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Subject: Applied Chemistry

Faculty: Dr. P Vinodkumar

Topic: BATTERIES

Battery:

Battery is a device consisting of one or more galvanic cells connected in series or parallel or both. It converts chemical energy into electricity through redox reactions.

Basic Components of Battery

Batteries consist of four major components:

- **Anode (–ve):** It undergoes oxidation and release electrons to the external circuit.
- **Cathode (+ve):** Active species at cathode undergoes reduction by accepting electrons from external circuit.
- **Electrolyte:** It is a solution of salt or alkali or acid. It allows the movement of ions inside the cell between anode and cathode. *Example:* NaCl, KOH, H_2SO_4, etc.
- **Separator:** It separates anode and cathode to prevent internal short circuiting, but allows transport of ions between anode and cathode and maintains electrical neutrality. *Example:* cellulose, nafion membranes, etc.
- Cathode current collector, anode current collector, rubber seal and container are the minor components of battery.

Classification of Batteries

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: Zn-MnO_2 battery, Li-MnO_2 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.

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.

Another 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.

DIFFERENCES BETWEEN PRIMARY BATTERIES AND SECONDARY BATTERIES

PRIMARY BATTERIES	SECONDARY BATTERIES
Cell reactions are irreversible.	Cell reactions are reversible.
Must be discarded after use.	Can be reused.
Have shorter shelf life.	Have longer shelf life.
They function only as galvanic cell.	They function as both galvanic and electrolytic cell.
Cannot be used as energy storage devices.	Can be used as energy storage devices.
They cannot be recharged.	They can be recharged.
Ex- Dry cell.	Ex-Lead acid storage battery.

Advantages of Batteries:

(1) Batteries act as a portable source of electrochemical energy.

(2) The portability of electronic equipment in the form of handsets has been made possible by batteries.

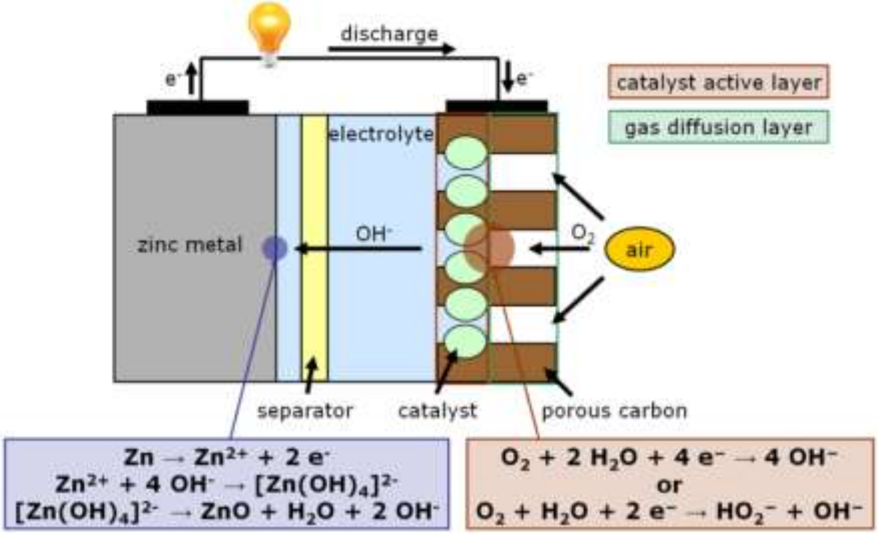
(3) A variety of electronic gadgets have been made more useful and popular with the introduction of rechargeable storage batteries having reliability, better shelf life and tolerance to service.

(4) For all commercial applications, batteries are constructed for their service. For example batteries for automotives and aircrafts, stand by batteries etc.

Zn-Air batteries:

Metal air batteries have attracted much attention because of their extremely high energy densities. The notable characteristic of these batteries is their open cell structure since these batteries use oxygen gas accessed from air as their cathode material.

Among metal air batteries zn-air batteries have powerful potential for the use as alternative energy device, low cost, abundance, low equilibrium potential, flat discharge voltage, and long shelf-life. The most important merit of the Zn-air batteries is that non-noble metal catalyst is used for the reduction reaction.



- Zn-air cells are composed of three parts zinc-metal as anode, an air electrode as cathode which is divided into a gas diffusion layer and a catalytic active layer along with a separator.
- Because of the low solubility of O_2 at atmospheric pressure it is necessary to use O_2 in the gas phase not in liquid.
- O_2 from atmosphere diffuses into the porous carbon electrode due to difference in pressure of O_2 outside and inside of the cell.
- Catalyst facilitates the reduction of O_2 to OH^- in the alkaline electrode by using the e^- generated by the Zn metal as anode reaction.
- This way we call the process a three-phase reaction catalyst (solid), electrolyte (liquid) and O_2(gas).
- Finally, the OH^- ion migrates from the air cathode to Zn anode to complete the cell reaction.

