

## UNIT – II Battery Chemistry & Corrosion

Introduction - Classification of batteries- primary, secondary and reserve batteries with examples. Basic requirements for commercial batteries. Construction, working and applications of Zn-air and Lithium-ion battery. Applications of Li-ion battery to electrical vehicles. Fuel Cells- Differences between battery and a fuel cell, Construction and applications of Methanol Oxygen fuel cell and Solid oxide fuel cell. Solar cells - Introduction and applications of Solar cells.

Corrosion: Causes and effects of corrosion – theories of chemical and electrochemical corrosion – mechanism of electrochemical corrosion, Types of corrosion: Galvanic, water-line and pitting corrosion. Factors affecting rate of corrosion, Corrosion control methods- Cathodic protection – Sacrificial anode & impressed current methods and Electroless plating.

---

### Battery

A battery is a storage device, used for the storage of chemical energy, and for the transformation of chemical energy into electrical energy.

Battery consists of groups of two or more electrical cells connected together electrically in series.

### Classification

Batteries can be classified into

1. Primary Batteries
2. Secondary Batteries

### **Primary Batteries:**

“These are **non-rechargeable** and are meant for single use and to be discarded after use”.

In these batteries, reactants have been converted to products, no electricity is produced and the cell becomes dead and cannot be used after that. This battery acts as electrochemical cell.

These are non-reversed and are less expensive and are offer used in ordinary gadgets like torch lights, watches and toys.

Eg: Leclanche cell, Dry cell, Lithium cells.

### Secondary Batteries:

These are rechargeable and are meant for multi cycle use. In the secondary batteries cell reaction is reversible, once the battery gets exhausted, it can be recharged. This acts as electrochemical cell as well as electrolytic cell.

Eg: Lead-acid cell, Ni/cd cell, Lithium-Ion Batteries.

### Reserved batteries:

Reserve batteries are special purpose primary batteries usually designed for emergency use. The electrolyte is usually stored separately in a dry inactive state from the electrodes to avoid self-discharge and minimize chemical deterioration. This allows the electrolyte to remain inert and makes reserve batteries well-suited for military and aerospace applications. The battery is only activated when it is actually needed by introducing the electrolyte into the active cell area. They can thus be stored for 10 years or more yet provide full power in an instant when it is required. . Most reserve batteries are used only once and then discarded.

Reserve cells are typically classified into the following 4 categories.

Water activated batteries.

Electrolyte activated batteries.

Gas activated batteries.

Heat activated batteries.

These batteries have many **marine and military applications**.

Examples: Aluminium battery, zinc-air battery, Silver-zinc battery,

### Differences between Primary and secondary batteries:

Primary cells	Secondary cells
These are non-rechargeable and meant for a single use and to be discarded after use.	These are rechargeable and meant for multi cycle use.
Cell reaction is not reversible.	Cell reaction can be reversed.
Cannot be rechargeable.	Can be rechargeable.
Less expensive.	Expensive.
Can be used as long as the materials are active in their composition.	Can be used again and again by recharging the cell.
Eg: Leclanche cell, 'Li' Cells.	Eg; Lead- acid cell, Ni-cd cells

## Basic requirements for commercial batteries.

A useful battery should fulfil the following requirements

1. It should be light and compact for easy transport.
2. It should have long life both when it is being used and when it is not used.
3. It should have high energy efficiency.
4. The voltage of the battery should not vary appreciably during its use.
5. It should be rechargeable so that it can be used again and again.
6. Adaptable: The battery should be able to handle and endure changing and various climatic conditions.

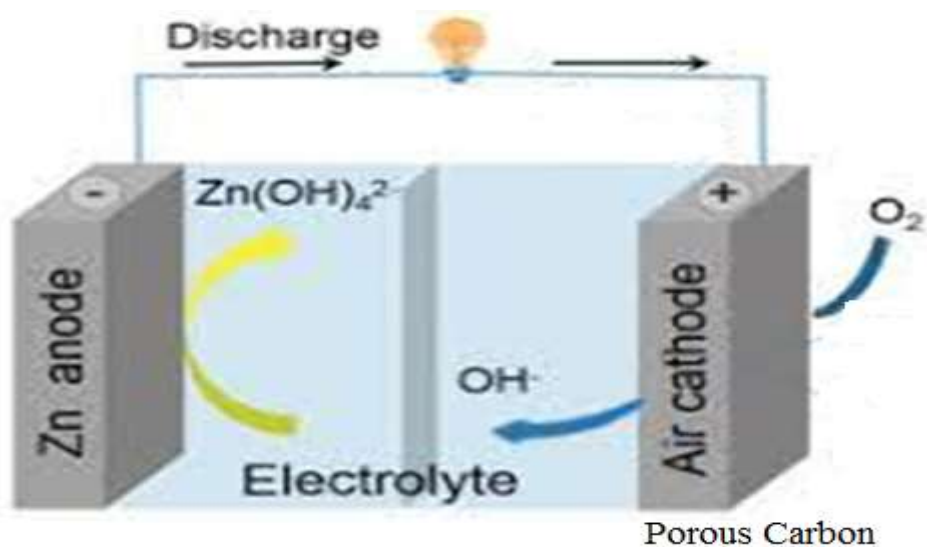
## Construction, working and applications of Zn-air battery

The zinc air battery is basically a primary battery (reserved battery) i.e. non-rechargeable battery. Zinc air cell converts chemical energy into electrical energy.

In these batteries, with the removal of a sealing tab, oxygen from the air is introduced into the cell. A zinc-air battery usually reaches full operating voltage within 5 seconds of being unsealed.

The primary components of the Zn-air battery are

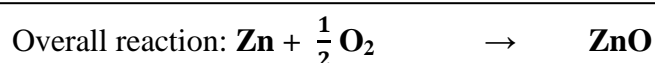
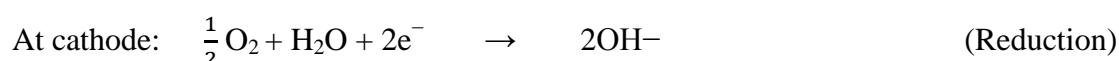
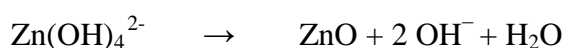
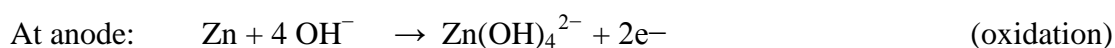
1. Anode (A negative electrode) → Zn metal
2. Cathode (A positive electrode) → air/Porous carbon.
3. An electrolyte → Potassium hydroxide (KOH) aqueous solution



The anode and cathode are separated by a separator allowing ions to transfer across the cell. Oxygen from the air enters the cathode region (porous body made of carbon with air access) and it reacts with water from the electrolyte to form a hydroxide.

