BATTERIES

BATTERY**:** Adevice that stores chemical energy for later release as electricity

Several eectrochemical cels connected in a series that can be used as a source of direct electric current at a constant voltage.

CLASSIFICATION :

Primary battery: In which the cel reaction is not reversible.When the reactants have for the most part been converted to products

Secondary battery: Cell reaction can br reversibe.Passing dc current in opposite directions.The Secondary battery may be used through a arge number of cyces of dischargining and charging

Flow battery or Fuel cell; In which materials (reactanmts, products, electrolytes) pass through the battery which is simpy an eectrochemical cell that converts chemica to eectric energy.

Dry cell (or Lacance cell): It is called dry battery as it does not have any iquid electroyte.The Zinc vessel serves as the anode (Fig.1) .The cathode is graphite rod in the centre of the cell.It is surrounded by the electrolyte which consosts of a past of NH_4Cl, $ZnCl_2$,MnO_2.Trace of acetylene black, graphite powder are also added.starch is added to make the mixture ike a thick paste.the cel is reperesented as

$$\mathbf{Zn/\ Zn^{2+},\ NH_4/\ MnO_2,\ C}$$

The cell reactions involved are

At anode, $Zn\ (s) \rightarrow Zn^{2+}(aq)+2e-$

At cathode, $2NH_4+(aq)2\ MnO_2(s)+\ 2e- \longrightarrow 2\ NH_3\ (aq)\ +Mn_2O_3(s)+\ H_2O\ (l)$

Net cell reaction; $Zn\ (s) + 2NH_4+(aq)+2MnO_2(S) \rightarrow Zn^{2+}(aq) +2\ NH_3(aq) +Mn_2O_3\ (s)+H2O\ (l)$

The cell is primary and gives votage of 1.5 V.

Applications:Used in transistors, tap recorders,toys, portable eectronic gadgets

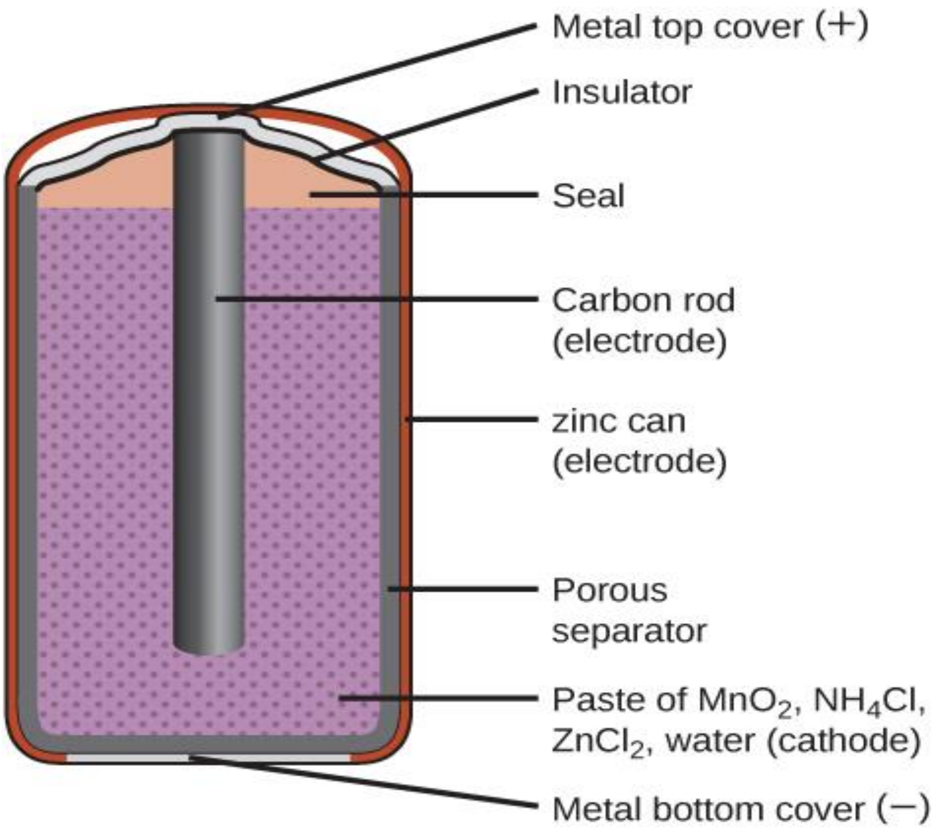
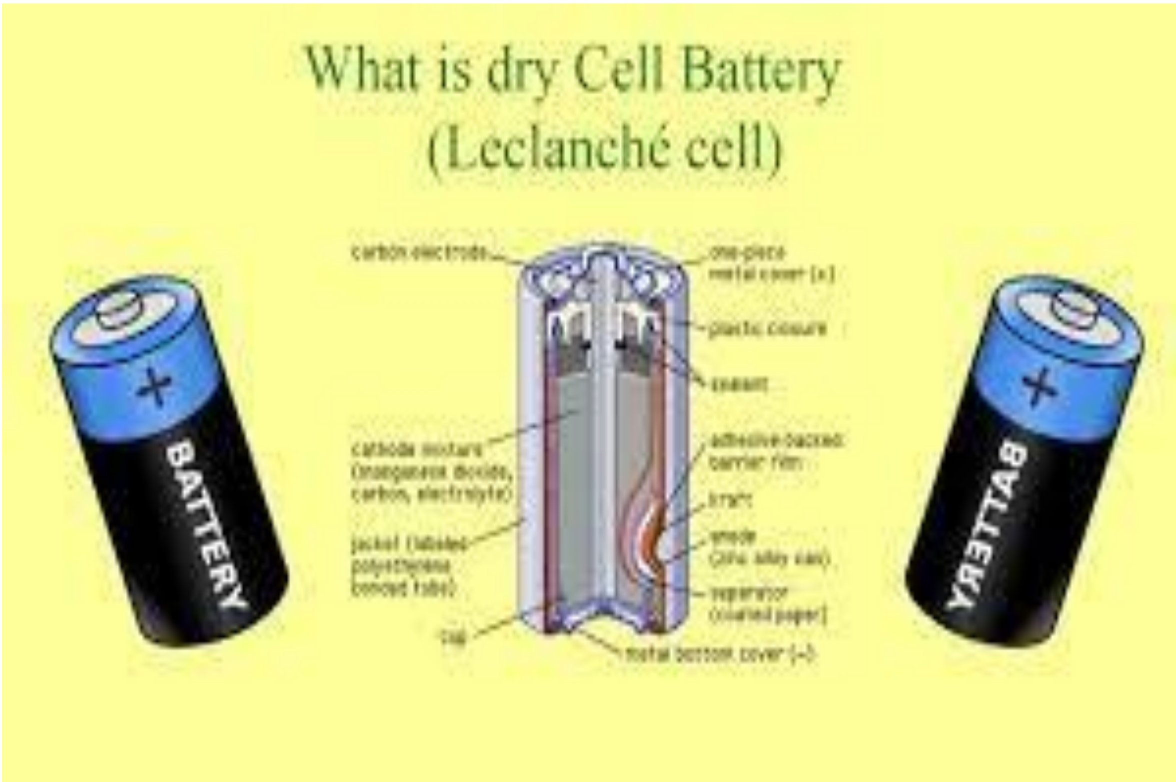


