

### Unit-III Electrochemistry & Corrosion

#### Basic terms and definition:

Electrochemistry	Electrochemistry is the branch of physical chemistry that deals with convert's ion of chemical to electrical energy and vice versa.
Electrolyte	A substance, which decomposes as a result of passage of electric current is called electrolyte.
Electrolysis	The phenomenon of decomposition of electrolyte through passage of electricity is called electrolysis.
Redox reactions	Both oxidation and reduction reactions are called redox reactions.
Oxidation potential	The tendency of an electrode to lose electrons, when it is in contact with solution of its own ions.
Reduction potential	The tendency of an electrode to gain electrons, when it is in contact with solution of its own ions.
Electrochemical cell	A device consisting of two electrodes, each in contact with a solution of its own ions transforms the free energy change of redox reaction at electrodes into electrical energy.
Conductors	The Substances which allows electricity to pass through them are called conductors. Ex :- Metals, metal sulphides, acids, alkalis, salt sol. and fused salts.
Non-conductors	The substances which do not allow electricity are called non-conductors. Ex: Pure water, dry wood, rubber, paper, non-metals etc.
E.M.F	The difference of potential which causes flow of electrons from an electrode of higher potential to an electrode of lower potential is called Electro motive force (EMF) of the cell.
Standard electrode potential( $E^0$ )	The potential exhibited by single at unit concentration of its metal ion at $25^0$ ° is called standard electrode potential ( $E^0$ )
Primary Batteries	These are non-rechargeable and are meant for single use and to be discarded after use.
Secondary batteries	In secondary batteries, the chemical reactions are reversed by passing direct current in opposite direction. The cells are designed for repeated use and they are able to be rechargeable.
Nernst equation	Nernst derived a mathematical relationship which enable us to calculate the half cell potential (E), from the standard potential ( $E^0$ ) and the temperature of the cell. This relation known as Nernst equation. At $25^0$ C $E_{cell} = E^0_{cell} \pm \frac{2.303RT}{nF} \times \log K$
Fuel cell Corrosion	A fuel cell is an electrochemical cell in which the chemical energy of fuel oxidant system is directly converted into electrical energy.

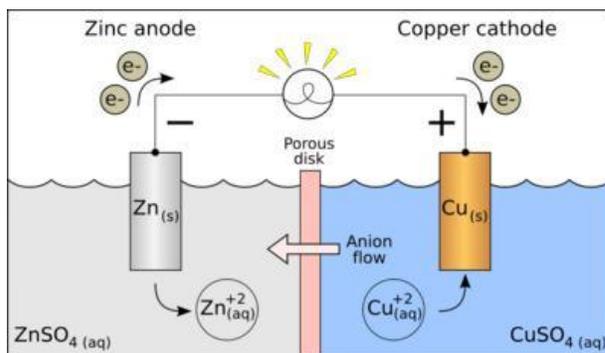
	The surface of almost all the metals begin to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium.
Dry corrosion	This type of corrosion occurs mainly through direct chemical action of atmospheric gases with metal surface in its immediate proximity.
Wet corrosion	This type of corrosion mostly takes place: where a conducting liquid is in contact with metal or two dissimilar metals or alloys are either dipped or immersed partially in solution.
Pilling – Bedworth rule	The rule states that “an oxide is protective or non-porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed”.
Galvanic corrosion	When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is known as galvanic corrosion.
Corrosion Inhibitors	A substance which on addition in small quantities to the aqueous corrosive environment decreases the corrosion of metal effectively is called corrosion inhibitors.
Electroplating	Electroplating is the process of deposition of coating metal in the base metal by passing a direct current through an electrolytic solution which contains the soluble salt of the coating metal.
Electroless plating	It involves base metal to be immersed in a bath of noble metal salt used for plating. The noble metal ion is displaced from its salt solution by the base metal ion and forms a thin uniform deposit on the base metal without current.

### Concepts:

**Definition:-** Electro chemistry is a branch of physical chemistry that is concerned with interrelationship of electricity and chemistry.

**Conductance:-** The conductance is the property of the conductor, which facilitates the flow of electricity through it. “The reciprocal of resistance is known as Conductance”.

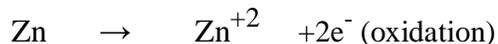
**Electro chemical cell (or) Galvanic cell:-** Galvanic cell is a device in which chemical energy is converted into electrical energy. These cells are called Electrochemical cells or voltaic cells. Daniel cell is an example for galvanic cell.



