

16.6 COMMERCIAL CELLS/BATTERIES

As is evident from the previous section, there are many kinds of electrodes. All these electrodes may combine in different ways to give a large number of galvanic cells. Combination of two or more galvanic cells electrically connected to work together, to produce electric energy is called a battery. Commercially, batteries are used as a source of electrical energy for various purposes. Various combinations of electrolytes and electrodes are employed to make batteries for specific purposes. Thus commercial batteries can be made from different types of electrochemical cells.

The term battery should not be used while referring to a single cell. The batteries act as a portable source of electrical energy.

There are many different types of batteries ranging from the relatively large 'flash light' batteries to the miniature versions used for wrist watches or calculators. Batteries consist of either of two types of cells:

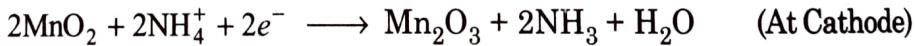
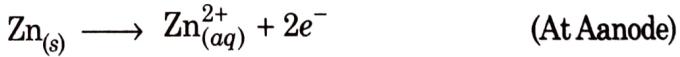
- (i) Primary cells
- (ii) Secondary cells.

16.6.1 Primary Cells

In primary cells, there is fixed amount of energy stored and once that energy has been used up, the cell is considered dead. In other words, the chemical reaction occurs only once and the cell then becomes dead and cannot be used again. Some of the important primary cells are described below:

(a) Dry Cell (Leclanche Cell): This is the most familiar type of dry cell. It consists of a zinc anode which is draped as a container. The cathode is comprised of a graphite rod surrounded by MnO_2 a moist electrolyte paste of NH_4Cl and ZnCl_2 . Starch is added to the electrolyte (NH_4Cl , ZnCl_2 and MnO_2) to make it a thick paste like. To reduce leakage the cell is enclosed in polypropylene cylinder.

The cell reactions are:



Thus, the reduction reaction occurs within the moist paste comprised of NH_4Cl and MnO_2 . The NH_3 which is liberated reacts with Zn^{2+} from ZnCl_2 to form the complex $[\text{Zn}(\text{NH}_3)_2]^{2+}$. The cell can be represented as:



The dry cell 'couple' produces about 1.5 volts.

Dry cells do not have indefinite life. The acidic NH_4Cl corrodes the zinc container even when not in use.

In alkaline version, a modified form of dry cell, the NH_4Cl is replaced by KOH or NaOH . Thus corrosion of Zn container is prevented because zinc does not dissolve readily in basic medium.

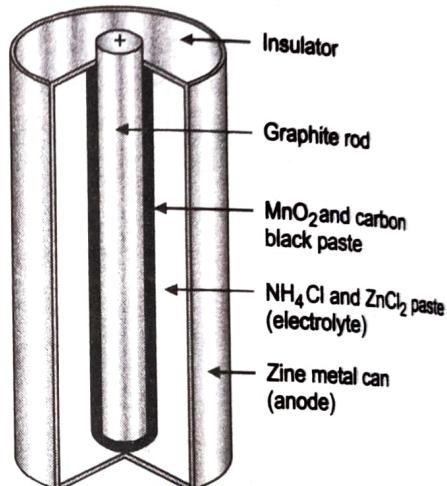
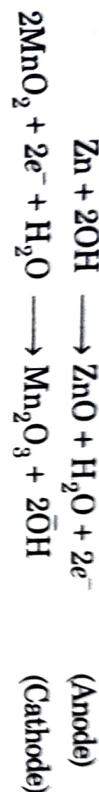


Fig. 16.2 Dry cell.

