI precipitates in the region between the two reactants. The LiI serves as the cell separator, electrolyte as well as the discharge product. The polyphase cathodic iodine is made conductive by adding pyridine containing polymer like poly-2-vinyl pyridine. In undischarged cells, the I_2/P2VP is in two-phase, liquid polymer and solid iodine. During discharging reactions, a layer of LiI formed becomes thicker which increases the resistance of the cells. At the same time, the iodine content of the cathode decreases during discharging, the remaining cathodic material changes its phase and becomes hard at depleted state.

3.8.2 Lithium-ion batteries

Lithium-ion batteries comprised of cells in which lithium intercalation compounds acts as the positive and negative materials. The lithium ions exchange between the positive and negative electrodes. They are referred as ‘rocking chair’ batteries as lithium ions moves back and forth between the electrode materials during the charging and discharging reactions of the cell. The construction of lithium-ion battery consists of a positive electrode, negative electrode and an electrolyte. The positive electrode material consists of a metal oxide with a layered structure such as lithium cobalt oxide ($LiCoO_2$) or metal oxide with a tunnel structure as lithium manganese oxide ($LiMn_2O_4$) adhered to a current collector of aluminium foil. The negative electrode is a layered graphitic carbon adhered on a copper current collector. The electroactive materials are adhered to the metal collector by a binder, polyvinylidene fluoride (PVDF) or copolymer of polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) and conductive diluents of carbon black or graphite. The positive and negative electrodes are separated by thin (10-30 µm) microporous polyethylene or polypropylene. Lithium hexa fluorophosphate ($LiPF_6$) or lithium tetrafluoroborate ($LiBF_4$) in propylene carbonate (PC) are most commonly used electrolytes. The conductivity of $LiPF_6$ in PC at 20°C is 5.2mS/cm.

Lithium –ion batteries are developed in various designs like wound spiral, cylindrical, wound prismatic and flat prismatic in small (0.1Ah) to large (100Ah) sizes. These batteries are applied in consumer electronics such as cell phones, laptops, cameras, camcorders and military electronics such as radios, mine detectors and thermal weapon sights.

Intercalation process

The active materials in Li-ion batteries are lithium metal oxide as positive electrode and lithiated carbon as negative electrode. These materials operate reversibly by incorporating lithium in an intercalation process where Li^+ ions are reversibly removed or inserted into a ‘host’ without any significant structural change to the host. The lithium metal oxide has either a layered or tunnel structure. The graphitic carbon has a layered structure similar to graphite. The metal oxide, graphite and other materials act as hosts, incorporating Li^+ ions as ‘guests’ which reversibly forms sandwich like structures. When a lithium-ion battery is charged, the positive material is oxidized and the negative material is reduced. In this process, Li^+ ions are de-intercalated from the positive electrode and intercalated to the negative electrode. The reverse reaction occurs in the discharging process. As metallic lithium is not used in these batteries, they are chemically less reactive and offer longer cycle life than lithium primary cells. The charging and discharging reactions are illustrated graphically. In the Fig 3.13, the layered active materials are shown on metallic current collectors.

Charging reactions:

During charging, Li^+ ions are extracted from cathode and are inserted into the anode together with the oxidation of transition metal (Co^{+3} to Co^{+4}) at the cathode (positive electrode)

