

# Battery chemistry and Corrosion

## ❖ Storage batteries:

A device that stores chemical energy and releases it as electrical energy is called as battery or storage battery.

Cell is a device in which chemical energy is converted into electrical energy. Many cells connected in series are called battery.

Batteries are classified as follows;

- i) Primary battery.
- ii) Secondary battery.
- iii) reserve battery

Not all batteries are equal; often they are classified under the following categories:

- **Primary battery:** In primary batteries, chemical energy stored in the battery is converted to electrical energy spontaneously as long as active materials are present. In other words, the batteries in which irreversible chemical reaction takes place are called as *primary batteries*. This battery cannot be recharged, because cell reaction is irreversible.

*Example:* Dry cell, Laclanche cell, Li-MnO<sub>2</sub> battery.

- **Secondary battery:** Secondary cells are the batteries in which reversible chemical reaction takes place. This battery can be recharged by passing electric current. Redox reaction is reversed during recharging. Electrical energy is stored in the form of chemical energy in these batteries and used when needed.

*Example:* Lead acid battery, Ni-MH battery, Li-ion battery.

Primary cells act only as galvanic cell, whereas, a secondary cell can act both as galvanic cell and electrolytic cell. During discharging it acts as galvanic cell converting chemical energy to electrical energy and during charging process it acts as electrolytic cell converting electrical energy to chemical energy

- **Reserve battery:** In this battery, one of the key component is stored separately, and is incorporated into battery when required. When long storage is required, reserve batteries are often used, since the active component of the cell is separated until needed, thus reducing self-discharge.

Reserve batteries effectively eliminate the possibility of self-discharge and minimize chemical deterioration. Most reserve batteries are used only once and then discarded.

These batteries are used primarily to deliver high power for relatively short periods of time after activation in such applications as radiosondes, fuzes, missiles, torpedoes, and other weapon systems.

The reserve batteries can be classified by the type of activating medium or mechanism that is involved in the activation:

**a) Water-activated batteries:** Activation by fresh- or seawater.

*Example:* Mg-AgCl battery. They are activated by adding sea water. These batteries have high reliability and long shelf life, hence they find applications in missiles and submarines.

**b) Gas-activated batteries:** Activation by introducing a gas into the cell. The gas can be either the active cathode material or part of the electrolyte.

**Example** is zinc-air batteries where the cell is sealed until use, the seal is removed to admit air and activate the cell when needed.

**c) Electrolyte-activated batteries:** Activation by the complete electrolyte or with the electrolyte solvent. The electrolyte solute is contained in or formed in the cell.

**d) Heat-activated batteries:** A solid salt electrolyte is heated to the molten condition and becomes ionically conductive, thus activating the cell. These are known as thermal batteries. Another

---

### Basic requirements for commercial batteries

- A battery should be reasonably light, compact
- It should have a low self-discharge rate. (Self discharge rate is a measure of how quickly a cell will lose its energy due to unwanted chemical reaction that occur within the cell).
- The internal parts of the battery shouldn't corrode or convert to its inactive forms. (Corrosion affects the functioning of the battery).
- Fast charging increases the changes in the components, shortening the life span of the battery. Therefore should have a slow charge or discharge rate.
- Battery should have a long life even when not in use.
- The voltage of the battery should not vary appreciably during its use.
- Battery size: Primary batteries ranges from tiny button cells (watches) to No. 6 cell used for signal circuit or other long duration applications. Secondary batteries are made in large size(submarines).

---

### ❖ Explain the construction and working of Zinc air battery (or) Modern battery?

| Zinc air cell : ( Modern battery ) |                           |
|------------------------------------|---------------------------|
| Anode :                            | Zinc (Zn)                 |
| Cathode :                          | Oxygen                    |
| Electrolyte :                      | Potassium hydroxide (KOH) |

Metal –air batteries have attracted much attention because of their extremely high energy densities.

The notable characteristic feature of these batteries is their open-cell structure. Since these batteries use oxygen-gas from air as their cathode.

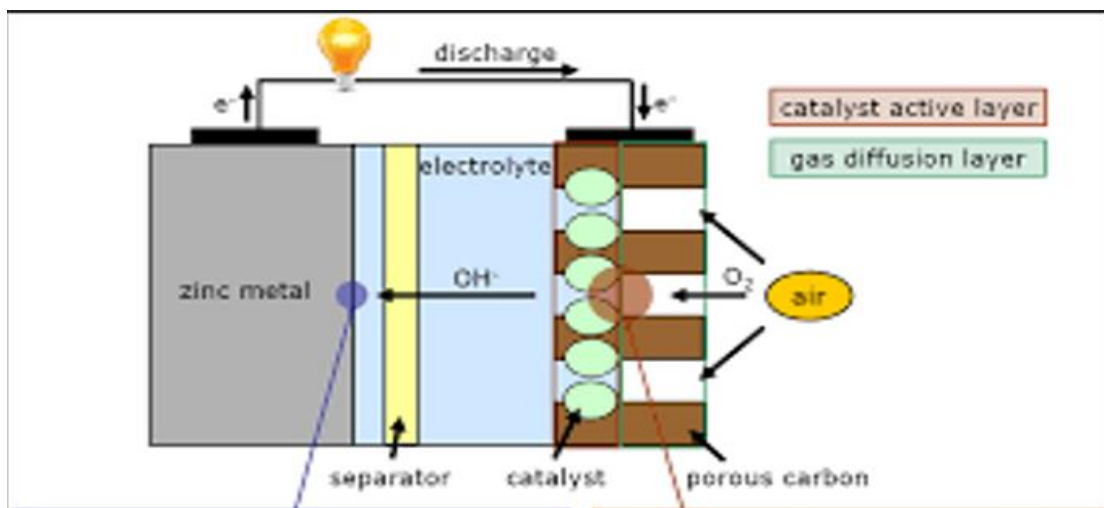
Among the metal –air batteries, zinc-air batteries have powerful potential for use as alternative storage device, low cost, abundance low, potential environmental benignity, flat discharge voltage and long shelf life.

#### Working :

1. Zinc air battery is a primary battery, it consists of anode containing granules of zinc mixed with 20% KOH electrolyte.
2. Carbon is catalytically activated to absorb O<sub>2</sub> gas. The solubility of Oxygen was very low at atm. pressure, so, it is necessary to use O<sub>2</sub> in the gas phase.

3. Cathode contains a porous carbon plate which provides site for the reduction reaction  $O_2$  to  $OH^-$  by using the  $e^-$  s generated by zinc metal.
4. The  $OH^-$  ion migrate from air cathode to zinc anode to complete the cell reaction.
5. The anode and cathode compartments are separated by a separator and both are encased in plastic or ebonite insulator.

The reactions are as follows.



