

UNIT 1

ELECTRODE SYSTEM AND CORROSION SCIENCE

Electrode and Cells

Electrochemistry is the branch of chemistry which deals with the study of interconversion of electrical energy and chemical energy and study of behaviour of electrolytes.

Chemical reactions that involved in the interconversion of electrical energy and chemical energy are called as **electrochemical reactions**.

Electrochemical cell is a device which is used to interconvert chemical energy and electrical energy. It consists of two electrodes and an electrolyte solution.

A metal rod which is dipped in a solution containing its own ions is called an electrode. The electrode at which oxidation takes place (loss of electrons) is called anode and the electrode at which reduction takes place (gain of electrons) is called cathode.

Ex : Zn in contact with ZnSO_4 solution.

Cu in contact with CuSO_4 solution.

Each electrode of the cell is called half cell.

A spontaneous chemical process is the one which can take place on its own and in such a process Gibbs free energy of a system decreases.

Types of Electrochemical Cell

1. Galvanic cells
2. Electrolytic cells

Galvanic Cell

The galvanic cell converts chemical energy into electrical energy i.e, electricity can be obtained with the help of redox reaction. The oxidation and reduction take place in two separate compartments. Each compartment consists of an electrolyte solution and metallic conductor which acts as an electrode. The compartment containing the electrode and the solution of the electrolyte is called half cells. **Ex: Daniel cell.**

Electrolytic Cell

The electrolytic cell converts electrical energy to chemical energy. Here the electrodes are dipped in an electrolytic solution containing cations and anions. On supplying current the ions move towards electrodes of opposite polarity and simultaneous reduction and oxidation take place.

Ex: - Electroplating of Cu, Ni, Zn etc.

Differences between Galvanic cell and Electrolytic cell:

	Galvanic cell	Electrolytic cell
1	Chemical energy is converted into electrical energy	Electrical energy is converted into chemical energy
2	Anode is -ve electrode & Cathode is +ve electrode	Anode is +ve electrode & Cathode is -ve electrode
3	It can be used as a source of energy	It cannot be used as a source of energy

Concentration cells:

Concentration cells can be defined as electrochemical cells that consist of two half-cells wherein the electrodes are the same, but they vary in concentration. As the cell as a whole strives to reach equilibrium, the more concentrated half cell is diluted and the half cell of lower concentration has its concentration increased via the transfer of electrons between these two half cells. Therefore, as the cell moves towards chemical equilibrium, a potential difference is created.

The cell potential depends on the concentration of electrolyte. **A concentration cell is defined as a galvanic cell obtained by dipping the same electrode in the same electrolyte of different concentrations.**

Consider 2 silver rods dipped in AgNO_3 solution of different concentration say C_1 and C_2 such that $C_2 > C_1$, The two electrodes are connected externally by a metallic wire and internally through a salt bridge.

The cell is represented as $\text{Ag}/\text{Ag}^+ (C_1) // \text{Ag}^+/\text{Ag} (C_2)/\text{Ag}$

Electrode reaction:

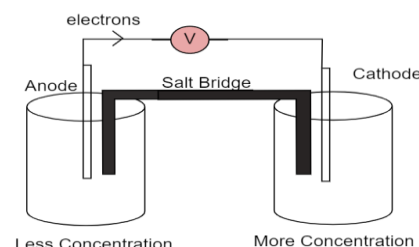
At anode : $\text{Ag} \rightarrow \text{Ag}^+ (C_1) + e^-$

At cathode : $\text{Ag}^+ (C_2) + e^- \rightarrow \text{Ag}$

EMF of the cell:

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\
 &= E^0_{\text{cell}} + \frac{0.0591}{n} \log[C_2] - E^0_{\text{cell}} + \frac{0.0591}{n} \log[C_1] \\
 &= E^0_{\text{cell}} + \frac{0.0591}{n} \log[C_2] - E^0_{\text{cell}} - \frac{0.0591}{n} \log[C_1]
 \end{aligned}$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$



- When $C_2=C_1$, $E_{\text{cell}}=0$ Hence no net current flows through the cell.
- When $C_2>C_1$ E_{cell} is positive. Hence net cell reaction is spontaneous
- Higher the C_2/C_1 ratio, higher is the cell potential

REFERENCE ELECTRODES may be defined as an electrode whose electrode potential value is either arbitrarily fixed or exactly known, using which it is possible to determine the potential of the electrodes.

Classification of reference electrodes

There are two types of reference electrodes viz.,

- (1) **Primary reference electrode** Ex: Standard hydrogen gas electrode whose potential is fixed as zero and
- (2) **Secondary reference electrode** Ex: Calomel electrode and Ag-AgCl electrode.

Limitations of standard hydrogen electrode:

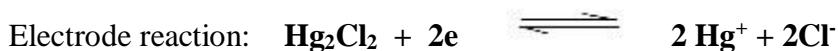
1. It is difficult to maintain the pressure of hydrogen gas uniformly at 1 atmosphere
2. It is difficult to maintain the H^+ ions concentration at 1M throughout.