Electrode reactions:

Anode: $Zn \rightarrow Zn^{+2} + 2e^-$

$Zn^{2+} + 4OH^- \rightarrow 2Zn(OH)_4^{-2}$

$Zn(OH)_4^{-2} \rightarrow ZnO + H_2O + 2OH^-$ ($E_o = 1.25$ V)

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (O_2 reduction reaction) $E_o = 0.4$ V

Overall reaction: $2Zn + O_2 \rightarrow 2ZnO$ ($E_o = +1.65$ V)

The drawback of this battery is the working voltage of battery is much lower due to internal losses.

Lithium-ion batteries (or) Lithium-ion cells:

- These batteries are rechargeable battery best suited for mobile devices that requires small size, light weight and high performance.
- Lithium-ion battery is a secondary battery.
- It works on the principle Intercalation Mechanism.
- As the name suggests, the movement of lithium ions are responsible for charging '& discharging.

Construction:

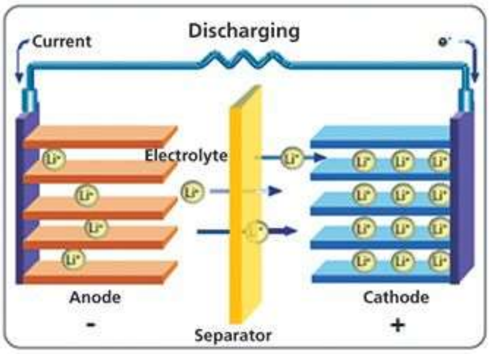
- Anode: Lithium intercalated graphite/carbon, metal matrix or polymer. A negative electrode.
- Anode current collector: Copper foil
- Cathode: Partially Lithiated oxides of Ni, Co and Mn like Li_yNiO_2, Li_yCoO_2 and Li_yMnO_4
- Cathode current collector: Aluminium foil.
- Separator: fine porous polymer film.
- Electrolyte: Lithium salt ($LiPF_6$) in an organic solvent (propylene carbonate or 1,2 dimethoxyethane).

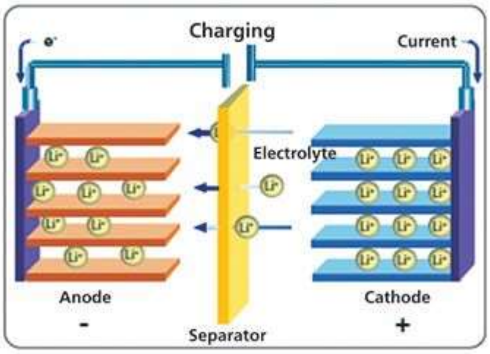
Working

Charging Reaction:

During charging, Li^+ ions flow from the positive electrode ($LiCoO_2$) to the negative electrode (graphite) through the electrolyte. Electrons also flow from the positive electrode to the negative electrode. The electrons and Li^+ ions combine at the negative electrode and deposit there as Li.

