UNIT-II

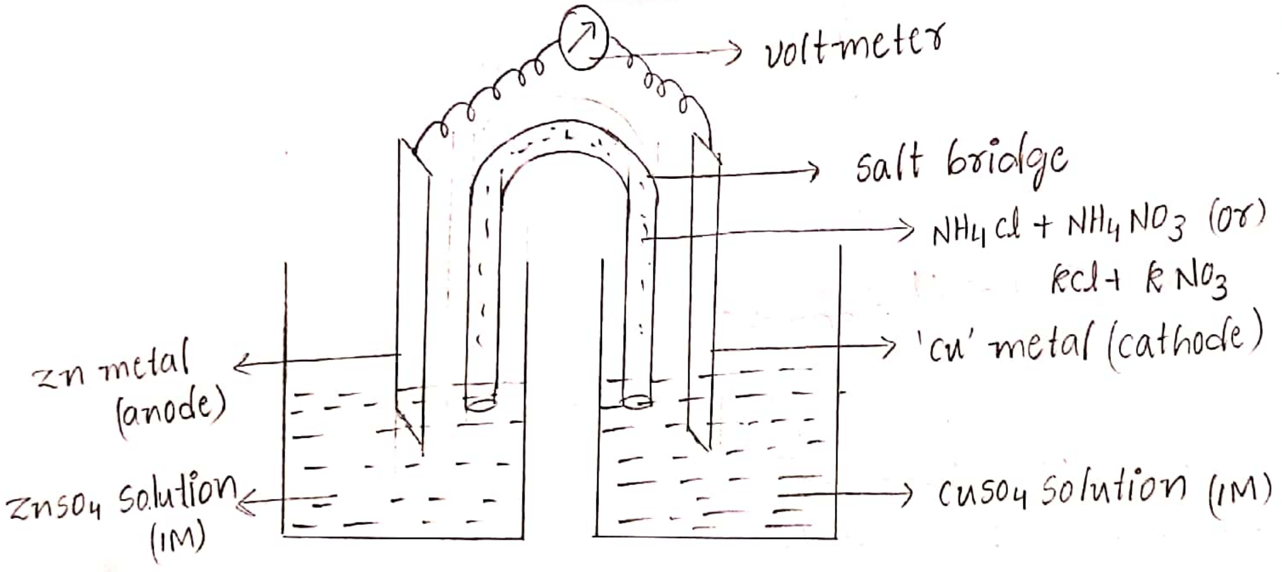
ELECTROCHEMICAL CELLS AND CORROSION

①

Introduction: Electro chemistry is the branch of physical chemistry which explains electricity and chemical reaction.

Electro chemical cells:

A device which converts chemical energy into electrical energy by spontaneous redox reaction is known as electro chemical cell (or) voltaic cell (or) galvanic cell (or) Daniel cell.



It consists of two half cells the half cell on the left side consists a 'zinc metal electrode' dipped in '$ZnSO_4$' solution. The half cell on the right side consists a 'cu' electrode dipped in $CuSO_4$ solution. These two half cells are joined by salt bridge. In which zn and cu electrodes are connected to voltmeter and electrolytes ($ZnSO_4$, $CuSO_4$) connected by salt bridge.

Cell Representation:

⟹ Anode half cell is written on left hand side and cathode half cell is written on right hand side.

⟹ Anode is represented by first metal electron and then electrolyte. These two are seperated by vertical line (or) semi colon.

$$Zn / ZnSO_4 \quad (or) \quad Zn ; ZnSO_4$$

⟹ cathode is represented by first metal electron and then electrolyte. These two are seperated by vertical (or) semi colon

$$CuSO_4 / Cu \quad (or) \quad CuSO_4 ; Cu$$

⟹ These two ~~cell~~ are seperated by salt bridge which is indicated by double vertical line.

Cell reaction – $Zn / \underset{(1M)}{ZnSO_4} // \underset{(1M)}{CuSO_4} / Cu$

Oxidation half cell reaction: 'zinc metal' acts as anode undergoes oxidation reaction by losing of electrons to form 'Zn^{+2}'.

At anode: $Zn \longrightarrow Zn^{+2} + 2e^-$ (oxidation)

Reduction half cell reaction: 'copper metal' acts as cathode undergoes reduction reaction by gainning of electrons to form 'Cu'.

