
INTRODUCTION OF ELECTROCHEMISTRY

Concept of electrochemistry: The branch of science which deals with the relationship between electrical energy and chemical energy and their inter-conversion of one form to another is called electrochemistry.

Electrolysis: The changes in which electrical energy causes chemical reaction to occur.

Electro chemical cells: The changes in which electrical energy is produced as a result of chemical change.

Conductors: The substances which allow the passage of electric current are called conductors.
Eg. Metals like Cu, Ag, Sn etc.

Insulators: The substances which do not allow the electric current to pass through them are called insulators or non-conductors. Eg. Rubber, wood, wax, wool, glass etc.

Metallic conductors: These are the metallic substances which allow the electric current to pass through them without undergoing any chemical change. The flow of electric current in metallic conductors is due the flow of electrons in the metal atoms. Eg. Metals like Cu, Ag, Sn etc.

Electrolytes: These are the substances which allow the electric current to pass through them in their molten states or in the form of their aqueous solutions and undergo chemical decomposition. The flow of electric current through an electrolytic solution is called electrolytic conduction in which charge is carried by ions. These substances do not conduct electricity in the solid state but conduct electricity in the molten state or aqueous solutions due to movement of ions. Eg. Acids, bases and salts.

Non-electrolytes: The substances which do not conduct electricity either in their molten state or through their aqueous solutions are called non-electrolytes. Eg. Sugar, glucose, urea, ethyl alcohol etc.

Strong electrolytes: The electrolytes which are almost completely dissociated into ions in are called strong electrolytes. Eg: NaCl, KCl, HCl, NaOH, NH_4NO_3

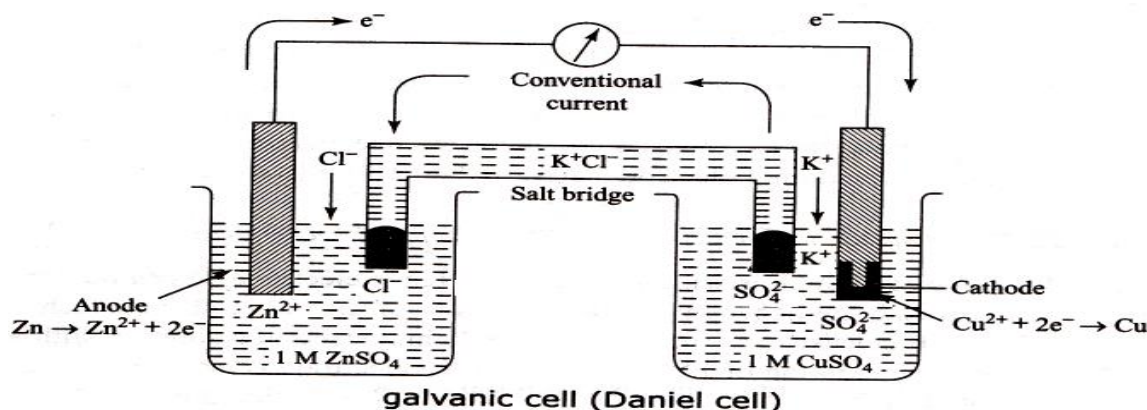
Weak electrolytes: The electrolytes which do not ionize completely in solution are called weak electrolytes. Equilibrium is established between unionized electrolyte and the ions formed in the solution.

ELECTRO CHEMICAL CELLS

- An electrochemical cell is a device which converts chemical energy into electrical energy.
- The redox reaction is utilized for generation of electrical energy.
- The electrochemical cells are commonly referred as Voltaic or Galvanic cells.
- The electromotive force (EMF) of such cell is directly proportional to intensity of chemical reaction taking place in it.
- The electrochemical cell is divided into two half cells. The half cell electrode where oxidation (loss of electrons) occurs is called anode (negative electrode). The half cell electrode where reduction (gain of electrons) occurs is called cathode (positive electrode). An electrochemical cell is the coupling of these two half cells.

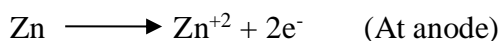
DANIEL CELL:

- The Daniel cell is a typical example of Galvanic cell.
- Daniel cell consists of a beaker containing copper rod dipped in CuSO_4 solution which is connected to another beaker containing zinc rod dipped in ZnSO_4 solution by a salt bridge.
- Salt bridge is an inverted U-tube containing saturated solution of some electrolyte such as KCl , KNO_3 , NH_4NO_3 which does not undergo chemical change during the process. The saturated solution is generally taken in agar-agar jelly or gelatin.
- The salt bridge allows the flow of ions to pass through it when the flow of electric current takes place. It completes the electrical circuit and maintains the electrical neutrality of two half cell solutions.
- When the circuit is completed, electric current flows through the external circuit as indicated by an ammeter. The following observations are made:
 1. Zinc rod gradually loses its weight.
 2. The concentration of $\text{Zn}^{+2}(\text{aq})$ in the $\text{ZnSO}_4(\text{aq})$ solution increases.
 3. Copper gets deposited on the electrode.
 4. The concentration of $\text{Cu}^{+2}(\text{aq})$ in $\text{CuSO}_4(\text{aq})$ solution decreases.
 5. The flow of electrons is from Zn-electrode (anode) to Cu-electrode (cathode).
 6. The flow of electric current is from Cu-electrode (cathode) to Zn-electrode (anode).



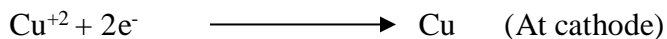
The above observations can be explained as follows:

- Zn is oxidized to Zn^{+2} ions which go in the solution and therefore Zn rod gradually loses its weight (oxidation half cell).



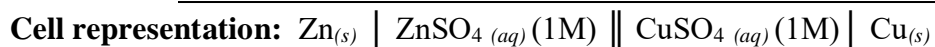
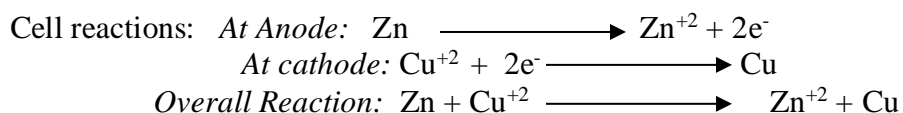
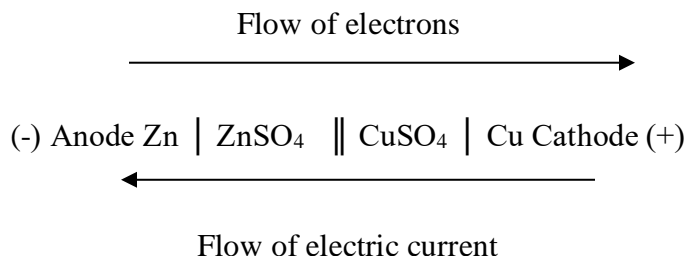
- The electrons released at the Zn electrode move towards Cu electrode through external circuit.
- These electrons are accepted by the Cu^{+2} ions in the solution and get reduced to copper which gets deposited on the Cu-electrode (reduction half cell).

