CHAPTER-8

ELECTROCHEMISTRY

You will learn in this chapter about:

- Electrolytes and non-electrolytes.
- Electrolysis.
- Electrolysis of molten NaCl.
- Electrolysis of water.
- Faraday's laws of electrolysis.
- Electrochemical equivalent.
- Uses of electrolysis.
- Electroplating.
- Electrochemical cells.
- Batteries.

INTRODUCTION

Chemical energy is associated with chemical reactions and the electrical energy is obtained from electricity. Thus chemical and electrical energies are the two forms of energy which are interconvertible.

The branch of chemistry that deals with the relationship between electricity and chemical reactions. It deals with the conversion of electrical energy into chemical energy and chemical energy into electrical energy is defined as electrochemistry.

8.1 ELECTROLYTES AND NON-ELECTROLYTES

The chemical compound which conducts electricity in molten condition or through its aqueous solution with chemical change is called an electrolyte.

All acids, bases and salts are electrolytes (in aqueous solutions or fused state). Such as Hydrochloric acid (HCl), Sulphuric acid (H_2SO_4), Sodium hydroxide (NaOH), Sodium chloride (NaCl), Copper sulphate ($CuSO_4$) etc, are electrolytes.

You cannot electrolyse something unless it conducts electricity. But all the conductors are not electrolytes,You can pass electric current through a metal for years but it will not decompose. Metals are good conductors but are not electrolytes. Metals are used as electrodes through which electric current enters and leaves the electrolytes.

All electrolytes are ionic compounds or polar compounds like acids and bases. Salts are ionic compounds and are solids. These solids do not conduct electricity because in the solid state the ions are very tightly packed or held together showing no movement of the ions. They cannot move. However when an ionic solid is melted or dissolved in water, its ions become free to move. Thus ionic compounds in molten states or in aqueous solution, conduct electricity. This conduction is due to the free movement of ions.

Non - Electrolytes:

The chemical compounds which do not conduct electricity in molten or in aqueous solutions are called non-electrolytes; such as Sugar, Petrol, Benzene etc.

8.2 ELECTROLYSIS OR ELECTROLYTIC CONDUCTION

A chemical process or reaction which does not have the capability to take place spontaneously, can be made to take place by passing electric current. If appropriate quantity of current is passed under suitable condition through an electrolytic solution, the reactions occurs non-spontaneously i.e. under stress.

The cell used for the reaction to occur by passing electric current is called electrolytic cell. Thus electrolytic cell is a device which is used to convert electrical energy into chemical energy (a non-spontaneous chemical reaction takes place by the loss and gain of electrons), for example a device for electroplating proceses or electrolysis of water in the presence of an acid. The process is called electrolysis or electrolytic conduction.

Electrolysis may be defined as a process in which movements of the ions take place towards their respective electrodes to undergo chemical changes under the influence of an applied electric field.

1. Electrolysis of Molten Sodium Chloride:

Sodium chloride, (Salt) does not conduct electricity in the solid state. To make it conduct electricity, either fuse or melt the salt or dissolve it i water. So there are two ways of doing electrolysis of sodium chloride. We are doing electrolysis of molten sodium chloride. Sodium chloride melts at 800°C. It is easy to predict the result of electrolysing a molten electrolyte. The salt just splits into two parts, sodium (metal) positive ion (Na^+) and chloride (non-metal) negative ion (Cl^-). We can write the ionization reaction as :

$$NaCl(s) \xrightleftharpoons{\text{fused}} Na^+(l) + Cl^-(l)$$

In solid sodium chloride, the ions are held together tightly in a regular lattice arrangements. In solid the ions cannot move, but when sodium chloride is melted, the ions are freed from their lattice and they can move freely to conduct electricity.

Some fused NaCl is taken in an electrolytic cell i.e. in a glass vessel. Two platinum rods (electrodes) are dipped into the fused salt (NaCl). The two electrodes are connected to a source of electricity i.e. to a battery outside the cell by wires. The electrode connected to the negative terminal of the battery is called cathode and the electrode connected to the positive terminal of the battery is called anode.

When an electrical potential is passed through the molten sodium chloride salt, electrolysis starts. The positive ions i.e. cations (Na^+) are attracted towards cathode and the negative ions i.e. anions (Cl^-) are attracted towards anode. At the two electrodes chemical reactions take place.

At Cathode:

Sodium ions (Na^+) which are positively charged,move towards cathode and gain electrons to get neutralized. Thus Na^+ ions are discharged at cathode and form neutral molten sodium metal.

We can represent the happening at cathode as :

$$\text{Sodium ion} + \text{electron} \longrightarrow \text{Sodium metal}$$

$$Na^+(l) + \bar{e} \longrightarrow Na(l)$$

At Anode:

Chloride ions (Cl^-) which are negatively charged move towards anode; Cl^- ions have one electron in excess. The anode has a shortage of electrons and is positively charged. When Cl^- ions arrive at anode, the anode attracts their electrons and Cl^- ions lose their extra electrons at anode, forming neutral chlorine (Cl) atoms but we know Cl atoms do not exist in the free state. They combine to form Cl_2 molecules. So Cl^- ions are discharged at anode to liberate Cl_2 gas by the loss of electrons at anode.

$$\text{Chloride ion} \longrightarrow \text{Chlorine atom} + \bar{e}$$

or $$Cl^-(l) \longrightarrow Cl(g) + e^-$$

Then $$Cl(g) + Cl(g) \longrightarrow Cl_2(g)$$

Over all it amounts to

$$2Cl^-(g) \longrightarrow Cl_2(g) + 2\bar{e}$$

The over all reaction can be described as:

$2(Na^+(l) + e^- \longrightarrow Na(l))$ Cathode reaction

$2Cl(g) \longrightarrow Cl_2(g) + 2e^-$ Anode reaction

On adding the two reactions, the loss and gain of electrons cancel and we get final result.

$$2Na^+(l) + \cancel{2}e^- \longrightarrow 2Na(l)$$

$$2Cl^-(l) \longrightarrow Cl_2(g) + \cancel{2}e^-$$

$$2Na^+(l) + 2Cl^-(l) \longrightarrow 2Na(l) + Cl_2(g)$$

The electrolysis of molten sodium chloride shows that we get sodium metal at cathode and Cl_2 gas is liberated at anode. The following fig 8.1 describes the electrolysis of molten NaCl.