Fig:1: Dry cell



Zinc-air battery:

In zinc-ai battery, the anode is made of zinc plate, a perforated carbon pate treated with water repelants acts as a cathode (Fig.2) NaOH (5M) Or KOH is used as electrolyte . The anode, cathode and the eectroyte are contained in an ebonite or poymeric case.At the anode, zinc react with electrolyte (NaOH or KOH) to form zincate ions which decay into zinc oxide and water. The eectrons reeased at the anode travel to the cathode where oxygen of thew air accepts the eectrons to form hydroxide ions.

The cell is represented as

Zn / NaOH(5M) /Air / C

The cell reactions are

$$2\ Zn\ (s) + 4\ OH^-\ (aq) \rightarrow 2\ ZnO\ (s) + 2\ H_2O\ (l) + 4e^- \quad \text{at anode}$$

$$O_2\ (g) + 2H_2O(l) + 4e^- \rightarrow 4\ OH^-\ (aq) \quad \text{at cathode}$$

$$2Zn\ (s) + O2\ (g) \rightarrow 2ZnO\ (s) \quad \text{Overall cell reaction}$$

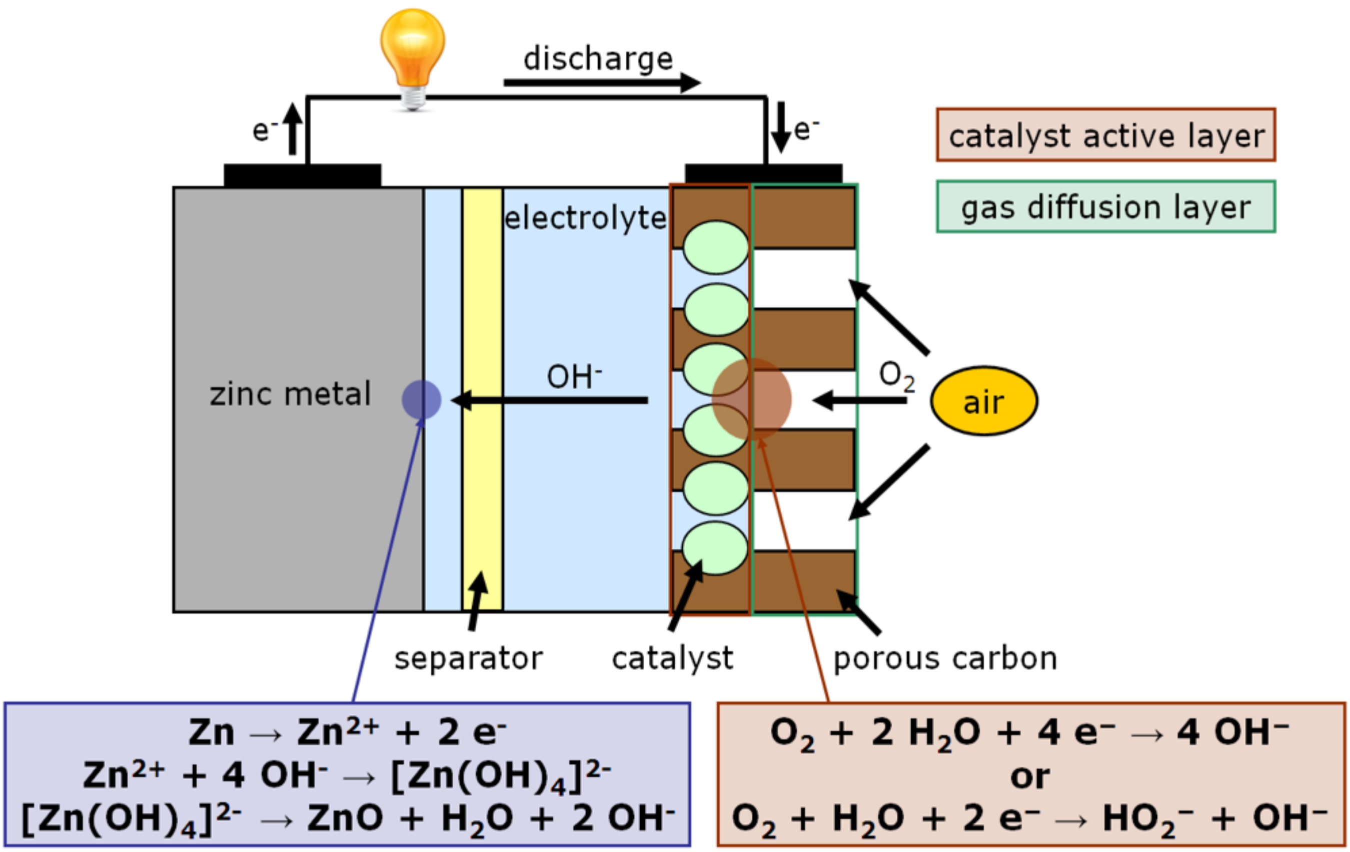


Fig.2: Zinc-air battery

They produce 1.65 v. They are very cheap and are increasingy being used instead of mercury battery

Lithium-MnO_2 battery:

These are primary battery that canot be recharged. In these batteries ithium metal or ithium compounds are used as anode(Fig:3). The cathode is made of specially treated MnO2 crystas obtained by special heat treatment. Since ithum is highey reactive with water and non-aqueous solvents.These sovents cannot be used as electrolyte. Instead, ithium sat solution in propylene carbonate and dimethoxy sats is used as the electrolyte. Sovents ike thionyl choride containing lithium compounds such as LiCl, LiBr, $LiAlCl_4$, $LISO_3CF_3$ can also be used.

THE CELL CAN BE REPRESENTED

At anode, Li→ Li+ + e-

At cathode, $Mn(IV)O_2 + LI^+ + e^- \rightarrow Mn(III)\ O_2\ (Li^+)$

The net cell reaction,

Mn(IV)O2 + Li→ Mn(III) O2 (Li+)

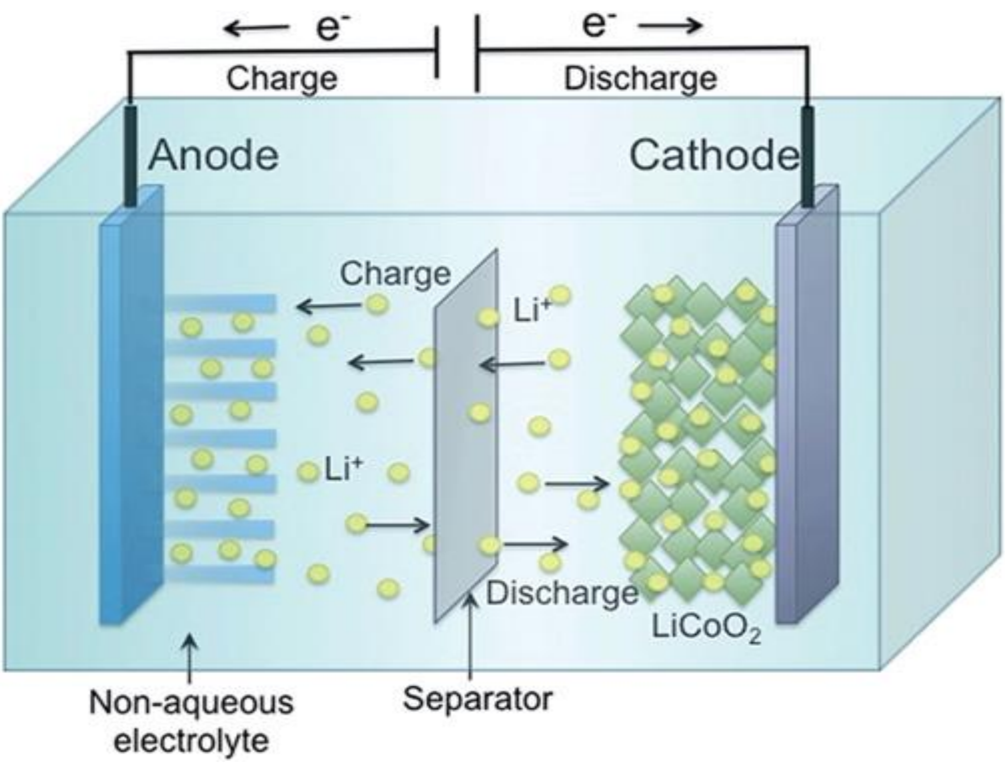


Fig:3: Lithium-MnO2 battery

Applications:

(−) *Anode*	*Li^+* *Polymer electroyte*	*(+)* *MnO2 Cathode*

Use in cocks, cacuators, toys, digita camersa, watches, medica equipment ike pacemakers, thermometers and remote car locks etc.

Fuel cells

A fuel cell is a device that converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines

Eectric energy is obtained without combustion from oxygen and gas that can be oxidized. Fuel cell convertes the chemical energy of the fuel directy to electricity.

$$\text{Fuel+ oxygen-} \longrightarrow \text{Oxidation products + electricity}$$

H_2-O_2 fuel cell:

H2-O2 fuel cell consists of porous screens of graphite coated with a layer of platinum catalyst (Fig.4)). The electrolyte is a cation exchange resin (poly styrene sulphonic acid). The water balance is maintained in the resin by means of a wick. The water formed during the cell reaction is drained out and used for drinking. Several such cells are connected together to obtain desired voltage.