➤



- The oxidation of Zn occurs at anode (negative terminal) and reduction of Cu^{+2} occurs at cathode (positive terminal).

➤ The flow of electrons is from negative terminal (anode) to positive terminal (cathode).



TYPES OF ELECTRODES

Electrode potential (or) Single Electrode potential (E): It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

Standard Electrode potential (E°): It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of one molar concentration at 25°C.

Types of Electrodes: An electrochemical cell consists of two electrodes, positive and negative. Each electrode constitutes a half cell or a single electrode.

CONSTRUCTION AND FUNCTIONING OF SOME STANDARD ELECTRODES:

The single electrode potential is conveniently measured by combining the half cell with a standard electrode and measuring the total EMF of the cell.

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$E_{\text{cell}} = E_{\text{right}} - E^{\circ} \text{ (if standard electrode is anode)}$$

$$E_{\text{cell}} = E^{\circ} - E_{\text{left}} \text{ (if standard electrode is cathode)}$$

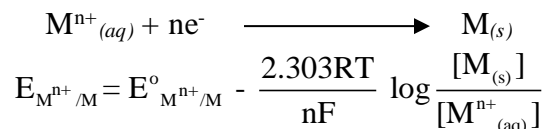
Where E° is the standard electrode potential.

Eg. Standard hydrogen electrode, Calomel electrode, Quinhydrone electrode

NERNST EQUATION

Standard electrode potentials are measured at standard states i.e at 1M concentration of electrolyte, temperature at 298 K and 1atm pressure. However the electrode potentials depend upon concentration of electrolyte solutions and temperature. Nernst equation gives the relationship between electrode potentials and concentration of electrolytic solutions.

For the general reduction reaction occurring at an electrode,



Where E° = Standard EMF of the cell for 1 M solution at 298 K;

R = Gas constant;

T = Kelvin temperature;

n = number of electrons involved in the cell reaction;

F = Faraday of electricity;

E = electrode potential of the metal;

$[M]$ = activity of metal in the metal phase and is taken as unity;

$[M^{n+}]$ = activity of metal ions in the solution is taken equal to their molarities;

But at STP conditions, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$; $T = 298 \text{ K}$; $F = 96500$ coulomb charge. Then the Nernst equation becomes

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{1}{[M^{n+}_{(aq)}]} \quad \text{considering } [M^{n+}_{(s)}] = 1$$

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} - \frac{0.0592}{n} \log \frac{1}{[M^{n+}_{(aq)}]}$$

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{0.0592}{n} \log [M^{n+}]$$

Nernst equation enables us to calculate the following:

1. Half cell potential or single electrode potential.
2. Cell potential or EMF of the cell.
3. Equilibrium constant for the cell reaction.

Definition of Battery:

A battery is an arrangement of several electrochemical cells connected in series that can be used as a source of direct electric current, thus, a cell contains only one anode and cathode. A Battery contains several anodes and cathodes.

TYPES OF BATTERYS

1. Primary Battery (or) Primary cells:

In these cells, the electrode and the electrode reactions cannot be reversed by passing an external electrical energy. The reactions occur only once and after use they become dead. Therefore, they are not chargeable.

Example: Dry cell, alkaline Cell and Li Cell.

2. Secondary Battery (or) Secondary cells:

In these cells, the electrode reactions can be reversed by passing an external electrical energy. Therefore, they can be recharged by passing electric current and used again and again. These are also called **Storage cells** (or) **Accumulators**.

Example: Lead Acid storage cell, Nickel-Cadmium cell and Li-Ion Cell.

3. Fuel cell

In these cells, the reactants, products and electrolytes are continuously passing through the cell. In this chemical energy gets converted into electrical energy.

Example: Hydrogen-Oxygen fuel cell. Methanol-Oxygen fuel cell.

BASIC REQUIREMENTS FOR COMMERCIAL BATTERIES

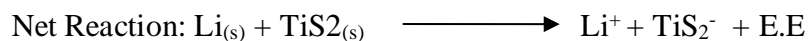
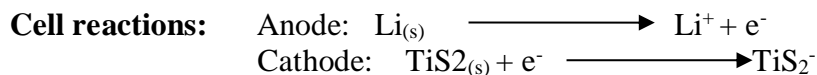
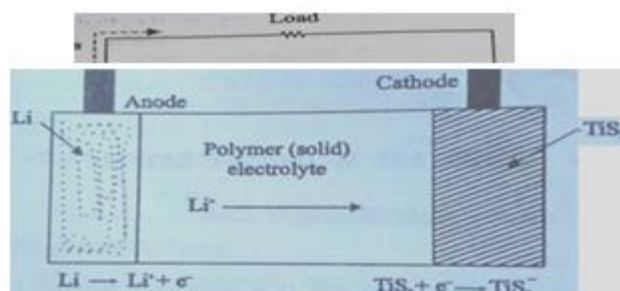
1. Battery should be light weight and compact for easy transport.
2. Battery should have long life both when it is being used and when it is not used.
3. Battery voltage should not vary appreciably during its use.
4. Battery should need **adaptability** to handle and endure changing and various climatic conditions.
5. The batteries need **durability** for a long time without breaking and high usage
6. The **cycle life** of a rechargeable battery is the number of discharge/charge cycles it can undergo before its capacity falls to 80%.
7. Battery should give sufficient performance for the **lowest possible price**.

COMPARISON BETWEEN PRIMARY, SECONDARY AND FUEL CELLS

Sl. No.	Primary cells	Secondary cells	Fuel cells
1.	Cell reaction is irreversible	Cell reaction is reversible.	Energy can be withdrawn indefinitely as long as outside supply of fuel is Maintained.
2.	Must be discarded after use.	May be recharged.	Cannot be reused.
3.	Have relatively short shelf life.	Have long shelf life.	Have life as long as the fuel is supplied.
4.	Function only as galvanic cells.	Functions both galvanic Cell & as electrolytic cell.	Functions as only galvanic cell.
5.	They cannot be used as storage devices	They can be used as energy storage devices (e.g. solar/ thermal energy converted to electrical energy)	Do not store energy.
6.	They cannot be recharged	They can be recharged.	They cannot be recharged.
7.	Eg. Dry cell, Alkaline cell and Li- battery.	Eg. Lead acid storage cell, Ni-Cd battery.	Eg: H ₂ -O ₂ fuel cell and CH ₃ OH-O ₂ fuel cell

LITHIUM CELL - PRIMARY BATTERY

- Lithium cell is a primary cell, Lithium metal acts as anode.
- Metal oxide or TiS₂ acts as cathode.
- Solid polymer will act as an electrolyte; this polymer is packed in between the electrodes. The electrolyte permits the passage of ions but not that of electrons.
- The EMF of the cell is 3.0V



Advantages:

1. In this cell voltage is high, 3.0V.
2. Lithium is a light weight metal (7gms).
3. Lithium has the most negative E° value.
3. In Lithium cell all constituents are in solid form so that there is no leakage.
4. The battery can be made in a variety of sizes and shapes.

Applications:

Button sized Lithium batteries are used in calculators, watches, cameras, mobile phones, laptop computers, etc.