#### Cell reactions:

**At anode:**  $Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$

**At cathode:**  $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

**Over all reaction:**  $Zn + \frac{1}{2} O_2 + H_2O \rightarrow Zn(OH)_2$

**Advantages:** 1) High energy density. 2) Low cost and compact 3) Does not produce harmful products.

**Applications:** Used in Military radio receivers, transmitters, hearing aids.

### ❖ Write about Lithium ion battery:

- These batteries are rechargeable battery best suited for mobile devices that requires small size, light weight and high performance.
- In this type of batteries lithium compounds are used.
- These batteries are considered as best than pure Lithium based batteries.
- It works on the principle Intercalation Mechanism.
- Lithium-ion battery is a secondary battery. As in lithium cell, it does not contain metallic lithium as anode.
- As the name suggests, the movement of lithium ions are responsible for charging '& discharging. Lithium-ion cell has the following three components.

| Lithium ion battery |  |
|---------------------|--|
| Anode :             | Lithium doped graphite                                   |
| Cathode :           | Lithium Cobalt (III) Oxide                               |
| Electrolyte :       | Complex Lithium compounds dissolved in organic solvents. |

### Discharging Reaction:

During discharging, the  $\text{Li}^+$  ions flow anode to the cathode through the non-aqueous electrolyte. Electrons flow from the anode to the cathode through external circuit. The  $\text{Li}^+$  ions and electrons combine at the positive electrode and deposit there as Li.

### Cell reactions:

**At anode:**  $\text{Li}_x\text{C}_6 \leftrightarrow x\text{Li}^+ + x\text{e}^- + 6\text{C}$

**At cathode:**  $\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + x\text{e}^- \leftrightarrow \text{LiCoO}_2$

**Over all reaction:**  $\text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{CoO}_2 \leftrightarrow 6\text{C} + \text{LiCoO}_2$

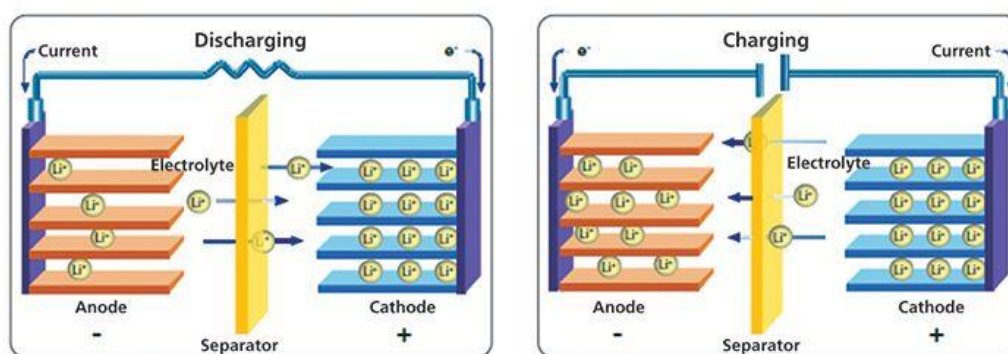
### Charging Reaction:

During charging, an external power source, the current to pass in the reverse direction. The positive terminal of the charging circuit is connected to the cathode of the battery, and negative terminal is connected to the anode.

The cathodic half reaction:  $\text{LiCoO}_2 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + x\text{e}^-$

The anodic half reaction:  $x\text{Li}^+ + x\text{e}^- + 6\text{C} \leftrightarrow \text{Li}_x\text{C}_6$

In lithium ion battery the  $\text{Li}^+$  ions are transported to and from cathode or anode, by the transition metal Cobalt [Co] where cobalt was oxidized from  $\text{Co}^{+3}$  to  $\text{Co}^{+4}$  during charging, and reduced from  $\text{Co}^{+4}$  to  $\text{Co}^{+3}$  during discharging.



### Advantages:

- They have high energy density than other rechargeable batteries.
- They are light weight.
- They produce high voltage out of 4 V.
- They have improved safety, i.e., more resistance to overcharge.
- No liquid electrolyte means they are immune from leaking.
- Fast charge and discharge rate.

### Disadvantages:

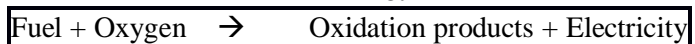
- 1) They are expensive.
- 2) They are not available in standard cell types.

### ❖ Applications of lithium ion in electronics and electrical vehicles

- The Li-ion batteries are used in portable devices: these include mobile phones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).
- Li-ion batteries are used in tools such as cordless drills, sanders, saws and a variety of garden equipment including whipper-snippers and hedge trimmers.
- Because of their light weight, Li-ion batteries are used for energy storage for many electric vehicles from electric cars to pedelec (pedelec is a bicycle where the rider's pedalling is assisted by a small electric motor), from hybrid vehicles to advanced electric wheelchairs, from radio-controlled models and model aircraft to the Mars Curiosity rover.
  - They are used in cardiac pacemakers and other implantable devices.
  - They are used in telecommunication equipment, instruments, portable radios and TVs, pagers.

### ❖ Define fuel cell. How fuel cells are represented. Mention its advantages and disadvantages?

**Definition:** Fuel cells are the galvanic cells which convert chemical energy of fuels into electrical energy by the combustion of fuels.



**Fuel cell Representation:** A fuel cell essentially consists of the following arrangement:

Fuel / electrode / electrolyte / electrode / oxidant.

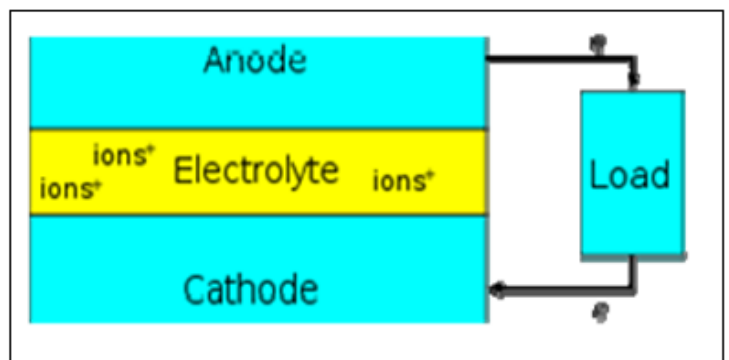
At the anode, fuel undergoes oxidation:  $\text{Fuel} \rightarrow \text{Oxidation product} + ne^-$

At the cathode, the oxidant gets reduced:  $\text{Oxidant} + ne^- \rightarrow \text{Reduction products}$ .

The electrons liberated from the oxidation process at the anode can perform useful work when they pass through the external circuit to the cathode.

#### **Advantages of the Fuel cells:-**

- 1) Their power efficiency is high.
- 2) The cells have high energy density.
- 3) They are ecofriendly.
- 4) Space required for fuel cell is less.
- 5) Produce harmless byproducts.
- 6) Produces direct current for a long time.
- 7) No moving parts and so elimination of wear and tear.
- 8) They operate very silently.
- 9) Absence of harmful waste products.
- 10) No need of charging.



#### **Limitations of Fuel cells:-**

- 1) Fuel cells produce energy only as long as fuels and oxidants are supplied.
- 2) Electrodes are very costly.
- 3) Power output is very costly.
- 4) Fuels in the form of gases and oxygen need to be stored in tanks under high pressure.
- 5) Reactions are constantly supplied and the products are constantly removed from the cell.

