Electrochemistry - Part 4

Objectives

After going through this lesson, the learners will be able to understand the following:

- Understand the quantitative aspects of electrolysis,
- Apply the Faraday's laws to electrolysis,
- Describe the construction of some primary, secondary batteries and fuel cells,
- Explain corrosion as an electrochemical process.

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- Electrolytic Cells and Electrolysis
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- Primary Batteries
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Introduction

One of the oldest and most important applications of electrochemistry is the storage and conversion of energy. Batteries are devices that carry out these conversions. In ordinary batteries the chemical components are contained within the device itself. If the reactants are supplied from an external source as they are consumed, the device is called a fuel cell. This module deals with Faraday's laws of electrolysis, product of electrolysis and it's application namely; the primary and secondary batteries and corrosion.

Electrolytic Cells and Electrolysis

In an electrolytic cell external source of voltage is used to bring about a chemical reaction. The electrochemical processes are of great importance in the laboratory and the chemical industry. One of the simplest electrolytic cells consists of two copper strips dipping in an aqueous solution of copper sulphate. If a DC voltage is applied to the two electrodes, then

Cu^{2+} ions discharge at the cathode (negatively charged) and the following reaction takes place:

$$Cu^{2+}(aq) \ + \ 2e^- \rightarrow Cu\,(s)$$
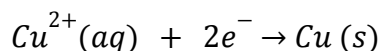
Copper metal is deposited on the cathode. At the anode, copper is converted into Cu^{2+} ions by the reaction:

$$Cu(s) \rightarrow Cu^{2+}(s) \ + \ 2e^-$$
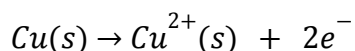
Thus copper is dissolved (oxidized) at anode and deposited (reduced) at cathode. This is the basis for an industrial process in which impure copper is converted into copper of high purity. The impure copper is made an anode that dissolves on passing current and pure copper is deposited at the cathode. Many metals like Na, Mg, Al, etc. are produced on large scale by electrochemical reduction of their respective cations where no suitable chemical reducing agents are available for this purpose. Sodium and magnesium metals are produced by the electrolysis of their fused chlorides and aluminium is produced by electrolysis of aluminium oxide in presence of cryolite.

Faraday's Laws of Electrolysis

Michael Faraday was the first scientist who described the quantitative aspects of electrolysis. Now Faraday's laws also flow from what has been discussed earlier. After his extensive investigations on electrolysis of solutions and melts of electrolytes, Faraday published his results during 1833-34 in the form of the following well known Faraday's two laws of electrolysis:

First Law: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

Second Law: The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

There were no constant current sources available during Faraday's times. The general practice was to put a coulometer (a standard electrolytic cell) for determining the quantity of electricity passed from the amount of metal (generally silver or copper) deposited or

consumed. However, coulometers are now obsolete and we now have constant current (I) sources available and the quantity of electricity Q, passed is given by: $Q = I \times t$

Q is in coulombs when I is in ampere and t is in second. The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction.

For example, in the reaction: $Ag^+(aq) + e^- \rightarrow Ag(s)$

One mole of the electron is required for the reduction of one mole of silver ions. We know that charge on one electron is equal to 1.6021×10^{-19} C. Therefore, the charge on one mole of electrons is equal to:

$N_A \times 1.6021 \times 10^{-19}$ C $= 6.02 \times 10^{23}$ mol^{-1} $\times 1.6021 \times 10^{-19}$

C $= 96487$ C mol^{-1}

This quantity of electricity is called **Faraday** and is represented by the symbol F.

For approximate calculations we use $1F = 96500$ C mol^{-1}.

For the electrode reactions:

$$Mg^{2+}(l) + 2e^- \rightarrow Mg(s)$$

$$Al^{3+}(l) + 3e^- \rightarrow Al(s)$$
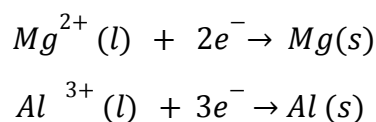
It is obvious that one mole of Mg^{2+} and Al^{3+} requires 2 mol of electrons ($2F$) and 3 mol of electrons ($3F$) respectively. The charge passed through the electrolytic cell during electrolysis is equal to the product of current in amperes and time in seconds. In commercial production of metals, current as high as 50,000 amperes are used that amounts to about 0.518 F per second.