The hydroxide formed at the cathode surface travels to the anode and it reacts with the zinc in the anode to release energy that provides the power.

The zincate at the anode decays to form zinc oxide and also water which returns to the electrolyte.



### Advantages

High energy density but low power

Inexpensive materials

The zinc-air system, when sealed, has excellent shelf life, with a self-discharge rate of only 2 percent per year.

### Applications

- The system is well known as a primary battery.
- Zinc air button cells are commonly used for watches and hearing aids.
- Telecoms and railway remote signalling, safety lamps at road and rail construction sites.

## Construction, working and applications of Lithium-ion battery

Lithium-ion battery is a secondary battery.

It is rechargeable portable battery in which Li ions move from negative electrode to the positive electrode. The movement of lithium ions are responsible for charging & discharging.

The primary components of the lithium-ion battery are

Anode (A negative electrode) → Layers of porous carbon (Graphite).

Cathode (A positive electrode) → Layers of lithium-metal oxide ( $\text{LiCoO}_2$ ).

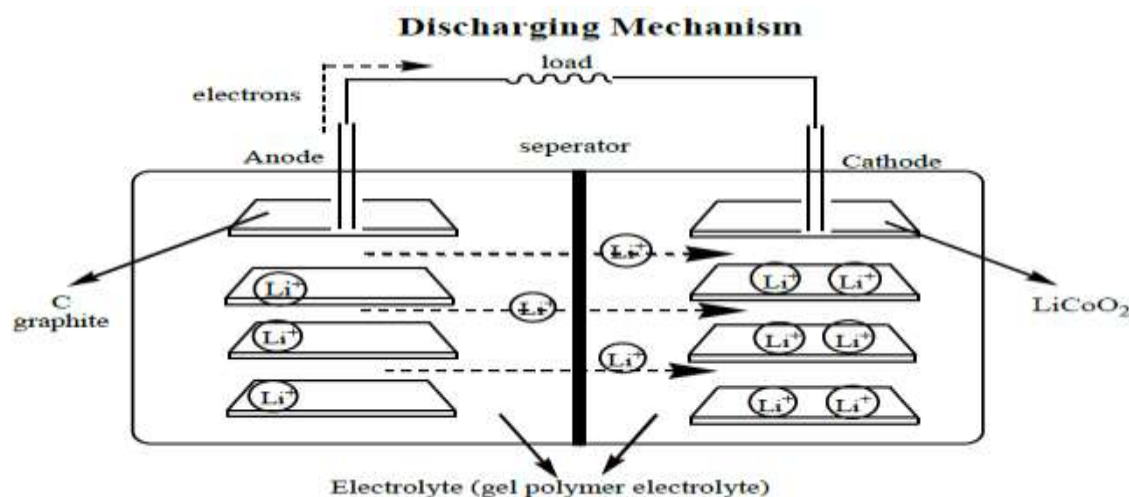
An electrolyte → Li salt Ex:  $\text{LiPF}_6$ ,  $\text{LiClO}_4$

**Construction:**

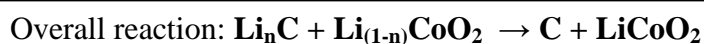
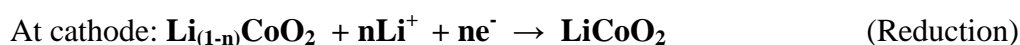
The positive electrode is typically made from layers of chemical compound called lithium cobaltoxide ( $\text{LiCoO}_2$ ).

The negative electrode is made from layers of porous carbon (C) (graphite).

Both the electrodes are dipped in a polymer gel electrolyte (organic solvent) and separated by a separator, which is a perforated plastic and allows the  $\text{Li}^+$  ions to pass through.

**Working****Discharging Reaction:**

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

**Charging Reaction:**

During charging,  $\text{Li}^+$  ions flow from the positive electrode ( $\text{LiCoO}_2$ ) to the negative electrode (Graphite) through the electrolyte. Electrons also flow from the positive electrode to the negative electrode. The electrons and  $\text{Li}^+$  ions combine at the negative electrode and deposit there as Li.



**Advantages (or) Characteristics:**

1. Lithium-ion batteries possess high energy density, tiny memory effect and low self-discharge.
2. Smaller in size.
3. They are high voltage and light weight batteries
4. rechargeable portable batteries
5. Less toxic and recycled
6. No thermal runaway due to overheating or over recharge with these batteries.

**Applications**

- Most commonly used for home electronics, used in telecommunication equipment, cell phone, Laptops, computers, portable LCD TV, semiconductor driven audio, etc.
- Power backups/UPS
- aerospace applications
- In air craft industries.
- Flashlights (Torches), handheld game consoles, electronic cigarettes, camcorders, digital cameras, tablets, are included in these.

**Applications of Li-ion battery to electrical vehicles**

- Lithium-ion batteries have higher energy densities than lead-acid batteries or nickel-metal hydride batteries, so it is possible to make the battery size smaller than others while retaining the same storage capacity.
- Currently, the most appropriate energy storage device for powering electric vehicles (EVs) is lithium-ion batteries because of their interesting characteristics like high power density, high energy density, long life cycle, lack of memory effect, and high energy efficiency.
- The electric vehicle batteries are utilized in advanced electric wheelchairs, personal transporters, electric bicycles, electric scooters and motorcycles, hybrid vehicles, and electric cars. They were also used in Mars Curiosity Rover, aircraft, model aircraft, radio-controlled models, and telecommunications applications. Li-ion batteries are discussed usually as a possible option for grid energy storage.

## Fuel Cells

A fuel cell can be defined as an electrochemical cell that generates electrical energy from fuel via an electrochemical reaction. These are also primary cells.

Fuel cells require a continuous input of fuel and an oxidizing agent (generally oxygen) in order to sustain the reactions that generate the electricity. Therefore, these cells can constantly generate electricity until the supply of fuel and oxygen is cut off.