❖

### Difference between Conventional Cell (Battery) & Fuel Cell

| Conventional Cell                                 | Fuel Cell  |
|---|--|
| 1. These store chemical energy                    | 1. These don't store chemical energy                                       |
| 2. Not necessary to supply reactants continuously | 2. Reactants are supplied continuously and products are removed constantly |
| 3. Less efficient operation                       | 3. More efficient operation  |
| 4. It requires charging                           | 4. No need to charge   |
| 5. It does not require metal catalysts            | 5. It requires metal catalysts   |
| 6. They are less expensive                        | 6. They are more expensive   |

### ❖ Describe the construction and working of Methanol-Oxygen Fuel cell?

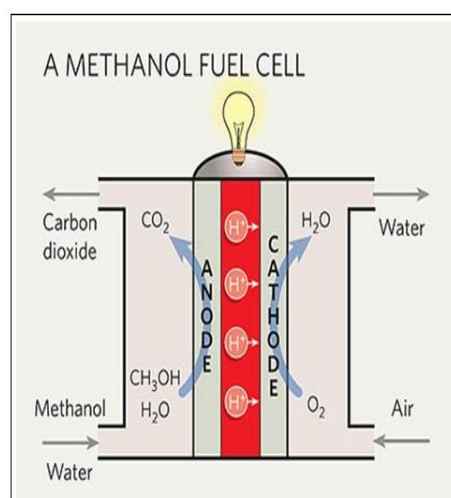
#### Methanol-Oxygen Fuel cell:- (DMFC)

- ★ Methanol is preferred as a fuel in fuel cells because of the following reasons.
- ★ It has low carbon content.
- ★ It possesses a readily oxidisable alcoholic group.
- ★ It has high solubility in aqueous electrolytes.

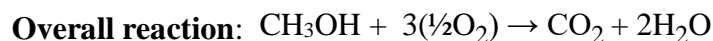
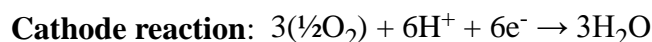
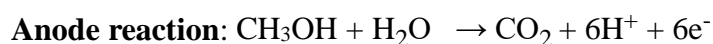
#### Construction:-

It consists of anodic and cathodic compartments and both the compartments contain platinum electrode.

Methanol containing  $\text{H}_2\text{SO}_4$  is passed through anodic compartments. Oxygen is passed through cathodic compartments. Electrolyte consists of sulphuric acid. A membrane is provided which prevents the diffusion of methanol into the cathode.



**Working:** - At anode,  $\text{CH}_3\text{OH}$  undergoes oxidation to  $\text{CO}_2$  liberates electrons, the liberated electrons taken by oxygen gets reduced into water with liberation of energy at cathode..



Fuel (methanol) and air or oxygen are fed to the electrodes. The cell potential is 1.21 V at 25 °C. The acid electrolyte offers the advantage of easy removal of CO<sub>2</sub>, a product of the cell reaction.

#### Uses:

- ★ In all kinds of portable, automotive and mobile applications like, Powering laptop, computers, cellular phones, digital cameras.
- ★ In Fuel cell vehicles (FCVs).
- ★ It is used in Spacecraft applications.
- ★ It is used in any consumables which require long lasting power compared to Li-ion batteries.
- ★ It is also used in Military applications.

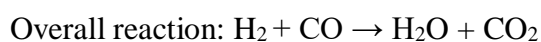
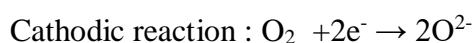
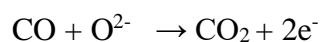
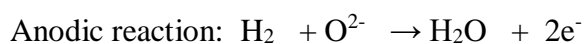
### Solid oxide fuel cells

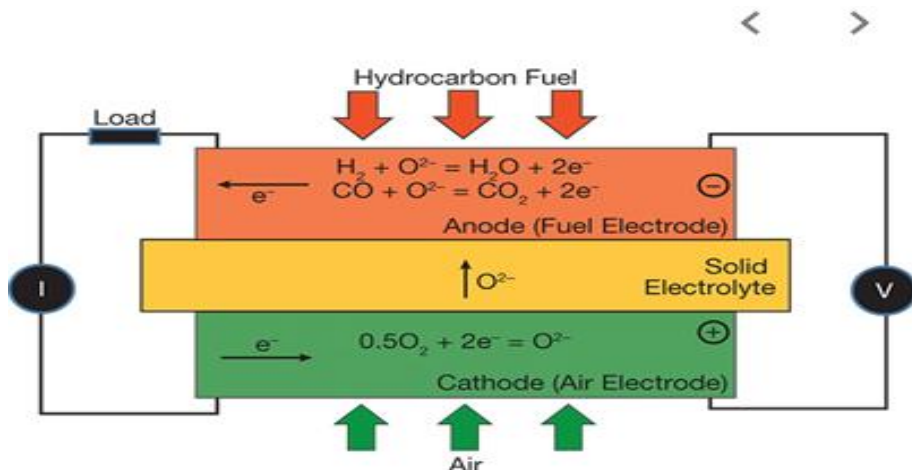
|                       |  |
|-----------------------|--|
| Fuel                  | H <sub>2</sub> , CO                                |
| Oxidant               | O <sub>2</sub>                                     |
| Electrodes            | Ceramic material                                   |
| Electrolyte           | Solid mixture of yttrium oxide and Zirconium oxide |
| Catalyst              | Perovskite   |
| Operating temperature | 700 to 1000°C                                      |
| Power density         | 0.1 to 1.5 KW/m <sup>2</sup>                       |
| Efficiency            | 55 to 65%  |

Working: Solid oxide fuel cell utilizes the movement of e<sup>-</sup>s and generate electricity in few basic steps:

Reduction of O<sub>2</sub> into O<sup>2-</sup> occurs at the cathode these ions can diffuse through the solid oxide electrolyte to the anode, where they can electrochemically oxidize the fuel.

Water was the byproduct is given off as well as two e<sup>-</sup>s. These e<sup>-</sup>s then flow through an external circuit. Where they can do work. The cycle repeats as that e<sup>-</sup>s enter the cathode material again.





### Advantages:

- 1) SOFC has a solid oxide or ceramic electrolyte. Ceramic are used not to become electrically and ionically active until they reach very high temperature.s
- 2) AOFC include high combined heat and power efficiency, long term stability, fuel flexibility, low emission and relatively low cost.

**Disadvantages :** Due to high operating temperature which are results is longer startup times and mechanical and chemical compatibility issues.

### Applications :

It is used for generating electiricity I motor vehicles.

It is used as power transmission system

Here are three main application of SOFC such as combined cycle power plant, cogeneration and trigeneration and residential application.



## Corrosion

❖ **Definition:** Corrosion is defined as the deterioration of a metal by chemical or electro chemical reactions with its environment.

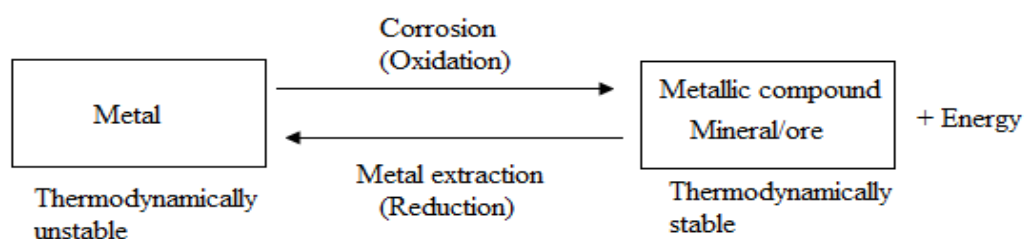
Due to corrosion the useful properties of a metal like malleability, ductility, electrical conductivity and also the surface appearance are lost. The most familiar example of corrosion is rusting of iron when exposed to atmospheric conditions.