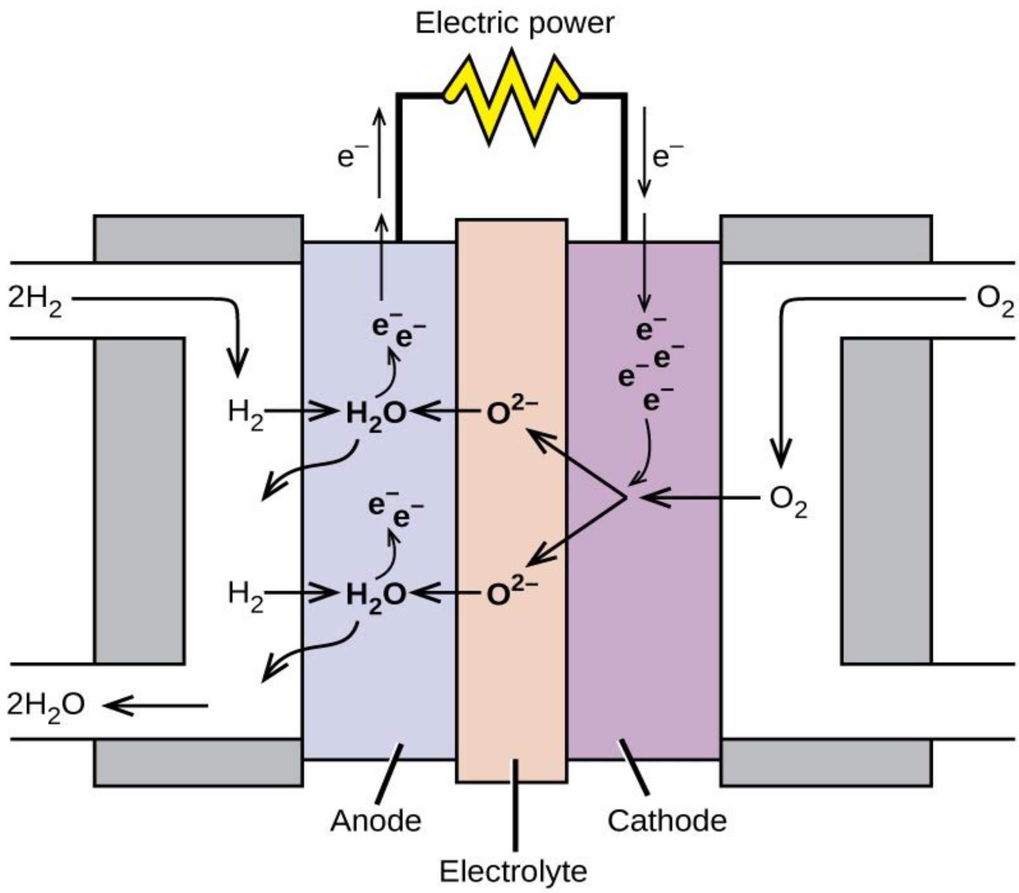


Fig: 4: H_2-O_2 Fuel cell

In a hydrogen fuel cell, the reactions are

Anode reactions; $H_2 \rightarrow 2H^+ + 2e^-$

Cathode reaction; $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Overall cell reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

The voltage is about 1.2 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust. Currently, fuel cells are rather expensive and contain features that cause them to fail after a relatively short time.

Phosphoric acid fuel cells:

The electrodes are made up with porous carbon catalysed by platinum metal with a graphite cloth support. The electrodes used (Fig. 5) in liquid phosphoric acid which is contained in a

Teflon coated silicon carbide matrix placed between the electrodes . phosphoric acid is a non-conductive electrolyte. Which passes hydrogen ions from the anode to the cathode. The production of hydrogen ions is increased by

