

UNIT-IV
ELECTROCHEMISTRY AND
CORROSION

ELECTROCHEMISTRY

Introduction

- ✚ Electrochemistry is a branch of chemistry which deals with the relationship between electrical energy and chemical energy.
- ✚ Some applications in which electrical energy is converted into chemical energy are:
 - ❖ Electrolysis
 - ❖ Electroplating
 - ❖ Extraction and purification of metals and some non-metals (F_2 , Cl_2) etc.
 - ❖ Recharging of secondary batteries etc.
- ✚ Batteries and electro analytical techniques to find the concentration of solutions are some applications in which chemical energy is converted to electrical energy.

Classification

Depending on the ability to conduct electricity substances are divided as

- ❖ Conductors
- ❖ Non-Conductors
- ❖ Semi Conductors
- ❖ Super Conductors

Conductors:

Substances which allow the electric current to pass through them are called conductors.

Ex: Acids, Bases and salt solutions, fused salts etc.

Non-Conductors:

Non-conductors do not allow the electricity to pass through them.

Ex: Wood, Rubber, Cloth, Plastic, Pure water, Paper, Non-metals except Carbon.

Semi Conductors:

- ✚ Possess properties between the metals and non-metals
- ✚ Partially allow the current
- ✚ Conducting property is increased by the addition of impurities called doping agents.

Depending on doping material, semiconductors are of two types:

- ✚ n-type semiconductors - Addition of V group elements
- ✚ p-type semiconductors - Addition of III group elements

Super conductors:

The compounds which allow the flow of current with zero resistance are called Super Conductors.

Ex: Mixture of Cu, Ba and rare earth metal oxides show zero resistance and exhibit super conductivity.

Types of Conductors

Conductors are of two types

Metallic or Electronic Conductors

✚ Metallic or electronic conductors conduct electricity without undergoing any chemical change.

✚ In these substances, conduction is due to the movements of electrons.

Ex: Metals-Cu, Fe, Al, Ag, Graphite etc.

Electrolytic Conductors or Electrolytes

✚ Electrolytic conductors undergo decomposition when electric current is passed through them.

✚ In these conductors, the flow of electricity or conductance is due to the movement of ions.

Ex: Solutions of acids, bases, salts in aqueous medium and in fused state.

Differences between Electronic and Electrolytic conductors

Electronic Conductors	Electrolytic Conductors
Conductance is due to the flow of electrons	Conductance is due to the flow of ions
No chemical change takes place	Chemical decomposition takes place
Conductance decreases with the increase of temperature Ex: Metals, Alloys, Salts like Cds, Zns etc	Conductance increases with the increase of temperature Ex: Acids, Bases, Salts in fused or aqueous state

Classification of Electrolytes

Electrolytes can be classified into two types depending on their value of their equivalent conductance

- ❖ Strong Electrolytes
- ❖ Weak Electrolytes

Strong Electrolytes:

The electrolytes possess a high value of equivalent conductance even at high concentration.

Ex: Mineral acids like HCl, H_2SO_4

Alkalies like NaOH, KOH etc.

Alkaline earth hydroxides like $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$ etc.

Salts like NaCl, KCl etc.

Weak Electrolytes:

These electrolytes possess a low value of equivalent conductance at ordinary concentration.

Ex: CH_3COOH , NH_4OH etc.

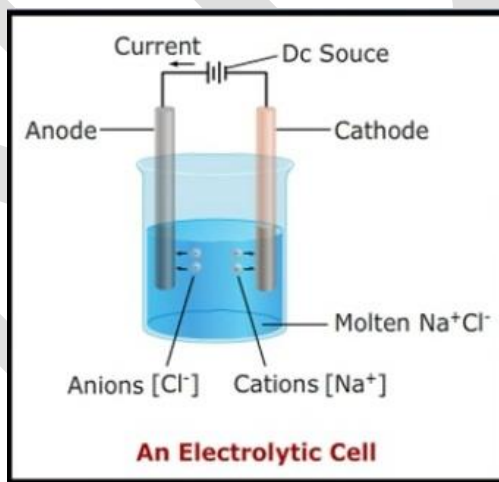
Electrolytic Cell

✚ The cell which converts electrical energy into chemical energy is called electrolytic cell.

✚ In this cell, electrical energy induces chemical reactions.

Ex: Electrolysis of molten NaCl using graphite electrodes.

Cell Reactions: NaCl dissolves when current is passed through it.



Electrochemical or Galvanic or Voltaic cells

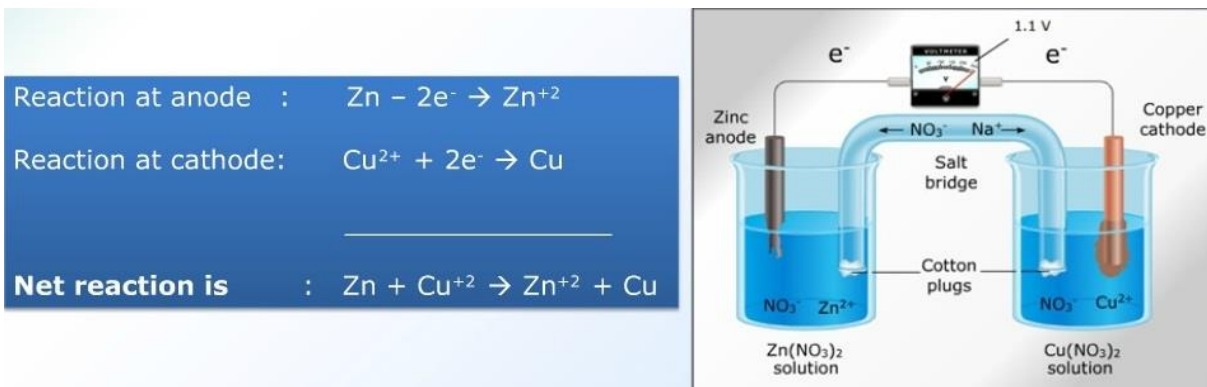
The device which converts chemical energy into electrical energy due to spontaneous redox reaction is called Galvanic Cell

Ex: Daniel cell, Laclenche cell, Fuel cell

Note: Daniel cell is a typical example of a galvanic cell.

Daniel Cell

It consists of two half cells or single electrodes one is oxidation half cell in which oxidation takes place and the other is reduction half cell in which reduction takes place. These two half cells are connected by a salt bridge.



Working of Salt Bridge:

- ✚ Salt bridge is an inverted U-shaped glass tube filled with a paste of KCl or KNO₃ with agar-agar gel.
- ✚ Salt bridge maintains electrical neutrality in the Galvanic cell by providing anions and cations of almost same speed.
- ✚ It prevents accumulation of charges.

Differences between electrolytic and Galvanic Cells

Electrolytic Cell	Galvanic Cell
In this cell electrical energy is converted into chemical energy	In this cell chemical energy is converted into electrical energy
It involves non-spontaneous reaction	It involves spontaneous reaction
$\Delta G > 0$	$\Delta G < 0$
E.M.F < 0	E.M.F > 0
In this cell anode is +Ve and cathode is -Ve.	Anode is -Ve and cathode is +Ve
Electricity is consumed	Electricity is produced

Electrode Potential

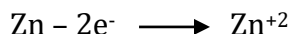
- ✚ It is the potential difference that exists at the surface of separation of a metal or a non-metal and its own ions which are in equilibrium in electrons.
- ✚ It is a measure of tendency of an electrode to loose or gain of electrons. (OR)
- ✚ It is the ability of a metal either to undergo oxidation or reduction.
- ✚ It is indicated by 'E' and its units are volts (V)

Electrode Potential Equation

✚ Electrode potential is two types

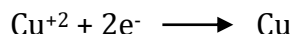
Oxidation Potential:

✚ It is the measure of tendency of electrode to lose electrons



Reduction Potential:

✚ It is the measure of tendency of electrode to gain electrons.



Standard Electrode Potential

✚ The electrode potential of given electrode at 25°C at unit activity (1molar concentration of an electrolyte and 1 atm pressure in case of gas) is known as "Standard Electrode Potential"

SEP is of two types

✚ SOP - Standard Oxidation Potential

✚ SRP - Standard Reduction Potential

According to IUPAC conversion, SRP is taken as SEP

SOP and SRP of an electrolyte are equal in magnitude but opposite in sign.