✓ Examples:

- ◆ Rusting of iron: A layer of reddish brown scale ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) is formed on the surface of the iron.
- ◆ Formation of green layer of basic copper carbonate [ $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ ] on the surface of copper.
- ◆ Tarnishing of silver: Blackening of surface of silver due to the formation of black layer of silver sulphide on it.

### Cause of corrosion:

- ▲ The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc.
- ▲ During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy.
- ▲ Hence the isolated pure metals are regarded as excited states than their corresponding ores.
- ▲ So metals have natural tendency to go back to their combined state (minerals/ores).
- ▲ When metal is exposed to atmospheric gases, moisture, liquids etc., the metal surface reacts and forms more thermodynamically stabled compounds.



### Consequences of corrosion:

- ♣ Enormous waste of machineries and different types of metallic materials
- ♣ It leads to sudden failure of machines.
- ♣ It leads to the decrease in efficiency of machine and frequent replacement of corroded equipment which is an expensive.
- ♣ It may leakage of inflammable gas from the corroded pipe lines resulting into fire accidents etc.
- ♣ It causes contamination of potable water.
- ♣ It has been estimated that 25% of annual world production of iron is wasted due to corrosion.

## ❖ Theories of corrosion

There are two different types of theories of corrosion 1) Chemical theory 2) Electro chemical theory of corrosion

**Dry corrosion (or) Chemical corrosion (or) Direct chemical attack theory (or)**

**Mechanism of dry corrosion:**

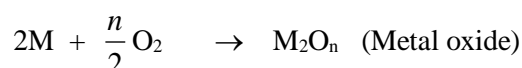
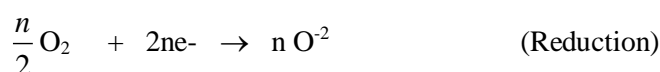
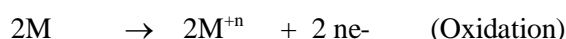
This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses like O<sub>2</sub>, halogens, H<sub>2</sub>S, SO<sub>2</sub>, N<sub>2</sub> or anhydrous inorganic liquid with the metal surface.

There are three types of chemical Corrosion:

(1.) Oxidation corrosion (2.) Corrosion due to other gases (3.) Liquid metal corrosion.

**(1.) Oxidation corrosion:**

- ★ This is carried out by the direct action of oxygen at low or high temperatures on metals in absence of moisture.
- ★ This theory explains dry corrosion.
- ★ Corrosion is initiated in a metal, when it is contacted directly with oxygen.
- ★ Then the metal gets oxidized to metal ions and the electrons so released reduce oxygen to form oxide ion.
- ★ The metal ion and oxide ion combine to form metal oxide on the metal surface.

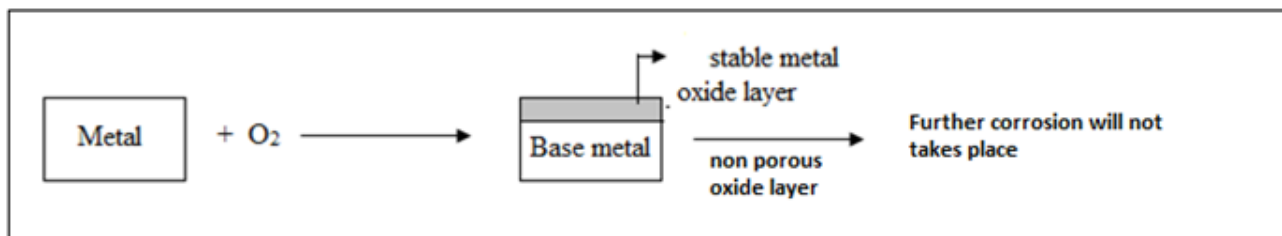


- ★ The extent of corrosion depends upon the nature of metal oxide.
- ★ The nature of metal oxide layer formed plays an important role in determining further corrosion.

**a) Stable oxide layer (or) Protective and non porous oxide film :**

If the metal oxide is stable, it behaves as a protective layer which prevents further corrosion.

E.g., The oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.

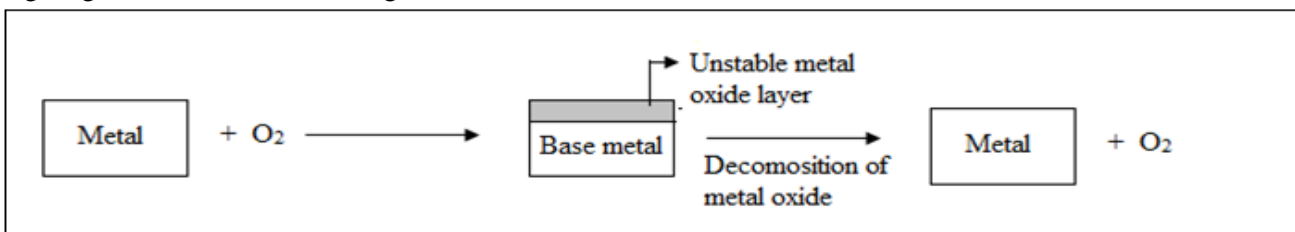


**(b) Unstable oxide layer:**

If the metal oxide layer is unstable, the oxide layer formed decomposes back into metal and oxygen.

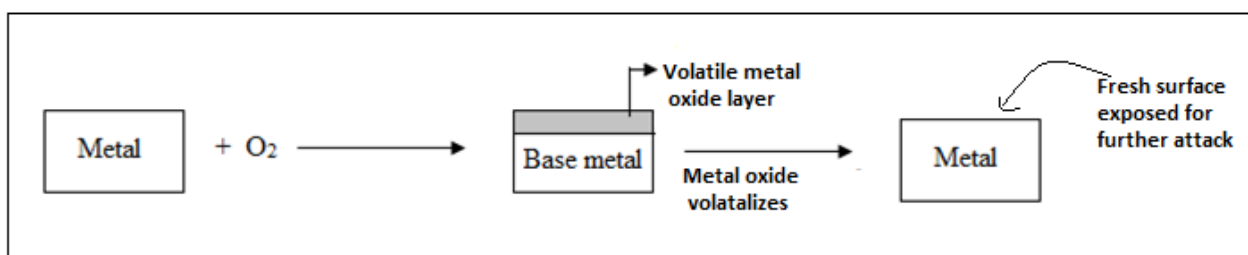
So, oxidation corrosion is not possible.

E.g., Ag, Au and Pt do not undergo oxidation corrosion.