1. CONSTRUCTION, WORKING AND APPLICATIONS OF LI-ION

Li – ion is a rechargeable secondary battery. This battery having number of charge – discharge cycles. In Discharge process it will act as voltaic cell and charging process it will act as Electrolytic cell.

Construction:

Anode: Layers of Lithium-Cobalt oxide (LiCoO_2).

Cathode: Layers of Carbon (graphite).

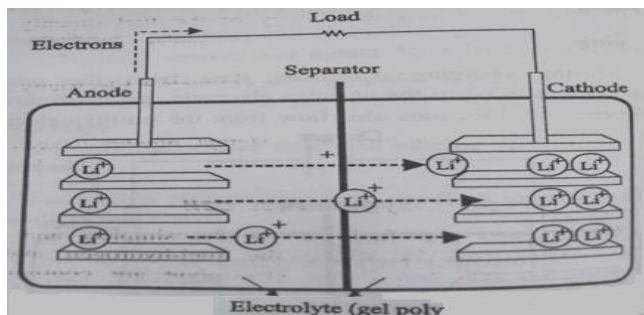
Electrolyte: Organic polymer. (Generally a polymer gel, act as separator between the electrodes. The separator permits the passage of ions but not that of electrons)

Working:

In Discharge process it will act as voltaic cell and charging process it will act as Electrolytic cell.

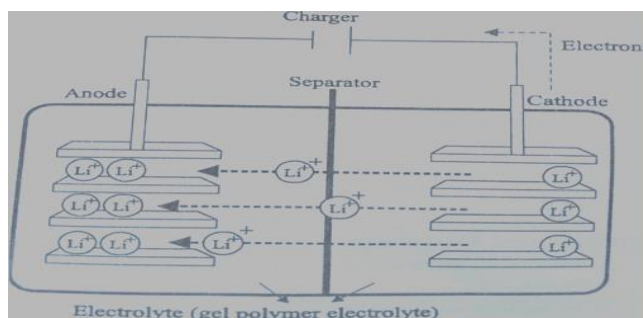
Discharging (voltaic cell):

During discharging, the Li^+ ions flow through the electrolyte from negative electrode to the positive electrode. Electrons flow from the negative electrode to the positive electrode. The Li^+ ions and electrons combine at the positive electrode and deposit there as lithium.



Charging (electrolytic cell):

During charging, the Li^+ ions flow back from the positive electrode to negative electrode through electrolyte.

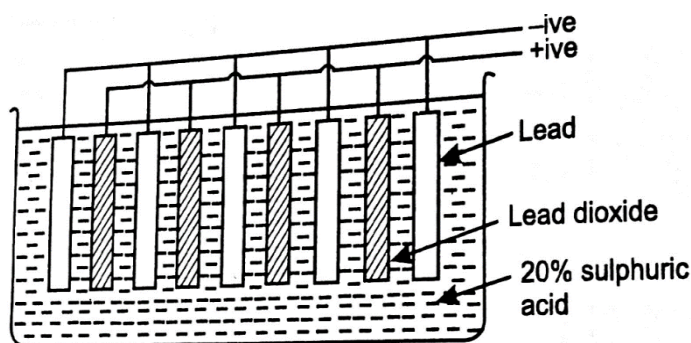


Applications:

1. The Li-ion batteries are used in cameras, calculators, smart phones and most of the consumer electronics device.
2. They are used in cardiac pacemakers and other implantable device.

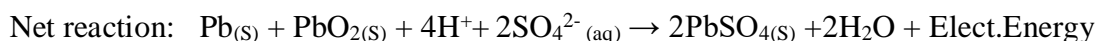
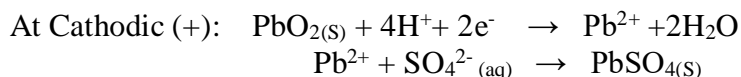
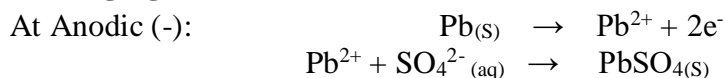
2. LEAD ACID STORAGE CELL - SECONDARY BATTERY

- It consists of lead –antimony alloy coated with lead dioxide (PbO_2) as cathode and spongy lead as anode. The electrolyte is a 20% solution of H_2SO_4 .
- The storage cell can operate both as voltaic cell and electrolytic cell.
- It acts as voltaic cell when supplying energy and as a result eventually becomes rundown.
- The cell operates as electrolytic cell when being recharged.



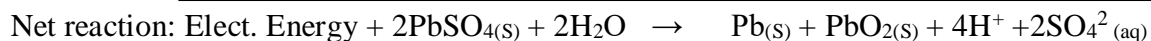
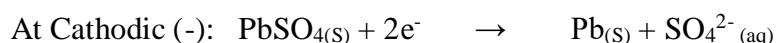
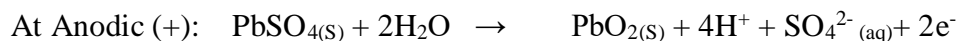
- The cell consists of a series of Pb-plates (negative plates) and PbO_2 plates (positive plates) connected in parallel. The plates are separated from adjacent one by insulators like wood, rubber or glass fiber.

Discharging (voltaic cell):



During the discharging the battery, H_2SO_4 is consumed the density of H_2SO_4 falls to 1.20g/cm^3 , then battery needs recharging. In discharging, the cell acts as a voltaic cell where oxidation of lead occurs. In charging, the cell is operated like an electrolyte cell and electric energy is supplied to it.

Recharging (electrolytic cell):



During this process, lead is deposited at the cathode, PbO_2 is formed at the anode and H_2SO_4 is regenerated in the cell.

Applications: The lead storage cells are used to supply current for electrical vehicles, gas engine ignition, telephone exchanges, electric trains, mines, laboratories, hospitals, broadcasting stations, automobiles and power station.

APPLICATIONS OF LI-ION BATTERY TO ELECTRICAL VEHICLES

1. Due to light weight Li-ion batteries are used for propelling a widerange of electric vehicles such as aircraft, electric cars and hybrid vehicles.
2. Advanced electric wheelchairs,
3. Radio-controlled models,
4. Model aircraft and the Mars Curiosity rover.

FUEL CELLS

A fuel cell is a galvanic cell in which chemical energy of a fuel – oxidant system is converted directly into electrical energy in a continuous electrochemical process. The chemical energy provided by the fuel cell is stored outside the cell. The fuel and oxidants are continuously and separately supplied to the electrodes of the cell where they undergo reactions. Fuel cells are capable of supplying current as long as reactants are supplied.



Example: Hydrogen-Oxygen fuel cell and Methanol-Oxygen fuel cell.