- Examples for fuel cells:
1.  $\text{H}_2\text{-O}_2$  fuel cell
  2.  $\text{CH}_3\text{OH-O}_2$  fuel cell

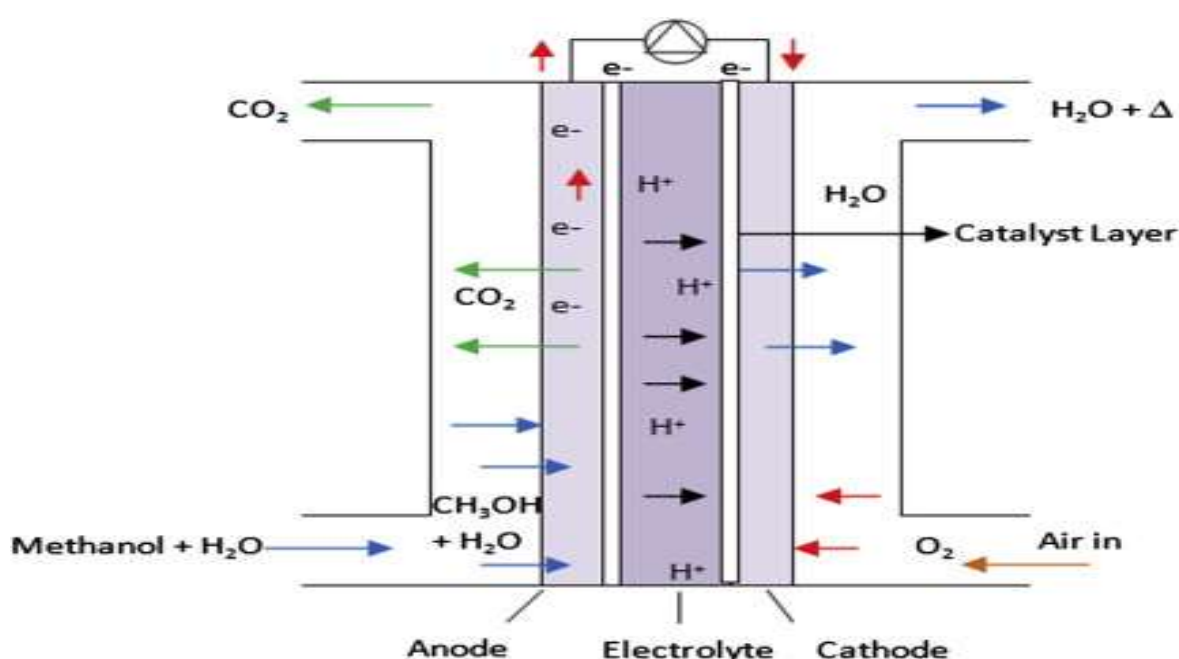
## Differences between battery and a fuel cell

Battery	Fuel cell
They store energy in the form of chemical energy	They cannot store energy. Fuel cell converts chemical energy to electrical energy.
Reactants are inside the cell itself.	Reactants for chemical reaction are supplied continuously.
Rechargeable	Not rechargeable
Can produce electrical energy using chemical energy.	Can produce electrical energy using chemical energy.
Contains limited amount of reactants, decrease with time, so this device cannot produce electrical for a long period of time.	Continuously Supplied with fuel and oxygen from an external source. This makes it work for a long period of time.
Less expensive	They are expensive
Example : lithium ion batteries	Example : hydrogen-oxygen fuel cell

## Construction and applications of Methanol Oxygen fuel cell

It consists of two electrodes made up of platinum, in between the electrodes  $\text{H}_2\text{SO}_4$  is placed as an electrolyte.

- Methanol and water is supplied at the anode and pure oxygen gas is supplied at the cathode.
- In this cell  $\text{H}^+$  ions moves from anode to cathode.
- At anode oxidation takes place, at cathode reduction takes place.
- The methanol is oxidised to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  with the liberation of electrical energy.



The cell reactions are as follows

At anode:  $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$  (Oxidation)

At Cathode:  $\frac{3}{2} \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$  (reduction)

---

Overall:  $\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

---

The cell delivers the emf of 1.20V

---

### Applications

They can produce a small amount of power over a long period of time. This makes them ill-suited for powering large



- But ideal for smaller vehicles such as forklifts and tuggers and consumer goods such as mobile phones, digital cameras or laptops.
- Military applications
- Space applications

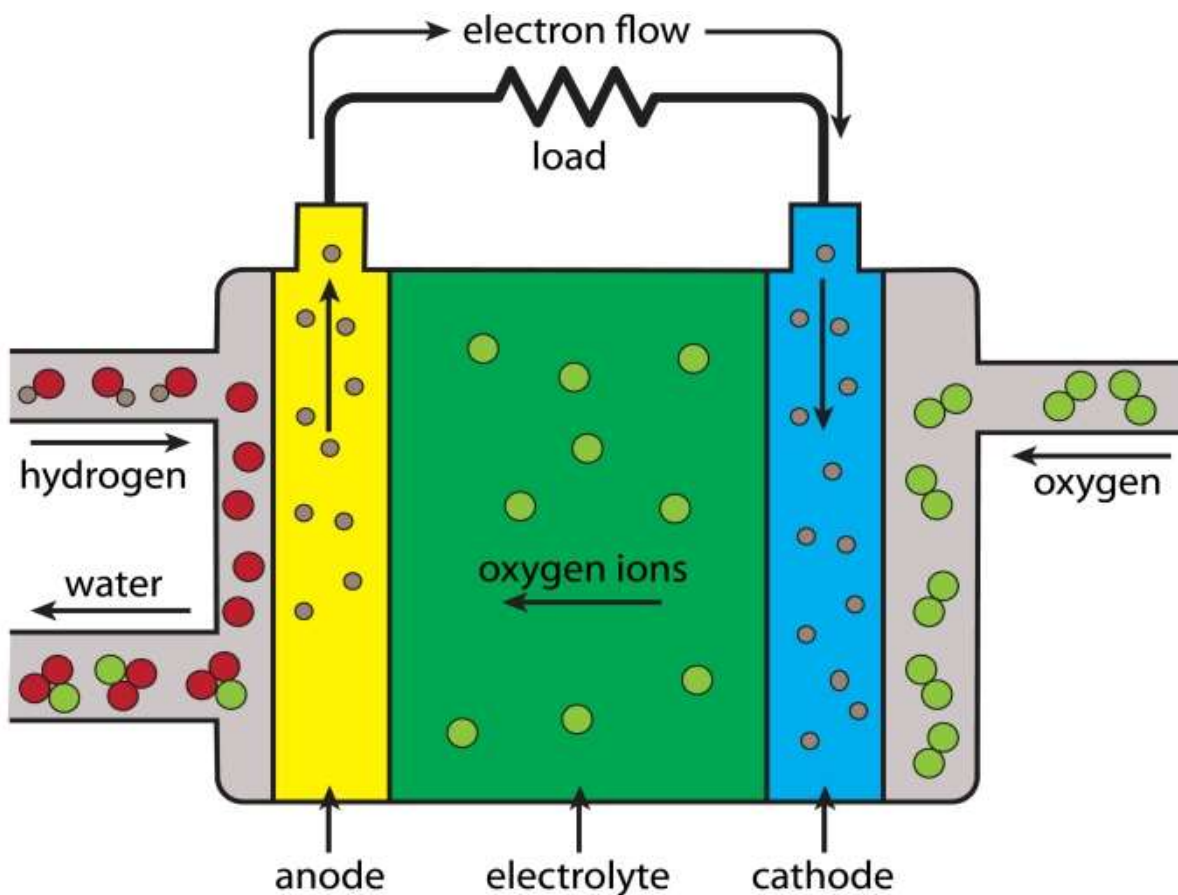
### Advantages of fuel cells

- Highly eco-friendly i.e. there is no harmful product
- Does not cause any pollution. The water produced is used as fresh water by astronauts.
- Noise and thermal pollution are very low.
- They have low maintenance cost.
- They have quick start system.