**(c) Volatile oxide layer:**

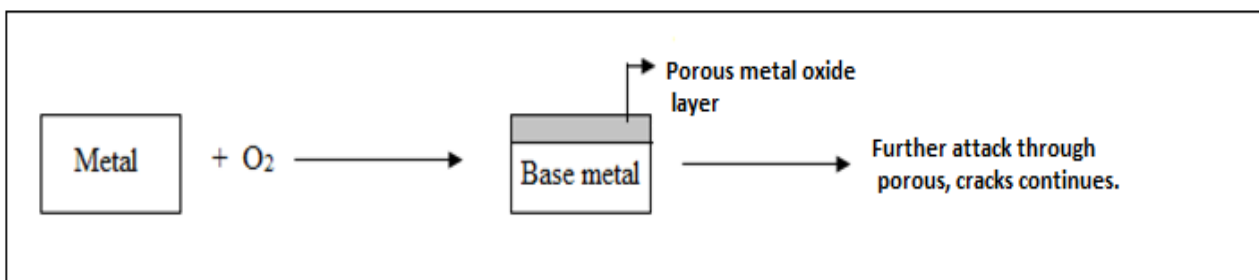
If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO<sub>3</sub>)



**(d) Porous and non protective oxide layer:**

If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This cause continuous corrosion till conversion of metal into its oxide is completed.

Ex: Alkali and alkaline earth metals (Li, Na, K, Mg etc.)



**Pilling-Bedworth Rule:**

This rule states the extent of protection given by the corrosion layer. An oxide is protective or non – porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed.

It is the ratio of the volume of metal oxide to volume of metal.

$$\text{specific ratio} = \frac{\text{volume of metal Oxide}}{\text{Volume of Metal}}$$

The smaller the specific ratio, greater the oxide corrosion since the formed oxide film will be porous through which the oxygen can diffuse and increases the corrosion further.

- 1) If the volume of the metal oxide layer is at least as great as the volume of the metal, no corrosion occurs as the oxidation of metal reaches to zero. i.e; specific ratio  $\geq 1$   
For example, the specific volume ratios of W, Cr and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in Tungsten (W).
- 2) If the volume of metal oxide is less than the volume of the metal, the oxide film will develop cracks and pores. The atmospheric oxygen reaches the metal and increases the corrosion. In this case corrosion is continuous and rapidly increases. i.e; specific ratio  $< 1$   
For example, Li, Na and K.

**(2)Corrosion due to other gases:**

- ★ This type of corrosion is due to gases like SO<sub>2</sub>, CO<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub>S, F<sub>2</sub> etc.
- ★ In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved.
- ★ The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bedworth rule.

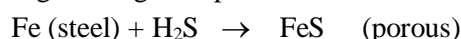
(i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous does not allow the penetration of corrosive gases. For example when Cl reacts with Ag forms AgCl film which prevents further reaction of Cl with Ag.



(ii) If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow

the penetration of corrosive gases leading to corrosion of the underlying metal.

Ex. In petroleum industry,  $\text{H}_2\text{S}$  gas at high temperature reacts with steel forming a FeS scale.



### (3.) Liquid metal corrosion:

- ★ This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy.
- ★ The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

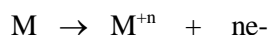
Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

### Wet Corrosion (or) Electrochemical corrosion:

- ★ This type of Corrosion occurs where a conducting liquid is in contact with the metal.
- ★ 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.

**Mechanism:** Electrochemical corrosion involves flow of electrons between anode and cathode.

The anodic reaction involves dissolution of metal liberating free electrons.

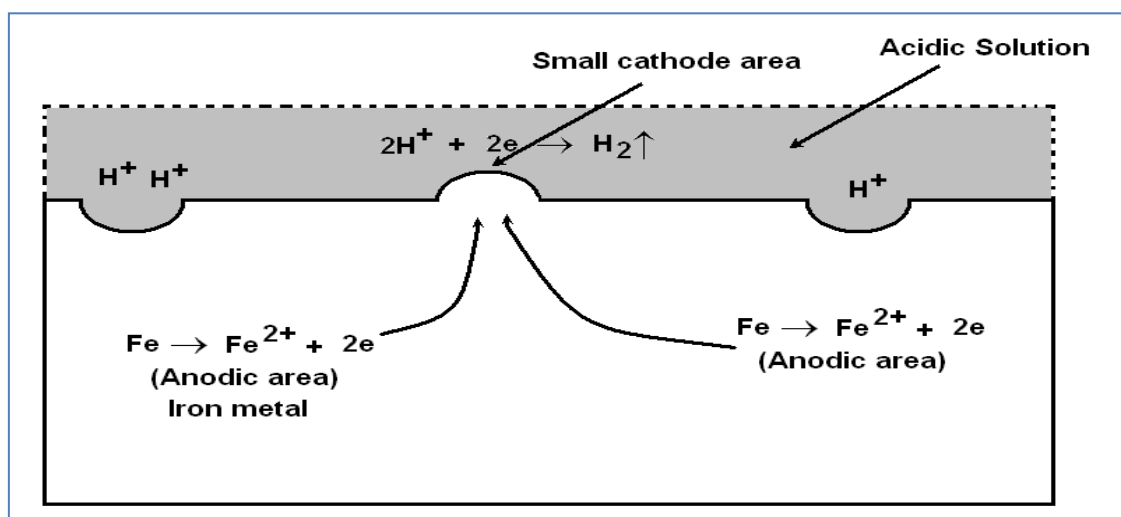


The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of

oxygen which depends on the nature of corrosive environment.

**Evolution of hydrogen :** [ Formation of Rust with evolution of  $\text{H}_2$  in Wet corrosion ]:

★



This type of corrosion occurs in acidic medium.

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

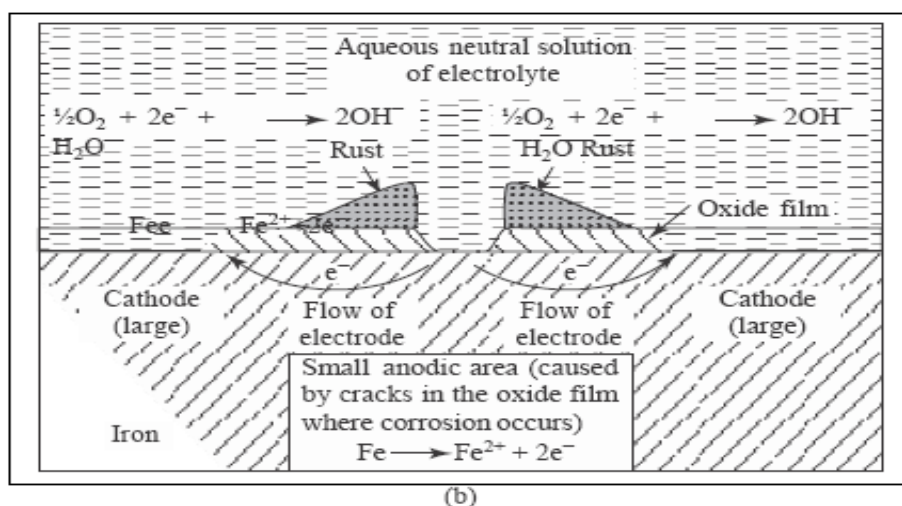
**Anode:**  $\text{Fe} \rightarrow \text{Fe}^{+2} + 2\text{e}^-$  (Oxidation)

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

**Cathode:**  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  (Reduction)

- ★ **The overall reaction** is:  $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{+2} + \text{H}_2$
- ★ 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  $\text{H}_2$  gas. The anodes are large areas, where as cathodes are small areas.