DIFFERENCES BETWEEN BATTERIES AND FUEL CELLS

Sl.No.	BATTERY	Fuel cells
1.	A battery is a device containing two or more electrochemical cells that can convert chemical energy into electrical energy directly	A fuel cell is a device that can convert chemical energy into electrical energy
2.	Produces electrical energy for a comparatively short time period	Can provide us with electrical energy for a long period of time
3.	Contains a limited amount of fuel and oxidant and these two components decrease with time, so this device cannot supply electrical energy for a long period of time	Continuously supplied with fuel and oxygen from an external source. which makes it work for a long time period

CONSTRUCTION AND APPLICATIONS OF METHANOL OXYGEN FUEL CELL

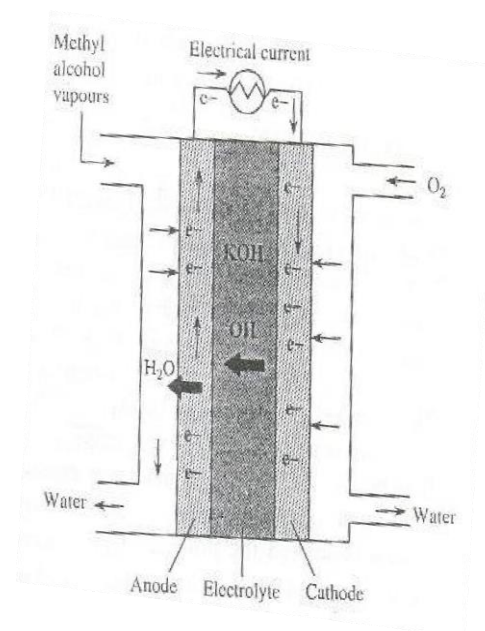
Construction: The cell consists of methanol and used as the fuel and oxygen (or) air as the oxidant.

Anode: Nickel sheet covered by Pt-Pd catalyst.

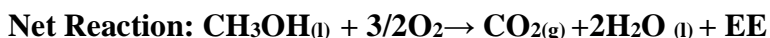
Cathode: Silver on nickel sheet.

Electrolyte: KOH solution.

In this cell methanol and oxygen are fed to the electrolyte. CO_2 produced is absorbed by the electrolyte KOH and converted in carbonates. Formation of carbonates decreases the cell efficiency because of the increasing, concentration and polarization at the electrode surface and decreases the conductivity of the electrolyte.



Working:



Advantages of methyl alcohol-oxygen fuel cell:

1. Easy to transport.
2. Do not require complex steam reforming operations.
3. These fuel cells are targeted to portable applications
4. It is excellent fuel due to presence of high concentration of hydrogen in methanol.
5. There is zero emission by the cells hence the fuel cells are eco-friendly.

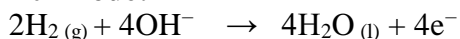
Applications of methyl alcohol-oxygen fuel cell:

1. Because of light weight these fuel cells are preferred for space crafts and product H_2O is a valuable fresh water source for astronauts.
2. The major application of methyl alcohol-oxygen fuel cells is a fuel for fuel cell motor vehicles like NECER-5(Japan), USA.

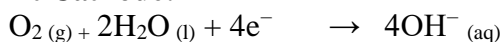
CONSTRUCTION AND APPLICATIONS OF HYDROGEN OXYGEN FUEL CELL

Hydrogen-Oxygen fuel cell: The cell consists of two inert porous electrodes, these electrodes are made of granite impregnated with platinum or lead with silver or nickel (75:25) and electrolyte solution 2.5% KOH through the anode hydrogen gas is bubbled and through cathode oxygen gas bubbled.

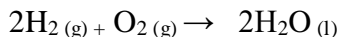
At Anode:



At Cathode:



Net Reaction:



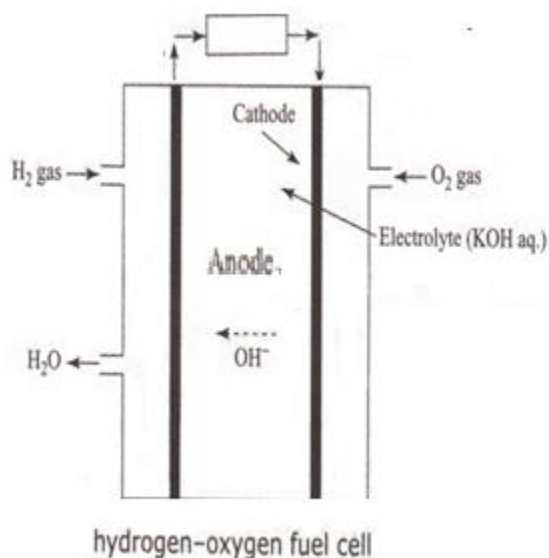
The product discharged is water and the standard EMF as the cell is $E^\circ = 1.23$ volts

Applications:

1. They are used as auxiliary energy source in space vehicle, submarines and military vehicles.
2. Because of light weight these fuel cells are preferred for space crafts and product H_2O is a valuable fresh water source for astronauts.

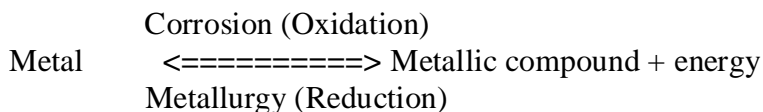
Limitations:

1. The life time of fuel cells is not accurate known.
2. Their initial cost is high.
3. The distribution of hydrogen is not proper.

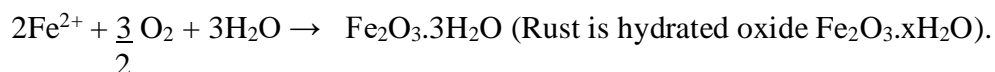


CORROSION AND ITS CONTROL

Definition: Corrosion may be defined as the disintegration or eating away of a metallic material from its surface by chemical or electrochemical reaction with its environment.

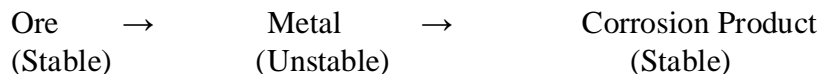


Example: Rusting of iron when exposed to atmospheric conditions.



CAUSES OF CORROSION

In nature metals have a natural tendency to revert back to combined states. During this process mostly oxides are formed though in some cases sulphides, carbonates. Any process of deterioration and loss of solid metallic material by chemical or electrochemical attack by its environment is called corrosion. Corrosion is the reverse process of metallurgy.



EFFECT OF CORROSION

- Poor appearance
- Maintenance and operating costs
- Plant shutdowns
- Contamination of product
- Loss of valuable products due to leakage
- Effects on safety and reliability in handling hazardous materials
- Product liability
- Valuable metallic properties such as conductivity, malleability, ductility, etc. are lost due to corrosion.

THEORIES OF CORROSION

There are two theories of corrosion

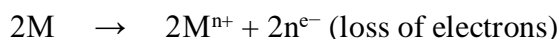
1. Dry/Chemical theory
2. Wet/Electrochemical/galvanic theory

1. Dry (or) chemical Corrosion: According to this theory type of corrosion occurs mainly through the direct chemical action of atmospheric gasses (O_2 , H_2S , SO_2 , and N_2) with metal.