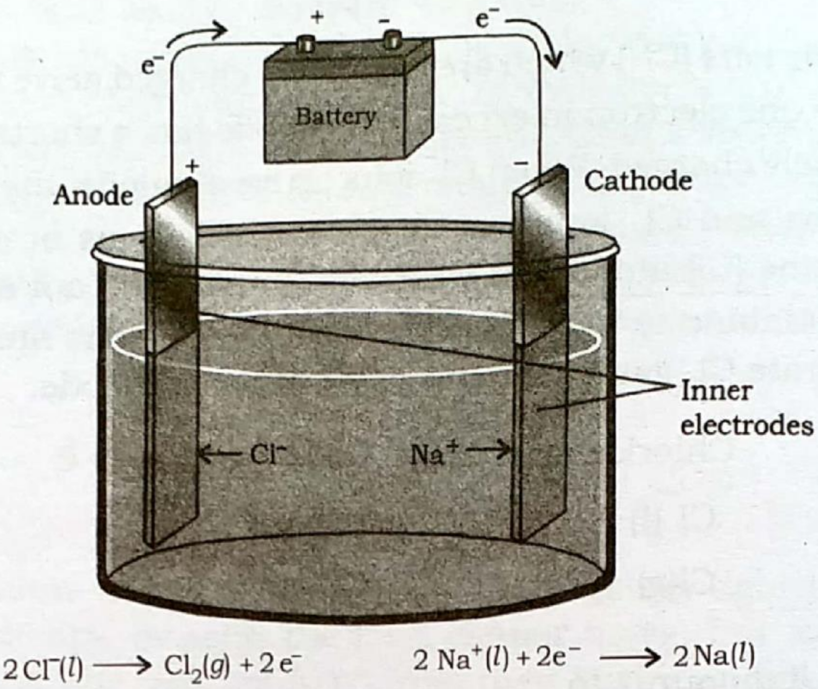


Fig. 8.1 Electrolysis of molten NaCl

2. Electrolysis of Water:

Pure water on its own hardly conducts electricity because it ionizes feebly into ions. But when few drops of acid or base or very small quantity of a salt is added in water, it makes water to conduct electricity and then water can be electrolysed to produce hydrogen gas at cathode and oxygen gas at anode.

Consider an electrolytic cell containing acidulated water. Two electrodes are dipped in the acidulated water. Water in the presence of few drops of acid ionizes as:

$$2H_2O(l) \xrightleftharpoons{acid} \underset{\text{Hydronium ion}}{H_3O^+(aq)} + \underset{\text{hydroxide ion}}{OH^-(aq)}$$

When electricity is passed from the battery, the positive ions (H_3O^+) move towards cathode. They gain electrons and get neutralized to liberate H_2 gas.

At Cathode:

$$2H_3O^+(aq) + 2e^- \longrightarrow H_2(g) + 2H_2O(l)$$

Hydroxide ion (OH^-) move towards anode. OH^- ions lose electrons at anode and get neutralized to liberate O_2 gas.

At Anode:

$$4OH^-_{(aq)} \longrightarrow O_2(g) + 2H_2O_{(l)} + 4e^-$$

The over all reaction should be balanced according to gain and loss of electrons at the two electrodes so the cathode reaction is multiplied by 2 and then added in the anode reaction.

$$2(2H_3O^+ + 2e^- \longrightarrow H_2(g) + 2H_2O(l)) \quad \text{Cathode reaction}$$

$$\text{or} \quad 4H_3O^+ + \cancel{4e^-} \longrightarrow 2H_2(g) + 4H_2O(l)$$

$$4OH^- \longrightarrow O_2(g) + 2H_2O(l) + \cancel{4e^-} \quad \text{Anode reaction}$$

$$4H_3O^+ + 4OH^- \longrightarrow 2H_2(g) + O_2(g) + 6H_2O(l)$$

$4H_3O^+$ and $4OH^-$ together will be equivalent $8H_2O$, So

$$8H_2O \longrightarrow 2H_2(g) + O_2(g) + 6H_2O$$

$$\text{or} \quad 8H_2O - 6H_2O \longrightarrow 2H_2(g) + O_2(g)$$

$$\text{or} \quad 2H_2O \longrightarrow 2H_2(g) + O_2(g)$$

For simplicity of the electrolysis of water, we write the equation as:

$$2H_2O(l) \xrightarrow{\text{Electric current}} \underset{\text{cathode product}}{2H_2(g)} + \underset{\text{anode product}}{O_2(g)}$$

It is observed that on electrolysis of water, we get two volumes of hydrogen gas per each volume of oxygen gas. Humphry Davy who first did the electrolysis of water, confirmed the formula of water is H_2O (2:1 ratio of Hydrogen and Oxygen).