This cell is made up of two half cells. One is oxidation or anodic half cell. The other is reduction or cathodic half cell. The first half cell consists of 'Zn' electrode dipped in ZnSO<sub>4</sub> solution and second half cell consists of 'Cu' electrode dipped in CuSO<sub>4</sub> solution. Both the half cells are connected externally by metallic conductor. And internally by 'salt bridge' salt bridge is a U - tube containing concentrated solution of KCl or NH<sub>4</sub> NO<sub>3</sub> in agar-agar gel contained porous pot. It provides electrical contact between two solutions.

The following reactions take place in the cell.

At cathode:



At cathode:



The movement of electrons from Zn to Cu produces a current in the circuit.



The galvanic cell can be represented by



The passage of electrons from one electrode to other causes the potential difference between them which is called E.M.F

**Nernst equation:** Nernst derived a mathematical relationship which enable us to calculate the half cell potential (E), from the standard potential (E<sup>0</sup>) and the temperature of the cell. This relation known as Nernst equation.

$$\text{At } 25^\circ\text{C } E_{\text{cell}} = E^0_{\text{cell}} \pm 2.303RT/nF \times \log K$$

**ELECTROCHEMICAL CELLS:-** Electrochemical cell is defined as "a device in which a redox reaction takes place indirectly and the decrease in potential energy of the reaction appears largely in the form of electrical energy".

**Measurement of EMF: - EMF** stands for Electro Motive Force.

The EMF of a cell can be measured by connecting two electrodes to the two terminals of a voltmeter. This method is inaccurate due to the following reasons.

- Some current drawn from the cell by voltmeter causes alteration of chemical equilibrium.
- With flow of current, a part of EMF is used in overcoming the internal resistance of the cell.

To measure EMF value accurately without disturbing the electrochemical equilibrium, "Poggendorff's compensation" principle is widely used.

**Poggendorff's compensation technique:-** In this tech, the EMF to be measured is balanced by equal and opposite EMF from another cell or battery and there is no net flow of current in the circuit. The electrical assembly used is known as "Potentiometer". It consists of a uniform wire AB of high resistance connected to a storage battery of constant EMF which should be longer than the EMF of cell to be measured is connected at the ends A and B of the wire. The cell X the EMF of which is to be determined is included in the circuit by connecting the positive pole at the same point A and then through a galvanometer G to a sliding contact D as shown in the figure.

**Batteries:** When two or more electrochemical cells are electrically inter connected each of which containing two electrodes and an electrolyte is called a Battery.

Batteries are classified into a two categories depending on their recharging capabilities.

**Primary Batteries:-** These are non-rechargeable and are meant for single use and to be discarded after use. These are non-reversed and are less expensive and are offer used in ordinary gadgets like torch lights, watches and toys.

**Secondary Batteries:** - In secondary batteries, the chemical reactions are reversed by passing direct current in opposite direction. The cells are designed for repeated use and they are able to be rechargeable  
Eg: Lead-acid cell, Ni/Cd cell.

**Differences between Primary and secondary batteries:**

Primary Batteries	Secondary Batteries
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.

**Primary Batteries:**

**Dry cell (Leclanche cell):**

**Anode:** Zinc

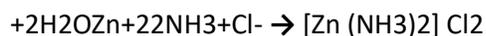
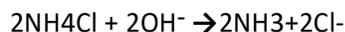
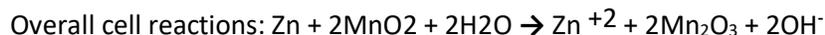
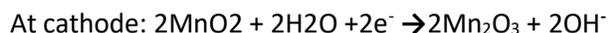
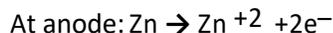
**Cathode:** Graphite rod

**Electrolyte:** paste of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$

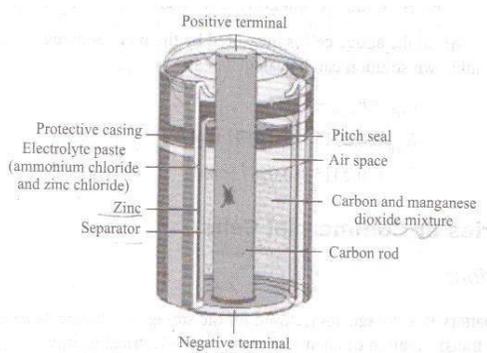
**Emf:** 1.5V.