Example 1: A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

Solution: $t = 600$ s charge = current × time = 1.5 A × 600 s = 900 C

According to the reaction: $Cu^{2+}(aq) + 2e^- = Cu(s)$

We require 2F or 2 × 96487 C to deposit 1 mol or 63 g of Cu.

For 900 C, the mass of Cu deposited = (63 g mol^{-1} × 900 C) / (2 × 96487 C mol^{-1})
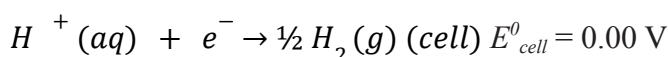
= 0.2938 g.

Product of Electrolysis

Products of electrolysis depend on the nature of material being electrolysed and the type of electrodes being used. If the electrode is inert (e.g., platinum or gold), it does not participate in the chemical reaction and acts only as source or sink for electrons. On the other hand, if the

electrode is reactive, it participates in the electrode reaction. Thus, the products of electrolysis may be different for reactive and inert electrodes. The products of electrolysis depend on the different oxidizing and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes, although feasible, are so slow kinetically that at lower voltages these don't seem to take place and extra potential (called o*ver-potential*) has to be applied, which makes such processes more difficult to occur. For example, if we use molten NaCl, the products of electrolysis are sodium metal and Cl_2 gas. Here we have only one cation (Na^+) which is reduced at the cathode: $(Na^+ + e^- \rightarrow Na)$ and one anion (Cl^-) which is oxidised at the anode: $(Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-)$

During the electrolysis of aqueous sodium chloride solution, the products are NaOH, Cl_2 and H_2. In this case besides Na^+ and Cl^- ions, we also have H^+ and OH^- ions along with the solvent molecules, H_2O. At the cathode there is competition between the following reduction reactions:
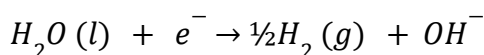
$Na^+ + e^- \rightarrow Na\ (s)$ $\qquad\qquad\qquad E^0_{cell} = -2.71$ V

$H^+\ (aq) + e^- \rightarrow \frac{1}{2}\ H_2\ (g)\ (cell)\ E^0_{cell} = 0.00$ V

The reaction with higher value of E^0 is preferred and, therefore, the reaction at the cathode during electrolysis is:
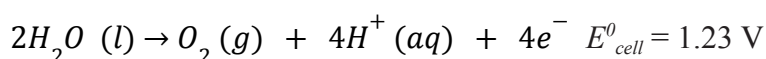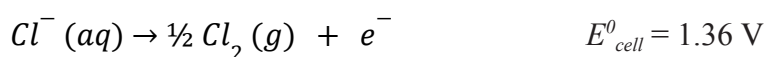
$H^+(aq) + e^- \rightarrow \frac{1}{2}\ H_2(g)$
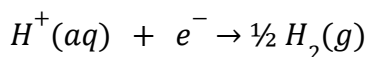
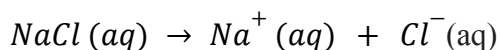but H^+ (aq) is produced by the dissociation of H_2O, i.e.,

$H_2O\ (l) \rightarrow H^+(aq) + OH^-(aq)$
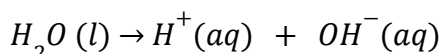
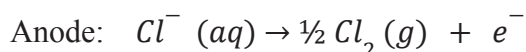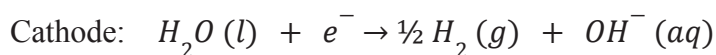Therefore, the net reaction at the cathode may be written as the sum of the above two cathode reactions and we have:

$H_2O\ (l) + e^- \rightarrow \frac{1}{2}H_2\ (g) + OH^-$

At the anode the following oxidation reactions are possible:

$Cl^-\ (aq) \rightarrow \frac{1}{2}\ Cl_2\ (g) + e^-$ $\qquad\qquad E^0_{cell} = 1.36$ V

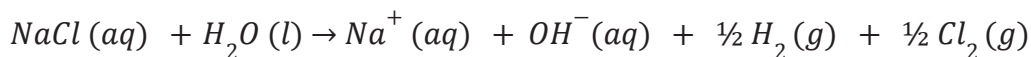$2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-\ E^0_{cell} = 1.23$ V