At cathode: $Cu^{+2} + 2e^- \longrightarrow Cu$ (reduction)

Net Reaction:

$$Zn \longrightarrow Zn^{+2} + 2e^-$$
$$Cu^{+2} + 2e^- \longrightarrow Cu$$
$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

Role of salt bridge: salt bridge is inverted U-shaped tube which have KCl, KNO_3 and gelatin (or) NH_4Cl, NH_4NO_3 and gelatin. is gel state is known as "agar agar gel"

⟹ It prevents accumulation charge of liquid junction potential

⟹ It allows electrons from anode to cathode.

⟹ It does not allows electrolyte substance from anode to cathode.

Single electrode potential:

when a metal rod dipped in its salt solution The metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction) the process of oxidation (or) reduction depends on the nature of metal. In this process there develops a potential between the metal atoms and its corresponding ions called the electrode potential. There is a between metal and metal ion and the potential value of electrolyte is zero and hence is called single electrode potential. It is measured in volts.

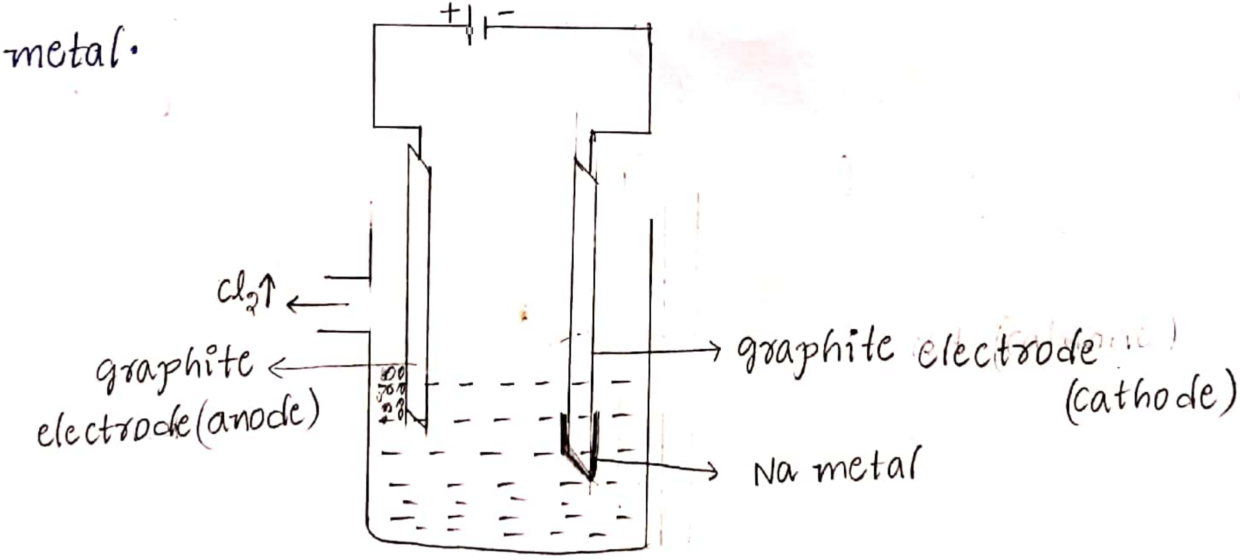
Electrolytic cell (or) irreversible cell:

A device which converts electrical energy into chemical energy by spontaneous redox reaction is called electrolytic cell (or) irreversible cell.

Electrolysis of fused Nacl:

In this process two platinum electrodes are immersed into fused Nacl electrolyte solution, in this two platinum electrodes are connected to battery. positive cell terminal connected platinum electrode acts as anode and undergoes oxidation, negative cell terminal acts as cathode and undergoes reduction.

At anode position chloride irons combine to release Cl_2 gas, at cathode position sodium ions gains electrons to form sodium metal.