Dry cell consists of a cylindrical Zinc container which acts as an anode. A graphite rod displaced in the center. The graphite rod does not touch the base and it acts as a cathode. The graphite rod is surrounded by powdered  $\text{MnO}_2$  and carbon. The remaining Space in between cathode and anode is filled with a paste of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$ . The graphite rod is fitted with a Metal cap and the cylinder is sealed at the top with a pitch.

The reactions takes place in the cell are:



Diaminedichlorozinc



## Secondary Batteries:-

### 1) Lead – acid cell:

**Anode:** Sponge metallic lead

**Cathode:** Lead dioxide  $PbO_2$

**Electrolyte:** Aqueous  $H_2SO_4$ .

**Emf:** 2V

Cell reactions:



Applications:

Automobile and construction equipment. Standby / backup system. for engine batteries

Advantages:-

Low cost, long life cycle, Ability to withstand mistreatment, perform well in high and low temperature.

### 2) Nickel – Cadmium cell:-

**Anode:** Cd

**Cathode:** Nickel oxy hydroxide  $Ni(OH)_2$

**Electrolyte:** Aqueous KOH

**Emf:** 1.4V

Cell reaction:



Applications: Calculators, digital cameras, pagers, laptops, tape recorders, flash lights, medical devices, electrical vehicles, space applications.

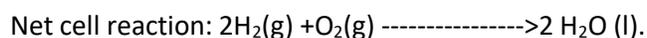
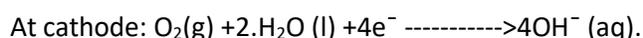
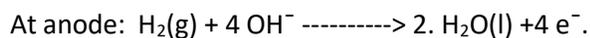
**Advantages:** -Good performance in low temperature long life.

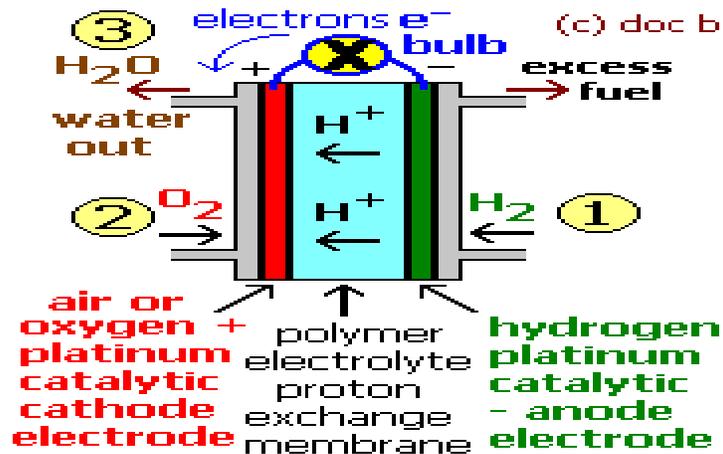
**STANDARD ELECTRODE POTENTIAL:-** The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in solution is called "Electrode potential". The magnitude of acquired electrons and proceed as a reduction is expressed by the half-reaction's potential. When it is measured under standard conditions namely  $25^\circ C$ , conc. of 1.0 M for all solute and pressure of 1 atmosphere, the reduction potential is called 'Standard electrode potential'. Standard electrode potential is also called 'Standard reduction potential'. To represent standard electrode potential, add subscript to the symbol  $E^\circ$  cell.

**FUEL CELLS:-** A cell in which one or both of the reactants are not permanently contained in the cell, but are continuously supplied from a source external to the cell and the reaction products continuously removed is called a fuel cell. The important process in the fuel cell is



**HYDROGEN-OXYGEN FUEL CELL:-** The best example of fuel cell is hydrogen-oxygen fuel cell. The cell consists of two inert porous electrodes and an electrolyte solution  $2.5\% KOH$ . Through the anode hydrogen gas is bubbled and through cathode oxygen gas is bubbled. The following cell reactions take place.





The product discharged is water and the standard EMF of cell is  $E^\circ=1.23\text{v}$ . A number of such fuel cells are stocked together in series to make a battery.

