5.84 Calculate the number of coulombs required to deposit 5.4 g of Al, when the electrode reaction is, $Al^{3+} + 3e^- \longrightarrow Al$.
(Given : Atomic mass of Al = 27 g mol^{-1}, F = 96500 C mol^{-1}). *(CBSE Delhi, 1994)*
[Ans. 57900 C]

5.85 Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency is 50%. If the potential drop across the cell is 3 volts, then how much energy will be consumed? *(I.I.T., 1990)*
[Ans. 115800 C, 347400 J]

5.86 How many molecules of chlorine should be deposited from sodium chloride in 1 minute by a current of 300 mA?
[Ans. 5.61×10^{19}]

5.87 A constant current was passed through a solution of $AuCl_4^-$ between gold electrodes. After a period of 14 minutes, the cathode required an increase in mass of 1.808 g. Calculate the quantity of current passed in solution. What was the magnitude of current? (Atomic mass of gold = 197.0).
[Ans. 2656.9 C, 3.163 amp]

5.88 A current of 4 amperes was passed for 2 hours through a solution of copper sulphate when 5.0 g of copper was deposited. Calculate the current efficiency.
[Ans. 52.77%]

5.89 Two voltameters containing $CuSO_4$ and acidulated water respectively are connected in series and the same current is passed for some time. 0.3177 g copper is deposited in the first. Calculate the weight of liberated hydrogen in the second. (At. wt. of Cu = 63.5 and H = 1.008). *(BITS Ranchi, 1991)*
[Ans. 1.008×10^{-2} g]

5.90 What is meant by Faraday constant? *(CBSE Outside Delhi., 1999)*

5.91 Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write overall reaction.

[Given : $E^\circ_{Na^+/Na} = -2.71$ V, $E^\circ_{Cl_2/2Cl^-} = 1.36$ V and $\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O(l)$; $E^\circ = 1.23$ V]. *(CBSE Outside Delhi Comptt., 2003)*

5.92 Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write overall reaction. *(CBSE Delhi Comptt., 2004)*

5.93 Silver is electrodeposited on a metallic vessel of surface area 800 cm^2 by passing current of 0.2 amp for 3 hours. Calculate the thickness of silver deposited.
(Density of silver = 10.47 g cm^{-3}, atomic mass of silver = 107.92 amu). *(CBSE Outside Delhi Comptt., 2004)*
[Ans. 2.89×10^{-4} cm]

5.94 Predict the products of electrolysis obtained at the electrodes in each case when the electrodes used are of platinum :
(i) An aqueous solution of $AgNO_3$ (ii) An aqueous solution of H_2SO_4. *(CBSE Outside Delhi, 2005)*

5.9. SOME COMMERCIAL CELLS

A galvanic cell (electrochemical cell) converts the chemical energy of a redox reaction into electrical energy. Thus a galvanic cell constitutes a source of electrical energy. In principle, any redox reaction can be used to generate electrical energy in a galvanic cell, but practically it is not possible to use most of the redox reactions for the generation of electrical energy in a galvanic cell. Only a few redox reactions have been found suitable for the construction of commercial cells. The commercial cells are popularly known as **batteries.** The term battery is not strictly correct when used to refer a single cell. In true sense, *a battery is an arrangement of two or more galvanic cells connected in series.*

A commercial cell or battery should meet the following requirements.
(i) It should be light in weight and compact in size.
(ii) Its voltage should not vary appreciably during the use.
(iii) It should have a reasonably long life.
Commercial cells (or batteries) are of following two types :
(a) Primary cells (b) Secondary cells
In the forthcoming subsections we shall study important characteristics of these cells. We shall also learn about some important commerical cells.

5.9.1. Primary Cells

Primary cells are those cells in which the cell reaction occurs only in one direction and the reaction can not be reversed by an external energy source. Thus, in primary cells, the reaction occurs only once and after a certain period of time the battery becomes dead and can not be used again. Such cells can not be recharged. Some important primary cells are Daniell cell, dry cell, mercury cell etc. A brief description of dry cell and mercury cell is given below.