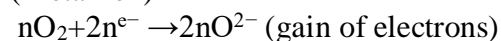
There are three main types of dry Corrosion:

- i. Oxidation corrosion
- ii. Corrosion of the other gases
- iii. Liquid metal corrosion.

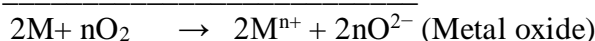
i. Oxidation corrosion: This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture at ordinary temperature metals or very slightly attacked. The exceptions are Alkali metals and Alkaline earth metals. At high temperature all metals are oxidized. The exception is Ag, Au and Pt.



(Metal ion)



(Oxide ion)



Mechanism: During oxidation of a metal, metal oxide is formed as a thin film on the metallic surface which protects the metal from further corrosion. If diffusion of either oxygen or metal is across this layer, further corrosion is possible. Oxides of Pb, Al, Sn are stable, and hence inhibit further corrosion.

ii. Corrosion of the other gases: Cl_2 , SO_2 , H_2S , NO_x gases react with metal and form corrosion products which may be protective or non-protective. Dry Cl_2 reacts with Ag and forms AgCl which is a protective layer, while $SnCl_4$ is volatile in petroleum industries at high temperatures, H_2S attacks steel forming FeS scale which is porous and interferes with normal operations.

iii. Liquid metal corrosion: In several industries, molten metals pass through metallic pipes and causes corrosion due to dilution or due to internal penetration.

Example: Coolant (sodium metal) causes cadmium corrosion in nuclear reactor. Liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.

2. Wet (or) Electrochemical Corrosion:

This type of Corrosion occurs where a conducting liquid is in contact with the metal (or) when two dissimilar metals (or) alloys are dipped partially in a solution. This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution. At anodic area, oxidation reaction occurs thereby destroying the anodic metal either by dissolution (or) formation of compounds. Hence corrosion always occurs at anodic parts. M^{n+} dissolution formation of compound at cathodic part, reduction reaction (electronation) occurs. It does not affect the cathode, since most metals cannot be further reduced. At cathodic part, the dissolved constituents in the conducting medium accept the electrons forming ions (OH^{-} , O^{2-}).

The metallic ions formed at anodic part and the ions formed at cathodic part diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode.

Mechanism: Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.



The cathodic reaction consumes electrons with either *evolution of hydrogen* or *absorption of oxygen* which depends on the nature of corrosive environment.

i. Evolution of hydrogen: This type of corrosion occurs in acidic medium.

Ex: Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

The electrons released flow through the metal from anode to cathode, whereas H^{+} ions of acidic solution are eliminated as hydrogen gas.

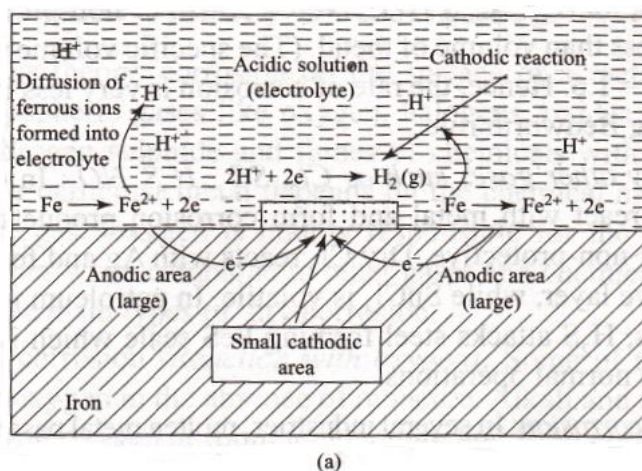
At Anode: $Fe \rightarrow Fe^{2+} + 2e^{-}$ (Oxidation)

At Cathode: $2H^{+} + 2e^{-} \rightarrow H_2$ (Reduction)

Overall reaction: $Fe + 2H^{+} \rightarrow Fe^{2+} + H_2$

This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas.

The anodes are large areas, whereas cathodes are small areas.

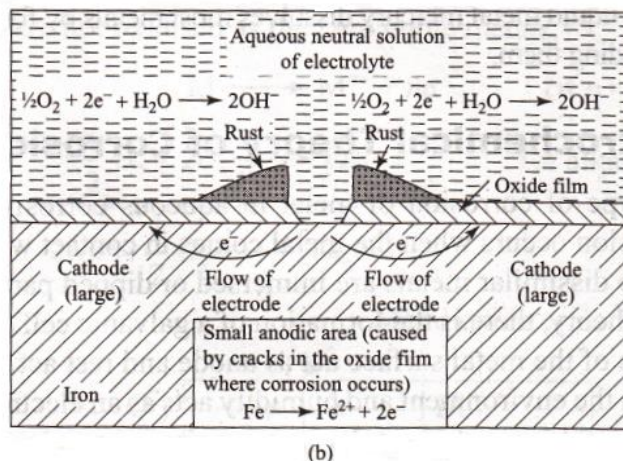


ii. Absorption of oxygen:

This type of corrosion occurs in neutral (or) basic medium.

Ex: Rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen.

Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes.

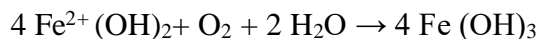


At anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$ (Oxidation)

At cathode: $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^-$ (Reduction)

Overall reaction: $\text{Fe} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{OH}^-$ ($\text{Fe}(\text{OH})_2$)

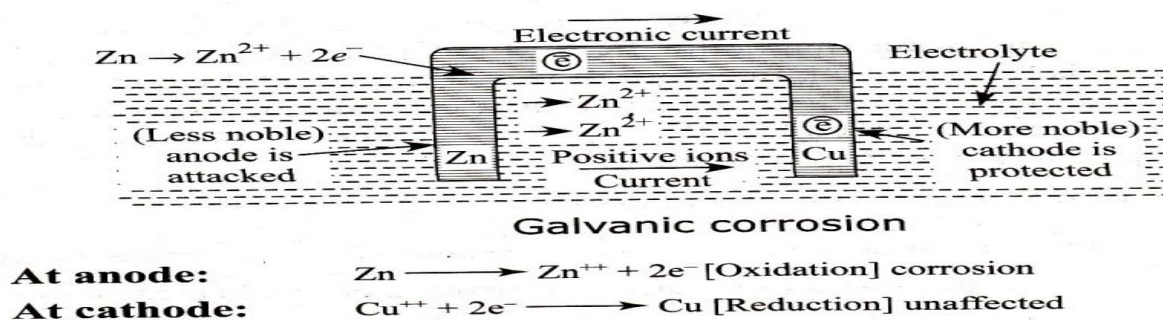
If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.