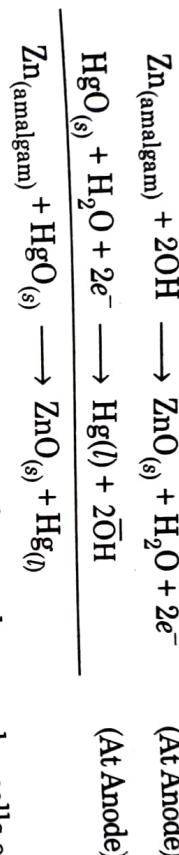
The half cell reactions of alkaline cell are:



The alkaline dry cell lasts much longer compared to Leclanche cell.

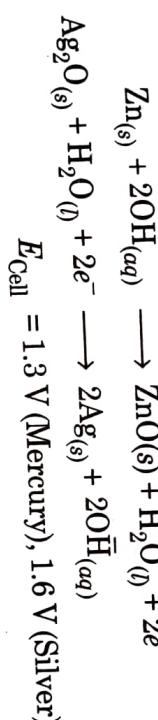
(b) Mercury Cell: The type of cell commonly used for calculations, hearing aids, digital watches and cameras is the mercury cell. The mercury cell, also known as Ruben Cell was developed in 1947. The anode consists of zinc-mercury amalgam and cathode is comprised of a paste of HgO and carbon. A paste of KOH and ZnO forms the electrolyte.

The cell reaction is:



Mercury cells are much more expensive to manufacture than are dry cells or alkaline cells. This is due to high cost of the mercury (II) oxide they contain. At 25°C the cell voltage is 1.344 V. Since the overall cell reaction does not involve any ion in solution whose concentration can change, the cell shows constant potential throughout its life. This makes it useful in sensitive instruments.

Similarly is silver button cell the anodic reaction is the same as mercury cell whereas anodic reaction involves Ag_2O :



Other types of primary cell include lithium cell which has been developed for special uses where long life, small size and very low power are required. Cameras, heart pacemakers and electronic wrist watches are powered by these cells.

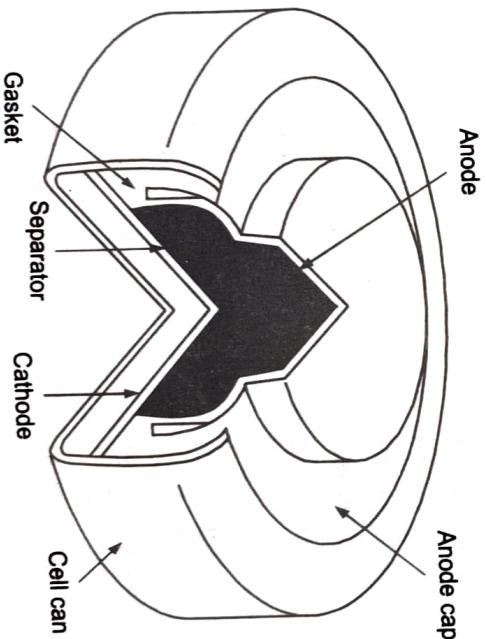


Fig. 16.3 Mercury cell.