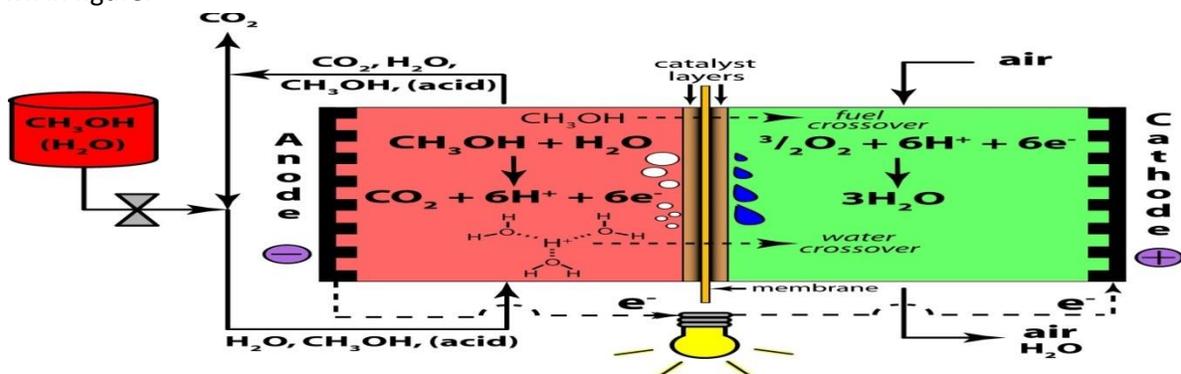
#### Applications:-

- They are used as auxiliary energy source in space vehicle, sub marines or other military vehicles.
- Because of the light weight these fuel cells are preferred for space crafts, and product of water proves to be a valuable source of fresh water to the astronauts.

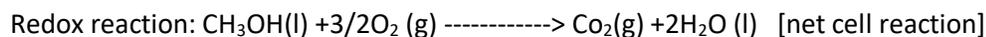
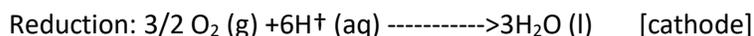
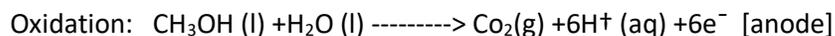
#### Advantages:-

- The energy conversion is very high(75-82/)
- The product  $\text{H}_2\text{O}$  is a drinking water source for astronauts.
- Noise and thermal pollution are low.
- Fuel cells offer an excellent method for use of fossil fuels.
- The maintenance cost is low for these fuels.
- The regenerative  $\text{H}_2\text{-O}_2$  fuel cell is an energy storage system for space applications.

**Methanol Fuel Cell:** - Methanol oxygen is another important fuel cell. It is a sub-category of proton exchange fuel cell relies upon the oxidation of methanol on catalyst layer to form  $\text{CO}_2$ . Water is consumed at the anode which produced at cathode. The position ions ( $\text{H}^+$ ) are transferred across the proton exchange membrane. Often made from anode to cathode where they react with oxygen to produce water. Electrons are transferred through an external circuit from anode to cathode, providing power to a connected device. Currently, platinum is used as catalyst in both half reactions. Methanol and water are absorbed on a catalysts usually made of platinum particles and lose protons until  $\text{CO}_2$  is formed. Methanol or water mixture is circulated through an anode of cell while  $\text{O}_2$  or air is circulated at cathode of the cell as shown in figure.



The half cell reactions are;



#### Limitations:-

- Methanol is toxic and flammable. Hence utmost care has to be taken.
- Limited in the power they produce.
- During the methanol oxidation reaction, CO is formed which is strongly adsorbed on to platinum catalyst, reducing the surface area and lowering the performance.

#### Advantages:-

- Storage of methanol is much easier than  $\text{H}_2$  as it does not need high pressure or low temp since methanol is liquid form.
- $97.0^\circ\text{C}$  to  $64.7^\circ\text{C}$  ( $-142.6^\circ\text{F}$  to  $148^\circ\text{F}$ ).
- The energy density of methanol is an order of magnitude greater than even highly compressed hydrogen.

**Corrosion:** The surface of almost all the metals begins to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium.

The process of decay of metal by environmental attack is known as corrosion.

Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides etc.

E.g. Iron undergoes corrosion to form reddish brown color rust [ $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ].