CONSTRUCTION AND WORKING OF CALOMEL ELECTRODE:

In order to overcome the practical difficulties in setting primary reference electrode, SHE, calomel electrode is devised and since potential of calomel electrode is determined with respect to SHE, it is called as secondary reference electrode.

Calomel electrode consists of a glass vessel containing mercury at its bottom and is covered with a paste of Mercurous chloride (Hg_2Cl_2) called calomel. The vessel is then filled with a saturated solution of KCl and it is provided with a platinum wire which dips in mercury for establishing electrical connection. It has a side U-tube which acts as salt bridge to combine this electrode with other electrode to form an electrochemical cell.

It is represented as **$Hg, Hg_2Cl_2(s) / KCl(aq)$**



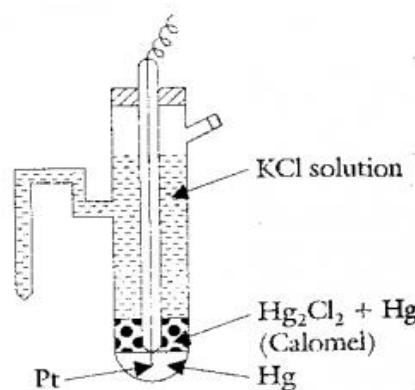
According to Nernst equation, electrode potential is given by the expression

$$E = E^0 - 0.0591 \log [Cl^-]$$

The potential of calomel electrode depends on the concentration of KCl. The potential of calomel electrode w.r.t. SHE at 25°C for various concentrations of KCl are

$$0.1 \text{ N KCl solution } E = 0.334 \text{ V}$$

$$1 \text{ N KCl solution } E = 0.280 \text{ V}$$



Saturated KCl solution $E = 0.242 \text{ V}$

Advantages:

- It is very easy to construct.
- Its potential does not vary with temperature.
- It is not susceptible to poisoning.

Applications:

- The electrode potential of any electrode can be conveniently measured by coupling it with calomel electrode and measuring its cell potential using voltmeter.
- It is used as a reference electrode along with glass electrode to measure the pH of an unknown solution.

ION SELECTIVE ELECTRODES:

Ion Selective Electrodes are sensitive to certain specific ions in a solution containing a mixture of ions and develop a potential which depends on the concentration of specific ions. Ion selective electrode consists of reference electrode and membrane that is sensitive only to a particular ion.

Applications:

- Ion selective electrode are used to determine pH of the solution
- To determine the concentration of the ions F^- , S^{2-} , NO_3^- , Br^- , Cl^- etc...
- To determine the concentration of the cations K^+ , Na^+ , Li^+ , Ag^+ , Ca^{2+} , Pb^{2+} , Cd^{2+} etc....
- To determine the concentration of the gases CO_2 , NH_3 , SO_2 , NO_2 etc...

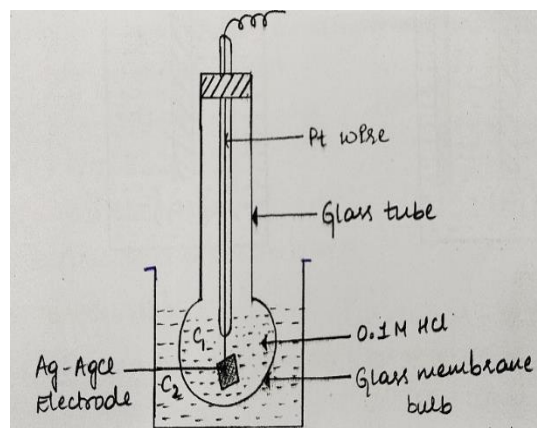
CONSTRUCTION AND WORKING OF GLASS ELECTRODE:

Glass electrode consists of glass tube with a thin walled membrane at the bottom. It is a special variety of glass having a low melting point and high electrical conductance. The composition of the glass is SiO_2 72%, Na_2O 22% and CaO 6%. An Ag-AgCl electrode is dipped in 0.1 M HCl taken in the glass bulb and is connected to platinum wire for electrical contact.

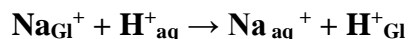
The glass electrode is represented as



When a glass membrane bulb containing a solution of known H^+ ion concentration is immersed in another solution of different H^+ ion concentration, a potential is developed across the glass membrane. This is due to the ion exchange reaction.



The Na^+ ions of the glass membrane are exchanged for H^+ ions of the external solution as follows



As the glass electrode is in contact with H^+ ions, it attains certain potential which is given by

$$E_{\text{G}} = E_{\text{G}}^0 + 0.0591 \log [\text{H}^+],$$

In terms of pH the above equation can be written as

$$E_{\text{G}} = E_{\text{G}}^0 - 0.0591 \text{ pH} \quad (\text{Since } \text{pH} = -\log (\text{H}^+))$$

Advantages:

- It is not easily poisoned by impurities present in the solution
- It can be readily used in presence of oxidising or reducing agents.
- It can be used for pH determination of coloured solutions, colloids and biological fluids

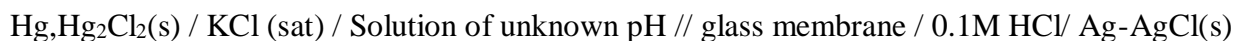
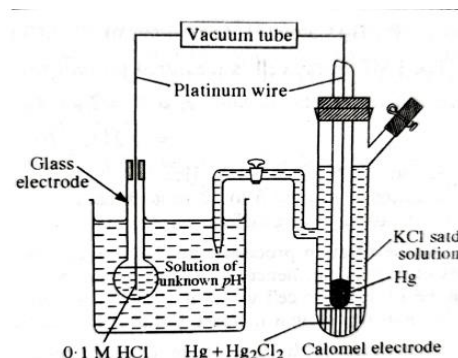
Limitations:

- It cannot be used in presence of F^- ions because HF dissolves glass.
- Glass membrane has a high resistance and hence expensive electronic voltmeter should be used.
- It cannot be used for pH determination > 10 as it leads to alkaline error.