The reaction at anode with lower value of E^0 is preferred and therefore, water should get oxidised in preference to Cl^-(aq). However, on account of overpotential of oxygen, reaction is preferred. Thus, the net reactions may be summarized as:

$NaCl\ (aq) \rightarrow Na^+\ (aq) + Cl^-(aq)$

Cathode: $H_2O\ (l)\ +\ e^-\rightarrow\frac{1}{2}\,H_2\ (g)\ +\ OH^-\ (aq)$

Anode: $Cl^-\ (aq)\rightarrow\frac{1}{2}\,Cl_2\ (g)\ +\ e^-$

Net reaction:

$NaCl\ (aq)\ +\ H_2O\ (l)\rightarrow Na^+\ (aq)\ +\ OH^-\ (aq)\ +\ \frac{1}{2}\,H_2\ (g)\ +\ \frac{1}{2}\,Cl_2\ (g)$

The standard electrode potentials are replaced by electrode potentials given by Nernst equation to take into account the concentration effects. During the electrolysis of sulphuric acid, the following processes are possible at the anode:

$2\,H_2O\ (l)\rightarrow O_2\ (g)\ +\ 4H^+\,(aq)\ +\ 4e^-\quad E^0{}_{cell}=+1.23\ \text{V},$
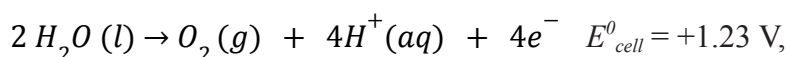
For dilute sulphuric acid the above reaction is preferred but at higher concentrations of H_2SO_4 the reaction given below is preferred.

$2[SO_4]^{2-}\ (aq)\rightarrow[S_2O_8]^{2-}\ (aq)\ +\ 2e^-\quad E^0{}_{cell}=1.96\ \text{V}$
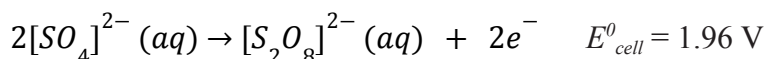
Primary Batteries

Any battery (actually it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries. In the primary batteries, the reaction occurs only once and after use over a period of time the battery becomes dead and cannot be reused again. The most familiar example of this type is the dry cell (known as Leclanche cell after its discoverer) which is used commonly in our transistors and clocks. The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon (Fig.1). The space between the electrodes is filled by a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$). The electrode reactions are complex, but they can be written approximately as follows:
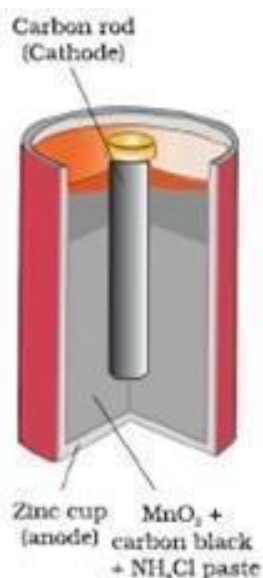
Anode: $Zn(s)\rightarrow Zn^{2+}\ +\ 2e^-$

Cathode: $MnO_2\ +\ NH_4\ +\ e^-\ +\ \rightarrow MnO(OH)\ +\ NH_3$
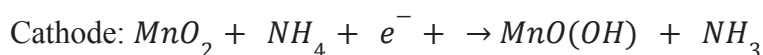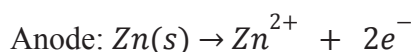
Fig. 1: A commercial dry cell consists of a graphite (carbon) cathode in a zinc container; the latter acts as the anode.