Ionisation reaction: $2NaCl \rightleftharpoons 2Na^+ + 2Cl^-$

At anode: $2Cl^- \longrightarrow Cl_2\uparrow + 2e^-$ (oxidation)

At cathode: $2Na^+ + 2e^- \longrightarrow 2Na$ (reduction)

∴ Net reaction: $2Cl^- \longrightarrow Cl_2\uparrow + \cancel{2e^-}$

$2Na^+ + \cancel{2e^-} \longrightarrow 2Na$

$$2Na^+ + 2Cl^- \longrightarrow 2Na + Cl_2\uparrow$$

Electro chemical series (galvanic series):

A series of metals arranged in increasing order of standard reduction potential and decreasing order of standard oxidation potential is known as "<u>electro chemical series</u>"

$$\left.\begin{array}{lcl}
Li & \longrightarrow & Li^{+1} + 1e^{\ominus} \\
K & \longrightarrow & K^{+1} + 1e^{\ominus} \\
Ca & \longrightarrow & Ca^{+2} + 2e^{\ominus} \\
Na & \longrightarrow & Na^{+1} + 1e^{\ominus} \\
Mg & \longrightarrow & Mg^{+2} + 2e^{\ominus} \\
Al & \longrightarrow & Al^{+3} + 3e^{\ominus} \\
Zn & \longrightarrow & Zn^{+2} + 2e^{\ominus} \\
Cr & \longrightarrow & Cr^{+3} + 3e^{\ominus} \\
Fe & \longrightarrow & Fe^{+2} + 2e^{\ominus} \\
Sn & \longrightarrow & Sn^{+2} + 2e^{\ominus} \\
Pb & \longrightarrow & Pb^{+2} + 2e^{\ominus}
\end{array}\right\} \text{ANODE}$$

$$H_2 \longrightarrow 2H^{\oplus} + 2e^{\ominus} \quad \Big\} \text{ BOTH ANODE AND CATHODE}$$

$$\left.\begin{array}{lcl}
Cu & \longrightarrow & Cu^{+2} + 2e^{\ominus} \\
Ag & \longrightarrow & Ag^{+1} + 1e^{\ominus} \\
Fe & \longrightarrow & Fe^{+3} + 3e^{\ominus} \\
Pt & \longrightarrow & Pt^{+3} + 3e^{\ominus}
\end{array}\right\} \text{CATHODE}$$

Significance:

1. we understood reactivity of the metals

2. Hydrogen acts as both anode and cathode because of which undergoes oxidation, reduction reaction.

3. Above the hydrogen element the metals acts as anode undergoes oxidation reaction which have negative electrode potential value.

4. below the hydrogen element the metals acts as cathode undergoes reduction reaction which have positive electrode potential value.

5. we should calculate electro motive force EMF using electro chemical series

$$\boxed{EMF = E_{cathode} - E_{anode}}$$

6. In metallurgy concept we should seperate metals from ore.

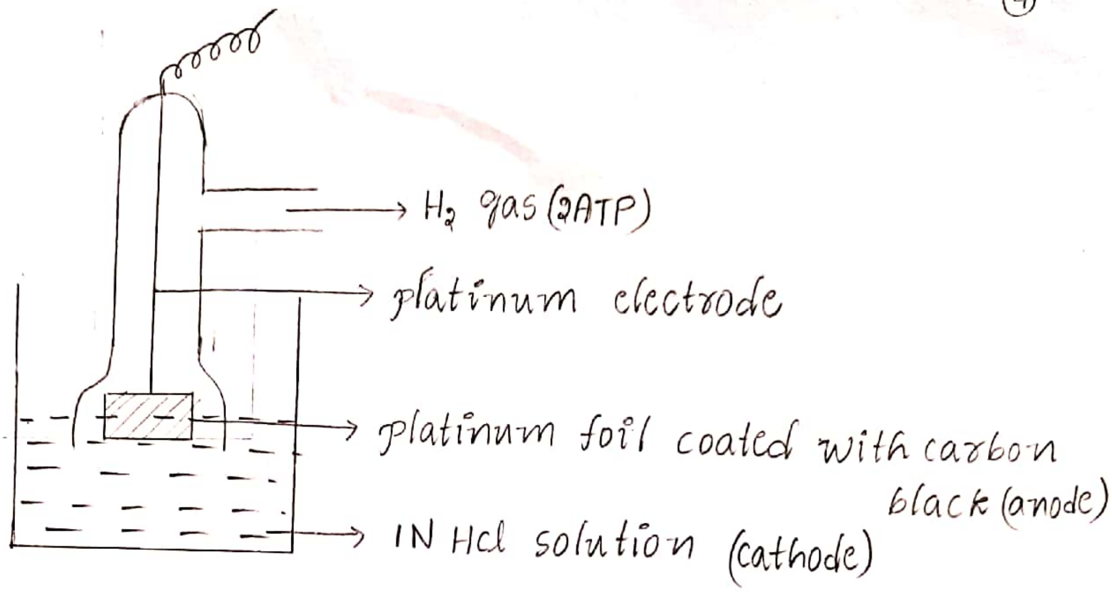
7. Above the hydrogen element which acts as anode undergoes rapid corrosion when compared to lower position of metals.