The use of platinum catalyst

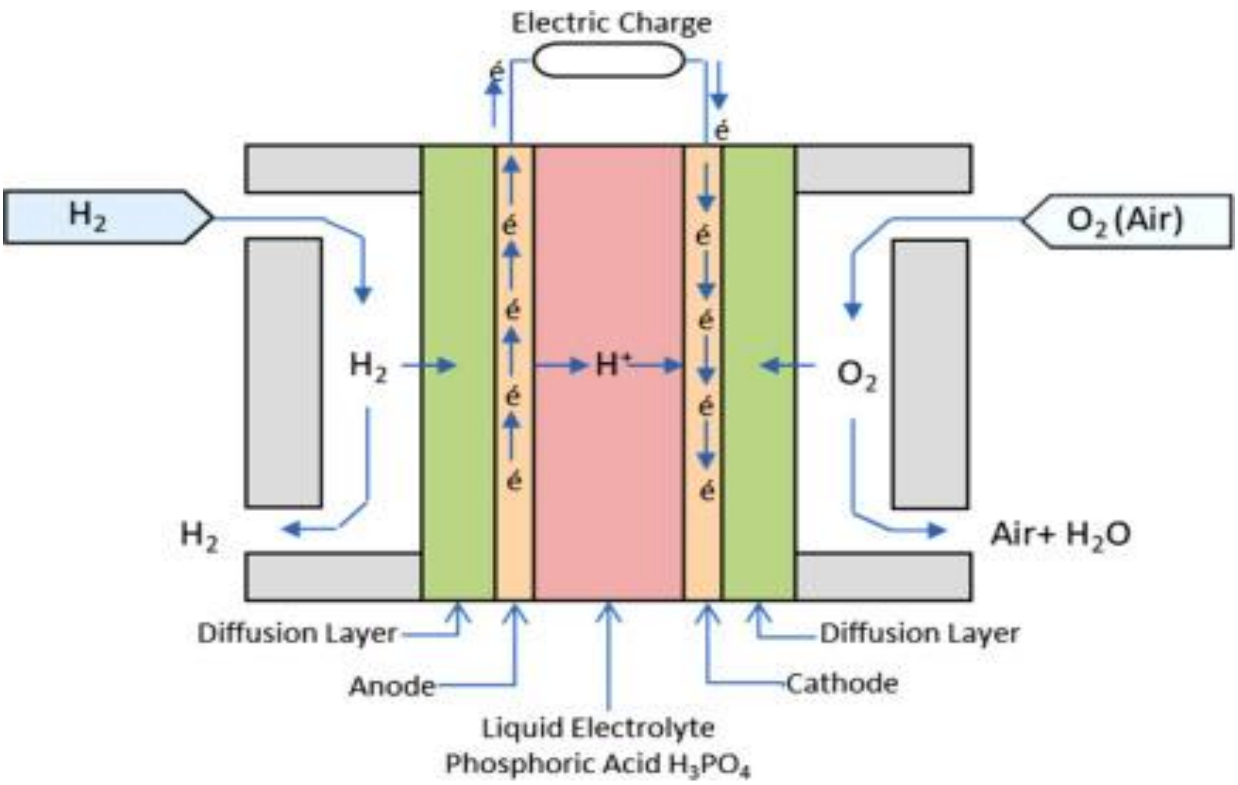
Operating the cell at high temperature (150-200^0 C)

\The hydrogen ions migrate through the electrolyte and combine with oxygen or air at the cathode. To form water. However, the use of platinum catalyst increases the cost of the cell. The cell reactions are as follows:

Anode $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode; O_2 (g) + $4H^+ + 4e^- \rightarrow 2H_2O$(l)

Net cell reactions: $2H_2 + O_2 \rightarrow 2H_2O$



Fig; 5; Phosphoric acid fuel cells

Molten carbonate fuel-cell:

The fuel-cell consists of an anode made up of a porous structure of nickel treated with oxides to prevent sintering. The cathode is made up of lithiated sintered nickel oxide (Fig.6). A molten mixture of carbonate salts like lithium carbonate Li_2CO_3, potassium carbonate and sodium carbonate is used as an electrolyte. The electrolyte is suspended in a porous, chemically inert ceramic lithium aluminium oxide ($LiAlO_2$) matrix. The cell operates at the very high temperature of 650^0 C to enable to melt and to increase ionic mobility through the electrolyte. At high temperature, natural gas, methane and steam are converted into hydrogen rich gas inside the fuel cell. The reacts with the carbonate ions at the anode to form CO_2 and water. The electrons pass to the cathode through the external circuit where the oxygen from the air and CO_2 from the anode reacts with electrons to form carbonate ions. The cell reactions are: Anode reaction $CO_3^{2-}+H_2 \rightarrow H_2O+CO_2+2e^-$

Cathode reaction $CO_2+1/2\ O_{2+}\ 2e^- \rightarrow CO_3^{2-}$

Overall cell reaction $H_2(g)+1/2\ O_2(g) \rightarrow H_2O(g)$

However, due to the use of corrosive electrolytes and high temperature, these cells are less durable, although, they are not easily poisoned by carbon monoxide and carbon dioxide.