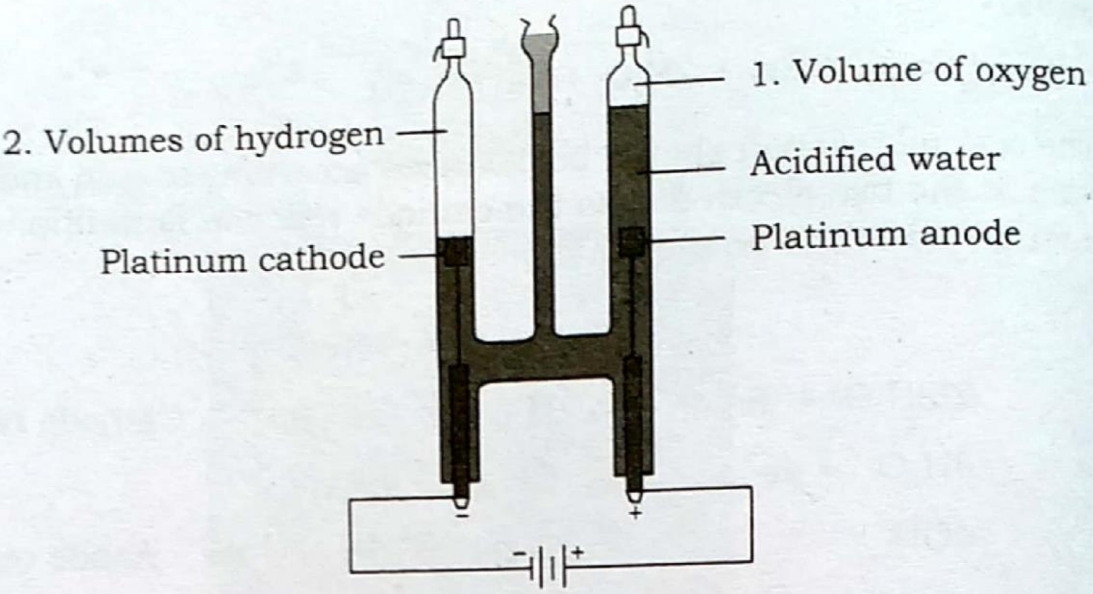


Fig. 8.2 Electrolysis of water

8.3 FARADAY'S LAWS OF ELECTROLYSIS

Michael Faraday in 1833, discovered the quantitative laws governing the process of electrolysis, which are known as Faraday's laws of electrolysis. There are two laws of electrolysis put forward by Faraday.

1. Faraday's First Law of Electrolysis:

It states that the amount of any substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of current passed through the electrolyte.

Explanation:

If 'w' be the weight or amount of a substance deposited or liberated, and 'A' ampere of current is passed for 't' seconds, then according to the law:

$$w \propto A \times t$$

$$\boxed{\text{or} \quad w = Z A t}$$

Where Z is a constant, known as "electro chemical equivalent" of the substance. If one ampere of current is passed for one second; then w = Z. This means when one ampere of current is passed for one second; then the weight or amount of the substance deposited or liberated is exactly equal to its electrochemical equivalent. The current in ampere, multiplied by the time in second is known as coulomb which is the electric charge.

Ampere (A) x time (s) = coulomb (C)

Electrochemical Equivalent:

Electrochemical equivalent of a substance may be defined as the weight (amount) of the substance deposited or liberated, when one coulomb of electric charge is passed through an electrolyte. It is denoted by Z and in S.I unit it is expressed in Kg / coulomb. Each element has its own electrochemical equivalent.

Example - 1

A current of 0.5 ampere was passed through a solution of $CuSO_4$ for one hour. Calculate the mass of copper metal deposited on the cathode. Electrochemical equivalent of Cu=0.000329g/C = 3.29×10^{-4} g/C

Or 3.294×10^{-7} Kg/C.

Solution:

Data:

1. Current in ampere (A) = 0.5
2. Time in second (1 hr) = 1 x 60 x 60 = 3600 s
3. Z for Cu metal = 3.294×10^{-4} g/C = 3.294×10^{-7}Kg/C

Formula

$$w = Z \times A \times t$$
$$= 3.294 \times 10^{-7} \times 0.5 \times 3600$$
$$= 5.929 \times 10^{-4} \text{ Kg/C}$$

Mass of copper metal deposited = 5.929×10^{-4} Kg/C or 0.5929 g/C

Example - 2

A current of 10 amperes was passed for 15 minutes in a solution of silver nitrate ($AgNO_3$). The mass of silver deposited was found to be 1.0062×10^{-2} Kg. Calculate the electrochemical equivalent (Z) of Ag metal.

Solution :

Data :

1. Current in ampere = 10
2. Time in seconds (15 minutes) = 15 x 60 = 900 s
3. Mass of Ag metal deposited (w) = 1.0062×10^{-2} Kg

Formula

$$w = Z A t$$

or $$Z = \frac{w}{At} = \frac{1.0062 \times 10^{-2}\,\text{Kg}}{10\text{A} \times 900\,\text{s C}}$$

$$= \frac{1.0062 \times 10^{-2}}{9 \times 10^{-3}} = \frac{1.0062 \times 10^{-2} \times 10^{-3}}{9}$$

$$= 0.1118 \times 10^{-5}\ \text{Kg/C}$$

$$= 1.118 \times 10^{-6}\ \text{Kg/C}$$

$$= 0.00118\ \ \text{g/C}$$

2. Faraday's Second Law Of Electrolysis:

It states that the masses of different substances deposited or liberated, when same quantity of current is passed through different electrolytes, connected in series are proportional to their chemical equivalent masses.

Consider three different electrolytes, $AgNO_3$, $CuSO_4$ and $Al\ (NO_3)_3$ solutions, connected in series. Same quantity of current is passed through them, then the masses of Ag, Cu and Al, deposited on their respective electrodes would directly proportional to their equivalent masses.

According to Faraday if exactly 96,500 coulombs of electric charge is passed then the mass of Ag deposited would be equal to 108g (108/1), that of copper is 31.75g (63.5/2) and Al is 9g (27/3) which are their equivalent masses respectively.

$$\text{Equivalent mass of an element} = \frac{\text{Atomic mass of the element}}{\text{Valency of the element}}$$

The current of 96,500 coulombs is called as one Faraday (F) charge after the name of Faraday. Thus Faraday is defined as the quantity of charge which deposits or liberates exactly one gram equivalent of a substance.