$$LiCoO_2 + C \rightarrow Li_{1-x}CoO_2 + CLix$$



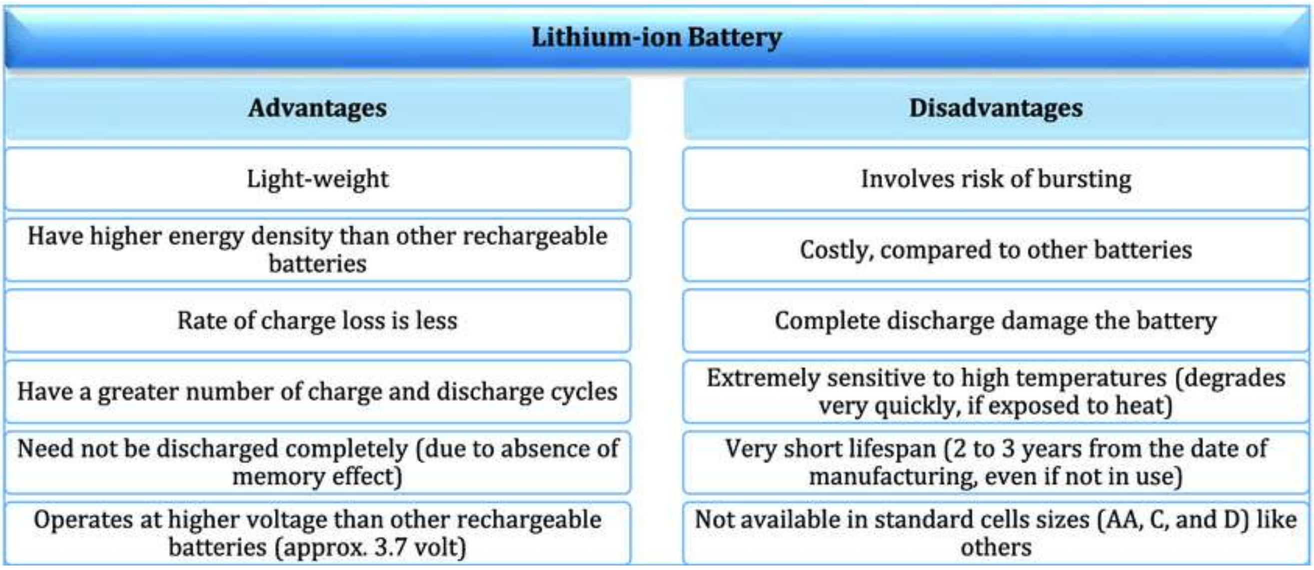


Discharging Reaction:

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

$$Li_{1-x}CoO_2 + CLi_x \rightarrow LiCoO_2 + C$$

Advantages (or) Characteristics:



Lithium-ion Battery

Advantages	Disadvantages
Light-weight	Involves risk of bursting
Have higher energy density than other rechargeable batteries	Costly, compared to other batteries
Rate of charge loss is less	Complete discharge damage the battery
Have a greater number of charge and discharge cycles	Extremely sensitive to high temperatures (degrades very quickly, if exposed to heat)
Need not be discharged completely (due to absence of memory effect)	Very short lifespan (2 to 3 years from the date of manufacturing, even if not in use)
Operates at higher voltage than other rechargeable batteries (approx. 3.7 volt)	Not available in standard cells sizes (AA, C, and D) like others

Applications:

Some of the most common applications of lithium-ion batteries are:

- Power backups/UPS
- Mobile, Laptops, and other commonly used consumer electronic goods
- Electric mobility
- Energy Storage Systems

in health centers for surgery

5) In agriculture sectors like irrigation , in animal husbandry for watering & milking.

6 In production activities such as milling, sawing and sewing.

Fuel cell

Fuel cell is a device which converts the chemical energy of a fuel (hydrogen, natural gas, methanol, gasoline) into electrical energy by oxidation of fuel with the help of oxidant.

Introduction: Fuel cell consists of two electrodes and an electrolyte. Fuel is oxidized at anode and oxidant (oxygen) is reduced at cathode. In fuel cells, fuel is passed through anode compartment and oxidant is passed through cathode compartment. Electrons liberated at anode are consumed at the cathode trough external circuit.

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

Advantages

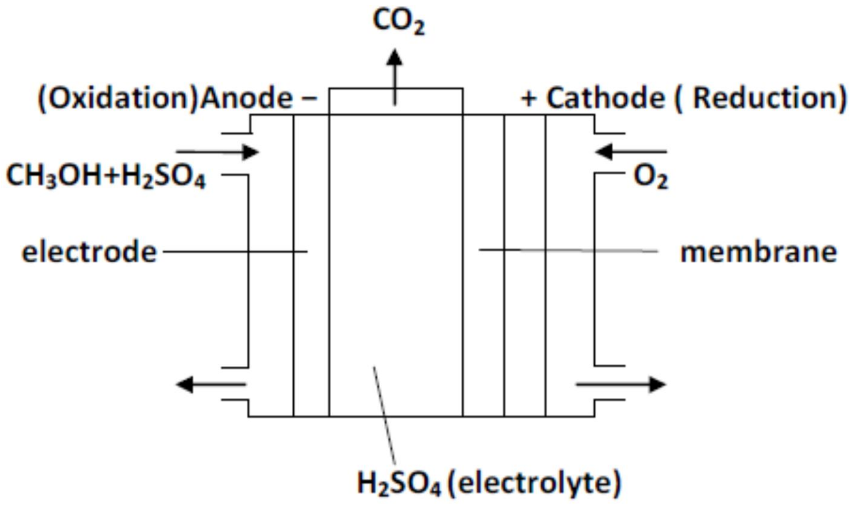
1) No need of charging
2) No harmful waste products and hence eco friendly
3) Silent operation
4) High efficiency of the energy conversion process
5) No moving parts, hence no wear and tear

Limitations

1) Electrodes are expensive
2) Fuels in the form of gases and oxygen should be stored in tanks under high pressure.
3) Power output is moderate

Methanol–Oxygen Fuel Cell

Anode Material: CH_3COOH & H_2SO_4
Cathode Material: Oxygen gas
Electrodes: Both are made up of platinum
Electrolyte: H_2SO_4



Construction &Working

Methanol is mixed with sulfuric acid and circulated through anode chamber. Pure oxygen is passed through the cathode. Sulfuric acid is kept as electrolyte between two platinum electrodes. A membrane is inserted close to cathode to avoid diffusion of methanol into cathode. Otherwise methanol undergo oxidation. Methanol diffuses through the anode is absorbed at the electrode surface. At cathode oxygen diffusing through the electrode is absorbed and get reduces.