A brief account of primary cells is given in Table 16.2

Tabel 16.2: Primary Cells

Type	Anode (-)	Cathode (+)	Electrolyte	Voltage	Uses
(1) <i>Léclanche or dry cell</i> $\text{Zn} \mid (\text{ZnCl}_2)_\text{l}$, $\text{NH}_4\text{Cl} \mid$ MnO_2, C	Zinc case $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq})$ $+ 2e^-$	Carbon rod in contact with carbon & MnO_2 $\text{NH}_4^+(\text{aq}) + \text{MnO}_2(\text{s})$ $+ e^- \rightarrow \text{NH}_3(\text{aq})$	Paste of NH_4Cl , ZnCl_2 (acid electrolyte)	1.5 volt	Low drain applications such as radios, torches, liquid crystal calculators, toys.
(2) <i>Alkaline cell</i> $\text{Zn, ZnO} \mid \text{KOH}$ (paste) MnO_2, C	Brass rod in contact with powdered zinc $\text{Zn(s)} + 2\text{OH}^-(\text{aq}) \rightarrow$ $\text{ZnO(s)} + \text{H}_2\text{O(l)}$ $+ 2e^-$	Steel case in contact with carbon & MnO_2 $\text{MnO}_2(\text{s}) + \text{H}_2\text{O(l)} +$ $e^- \rightarrow \text{MnO(OH)(s)} +$ $\text{OH}^-(\text{aq})$	Paste of 7 M KOH (alkaline electrolyte)	1 volt	High current or high capacity such as electronic graphic flash units, tape recorders, radios, tape can deliver higher current than Leclanche cell without severe voltage drop.
(3) <i>Mercury button Cell</i>	Steel cap in contact with powdered zinc	Steel case in contact with powdered HgO $\text{HgO(s)} + \text{H}_2\text{O(l)} +$ $2e^- \rightarrow \text{Hg(l)} +$ $2\text{OH}^-(\text{aq})$	Paste of KOH (alkaline electrolyte)	1.3 volt	Watches, pacemakers, hearing aids, microphones.
(4) <i>Silver button cell</i> $\text{Zn, ZnO} \mid \text{KOH(paste)}$ $\text{Ag}_2\text{O, Ag}$	Steel cap in contact with powdered zinc $\text{Zn(s)} + 2\text{OH}^-(\text{aq})$ $\rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)}$ $+ 2e^-$	Steel case in contact with powdered Ag_2O $\text{Ag}_2\text{O(s)} + \text{H}_2\text{O(l)} +$ $2e^- \rightarrow 2\text{Ag(s)} +$ $2\text{OH}^-(\text{aq})$	Paste of KOH (alkaline electrolyte)	1.3 volt	Watches, pacemakers, hearing aids, microphones.

16.6.2 Secondary Cells

A secondary cell is one in which electrodes and the electrolyte are altered by the chemical action that takes place when cell delivers the current. However, these cells can be restored to their original condition by forcing an electric current through them. In other words, such batteries can be recharged and the cycle is repeated a number of times.

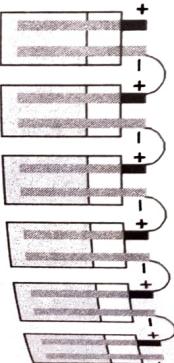
The automobile battery (lead storage battery) and nickel cadmium cells fall under this category.

(i) Lead Storage Cell: In 1859, the French physicist Gaston Planté (1834-89) invented a device called the lead-acid accumulator, which is still used today as motor car battery with minor changes. It is an example of secondary electrochemical cell, since it can be recharged.

The cell consists of a lead grid filled with a spongy lead as anode and a lead grid packed with lead oxide as cathode. A solution of H_2SO_4 (38% by mass) is used as an electrolyte. This is the battery acid which one can buy at service stations.

The battery consists of 6 such cells connected in series, each cell having an emf of about 2 V, giving 12 V as the overall emf of the battery.

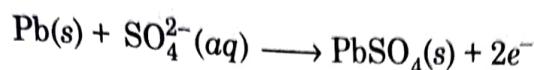
When the battery is discharging, i.e., when it is supplying a current, the reactions are



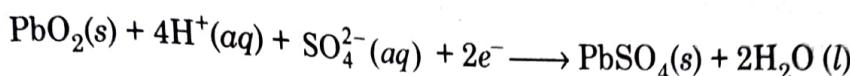
$$6 \times 2 \text{ V} = 12 \text{ V}$$

Fig. 16.4

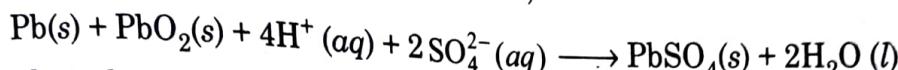
At the anode:



At the cathode:



The overall reaction (during discharge) is, therefore,



Note that the electrolyte is sulphuric acid (H_2SO_4), which is gradually used up. Both electrodes become coated with an insoluble layer of lead sulphate, which, being an insulator, would eventually ruin the battery.