Electrodes

The various types of electrodes in an electrochemical cell are as follows

1. Metal-Metal ion electrode
2. Gas electrode
3. Metal-Amalgam electrode
4. Redox electrode
5. Metal-Metal insoluble salt electrode

Reference Electrode

There are two types of reference electrodes

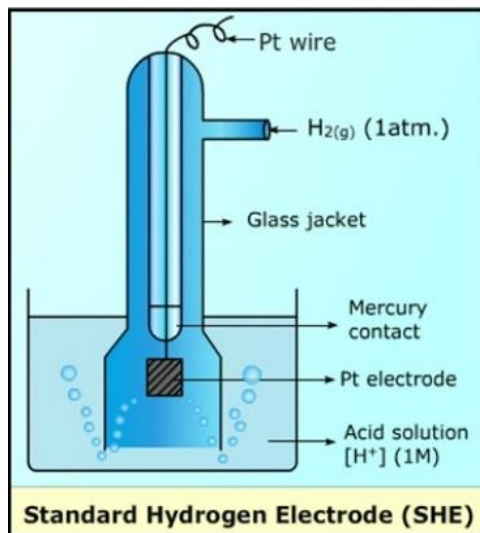
1. Primary reference electrode

Ex: Standard Hydrogen electrode

2. Secondary reference electrode

Ex: Saturated calomel electrode, Quinhydrone electrode, Glass electrode

Gas Electrode

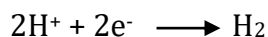


It is also called gas ion electrode

Ex: Hydrogen electrode

Introduction

- It is an electrode possessing stable and constant potential
- It is used as one of the half cell of electrochemical cell for determining the potential of the other half cell.
- The standard reduction potential of this electrode is assumed as zero and this electrode is used to measure the SRP of other electrodes.
- In a cell when this electrode acts as anode, the H_2 has undergoes oxidation as
$$H_2 \longrightarrow 2H^+ + 2e^-$$
- When this electrode acts as cathode the reduction reaction takes place is



Construction

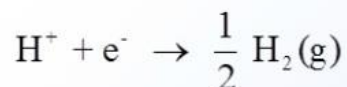
It is a primary reference electrode (S.H.E or N.H.E).

- It consists of a platinum electrode coated with platinum black immersed in a 1M solution of H^+ ions (HCl) maintained at $25^\circ C$.
- Hydrogen gas at 1 atm pressure is bubbled through the electrode.
- The electrode notation for hydrogen electrode is $Pt \ H_2 (g) / H^+ (aq)$.

Nernst Equation

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

The reduction reaction is



$$E = 0 - \frac{0.0591}{1} \log \frac{[\text{H}_2]^{\frac{1}{2}}}{[\text{H}^{+}]} \quad [\because \text{pH}_2 = 1 \text{ atm}]$$

$$E = -0.0591 \log \frac{1}{\text{H}^{+}}$$

$$\therefore \boxed{E = -0.0591 \text{ pH}}$$

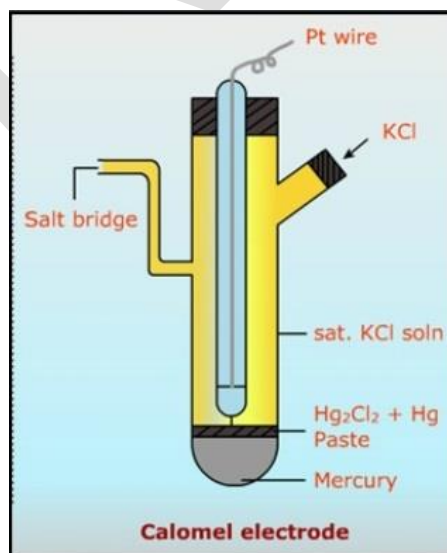
Advantages:

- ✚ Results are highly accurate.
- ✚ It can be used over entire range of pH.

Drawbacks:

- ✚ It is cumbersome to step up and maintain the hydrogen gas pressure.
- ✚ It has to be carefully handled as Hydrogen forms explosive mixture with air.
- ✚ It cannot be used in presence of oxidizing agents such as Fe^{+3} , MnO_4^{-} , $\text{C}_2\text{O}_4^{-2}$ etc.
- ✚ It gets easily poisoned by cyanide, mercury, arsenic, sulphate etc.

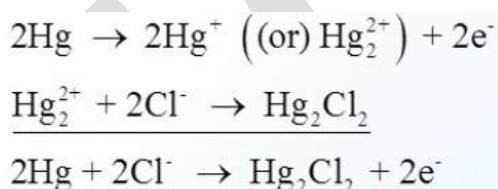
Calomel Electrode



- ✚ It is a secondary reference electrode.
- ✚ It consists of a wide glass tube. Pure mercury is taken at its bottom and above this Hg & Hg₂Cl₂ (Calomel) paste is placed.
- ✚ The remaining portion of the tube is filled with a solution of KCl.
- ✚ A platinum wire sealed through a glass tube is dipped into mercury and makes contact with the circuit.
- ✚ This tube has two side tubes one for introducing KCl solution and the other for connecting to a salt bridge and other half cell.
- ✚ The electrode notation is Pt, Hg_(L), Hg₂Cl_{2(S)}/KCl.

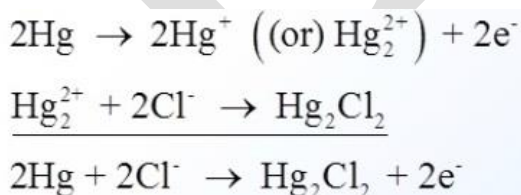
Working:

When this electrode acts as anode, mercury undergoes oxidation



∴ Concentration of chloride ions decrease

When this electrode acts as cathode, Hg₂Cl₂ is reduced to mercury



∴ Concentration of chloride ions decrease

Hence calomel electrode is reversible w.r.t. chloride ion concentration

Standard E.M.F. Values (E⁰)

E⁰ values of calomel electrode depend on the concentration of KCl solution.

- ✚ Saturated Calomel Electrode (SCE) : 0.2422V
(Saturated KCl)
- ✚ Normal Calomel Electrode (NCE) : 0.2800V
(1N, KCl)
- ✚ Deci-Normal Calomel Electrode (DCE) : 0.3335V
(0.1N, KCl)

Advantages:

- ✚ It is simple to construct.
- ✚ Results of cell potential measurements are reproducible and stable over a long period and do not vary with temperature.

Electro Chemical Series

- ✚ The series in which elements are arranged in increasing order of standard reduction electrode potential as compared to that of standard hydrogen electrode is called electrochemical series.

E.C. series at 25°C	
Electrode	E° (Volts)
Li (Li ⁺ /Li)	-3.045
K (K ⁺ /K)	-2.925
Ca (Ca ²⁺ /Ca)	-2.87
Na (Na ⁺ /Na)	-2.714
Mg (Mg ²⁺ /Mg)	-2.37
Zn (Zn ²⁺ /Zn)	-0.763
Fe (Fe ²⁺ /Fe)	-0.440
Cd (Cd ²⁺ /Cd)	-0.403
Pb (Pb ²⁺ /Pb)	-0.126
H ₂ (H ⁺ /H)	0.000
Cu (Cu ²⁺ /Cu)	+0.337
Ag (Ag ⁺ /Ag)	0.799
Cl ₂ (Cl ₂ /2Cl ⁻)	+1.36
Au (Au ³⁺ /Au)	+1.5
F (F ₂ /2F ⁻)	+2.0

Features:

- ✚ Electrodes present above hydrogen have -ve S.R.P values and those below H₂ have +ve S.R.P values.
- ✚ Li is at the top most position of the series with S.R.P -3.045V and F₂ is at the bottom most with S.R.P +2.87V.
- ✚ The element present above in the series act as anode and below in the series act as cathode.
- ✚ The reactivity of elements decrease down the series.
- ✚ The metals above the hydrogen in the series can be easily oxidized and hence undergo corrosion easily.

Applications:

- ✚ To know the relative reducing or oxidizing abilities of given system.
- ✚ Replacing ability of metals can be predicted.
- ✚ The feasibility of given redox reaction can be predicted.
- ✚ The E^0 cell can be calculated.
- ✚ The corrosion tendency of the metal can be predicted.

Batteries

A Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at constant voltages.

Or

A device which converts chemical energy into electrical energy is called Battery.

Advantages of Battery

- ✚ Batteries act as a portable source of electric energy.
- ✚ The portability of electronic equipments in the form of hand sets are made possible by batteries.
- ✚ Rechargeable batteries have better shelf life tolerance. These batteries have increased the usage of electronic gadgets in recent times.
- ✚ Batteries are used in all commercial applications.
- ✚ **Ex:** Batteries for automobiles, aircrafts etc.

Classification

Batteries are classified into three types

1. Primary cells
2. Secondary cells
3. Fuel cells

1. Primary Cells

- ✚ The cell in which the cell reactions are not reversible are said to be primary cells.
- ✚ Non rechargeable and meant for single use and can be discarded after use.
- ✚ Can generate electricity as long as the reactants are present in the cell.
- ✚ When all the reactants are converted into products, the battery is dead.

- ✚ Cannot be recharged because the cell reaction cannot be reversed by applying internal e.m.f. in opposite direction.

Dry Cell



Dry cell

- ✚ Invented by Georges Laclenche in 1886.
- ✚ The Battery contains a conducting solution of NH_4Cl , a cathode of carbon, a depolarizer of MnO_2 and an anode Zinc.