At Anode $CH_3OH_{(l)} + H_2O_{(l)} \longrightarrow CO_{2\,(g)} + \cancel{6H^+}_{(aq)} + \cancel{6e^-}$

At Cathode $3/2O_2 + \cancel{6H^+}_{(aq)} + \cancel{6e^-} \longrightarrow 3\,H_2O_{(l)}$

Net reaction $CH_3OH_{(l)} + 3/2O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 2H_2O_{(l)}$

Acid electrolyte removes CO2 easily. The cell potential is 1.2V at 25 C. The methanol oxygen fuel cell is used in military applications and in large scale power production.

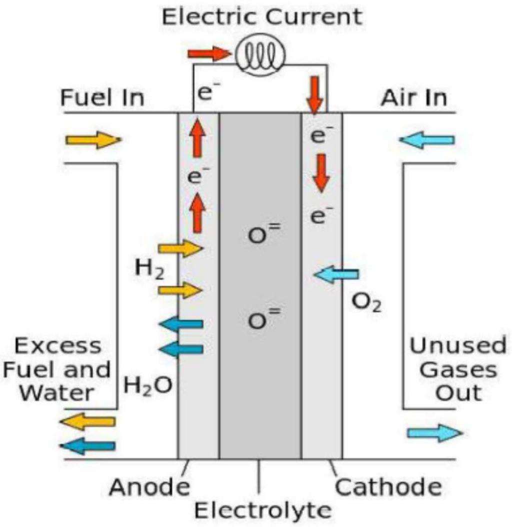
Advantages

1. It has low carbon content
2. It has readily oxidizable OH group
3. It has high solubility in aqueous electrolyte

SOLID OXIDE FUEL CELL (SOFCs)

Solid Oxide Fuel Cell is an electrochemical conversion device that produces electricity directly from oxidizing a fuel and are characterized by the use of a solid oxide material as the electrolyte.

SOFCs use a solid oxide electrolyte to conduct negative oxygen ions from cathode to anode.



Anode Material: Nickel doped Zirconia (Ni-Zr) Catalyst for oxidation of fuel

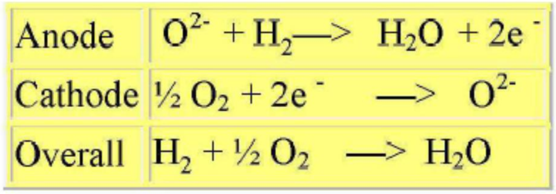
Cathode Material: Lanthanum–Manganate

Fuel: H2/CO2

Temperature: 500 to 1000^{o}C

Construction and Working:

SOFCs consist of two porous ceramic electrodes separated by dense oxide conducting electrolyte. The operating principle is oxygen supplied at cathode undergoes reduction to form oxide ions, which migrate to the anode through oxide ion conducting electrolyte. At anode oxide ions combines with H_2 or CO in the fuel to form H_2O or CO_2 liberating electrons. These electron flow from the external circuit.



Anode	$O^{2-} + H_2 \longrightarrow H_2O + 2e^-$
Cathode	$\frac{1}{2} O_2 + 2e^- \longrightarrow O^{2-}$
Overall	$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

Advantages: High efficiency, long-term stability, fuel flexibility, low emissions and low cost.

Disadvantages: High operating temperature which result in longer start up time, mechanical and chemical stabilities.

Subject: Applied Chemistry

Faculty: Dr. P Vinodkumar

Topic: Introduction-Causes and Effects of corrosion

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Corrosion:

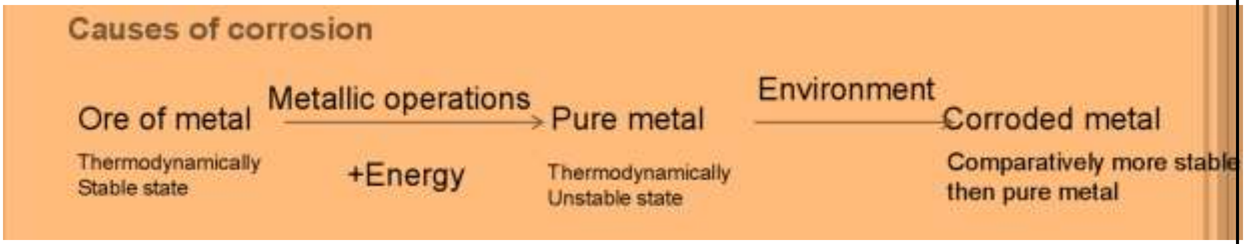
Scientific Definition: Corrosion is defined as the gradual destruction of metals or alloys by the chemical or electrochemical reactions with its environment.