DISCHARGING

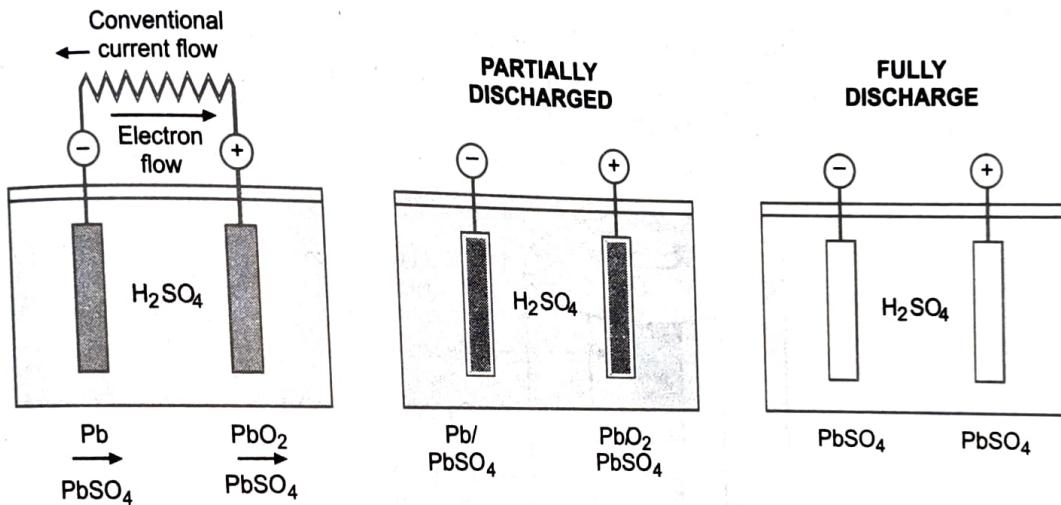


Fig. 16.5

As the battery provides energy, it is discharged and this leads to the gradual formation of lead sulphate at the electrodes, and a steady decrease in the concentration of the sulphuric acid:

If the battery is totally discharged, both electrodes will have been converted to lead sulphate. It will no longer be able to provide a current, and cannot be recharged. It is only good for scrap!

CHARGING

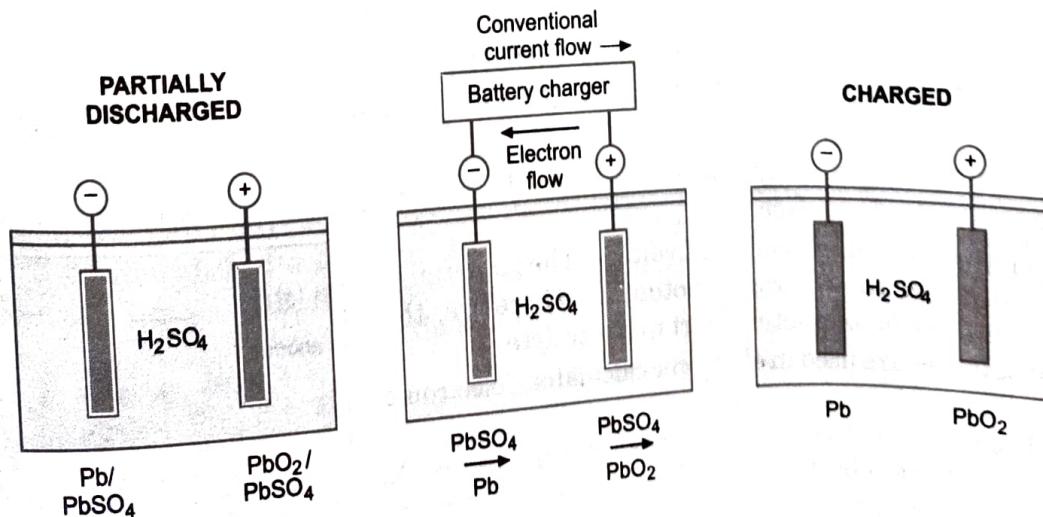
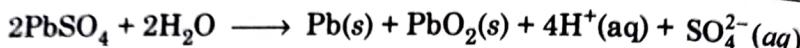
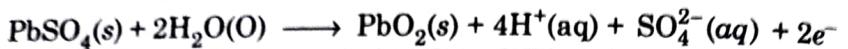
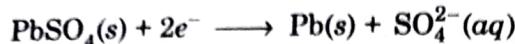