At positive electrode,

$$Li_xCoO_2 \longrightarrow Li_{(1-x)}CoO_2 + xLi^+ + xe^-$$

At negative electrode,

$$C + xLi^+ + xe^- \longrightarrow Li_xC$$

The overall reaction is,

$$Li_xCoO_2 + C \longrightarrow Li_{(1-x)}CoO_2 + Li_xC$$

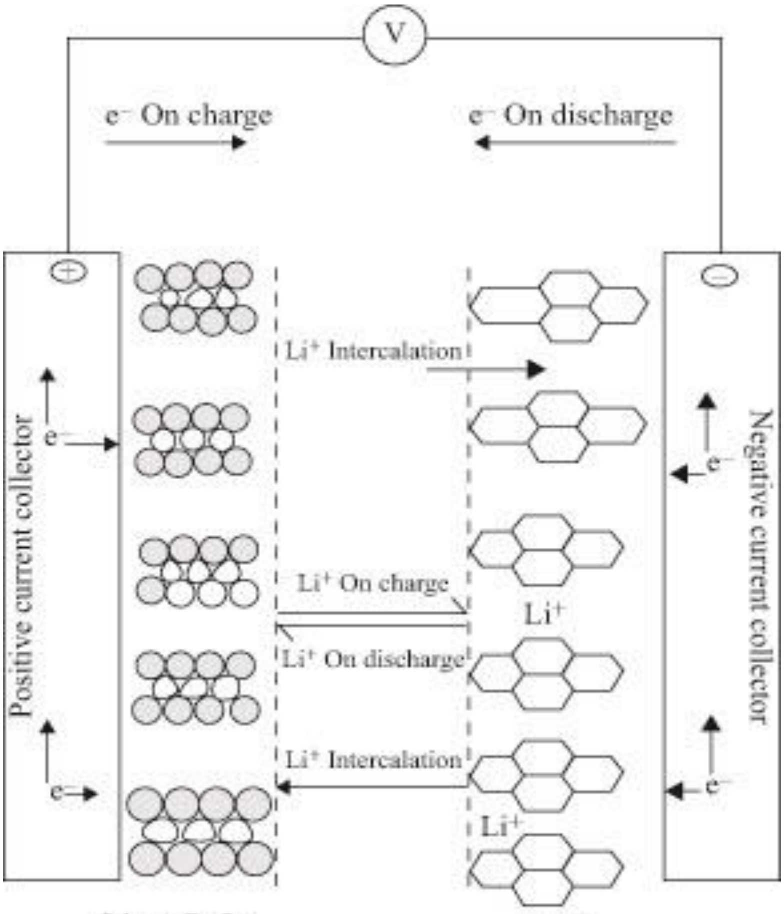


Fig 3.13 Representation of Lithium ion batteries

Discharging reactions:

When a cell delivers current to an external circuit, the Li^+ ions are shuttled from negative electrode back to positive electrode with the reduction of transition metal, Co^{+4} to Co^{+3}.

At positive electrode,

$$Li_{(1-x)}CoO_2 + xLi^+ + xe^- \longrightarrow Li_xCoO_2$$

At negative electrode,

$$Li_xC \longrightarrow C + xLi^+ + xe^-$$

The overall reaction is,

$$Li_{(1-x)}CoO_2 + Li_xC \longrightarrow Li_xCoO_2 + C$$

The advantage of lithium-ion battery is high energy density (150Wh/Kg) making them attractive for weight/volume sensitive applications. They also offer low self-discharge rate, long cycle life (> 1000 cycles) and broad range of temperature (-20°C to +60° C). The major disadvantage of these batteries is that they are degraded when discharged <2V and may vent when overcharged. They permanently lose their capacity at elevated temperatures of >65°C.

3.9 FUEL CELLS

A fuel cell is a galvanic cell which can convert the chemical energy of a fuel into electrical energy by an electrochemical reaction. The fuel is made to react with an oxidant or oxidizing agent. Hydrogen is the most commonly used fuel and hydrocarbons like natural gas, methanol, etc are also used. The oxidant is usually oxygen. A single fuel cell consists of two electrodes, an anode and a cathode with an electrolyte between them. At the anode, hydrogen reacts with a catalyst, creating a positively charged ion and a negatively charged electron. The positively charged ion called proton then passes through the electrolyte, while the electron travels through a circuit, creating a current. At the cathode, oxygen reacts with the positively charged ion and electron, forming water and heat. The electrolyte is either a solid or liquid medium which allows the movement of ions through it, but not the electrons. This single cell generates about 0.7 volts, which is enough to power a single light bulb. When these cells are stacked in series the output increases, resulting in fuel cells anywhere from several watts to multiple megawatts. Usually the anode and the cathode are impregnated with a catalyst like Pt, Pd, Mg or Ni to enhance the reaction at the electrodes.