**Absorption of oxygen:** [ Formation of Rust with evolution of  $\text{O}_2$  in wet reaction ] :



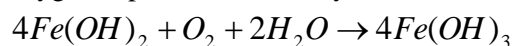
For example, rusting of iron in neutral aqueous solution of electrolytes in

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. The released electrons flow from anode to cathode through iron metal.

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

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

- ★  $\text{Fe}^{2+}$  ions and  $\text{OH}^-$  ions combine to form  $\text{Fe}(\text{OH})_2$  precipitate.
- ★ If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.

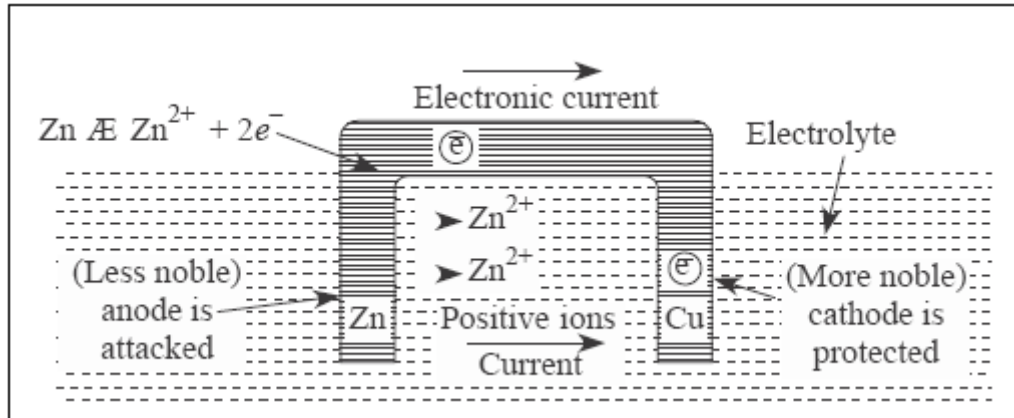


- ★ This product called yellow rust actually corresponds to  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .
- ★ If the supply of oxygen is limited, the corrosion product may be black magnetite  $\text{Fe}_3\text{O}_4$ .

## ❖ Types of Corrosion

**What is galvanic corrosion? How is it prevented? Give examples?**

Galvanic corrosion: This type of electrochemical corrosion is also called bimetallic corrosion. When two dissimilar metals are connected and exposed to an electrolyte, they will form a galvanic cell. The anodic metal will be oxidised and it will undergo corrosion. Zinc and copper metals connected with each other in an electrolyte medium form a galvanic cell. Zinc acts as anode and undergoes corrosion while cathode will be unaffected.



**Eg:** When Zn and Cu are connected and exposed to a corroding environment, Zinc (higher in electrochemical series) forms the anode; undergoes oxidation and gets corroded. Cu (lower in electrochemical series) acts as the cathode; undergoes reduction and is protected as the electrons released by Zn flow towards Cu.

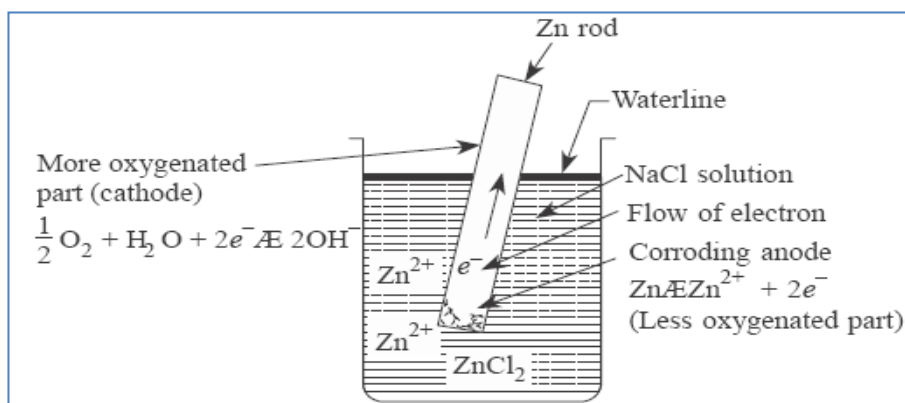
**Prevention:**

- 1) Galvanic corrosion can be avoided by coupling metals close to the electrochemical series.
- 2) Fixing insulating material between two metals.
- 3) By using larger anodic metal and smaller cathodic metal.

**Example of galvanic corrosion:**

- 1) Steel screws in brass marine hardware,
- 2) steel pipe connected to copper plumbing,
- 3) steel propeller shaft in bronze bearing,
- 4) zinc coating on mild steel,
- 5) lead-tin solder around copper wires.

❖ **Differential aeration corrosion: or Concentration cell corrosion:**

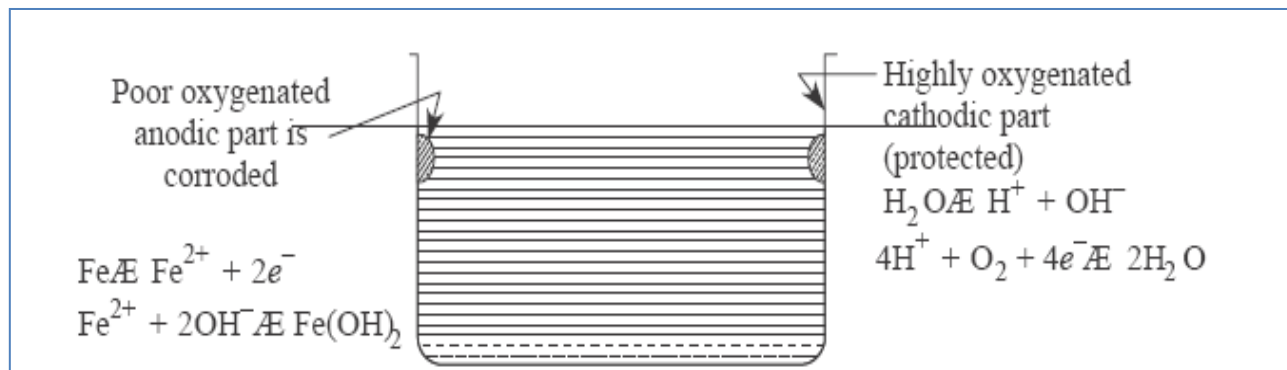


If a metal rod is dipped in an electrolyte, the portion dipped in water is poor in oxygen concentration and works as anode which gets corroded and the portion above water acts as cathode which is protected. The system will act as a concentration cell and the chemical reactions for zinc dipped in water are given as:

$\text{Zn(OH)}_2$  appears as corrosion products. Examples: Water line corrosion, Drop corrosion.

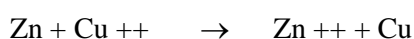
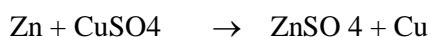
### Waterline corrosion:

It has been observed in the case of an 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. Corroding portion is poor in oxygen and acts as anode.



### ❖ What is Galvanic series? Explain.

Electrochemical reactions are predicted by electrochemical series. A metal having higher position can replace (reduce) other metals that have lower position in the series. For example, that is,



Or in other words, zinc will corrode faster than copper.

Some exceptions have been observed in this generalisation. For example, Ti is less reactive than Ag.