Standard hydrogen electrode (or) normal hydrogen electrode:

Placing platinum foil into 1N of Hcl solution. The foil is coated with carbon black powder which absorbs hydrogen gas. The foil is closed with open bell like glass tube which have inlead for the supplying of hydrogen gas at 2ATP. The platinum foil absorbs hydrogen gas then converted into hydrogen electrode.

1. Here, hydrogen electrode acts as anode.

2. The electrolyte solution acts as cathode.

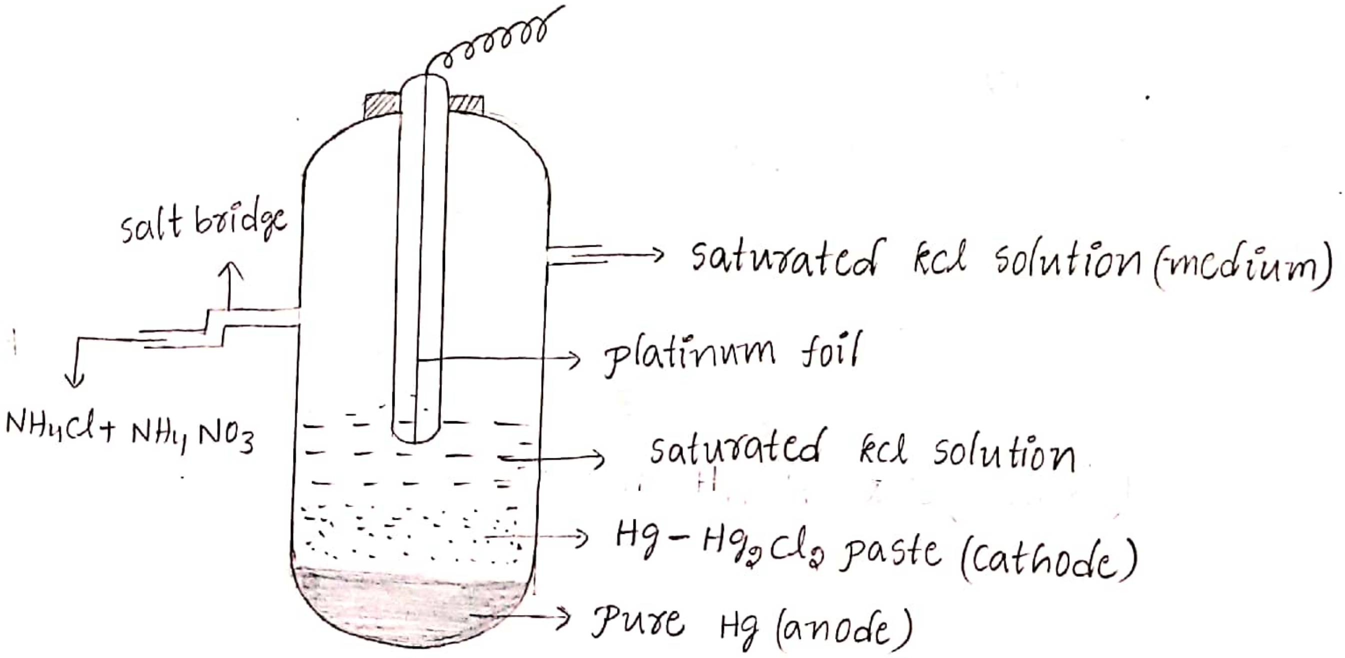


At anode: $H_2 \longrightarrow 2H^+ + 2e^-$ (oxidation)

At cathode: ~~$2H^+$~~ $2H^+ + 2e^- \longrightarrow H_2 \uparrow$ (reduction)

$\Longrightarrow$ Here, net reaction is 'zero', the electrode potential also zero.