Carbon rod (Cathode)

Zinc cup (anode)   MnO₂ + carbon black + NH₄Cl paste

In the reaction at cathode, manganese is reduced from the +4 oxidation state to the +3 state. Ammonia produced in the reaction forms a complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$. The cell has a potential of nearly 1.5 V. Mercury cell, (Fig. 2) suitable for low current devices like hearing aids, watches, etc. consists of zinc–mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are given below:

Anode: $Zn\ (Hg)\ +\ 2OH^-\ \rightarrow ZnO\ (s)\ +\ H_2O\ +\ 2e^-$

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

Anode   Anode cap
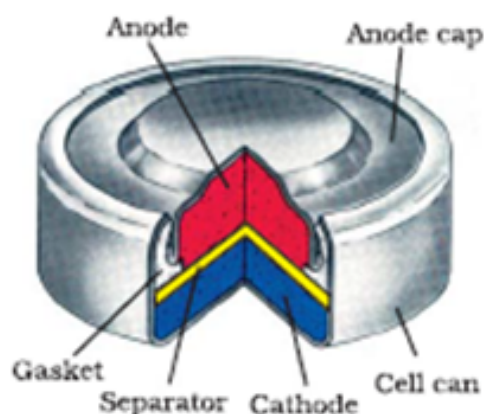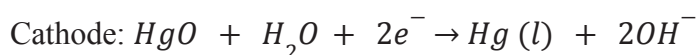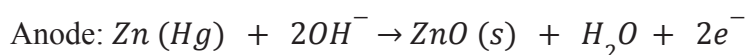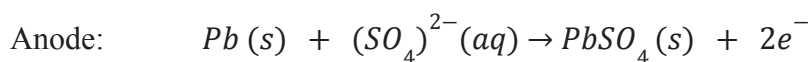
Gasket   Cell can

Separator   Cathode

Fig. 2: Commonly used mercury cell. The reducing agent is zinc and the oxidising agent is mercury (II) oxide.

The overall reaction is represented by: $Zn\,(Hg)\ +\ HgO\,(s) \rightarrow ZnO\,(s)\ +\ Hg\,(l)$
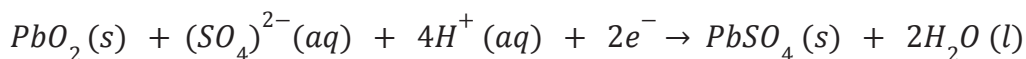
The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its lifetime.
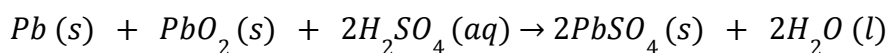
Secondary Batteries

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles. The most important secondary cell is the lead storage battery (Fig. 3) commonly used in automobiles and inverters. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte. The cell reactions when the battery is in use are given below:

Anode: $Pb\,(s)\ +\ (SO_4)^{2-}\,(aq) \rightarrow PbSO_4\,(s)\ +\ 2e^-$

Cathode:

$PbO_2\,(s)\ +\ (SO_4)^{2-}\,(aq)\ +\ 4H^+\,(aq)\ +\ 2e^- \rightarrow PbSO_4\,(s)\ +\ 2H_2O\,(l)$

i.e., overall cell reaction consisting of cathode and anode reactions is:

$Pb\,(s)\ +\ PbO_2\,(s)\ +\ 2H_2SO_4\,(aq) \rightarrow 2PbSO_4\,(s)\ +\ 2H_2O\,(l)$

On charging the battery the reaction is reversed and $PbSO_4$ (s) on anode and cathode is converted into Pb and PbO_2, respectively.
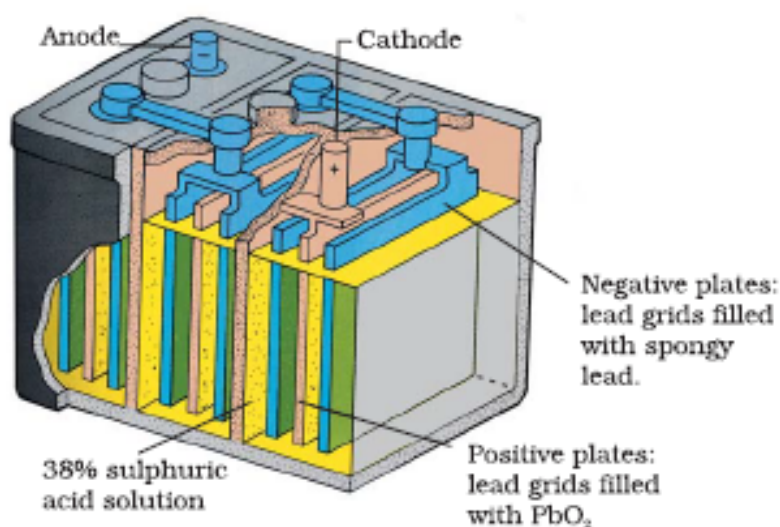

Fig. 3 : The Lead storage battery.