Galvanic series is the series of metals that is made keeping in view the process of corrosion of a metal in a particular atmosphere, i.e. sea water. In galvanic series, oxidation potential of metals is arranged in the decreasing order of activity of a series of metals. The series is towards the increasing noble nature.

More anodic: Mg, Mg alloys, Zn, Al, Cd, Fe, Pb, Sn, Ni–Mo–Fe alloys) Brasses, Cu, Ni, Cr–steel alloy, Ag, Ti, Au, Pt towards noble nature.

### ❖ Explain about the Factors Influencing rate of Corrosion:

The rate and extent of corrosion depends upon various factors.

1. Nature of metal
2. Nature of corroding atmosphere

#### Nature of the metal:

##### 1. Position in the galvanic series:

Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily. Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected.

##### 2. Purity of metal:

Heterogeneity is produced if impurities are present in a metal, which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded. As the extent of exposure and impurities increase, the extent of corrosion increases.

For example in case of zinc metal;

|                |        |       |       |      |
|----------------|--------|-------|-------|------|
| % Purity       | 99.999 | 99.99 | 99.95 | 99   |
| Corrosion rate | 1      | 2650  | 5000  | 7200 |

### 3. Relative areas of the anodic and cathodic parts:

When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts. i.e, the corrosion is more rapid, severe and highly localised if the anodic area is small.

For example, a small pipe made of steel fitted in a large copper tank.

$$\text{In general Rate of corrosion of anodic region} \propto \frac{\text{CathodicArea}}{\text{AnodicArea}}$$

### 4. Nature of surface film:

In aerated atmosphere, practically all metals produce a thin surface film of metal oxide.

The ratio of the volumes of the metal oxide formed to the metal is called "specific volume ratio".

$$\text{specific ratio} = \frac{\text{volume of metal Oxide}}{\text{Volume of Metal}}$$

If the specific volume ratio is more, the rate of corrosion is less, because the surface of the metal is completely covered by the film, offering protection to the metal surface.

For example, the specific volume ratios of Ni, Cr, and W are 1.6, 2.0 and 3.6 respectively. The rate of corrosion for tungsten (W) is least even at elevated temperatures.

### 5. Physical state of metal:

The grain size, orientation of crystals, stress etc. of the metals influence the rate of corrosion. The smaller the grain size of the metal or alloy greater will be the rate of corrosion, because of its high solubility. The areas under stress become anodic and corrosion takes place in these areas.

### 6. Volatility of corrosion products:

If the corrosion produced volatilizes as soon as it is formed, the metal surface is exposed for further attack. This creates rapid and excessive corrosion.

For example the corrosion product of molybdenum as molybdenum oxide ( $\text{MoO}_3$ ) is volatile.

### 7. Passive character of metal:

Metals like Ti, Al, Cr, Mg, Ni and Co are passive and they exhibit much higher corrosion resistance than expected from their position in the electrochemical series. This is because the metal forms very thin, highly protective corrosion film, by reacting with atmospheric oxygen. If the film is broken, it compensates the film by re exposure to oxidising conditions. Thus they produce "self healing film". This property is called passive character of metal.

For example the corrosion resistance of "stainless steel" is due to passive character of chromium present in it.



### **Nature of corroding environment:**

**1. Temperature:**

The rate of corrosion reaction and diffusion rate increases with increase in temperature, causing the increase in rate of corrosion.

**2. Humidity of air:**

The humidity of air is a deciding factor for rate of corrosion. The relative humidity above which, the rate of corrosion increases sharply is called "critical humidity". The value of critical humidity depends on the physical characteristics of the metal and the nature of corroding atmosphere.

The reasons for increase of corrosion with humidity are,

1. The moisture or vapours present in atmosphere furnish water to the electrolyte, essential for setting up an electrochemical cell.

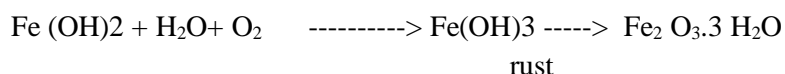
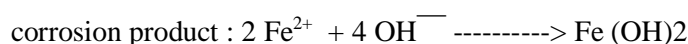
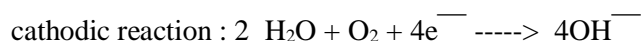
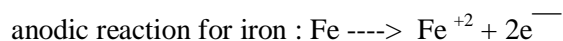
**3. Presence of impurities in atmosphere:** Atmosphere is contaminated with gases like CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S; fumes of H<sub>2</sub>SO<sub>4</sub>, HCl etc. and other suspended particles in the vicinity of industrial areas. They are responsible for electrical conductivity, thereby increasing corrosion

**4. Nature of ions present in the medium :**

The presence of ions like silicates in the medium leads to the formation of "insoluble reaction products" like silica gel, on the metal surface which "inhibit" further corrosion. On the other hand chloride ions, if present in the medium destroys the protective film on the surface of the metal.

**5. Amount of oxygen in atmosphere:**

As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.



**6. Velocity of ions which flow in the medium:**

As the velocity of the diffusion of ions in the medium increases, the rate of corrosion increases.

**7. pH value of the medium:**

pH value of the medium has greater effect on corrosion. When pH value is lowered, the corrosion is increases.

---

### **❖ Corrosion Control Methods:**

As we have discussed the disadvantages and different mechanisms of corrosion so far, it is essential to know the different corrosion control methods. The following are the important control methods of corrosion.

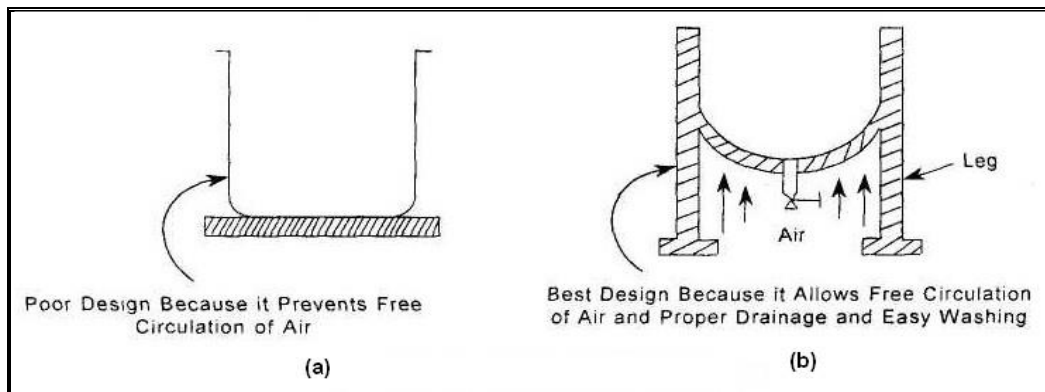
- 1) Proper designing
- 2) Using pure metal

- 3) Using metal alloys
- 4) Modifying the environment
- 5) Use of inhibitors
- 6) Cathodic protection
- 7) Application of protection coatings.

#### **Proper designing & Selection of material:**

The design of the metal under corroding atmosphere must be such that it is uniform and does not produce intense and localised corrosion, important principles of proper designing are:

The design of the equipment should allow free circulation of air proper drainage and easy washing as shown below.