Fig. 16.6

When the battery is being charged, (using a battery charger or the motor car's alternator), electrons are supplied to the anode of the battery and this converts the lead sulphate to lead. At the same time, the lead sulphate at the anode is converted to lead dioxide. That is the cell reactions are reversed and the cell operates like an electrolyte cell.

The reactions are:



(at cathode)

(at anode)

The concentration of H_2SO_4 decreases during discharging whereas it increases during charging. Thus the extent to which the battery is discharged can be checked by measuring the density of H_2SO_4 by hydrometer.

The lead storage cell is both a voltaic cell and an electrolytic cell. When electricity is being drawn from the cell to start the car it acts as voltaic cell. Whereas when the car is running, the cell is being recharged, it acts as an electrolytic cell. Actually, the alternator forces electrical energy generated due to its motion into the cell causing electrolytic reaction to take place.

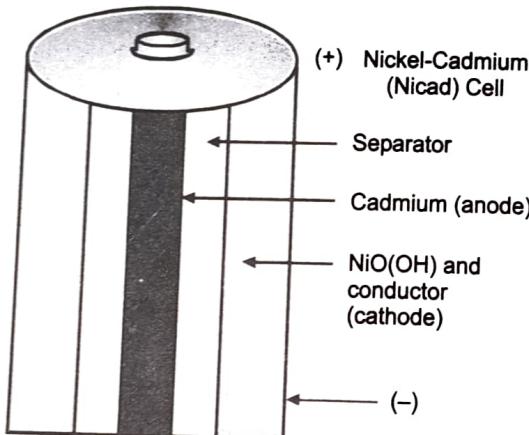
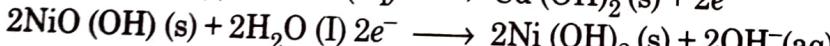


Fig. 16.7 Nicad cell.

(ii) Nickel-Cadmium (Nicad) Cell: Nickel-cadmium cell consists of a cadmium anode and a paste of $\text{NiO(OH)}_{(s)}$ comprises the cathode. The cell reactions are:



(At Anode)



(At Cathode)

$$E_{\text{cell}} = 1.4 \text{ V}$$

The reactions can be easily reversed, because the reaction products, $\text{Ni}(\text{OH})_{2(s)}$ and $\text{Cd}(\text{OH})_{(s)}$ adhere to the electrode surface.

Nicad battery has fairly constant voltage. The potential of Cd anode is below the hydrogen potential. Therefore, the cadmium electrode is completely inert to electrolyte.

Nicad batteries are used in electronic calculators, electronic flash units, transistors etc.

(iii) Lithium Solid-State Battery (Rechargeable): These are Lightweight batteries which produce high voltages. Lithium solid-state batteries are common in computers, digital cameras, cell phones, etc. The cell reactions are:

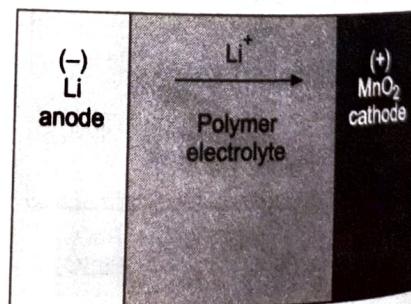
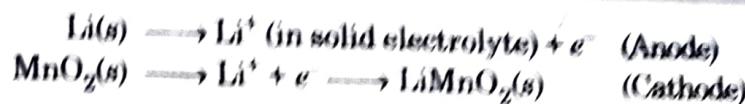


Fig. 16.8 Lithium Solid-state Battery



A brief account of secondary batteries is given in Table 16.3.