Copper undergoes corrosion to form a green film of basic carbonate [ $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ ]

#### Causes of corrosion:

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

#### Effects of corrosion:

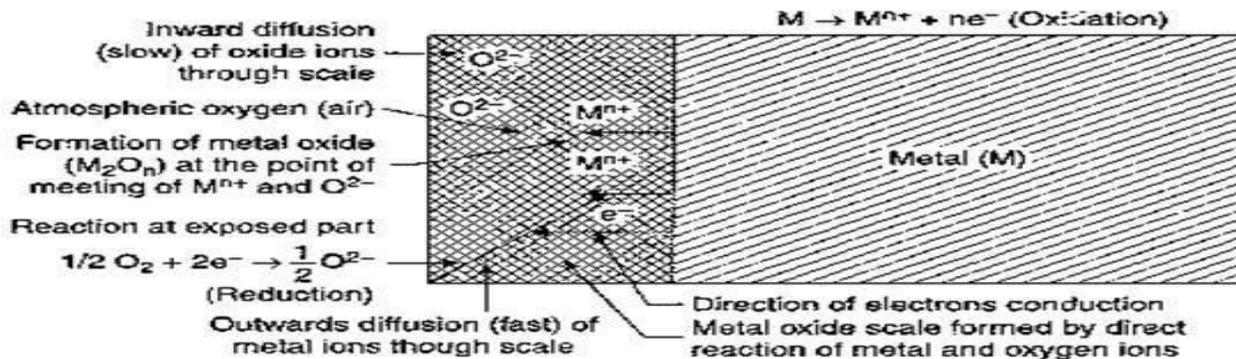
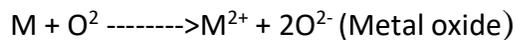
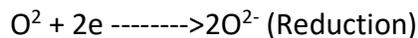
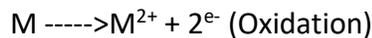
1. Wastage of metal in the form of its compounds.
2. The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
3. Life span and efficiency of metallic parts of machinery and fabrications is reduced.

#### Theories of corrosion:

**1) Dry corrosion or Chemical corrosion:** This type of corrosion occurs mainly through the direct chemical action of atmospheric gases like  $\text{O}_2$ , halogens,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{N}_2$  or anhydrous inorganic liquid with the metal surface. There are three types of chemical corrosion.

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

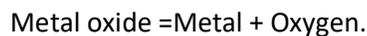
**1. Oxidation corrosion:** This is carried out by the direct action of oxygen low or high Temperatures on metals in absence of moisture. Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, and Pt).



**i) Stable:-** A stable layer is adhering tightly to the parent metal surface. Such a layer behaves as protective coating in nature, there by shielding the metal surface. Therefore further oxidation corrosion is prevented.

**Eg:-** Al, Au, Pt.

**ii) Unstable:-** If the layer is unstable , the forward layer decomposes back into the metal and oxygen.



Therefore oxidation corrosion is not possible in Ag, Au, Pt.

**iii) Volatile:-** If the layer is volatile ,the oxide layer volatilizes as soon as it is formed and leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion.

**b) Corrosion by other gases:-**The corrosion of this type depends mainly on the chemical affinity b/w the metal and gas involved. The intensity of attack depends on the formation protection or non-protective films on the metal surface.

- If the film is protective or non-porous they expect of corrosion decreases due to the formation of AgCl film which protects metal from further attack.

**Eg:-**AgCl results from attack of  $Cl_2$  on Ag.

- If the film is non-protective or porous the metal surface is gradually destroyed.

**Eg:-**Formation of volatile  $SnCl_4$  by the attack of  $Cl_2$  gas on tin.

**c) Liquid metal corrosion:-**

- This type of corrosion occurs by the chemical attack of following liquid metal at high temp, on solid.
- The corrosion reaction involves either,

i)Dissolution of a solid metal by a liquid metal. (Or)

ii) Internal penetration of the liquid metal in to the solid.

**II) Electrochemical or Wet Corrosion:-**

i)This type of corrosion mostly takes place;

Where a conducting liquid is in contact with metal (or) when two dissimilar metals immersed or dipped partially in a solution.

ii) In this corrosion, existence of anodic area and cathodic areas are takes place.

iii)At anodic area oxidation reaction takes place. Hence, corrosion always occurs at anodic area.

AT ANODE:  $M \rightarrow M^{n+} + ne^-$ .(loss of  $e^-$ )

$M^{n+}$  -----> dissolves in solution.

iv) At cathodic areas reduction reaction takes place.

v) Thus, at the cathodic reaction consumes electrons with either by (a) Evolution of hydrogen (b) Absorption of Oxygen, takes place based on the nature of corrosion environment.