### **Construction and applications of Solid oxide fuel cell (SOFC)**

A solid oxide fuel cell (or SOFC) is an electrochemical device that produces electricity directly from oxidizing a fuel. The SOFC has a solid oxide or ceramic electrolyte.

They produce electricity at a high operating temperature of 800 to 1000 °C.



In this cell

**Anode:** Ni-ZrO<sub>2</sub> or Co-ZrO<sub>2</sub>

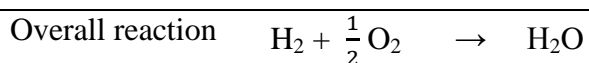
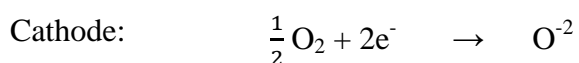
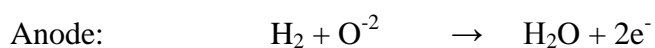
**Cathode:** LaMnO<sub>3</sub> (Lanthanum Manganate)

**Electrolyte:** Solid ceramic material consists of ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>

**Fuel:** H<sub>2</sub>

**Oxidant:** O<sub>2</sub>

At anode, oxidation of hydrogen (H<sub>2</sub>) takes place and at cathode oxygen reduction reaction takes place



### Advantages

- Operate at a higher temperature, do not require precious metal catalyst
- Produce the highest electrical efficiency
- Near zero emissions
- relatively low cost
- less corrosive
- long term stability

### Disadvantages

- High operating temperature which results in longer start-up times and mechanical and chemical compatibility issues.

### Applications

- Used for stationary power generation for homes and businesses.
- Auxiliary power units in electrical vehicles

## **Solar cells**

Solar cell (semi-conductor devices) or photovoltaic cell is a device that converts sunlight into electricity by the photovoltaic effect.

These cells are made of semiconductor materials like Si, Ge.

Basically, a solar cell is a P-N junction that absorbs light, releases electrons and holes, creating a voltage in the cell, and electric flow in the cell.

## **Applications of Solar cells**

Solar cells mostly used in

- In powering space vehicles such as satellites and telescopes.
- Solar cell panels
- Solar cells in power calculators
- Field of electric fence.
- Field of remote lighting system area.
- Field of satellites.
- Military uses, transportation, power in space.

## **Advantages**

- Renewable source
- Free of charge
- does not cause pollution
- Can be used in remote areas.

## **Corrosion:**

The process of decay of a metal from its surface due to unwanted chemical (or) electro chemical interactions with its environment is called corrosion.

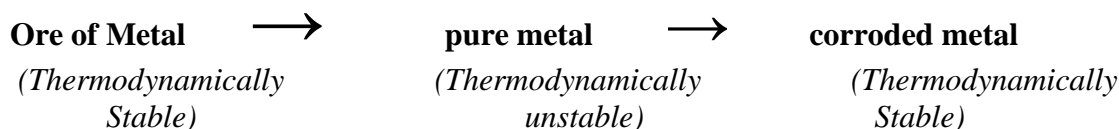
Ex:- Formation of reddish brown layer of rust on the surface of iron ( $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ).

Almost all metals except the least active metals such as gold, platinum and palladium are attacked by environment i.e. undergo corrosion.

- **Units:** milli inches /years (or) mm/ year.

## **Causes of corrosion:-**

- In nature, metals are not found in Free State due to their reactivity.
- Metals exist in nature in the form of oxides, chlorides, sulfates, carbonates and sulphides.
- These combined states of metal (Ore) has low energy is thermodynamically stable state for metals. Pure metals are thermodynamically unstable.
- During extraction of metals these are reduced to free metallic state which is unstable so metals have the natural tendency to go back to their stable combined state. Therefore they undergo corrosion to get stability.



The corrosion is the exactly the reverse process of metallurgy.

## **Effects of corrosion:**

Corrosion taking place mainly on the surface of the metals, but damage caused by it is enormous.

- 1) Corrosion reduces the thickness of the metal, resulting in the loss of mechanical strength and failure of the structure.
- 2) The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
- 3) Buildings and historic monuments are damaged due to corrosion (Eg: Taj Mahal)

- 4) The process of corrosion is very harmful and is responsible for the enormous wastage of metallic products.
- 5) Life span of the metallic parts of the machineries is reduced.

## **Theories of Corrosion**

- 1) Dry or Chemical Corrosion
- 2) Wet or Electrochemical Corrosion

### **Theories of Corrosion**

#### **Dry or Chemical Corrosion**

Types of dry or chemical corrosion

1. Oxidation Corrosion
2. Corrosion by other gases
3. Liquid - Metal Corrosion

#### **Wet or ElectroChemical corrosion**

This corrosion by evolution of hydrogen or absorption of oxygen

Types of wet or electrochemical Corrosion

1. Galvanic Corrosion
2. Water line corrosion
3. Pitting Corrosion

## **Dry or Chemical corrosion**

According to this theory, Corrosion on the surface of a metal is due to direct reaction of atmospheric gases like  $O_2$ ,  $SO_2$ ,  $H_2S$ , halogens, oxides of nitrogen, with metal in the absence of moisture.

There are three types of dry or chemical corrosion.

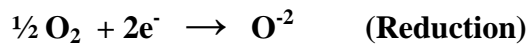
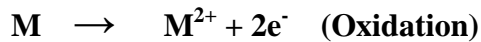
- 1) Oxidation Corrosion
- 2) Corrosion by Hydrogen
- 3) Liquid Metal Corrosion

### **Oxidation Corrosion**

Direct attack of oxygen at low or high temperatures on metals in the absence of moisture is called oxidation corrosion.

Alkali metals (IA) and alkaline earth metal (IIA) are oxidized at low temperature.

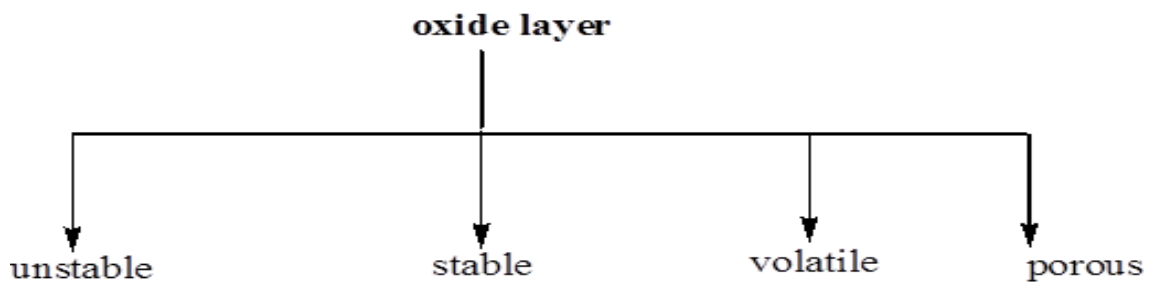
At high temperatures, almost all metals (except Ag, Au, Pt) are oxidized.