Table 16.3

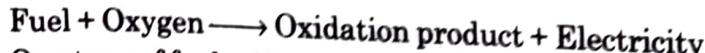
Type	Anode (-)	Cathode (+)	Electrolyte	Voltage	Uses
(1) Lead-acid battery (or accumulator)	Lead plates $\text{Pb}(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^-$ $\text{Pb}, \text{PbSO}_4 \text{H}_2\text{SO}_4(aq) \text{PbO}_2, \text{Pb}$	Lead plates covered with PbO_2 $\text{PbO}_2(s) + 3\text{H}^+(aq) + \text{HSO}_4^-(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$	4M H_2SO_4	2.1 volts per cell (6 cells in series makes up a 12 volt car battery)	Motor vehicle batteries. As cell delivers current, lead sulfate deposits on electrodes and $[\text{H}_2\text{SO}_4]$ falls. Six 2 V cells connected in series make up a 12 V battery. To obtain high current output from the battery, the surface area of the electrodes in contact with the electrolyte must be large and the plates close together.
(2) Nickel-cadmium cell (NiCad)	Grid covered with cadmium $\text{Cd}(s) + 2\text{OH}^-(aq) \rightarrow \text{Cd}(\text{OH})_2(s) + 2e^-$ $\text{Cd}, \text{Cd}(\text{OH})_2 \text{KOH} \text{NiO}_2, \text{Ni} \text{Ni}(\text{OH})_2, \text{Ni}$	Grid covered with nickel (III) hydroxide $\text{NiO(OH)}(s) + \text{H}_2\text{O}(l) + e^- \rightarrow \text{Ni}(\text{OH})_2(s) + \text{OH}^-(aq)$	KOH	1.25 volts	Video cameras, phones, cordless drills, laptop computers

16.7 FUEL CELLS

These are the electrical cells which convert the energy from the combustion of fuels into the electrical energy. It differs from an ordinary battery that the reactants are not contained within the cell, but are continually supplied from outside i.e. the fuel and the oxidant are supplied from outside the cell to the electrodes at which they undergo reactions.

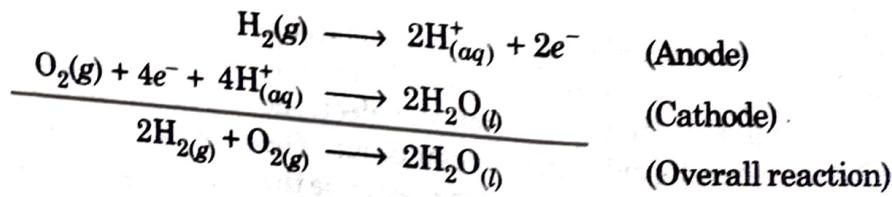
Fuel cells is not a primary cell, since neither the reactants nor products are stored. It is not a secondary cell which can be recharged. Rather, the reactants have to be fed continuously and the product have to be removed. So it is reasonable to keep fuel cell in a separate category.

The fuel cell converts the chemical energy of the fuel directly to electricity. The essential process in a fuel cell is:



One type of fuel cell, used in space crafts and advanced non-linear submarines, is hydrogen-oxygen fuel cell.

Hydrogen-Oxygen Fuel Cell: It consists of two inert porous electrodes which are made up of either graphite impregnated with finely divided Pt or a 75/25 alloy of Pd with Ag or Ni. The electrolyte solution is 25% KOH. Hydrogen and oxygen are bubbled through the anode and cathode compartment respectively. The cell reactions are:



The theoretical e.m.f. of the cell is 1.23 V

$$E^\circ = E_{\text{oxd.}}^\circ + E_{\text{red.}}^\circ = 0.83 \text{ V} + 0.40 \text{ V} = 1.23 \text{ V}$$

However, in actual practice, the e.m.f. of the cell is about 0.8 V to 1.0 V.