IF = 96500 Coulombs

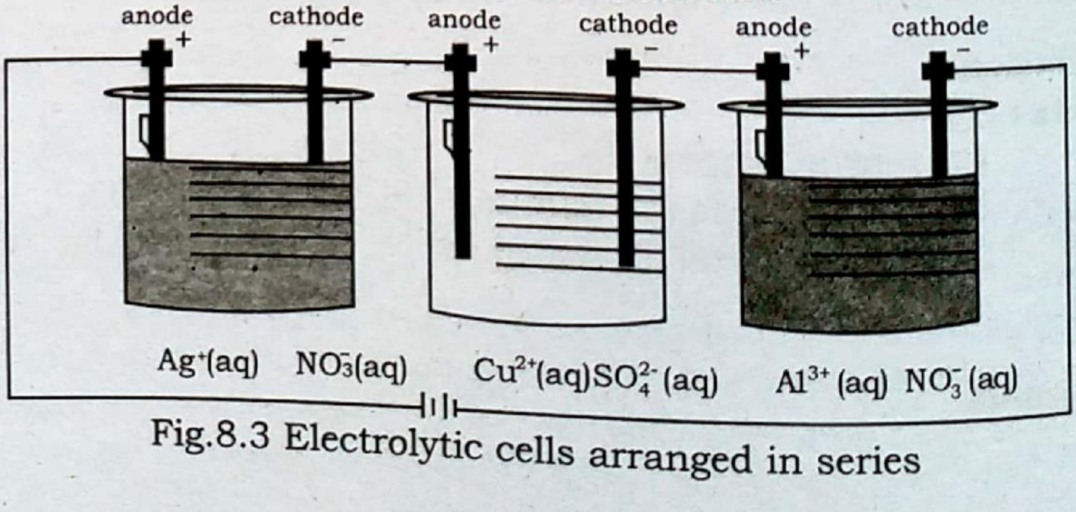


Fig.8.3 Electrolytic cells arranged in series

Relationship Between Equivalent Mass And Electrochemical Equivalent:

Since 96,500 C (IF) electric charge is required to liberate one gram equivalent mass of a substance, so it is clear that the gram equivalent mass of a substance is 96,500 times greater than its electrochemical equivalent.

Gram Eq.mass = 96,500 x E.C.E (Z)

In other words if e is the gram equivalent mass and Z is the E.C.E, then we can write it as :

$e = 96{,}500 \times Z$ or $e = F \times Z$.

UNITS OF CURRENT AND ELECTRIC CHARGE

1. **Ampere :**

It is the basic unit of current in the international system (S.I). It may be defined as the current when passed through a circuit for one second, can liberate 0.001118 g or 1.118×10^{-6} Kg of Ag from silver nitrate solution.

2. **Coulomb :**

It is the SI unit of electric charge and is defined as the quantity of charge when one ampere of current is passed for one second.

$$\begin{aligned} C &= \text{ampere} \times \text{time (s)} \\ 1 \text{ coulomb} &= 1\text{ A} \times 1\text{ s} \end{aligned}$$

A coulomb is equivalent to ampere multiplied by seconds. For example, a current of 0.5 ampere flowing for 80 seconds, gives a charge $0.5 \times 80 = 40$ coulombs.

If we are given the current and the time of electrolysis, we can calculate the amount of the substance produced at an electrode. On the other hand if we are given the amount of the substance produced at an electrode and the length of the time of electrolysis, we can determine the current or electrical charge.

Example-1:

When an aqueous solution of copper sulphate is electrolysed, copper metal is deposited at the cathode.

$$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s) \text{ -- at cathode}$$

If a constant current was passed for 5 hours and 404 mg of Cu was deposited, calculate the current passed through $CuSO_4$.

Solution:

Amount of Cu deposited = 404mg = 0.404g.

Gain of $2e^-$ means 2F electric charge

Atomic mass of Cu = 63.5

According to cathode reaction.

63.5 g of Cu is deposited by 2 F electric charge

$$\therefore 0.404\text{g of Cu is deposited by } \frac{2}{63.5} \times 0.404$$
$$= 0.0127 \text{ F}$$

We know

$$\text{IF} = 96{,}500 \text{ coulomb}$$
$$\therefore 0.0127\text{F} = 0.0127 \times 96{,}500 = 1225.6\text{C}$$

$\therefore$ Coulomb = Ampere x t sec. (time = 5hours)

$$\therefore \text{Ampere} = \frac{C}{ts} = \frac{1225.6}{5 \times 60 \times 60} = 0.0680$$
$$= 6.80 \times 10^{-2} \text{ ampere}$$

Example-2:

How many grams of oxygen gas is liberated by the electrolysis of water after passing 0.0565 ampere for 185 second.

Solution:

Equation: $2H_2O \longrightarrow O_2(g) + 4H^+ + 4e^-$

According to equation (four) Faraday is required to liberate 32 g of O_2

Data:

Current in ampere = 0.0565

Time in second = 185

Coulomb = ampere x time (s)

= 0.0565 x185 = 10.45 C.

$$F = \frac{C}{96{,}500} = \frac{10.45}{96{,}500} = 0.000108 \text{ F}$$

Now

4 F electric charge liberates 32 g O_2

$\therefore$ 0.000108 electric charge liberates $\frac{32}{4} \times 0.000108$

$= 0.000864$ g

$= 8.64 \times 10^{-4}$ g O_2

8.4 USES OF ELECTROLYSIS

Electrolysis is an important process, used for the extraction of certain metals from their ores. It is also used in electroplating. Electroplating means to coat one metal on other metal through the process of electrolysis in order to protect the baser metals from corrosion and to make them more attractive.

In 1852, the price of Aluminium metal was very high and it was considered as an expensive oddity, because of its silvery - white shining property. However, by 1890, the price of Aluminium metal had fallen very low to a fraction of the price of silver. What had happened ?