1. Dry Cell : The dry cells are the most familiar type of commercial cells. Dry cell is a compact form of *Leclanche cell* which was discovered by *G. Leclanche* (1868). A dry cell is shown in Fig. 5.16. It consists of a zinc metal container which works as anode. A graphite rod surrounded by powdered MnO_2 and carbon acts as cathode. The space between the zinc container (anode) and graphite rod (cathode) is filled with a moist paste of NH_4Cl and $ZnCl_2$ as shown in Fig. 5.16. The zinc metal container is wrapped with a card board cover or thick paper lining. The cell is sealed on the top with pitch or wax.
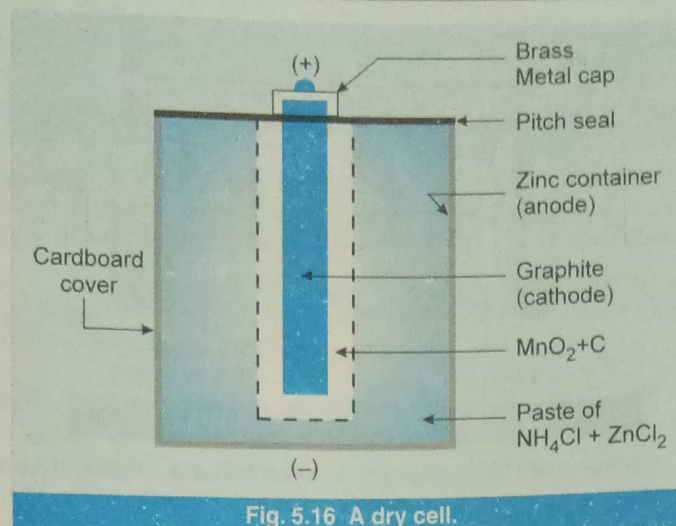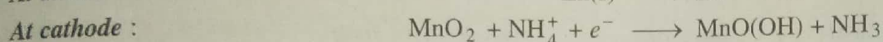
Fig. 5.16 A dry cell.

The electrode reactions involved during the operation of the cell are complex. However, they can be written approximately as given below.
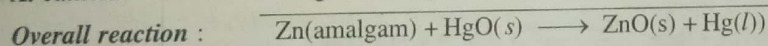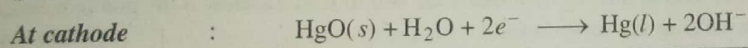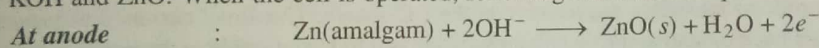
At anode :
$$Zn(s) \longrightarrow Zn^{2+} + 2e^-$$

At cathode :
$$MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$$

At anode, zinc (from the container) gets oxidised to Zn^{2+} ions. At cathode, manganese is reduced from +4 state to +3 state. Ammonia produced in the cathode reaction combines with Zn^{2+} ions liberated in the anodic reaction to form $Zn(NH_3)_4^+$ ion. The complexation of Zn^{2+} by NH_3 molecules decreases the concentration of free Zn^{2+} ions. This increases the voltage of the cell.

The cell potential of a dry cell is approximately 1.25 V to 1.5 V. Dry cells do not have a long life because NH_4Cl paste used in a dry cell is acidic in nature and corrodes the zinc container even when not in use. A dry cell is a primary cell and can not be recharged.

2. Mercury cell : Mercury cell is a new type of dry cell and is a very convenient source of electrical energy for applications having small electrical circuits such as watches, camera, hearing aids etc.

It consists of zinc-mercury amalgam as the anode. A paste of HgO and carbon acts as the cathode. The electrolyte used in the cell is a paste of KOH and ZnO. When the cell is operated, following reactions take place.