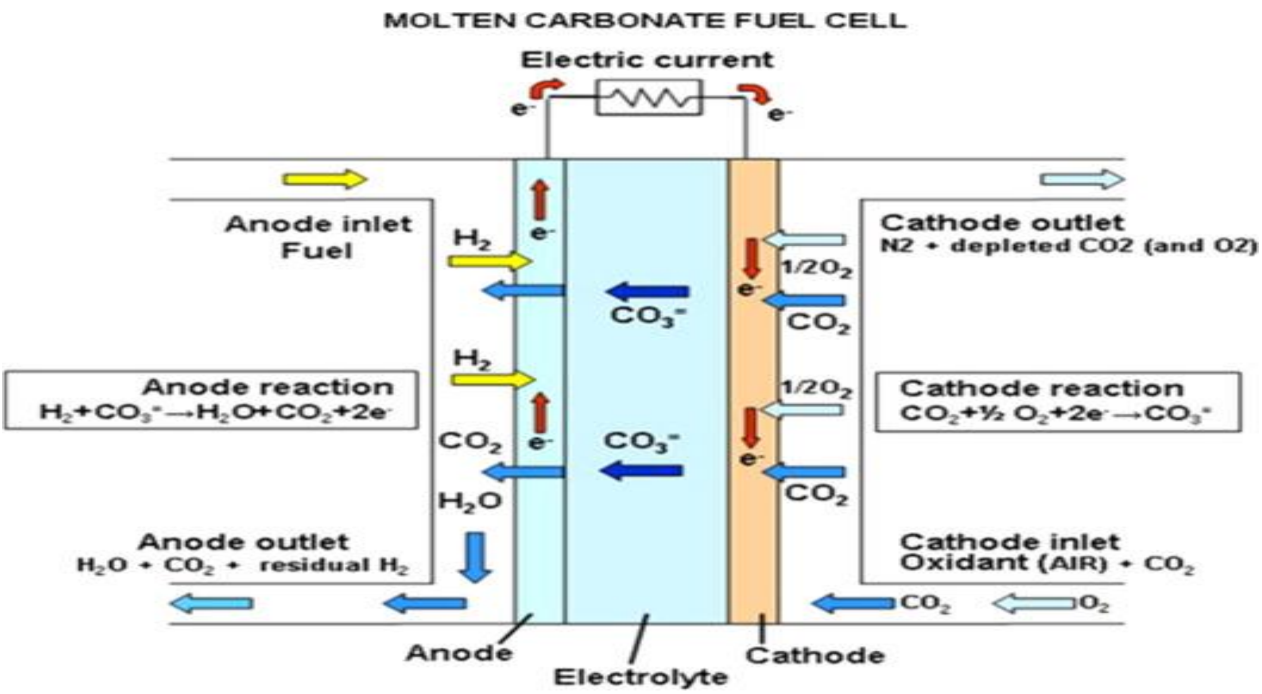


Fig:6: Molten carbonate fuel-cell

ELECTROCHEMICAL SERIES:

When elements are arranged in increasing order (Downwards) of their standard electrode potential, a series called electrochemical series

Standard electrode potential (reduction) at 25^0 C

METAL ION		POTENTIAL IN VOLTS	
$Li^+ + e^- \longrightarrow Li$	(BASE)	-3.05	(ANODE)
$K^+ + e^- \longrightarrow K$		-2.93	
$Ca^{2+} + 2e^- \longrightarrow Ca$		-2.90	
$Na^+ + e^- \longrightarrow Na$		-2.71	
$Mg^{2+} + 2e^- \longrightarrow Mg$		-2.37	
$Al^{3+} + 3e^- \longrightarrow Al$		-1.66	
Zn^{2+} +2e-$\longrightarrow$Zn		-0.76	
$Cr^{3+} + 3e^- \longrightarrow Cr$		-0.74	
$Fe^{2+} + 2e^- \longrightarrow Fe$		-0.44	
$Ni^{2+} + 2e^- \longrightarrow Ni$		-0.23	
$Sn^{2+} + 2e^- \longrightarrow Sn$		-0.14	
$Pb^{2+} + 2e^- \longrightarrow Pb$		-0.13	
$H^+ + e^- \longrightarrow 1/2\ H$		0.00	(REFERENCE)
$Cu^{2+} + 2e^- \longrightarrow Cu$		+0.34	
Ag+ +e-$\longrightarrow$Ag		+0.80	
$Pt^{4+} + 4e^- \longrightarrow Pt$		+0.86	
$Au^+ + e^- \longrightarrow Au$		+1.69	
½ F_2+ +e-$\longrightarrow F^-$	(NOBLE)	+2.87	(CATHODIC)

Applications of Electrochemical Series:

(i)It helps to predict a redox reaction:. A given ion will oxidise all the metals below it and a given metal will reduce ions of any metal placed above it in the series.

Example 1 : Predict the redox reaction between zinc and iron. Given E^0 of Zn^{2+} / Zn is –0.763 and E^0 for Fe^{2+} / Fe is –0.44 V.

The E^0 value of Zn2+/Zn is lower than Fe2+/Fe. It means Zn has a greater reducing power than Fe or zinc can undergo oxidation more quickly than Fe. Zinc will reduce Fe^{2+} ions and itself undergoes oxidation. The given reaction between Zn and Fe will take place as shown.

$$Zn + Fe^{2+} \longrightarrow Fe + Zn^{2+}$$

(ii)It helps to calculate the emf of a galvanic cell;

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

E^0 cell should always be positive. If E^0 cell comes as –ve it means the cell cannot work and electrodes should be interchanged.

Example : Predict the E° for the cell

$$Mg \mid Mg^{2+}(1M) \parallel Ag^{+}(1M) \mid Ag$$

From the table

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

$$E^0 Mg^{2+}/Mg = –2.365V \text{ and}$$

$$E^0 Ag^{+}/Ag = 0.80V$$

$$E0cell = 0.80 – (–2.365)V$$

$$= 0.80 + 2.365$$

$$= 3.165 \text{ V}$$

(iii) It helps to predict the feasibility of a redox reaction:

The feasibility of a redox reaction can be predicted by calculating E0 cell for the redox reaction. The redox reaction is broken in two half reactions : oxidation half reaction acts as anode and reduction half acts as cathode. The positive E^0 cell indicates the redox reaction is possible.

Example 13.3 : Predict whether the following reaction is feasible or not?

$$Cu^{2+}(aq) + 2Ag(s) \rightarrow Cu(s) + 2Ag^{+}(aq)$$

Given $E^0 Ag^{+}/Ag = 0.80V$ and $E^0 Cu^{2+}/cu = 0.34V$

The given redox reaction can be written as two half reactions

Anode (Oxidation) $2Ag(s) \rightarrow 2Ag^{+}(aq) + 2e^{-}$.

Cathode (Reduction) $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

$$E^0cell = E^0 \text{ cathode} — E^0 \text{ anode}$$

$$= E^0\ Cu^{2+}/Cu — E^0 Ag^{+}/Ag$$

$$= 0.34 \text{ V} – 0.80 \text{ V}$$

$$= –0.46V$$

The –ve E^0 value indicates that the above reaction will never take place and silver cannot displace Copper from a solution of Cu^{2+} ion. Instead the reverse reaction would be feasible.