---

Overall reaction:  $\text{M} + \frac{1}{2} \text{O}_2 \rightarrow \text{M}^{2+} + \text{O}^{2-} = \text{MO}$  (Metal oxide)

When oxidation starts, a thin layer of oxide is formed on the metal surface. Nature of the oxide formed plays an important role in oxidation corrosion process.



### Dry or Chemical corrosion

According to this theory, Corrosion on the surface of a metal is due to direct reaction of atmospheric gases like  $\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , halogens, oxides of nitrogen, with metal in the absence of moisture.

There are three types of dry or chemical corrosion.

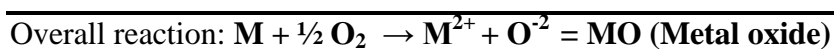
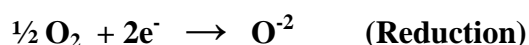
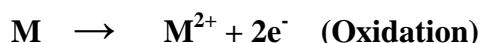
- 1) Oxidation Corrosion
- 2) Corrosion by Hydrogen
- 3) Liquid Metal Corrosion

### Oxidation Corrosion

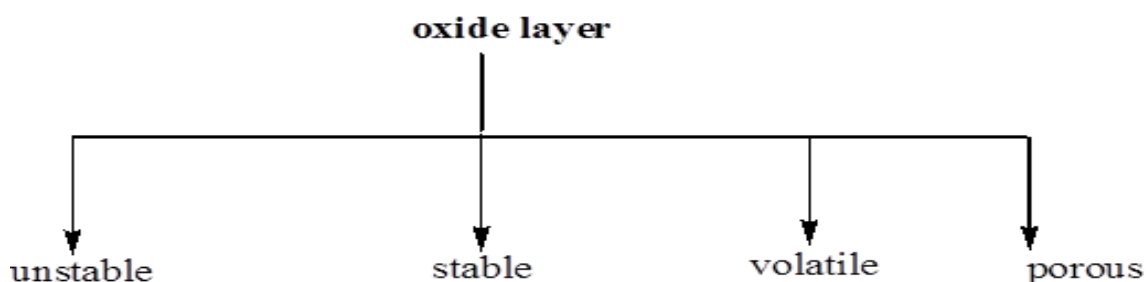
Direct attack of oxygen at low or high temperatures on metals in the absence of moisture is called oxidation corrosion.

Alkali metals (IA) and alkaline earth metal (IIA) are oxidized at low temperature.

At high temperatures, almost all metals (except Ag, Au, Pt) are oxidized.



When oxidation starts, a thin layer of oxide is formed on the metal surface. Nature of the oxide formed plays an important role in oxidation corrosion process.



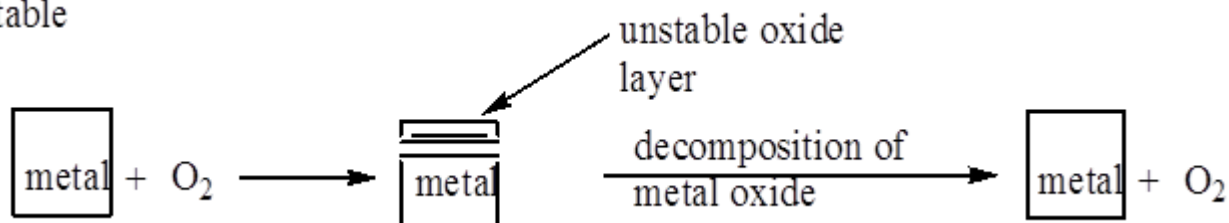
#### Unstable oxide layer:

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

Consequently, oxidation corrosion is not possible in such a case.

Thus, Ag, Au, and Pt do not undergo oxidation corrosion

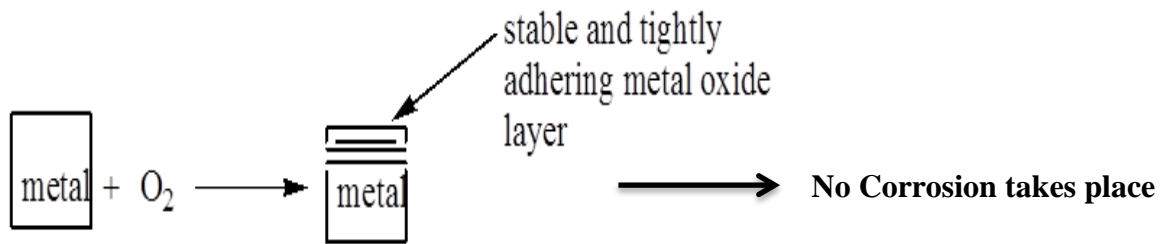
unstable



#### stable oxide layer:

Metals like copper, aluminum, tin, lead can form stable oxide layer, thereby preventing the metal from further corrosion. The oxide layer is tightly adhering which acts as a barrier to prevent the entry of oxygen, there by shielding the metal from further corrosion.

Ex; The oxide film on Al, Sn, Pb, Cu, Cr, W etc

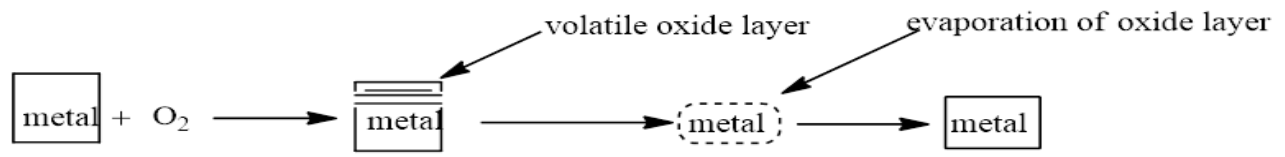


### Volatile oxide layer

If the metal oxide layer is volatile, it evaporates as soon as it is formed, leaving the underlying metal surface exposed for further attack.

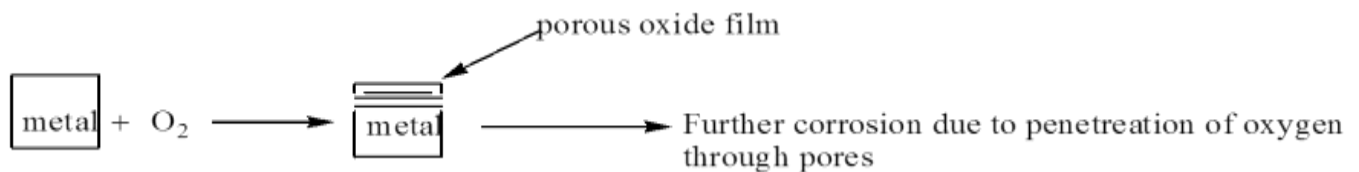
This causes rapid and continuous corrosion, leading to excessive corrosion.