At anode :
$$Zn(amalgam) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$$

At cathode :
$$HgO(s) + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$$

Overall reaction :
$$Zn(amalgam) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

The overall reaction (cell reaction) does not involve any ion is solution whose concentration may change. Therefore, the potential of the cell remains constant not only during its operation but throughout its life. The cell potential of a mercury cell is approximately 1.35 V.

5.9.2. Secondary Cells

The cells which can be recharged by passing a direct current through them are called secondary cells. These are *repeated action cells*. After every use they can be recharged and thus can be used again and again. Secondary cells are also called *storage cells* or *accumulators* because they are capable of storing electrical energy in the form of chemical energy. Some typical secondary cells are lead storage cell, nickel-cadmium cell etc. A brief description of some of the important secondary cells is as follows.

1. Lead storage battery : The most commonly used battery in automobiles (*e.g.*, cars, buses, trucks etc.) and in household power invertors is *lead storage battery.* It consists of a number of *lead storage cells* (usually six or twelve) connected in series.

A **lead storage cell** is a galvanic cell in which anode is made of a grid of lead (or an alloy of lead and antimony) packed with finely divided sponge lead, while cathode is a grid of lead coated with red brown lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulphuric acid (appoximately 38% by mass) having density of 1.3 g mL^{-1}. A lead storage cell may be represented as

$$Pb \mid PbSO_4(s) \mid H_2SO_4(38\%) \mid PbO_2(s) \mid Pb$$
$$\text{(anode)} \qquad\qquad\qquad\qquad \text{(cathode)}$$
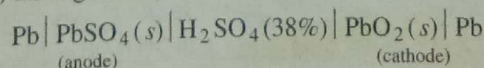
The cell potential of a lead storage cell is 2 volts.

As mentioned above, a lead storage battery is constructed by connecting a number of lead storage cells in series. A battery consisting of six cells gives an emf of 12 V. In order to obtain an emf of 24 V, twelve cells need to be connected together in series. In a lead storage battery, the anode and cathode plates (called *grids*; anode : Pb grid packed with finely divided sponge lead, cathode : Pb grid coated with PbO_2) are arranged alternatively and are immersed in a bath of 38% sulphuric acid solution as shown in Fig. 5.17. The container is made of a tough insulating material. The anode and cathode plates are separated from each other by *separators* made of some
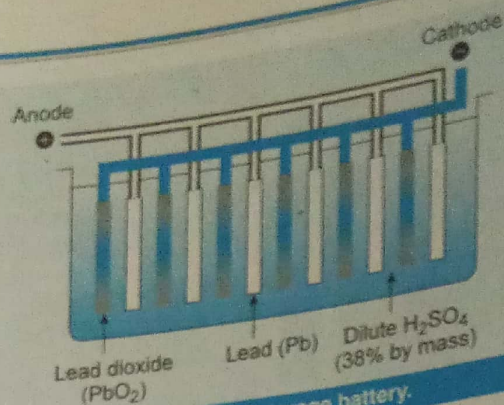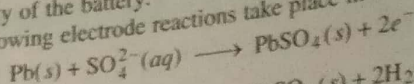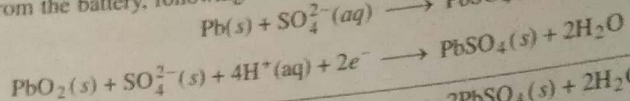
Fig. 5.17 A lead storage battery.

insulating material. The anode and cathode plates are separately connected to one another. This increases the surface area of the electrodes and hence the current producing capacity of the battery.