Practical Definition: Tendency of a metal to Revert to its Native State

Examples: Rusting of Iron, Tarnishing of Silver, Bluish-green Tinge by Copper

1. Causes of Corrosion

- In nature, metal exists in combined mineral forms as compounds like Oxides, Nitrates, Silicates etc., in ores.
- Pure metals are extracted from those ores, through different metallurgical processes such as crushing, grinding, cleaning with solvent, chemical treatment, roasting in a furnace and electrolytic refining.
- The metallurgical process requires an enormous amount of energy to obtain pure metal because the ore form of the metal is thermodynamically stable.
- The pure metal which is obtained from ore is thermodynamically unstable, this causes metal to revert back to thermodynamically stable state by interacting chemically or electrochemically with the environment.
- The metal gets the minimum needed energy from temperature, Sun light, chemicals from enviranment to go to stable compound.
- This natural tendency of pure metal to revert back to its stable form leads to corrosion.



2. Effects of Corrosion

- ✓ Metals loses their thickness and mechanical strength during corrosion.
- ✓ Valuable properties like malleability, ductility and conductivity are changed due to corrosion.
- ✓ Metal loses their efficiency and Lifetime.
- ✓ Because of deterioration of appearance, the cost of machine is reduced.
- ✓ Replacement is time consuming; hence the production and maintenance cost increases.

Subject: Applied Chemistry

Faculty: Dr. P Vinodkumar

Topic: Classification of corrosion

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3. Classification of Corrosion Mechanism

Based on the interaction of metal with environment the corrosion mechanism can be classified into 2 types:

1. Dry / Chemical Corrosion
2. Wet / Electrochemical Corrosion

3.1. Chemical Corrosion/ Dry Corrosion

This type of corrosion occurs due to chemical reaction between metal and atmospheric gases like CO_2, O_2, H_2S, halogens and SO_2 etc. that attack the metal surface.

The chemical corrosion can be further divided into three types:

(1) Oxidation corrosion

(2) Corrosion due to other gases

(3) Liquid metal corrosion

3.1.1. Oxidation corrosion:

This is carried out by the direct action of oxygen on metals in absence of moisture. Being an high electronegative element and due to sufficient abundance, alkali metals and alkaline earth metals are rapidly oxidized even at low temperatures. Whereas at higher temperatures almost all metals gets oxidized (except Ag, Au, and Pt).

Basic Reaction during Chemical Corrosion:

M (metal) $\rightarrow M^{2+} + 2e^-$ (Oxidation)

$O_2 + 2e^- \rightarrow 2O^{2-}$ (Reduction)

Overall reaction: $M + O_2 \rightarrow MO_2$ (metal oxide)

The nature of oxide film formed on the metal surface plays an important role in oxidation corrosion.

This layer can be classified into four types

(i) **Stable Oxide Layer / Non-Porous Oxide Layer**

A stable oxide layer behaves as a protective coating and no further corrosion can develop.

Example: oxides of Al, Ag, Pb, Cu etc., are stable oxide layers

(ii) **Unstable Oxide Layer**

When oxide layer formed is unstable, metal oxide gets decomposed back into the metal and oxygen. As a result, metals like Ag, Au, Pt do not undergo corrosion.

(iii) **Volatile Oxide Layer**

A Volatile oxide layer is developed making further corrosion to take place due to evaporation of layer and by exposing the fresh metal surface to environment so that the process continues till the all metal is corroded.

Example: Molybdenum forms its trioxide layer (MoO_3)

(iv) **Porous Oxide Layer**

This layer allows passage of atmospheric gases through pores and react with metal and goes on till all the metal is being converted to its metal oxide

Example: Rusting of Iron

3.1.2. Corrosion by Other Gases

Gases like SO_2, CO_2, Cl_2, H_2S etc. – Induce action on metals in dry atmosphere forming protective or non –protective layers

Eg: When Cl_2 reacts with Ag, it forms AgCl which is protective in nature whereas reaction with Sn forms $SnCl_4$ which forms volatile layer

3.1.3. Liquid - Metal Corrosion

This is due to the chemical action of flowing liquid metal at high temperature. The corrosion reaction involves either,

(i) Dissolution of a solid metal by a liquid metal (or)

(ii) Liquid metal may penetrate into the solid metal

Eg: Mercury forms amalgams with metals; and corroding them

3.2. Wet Corrosion / Electrochemical Corrosion

If the corrosion happens in the presence of moisture by forming small electrochemical cells (anodes and cathodes) on the surface of the metal, then it is called Wet corrosion or Electro Chemical Corrosion. Usually this happens when there is some kind of non-uniformity or heterogeneity (two dissimilar metals are in contact with each other, differences in stress/Strain, differences in the concentration).

At the anodic part of the metal, metal gets oxidized to form metal ions with liberation of electrons. The liberated electrons flow towards cathode through conductor (metal itself). Now, some other species (usually O_2) gets reduced.

Metal ions liberated at the anode and some anions formed at the cathode diffuse towards each other through the electrolyte and form a corrosion product between anode and cathode.