3.9.1 Advantages Of Fuel Cells

- High efficiency of energy conversion from chemical to electrical energy.
- No emission of gases and pollutants.
- Produces drinking water of potable quality.
- Low noise and thermal pollution.
- Negligible air pollution
- Constant efficiency at low load
- Flexible output with fast adjustments.
- Low cost fuels can be used with high temperature systems.
- Low maintenance costs.
- Saves fossil fuels.

3.9.2 Limitations Of Fuel Cells

- Large weight and volume of gas-fuel storage systems.
- High initial cost.
- Lifetime is less.

3.9.3 Classification Of Fuel Cells

Fuel cells can be classified into three categories:

1. Direct fuel cells - the products of the cell reaction are discarded.
2. Indirect fuel cells - the fuel of the cell is obtained from organic fuel.

3. Regenerative fuel cells - the spent reactants are regenerated from the products by using thermal, electrical or photochemical methods.

Fuel cells are further classified into various categories based on,

a. The temperature range used

1. Low temperature fuel cell (25-100^oC)
2. Intermediate temperature fuel cell (100-500^oC)
3. High temperature fuel cell (500-1000^oC)
4. Very high temperature fuel cell (>1000^oC)

b. The type of fuel used

1. Gaseous fuel cells (H_2, NH_3, etc)
2. Liquid (alcohols, hydrocarbons)
3. Solid (coal, hydrides)

c. The type of electrolytes used

1. Alkaline fuel cells
2. Solid oxide fuel cells
3. Polymer electrolyte fuel cells
4. Phosphoric acid fuel cells
5. Molten carbonate fuel cells

3.9.4 ALKALINE FUEL CELL

These cells use an aqueous solution of KOH as electrolyte. These cells are low temperature fuel cells and also use non noble electro-catalyst metal. Oxygen reduction is fast in alkaline electrolyte cells than in acid electrolyte cells.

Ex : $H_2 – O_2$fuel cell (Hydrogen - oxygen fuel cell)

3.9.4.1 Hydrogen-Oxygen Fuel Cell

Hydrogen-oxygen fuel cell uses hydrogen gas as a fuel and oxygen gas as oxidant. The cell consists of two electrodes namely anode which is a porous carbon electrode impregnated with catalyst such as finely divided platinum or palladium and the cathode which is also a porous carbon electrode impregnated with platinum or silver as catalyst. The electrolyte is an aqueous solution of KOH. The cell operating temperature is 150 – 200^{0}C and represented as,

C, Pt or Pd / KOH / C, Pt or Ag

Working Of H_2-O_2 Cell

The hydrogen gas fuel is continuously supplied at the anode and oxygen gas is supplied at the cathode. As the hydrogen gas diffuses through the anode, it is adsorbed on the electrode surface and reacts with hydroxyl ions to form water and liberate electrons. At the cathode oxygen diffusing through the electrode is absorbed by the liberated electrons and reduced to hydroxyl ions. The efficiency of the cell is about 70%. The cell output ranges from 300 watts (W) to 5 kilowatts (KW). These electrode reactions are given below:

At the anode: $2H_2 \rightarrow 4H^+ + 4e^-$

$4H^+ + 4OH^- \rightarrow 4H_2O$

$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

At the cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

The net cell reaction is: $2H_2 + O_2 \rightarrow 2H_2O$

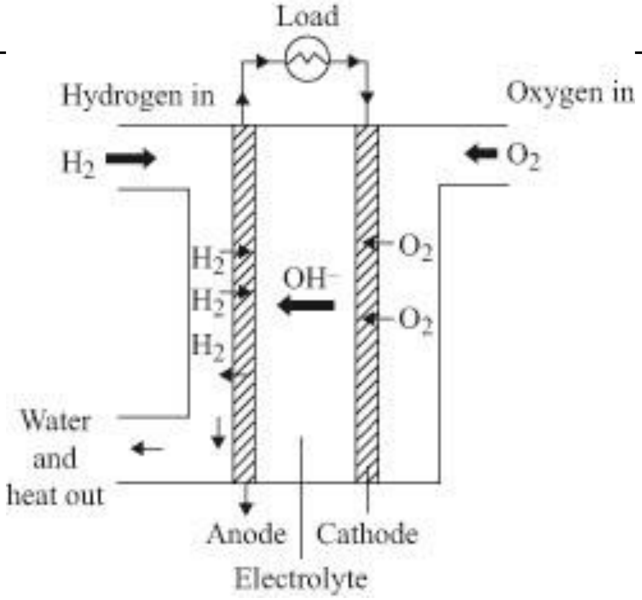


Fig 3.14:H_2-O_2 fuel cell

3.9.4.2 Applications

$H_2 – O_2$ fuel cells are used in,

- Space applications
- Automotive applications

Note: When methanol is used as a fuel and oxygen as oxidant, the use of alkali as an electrolyte creates problems. The CO_2 produced is absorbed by the electrolyte and the electrolyte is gradually converted into carbonate. This decreases the cell efficiency because of the increasing concentration polarization at the electrode surface and the decreasing conductivity of the electrolyte. Therefore acid electrolytes are a better option.

3.9.5 Solid Oxide Fuel Cell (SOFC)

SOFCs differ from other fuel cells in many aspects. First, they are composed of ceramic substances. Second, the cell can operate at high temperatures such as 1000^0C which cannot be operated in any other fuel cell. Third, these cells can be configured either as rolled tubes or as flat plates. These cells are clean, reliable and entirely non- polluting. There are two porous electrodes which sandwich an electrolyte. Both electrodes (cathode and anode) and the electrolyte are made of ceramic materials, since the high operating temperature prevent the use of cheaper metals. Both hydrogen and carbon monoxide serve as fuels. Common hydrocarbon fuels such as diesel, natural gas, gasoline, alcohol etc can also be used in SOFC.

The anode material is Co-ZrO_2 (Zirconia)or Ni-ZrO_2cermets and the cathode material is Sr doped $LaMnO_3$ (Lanthanum manganite) called LSM [$La_{0.8}Sr_{0.2}MnO_3$]. The electrolyte used in this fuel cell is a solid, nonporous metal oxide powder, usually ZrO_2 doped with 8-10 mole percentage of Y_2O_3 (Yttria) and denoted as YSZ .The cell operates at 650-1000^{0}C. The anode contains nickel, for better electron conduction and catalysis. The cell may be represented as,

Ni-ZrO_2 / YSZ / LSM

.

3.9.5.1 Working OfSOFC

In this cell operation, the oxygen atoms are reduced on the porous cathode surface by electrons. These oxide ions diffuse through the electrolyte to the fuel rich and porous anode, where they react with the fuel (hydrogen) and give off electrons to an external circuit. A large amount of heat is produced by the electrochemical reaction, which can be used by an integrated heat management system. The efficiency is about 80-85%. The cell power output is given as 100kw. These electrode reactions are given below:

At the anode: $H_2 + O^{2-} \rightarrow H_2O + 2e^-$

At the cathode: $\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$

The net cell reaction is: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

3.9.5.2 Advantages

- High operating temperature avoids expensive catalyst.

- High tolerance to impurities.
- No liquid formation in the cell.

3.9.5.3 Disadvantages

- Highly expensive.

3.9.5.4 Applications

- Stationary power plants.
- Auxiliary power supplies.
- Start-up time problems could be solved by using super capacitor batteries for the first few minutes of operation in mobile applications.