Another important secondary cell is the nickel cadmium cell (Fig.4) which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:

$$Cd\ (s)\ +\ 2Ni(OH)_3\ (s) \rightarrow CdO\ (s)\ +\ 2Ni(OH)_2\ (s)\ +\ H_2O\ (l)$$
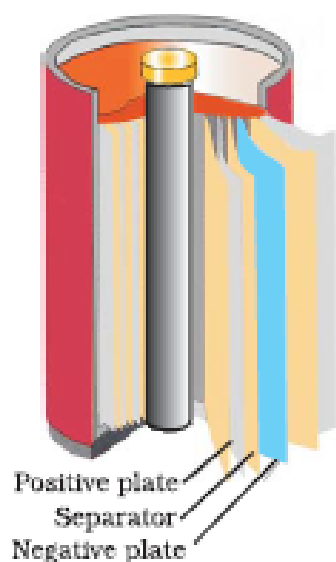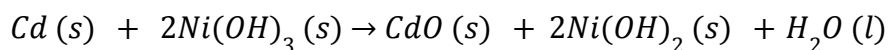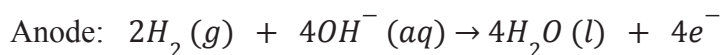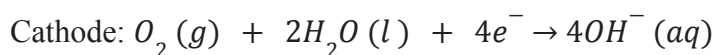

Fig 4: A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide.

Positive plate
Separator
Negative plate

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water (Fig. 5). The cell was used for providing electrical power in the Apollo space program. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

Cathode: $O_2 (g) + 2H_2O (l) + 4e^- \rightarrow 4OH^- (aq)$

Anode: $2H_2 (g) + 4OH^- (aq) \rightarrow 4H_2O (l) + 4e^-$

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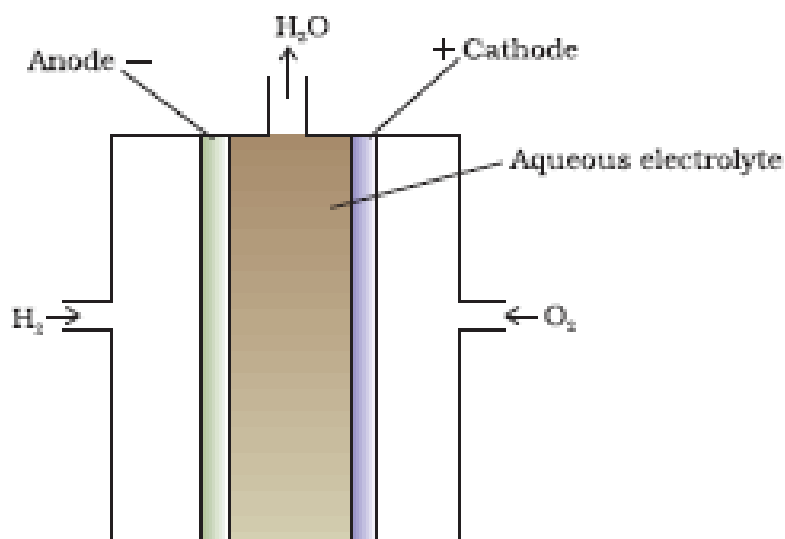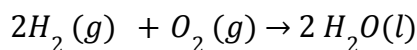
$2H_2 (g) + O_2 (g) \rightarrow 2 H_2O(l)$

Figure 5 : *Fuel cell using H₂ and O₂ produces electricity.*

The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried.

Corrosion

Metallic objects corrode slowly and over a period of time a coating of oxides or other salts of the metal develops on its surface. Few examples of corrosion are: Rusting of iron, green coating on copper and bronze metal statues or coins, tarnishing of silverware. Corrosion is one of the major factors that damage the metallic structures all over the world. Particularly the buildings, ships, bridges, towers etc., structures made from metals especially iron. Governments lose a lot of money every year due to the corrosion of metallic objects.