Aluminium metal is a reactive metal which makes it difficult to extract it from its ore. Before 1886 the only way to get it, was by heating its salt Aluminium chloride with sodium metal. Sodium itself was expensive which made it even more expensive.

$$AlCl_3(s) + 3Na(s) \xrightarrow{heat} Al(s) + 3NaCl(s)$$

Then in 1886 a new process was developed which involved the electrolysing a molten Aluminum compound. The same basic method of electrolysis is still used for the extraction of Al-metal. Now-a-days Al is extracted by the electrolysis of Alumina (Al_2O_3) which is obtained from the chief ore of Al, bauxite (Al_2O_3 nH_2O). Due the process of electrolysis, the price of Aluminum quickly falls. Today Aluminum is so cheap that we can use disposable plates of Aluminum for eating and throw them away afterwords.

Many metals are extracted by the electrolysis of their molten compounds, usually their chlorides, because the chlorides of most of the metals have low melting points. For example sodium metal is extracted by the electrolysis of molten sodium chloride to deposit Na metal at cathode by Down's process.

Many metals are purified into pure metals by the process of electrolysis for example impure copper (blister Cu) is purified by the process of electrolysis. In this process, the impure copper i.e. Blister copper is made as anode in the electrolytic cell, cathode is a thin plate or sheet of pure copper metal and the two electrodes are dipped in the electrolytic solution of copper sulphate ($CuSO_4$), containing few drops of sulphuric acid. The two electrodes are connected with a battery (source of electricity), when an electric current is passed through the electrolytic solution. The copper anode dissolves in the solution as Cu^{2+} ions which move towards cathode and gain electrons to get neutralized, depositing pure copper metal over cathode plate. Most of the impurities of anode fall to the bottom of the cell, called as "anode mud". Copper thus deposited at cathode is 99.99% pure. In this way copper anode (Blister copper) dissolves completely to form pure copper at cathode. This process of electrolysis is similar to electroplating.

Electroplating:

Electroplating is the process of electrolysis which is used to coat one metal onto another. Usually the object to be electroplated is made up of cheaper or baser metal, such as iron, steel etc. It is then coated with a thin layer of more attractive corrosion - resistant and costly metal, like silver, gold, nickel, chromium, tin etc. The cost of the finished product is far less than the objects entirely made of these metals. Gold coated object is much cheaper than the gold object.

1. Nickel Plating:

A cell for electroplating of nickel is shown in the fig 8.4. A piece of pure nickel is the anode and the spoon or any object to be nickel plated is cathode. A solution of nickel sulphate ($NiSO_4$) is used as the electrolyte in the electrolytic cell. The two electrodes are joined with a battery (an external source of direct electric current). On passing the electric current, the anode which is Ni, dissolves in the electrolytic solution forming Ni^{2+}ions by the loss of electrons. Ni^{2+}ions from the solution move towards the cathode, where they gain electrons and are reduced to Ni metal on the surface of spoon (cathode).

$$Ni(s)\ (anode) \longrightarrow Ni^{2+}(aq) + 2e^- \qquad \text{(Anode reaction oxidation)}$$

$$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s) \qquad \text{(Cathode reaction reduction)}$$

The net reaction is simply the transfer of Ni as Ni^{2+} through $NiSO_4$ solution towards the cathode i.e. spoon and get it coated with Ni metal on the surface. The sum of reduction and oxidation is :

$$\text{Ni(s) (anode)} \longrightarrow \text{Ni(s)} \quad \text{(cathode)}$$

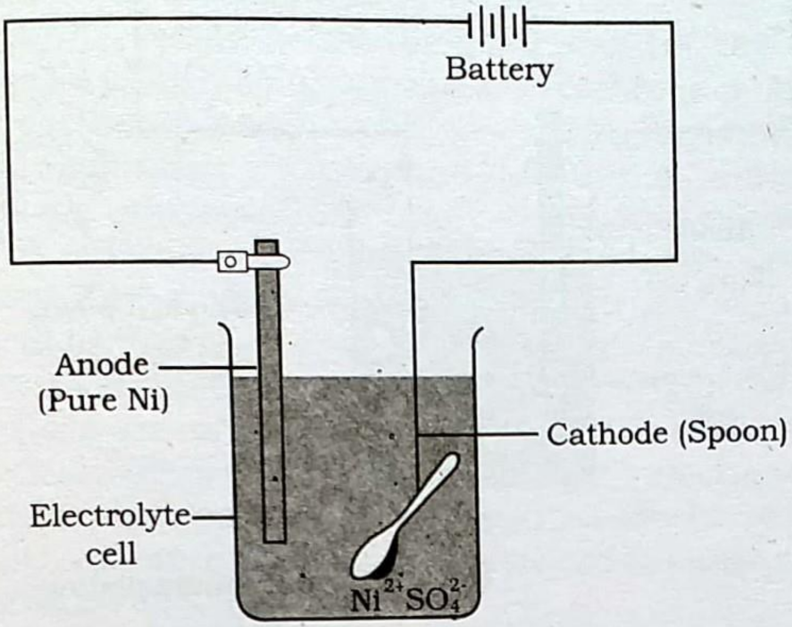


Fig. 8.4 Nickel plating

2. Chromium Plating:

Chromium metal can also be coated over baser or cheap metals by the process of electrolysis i.e. electroplating.