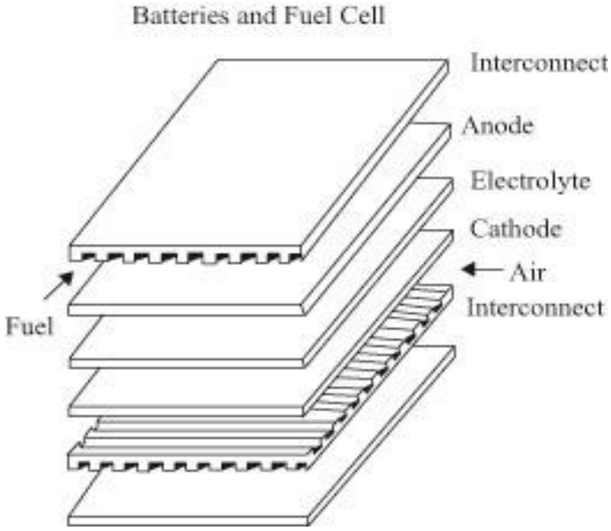


Fig 3.15: CONFIGURATION OF FLAT SOFC

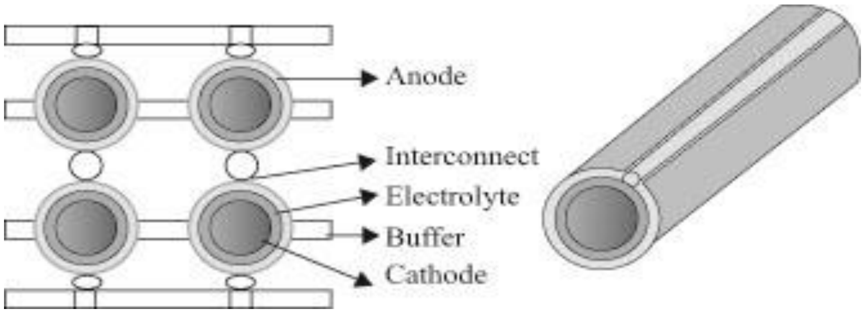


Fig 3.16: CONFIGURATION OF TUBULAR SOFC

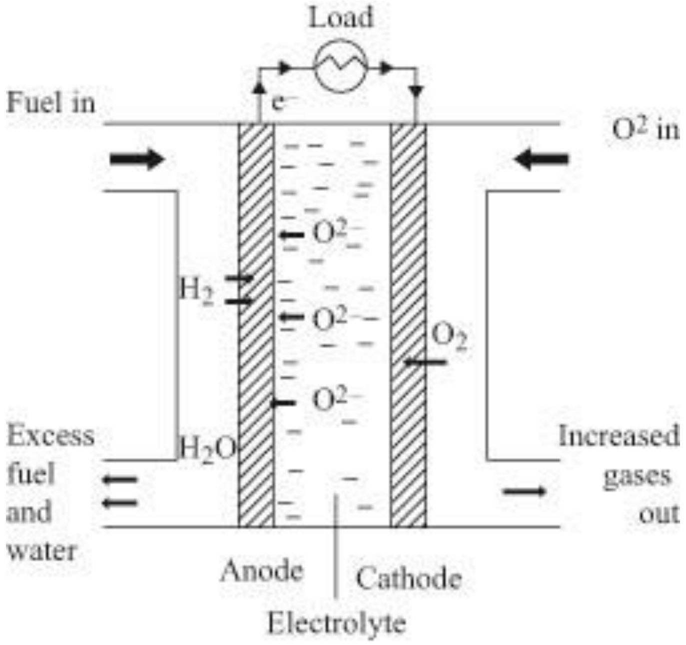


Fig 3.17:CELL DIAGRAM OF SOFC

3.9.6 Ion Exchange Membrane Fuel Cell (IEMFC)

The IEMFC uses a proton exchange membrane as its electrolytes and hence these cells are referred as proton exchange membrane fuel cells (PEMFC).