Working

- ✚ The chemical process which produces electricity in the cell begins when the zinc atoms on the surface of the anode oxidize, as the Zn^{+2} moves away from the anode, leaving these electrons on the surface, the anode becomes more negatively charged than the cathode.
- ✚ When the cell is connected in an external electrical circuit, the excess electrons of zinc flow through the circuit to the carbon rod, due to which the movement of electrons form an electric current.
- ✚ After passing through the circuit, electrons enter the cathode and combine with MnO_2 and water which react with each other to produce Mn_2O_3 and OH^- ions.
- ✚ The OH^- ions react with NH_4Cl to produce ammonia, which is not liberated as has but immediately combines with Zn^{+2} and Cl^- ions to form a complex salt $[\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$



- ✚ A dry cell battery is a subtype of battery. It stores energy in an immobilized electrolyte paste which minimizes the need of water.
- ✚ The dry cell finds its applications in flashlights, transistor radios, calculators etc.

2. Secondary Cells:

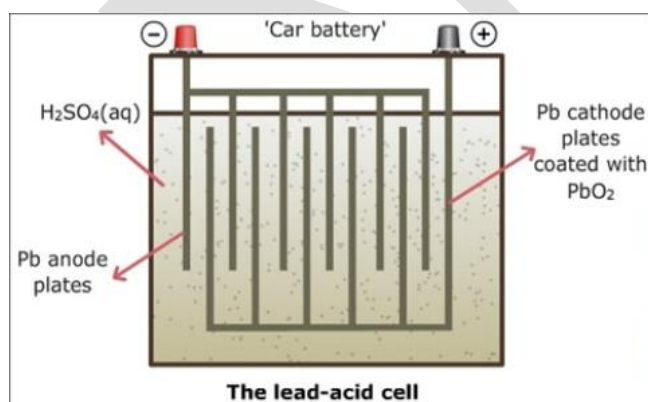
- ✚ The batteries in which cell reaction can be reversed by applying external e.m.f. in opposite direction are called secondary batteries or accumulators.
- ✚ These batteries are used for multi-cycle purpose (discharging and recharging).
- ✚ Cycle is reversed till the capacity fades or lost due to internal short circuit or leakage.
- ✚ These batteries have large capacitance and low-current rate discharge.

Ex: Lead acid storage cell, Nickel-Cadmium cell and Lithium cell.

Lead Acid Storage Cell

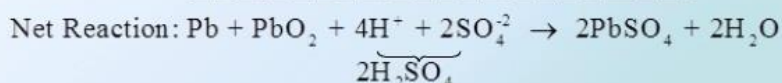
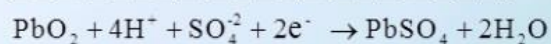
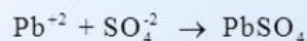
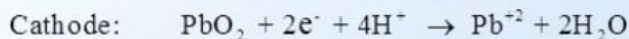
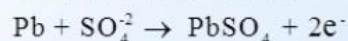
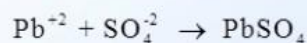
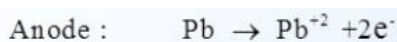
It is a secondary battery because the cell reaction can be reversed by applying external e.m.f. on opposite direction.

- ✚ The Pb and PbO₂ plates are arranged alternatively and this arrangement is immersed in H₂SO₄ taken in a container made up of hard rubber.
- ✚ The battery acts as Galvanic cell while discharging and electrolytic cell while recharging.



Anode : A grid of Pb
 Cathode : A grid of PbO₂
 Electrolyte : 20 – 21% H₂SO₄

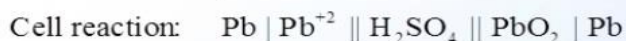
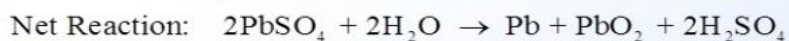
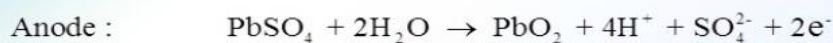
Discharging Reactions (Cell acting like galvanic cell)



- Due to anodic and cathodic reactions, the Pb and PbO₂ are covered with PbSO₄ and the specific gravity of H₂SO₄ decreases.
- If it reaches a voltage less than 1.2V, the cell can be recharged by applying external e.m.f.

$E_{\text{cell}} = 2\text{V}$. The commercial lead acid storage cells used in automobiles consists 6(12V) cells connected in series

Recharging Reactions: (Cell acting like electrolytic cell)



Applications:

- Used in automobiles and power inverters.
- Also used to supply current for electric vehicles, telephone exchanges, electric trains, mines, laboratories, hospitals, broadcasting stations, power stations etc.

Advantages:

- It is rechargeable.
- It is less expensive and has long life.
- Ability to withstand mistreatment.
- It can generate electricity at constant voltage.
- Perform well in high and low temperature and in high-drain applications.

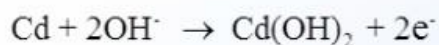
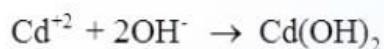
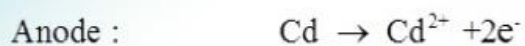
Drawbacks:

- ✚ Use of H_2SO_4 is dangerous
- ✚ Use of Pb and PbO_2 is harmful to environment.

Nickel Cadmium Battery

- ✚ It is also known as Ni-Cd cell or Ni-Cd battery.
- ✚ It is a secondary battery
- ✚ It is an alkaline battery

Discharging Reactions: (Functions as Galvanic Cell)



$$E_{\text{Cell}} = 1.4\text{V}$$

Cell Notation: $\text{Cd}/\text{CdO} // 6\text{MKOH} // \text{NiO}(\text{OH}), \text{Ni}(\text{OH})_2/\text{Ni}$

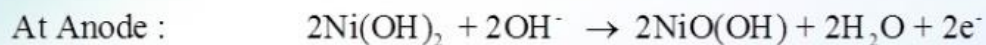


Anode : Spongy Cd/CdO

Cathode : $\text{NiO}(\text{OH})/\text{Ni}$

Electrolyte : 6M KOH

Recharging Reactions: (Functions as Electrolytic Cell)



Since the net reaction does not consume electrolyte, small amount of electrolyte is sufficient which reduces the weight of the battery.

Advantages:

- ✚ Light weight
- ✚ Rechargeable
- ✚ Compact
- ✚ Long shelf life
- ✚ Long cycle life and sturdy.

Drawbacks:

- ✚ Expensive
- ✚ Lower power density

Applications of secondary batteries in E-vehicles

- ✚ There are two basic types of EVs: All-Electric Vehicles (AEVs) and plug-in hybrid electric vehicles (PHEVs). AEVs include Battery Electric Vehicles (BEVs) and Fuel Cell Electric Vehicles (FCEVs).
- ✚ In addition to charging from the secondary batteries, both types are charged in part by regenerative braking, which generates electricity from some of the energy normally lost when braking.
- ✚ All-electric vehicles (AEVs) run only on electricity. Most have all-electric ranges of 80 to 100 miles, while a few luxury models have ranges up to 250 miles.
- ✚ When the battery is depleted, it can take from 30 minutes (with fast charging) up to nearly a full day (with Level 1 charging) to recharge it, depending on the type of charger and battery.

3. Fuel Cells

- A fuel cell converts the chemical energy of the fuels directly to electricity. The essential process in a fuel cell is:

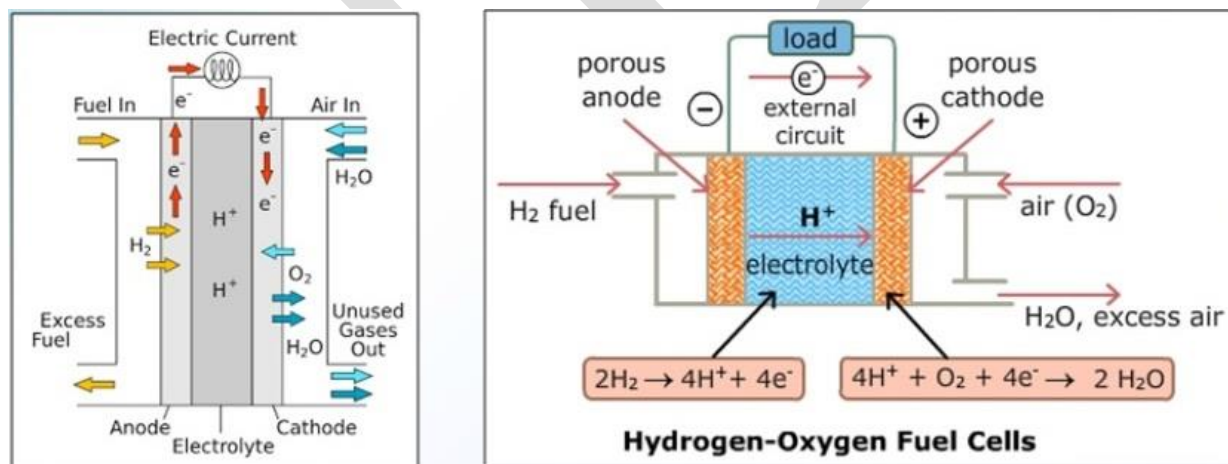


- These are special type of galvanic cells which convert free energy of a chemical reaction between the fuel and oxidant directly into electrical energy.
- In these cells, electricity is generated continuously as long as the fuel and oxidant are supplied continuously and separately at the two electrodes.
- The fuel cell system may be represented as:

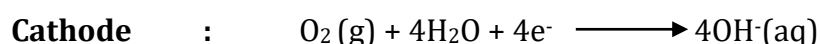
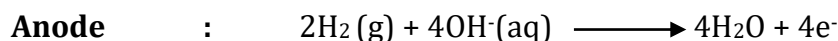


- Fuel undergoing oxidation at the anode releases electrons and the oxidant gets reduced at the cathode by the electrons flowing through the external circuit to the cathode.
- Anode:** Fuel = Oxidation products + ne^-
- Cathode:** Oxidant + ne^- = Reduction products
- One of the simplest and most successful fuels is hydrogen-oxygen fuel cell.