Corrosion involves loss of electrons by a metal atom and gain of the same electron by the oxygen in the air to form oxides. Rusting of iron which is actually corrosion of iron occurs in the presence of water and air. Corrosion chemistry is a complex process but it may be considered essentially as an electrochemical phenomenon.
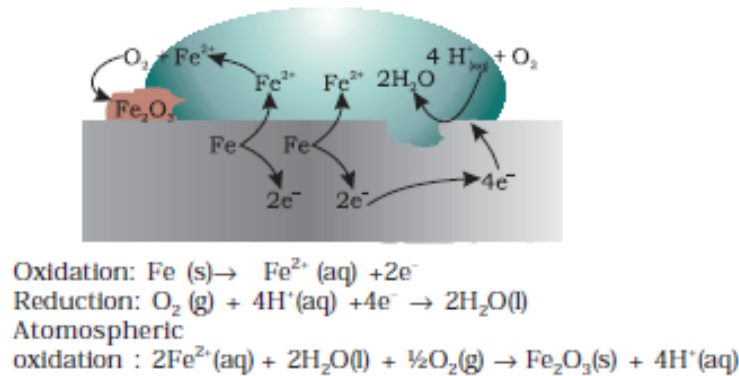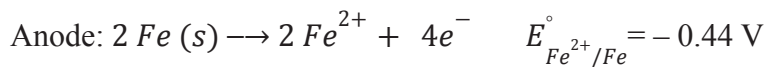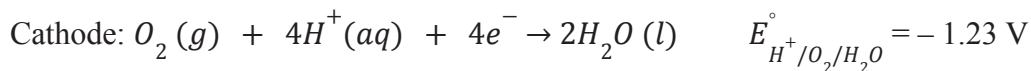

Oxidation: Fe (s)→ Fe²⁺ (aq) +2e⁻
Reduction: O₂ (g) + 4H⁺(aq) +4e⁻ → 2H₂O(l)
Atomospheric
oxidation : 2Fe²⁺(aq) + 2H₂O(l) + ½O₂(g) → Fe₂O₃(s) + 4H⁺(aq)

Fig.7: *Corrosion of iron in atmosphere.*
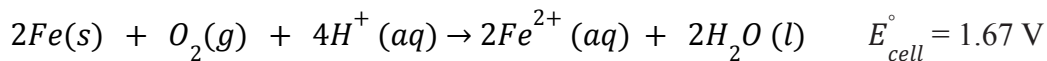
At a particular spot (Fig 7.) of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction as:

Anode: $2\ Fe\ (s) \longrightarrow 2\ Fe^{2+} + 4e^{-}$ $E^{\circ}_{Fe^{2+}/Fe} = -0.44$ V

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ions in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction

Cathode: $O_2\ (g)\ +\ 4H^+(aq)\ +\ 4e^{-} \rightarrow 2H_2O\ (l)$ $E^{\circ}_{H^+/O_2/H_2O} = -1.23$ V

The overall reaction being:

$2Fe(s)\ +\ O_2(g)\ +\ 4H^+\ (aq) \rightarrow 2Fe^{2+}\ (aq)\ +\ 2H_2O\ (l)$ $E^{\circ}_{cell} = 1.67$ V

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3 . xH_2O$) and with further production of hydrogen ions.
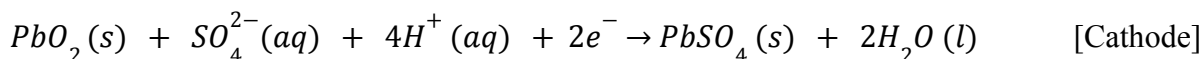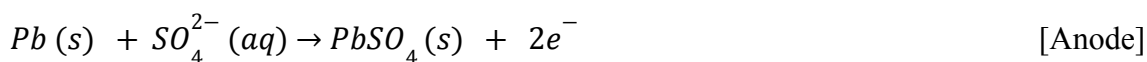
Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic

object to come in contact with the atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.
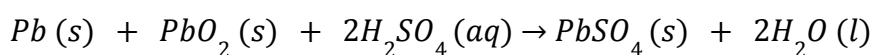
Example 2: Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

Solution: Anode of lead storage battery consists of lead, lead oxide (PbO_2) (a grid of lead packed with PbO_2) as the cathode and sulphuric acid (38% solution) as an electrolyte.