A cell of chromium electroplating is shown in fig. 8.5. A piece of chromium metal is the anode and the spoon or any other object to be chromium plated is the cathode. A solution of chromium sulphate [$Cr_2(SO_4)_3$] is used as an electrolyte in the electrolytic cell. The two electrodes are joined with a battery (an external source of direct electric current). On passing electric current, the anode which is chromium dissolves in the solution, forming Cr^{3+} ions by the loss of electrons, Cr^{3+} ions from the solution move towards the cathode, where they gain electrons and are reduced to deposit chromium metal on the surface of cathode.

$$\text{Cr(s) (anode)} \longrightarrow Cr^{3+}(aq) + 3e^- \quad \text{(Anode reaction oxidation)}$$

$$Cr^{3+}(aq)\ 3e^- \longrightarrow \text{Cr(s)} \quad \text{(Cathode reaction reduction)}$$

The net process is simply the transfer of Cr as Cr^{3+} ions through $Cr_2(SO_4)_3$ solution towards cathode and coating it with Cr-metal. The sum of oxidation and reduction is :

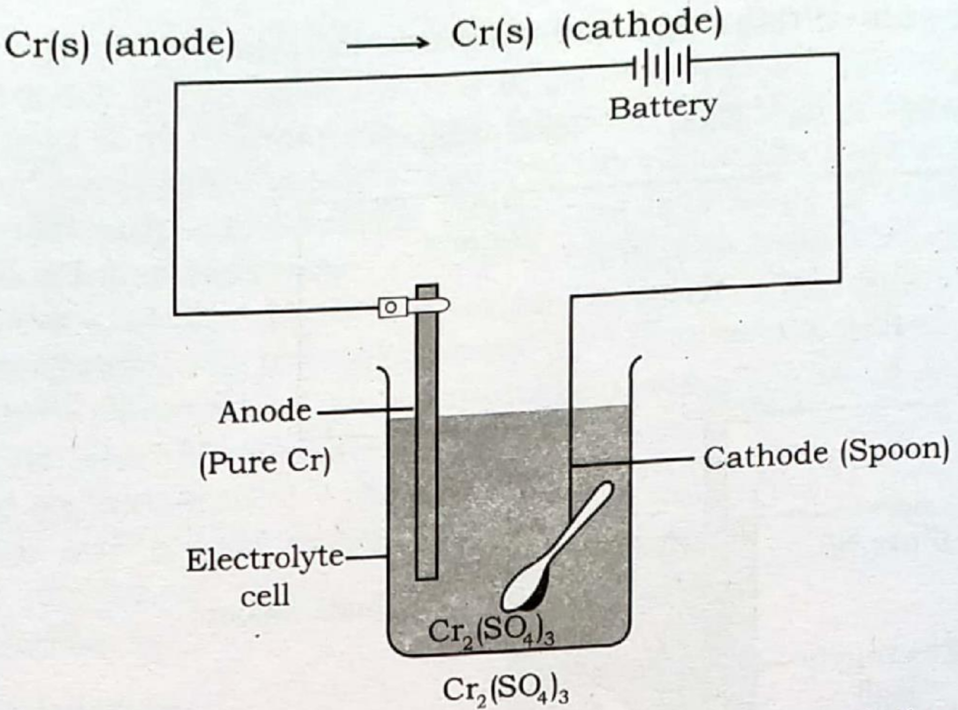


Fig. 8.5 Chromium plating

Looking for Electro plate:

Look around in your home for articles that are electroplated. Decide as far as you can :

1. What metal is plated on top.
2. What metal is underneath.
3. What is the purpose of the plating ?

Choose one of the items and look very closely at it, specially look at cooking oil container. Is there any place where the plating is noting good?

8.5 ELECTROCHEMICAL CELLS:

The cell which is used to convert chemical energy into electrical energy or vice versa is called electrochemical cell. An electrochemical cell which converts chemical energy into electrical energy is known as Galvanic or voltaic cell. This is a very strange device to produce electric current.

Take strips of zinc and copper metals, sticking them into a lemon, producing electricity. Howdoes this happen? The two dissimilar metal strips (Zn and Cu) and the electrolyte of lemon juice are the key components of the device that convert chemical energy into electrical energy. Try it on your own. Insert the Zn and Cu strips into a lemon and join the two strips by a wire outside, you will feel the electricity passing through wire joining the two strips.

The simplest of the Galvanic or Voltaic cells is Daniell cell.

Daniell Cell:

A Daniell cell is the simplest of the Galvanic or Voltaic cells which is used to convert chemical energy into electrical energy spontaneously. Daniell cell consists of two half cells. One half cell is Zinc rod (Zn - metal) dipped in IM $ZnSO_4$ solution and the other half cell is Copper rod (Cu-metal) dipped in IM $CuSO_4$ solution. The two half cells or single electrodes are connected together to form a complete cell. The two half cells should be separated from each other by a porous partition or a salt bridge, when both electrodes are connected externally through a volt-meter by means of metal wire. The cell starts producing electric current at once. Zn undergoes oxidation to form Zn^{2+} ions by the loss of 2 - electrons to go into $ZnSO_4$ solution. Zn acts as anode or negative electrode. The electrons which are free at Zn - electrode travel through the wire externally to Cu - electrode. These electrons are accepted by Cu^{2+}ions of $CuSO_4$ solution and Cu^{2+}ions undergo reduction to deposit copper metal at Cu - electrode which acts as cathode or positive electrode. In this process Zn - electrode dissolves in the solution of $ZnSO_4$ and reduces in size, while copper electrode grows in size due to the deposition of Cu - metal.

VERY SURPRIZING

Heart Beats and Electrocardiography (ECG)

The human heart, generally in a whole day pumps more than 7000 litres of blood through the circulatory system. We generally think of the heart as a mechanical device, a muscle that circulates blood via regularly spaced muscular contractions. However, in the late 1800 two pioneers in electricity Luigi Galvani and Alesandro Volta discovered that the contractions of heart are controlled by electrical phenomenon, as are nerve impulses throughout the body. These electrical impulses that cause the contraction of heart muscle are strong enough to be detected at the surface of the body. This observation formed the basis for electrocardiography (ECG). It is quite striking that although the heart's major function is the mechanical pumping of blood, it is most easily monitored by using the electrical impulses generated by volatic cell.