The only by-product formed in fuel cell is water which is used by the spacecraft or submarine crews.

Fig. 16.10 shows a basic design of a fuel cell. However, in practice, it is very complex piece of equipment.

Let us look in more detail at the key cell components:

(a) **The Fuel:** Oxygen is usually taken from the air (filtered and cleaned before introduction to the cell) and hydrogen is generally made from the decomposition of a hydrocarbon source (such as methane). Any hydrogen rich material can serve as possible fuel source such as methanol, ethanol, propane etc.

(b) **The Electrodes:** The function of the electrodes is to bring about reaction between the reactant (fuel or oxygen) and the electrolyte, without itself being consumed or corroded. They must also, by definition, be an electronic conductor and bring the three phases (gaseous fuel, liquid electrolyte and electrode itself) to contact. They must be good electron sources or sinks.

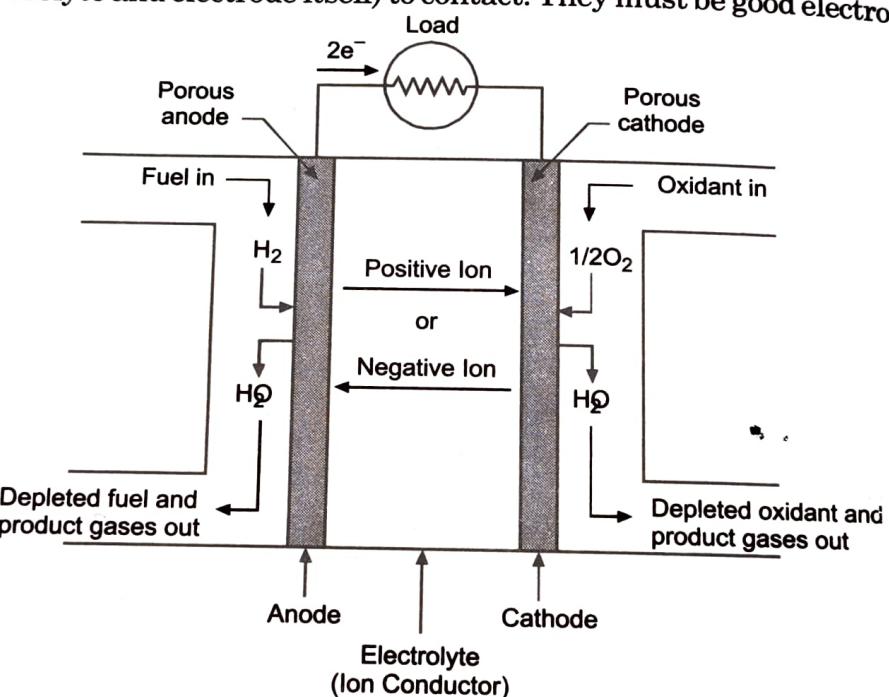


Fig. 16.9 Schematic of an individual fuel cell.

There are several methods for gas-liquid interface stabilisation which rely on capillary action. A biporous electrode allows liquid to penetrate the small pores and a gas pressure is applied that drives the liquid out of the large pores. All this is set-up within the structure of the electrode. Then the merging of the two phases may be achieved in several ways. The electrolyte will tend to form a thin wetting film over part of the internal surface of the electrode. The reactant gas, sparingly soluble in the electrolyte, can diffuse through this film and reach the electrode surface, where a solid-liquid reaction can occur. The electrode structure have to be designed to maximise the area of the wetted film (Fig. 16.10).