Hydrogen-oxygen fuel cell

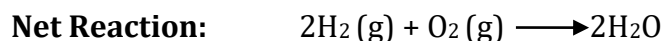
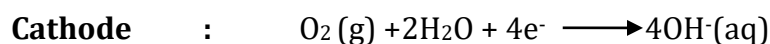
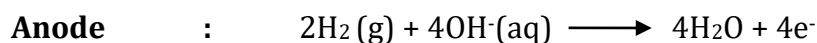


- It consists of an electrolytic solution such as 25% KOH solution and two inert porous electrodes.
- Hydrogen and oxygen gases are bubbled through the anode and cathode components respectively, where the following reactions takes place:



- ✚ Electrodes are made up of porous graphite. Platinum is used as the catalyst in low temperature and nickel in high temperature.
- ✚ The electrolyte is 25% KOH.
- ✚ Here, hydrogen gas is bubbled at anode and oxygen gas is bubbled at cathode.

Cell Reactions

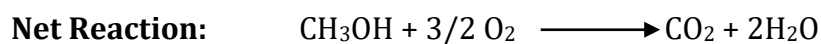
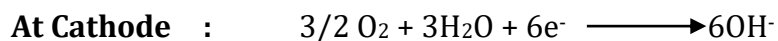
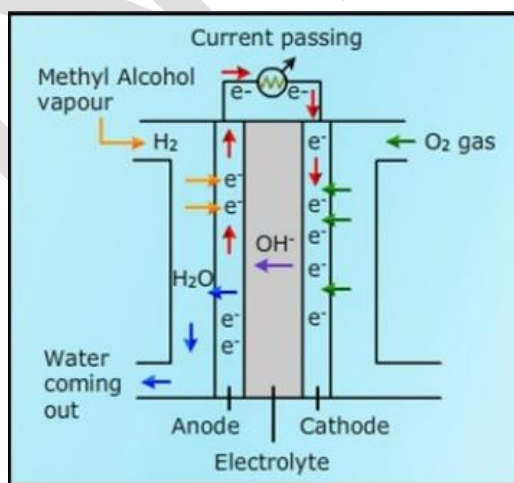


Uses

- ✚ Used as auxiliary energy sources in space vehicles (space craft), submarines and other military vehicles.
- ✚ For space craft, they are preferred due to their lightness and product water is available as a source of fresh water for the astronauts.

Methyl Alcohol-Oxygen Alkaline Fuel Cell

- ✚ The methyl alcohol-oxygen fuel cell has two electrodes.
- ✚ The anode is porous nickel electrode impregnated with Pt/Pd catalyst.
- ✚ Cathode is porous nickel electrode coated with silver catalyst.
- ✚ The electrolyte KOH, is taken in between the two electrodes.
- ✚ CH_3OH and O_2 are sent continuously into their electrodes and electrical energy is produced due to the following cell reactions:



Advantages:

- ✚ Methanol fuel cells are reasonably stable at all environmental conditions
- ✚ Easy to transport
- ✚ Because of high hydrogen concentration in methanol, it is an excellent fuel.
- ✚ Methanol poses less risk to aquatic plants, animals and human beings than gasoline.
- ✚ Due to its low inflammability limit, methanol has less risk than gasoline
- ✚ There is zero emission by the cells. Hence the fuel cells are eco-friendly.

Applications:

- ✚ Methyl alcohol oxygen fuel cells are used in motor vehicles like NECAR in Japan, USA etc.

Advantages of Fuel Cells

- ✚ Eco-friendly, high efficient and offer an excellent use of our renewable energy sources.
- ✚ Low maintenance cost, compact and transportable.
- ✚ Less corrosive and can be operated up to 200°C.
- ✚ Fuel cell energy is economical and safe.
- ✚ These are good storage devices for future nuclear and solar energy economies.

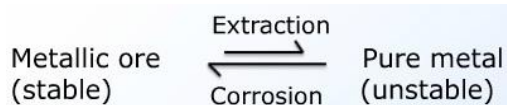
Limitations of Fuel Cells

- ✚ High initial cost.
- ✚ Large weight and volume of hydrogen gas fuel storage system
- ✚ Lack of infrastructure for distribution and marketing of hydrogen gas
- ✚ High cost of hydrogen cost.
- ✚ Most of the cells suffer from carbon dioxide leakage.

CORROSION

Why metals corrode: Reason

- ✚ All metals except gold and platinum corrode when exposed to atmosphere.
- ✚ Metals exist in the form of ores, which are in the combined form.
- ✚ Metals are extracted from their ores by reduction process.
- ✚ Corrosion is the reverse process of extraction of metals from ores by oxidation.



- ✚ Greater is the amount of energy required to separate the metal from its mineral, higher will be the tendency of the metal to revert back to its natural state resulting in the degradation of the metal.

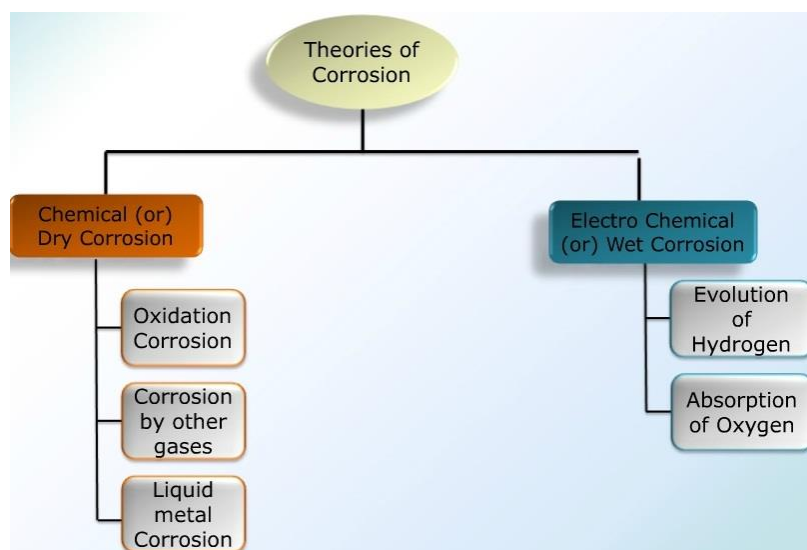
Consequences of Corrosion

- ✚ Leads to an enormous loss of metallic material such as machines, equipments, tools, structures etc.
- ✚ It leads to unpredictable machinery failure.
- ✚ It leads to decrease in the efficiency of equipment and machinery.
- ✚ Health due to a corrosion product or due to an escaping chemical from corroded equipment.
- ✚ Necessity for overdesign to allow for corrosion.
- ✚ Plant shutdown due to failure.
- ✚ Preventive maintenance.
- ✚ Losses, to the tune of millions of rupees or dollars per annum.

Theories of Corrosion

Chemical (or) Dry Corrosion

- ✚ It is the simplest cause of corrosion.
- ✚ Here corrosion takes place by direct chemical attack of atmospheric gases such as oxygen, halogen, hydrogen sulphide (H_2S), SO_2 etc. on metal surface.



Dry corrosion is of three types:

1. Oxidation corrosion
2. Corrosion by other gases
3. Liquid metal corrosion

1. Oxidation Corrosion

- ✚ Oxidation corrosion takes place by direct action of oxygen on metals, at low or high temperature forming oxides of the metal. It generally takes place in the absence of moisture.



- ✚ Oxidation first occurs at the surface of the metal and the resulting metal oxide scale forms a barrier that tends to restrict further oxidation.

Mechanism

- ✚ Oxygen is adsorbed at the surface of the metal by physical adsorption.
- ✚ When the temperature rises, the physical adsorption turns into chemical adsorption and the gets oxidized to metal ions.



- The electrons are taken up by the oxygen which gets reduced to oxide ion.