Cell Reaction

At Zn - Electrode (Anode)

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

At Cu - Electrode (Cathode)

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

The total cell reaction is the sum of two half cell reactions.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

The function of salt bridge or porous partition is to prevent the mixing of two solutions ($ZnSO_4$ and $CuSO_4$) and allows the ions to move through from one part to another. Zn^{2+} ions from the anode compartment move into the cathode compartment, while negative ions: SO_4^{2-} ions move from cathode compartment to anode compartment through the porous partition or salt bridge. It maintains the electrical neutrality in the two electrolytic solutions.

The cell voltage in Daniell cell is 1.10 volt.

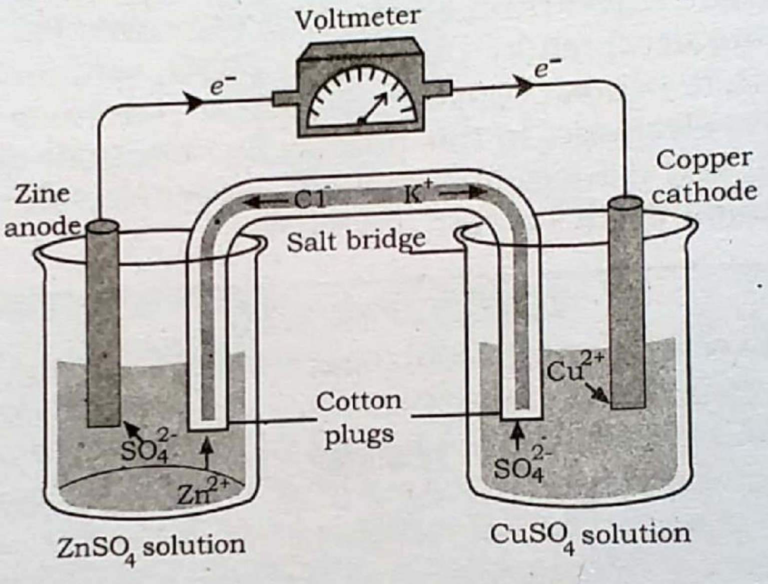


Fig.8.6 Daniell cell (A Zn - Cu voltaic cell)

8.6 Batteries:

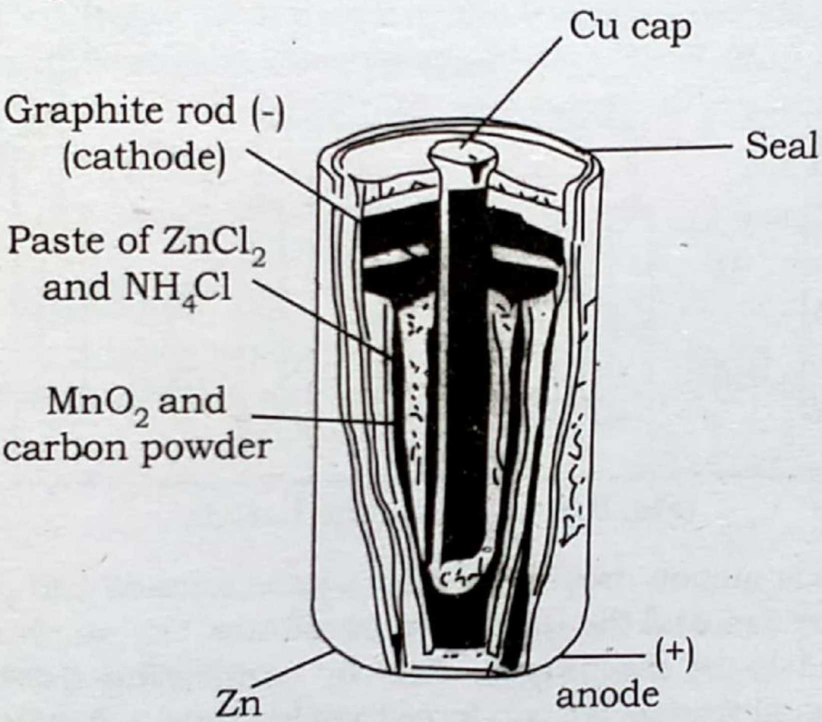
In every day life, we use the devices to produce electricity by the chemical reactions, known as batteries. A flash light "battery" consists of single voltaic cell with two electrodes in contact with one or more electrolytes. Some times a distinction is made between the terms "cell" and "battery". A battery is an assembly of two or more voltaic cells, connected together in series. By this definition, automobile or motor battery is a true battery. The most common types of cells or batteries are described as follows:

1. Dry Cell:

It is a primary cell, which is used to convert chemical energy into electrical energy. It is used in most of the flash lights, calculators, clocks, transistors and in portable electronic devices. It is an irreversible cell.

In a dry cell (fig 8.7), there is an outer zinc vessel which acts as anode and inert carbon (graphite) rod which acts as cathode. The graphite rod is surrounded by a mixture of manganese dioxide (MnO_2) and carbon powder. The electrolyte is a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$). The cell is called a dry cell because there is no free flowing liquid. The concentrated electrolytic solution is thickened into a gel like paste by an agent such as starch. The upper top position of the cell is sealed with wax (sealing material). A copper cap is fitted on the top of carbon rod (cathode) to make the electrical contact. The whole cell is covered with a safety cover.