DETERMINATION OF pH USING GLASS ELECTRODE:

In order to determine pH, the glass electrode is immersed in a solution of unknown H^+ ion concentration and combined with a reference electrode like calomel electrode through a salt bridge.

The cell is represented as



The potential of the above cell E_{cell} is measured using an electronic voltmeter. An ordinary potentiometer is not used because of the high resistance of the glass membrane. As the glass electrode is in contact with H^+ ions on either side, it attains certain potential the value of which is given by This potential is known as boundary potential (E_b).

$$\text{Thus } E_b = \frac{2.303RT}{nF} \log \frac{[\text{C}_2]}{[\text{C}_1]}$$

Where C_1 and C_2 are concentration of H^+ ions in solution inside and outside the glass bulb respectively.

$$E_b = \frac{2.303RT}{nF} \log \frac{1}{[C_1]} + \frac{2.303RT}{nF} \log [C_2]$$

Since the concentration of internal solution C_1 is constant

$$E_b = \text{Constant} + \frac{2.303RT}{nF} \log [C_2]$$

Substituting for R and F at 298 K

$$E_b = K + 0.0591 \log C_2$$

Where K is constant which depends on the pH of the solution inside the bulb and C_2 is the H^+ ion concentration of the external solution.

$$\begin{aligned} E_b &= K + 0.0591 \log (H^+) \\ &= K - 0.0591 \text{ pH} \quad [\text{Since } \text{pH} = -\log (H^+)] \end{aligned}$$

The boundary potential is mainly responsible for the glass electrode potential. Therefore the potential of the glass electrode is given by

$$\begin{aligned} E_G &= E_b + E_{\text{Ag-AgCl}} \\ &= K - 0.0591 \text{ pH} + E_{\text{Ag-AgCl}} \end{aligned}$$

The potential of Ag-AgCl electrode is constant and potential difference between the inner surface of the glass membrane and 0.1M HCl is also constant. Thus Glass electrode Potential is due to the difference between the outer surface of the glass membrane and the external solution.

Therefore $E_G = E_G^0 - 0.0591 \text{ pH}$, where $E_G^0 = K + E_{\text{Ag-AgCl}}$

E_G^0 is a constant for a particular glass electrode.

$$E_G = E_G^0 + 0.0591 \log [H^+]$$

In terms of pH the above equation can be written as

$$E_G = E_G^0 - 0.0591 \text{ pH}$$

Therefore,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_G - E_{\text{SCE}} \end{aligned}$$

Substituting for E_G from the above equation

$$E_{\text{cell}} = E_G^0 - 0.0591 \text{ pH} - E_{\text{SCE}}$$

$$0.0591 \text{ pH} = E_G^0 - E_{\text{SCE}} - E_{\text{cell}}$$

$$\text{pH} = \frac{E_G^0 - E_{\text{SCE}} - E_{\text{cell}}}{0.0591}$$

Knowing E_{cell} , E_{SCE} & E_G^0 , pH of the unknown solution can be calculated.

Corrosion Science

Corrosion may be defined as the destruction and loss of metal or alloy by the surrounding environment through chemical or electrochemical reaction.

Ex : 1. Rusting of iron, when iron is exposed to atmosphere a reddish brown scale due to hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) is formed.

2. When copper is exposed to air, a green scale of cupric carbonate [$\text{CuCO}_3 + \text{Cu}(\text{OH})_2$] is formed.

Corrosion may be

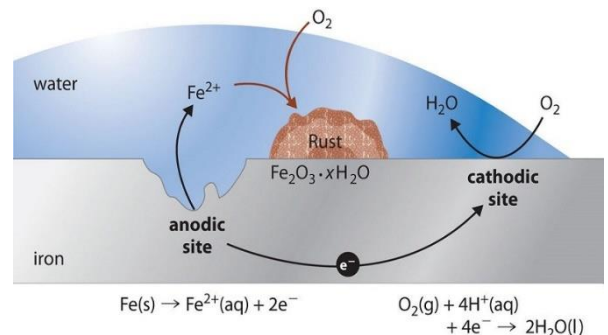
1. Chemical or Dry corrosion
2. Electrochemical or Wet corrosion

Chemical or dry corrosion occurs due to chemical reaction between the metal and gases present in the environment, whereas electrochemical or wet corrosion occurs when a conducting liquid is in contact with a metal or when two dissimilar metals are in contact with an aqueous solution.