When current is drawn from the battery, following electrode reactions take place in each cell in the battery.
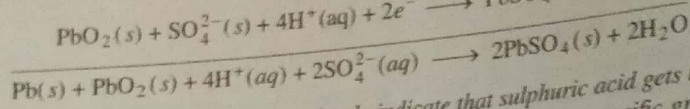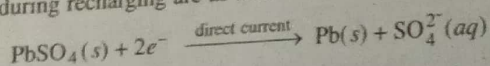
At anode :
$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

At cathode :
$$PbO_2(s) + SO_4^{2-}(s) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$$

Overall reaction :
$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$$
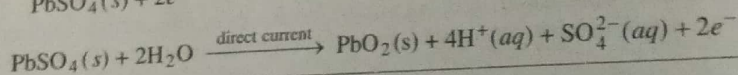
The electrode reactions and the overall cell reaction clearly indicate that sulphuric acid gets used up during the discharge of the cell. Therefore when current is drawn from the cell, sulphuric acid gets diluted and its specific gravity falls. Both the electrodes get coated with the white precipitate of lead sulphate ($PbSO_4$). When the specific gravity of sulphuric acid falls below 1.2 g cm^{-3} and both the electrodes get covered with $PbSO_4$, the cell reaction stops and the cell (or battery) is said to be **discharged.** At this stage the cell or battery needs recharging.

Recharging of a dischaged cell (or battery) : The discharged lead storage cell (or lead storage battery) can be recharged by passing a direct current through it in the opposite direction. For this purpose, the negative electrode of the storage cell is connected to the negative of the DC source and the positive electrode of the cell to the positive of the DC source. The direct current thus passed reverses the electrode reactions and converts lead sulphate back to lead at the negative electrode and to lead dioxide at the positive electrode. The reactions taking place at the two electrodes during recharging are as follows.
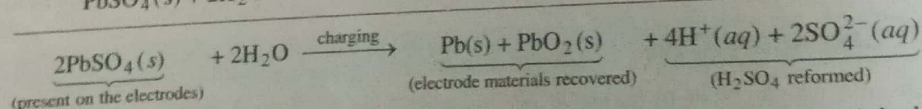
At negative electrode :
$$PbSO_4(s) + 2e^- \xrightarrow{\text{direct current}} Pb(s) + SO_4^{2-}(aq)$$

At positive electrode :
$$PbSO_4(s) + 2H_2O \xrightarrow{\text{direct current}} PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$$

Overall charging reaction :
$$\underbrace{2PbSO_4(s)}_{\text{(present on the electrodes)}} + 2H_2O \xrightarrow{\text{charging}} \underbrace{Pb(s) + PbO_2(s)}_{\text{(electrode materials recovered)}} + \underbrace{4H^+(aq) + 2SO_4^{2-}(aq)}_{\text{(H}_2\text{SO}_4 \text{ reformed)}}$$
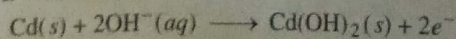
From the above reactions it is clear that during the recharging of the cell, the electrode materials are restored in their original forms. Due to formation of H^+ and SO_4^{2-} ions, the specific gravity of sulphuric acid increases and it attains the original value (1.3 g cm^{-3}). The cell (or battery) thus becomes ready for the fresh use and can generate electric current till it again gets discharged.
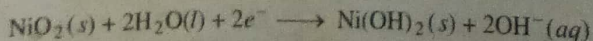
2. Nickel-cadmium storage cell (Nicad cell) : The *nickel-cadmium storage cell* or *nickel-cadmium accumulator* is also a rechargeable cell. Although it is more expensive as compared to a lead storage cell, yet it is becoming more and more popular because it is smaller, lighter and has a longer life. It is suitable for portable and cordless appliances.