The product called yellow rust corresponds to $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

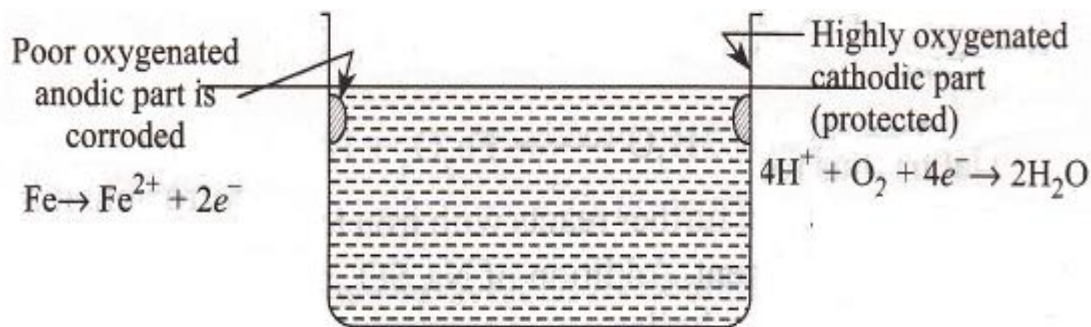
TYPES OF CORROSION

1. Galvanic Corrosion: When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called galvanic corrosion.



Galvanic corrosion can be avoided by coupling metals close to the electrochemical series, fixing insulating material between two metals, by using larger anodic metal and smaller cathodic metal.

2. Waterline Corrosion: This is also known as *differential oxygen concentration corrosion*. It has been observed in the case of iron tank containing water, that the portion of iron tank just below the water level undergoes corrosion. It is due to the difference in oxygen concentration.



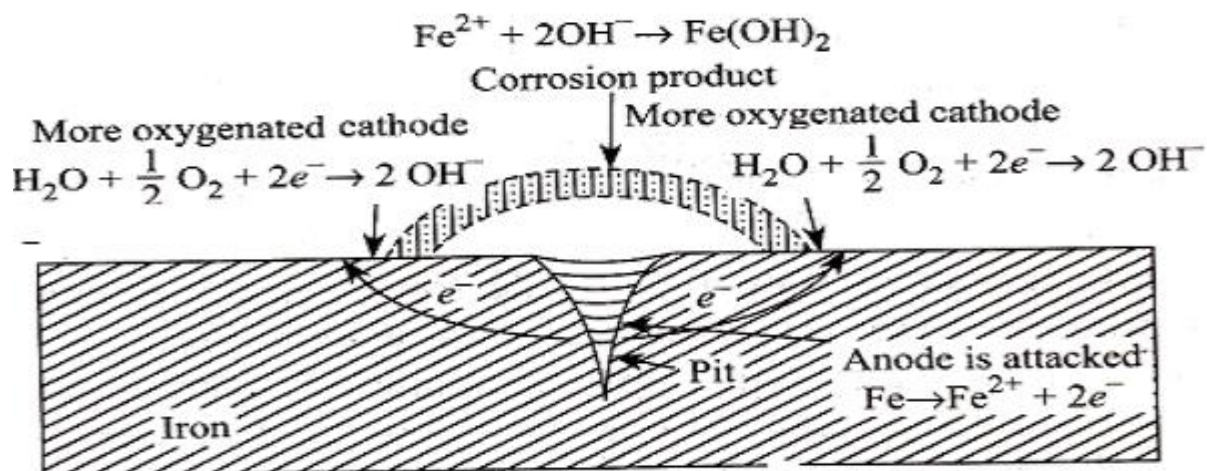
At anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$

At cathode: $2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{H}_2\text{O}$ ($\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$)

Overall reaction: $\text{Fe} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{OH}^-$ ($\text{Fe}(\text{OH})_2$)

The area above the waterline (highly oxygenated) acts as cathodic and is not affected by corrosion. However, if the water is relatively free from acidity, little corrosion occurs. This type of corrosion is prevented to a great extent by painting the sides of the ships by antifouling paints.

3. Pitting corrosion: Pitting corrosion is due to crack on the surface of a metal, there is a formation of a “local galvanic cell” (Pinholes, pits and cavities) in the metal.



Pitting is usually the result of the breakdown or cracking of the protective film on a metal at specific points. This gives rise to the formation of small anodic and large cathodic areas. In the corrosive environment this produces corrosion current.

FACTORS AFFECTING OF CORROSION

The rate and extent of corrosion depends on the nature of the metal and nature of corroding environment. Those are

1. Effect of metal
2. Effect of environment

1. Effect of metal: Different properties of a metal are responsible for corrosion. These properties are given below.

- a. Position of metal in galvanic series
- c. Nature of surface/oxide film

- b. Hydrogen over voltage
- d. Volatility of corrosion product

a. Position of metal in galvanic series: It decides the corrosion rate. A metal having higher position in galvanic series undergoes corrosion when connected to another metal below it.

b. Hydrogen over voltage: In case of Zinc metal placed in a normal solution of H_2SO_4 , reaction takes place forming bubbles of hydrogen gas on zinc surface. The process is slow due to high overvoltage of zinc metal (0.7 V) which reduces the effective potential to a small value. In presence of CuSO_4 the corrosion rate of zinc is accelerated.

c. Nature of surface/oxide film: In aerated atmosphere, all metals get covered with a thin surface film of metal oxides. The ratio of the volumes of metal oxides to the metal is known as specific volume ratio. Greater is this value lesser is the oxidation corrosion rate. Specific volume ratios of Ni, Cr and W are 1.6, 2.0 and 3.6 respectively suggesting Tungsten has least corrosion. Further the corrosion depends on nature of oxide film. Metals like Al have a firm oxide film in comparison to Fe and hence Al is less corrosive means it follows *Pilling-Bedworth Rule*. The iron oxide is porous in nature and this leads to extension of corrosion to inner surface.

d. Volatility of corrosion products: If the corrosion product is volatile, then the underlying surface is exposed for further attack. This causes rapid and continuous corrosion. E.g. MoO_3 is volatile.

2. Effect of environment: Different properties of an environment are responsible for corrosion. These properties are given below.

a. Effect of pH

b. Temperature

c. Humidity of air

a. Effect of pH:

In the corrosion reaction described H^+ or OH^- are also involved. Therefore the effect of pH is obvious. It can be easily seen from the chemical equation for a reaction the direction in which it will shift by change in concentration of H^+ or OH^- . As a general rule, acids are more corrosive than neutral or alkaline solutions.

b. Temperature:

As the temperature of environment is increased the reaction rate is increased thereby accelerating corrosion. The effect of temperature on the corrosion rate is complicated because of the fact that it affects the various factors in different ways. The rate of chemical reaction increases, with rise in temperature but the solubility of gases, like oxygen which affect corrosion, decreases. The temperature may affect the protective coatings in different ways. In general, the rate of corrosion due to oxygen or oxidizing agents is decreased with rise in temperature but the rate of hydrogen type corrosion is increased.

c. Humidity of air:

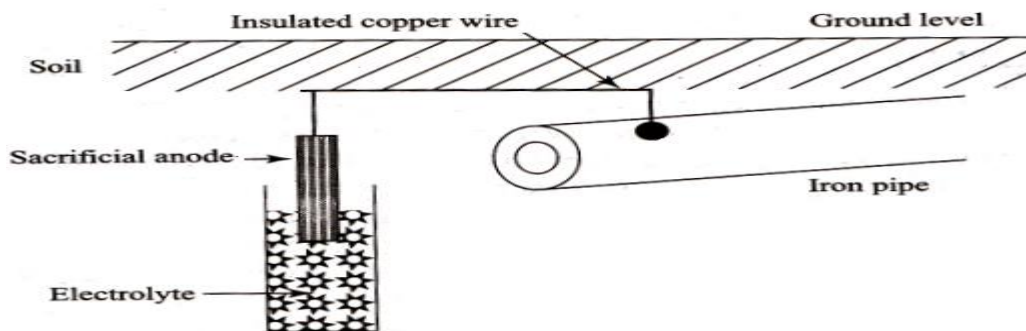
Corrosion of a metal is furnished in humid atmosphere because gases (CO_2 , O_2) and vapours present in atmosphere furnish water to the electrolyte essential to establish an electrochemical corrosion cell. The oxide film on the metal surface has the property to absorb moisture. In presence of this absorbed moisture, corrosion rate is enhanced. Rain water may also wash away the oxide film from the metal surface. This leads to enhanced atmospheric attack. The exceptions are Cr, Al.