- The metal oxide scale so formed forms a barrier between the metal and the oxygen and restricts further oxidation or corrosion of the metal.
- For oxidation to continue either the metal must diffuse outwards through the scale to the surface or oxygen must diffuse through the scale to the underlying metal.
- As the metal cation is much smaller in size, the outward diffusion of the metal ion is much more rapid than inward diffusion. Hence, corrosion continues by rapid diffusion of highly mobile cations.
- The extent of corrosion depends upon the nature of the corrosion product formed.
- Nature of the oxide film formed plays an important role in corrosion process. The nature of the oxide film decides further corrosion process.

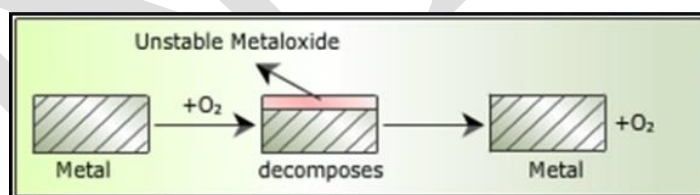
Stable:

- If metal oxide is stable in nature, it acts as a protective barrier between metal and oxygen, so further corrosion doesn't take place.

Ex: Al_2O_3 , Cr_2O_3 , Pb_2O_3

Unstable:

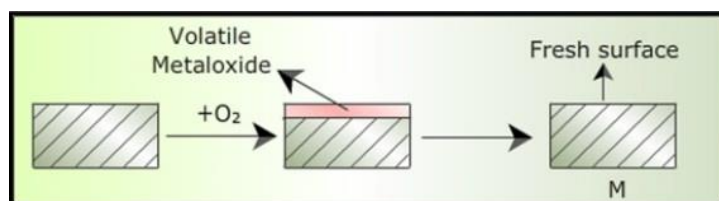
- The oxide layer formed decomposes back into the metal and oxygen. Hence further corrosion is possible.



Volatile:

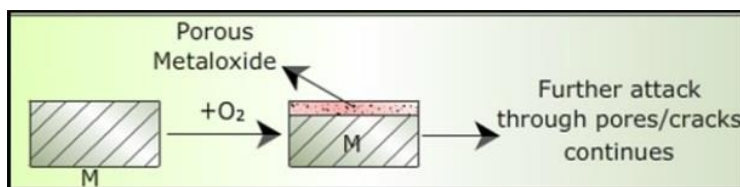
- The oxide layer volatilizes as soon as it is formed, thereby leaving underlying metal for further attack.

Ex: MoO_3



Porous:

- ✚ Have pores or cracks.
- ✚ In such case, the atmospheric oxygen has access to the underlying surface of metal through the pores or cracks.
- ✚ Further corrosion takes place continuously till the entire metal is converted into its oxide.



Pilling-Bed worth Rule (or) Ratio:

- ✚ The oxide layer can be protective or non-protective depending on the ratio of the volume of the metal oxide formed to the volume of metal consumed. This is known as "Pilling-Bed Worth ratio"

$$\text{Pilling Bed worth ratio} = \text{Vol. of metal oxide formed} / \text{Vol. of metal consumed}$$

According to the Pilling Bed worth rule

- ✚ If the volume of the oxide film is less than the volume of the respective metal from which it is formed and the ratio is less than the unity (1), then the oxide film will be non-protective in nature.

Ex: Alkali and alkaline earth metals such as Na, Ca, Mg (except Al).

Consequently the oxide film develops cracks and pores on its surface

- ✚ If the metal oxide film formed is equal or greater than the respective metal from which it is formed and the ratio is more than the unity (1), the metal oxide film is protective in nature. In such case, the oxide film formed is continuous, adhering and nonporous.

Ex: Al, Cr etc.

2. Corrosion by other gases

- ✚ In addition to oxygen, a number of other gases such as CO₂, SO₂, Cl₂, H₂S, F₂ etc. also have corrosion effect on metals.

✚ The extent of corrosion depends on the chemical affinity between the metal and the gas involved. In this case also the film so formed may be protective or non-protective in nature.

✚ If the film formed is protective in nature, the extent of attack of corrosion decreases.

Ex: Chlorine gas attacks silver metal.

✚ If the metal film formed is non-protective in nature, then it destroys the whole metal eventually.

Ex: Chlorine attacks Sn to form SnCl_4 film which is volatile.

H_2S attacks steel forming FeS layer which is porous in nature.

3. Liquid Metal Corrosion:

✚ Liquid metal corrosion is due to the chemical action of flowing liquid metal at high temperature on solid metal or alloy.

✚ Such corrosion in devices is used for nuclear power.

✚ The corrosion reaction involves either of the following.

- Dissolution of a solid metal by a liquid metal.
- Internal penetration of the liquid metal into the solid metal.

✚ Both these modes of corrosion cause weakening of the solid metal.

Electro Chemical (or) Wet Corrosion

✚ The corrosion of metals in aqueous medium is electrochemical in nature.

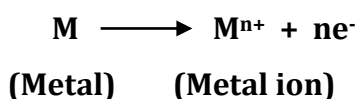
✚ This type of corrosion occurs:

- i. Where a conducting liquid is in contact with metal (or)
- ii. When two dissimilar metals or alloys are either immersed or dipped in a solution.

✚ The corrosion occurs due to the existence of separate anodic and cathodic areas, between which current flows through the conducting solution.

Cell Reactions:

a) **Anodic Reactions:** At anodic area oxidation takes place



Thus, anodic metal is destroyed by either dissolving or assuming combined state.

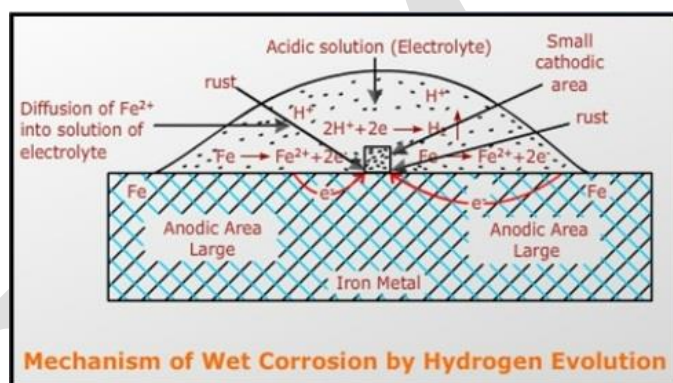
b) Cathodic Reactions:

- The electrons released at the anodic area are consumed in the reaction at the cathodic area forming ions like OH^- , O^{2-} etc.
- The metallic ions (at anodic part) and non-metallic ions (formed at cathodic part) diffuse towards each other through conducting medium and form a corrosion product between anode and cathode.

Wet corrosion takes place in two ways

- ❖ Evolution of hydrogen
- ❖ Absorption of oxygen

Evolution of hydrogen



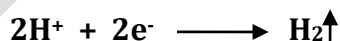
- It occurs in acidic environment.

Ex: Rusting of iron in acidic medium in the absence of oxygen.

- At anode, iron undergoes oxidation by releasing electrons and dissolves.



- The electrons flow from anode to cathode and absorbed by H^+ ions of acidic solution to form hydrogen gas. Thus H_2 gas evolved.

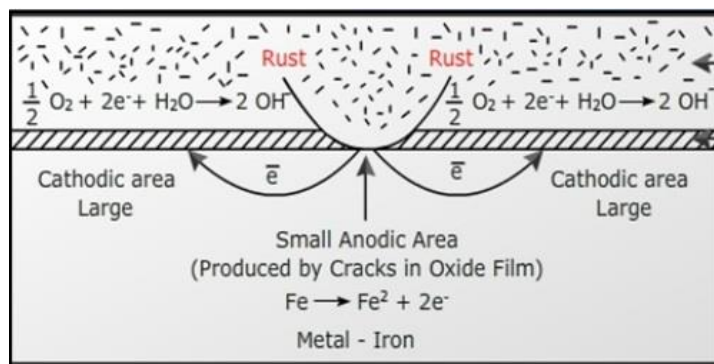


- Overall reaction is



- Hence, in this type of corrosion, hydrogen ions are displaced from the acidic solution by metal ions.

Absorption of Oxygen



✚ This type of corrosion reaction takes place in the presence of atmospheric oxygen.

✚ In neutral aqueous or weakly alkaline solution oxygen gets reduced as



Ex: Rusting of iron in neutral solution in the presence of oxygen.

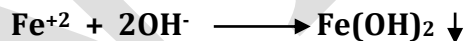
✚ Anodic reaction is



✚ The electrons are moved to the cathode and accepted by water oxygen to form OH^- ions by reduction.