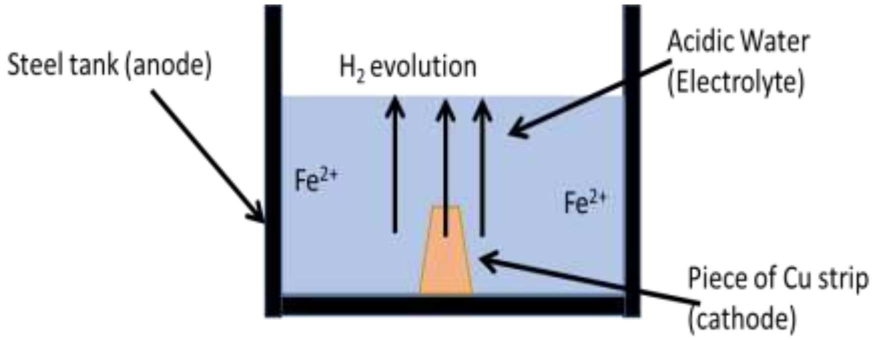
3.2.1. Wet Corrosion Mechanism:

Based on nature of environment or electrolyte involved there can be one of the following two mechanisms involves in electrochemical corrosion:

1. Hydrogen evolution mechanism (In acidic medium)
2. Oxygen absorption mechanism (Neutral or alkaline medium)

3.2.1.1. Hydrogen Evolution Mechanism

Hydrogen evolution mechanism occurs in acidic medium like – in industrial water and solution of non-oxidizing acids. e.g.- A steel (Fe) tank, acidic industrial water is in contact with a small copper scrap. The piece of copper and steel tank in contact with each other in presence of acid electrolyte form an electrochemical cell. In this process, steel acts as anode and Cu acts as cathode. It is observed that the steel tank portion in contact with the piece of Cu is corroded.



Corrosion Reactions:

At anode (steel tank): Fe is oxidized and passes into the solution as Fe^{2+}.

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (oxidation)}$$

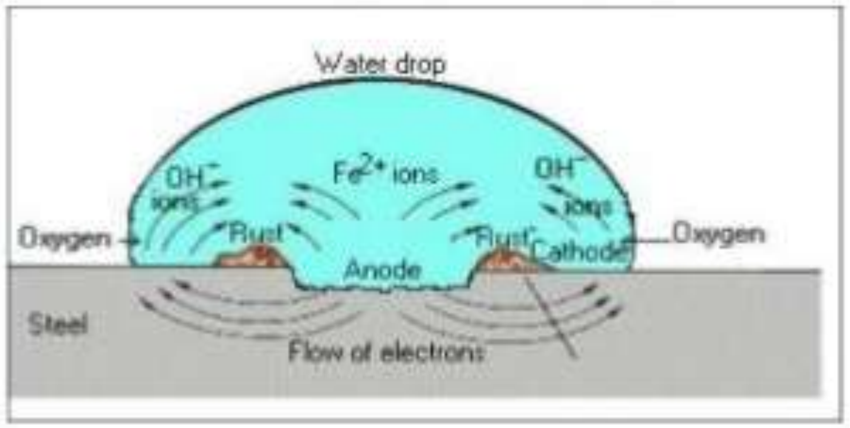
At cathode (Cu) : H^+ ions from acidic solution accept the free electrons obtained from oxidation of Fe and H_2 gas formed is liberated in the form of bubbles at cathode.

$$2H^+ + 2e^- \rightarrow H_2 (g) \quad \text{(reduction)}$$

Net Reaction: $Fe + 2H^+ \rightarrow Fe^{2+} + H_2 (g)$

This corrosion mechanism involves displacement of H^+ ions from acidic electrolyte by the metal ion and converting them to H_2 gas at cathode.

3.2.1.2. Oxygen Absorption Mechanism



Corrosion Reaction

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

At cathode: $Fe^{2+} + OH^- \rightarrow Fe(OH)_2$

The e- flow from anode (crack) to cathode (surface of steel plate covered with oxide film and moisture). These electrons react with moisture and dissolved oxygen present in the electrolyte forming hydroxyl ions.

Now, the Fe^{2+} ions at anode and OH^- ions at cathode diffuse and combine to form ferrous hydroxide ($Fe(OH)_2$) as the corrosion product. It further forms rust on oxidation.

$Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow Fe_2O_3.3H_2O$ (Rust)

Differences Between Chemical and Electrochemical Corrosion

Dry / Chemical corrosion	Wet / Electrochemical corrosion
1. Occurs in dry condition	Occurs in wet condition in the presence of moisture and electrolyte
2. It involves chemical attack of oxygen or other gases	It involves electrochemical reaction and formation of Electrochemical cells on the surface of metal.
3. Can happen on both homogeneous and heterogeneous surface	Can happen only on heterogeneous surface
4. Corrosion is uniform	Corrosion is non-uniform
5. Corrosion product accumulate at the site of attack	Accumulate between the area of anode and cathode.
6. It is a slow process because of involvement of gases	It is a fast process because of involvement of liquids

4. Factors Affecting Rate of Corrosion

The rate of corrosion depends on the following factors:

1. Nature of Metal (primary factor)
2. Nature of Environment (secondary factor)

4.1. NATURE OF METAL: (primary factor)

(a) **Position of metal in the galvanic series:** Metal placed higher in galvanic series (having lower electrode potential) becomes anodic and hence undergoes corrosion and the other metal is protected. e.g.- in combination of Zn and Cu, Zn undergoes corrosion whereas Cu is protected.

(b) **Purity of metals:** The impurities present in a metal form a minute galvanic cell with metal under appropriate environment, the metal then acts as anode undergo corrosion. e.g. – Impurities such as Pb, Fe in zinc leads to the formation of a tiny electrochemical cell. Here, Zn act as anode and its rate of corrosion increases. Pure metals have lesser chance of corrosion.

(c) **Physical state of metal**: The rate of corrosion of a metal is influenced by the physical state of the metal such as- grain size, orientation of crystal, stress etc. The Smaller the grain size the greater will be its solubility and hence faster is the rate of corrosion.

(d) **Nature of corrosion product:** If the corrosion product deposited on metal surface is uniform, stable, insoluble and non-porous, it acts as protective layer and prevent further corrosion of metal.

(e) **Relative areas of Anode and Cathode:** If the ratio of cathodic area to anodic area is more, the rate of corrosion is more. Smaller anodic area leads to more rapid, severe and localized corrosion because of more demand of electrons by the large cathodic area. More demand for electrons is fulfilled by the small anodic area with higher current density and rapid oxidation which leads to increase in rate of corrosion.

4.2. NATURE OF ENVIRONMENT (secondary factor)

(a) **Temperature**: The rate of chemical reaction and rate of diffusion increases with temperature; hence rate of corrosion also increases at higher temperature.

(b) **Humidity:** In a humid atmosphere the rate of corrosion is very fast. This is because moisture acts as electrolyte for the atmospheric gases like- O_2, CO_2 etc. to undergo electrochemical corrosion.

(c) **Impurities in the medium:** Impurities such as dissolved gases and suspended particles can act as conducting ions during corrosion. So, they can enhance the rate of corrosion.

(d) **Conductance of the medium:** The clay and mineralized soil has more conductance than the dry and sandy soil and therefore, rate of corrosion is higher in clay soil.

(e) **p^H of the medium:** The acidic medium (lower pH) increases the rate of corrosion. Every metal or alloy has its own safe pH range where they exhibit slow rate of corrosion. Ex: For Fe, pH range is ~11, and for Al it is ~5.5.

(f) **Oxygen Concentration:** Due to variation in the oxygen concentration from one region to another region on the metal surface, it develops anodic and cathodic areas. The low oxygen level area becomes cathode and the higher oxygen area becomes cathode.

5. Corrosion Control Methods

5.1. Cathodic Protection Method:

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 Anode Protection and (b) Impressed Current Cathodic Protection.

a) Sacrificial Anodic Protection:

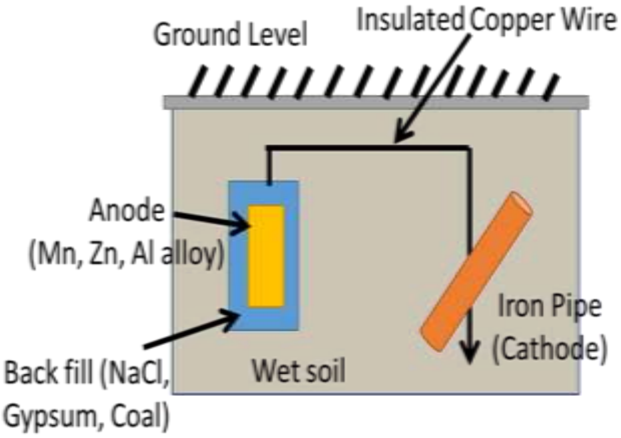
In this method metal to be protected is electrically connected to a small block or piece of metal which is placed higher in Galvanic series (more electroactive material).

The more electroactive material works as anode and the metal of concern act as cathode and is protected. Current flow from metal to the anode which results in rapid consumption of anode.

The corrosion attack is concentrated to the more active metal (anode) till it is completely consumed. Since the metal attached is acting as sacrificed anode, this method is termed as *sacrificial anode method*.

Example of sacrificial anode is galvanic anode such as Mg, Mg alloy, Zn, Al alloy etc.

To increase the electrical contact, the sacrificial anodic metal is placed in electrolyte (coal or gypsum).