**a) Evolution of hydrogen :-**

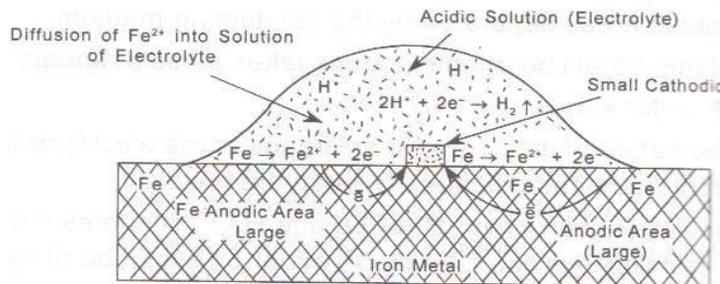
➤ This type of corrosion occurs in acidic environments, considering metal like Fe in acidic solution.

Anodic reaction:  $Fe \rightarrow Fe^{2+} + 2e^-$  (oxidation).

➤ These electrons flow through the metal, from anode to cathode, where  $H^+$  ions (of acidic solution) are eliminated as hydrogen gas.

Cathodic reaction:  $2H^+ + 2e^- \rightarrow H_2 \uparrow$  (reduction)

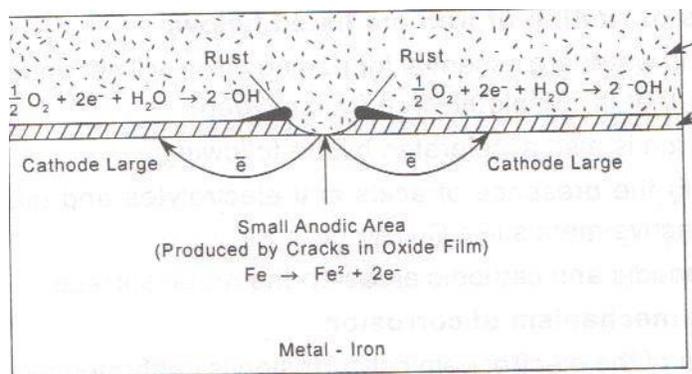
The overall reaction is,  $Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \uparrow$ .



**b) Absorption of Oxygen:-**

➤ The best example of this type of corrosion is rusting of iron in neutral aqueous solution of electrolyte (like NaCl solution) in the presence of atmospheric oxygen.

➤ The surface of iron is coated with a thin film of iron oxide however, if this iron oxide film develops some cracks.



➤ In absorption of oxygen, the cathodes are large areas, whereas anodes are small areas.

Anodic reaction:  $Fe \rightarrow Fe^{2+} + 2e^-$  (oxidation).

Cathodic reaction:  $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$  (reduction)

➤ The  $Fe^{2+}$  ions (at anode) and  $OH^-$  ions (at cathode) diffuse and when they meet, ferrous hydroxide is precipitated.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \downarrow$ .

➤ 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 is called yellow rust, actually corresponds to  $Fe_2O_3 \cdot H_2O$ .

- If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite,  $\text{Fe}_3\text{O}_4$ .

**GALVANIC SERIES:-** Electrochemical series will give useful information regarding chemical reactivity of metal and may not be able to provide sufficient information in predicting the corrosion behavior of metal in a particular set of environmental conditions. Passivation makes effective electrode potential of some metals more passive and acts as cathodic and exhibit noble behavior. This behavior is exactly opposite to that predicted by electrochemical series. For more practical series called Galvanic series, have been prepared by studying the corrosion of metals and alloys in a given environment like in sea water. This series gives real and useful information about corrosion behavior of metals and alloys in a given environment.

Mg	Brass
Mg alloy	Mantel
Zn	Silver solder
Al	Cu
Al alloy	Ni
Mild steel	Cr stainless steel
Cost iron	18-08 stainless steel
High Ni cost iron	18-08 Mo steel
Pb-Sn solders	Ag
Pb	Ti
Sn	Graphite
Iconel	Au
Ni-Mo-Fe alloy	Pt

In the galvanic series anodic character of the metals/alloys increases upward while cathodic character increases downward.