✚ The Fe^{+2} ions at anode and OH^- ions at cathode diffuse towards each other forming rust. i.e. $\text{Fe}(\text{OH})_2$

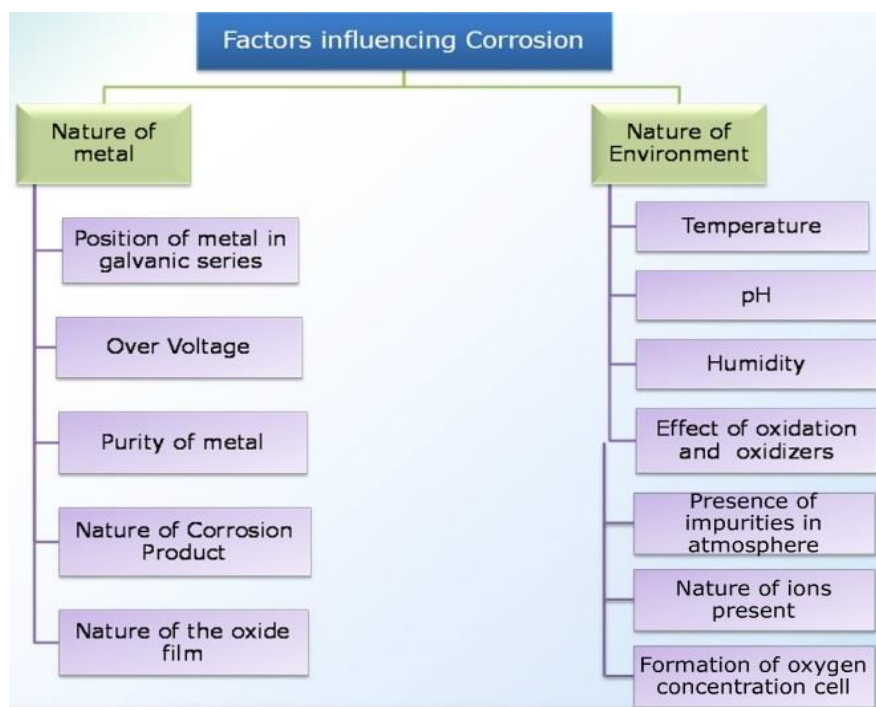


✚ If enough oxygen is present $\text{Fe}(\text{OH})_2$ is easily oxidized to $\text{Fe}(\text{OH})_3$



✚ Though corrosion occurs at the anode, the rust formed near the cathode because of smaller Fe^{+2} ions produced at the anode diffuse faster towards the cathode than the larger OH^- ions towards the anode.

Factors influencing Corrosion



Nature of Metal

Position of metal in galvanic series

- ✚ When two metals or alloys are in electric contact in the presence of an electrolyte, the metal high in series (more anodic) undergoes corrosion faster than the metal below it.
- ✚ Greater the difference, faster is the corrosion.
Ex: Li corrodes faster than Mg.

Over voltage

- ✚ Over voltage occurs when the voltage in a circuit or part of it is raised above its upper limit.
Ex: When Zn is placed in 1N H_2SO_4 , it undergoes corrosion forming a film and evolving hydrogen gas. The initial rate of corrosion is slow, due to high over voltage i.e. 0.76 volts.
- ✚ On addition of copper sulphate, the corrosion rate of Zinc is accelerated due to the deposition of copper, where the overvoltage of hydrogen is 0.33v. Thus, reduction in overvoltage of the corroding metal/alloy accelerates the corrosion rate.

Purity of metal:

- Heterogeneity is produced if impurities are present in a metal and form tiny electrochemical cells at the exposed parts.

- As the extent of exposure and impurities increases, corrosion increases.

Ex: Zinc metal containing impurity such as Pb or Fe undergoes corrosion due to the formation of local electrochemical cells.

Nature of corrosion product:

- If the corrosion product is volatile and soluble in both the cases, the corrosion will be faster. MnO_3 , SnCl_4 are volatile, so the corrosion of Sn is faster in Cl.
- In case of soluble corrosion product, it is enhanced by water and the metal surface is exposed for further corrosion.

Nature of oxide film

- All metals when exposed to atmosphere produce a thin film of metal oxide. The ratio of the volumes of the metal oxide to the metal is called specific volume ratio.
- If the volume is more, the rate of corrosion is less, because the surface of the metal is completely covered by the film which protects the metal surface.

Nature of Environment**Temperature**

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

pH

- pH has greater effect on corrosion. When pH is lowered, the rate of corrosion increases.

Humidity

- Corrosion of metals becomes faster in humid atmosphere.
- It provides water, which is essential for setting up an electrochemical corrosion.

Effect of oxidation and oxidizers

- When oxidizer is added, some metals achieve passivity due to the formation of oxide film which is protective in nature.

Presence of impurities in atmosphere

- ✚ Atmosphere, in the vicinity of industrial areas, contains corrosive gases like CO_2 , H_2S , SO_2 and fumes of HCl , H_2SO_4 , etc.
- ✚ In presence of these gases, the acidity of the liquid, adjacent to the metal surfaces, increases and its electrical conductivity also increases.
- ✚ This consequently, results in an increase of corrosion current flowing in the local electrochemical cells on the exposed metal surfaces.
- ✚ Similarly, in the marine atmosphere, the presence of sodium and other chlorides (of sea water) lead to increased conductivity of the liquid layer in contact with the metal surface, thereby corrosion is speeded up.

Nature of ions present

- ✚ Presence of anions like silicate in the medium, leads to the formation of insoluble reaction products (Ex. Silica gel), which inhibit further corrosion.
- ✚ On the other hand, chloride ions, if present in the medium, destroy the protective and passive surface film, thereby exposing the metal/alloy surface for fresh corrosion.
- ✚ Many metals, including iron, undergo corrosion rapidly, if corroding medium contains ammonium salts.
- ✚ Presence of even traces of copper (or any noble metal) in mine waters, accelerates the corrosion of the iron pipes, used for carrying such waters.

Formation of oxygen concentration cell

- ✚ With the increase in the supply of oxygen/air to the moist-metal surface, the corrosion is formed.
- ✚ Less oxygen concentration (Ex. Oxide-coated part or less-exposed part) parts becomes anodic, while the more-oxygenated regions (or parts more exposed to oxygen) becomes cathodic, thereby leading to the formation of oxygen concentration cell in which the anodic part suffers corrosion.

Corrosion controlling Methods

There are many corrosion control methods like; Proper designing, Using pure metal, Using metal alloys, Cathodic protection, Modifying the environment, Use of inhibitors and Application of protective coatings etc.

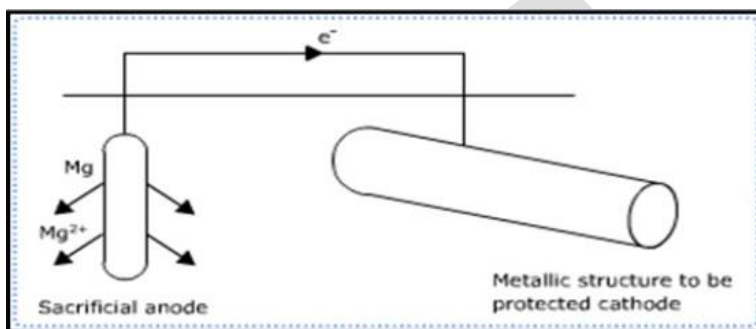
Cathodic protection

Principle: The metal to be protected is forced to act as cathode, so that the metal can be protected from corrosion.

There are two types of cathodic protection:

1. Sacrificial Anode protection
2. Impressed current cathodic protection

1. Sacrificial Anode protection

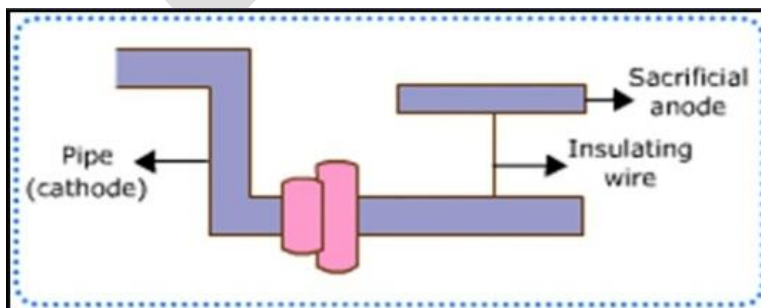


- ✚ In this method the metallic structure to be protected is connected to a more active metal through an insulated wire, so that active metal acts as an anode and gets corroded, the metallic structure acts as a cathode and gets protected.
- ✚ Since the anode is sacrificing itself, it is called sacrificial anodic. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. The commonly used sacrificial anodes are Mg, Alloys of Mg, Zn, Al, etc.