When in use, a battery undergoes the following reaction:

$$Pb\ (s)\ +\ SO_4^{2-}\ (aq) \rightarrow PbSO_4\ (s)\ +\ 2e^- \qquad\qquad \text{[Anode]}$$

$$PbO_2\ (s)\ +\ SO_4^{2-}(aq)\ +\ 4H^+\ (aq)\ +\ 2e^- \rightarrow PbSO_4\ (s)\ +\ 2H_2O\ (l) \qquad \text{[Cathode]}$$

The overall cell reaction is given by:

$$Pb\ (s)\ +\ PbO_2\ (s)\ +\ 2H_2SO_4\,(aq) \rightarrow PbSO_4\ (s)\ +\ 2H_2O\ (l)$$

While being charged, a battery undergoes the reverse of all the above reactions. Thus, the lead sulphate present at the anode gets converted to metal lead [Pb(s)] and at the cathode is converted into lead oxide [PbO_2(s)].

Example 3: Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Solution: Methane & Methanol.

Example 4: Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

Solution: In the process of rusting, the water molecules present at the surface of iron react with oxides and get dissociated to furnish H^+ ions

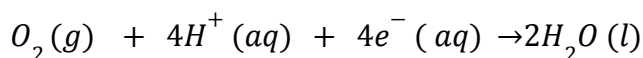$$H_2O\ +\ CO_2 \rightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow 2H^+\ +\ CO_3^{2-}$$
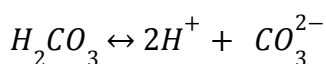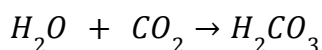
In presence of H^+ ions iron converts into Fe^{2+} ions, hence this part is acts as an anode

Reaction at anode:

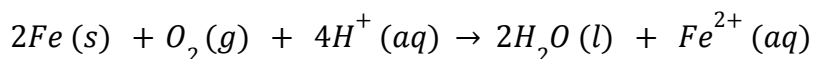$$Fe\ (s) \rightarrow Fe^{2+}\ (aq)\ +\ 2e^-$$
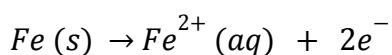
Electron released at the anode moves through the metal to another section on the surface of the metallic sheet and reduces oxygen at that spot which acts as the cathode.

Reaction at Cathode:

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

The overall reaction:

$$2Fe(s) \ + \ O_2(g) \ + \ 4H^+(aq) \rightarrow 2H_2O(l) \ + \ Fe^{2+}(aq)$$

Hence, rusting of iron is an apt example of an electrochemical cell.

The Hydrogen Economy

At present the main source of energy that is driving our economy is fossil fuels such as coal, oil and gas. As more people on the planet aspire to improve their standard of living, their energy requirement will increase. In fact, the per capita consumption of energy used is a measure of development. Of course, it is assumed that energy is used for productive purposes and not merely wasted. We are already aware that carbon dioxide produced by the combustion of fossil fuels is resulting in the 'Greenhouse Effect'. This is leading to a rise in the temperature of the Earth's surface, causing polar ice to melt and ocean levels to rise. This will flood low-lying areas along the coast and some island nations such as Maldives face total submergence. In order to avoid such a catastrophe, we need to limit our use of carbonaceous fuels. Hydrogen provides an ideal alternative as its combustion results in water only. Hydrogen production must come from splitting water using solar energy. Therefore, hydrogen can be used as a renewable and non-polluting source of energy. This is the vision of the Hydrogen Economy. Both the production of hydrogen by electrolysis of water and hydrogen combustion in a fuel cell will be important in the future. And both these technologies are based on electrochemical principles.

Summary

Any battery or cell that we use as a source of electrical energy is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries: primary batteries and secondary batteries. In the primary batteries, the reaction occurs only once and after use over a period of time the battery becomes dead and cannot be reused again. The most familiar example of this type is the dry cell (or Leclanche cell) which is used commonly

in our transistors and clocks. The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$). A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. The most important secondary cell is the lead storage battery commonly used in automobiles and inverters. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. Batteries and fuel cells are very useful forms of galvanic cell. Corrosion of metals is essentially an electrochemical phenomenon. In corrosion, a metal is oxidized by loss of electrons to oxygen and formation of oxides. A proper coating of metallic surface with paint or providing a sacrificial electrode of another metal with lower reduction potential values is effective in prevention of corrosion. Electrochemical principles are relevant to the Hydrogen Economy.