**GALVANIC CORROSION:-** When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is known as galvanic corrosion.

**FACTORES INFLUENCING CORROSION:-** The rate and extent of corrosion depends majorly on; the nature of the metal and the nature of the environment.

**a) Nature of the Metal:-** Many characteristic properties of metal are responsible for corrosion . These are;

**i) Position of galvanic series:-** When two metals or alloys are in contact with a conducting medium, then the metal at higher galvanic series is more active towards corrosion.

**ii) Over voltage:-** It can be defined as the difference of potential at which electrolysis actually place, and theoretical decomposition potential for the same solution is known as over voltage. For example, electrolysis of  $\text{H}_2\text{SO}_4$  with Pt occurs at 1.70 volts whereas its theoretical potential is 1.229 volts. The difference i.e., 0.471 volt is over voltage. Thus, the decrease in over voltage enhances the corrosion of the metal.

**iii) Relative areas of anode and cathode:-** Small anodic and large cathodic area causes severe corrosion . When two dissimilar metals/alloys are in contact, the corrosion of anodic part is directly proportional to the ratio of areas of the cathodic part and anodic part.

**iv) Purity of metal:-** Impurities in a metal cause heterogeneity and turn minute electrochemical cells and anodic part gets corroded. So purity of the metal do not undergo corrosion.

**v) Physical state of the metal:-** The rate of corrosion is influenced by physical state of metal such as grain size, stress, crystal orientation. Areas under stress, even in pure metal become anode and undergoing corrosion.

**vi) Nature of surface film:-** All the metals except Au, Ag, Pt interact with atmospheric air and form a thin surface film of metal oxide. The ratio of volume of metal oxide to the metal is known as specific volume ratio. Higher the volume of SVR, lower will be the corrosion rate.

**b) Nature of the environment:-** The process of corrosion will also decide on the basis of environment in which the metal is working.

**i) Temperature:-** An increased temp, enhances the rate of corrosion.

**ii) Presence of corrosion gases in atmosphere:-** The corrosion gases like  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and fumes of HCl,  $\text{H}_2\text{SO}_4$  etc., Present in atmosphere produce acidic medium coming with moisture and causes electrochemical corrosion.

**iii) Effect of  $\text{pH}$ :-** The acidic media ( $\text{pH} < 5$ ) facilitate the corrosion of metals while in alkaline media ( $\text{pH} > 11$ ) the rate of corrosion is minimum.

**iv) Presence of suspended solid particles in atmosphere:-** Presence of suspended solid particles like NaCl,  $(\text{NH}_4)_2\text{SO}_4$  absorb moisture and act as strong electrolyte thereby enhancing electrochemical corrosion.

**v) Humidity of air:-** Humidity of air gives rise to atmospheric corrosion because of the moisture content in atmosphere. Since the moisture acts as the solvent for oxygen in air, electrochemical type corrosion occurs.

**CONTROL OF CORROSION:-** Following are some of the methods for control of corrosion.

**Cathodic protection:-** The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur. There are two types of cathodic protection;

**i) Sacrificial anodic protection method:-** In this method, the metal structure to be protected is connected by a wire to a more active metal so that all the corrosion is concentrated at more active metal and saving the metal structure from the corrosion. The more active metal so used is known as "Sacrificial anode". Examples of some of common sacrificial anode are Mg, Zn, Al and their alloys.

**Applications:-** Important applications of sacrificial anodic method are buried pipelines, underground cables, marine structures, i.e., Ship hulls, water tanks, etc.

**ii) Impressed current cathodic protection:-** In this method, an impressed current is applied in opposite direction to the corrosion current to nullify and convert the corroding metal from anode to cathode. Once the metal becomes cathodic, it is protected from corrosion.

This type of cathodic protection has been applied to open water box coolers, water tanks, buried oil, (or) water pipes transmission line towers, ships, etc.,

This kind of protection technique is particularly used for large structures for long term operations.

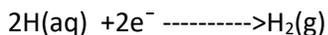
**Uses of Inhibitors:-** Inhibitors are the chemical substances, which when added to the corrosion environment, decrease the corrosion rate. Corrosion inhibitors are classified into two types. They are;

**i) Anodic inhibitor:-** They are adsorbed on the metal surface forming a protective coating, thereby reducing the rate of corrosion.

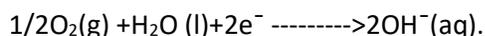
**Eg:-** Chromate, Phosphate, Tungstates or other ions of transition element with a high oxygen content.