ELECTROCHEMICAL THEORY OF CORROSION:

When a metal is exposed to environment the following electrochemical changes occur.

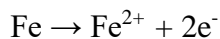
- Formation of large number of galvanic cells i.e. anodic and cathodic areas. Electrons liberated at the anodic area are taken up by the cathodic area.
- Oxidation (corrosion) takes place at the anodic area.
- Reduction of water and oxygen in the atmosphere to OH^- ions and H_2 occurs at cathodic area



Corrosion of iron

Reaction taking place in the cell are given below:

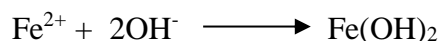
Anodic reaction: At the anode, oxidation takes place



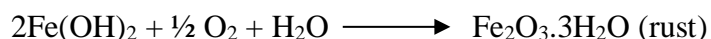
Cathodic reaction: Electrons flow from anodic to cathodic area and cause reduction depending on nature of the electrolyte. There are three ways by which reduction takes place

1. If the solution is aerated and neutral, oxygen is reduced to OH^- ions
$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-$$
2. If the solution is deaerated and neutral the reaction at cathode involve liberation of H_2
$$2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^-$$
3. If the solution is deaerated and acidic, H^+ ions are reduced to H_2 .
$$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2$$

Fe^{2+} ions formed at anode combine with OH^- ions liberated at the cathode to form corrosion product.



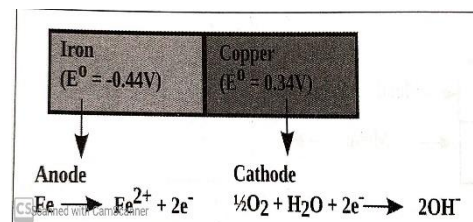
As $\text{Fe}(\text{OH})_2$ is not stable it gets oxidised to $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (rust)



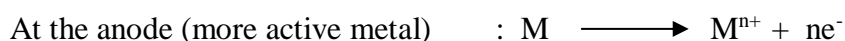
TYPES OF CORROSION:

1. DIFFERENTIAL METAL CORROSION

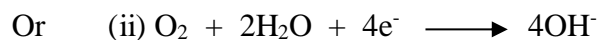
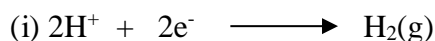
When two dissimilar metals are in contact with each other in a corrosion medium, the two metals differ in their tendencies to undergo oxidation. The one with lower reduction potential or the more active metal acts as anode and undergoes corrosion, while the one with higher reduction potential act as cathode. The greater the potential difference between the two electrodes higher is the rate of corrosion.



The following reactions occur during galvanic corrosion:



At the cathode (Less active metal): Depending on the nature of the corrosion environment the cathode reaction may be either hydrogen evolution or oxygen absorption.



When Fe is coupled with Cu --- Fe being anodic to Cu undergoes corrosion.

When Zn is coupled with Fe --- Zn being anodic to Fe undergoes corrosion.

Examples

- Steel screws/riverts in copper sheet
- steel pipes connected to copper plumbing

The rate of galvanic corrosion depends upon factors such as potential difference between the anodic and cathodic region, ratio of anodic area to cathodic area, environmental factors, tendency of the metal to exhibit passivity, etc.

2. DIFFERENTIAL AERATION CORROSION:

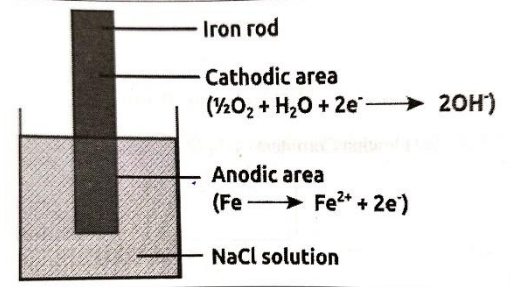
The difference in oxygen concentration over a metal surface develops galvanic cells called oxygen concentration cells which initiate corrosion. This type of corrosion is called differential aeration corrosion or oxygen concentration cell corrosion.

It is found that poorly oxygenated area acts as anode and undergoes corrosion where as well aerated part acts as cathode and remains unaffected.



At the cathode (more O_2 concentration): $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (Reduction)

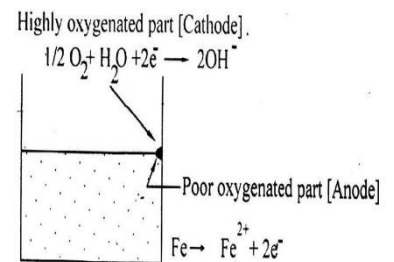
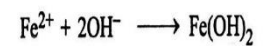
Corrosion of metals arising as a result of the formation of oxygen concentration cell due to uneven supply of air on the metal surface is known as differential aeration corrosion.