(iv) It helps to predict whether a metal can liberate hydrogen from acids:

Any metal which is above hydrogen in the electro chemical series can liberate hydrogen from acid since it is a better reducing agent than hydrogen. Thus metals like, Zinc, Magnesium, Calcium etc can displace hydrogen from HCl or H_2SO_4but metals like copper, silver cannot displace hydrogen from acid

(v) Calculation of equilibrium constant:

The standard electrode potential,

$$E0=RT/nF \ln K_{eq}= 2.303RT/ nF \log K_{eq}$$

$$K_{eq} = nFXE^0/2.303RT= nE^0/0.0592V$$

Calomel electrode:

The mercury and mercurous chloride electrode.The potential is vary with the KCl solution.When the potassium chloride solution is 0.1 N, 1.0 N and saturated decinormal or normal.The potential of this electrode is equal to the e.m.f. of the cell.

Pt^-, H_2(1atm)/H=?// KCl (0.1 N or N satd.)Hg_2Cl_2, Hg^+

Construction:

It consists of a tube in the bottom of which is a layer of mercury over which is placed a paste of Hg, Hg_2Cl_2.The remaining portion of cell is filled with a solution of normal or decinormal satd. KCl solution. A platinum wire dipping into the mercury layer, is used for making electrical contact. The side tube is used for making electrical contact with a salt bridge. The saturated calomel electrode formulated as:

Hg, Hg_2Cl_2(s), KCl (Satd. solution)

The electrode can be coupled with hydrogen electrode containing solution of unknown PH