Important applications of sacrificial anodic method

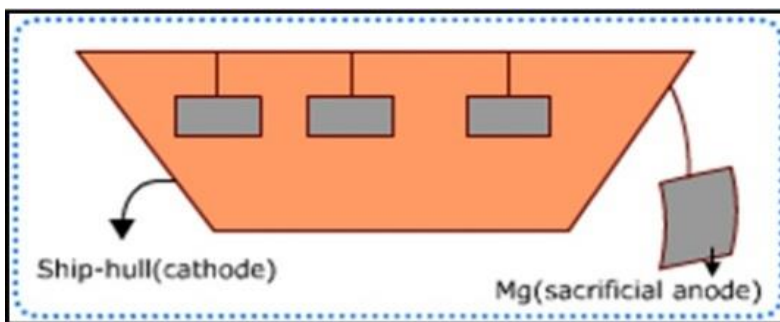
- ✚ Buried pipe lines, underground cables, marine structure, ship-hulls, water-tanks etc. are protected by this method.

Ex: 1. For the protection of underground cables.

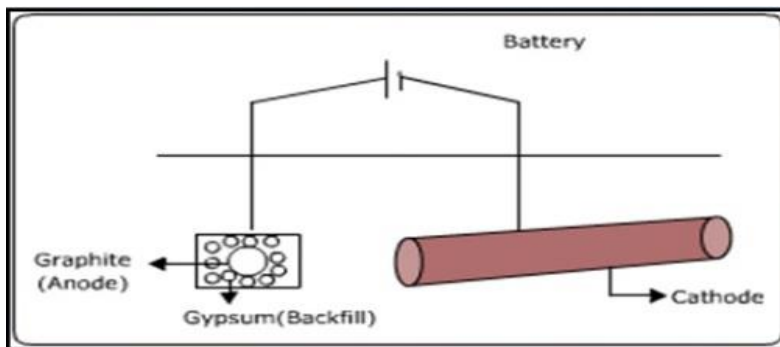


Ex: 2. For the protection of ships or boats

The sheets of Mg or Zn are hung using an insulating wire.



2. Impressed current cathodic protection



- ✚ In this method, an impressed current is applied in the opposite direction to nullify the corrosion current and to convert the corroding metal from anode to cathode.
- ✚ Generally anode is made up of insoluble materials such as graphite, platinum etc. which is buried in a black electric conductivity.
- ✚ This method is used for the long term protection of large structures like electrical transmission towers, underground pipes, water box coolers etc.

Surface Coatings

- ✚ The surface of the structure to be protected is covered with another material which forms a coating and acts as a barrier between the metal and its environment and offers protection to the metal.
- ✚ There are three types of surface coatings:
 1. Metallic coating (**Example:** Galvanization and Tinning)
 2. Organic coating (**Example:** Paint and varnish)
 3. Non-metallic coatings (**Example:** Enamel coating)

1. Metallic Coatings

The surface of the metal coated with another metal is called metal coating. It is of two types.

❖ Anodic Coating

❖ Cathodic Coating

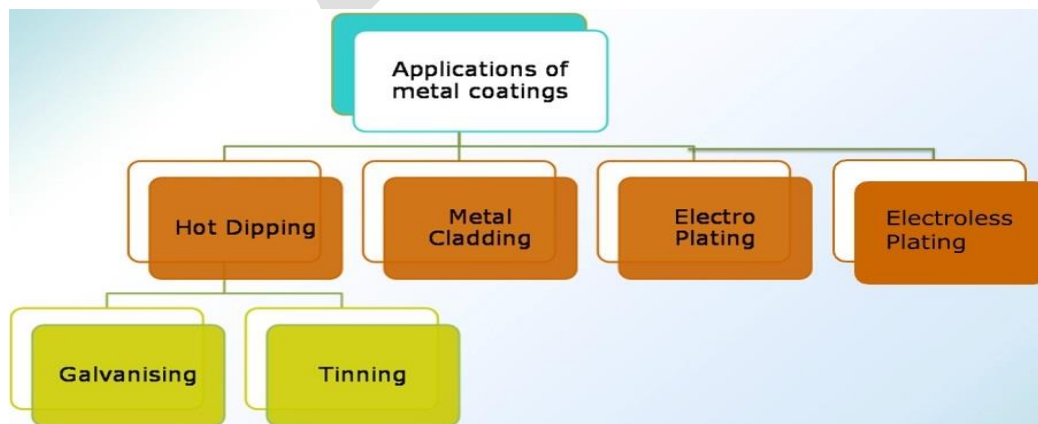
❖ Anodic Coating

- ✚ The surface of the base metal (to be protected) is coated with another more anodic metal.
- ✚ The coating metal acts as an anode and the base metal acts as cathode.
- ✚ **Example:** Galvanization of Fe/Steel
- ✚ Let us consider the surface of Fe/Steel coated with Zinc. Here, Zinc acts as anode and the base metal Fe acts as cathode.
- ✚ Anodic coating of Zinc protects the base metal iron sacrificially.
- ✚ Protection continues even if there are cracks or pin holes in the coating, in such a case, the exposed part of the base metal (Fe) acts as a cathode and its is protected.

❖ Cathodic Coating

- ✚ In this method the base metal is coated with a more noble metal that is a metal present below it in the galvanic series.
- ✚ Here, the coating metal acts as a cathode and the base metal acts as anode.
 - **Ex:** Coating of the surface of iron with metals like Sn, Ni, Cr etc.
- ✚ Cathodic coating protects the base metal due to its noble character.
- ✚ Cathodic coating can protect the base metal only as long as the coating is continuous.
- ✚ In the case of any discontinuity, the exposed part of the base metal (for **Ex:** iron) becomes anodic and the coating metal (for **Ex:** Sn) becomes cathodic in the galvanic cell formed. Severe corrosion occurs and iron gets corroded very badly.

Methods of Application of Metal Coatings



Hot Dipping

- ✚ Hot dipping is used for producing a coating of low melting metal such as Zn (M.P- 419°C), Sn (M.P = 230°C) Pb, Al etc., on iron and steel, which have relatively higher melting points.
- ✚ The process in general, consists of immersing the base metal in a bath of the molten coating metal covered by a molten flux layer.
- ✚ The flux cleans the base metal surface and prevents the oxidation of molten coating metal.

Galvanizing

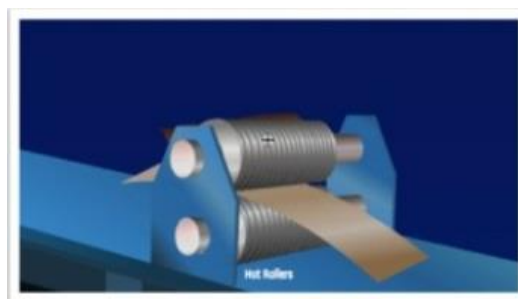
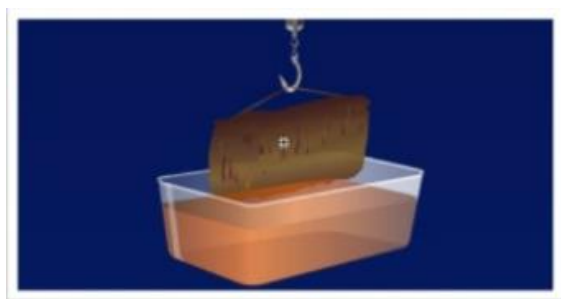
- ✚ The process of the coating of iron or steel with a thin layer of zinc to prevent them from rusting.
- ✚ Metal piece is carried by a spring balance.
- ✚ A metal piece is dipped in a solution of dil. H_2SO_4 (at 60°C-90°C temp. for 15-20 min.). It removes scale, rust and impurities.



- ✚ Again it is dipped in water.
- ✚ Metal piece is dried by using a drier.

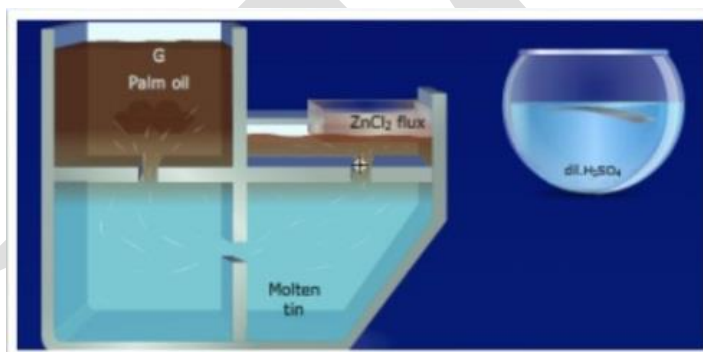


- ✚ Metal piece is dipped in a zinc bath (metal will be in irregular shape)
- ✚ It is maintained at 425°C-435°C and covered by NH_4Cl flux to avoid oxidation of Zinc.
- ✚ Metal is placed in between the rollers to get a regular shape and the excess of zinc will be melting down.