**ii) Cathodic inhibitors:-** The substances which slow down the diffusion of H<sup>+</sup> ions to the cathode or is capable of eliminating oxygen from the corroding medium are called Cathodic inhibitors.

a) In acidic solution the main cathodic reaction is the evolution of H<sub>2</sub>.



b) In neutral solution the cathodic reaction is the absorption of O<sub>2</sub>.



**ELECTROPLATING:-** Electroplating is the process of deposition of coating metal in the base metal by passing a direct current through an electrolytic solution which contains the soluble salt of the coating metal. The main objectives of electroplating are;

- To increase the resistance of the plated metal.
- Resistance to chemical attack.
- To improve physical appearance and hardness.
- For improvement of commercial value and decoration of metal.

**ELECTROLESS PLATING:-** Electro-less plating is also a widely used technique to protect the base metal from the corrosion. It is also called displacement plating or immersion plating. It involves base metal to be immersed in a bath of noble metal salt used for plating. The better example for electro-less plating is nickel plating. The base metal to be protected from corrosion is immersed in a bath containing sodium hypophosphate and nickel sulphate at pH 4.5-5.0 and maintains both temp, of about 100°C.

**ELECTROPLATING OF NICKEL:-** Nickel plating gives hard, adherent and good wear resistance surface. General nickel plating is used as an under coat for articles which are finally to be chromium plated.

**Requirements for electroplating:-**

1. Electrolytic bath: It consists of nickel sulphate (250g/l), nickel chloride (450g/l) and boric acid (30g/l).
2. pH: Maintained at 4.0 by boric acid buffer.
3. Operating temperature: 40-70°C.
4. Current density: 20-30mA/cm<sup>2</sup>.
5. Additive agent: Saccharin/coumarin derivatives.
6. Cathode: Metal article to be plated.
7. Anode: Nickel pallets/pieces taken in a titanium mesh basket.
8. Current efficiency: 95 %.

**ELECTROPLATING OF CHROMIUM:-** Chromium plating is a porous and non-adherent in which it requires that the article is first given under coat of copper or nickel. Chromium electroplating is carried out in acidic medium by insoluble anode.

1. Plating bath: Chromic acid ( $\text{H}_2\text{CrO}_4$ ) and  $\text{H}_2\text{SO}_4$  is 100:1 by volume.
2. Operating temp: 40-50°C.
3. Catalyst:  $\text{SO}_4^{2-}$  ion Cr(IV) converts to Cr(III) by complex anodic reaction in presence of  $\text{SO}_4^{2-}$ .
4. Current density: 100-200 mA/cm<sup>2</sup>.
5. Anode: Lead and antimony alloy is used for getting insoluble anodes.
6. Cathode: Article to be plated and pretreated with organic solvents to remove oils and greases.
7. Current density: 10-12 /.

**Electroless plating:** It involves base metal to be immersed in a bath of noble metal salt used for plating. The noble metal ion is displaced from its salt solution by the base metal ion and forms a thin uniform deposit on the base metal without current.

### Important questions:

1. With a neat diagram, explain the working of a Daniell cell (or) Galvanic cell. Do you use a salt bridge in this cell? If yes, explain why?
2. Explain construction, working principle & uses of Ni-Cd cell (or) NiCad cell.
3. Explain the working principle of lithium ion cell.
4. Explain primary lithium cell (Lithium Manganese dioxide cell)
5. What are the storage batteries? Explain Lead acid battery with neat sketch.
6. Discuss with a neat sketch, the construction and working principle of Hydrogen – oxygen fuel cell.
7. Discuss with a neat sketch, the construction and working principle of Methanol – oxygen fuel cell.
8. With a neat sketch explain the mechanism of Oxidation corrosion. (Chemical corrosion)
9. With a neat sketch discuss in detail electrochemical corrosion of evolution of hydrogen.
10. With a neat sketch discuss in detail electrochemical corrosion of absorption of oxygen.
11. Discuss in detail the factors influencing (or) affecting corrosion.
12. Explain various measures available for controlling of corrosion.
13. What is cathodic protection? Explain sacrificial anodic protection method.
14. What is anodic protection? Explain impressed current method.
15. Define electro plating. Explain electro plating of nickel and electro plating of chromium.
16. Define electro less plating. Explain electro less plating of nickel.