Pt-, H_2(1atm)/H=?// Hg_2Cl_2 (s), Hg^+

The e.m.f of the cell

$$E_{cell}= E_{right}-E_{left}=0.2422V+0.0592 V \, PH$$

$$PH= \frac{E_{cell}-0.2422V}{0.0592V}$$

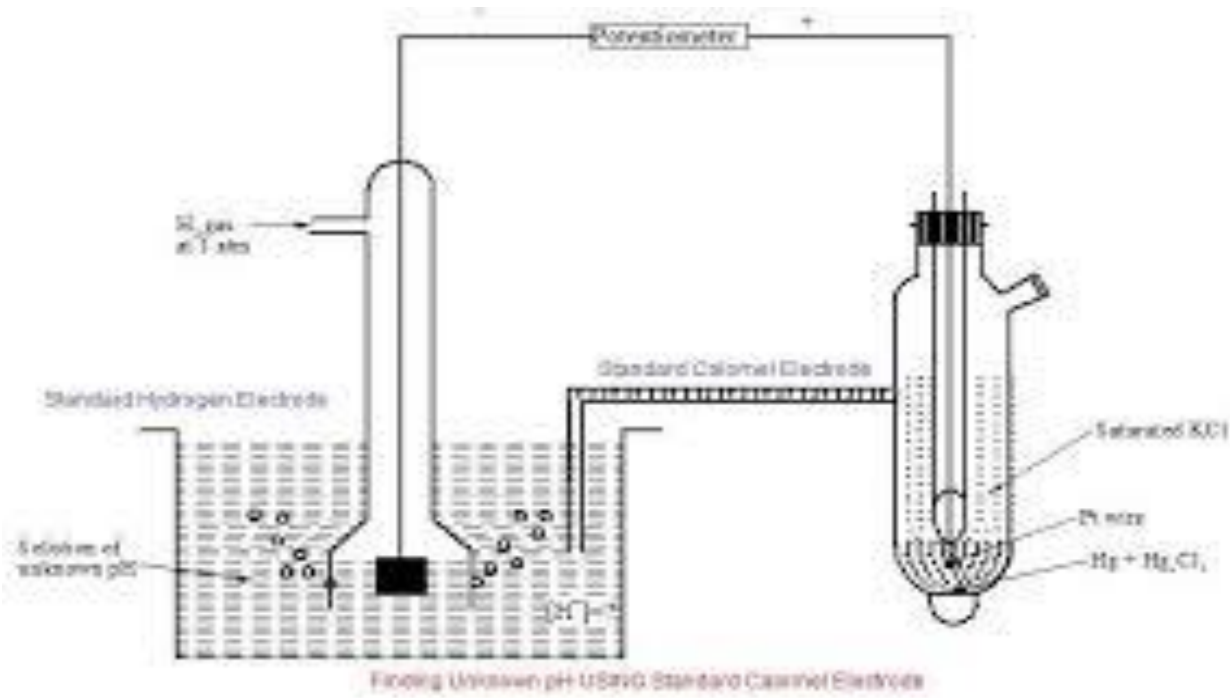


Fig: Determination of pH value of a solution using calomel electrode