Examples:

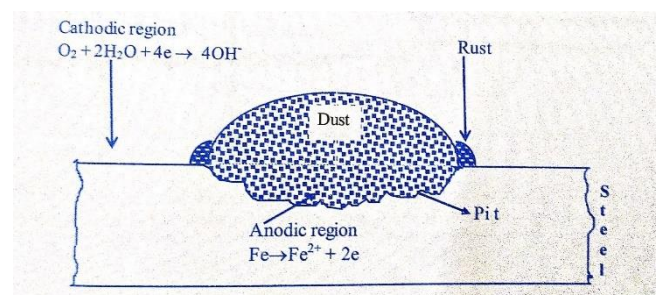
(i) Water line corrosion:

This type of corrosion is observed in ships, water storage steel tank etc. The area above the water line which is highly oxygenated part acts as cathode and is completely protected whereas the metal below the water line which is less oxygenated acts as anode and undergoes corrosion. A distinct brown line is formed just below the water line due to the deposition of rust. Water line corrosion is common in water lifting pipes, the ships going in ocean suffers from differential aeration corrosion, whereas ships sunk for many years under water are free from corrosion.



(ii) Pitting corrosion:

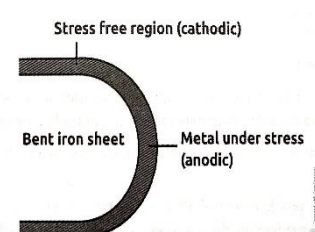
The deposition of impurities like dust, sand, scale etc. on the metal induces pitting corrosion. The portion covered by the impurities will be less oxygenated compared to the exposed surface. The gradient in oxygen concentration results in the formation of oxygen concentration cell. The covered



part act as anode with respect to the exposed surface and corrosion starts just beneath the impurity particles. It is often difficult to detect pits because of their small size and also because the pits are covered with corrosion products. Once pit is formed rate of corrosion increases.

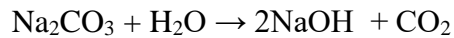
3. STRESS CORROSION:

In a metal stress results due to bending, pressing, welding, riveting, quenching etc. At stressed part the metal atoms are somewhat displaced creating an anodic zone of higher potential. Therefore stressed part which acts as anode undergoes corrosion while the unstressed part acts as cathode and is protected.



Ex: Caustic embrittlement of boilers:

Boilers undergo corrosion at the stressed part due to the presence of hairline cracks. Water containing alkaline impurities (Na_2CO_3) passes in to the cracks by capillary action. Alkaline water enters the cracks and dissociates under the existing conditions to form



Water evaporates leaving behind caustic soda in the cracks whose concentration gradually increases.

A galvanic cell is set up as given below:

Iron under stress		Con NaOH		Dil NaOH		Iron main body
		(In cracks)		(In boiler water)		(Unstressed part)
Anode						Cathode

Iron surrounded by dil NaOH acts as cathode and iron under stress surrounded by cons NaOH acts as anode and gets corroded

FACTORS AFFECTING RATE OF CORROSION:

Related to nature of metal:

- 1. Electrode potential:** When two different metals are in contact with each other, galvanic corrosion takes place. The greater the difference in electrode potential (E°) between the metals, faster will be the rate of corrosion. For ex. The potential difference between iron and copper is more than between iron and tin. Hence iron corrodes faster when in contact with copper than with tin.
- 2. Relative size of anodic and cathodic area:** The rate of corrosion is greatly influenced by relative size of anodic and cathodic areas. Smaller the anodic area and larger the cathodic area faster is the rate of corrosion because the demand for electrons in large cathodic area can be met only by small anodic area. If Sn is cathode (large) and Fe is anode, corrosion is fast. Larger the anodic area and smaller the cathodic area slower is the rate of corrosion because the consumption of electrons will be less. If Zn is anode (large) and Fe is cathode, corrosion is slow.
- 3. Nature of corrosion product:** The corrosion product i.e oxide layer on the metal surface determines the corrosion rate. If the corrosion product is insoluble, stable, nonporous and uniform it forms protective layer on the surface and prevents further corrosion as in the case of Al, Cr, Ti etc. A thin invisible continuous film formed on the surface acts as a barrier between the fresh metal surface and the corrosive environment. If the corrosion product is soluble, unstable, porous and non-uniform it forms non-protective layer on the surface as in case of Zn, Fe etc. The fresh

metal surface is continuously exposed to the corrosive environment and corrosion of metal takes place continuously.

Related to nature of the surrounding environment:

1. **pH of the medium:** The corrosion rate is high in acidic medium i.e $\text{pH} < 7$ than in alkali and neutral medium i.e $\text{pH} \geq 7$. If $\text{pH} > 10$ the rate of corrosion of iron stops due to the formation of protective coating of iron hydroxide. Between pH 10 and 3, the presence of O_2 is essential for corrosion of iron and if $\text{pH} < 3$, iron is severely corroded even in the absence of Oxygen. In general lower the pH of corrosion medium higher is the rate of corrosion.
2. **Temperature:** The corrosion rate is accelerated when the temperature is increased. Due to rise in temperature there is an increase in the conductance of aqueous medium and thereby rate of diffusion of ions. Hence rate of corrosion is faster at higher temperature.
3. **Humidity and presence of impurities in atmosphere:** At lower relative humidity rate of corrosion is slow. As the humidity of the medium increases, corrosion rate gradually increases. Severe corrosion of metal occurs in presence of impurities such as SO_2 , HCl etc. The higher the moisture content in the atmosphere greater is the rate of corrosion.