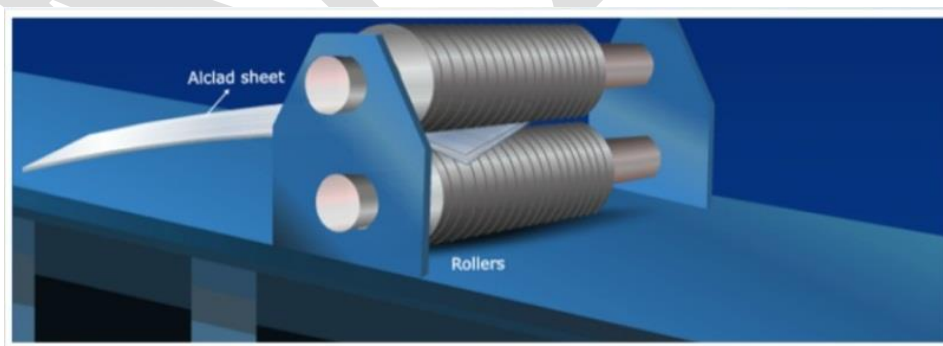


Tinning

- ✚ The process of coating of iron or steel with a thin coat of Tin.
- ✚ Base metal is cleaned by dipping in dil. H_2SO_4 .
- ✚ Metal is passed through a bath of ZnCl_2 flux.
- ✚ Metal is passed through molten tin.
- ✚ Metal piece is pressed between two rollers from a layer of palm oil.



Metal Cladding



- ✚ The choice of cladding of material depends on the corrosion-resistance is required for any particular environments.
- ✚ Nearly all existing corrosion resisting metals (like Nickel, Cu, Pb, Ag, Pt etc.) and alloys like (stainless steel, Ni alloy, Cu alloys, Pb alloys etc.) can be used as cladding materials. Among the base a metal on which cladding is done are, mild steel, Aluminum, Cu, Ni and their alloys.

- ✚ Generally, cladding is accomplished by arranging thin sheets of the coating metal and the base metal sheet in the form of a sandwich, which are then passed through rollers, under the action of heat and pressure.

Ex: Duralumin is sandwiched between two layers of 99.5% pure aluminum results in clad sheet known as “alclad”.

- ✚ It is used in aircraft industry.
- ✚ It is the process by which a dense, homogeneous layer of coating metal is bonded firmly and permanently to the base metal on one or both sides.

Electro Plating

It is the process by which the coating metal deposited on the base metal by passing a d.c. through an electrolytic solution containing the soluble salt of coating metal.



Electroless Plating

The driving force is autocatalytic redox reaction on pretreated catalytic surface. Various aspects of electroless plating are

Preparation of active surface of the object to be plated:

- ✚ This step is most important in this technique. This is achieved by using one of the following methods.
- ✚ Etching, i.e. by acid treatment.
- ✚ Electroplating a thin layer of the metal to be plated or any other suitable metal. This is usually followed by heat treatment.
- ✚ Treating with stannous chloride, followed by dipping in palladium chloride solution. This treatment yields thin layer of Pd on the treated surface. Usually, this is followed in case of plastics and printed circuit boards.

Plating bath is composed of

- ✚ Soluble salt of metal (like chloride or sulphate) to be plated.
- ✚ Reducing agent like formaldehyde, hypophosphite, etc.
- ✚ Complexing agent like tartarate, citrate succinate, etc. This improves the quality of deposit.
- ✚ Exaltant like succinate, flouride, glycinate, etc. This enhances the plating rate.
- ✚ Stabilizer like thiourea, cation of lead, calcium, thalium, etc. is added to prevent the decomposition of the plating bath solution.
- ✚ Buffer like sodium acetate, sodium hydroxide + Rochelle salt, etc. is added to control the pH of the bath. It may be pointed out that pH of the bath plays a critical role in getting a uniform, but thin deposit.

Advantages of electroless plating over electroplating

- ✚ No electrical energy is required.
- ✚ Better throwing power.
- ✚ Plating on articles made of insulators (like plastics) and semiconductors can be plated uniformly.
- ✚ Electroless plated coatings possess unique mechanical, chemical and magnetic features.

2. Organic Coatings

Organic coatings are inert organic barriers applied on metallic surfaces for protection against corrosion.

Ex: Paints



- ✚ Paint is a dispersion mixture of one or more pigments in a vehicle.
- ✚ Vehicle is a liquid consisting of non-volatile and film forming drying oil and a highly volatile solvent called thinner. Vehicle = Drying oil + Thinner

Constituents of paint

Pigment

- ✚ Pigment is a solid substance, which is an essential constituent of paint.
- ✚ Provides desired colour to paint
- ✚ Reflects harmful UV rays, thereby prevents cracking of paint film.

Ex: White Colour	-	White lead, lithophone
Red Colour	-	Red lead, Ferric oxide
Black	-	Carbon black
Blue	-	Prussian blue
Green	-	Chromium oxide
Brown	-	Brown Umbre etc.

Functions of pigments are:

- ✚ Provide capacity to paint
- ✚ Provide strength to paint
- ✚ Provide desired colour to paint
- ✚ Give aesthetical appeal (i.e. Pleasing to look at) to the paint film.
- ✚ Give protection to the paint film by reflecting harmful ultraviolet light.
- ✚ Provide resistance to paint film against abrasion/wear.
- ✚ Improve the impermeability of paint film to moisture.
- ✚ Increase weather-resistance of the film.

Pigment Volume Concentration:

The most important concept for a modern paint formulator is pigment volume concentration (PVC), which is the concentration by volume of the pigments expressed as a percentage of the total volume of non-volatile constituents of the paint. As non-volatile volume in paint is the sum of the volumes of the pigment and non-volatile vehicle. PVC can be expressed as

$$PVC = \frac{\text{Volume of pigment in paint}}{\text{Total volume of non – volatile constituents of the paint}}$$

$$PVC = \frac{\text{Volume of pigment in paint}}{\text{Volume of [pigment + non volatile constituents of the paint]}}$$

Drying oil

- ✚ A film forming constituent of the paint.
- ✚ These are glyceryl esters of high molecular weight fatty acids obtained from animal and vegetable sources.
- ✚ The most widely used drying oils are linseed oil, soyabean oil, and dehydrated castrol oil.

Functions of drying oil:

Drying oil supplies to paint-film:

- (i) Main film-forming constituent (ii) Vehicle or medium (iii) Toughness (iv) adhesion (v) Durability (vi) Water-proffness

Thinners

- ✚ Reduce the viscosity of the paints, so it can be easily handled and applied on metals
- ✚ Dissolve dry oil and other constituents.
- ✚ Suspend the pigments in them
- ✚ Help in the drying of the paint film, when they evaporate.
- ✚ Common thinners used are turpentine, mineral spirits (from petroleum), benzene, dipentene, naptha, xylol, kerosene, methylated naphthalene etc.

Driers:

- ✚ Driers are oxygen carrier catalysts.
- ✚ They accelerate the drying of the oil film through oxidation, polymerization and condensation.
- ✚ Thus, their main function is to improve the drying quality of the oil-film.
- ✚ The most effective dries are resonates, linoleates, tungstates and napthenates of Co, Mn, Pb and Zn.
- ✚ Cobalt substances are the most efficient of all and are surface-driers.

- ✚ Lead substances are bottom-driers.
- ✚ Manganese substances are through-driers. Too much of a drier tends to produce hard and brittle films. **Ex:** Resinates, Linoleate, tungstates etc.

Fillers

- ✚ Extenders or fillers are low refractive indices materials, generally of white colour, which are added to:
 - ✚ Reduce the cost.
 - ✚ Increase the durability of the paint.
 - ✚ Help reduce the cracking of dry paint film and sometimes help keep the pigments in suspension.
 - ✚ Serve to fill voids in the film.
 - ✚ Increase random arrangement of pigment particles, and
 - ✚ Acts as carrier for the pigment colour.
- ✚ **Ex:** Important extenders used are barites (Ba), talc, asbestos, ground silica, gypsum, ground mica, china clay, whiting (Ca), magnesium silicate, diatomite clay, calcium sulphate, etc.

Plasticizers

Sometimes, plasticizers are incorporated in paint

- ✚ To avoid elasticity to the film.
 - ✚ To minimize its cracking.
- Ex:** Common plasticizers used are tricresyl phosphate, triphenyl phosphate, tributyl phthalate, diamyl phthalate and dibutyl tartarate.

Anti Skinning Agents

Anti skinning agents are used to prevent gelling, cracking of paint films.

Ex: Polyhydroxy phenols.

UNIT-IV
ELECTROCHEMISTRY AND CORROSION
IMPORTANT QUESTIONS

1. What is reference electrode? Explain the construction of Hydrogen & Calomel electrode.
2. What is primary cell? Explain the mechanism of dry cell.
3. Explain the construction and discharging, charging reactions of Lead-acid and Ni-Cd battery.
4. Explain the construction and working of Fuel cells.
5. Describe the chemical and electrochemical theories of corrosion.
6. Explain how nature of metal and nature of environment influences the rate of corrosion?
7. Describe the cathodic protection.
8. What are the different constituents present in paints? Discuss the functions of each constituent.
9. Explain the following
 - a) Hot-dipping
 - b) Electroplating
 - c) Electro less plating
 - d) Metal Cladding