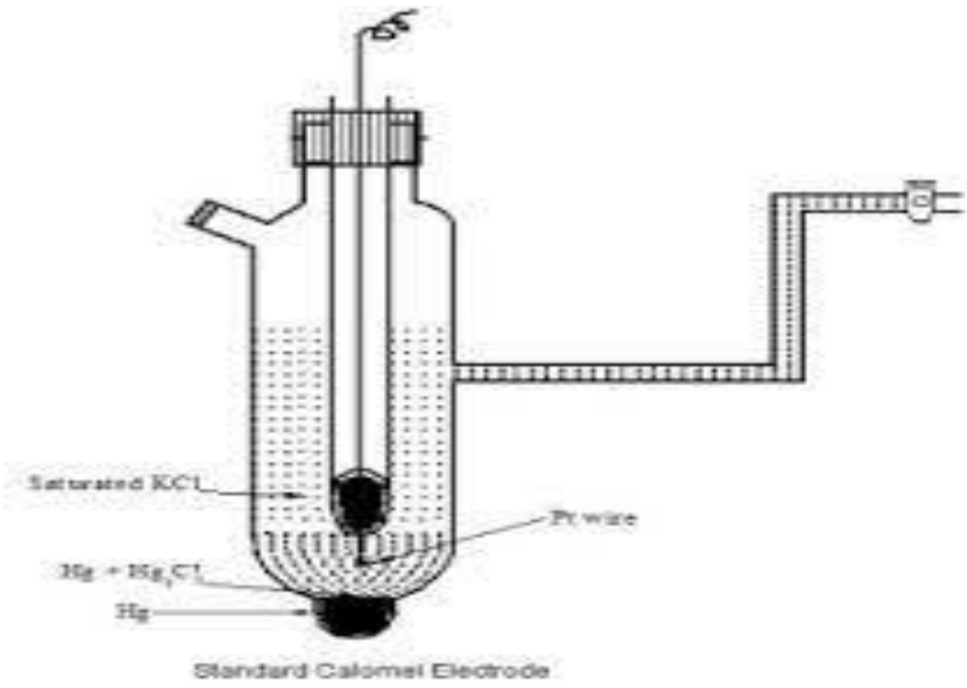
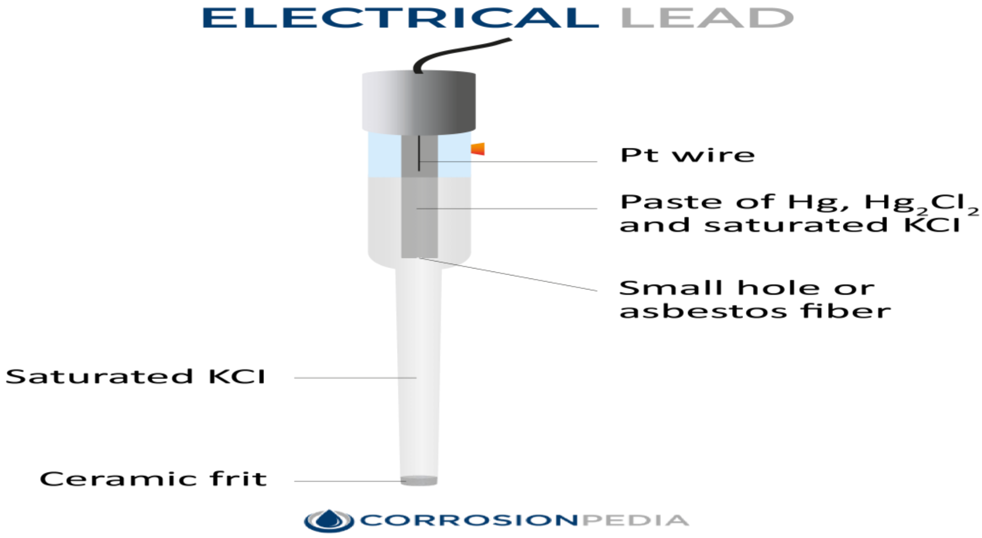
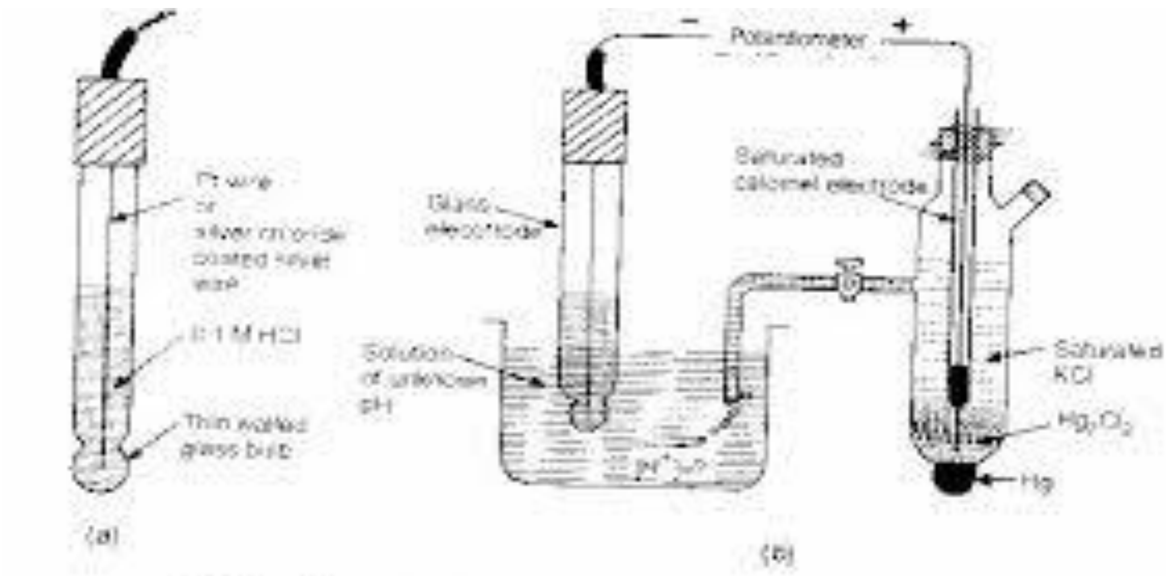


Fig: Saturated calomel electrode



Determination of pH value of a solution using glass electrode



(a) Glass electrode ; (b) determination of pH by using glass electrode.