In a nickel-cadmium storage cell, the anode is made of cadmium, while the cathode consists of a metal grid containing nickel (IV) oxide. The electrolyte is a solution of KOH. When the current is drawn from the cell, following reactions take place.
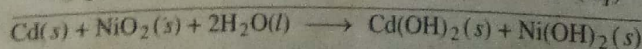
At anode :
$$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$$

At cathode :
$$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$$

Overall reaction :
$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

The cell has a potential (EMF) of about 1.4 V. As the cell reaction consumes water as the electrolyte, the voltage of this cell remains fairly constant during use. Moreover, the cell reaction does not involve any gaseous product. The products formed stick to the electrodes and can be reconverted into substances originally present before the discharge of the cell by *recharging process.* A discharged
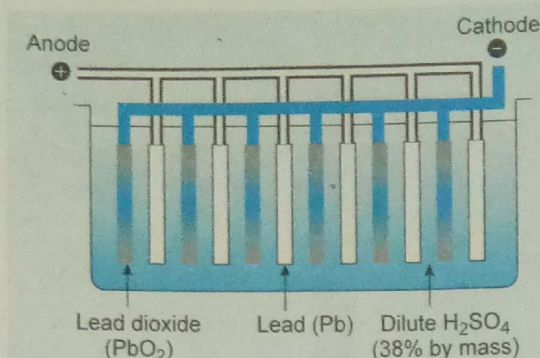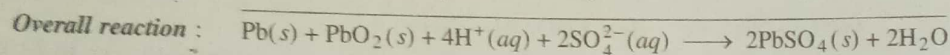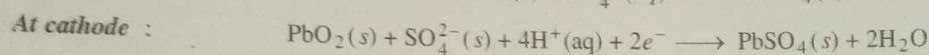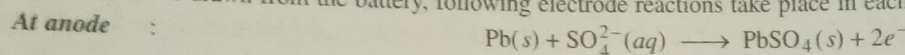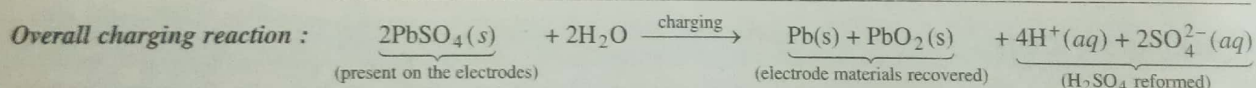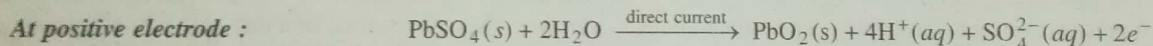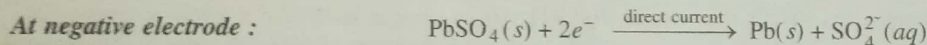
Fig. 5.17 A lead storage battery.

insulating material. The anode and cathode plates are separately connected to one another. This increases the surface area of the electrodes and hence the current producing capacity of the battery.

When current is drawn from the battery, following electrode reactions take place in each cell in the battery.

At anode :
$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

At cathode :
$$PbO_2(s) + SO_4^{2-}(s) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$$

Overall reaction :
$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$$

The electrode reactions and the overall cell reaction clearly indicate that sulphuric acid gets used up during the discharge of the cell. Therefore when current is drawn from the cell, sulphuric acid gets diluted and its specific gravity falls. Both the electrodes get coated with the white precipitate of lead sulphate ($PbSO_4$). When the specific gravity of sulphuric acid falls below 1.2 g cm^{-3} and both the electrodes get covered with $PbSO_4$, the cell reaction stops and the cell (or battery) is said to be **discharged.** At this stage the cell or battery needs recharging.
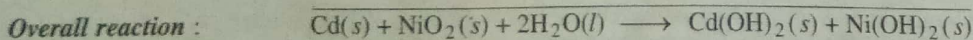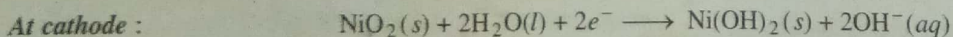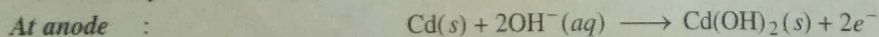
Recharging of a dischaged cell (or battery) : The discharged lead storage cell (or lead storage battery) can be recharged by passing a direct current through it in the opposite direction. For this purpose, the negative electrode of the storage cell is connected to the negative of the DC source and the positive electrode of the cell to the positive of the DC source. The direct current thus passed reverses the electrode reactions and converts lead sulphate back to lead at the negative electrode and to lead dioxide at the positive electrode. The reactions taking place at the two electrodes during recharging are as follows.