CORROSION PENETRATION RATE (CPR)

Corrosion penetration rate may also be known as corrosion rate

The corrosion penetration rate (CPR) is defined in three way :

- The speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment.
- The amount of corrosion loss per year in thickness.
- The speed at which corrosion spreads to the inner portions of a material.

The speed or rate of deterioration depends on the environmental conditions and the type and condition of the metal under study. Data required to calculate the corrosion penetration rate for any given metal:

- The weight lost (the decrease in weight of the metal during the period of reference).
- The density of the metal.
- The total surface area initially present.
- The time taken for the metal to corrode.

The CPR is calculated as follows:

$$\text{CPR} = (k \times W) / (D \times A \times T)$$

where k = a constant

W = total weight lost

T = time taken for the loss of metal

A = the surface area of the exposed metal

D = the metal density in g/cm³

The corrosion penetration rate is best expressed in terms of thickness or weight loss where the surface of the metal corrodes uniformly across an area.

This method involves the exposure of a weighed piece of test metal or alloy to a specific environment for a specific time. This is followed by a thorough cleaning to remove the corrosion products and then determining the weight of the lost metal due to corrosion.

The rate may vary if the rate expressed by the formula above is used to compare corrosion rates for a period of time longer than one year with rates calculated over short periods. This is because the short time periods are prone to fluctuating environmental changes from season to season and also from day to day.

CORROSION CONTROL:

1. INORGANIC COATING:

A surface layer of the metal is converted into a compound by chemical or electrochemical reaction, which forms a barrier between the metal and corrosion environment.

Anodizing of Aluminium:

In case of Al, Zr, Cr, Ti etc. the corrosion product formed (oxide film) is protective in nature i.e. passive to corrosion. But such an oxide layer is less resistant to corrosion as well as to mechanical damages. Hence corrosion can be effectively decreased by increasing the thickness of the oxide layer on the metal surface by making the base metal as anode in an aqueous medium. This process of increasing the thickness of the oxide layer on the surface of the base metal is called anodizing.

Aluminium article to be anodized is degreased, polished, washed and dried.

Anode- Aluminium article to be anodized

Cathode- copper or steel

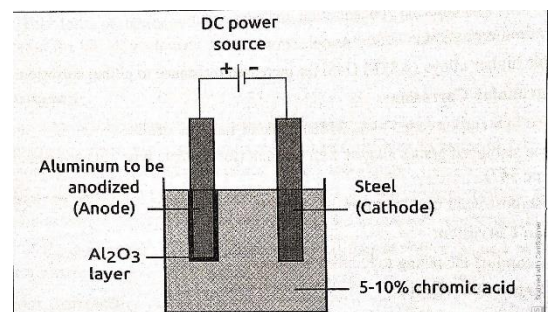
Electrolyte - 10% chromic acid

Temperature - 35°C

Current density of 10-20 mA/cm²

An oxide layer of 4 – 8 micro meter thickness is obtained.

Reactions:



Anodized aluminium is used in window frames, office partitions, house hold utensils etc.

Phosphating Or Phosphate Coatings:

Phosphate coating is obtained on steel surface by converting the surface metal atoms into their phosphates by chemical or electrochemical reactions. The phosphating bath contains

- Free phosphoric acid
- A primary metal phosphate like Fe, Zn or Mn
- An accelerator like such as nitrates, nitrites, chlorates etc

The pH is maintained between 1.8 and 3.2 and electrolysis is carried out at 35°C.

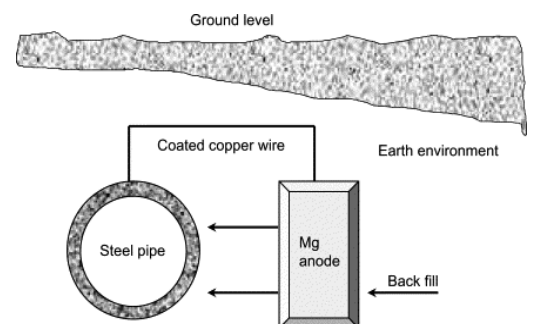
The most important application of phosphate coating is as an under layer for paint finishes. It is a standard pre-treatment before painting of automotive bodies and steel fabrications such as washing machines and refrigerators. It is widely applied for the protection of metal parts which cannot be painted or plated such as nuts, bolts and the moving parts of machinery.

CATHODIC PROTECTION:

Cathodic protection is a method of protecting a metal or an alloy from corrosion by converting it completely into cathode and no part of it is allowed to act as anode. Corrosion of a specimen occurs because of the flow of electrons from anodic to cathodic regions. The anodic region undergoes corrosion whereas cathodic region is unaffected. The technique of offering protection to specimen against corrosion by providing electrons from an external source is called cathodic protection. Cathodic protection is provided by Sacrificial anode method.

Sacrificial anode method:

In sacrificial anode method, the metal to be protected is connected to a more active metal which acts as auxiliary anode. Metals like Zn, Mg and Al being more active than iron act as anode and undergo preferential corrosion. They supply electrons to iron specimen which remains cathodic in the environment. This method is used to protect buried pipe lines storage tanks, ship hulls etc.