Ex: Molybdenum oxide (MoO<sub>3</sub>) is volatile.



### Porous oxide layer

In the case of a porous oxide film, atmospheric gases pass through the pores and react with metal. The process of corrosion continues to occur till the entire metal is converted into oxide.



### Corrosion by other gases

The gases like SO<sub>2</sub>, CO<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub>S and F<sub>2</sub> etc. also cause chemical corrosion and the extent of corrosion 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.
- If the film formed is protective or non-porous, the intensity or extent of attack decreases, because the film formed protects the metal from further attack.



Ex: AgCl film, resulting from the attack of Cl<sub>2</sub> on Ag. The AgCl film formed is very stable and sticks firmly to the surface preventing further corrosion.

- If the film formed is non-protective or porous, the surface of the whole metal is gradually destroyed.

Ex: dry Cl<sub>2</sub> gas attacks on tin (Sn) forming volatile SnCl<sub>4</sub>.

### **Liquid metal corrosion**

It is due to chemical action of flowing liquid metal on solid metal at high temperatures.

Such corrosion occurs in devices used for nuclear power. The corrosion reaction involves either dissolution (the act of breaking up) of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

Both these methods of corrosion cause weakening of the solid metal.

Ex:- Coolant Sodium leads to corrosion of Cadmium in nuclear reactor.

### **Electrochemical or Wet Corrosion:**

- This type of corrosion occurs when two dissimilar metals or alloys are in contact with each other in presence of an aqueous solution or moisture.
- This corrosion occurs, due to the existence of separate “anodic and cathodic” areas, between which current flows through the conducting solution.
- At anodic area, oxidation reaction takes place, so anodic metal is destroyed by either dissolution or formation of compounds. Hence, corrosion always occurs at anodic areas.

### **Mechanism:**

Electrochemical corrosion involves flow of electrons between anode and cathode.

The anodic reaction involves dissolution of metal liberating free electrons.

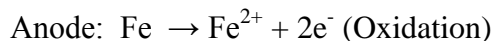


The cathodic reaction consumes electrons with either **evolution of hydrogen** or **absorption of oxygen** which depends on the nature of corrosive environment.

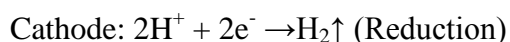
**a) Evolution of hydrogen:**

This type of corrosion occurs in **acidic medium**.

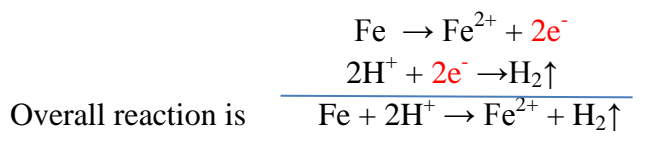
Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.



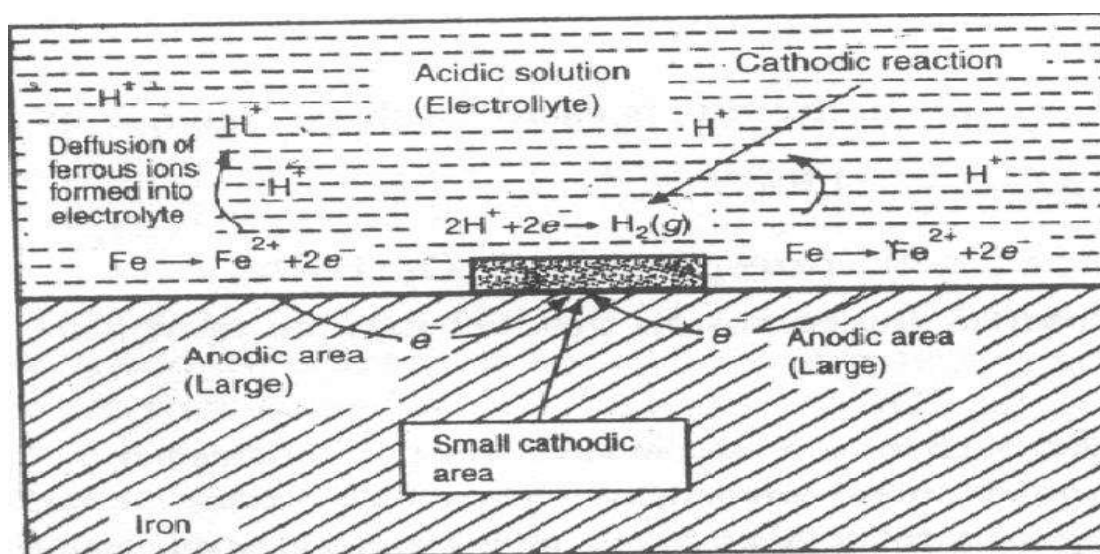
The electrons released flow through the metal from anode to cathode, where  $\text{H}^+$  ions (of acidic solution) are eliminated as hydrogen gas.



The overall reaction is



In this type of mechanism the anodes are large areas, whereas cathodes are small areas.



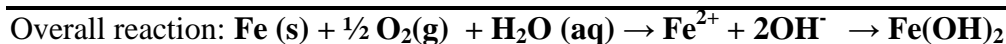
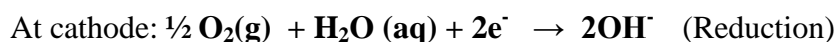
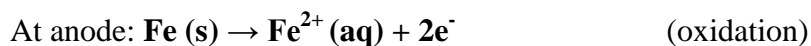
**Mechanism of wet corrosion by hydrogen evolution**

**b) Absorption of oxygen:**

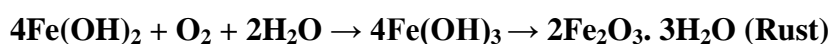
This type of corrosion takes place in **neutral or basic medium** in the **presence of oxygen**.