At negative electrode :
$$PbSO_4(s) + 2e^- \xrightarrow{\text{direct current}} Pb(s) + SO_4^{2-}(aq)$$

At positive electrode :
$$PbSO_4(s) + 2H_2O \xrightarrow{\text{direct current}} PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$$

Overall charging reaction :
$$\underset{\text{(present on the electrodes)}}{2PbSO_4(s)} + 2H_2O \xrightarrow{\text{charging}} \underset{\text{(electrode materials recovered)}}{Pb(s) + PbO_2(s)} + \underset{(H_2SO_4 \text{ reformed})}{4H^+(aq) + 2SO_4^{2-}(aq)}$$

From the above reactions it is clear that during the recharging of the cell, the electrode materials are restored in their original forms. Due to formation of H^+ and SO_4^{2-} ions, the specific gravity of sulphuric acid increases and it attains the original value (1.3 g cm^{-3}). The cell (or battery) thus becomes ready for the fresh use and can generate electric current till it again gets discharged.

2. Nickel-cadmium storage cell (Nicad cell) : The *nickel-cadmium storage cell* or *nickel-cadmium accumulator* is also a rechargeable cell. Although it is more expensive as compared to a lead storage cell, yet it is becoming more and more popular because it is smaller, lighter and has a longer life. It is suitable for portable and cordless appliances.

In a nickel-cadmium storage cell, the anode is made of cadmium, while the cathode consists of a metal grid containing nickel (IV) oxide. The electrolyte is a solution of KOH. When the current is drawn from the cell, following reactions take place.

At anode :
$$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$$

At cathode :
$$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$$

Overall reaction :
$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

The cell has a potential (EMF) of about 1.4 V. As the cell reaction consumes water as the electrolyte, the voltage of this cell remains fairly constant during use. Moreover, the cell reaction does not involve any gaseous product. The products formed stick to the electrodes and can be reconverted into substances originally present before the discharge of the cell by *recharging process*. A discharged

cell can be recharged by passing a direct current in the opposite direction when cell reaction gets reversed and original substances get recovered at the electrodes.
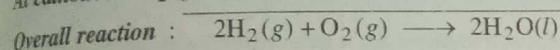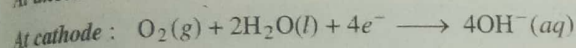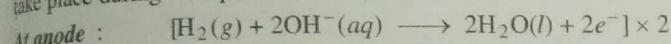
5.9.3. Fuel Cells

The cells which convert the chemical energy of a fuel directly into electrical energy are called **fuel cells**. In these cells, fuels like H_2, CO, CH_4, C_3H_8 etc. are used to generate electrical energy. The fuels are continuously supplied and the products are continuously removed. A large number of fuel cells are available. Among these, the most common one is *hydrogen-oxygen fuel cell.*

Hydrogen-oxygen fuel cell (Bacon Cell)

Hydrogen-oxygen fuel cell was designed by **Bacon** in 1959. Therefore, it is also known as **Bacon cell**. It is a potential source of electrical energy and was used as a primary source of electrical energy in the **Appollo space programme** of U.S.A.

A simple $H_2 - O_2$ fuel cell is shown in Fig. 5.18. The cell consists of two porous carbon electrodes impregnated with a suitable catalyst such as Pt, Ag, CoO etc. The space between the two electrodes is filled with a concentrated solution of KOH or NaOH which serves as an electrolyte. H_2 gas and O_2 gas are bubbled in the electrolyte through porous carbon electrodes as shown in Fig. 5.18. Following reactions take place during the operation of the cell.