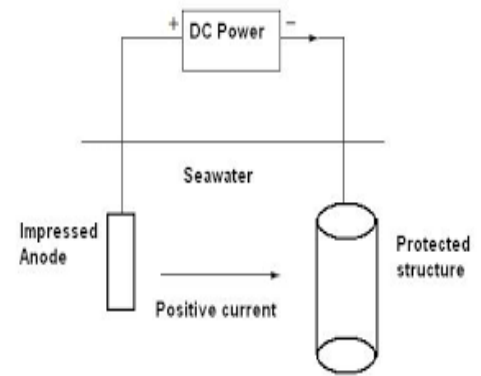


Impressed Voltage Method :

In this method, current is applied from opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. Thus electrons are supplied from an external source so that the object itself becomes cathodic and is not oxidized.

In Impressed Voltage Method the metal to be protected is connected to the negative (cathode) terminal of a DC source. The positive (anode) terminal is connected to an inert anode like graphite. DC current is applied to supply electrons to the metal to be protected.

Impressed Voltage/current Method is used to protect water storage tanks, marine structures and oil pipe lines. This method is particularly useful for large structures for long term operations.



Metal finishing

Metal finishing is a technique in which a metal is deposited on the surface of an object such as metal, alloy, plastic, ceramic, composite etc. in order to improve its surface properties.

Technological importance:

1. To offer corrosion resistance to the substrate metal Ex: Chromium plating on steel
2. To improve appearance of the substrate metal i.e., for decorative purposes

Ex: Au plating on Cu

3. To impart wear (abrasion) resistance Ex: Cr plating on wires
4. To induce specific thermal, optical and electrical properties.

5. Manufacture of electronic components, PCB's, capacitors, electro chemical machining, electro polishing, electrochemical etching, electroforming etc.

The above objectives can be achieved by

- (a) coating a single metal Cu, Cr, NI, Zn, Ag, Au etc. or
- (b) a combination of two metals Ni-Cr, CU-Zn, Pb-Zn etc.

Metal finishing is of two types 1. Electroplating. 2. Electroless plating

Electroplating, also known as electrochemical deposition or electrodeposition, is a process for producing a metal coating on a solid substrate through the reduction of cations of that metal by means of a direct electric current.

Uses of Electroplating - used in industry and decorative arts to improve the surface qualities of objects—such as resistance to abrasion and corrosion, lubricity, reflectivity, electrical conductivity, or appearance.

Electrolessplating is process of deposition of a metal from its salt solution on a catalytically active surface by employing a reducing agent without using electricity .Ex. Cu on PCB, Ni on Al etc.

Electroplating process

The electroplating process consists of an anode, a cathode and electrolyte (a conducting solution). Oxidation occurs at anode while reduction at cathode. The theoretical basis of electroplating is provided by Faraday's laws of electrolysis. The principle components of electroplating process include the following:

1. The coating metal or the inert metal forms the anode.
2. The base metal to be plated forms the cathode.
3. The electrolyte usually is a solution of metal. Buffer is added to maintain the pH and brightener's are added to get lustrous plating.
4. The plating bath generally called as VAT is constructed of a material which will not be attacked by the solution and which withstands temperature of operation. Materials used are steel or wood with rubber or PVC lining

Chromium plating:

The given metal object is subjected to cleaning with organic solvents to remove oil and grease and then subjected to cleaning with organic solvents to remove the corrosion products, washed with water and electroplating is carried out. If the plating is for decorative purposes, the article is first plated with copper and then with chromium. This will reduce the porosity of decorative chromium plating.

Plating bath composition – Chromic acid (CrO_3) and H_2SO_4 in 100:1 proportion

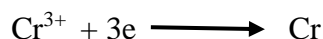
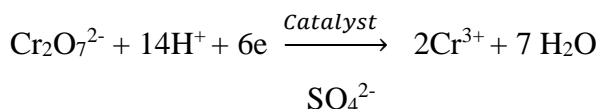
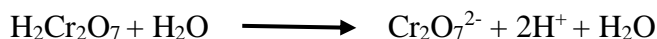
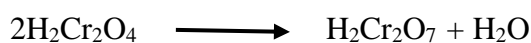
Operating temperature – 45 to 60°C

Current density – 100 to 200 mA/cm^2

Anode – Insoluble Pb –Sb , Pb-Sn coated with PbO_2

Cathode – Object to be plated

Reactions: $2\text{CrO}_3 + 2\text{H}_2\text{O} \longrightarrow 2\text{H}_2\text{Cr}_2\text{O}_4$



Chromium anode; is not used in chromium plating because chromium metal passivates strongly in acid sulphate medium.

Properties : Chromium plating gives hard, abrasion resistant and corrosion resistant surface as well as decorative finish.

Application: Chromium plating provides durable finish on cycles automobiles, furniture, house ;hold fittings,; surgical instruments. It is applied on cutting tools, piston rings, cylinder liners of diesel engines, machine tools etc.

Electroless plating:

It is the deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electricity. The reducing agent brings about the reduction of the metal ions which gets deposited over catalytically active surface.