Rusting of iron in neutral aqueous solution of electrolytes in the presence of atmospheric oxygen is a common example of this type of corrosion. 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

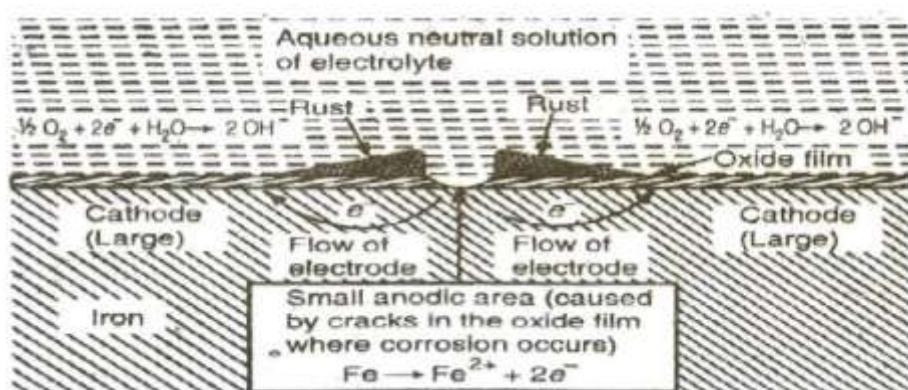
the rest metallic part forms large Cathodes. The released electrons flow from anode to cathode through iron metal.



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



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



### Types of electrochemical (Wet) Corrosion

Wet or electrochemical corrosion is of different kinds. Some of them are

- Galvanic corrosion
- Water-line corrosion
- Pitting corrosion

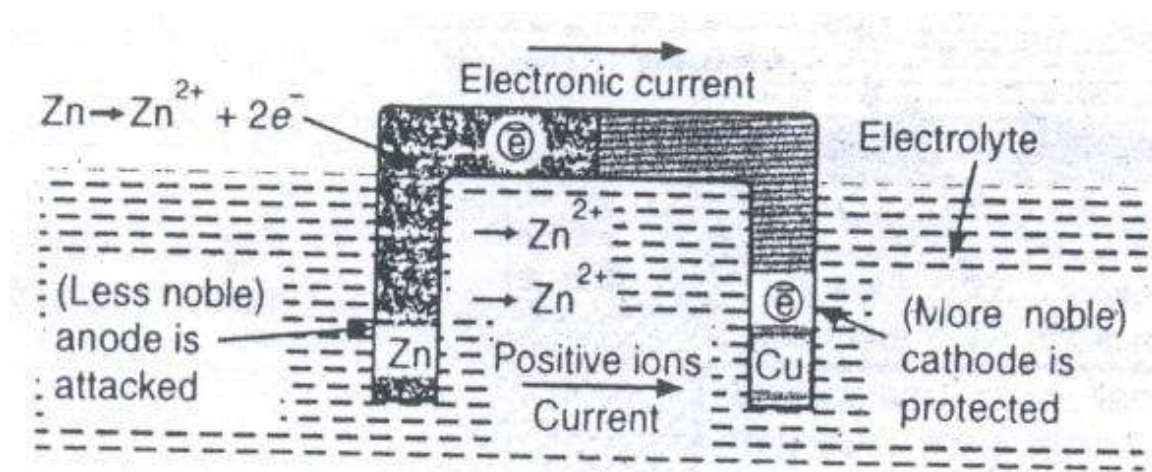
### Galvanic corrosion

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. The corrosion is more if the potential difference between the metals is more.
- 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 Cu will be unaffected.
- The electrons released by zinc reach copper through the metal.

## Reactions

At anode:	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	[Oxidation] corrosion
At cathode:	$\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$	[Reduction] unaffected
Net reaction is	$\text{Zn} + \text{Cu}^{+2} \rightarrow \text{Zn}^{2+} + \text{Cu}$	



Galvanic corrosion can be avoided by

1. 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

## Water-line corrosion

This is also known as differential oxygen concentration corrosion. When water is stored in a metallic tank, it is observed that the metal below the waterline gets corroded. It is because the water below the waterline is poorly oxygenated and acts as an anode. The metal above the waterline is highly oxygenated and acts as a cathode. Hence corrosion of metal below the waterline takes place.

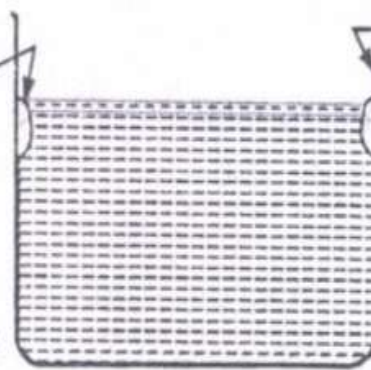
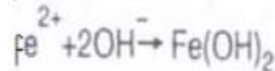
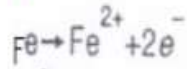
At anode:  $\text{Fe (s)} \rightarrow \text{Fe}^{2+} (\text{aq}) + 2\text{e}^-$

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

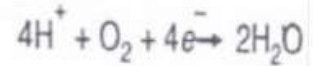
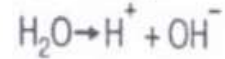
---

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

**Poor oxygenated  
anodic part is  
corroded**



Highly oxygenated  
cathodic part  
(protected)



### Pitting Corrosion:

The metal surfaces having pits or cavities undergo corrosion due to development of separate anodic and cathodic areas. When a metal is covered by some water or dirt, the part which is covered has low oxygen concentration acts as an anode. The part which is exposed to oxygen acts as cathode. The covered area gets corroded and small pits are formed on it.

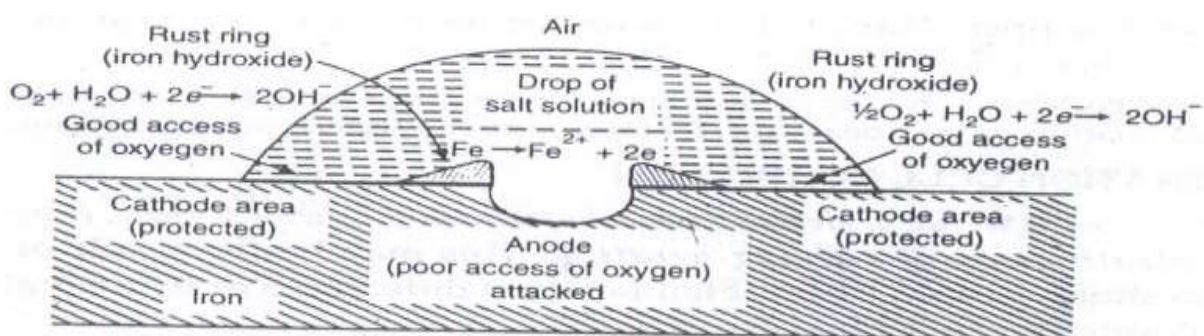
At anode:  $\text{Fe (s)} \rightarrow \text{Fe}^{2+} \text{ (aq)} + 2\text{e}^-$

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

---

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

(Oxidation)



Pitting of the metal occurs when there is a break in the protective layer. Pitting corrosion is a non-uniform corrosion resulting in the formation pits, cavities and pin-holes in the metal.

Once a small pit is formed the rate of corrosion will be increased.

### **Factors affecting the rate of corrosion**

The rate and extent of corrosion depends on the following factors.