At anode : $[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-] \times 2$

At cathode : $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Overall reaction : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Thus, the overall cell reaction involves the combination of $H_2(g)$ and $O_2(g)$ to form water. The cell runs continuously as long as the reactants (H_2 and O_2) are supplied. The cell operates efficiently in the temperature range 343 K – 413 K (70°C–140°C) and provides a potential of about 0.9 V.

Fig. 5.18 A simple H_2–O_2 fuel cell.

As mentioned above, this cell was used as a source of electrical energy in Appollo space programme. The water vapour produced in the cell reaction were condensed and water thus formed was used as drinking water by the astronauts.

Advantages of the fuel cells : Fuel cells are the potential source of electrical energy and have an edge over the conventional galvanic cells and the conventional methods used for the production of electrical energy by burning the fuel. Some significant advantages of fuel cells are as follows.

(i) *High efficiency* : Since fuel cells convert the energy of a fuel directly into electrical energy, they are potentially more efficient than the conventional methods used for the production of electrical energy by burning fuels such as hydrogen, carbon fuels or by using nuclear reactor. Theoretically, fuel cells should be 100% efficient but so far an efficiency of 60–70 percent has been attained. The efficiency of a conventional method involving the burning of a fuel is only about 40 percent.

(ii) *Pollution free working* : The by-products obtained from a fuel cell do not cause any pollution problem. For example a $H_2 - O_2$ cell produces only water which in no way can cause any pollution problem.

(iii) *Continuous supply of energy* : Fuel cells can supply energy continuously so long as the fuels are fed into them. Contrary to conventional cells or batteries, these cells do not involve any drop in the voltage or current during long usage.

Limitations of the fuel cells : Although fuel cells are superior to conventional cells, yet there are certain practical difficulties in their construction and use as a source of electrical energy. Some of these are as follows.

(i)   The handling of gaseous fuels is difficult. The fuel gases such as H_2, O_2 etc. are required to be stored as liquids at very low temperature and high pressure in specially designed cylinders. This increases the cost of the cell and involves several practical difficulties.

(ii) The catalysts needed for the electrode reactions such as Pt, Pd, Ag etc. are quite expensive and increase the cost of the cell.

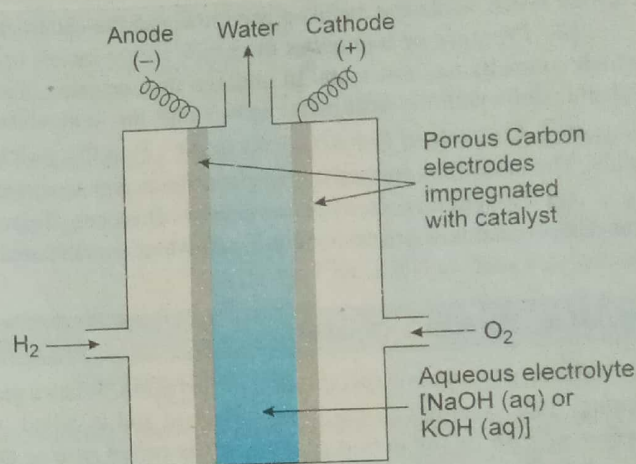(iii) The electrolytes used in fuel cells are highly corrosive and create several practical problems.

5.10. CORROSION

When a metal is exposed to a certain environment, it may get deteriorated due to its reaction with the environment and its surface may become rough. This phonomenon is called **corrosion.**

It is a common experience that most of the metals are affected in some way or the other when exposed to the atmosphere. The gases present in the atmosphere react with the metal and slowly deteriorate it. A large number of metals lose their shine due to deposition of the compounds such as oxides, sulphides, sulphates, carbonates etc. on their surface. Some metals lose their strength and become weak and brittle. The *tarnishing of silver* (loss of shine), *rusting of iron* (deposition of a brown coloured layer on its surface), *development of green coating on copper and bronze*, tarnishing of aluminium etc. are some familiar examples of corrosion.