CORROSION CONTROL METHODS

1. Cathodic Protection: The cathodic protection of metals is used to control corrosion metals where it is impartibly to alter the nature of the corrosion medium. The principle involved in this method is to protect metals and alloys from corrosion by making them completely cathodic. Since there will not be any anodic area on the metal, therefore corrosion does not occurs. The following are **two types** of cathodic protections.

a. Sacrificial anodic protection b. Impressed current cathodic protection

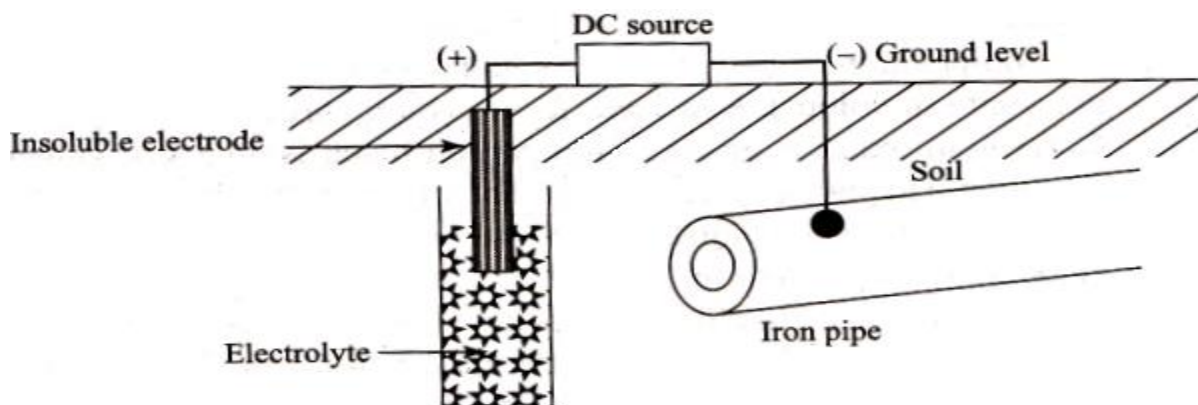
a. Sacrificial anodic protection: In this method, the metal structure can be protected from corrosion by connecting it with wire to a more anodic metal. As this more active metal is sacrificed in the process of saving metal from corrosion, it is known as sacrificial anode. The metals which are commonly used as sacrificial anodes are Mg, Zn, Al and their alloys.



The important applications of this method are:

- Protection of underground cables and pipelines from soil corrosion.
- Protection of ships and boat hulls from marine corrosion.
- Prevention of rusty water by inserting Mg sheets or rods into domestic water boilers or tanks.

b. Impressed current cathodic protection: As the name implies, an impressed current is applied to convert the corroding metal from anode to cathode. The applied current is in opposite direction since to nullify the corrosion current.



This can be accomplished by applying sufficient amount of direct current source like battery or rectifier to an anode like graphite, high silica iron, stainless steel or platinum buried in the soil or immersed in the corrosion medium, and connected to the corroding metal structure which is to be protected as shown in the diagram below. In impressed current cathodic protection, electrons are supplied from an external cell, so that the object itself becomes cathodic and not oxidized. This type of cathodic protection has been applied to buried structures such as tanks and pipelines, transmission line-towers, marine piers, laid-up ships etc. since, their operating and maintenance costs are less, they are well suited for large structures and long term operations.

2. Surface coatings/ Metallic coatings: These are produced by coating one metal on the surface of molten metal. The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

Methods of Application of Metallic coatings: Metallic coatings are done by the following methods:

I: Hot dipping.

II: Electroplating.

III. Electroless Plating.

I. HOT DIPPING

i. Hot-dipping: Hot dipping process is applicable to the metals having higher melting point than the coating metal. It consists of immersing well cleaned base metal in a bath containing molten coating metal, and a flux layer. The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

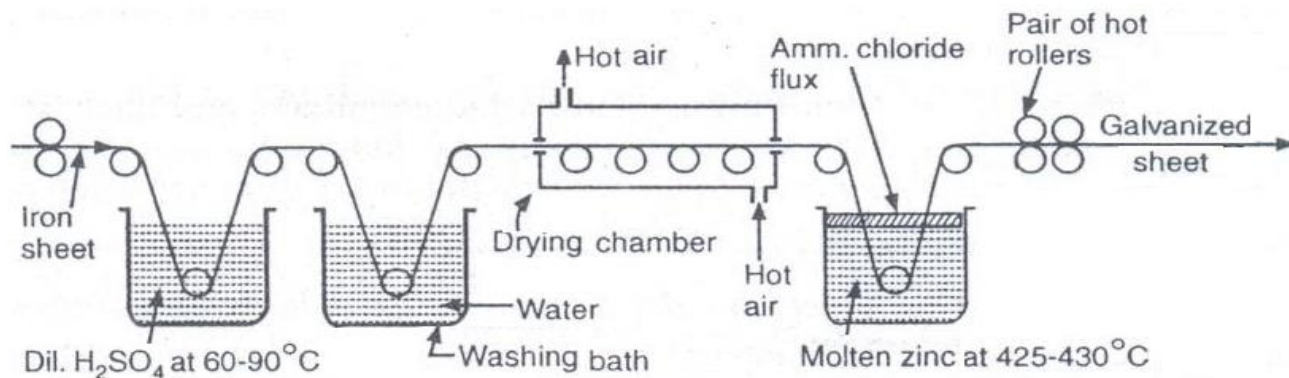
Examples: Coating of Zn, Sn, Pb, Al on iron, steel surfaces.

Most widely used hot dip process are:

a. Galvanizing.

b. Tinning.

a. Galvanizing: Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc. At first iron or steel is cleaned by pickling with dilute H_2SO_4 at a temperature range of $60\text{--}90^\circ\text{C}$ for 15 to 20 minutes. Therefore, it removes scale, rust and other impurities present. Then after dipped molten zinc in the bath at $425\text{--}450^\circ\text{C}$, to prevent it from oxide formation, the surface of bath is covered with a flux (NH_4Cl).