The cell diagram is as :



(Fig. 8.7 Dry cell)

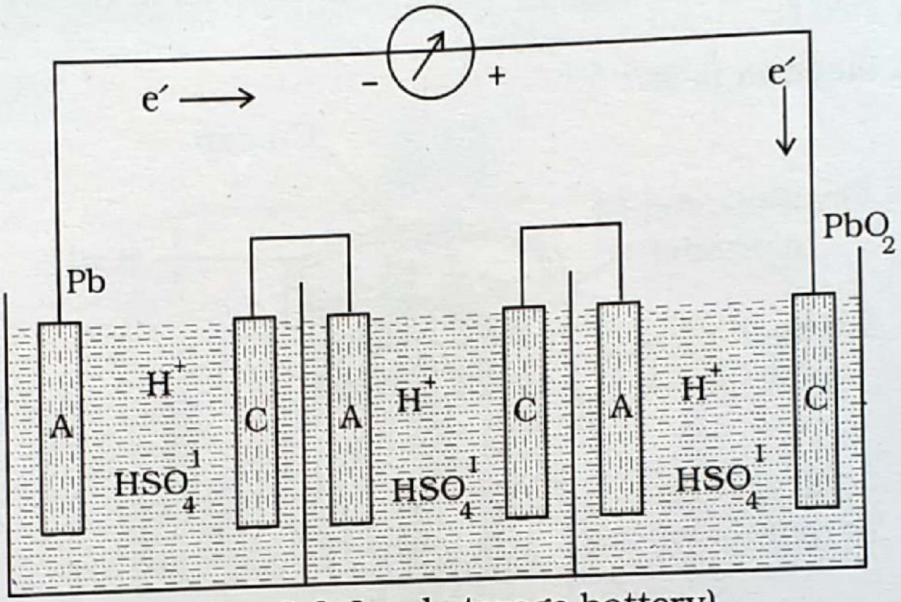
When zinc and graphite electrodes are connected by a metallic wire, Zn gets oxidized to form Zn^{2+}ions which pass into the wet paste leaving behind electrons on the Zn container and the electrons move from Zn electrode to carbon electrode through the external circuit. The cell reactions are complex.

2. Lead-Storage Battery (Motor - Battery)

Lead storage battery is used in automobiles. It is a secondary battery and is a reversible cell which can be restored to its original condition. The battery can be used through repeated cycles of discharging and recharging.

Fig 8.8 shows a portion of the cell in the lead storage battery. There are several anodes and several cathodes which are connected together in series; about six cells are connected together. Each cell has a voltage of 2V and overall voltage when six cells are connected together in series would be 12V.

In lead storage battery, anodes are the lead alloy and cathodes are made up of red lead dioxide (PbO_2). The electrolyte is dilute sulphuric acid having concentration of 30%



(Fig. 8.8 Lead storage battery)

As the cell reaction proceeds, $PbSO_4(s)$ precipitates and partially coats both the electrodes, and the water formed dilutes the sulphuric acid. The battery is said to be discharged. Now by connecting the battery to an external electrical source, we can force the electrons to flow in the opposite direction, i.e. the net cell reaction can be reversed and the battery is recharged.

SUMMARY

1. The chemical compounds which conduct electricity and as a result decompose by the loss and gain of electrons are called electrolytes. The chemical compounds which do not conduct electricity are called non - electrolytes.
2. Electrolytic cells are the cells, use external voltage to push a reaction non - spontaneously and are used to convert electrical energy into chemical energy while electrolysis may be defined as a process in which movements of the ions take place towards

their respective electrodes to undergo chemical changes under the influence of applied electric field. In the electrolysis of molten sodium chloride, sodium metal is formed at cathode, while chlorine gas is liberated at anode.

3. Electrochemical voltaic cell uses spontaneous chemical reactions to generate an electric current through oxidation reduction reactions. The half reactions take place in half cells. The half cell in which reduction occurs is called cathode; the half cell in which oxidation occurs is called anode. Electrons flow in the external circuit from anode to cathode. Voltaic cells are used commercially as portable energy sources (batteries). Electrolysis is an important process used for the extraction of certain metals, in purification of metals and in electroplating. Nickel - plating and chromium plating are very important techniques to protect baser metals from corrosions.

EXERCISE

1. **Fill in the blanks:**

(i) The substance used for electrolysis is called __________.

(ii) When molten sodium chloride is electrolysed ____________ is formed at cathode.

(iii) One Faraday is equivalent to __________ coulombs.

(iv) The electrolyte in lead storage battery is __________.

(v) Dry cell is a __________ cell.

2. **Write true or false:**

(i) Sugar is an electrolyte.

(ii) Electrolytic conductance is also known as electrolysis.

(iii) Z is called as electrochemical equivalent.

(iv) The unit of electrochemical equivalent is ampere x second.

(v) Daniell cell is a voltaic cell.

(vi) Lead storage battery is a primary cell.

3. **Write answers of the following questions:**

(i) Define the following terms:

(a) Electrolysis (b) Electrochemical cell

(c) Coulomb (d) Electrochemical equivalent

(e) Primary cell (f) Electroplating

(ii) Predict what would be formed (i) at the anode and (ii) at the cathode when each of the following molten salts are electrolysed using inert electrodes.

(a) NaCl (b) $MgBr_2$ (c) $CaCl_2$

(iii) State and explain Faradays first law of electrolysis.

(iv) Calculate the amount of silver deposited when 10 ampere of current is passed for 50 minutes through a solution of $AgNO_3$. (Z of Ag = 0.00118 g/C)

(v) Describe the construction and working of a dry cell.

(vi) What happens when electric current is passed through acidulated water? Give the reactions at two electrodes and mention the products at cathode and anode.

(vii) Predict the net electrolysis reaction when molten NaCl is electrolysed.

(viii) Describe the process of nickel plating.

(ix) What is the function of a salt bridge or porous partition in an electrochemical cell?

(x) Which of the following pairs of terms have the same meaning and which have a different meaning ?

(a) Voltaic cell and Galvanic cell.
(b) Electrolytic cell and Electrochemical cell.
(c) Cell and battery.

(xi) What is the difference between a primary and a secondary cell? Give an example of each. Discuss lead - storage battery.

(xii) When molten NaCl is electrolysed. Sodium metal is liberated at cathode by the reaction $Na^+ + e^- \longrightarrow Na(s)$. How many grams of sodium are liberated when 5×10^3 C of electric charge is passed through the cell.