Difference between electroplating and electroless plating

Electroplating	Electroless plating
Electrical power is required	Electrical power is not required
Bath has less throwing power	Bath has better throwing power
Driving force is electrolysis by passing electricity	Driving force is Autocatalytic reaction over catalytically active surface
Separate anode is necessary is required for anodic reaction	Anodic reaction takes place on the surface of the substrate

Advantages:

- It does not require electrical power.
- Non; metal surface such as semiconductor; and plastics can also be plated.
- Intricate parts can be uniformly coated.
- It gives better throwing power and more uniform coating over article irrespective of shape.

ELECTROLESS PLATING OF COPPER ON PCB'S

Activation: The surface is degreased followed by treatment by with acid .Copper electroless plating can be done on Ag, Au, Pt, Pd, Fe, Co, Ni etc in presence of reducing agent: plastics and PCB are activated by SnCl_2 followed by PdCl_2 .

Plating bath solution: CuSO_4 solution,

HCHO (Reducing agent),

NaOH and Rochelle salt (Buffer),

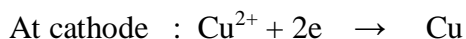
EDTA (Complexing agent & exaltant),

Na_2CO_3 , thiourea (stabilizer)

pH - 11 to 11.5

Temperature - 25°C

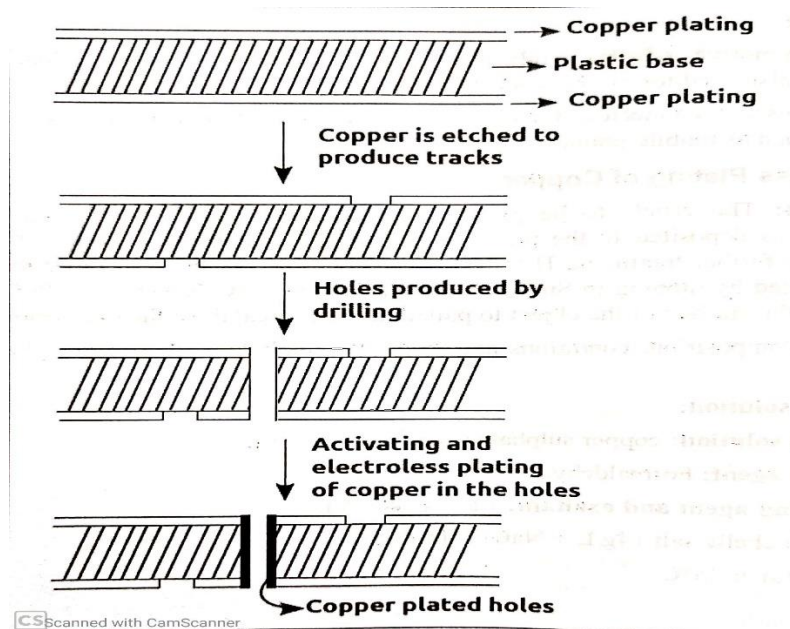
Reactions:



Application: Electroless plating of PCB where plating through holes is required.

Plating through holes

- Object is first electroplated with copper to 5 – 100 micro meter thickness.
- Selected area are protected by a photo resist or electroplated image and the rest of copper is etched away to produce circuit pattern.
- Connection between both sides is made by drilling.
- Subjected to electro less plating after activation using CuSO_4 , HCHO , NaOH , Rochelle salt, complexing agent and exultant.



Application: Applied on wave guides, for decorative on plastics and for decorative plating on plastics and for PCB's

Questions

1. Explain the construction and working of Calomel electrode. Mention its advantages.
2. Define concentration cell. Explain the determination of EMF of a Concentration cell with an example.
3. What are Ion selective electrodes? Explain the construction and working of Glass electrode. Mention its advantages and limitations.
4. Explain the determination of pH of a solution using glass electrode.

5. Define corrosion. Explain electrochemical theory of corrosion.
6. Define corrosion. Explain differential metal corrosion.
7. Discuss differential aeration corrosion, taking examples of pitting and water line corrosion.
8. Describe stress corrosion. Explain caustic embrittlement in boilers
9. Explain the following factors affecting the rate of corrosion.
 - Electrode Potential
 - Relative size of anode and cathode.
 - Nature of corrosion product.
 - pH
 - Temperature
 - Humidity
10. What is inorganic coating? Explain anodizing and phosphating.
11. What is cathodic protection? Explain the sacrificial anode method.
12. What is cathodic protection? Explain the impressed current method.
13. Explain the term metal finishing. Discuss its Technological importance.
14. Give brief accounts and application of electroplating of chromium.
15. What is electroless plating? How is it different from electroplating process?
16. Give an account of electroless plating of copper on PCB.

Numerical Problems for CPR Calculation

1. A piece of corroded metal alloy plate was found in a submersed ocean vessel, it was estimated that the original plate was 800 cm² and that approximately 7.6 Kg had corroded away during the submersion, assuming a corrosion penetration rate of 4 mm/yr for this alloy in seawater, estimate the time of submersion in years, the density of alloy is 4.5 g/cm³.
2. A thick steel sheet of area 100 in² is exposed to air near the ocean, after one year period it was found to experience a weight loss of 485 g due to corrosion, to what rate of corrosion in mpy and mm/yr does this correspond?