3.9.6.1 Polymer Exchange Membrane Fuel Cell (PEFC)

The PEMFC uses a polymer membrane as electrolyte which is an electronic insulator, but an excellent conductor of hydrogen ions. The polymer membrane provides an effective barrier against the leakages of gases between the electrodes. The membranes are very thin and reduce ohmic losses in the electrolyte and thereby producing high current densities. The membrane is made up of fluorocarbon polymer backbone, like Teflon, in which sulphonicacid groups are attached. The acid molecules are fixed to the polymer and cannot leak out but the protons on these acid groups are free to migrate through the membrane. The anode and cathode are made up of porous carbon electrodes which are impregnated with platinum catalyst. The cell may be represented as,

C, Pt/ PEM / C, Pt

3.9.6.2 Working OfPEMFC

The hydrogen from the fuel gas is supplied at the anode, yielding electrons and hydrogen ions, which enter the electrolyte. The hydrogen ions pass through the polymer electrolyte to the cathode, where they are combined catalytically with oxygen and electron to produce water. Since the cell operates at a temperature less than 100^0C, the water is produced as liquid water and is carried out of the fuel cell by excess oxidant flow. The efficiency of the cell is about 40-50 % and their outputs generally range from 50 to 250 kW. These electrode reactions are given below:

At the anode: $2H_2 \rightarrow 4H^+ + 4e^-$

At the cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

The net cell reaction is: $2H_2 + O_2 \rightarrow 2H_2O$

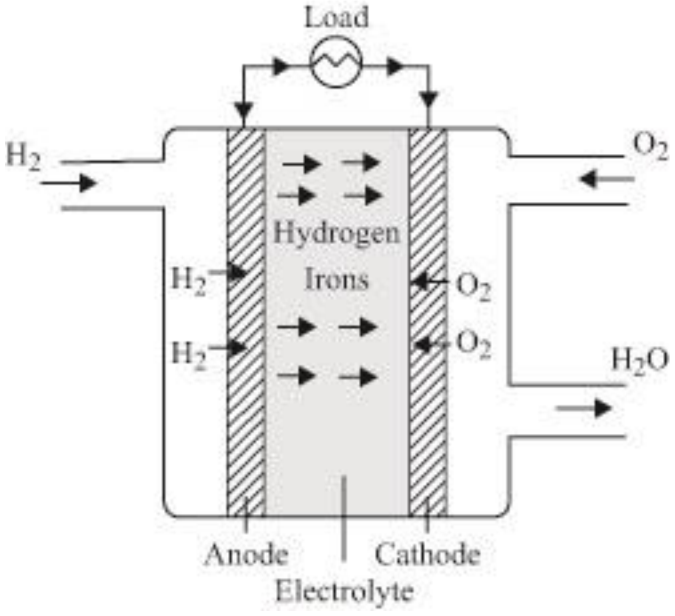


Fig 3.18: PEM FUEL CELL

3.9.6.3 Advantages

- Water with potable quality is produced.
- Easy to fabricate the cell.
- Can withstand high pressure
- Life time is more

3.9.6.4 Disadvantages

- Uses expensive electrolyte, therefore the cell cost is high.
- Water management in the membrane is difficult for effective operation.

3.9.6.5 Applications

- Transportation.
- Residential Power Generator (RPG).
- Portable Computers.

3.9.7 Phosphoric Acid Fuel Cell (PAFC)

Phosphoric Acid fuel cells (PAFC) use concentrated phosphoric acid as the electrolyte and operate at 160-220^{0}C. The electrodes are made up of carbon paper coated with a finely-dispersed platinum catalyst. The cell operates effectively only with pure hydrogen gas as the fuel and its performance will be affected if sulphur compounds and carbon monoxide are present. At the anode the positively charged hydrogen ions are liberated which is then migrate to the cathode through the electrolyte. Electrons generated at the anode travel through an external circuit, providing direct current and return to the cathode. Hence the electrons, hydrogen ions and oxygen will combine to form water, which is discharged from the cell. The efficiency of the cell is about 37-42%. The cell output ranges from 1kw-5mw. These electrode reactions are given below:

At the anode: $H_2 \rightarrow 2H^+ + 2e^-$

At the cathode: $1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$

The net cell reaction is: $H_2 + l/2O_2 \rightarrow H_2O$

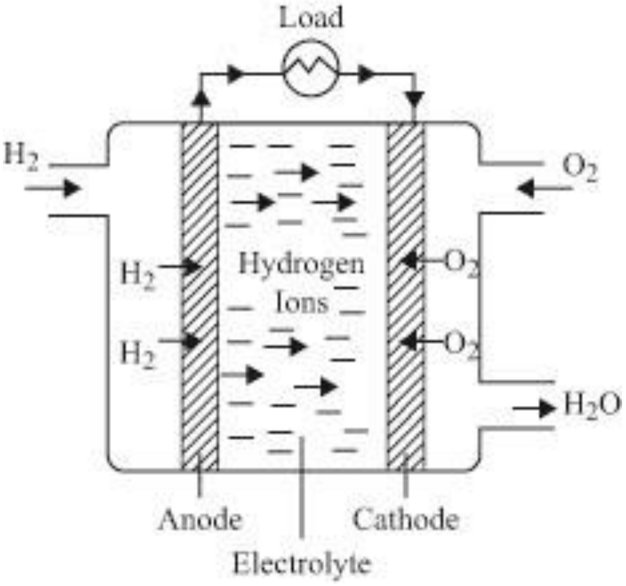


Fig 3.19:CELL DIAGRAM OF PAFC

3.9.7.1 Advantages

- Good thermal, chemical and electrochemical stability.
- Phosphoric acid will have low volatile nature above 150^0C compared to other acids.
- Catalytic poisoning due to CO is minimum because of the high operating temperature.

3.9.7.2 Applications

- Hotels.
- Hospitals.
- Office buildings.
- Large vehicles etc.,

3.9.8 Molten Carbonate Fuel Cell (MCFC)

Molten Carbonate fuel cells (MCFC) use high-temperature compounds of salt carbonates (like sodium or magnesium) as the electrolyte. The cell operates at a temperature of 600-650^0C. The efficiency of the cell is about 60-80%. This type of cell uses either hydrogen or CO as the fuel at the anode. The anode is porous nickel or nickel-chromium alloy and the cathode is porous nickel oxide (NiO). The electrolyte consists of 40% $LiAlO_2$, 28% K_2CO_3 and 32% Li_2CO_3 in the molten state is absorbed in a porous inorganic matrix. The matrix support material is a mixture of fine particles of r- $LiAlO_2$, coarse particles of α- Al_2O_3 and fibers of α- Al_2O_3. At the anode, hydrogen reacts with the carbonate ions to produce water, carbon dioxide and electrons. The electrons travels through an external circuit creating electricity and return to the cathode. There, oxygen from the air and carbon dioxide recycled from the anode react with the electrons to form CO_3^{2-} ions that replenish the electrolyte and transfer current through the fuel cell, completing the circuit. These electrode reactions is given as,

At the anode: $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$

At the cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$

The net cell reaction is: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

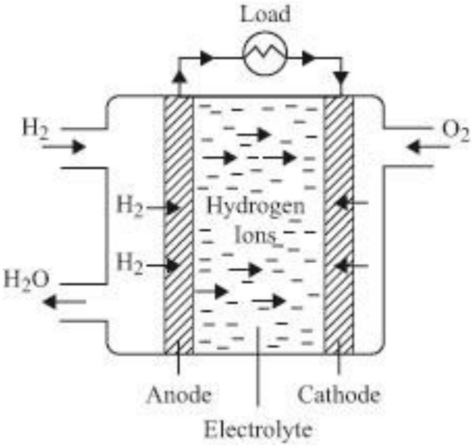


Fig 3.20: CELL DIAGRAM OF MCFC

3.9.8.1 Advantage

- Waste heat generated from the cell is recycled to make additional electricity.
- Used as medium to high power range plants for electric utility and industrial purpose.
- High temperature limits damage from carbon monoxide poisoning of the cell.
- Uses inexpensive catalyst like nickel compared to other cells.

QUESTION BANK

PART A

1. Define battery.
2. Define cycle life and capacity.
3. What are secondary batteries and give its characteristics?
4. Differentiate between primary and secondary batteries.
5. What is charging and discharging?
6. What is energy density and shelf life?
7. Give the representation of lead acid battery.