Advantages:

- No external current is required.
- Easy to install and inexpensive.
- Minimum maintenance is required.

Limitations:

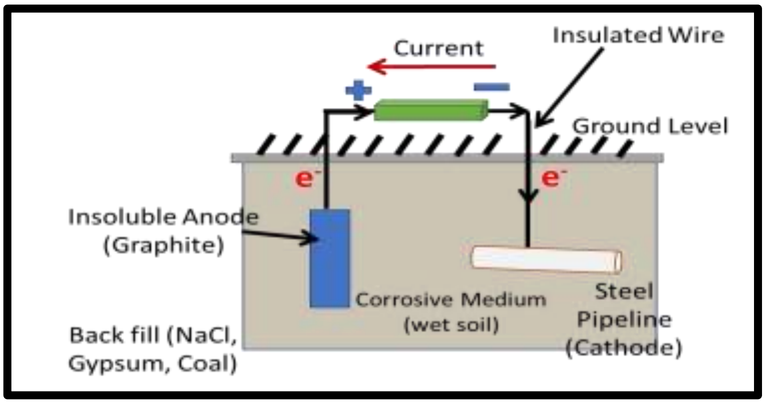
- Ineffective in high corrosive environment.
- Installation can be expensive if the anode installed after construction.

Applications:

Protection of buried pipelines, underground cables, water tanks etc

b) Impressed Current Cathodic Protection:

In this method the metal to be protected is connected to an insoluble electrode (Ti, Pt, graphite etc) and an external DC power supply. An external current is applied in the opposite direction to the metal to nullify the corrosion current. In this way the metal subject to corrosion is converted from anode to cathode and thus get protected, the insoluble anode being inert remains unaffected.



Advantages:

- Large structure can be protected for long term operations.
- It can be applied in high corrosive environment.
- Effective in protecting uncoated and poorly coated structures

Disadvantages:

- Requires periodic maintenance.
- Requires external power, resulting in monthly power cost.
- Over protection can cause coating damage.
- It is subject to power failure.

Applications:

Water tanks, Buried oil and water pipes, Marine Pipes etc.

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

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

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

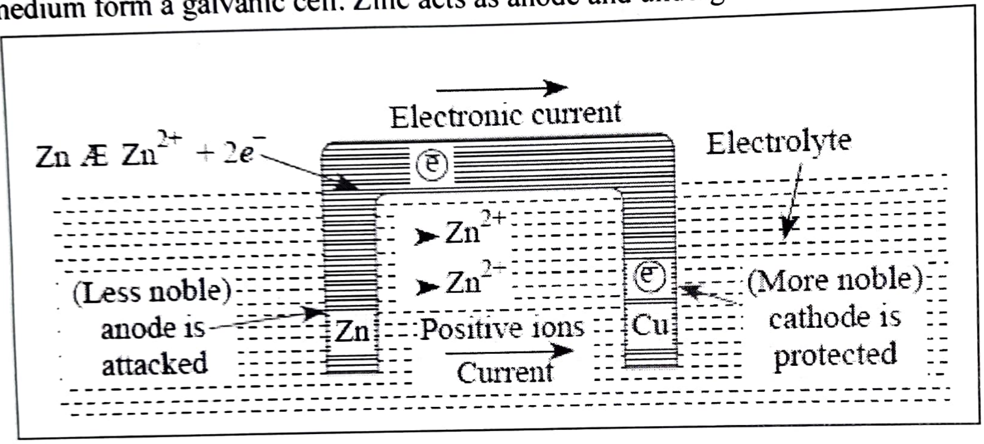
$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

- This product called yellow rust actually corresponds to $Fe_2O_3\ H_2O$.
- If the supply of oxygen is limited, the corrosion product may be black magnetite Fe_3O_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.



Prevention:

1) Galvanic corrosion can be avoided by coupling metals close to the elec- trochemical 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) zinc coating on mild steel,
4) 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 cath- ode which is protected. The system will act as a concentration cell and the chemical reactions for zinc dipped in water are given as:

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.

Drop corrosion:-

- For instance iron metal surface is covered with a drop of water.
- The area covered by a drop has low oxygen concentration and thus acts as an anode and suffers corrosion, the uncovered area of the metal acts as large cathode due to high O_2 concentration.

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

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

Write an account on pitting corrosion?

Pitting corrosion: Due to crack on the surface of a metal, local straining of metal, sliding under load, chemical attack, there is formation of a local galvanic cell. The crack portion acts as anode and rest of the metal surface acts as cathode. It is the anodic area which will be corroded and the formation of a pit is observed. This type of corrosion is thus called pitting corrosion (Fig.2.4). Metals owing to their corrosion resistance to their passive state show pitting and ultimately result in formation of passivity. Presence of external impurities such as sand, dust, scale embedded on the surface of metals lead to pitting. For example, stainless steel and aluminium show pitting in chloride solution.