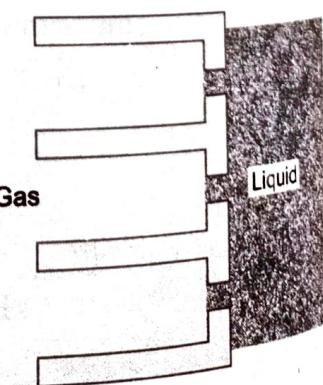


Fig. 16.10

(c) **The Electrolyte:** A large range of fuel cells have been developed using a variety of different electrolytes. These developments have been driven by the desire to improve the economics of the cells and the potential applications at a range of different temperatures. In fact fuel cells are usually classified in terms of their electrolyte contents. Electrolytes most often used are aqueous KOH or H_2SO_4 or ion exchange resin saturated with water.

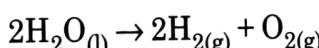
Depending upon the electrolyte used the fuel cell can be of different types. Table 16.4 gives an account on the different types of fuel cells.

Table 16.4 Fuel Cells

Type	Anode (-)	Cathode (+)	Electrolyte Voltage	Uses
Alkaline fuel cell	Porous carbon anode with catalyst in contact with $H_2(g)$ $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$	Porous carbon cathode with catalyst in contact with $O_2(g)$ $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	Hot KOH (aq) ~ 1 volt	<ul style="list-style-type: none"> Promising future More efficient than coal or gas-fired power stations. Non-polluting Porous electrodes lined with catalysts, eg. Ni or Pt, making it expensive
Acid fuel cell	Porous carbon anode with catalyst in contact with $H_2(g)$ $H_2(g) \rightarrow 2H^+(aq) + 2e^-$	Porous carbon cathode with catalyst in contact with $O_2(g)$ $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	hot H_3PO_4 (aq) ~ 1 volt	<ul style="list-style-type: none"> Systems required to continuously supply reactants and remove products CH_4, CH_3OH, C_3H_8 can be used instead of $H_2(g)$

16.8 ELECTROLYSIS

Electrolysis refers to the decomposition of a substance by an electric current. In other words, the process of decomposing a compound using electricity is called **electrolysis**.



Electrolysis is a most important industrial process with a wide application. However, the largest application is that of the manufacture of chlorine and sodium hydroxide from concentrated aqueous sodium chloride in the Chlor-alkali industry.

16.8.1 Electrolytic Cells

The apparatus used to bring about electrolysis is called *electrolytic cell* (Fig. 16.18). It consists of a glass vessel in which the electrolyte in the form of an aqueous solution or in the molten state is taken. Two metal rods are dipped into it and are connected to a source of electricity, i.e., battery. These rods are called electrodes; the one connected to the negative pole of the battery is called cathode and the other connected to the positive pole of the battery is called anode.

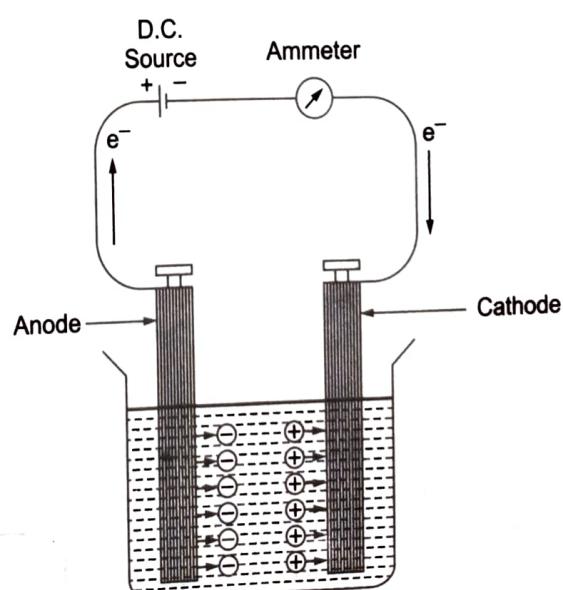


Fig. 16.11 Electrolytic cell.