8. What is NICAD battery?
9. What are the applications of lead acid battery?
10. Give the uniqueness of lithium battery.
11. Give the classification of lithium primary cells.
12. Give the cell representation of lithium-thionyl chloride cell.
13. What is lithium-ion battery?
14. What are fuel cells?
15. What are the advantages of fuel cells?
16. Classify fuel cells according to the type of electrolyte used.
17. What are the applications of hydrogen-oxygen fuel cell?
18. What is SOFC?
19. Give the cell representation of PEMFC.
20. What are the limitations of SOFC?
21. Compare SOFC and PEMFC.

PART B

1. Explain lead acid battery in detail.
2. What is NICAD battery? Give its characteristics and charging and discharging reactions.
3. What are the advantages of lithium cells? Explain lithium-iodine cell.
4. Explain lithium-thionyl chloride cell.
5. Explain lithium-ion batteries in detail.
6. Explain hydrogen-oxygen fuel cell with a neat diagram.
7. Describe SOFC and mention its advantages.
8. Describe PEMFC in detail with a neat diagram.

Problems:

1. Calculate the theoretical voltage or standard cell potential for the reaction:

$Zn + Cl_2 \longrightarrow ZnCl_2$ with half cell potential for Zn^{2+}/Zn is -0.76 V and Cl_2/Cl^- is 1.36V

Sol:

At anode : $Zn \longrightarrow Zn^{2+} + 2e^-$ (E^o= -0.76V)

At Cathode: $Cl_2 + 2e^- \longrightarrow 2Cl^-$ (E^o = 1.36V)

Standard cell potential = $E^o_{cathode} - E^o_{anode}$

= 1.36 - (-0.76)

= 2.12V

Ans: 2.12 V

2. Calculate the theoretical capacity of an electrochemical cell,

$Zn + Cl_2 \longrightarrow ZnCl_2$

Sol:

1 g equivalent of any substance have capacity of 26.8Ah

Hence, For $ZnCl_2$ (Mol.wt 136.4) have capacity of 0.3929 Ah/g

Ans: 0.3929 Ah/g.

3. Calculate the capacity of a battery which discharges current of 2 A for 2 h.

Sol:

Current I = 2A

Time t = 2 h

Capacity Q =?

Q = I x t

= 2 x 2 = 4 Ah.

Ans: 4 Ah

4. Calculate the power and power density of a battery with 2 kg weight discharging voltage and current at 2 V and 3 A respectively.

Sol;

Current I = 3 A

Voltage V = 2 V

Weight of battery w =2 Kg

Power P=?

Power density P D =?

Power = I X V

=3 x 2 = 6 W

Power density = I X V/w

= 6/2 = 3 W/Kg.

5. Calculate the energy, energy density of a battery of 0.5 kg discharging voltage and current of 5 V and 2 A for 1h?

Sol:

Voltage V = 5 V

Current I = 2 A

Time t = 1 h

weight w = 0.5 Kg

Energy E =?

Energy Density E D = ?

Energy E = V x Ix t

= 5 x 2 x 1 =10 Wh.

Energy Density ED = V X I X t /w

= 10/0.5 = 20 Wh/kg.

Ans: E= 10Wh; ED= 20Wh/Kg.

Exercise Problems.

1.Calculate the theoretical cell voltage for a lead acid battery with a standard reduction potential for Pb^{2+}/Pb = -0.36 V; and PbO_2/Pb^{2+}= 1.69 V. [Ans= 2.05V)

2. Calculate the capacity of a dry cell discharging 2A for 5h. [Ans = 10 Ah]

3. Calculate the power, power density, energy and energy density of a NiCad battery of 0.75Kg discharging voltage of 1.2 V and current of 3 A for 10 h. [Ans P = 3.6W; PD = 4.8 Wh/Kg; E = 36 Wh; ED = 48 Wh/Kg.]

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