- a. **Nature of the Metal**
- b. **Nature of the corroding environment**

### **Factors due to nature of metal**

#### **1. Galvanic series/ Electrochemical series**

When metals are arranged in decreasing order of their oxidation potentials, the series so formed is known as “Galvanic Series”.

- Which possess high oxidation potentials in the galvanic series undergo corrosion easily.
- Metals which possess low oxidation potentials in the galvanic series do not undergo corrosion and they get protected.
- When two different metals are in electrical contact in presence of an electrolyte, then the metal which is more active undergoes corrosion.
- The rate of corrosion depends on the difference in their position in Galvanic series. Greater the difference more will be the extent of corrosion at anode.

Eg. The potential difference between Fe and Cu is 0.78V which is more than that between Fe and Sn (0.30V). Therefore, Fe corrodes faster when in contact with Cu than that with Sn. on this account, the use of dissimilar metals should be avoided wherever possible (Eg. Bolt & nuts, screw & washer).

2. **Purity of the metal:** generally pure metal does not corrode as there is no cathode spot available to induce corrosion. Impurities present in the metal result in heterogeneity and thereby help in the development of separate anodic and cathodic areas. The anodic parts get corroded. The rate and severity of corrosion increase with increase in impurities.

#### **3. Nature of the corrosion product**

If the corrosion product is soluble in corroding medium, the corrosion proceeds at a faster rate.

If the corrosion product is volatile, the corrosion rate will be faster. Ex:  $\text{MoO}_3$  is volatile.



### **Factors due to nature corrosive environment**

1. **Temperature:** The rate of diffusion increases by rise in temperature, hence the corrosion also increased. At higher temperatures, passive metals also become active and undergo corrosion.  
 $\therefore$  the rate of corrosion increases with increase in temperature.
2. **Humidity in 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”.  
Most of the metals corrode faster in humid atmosphere than in dry air.  
The reasons for increase of corrosion with humidity are the moisture or vapours present in atmosphere furnish water to the electrolyte, essential for setting up an electrochemical cell.
3. **PH value:** pH value of the medium has the greater effect on corrosion. Acidic pH (or lowered pH) increases the rate of corrosion.

### **Corrosion control methods**

Due to corrosion there is a great loss of material and money. Therefore it is essential to protect metals from corrosion.

- Metal undergoes corrosion by its oxidation, when they behave like an anode.
- We can prevent the corrosion of metals by forcing the metals to behave like cathode.  
This is the principle of **cathodic protection**.
- There are two types of cathodic protection.

#### **1. Sacrificial anodic protection**

#### **2. Impressed current cathodic protection**

### **Sacrificial anodic protection**

In this protection method, the metallic structure to be protected (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.

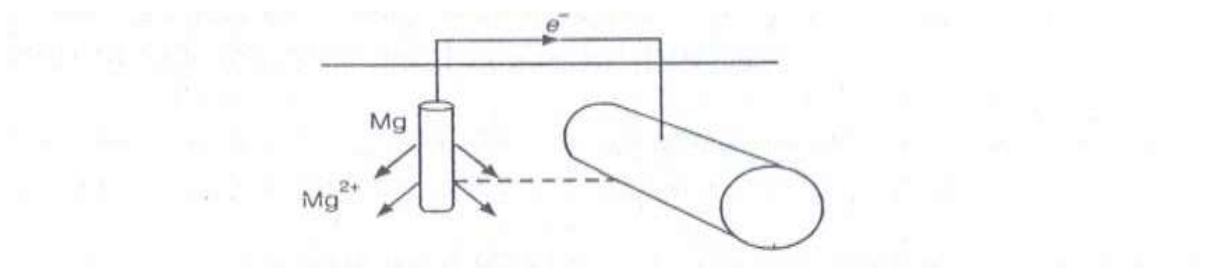
Examples are

To protect marine structures and ship parts which are made of steel are connected to a sacrificial anode (Zn (or) Mg).

- a. Buried pipelines, underground cables and water tanks also protected by sacrificial anode (Na, Mg) method.

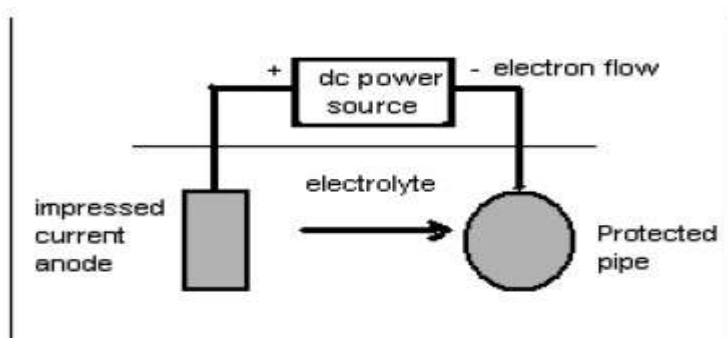
#### **Disadvantages**

- More than one anode is required. Anode must be replaced when it is consumed
- Current output is less
- It does not work properly in highly corrosive environment



#### **Impressed current cathodic protection**

- This is another method for the cathodic protection of metals. In this method, an impressed current is applied from an external source in opposite direction to nullify the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.
- The impressed current is slightly higher than the corrosion current.
- The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.
- The commonly used anodic materials are graphite, carbon, stainless steel, scrap iron, high silica iron and platinum.

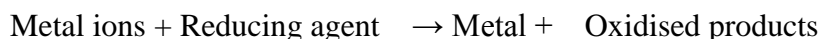




## Electroless plating:

It is technique of depositing a noble metal (from its salt solution) on a catalytically active surface of a less noble metal by employing a suitable reducing agent without using electrical energy.

The added reducing agent causes the reduction of the metallic ions to metal, which eventually gets plated over the catalytically activated surface giving a highly uniform, but thin coating thus:



## Electroless plating (Nickel plating)

Before performing electroless nickel plating, the material to be plated must be cleaned by a series of chemicals, this is known as the pre-treatment process.

Failure to remove unwanted "soils" from the part's surface result in poor plating.

Each pre-treatment chemical must be followed by water rinsing (normally two to three times) to remove chemicals that may adhere to the surface.

De-greasing removes oils from surfaces, whereas acid cleaning removes scaling.

Composition of bath:

Coating solution – NiCl<sub>2</sub> solution (20g/l)

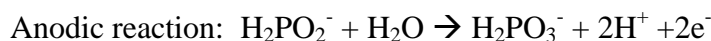
Reducing agent – sodium hypophosphite (20g/l);

Buffer – sodium acetate (10g/l);

Complex agent cum exhalant – sodium succinate (15g/L)

pH= 4.5 ; temp = 93°C

## Reactions:



In this pre-treated object (ex: stainless steel) is immersed in the plating bath containing NiCl<sub>2</sub> and a reducing agent, sodium hypophosphite for the required time. During the process, Ni gets coated over the