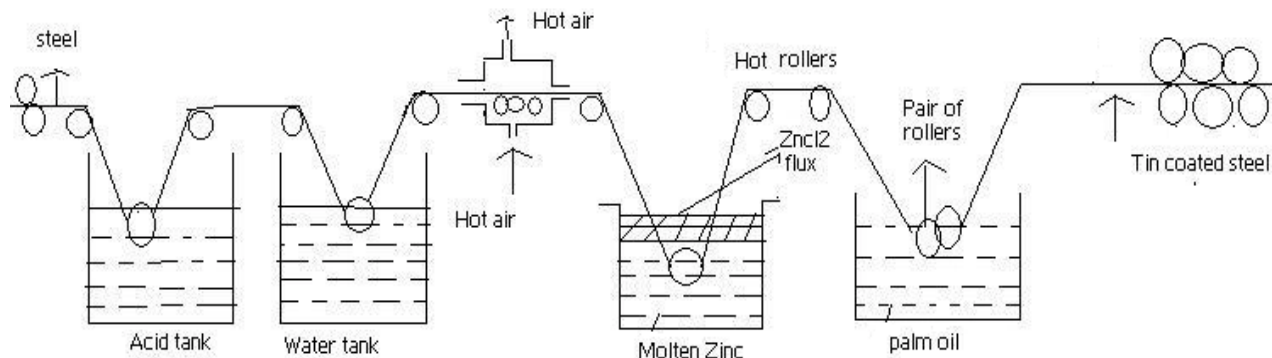


When the iron piece is taken out it is coated with a thin layer of zinc. And to remove excess zinc, it is passed through a pair of hot rollers; lastly, it is annealed at a temperature of 450°C and then cooled slowly.

Applications of Galvanizing:

- It is widely used for protecting iron exposed to the atmosphere, as is the case with roofs, wire fences, pipes and articles fabricated from galvanized sheets like buckets, tubes.
- Galvanized ware is not used for keeping eatables because of the solubility of zinc.
- The popularity of galvanizing is due the low cost of zinc.
- Easy application and the anodic protection offered by the zinc.

b. Tinning: The process of coating tin over the iron or steel articles to protect it from corrosion is known as tinning. Tin is a nobler metal than iron, therefore, it is more resistance to chemical attack. In this process, at first Iron sheet is treated in dilute H_2SO_4 (pickling) to remove any oxide film if present.



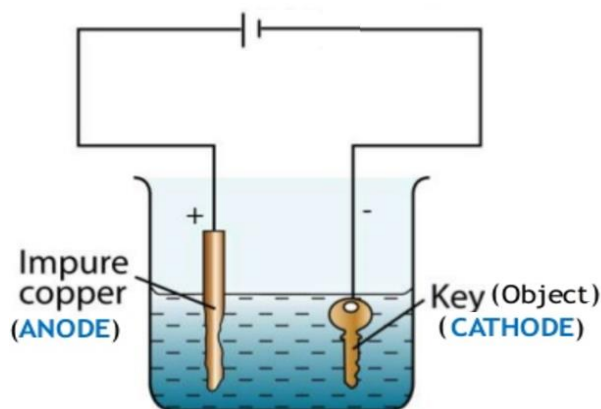
A cleaned Iron sheet is passed through a bath molten flux. Like Zinc chloride, then through molten tin and finally through a suitable vegetable oil. Tinning of mild steel plates is done mostly for the requirements of the food stuff industry. A cleaned iron sheet is passed through a bath of molten flux, like zinc chloride, then through molten tin and finally through a suitable vegetable oil. Lastly it is passed between rolls to adjust the thickness of the tin layer, which may be about 0.002 mm thick.

II. ELECTROPLATING

Electroplating is the process of coating metals and non-metals, to change their surface properties such as to improve the appearance, and corrosion or chemical attack. Electroplating is the electro-deposition of metal, by means electrolysis over surface of metals, alloys or non-metals.

Electro plating of copper over metal object:

The metal object, to be plated is first treated with dil.HCl or dil. H_2SO_4 . The cleaned object is the made cathode of an electrolytic cell and pure copper plate as anode. CuSO_4 and dil. H_2SO_4 solutions are taken as electrolyte. When the current is passed from the battery through the solution copper dissolves in the electrolyte and deposits uniformly on the metal object.



Chemical reactions:

At Anode: $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{e}^-$

At Cathode: $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$ deposited on base metal.

Conditions for Electro plating of copper over metal object:

Anode/coating metal: Pure copper plate

Cathode/Base metal: Metal object

Electrolyte: CuSO_4 and dil. H_2SO_4

Temperature: 40-45°C

Current: 30-40 mA/cm²

Applications of electroplating are:

- This process is widely used in automobiles, aircrafts, etc.
- Plating for decoration.
- This process is also used in Refrigerators, jewellery, radios, cameras, type-writers, umbrellas, watches etc.
- Plating on non-metallic materials.

III. ELECTROLESS PLATING COATING/ ELECTROLESS NICKEL PLATING

Electroless plating is a technique of depositing a noble metal (from its salt solution) on a catalytically active surface of the metal to be protected, by using a suitable reducing agent without using electrical energy.

The reducing agent reduces the metallic ions to metal, which gets plated was that catalytically activated surface giving a uniform thin coating.

Metal ions + Reducing agent \longrightarrow Metal (deposited) + oxidized products

IN ELECTRO LESS NICKEL PLATING HAVING THREE STEPS AS FOLLOWS:

Step I: Pretreatment and activation of the surface:

The surface to be plated is first degreased by using organic solvents or alkali followed by acid treatment.

Ex:

- The surface of the stainless steel is activated by dipping in hot solution of 50% dilute sulphuric acid.
- Metals and alloys like Al, Cu, Fe, Brass, etc., can be directly nickel-plated without activation.
- Non-metallic articles like plastics, glasses are activated by dipping them in the solution containing $\text{SnCl}_2 + \text{HCl}$, followed by dipping in PdCl_2 solution on drying a thin layer of freed is formed on the surface.

Step II: Plating bath: Plating bath consists of the following ingredients:

Coating solution: NiCl_2 .

Reducing agent: Sodium hypophospite.

Complexing agent: Sodium succinate.

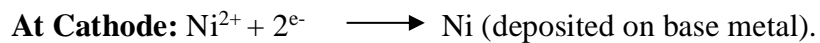
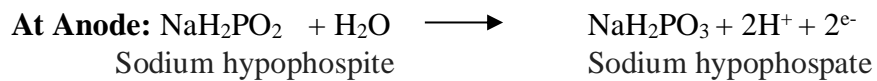
Buffer: Sodium acetate.

Optimum pH: 4.5

Optimum temperature: 93°C.

Step III: Procedure:

The pretreated object is immersed in the plating bath for the required time. During which of the following reducing another Nickel gets coated over the object.



Applications of Electroless-plating:

- Electroless Ni-plating is extensively used in electronic appliances.
- Electroless Ni-plating is used domestic as well as automatic fields.
- This application is used in making jewellery.
- Electroless Ni-coated Polymers are used in decorative and functional works.
- Electroless Copper and Nickel coated plastic cabinets are used in digital as well as electronic instruments.