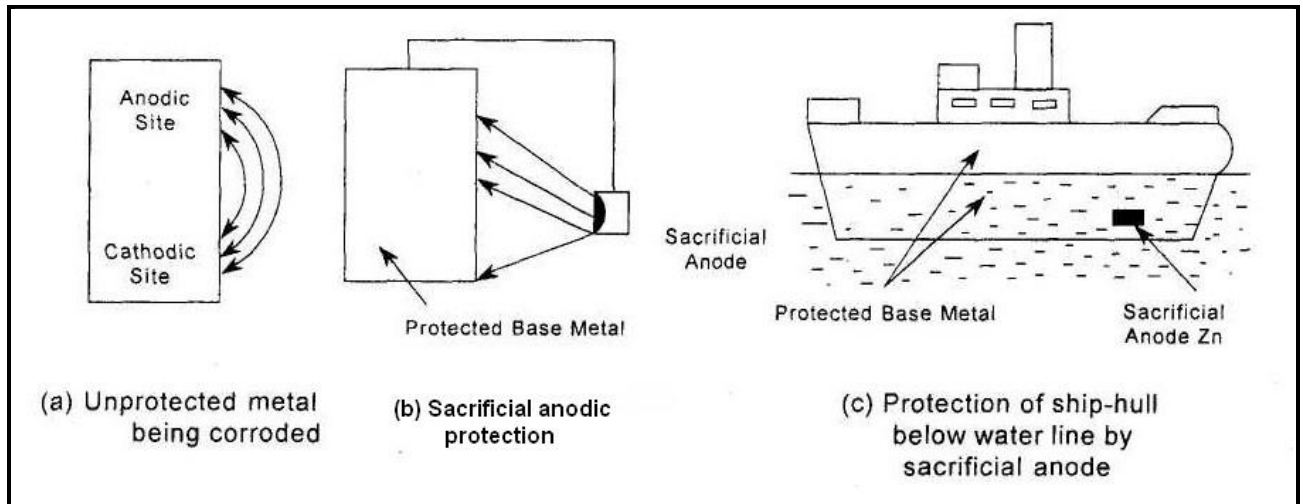
#### **1) Cathodic protection :**

- ★ The basic principle of cathodic protection is to force the metal to behave like a cathode.
- ★ The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.
- ★ There are two types of cathodic protection;
  - (a) Sacrificial anodic protection method.
  - (b) Impressed current cathodic protection method.

##### **a) Sacrificial anodic protection method :**

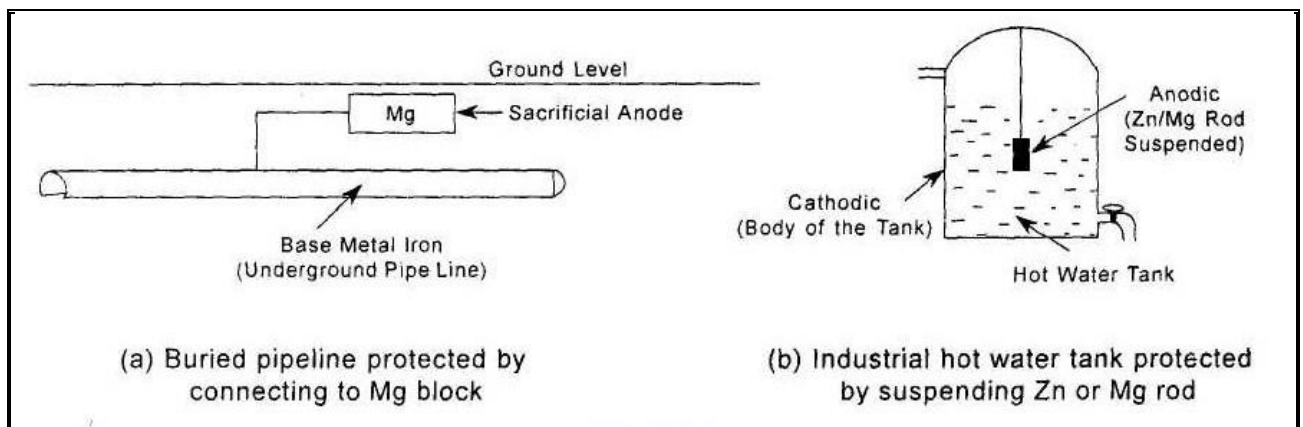
- ★ In this protection method, the metallic structure to be protected is called a base metal.
- ★ The base metal is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- ★ The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected.
- ★ The more active metal so employed is called sacrificial anode.
- ★ The corroded sacrificial anode is replaced by a fresh one, when consumed completely.
- ★ Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

Eg 1. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

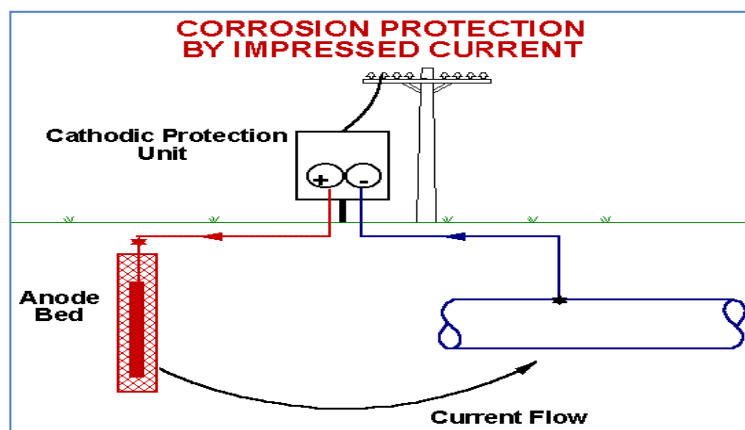


Example 2:

The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.



### (b) Impressed current cathodic protection:



★ In this method an impressed current little more than corrosion current is applied in the opposite

direction to nullify the corrosion current producing a reverse cell reaction.

★ Thus the anodic corroding metal becomes cathodic and protected from corrosion.

- ★ The impressed current is taken from a battery or rectified on A.C. line.
- ★ The anode is usually insoluble anode like graphite, high silica iron, scrap iron, stainless steel, or platinum.
- ★ Usually a sufficient D.C. current is passed on to the insoluble anode kept in a 'back fill' composed of coke or gypsum, so as to increase the electrical contact with the surrounding soil.
- ★ This type of impressed current cathodic protection is given to
  - (1) open water box coolers                      (2) water tanks                      (3) buried water pipe lines or oil pipelines
  - (4) condensers                      (5) transmission line towers                      (6) marine pipes
- ★ This type of protection is more useful for large structures for long term operations.

**Disadvantages of cathodic protection:**

1. The cathodic protection may be efficient in protecting a pipeline, yet may increase the corrosion of the adjacent pipelines or metal structure because of stray currents.
2. Capital investment and maintenance costs are more.
3. Special care must be taken that the metal is not over protected, i.e., the use of much higher potential than the open circuit voltage for the metal/metal ion couple in case of impressed current method and the higher anodic metal in the series must be avoided. Otherwise problems related to cathodic reactions like evolution of H<sub>2</sub> or formation and accumulation of OH<sup>-</sup> will take place.

In spite of these disadvantages, cathodic protection has been widely used with success, when suitable precautions are taken.