Calomel electrode (or) Hg - Hg_2Cl_2 electrode:



Construction:

It consists along glass tube the bottom to the glass is filled with pure 'Hg' above the pure Hg mecury-mercurous chloride electrode. The remaining portion of the tube is filled with saturated kcl solution. The glass having two inllets. one is used for filled saturated kcl and another one is acts as salt bridge. The platinum electrode immersed in the tube upto the paste.

⇒ The potential calomel electrode is depends on concentration of kcl solution.

⇒ If we take saturated kcl solution then the E° value is '0'v.

working:

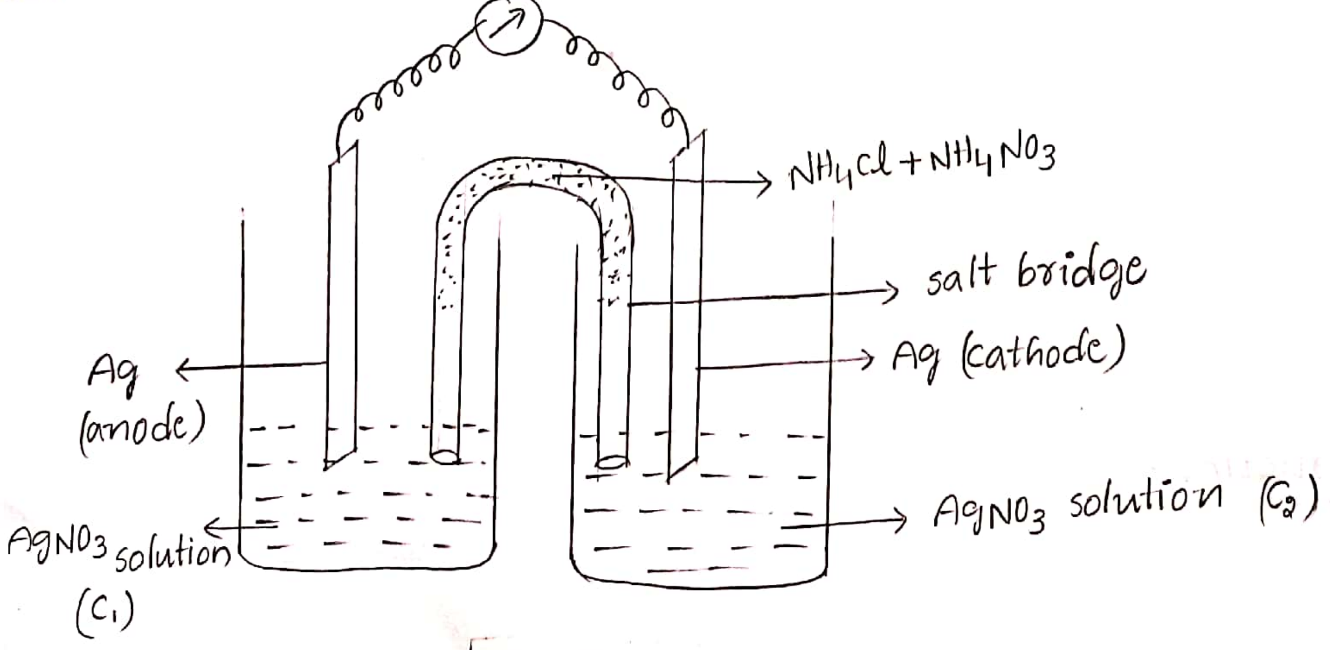
At anode: $2Hg \longrightarrow Hg_2^{+2} + 2e^-$ (oxidation)

At cathode: $Hg_2^{+2} + 2e^- \longrightarrow 2Hg$ (reduction)

⇒ The net reaction is zero. so, electrode potential is zero.

Concentration cell:

A device which converts chemical energy into electrical energy by spontaneous redox reaction. Here, the concentration of electrolyte is different is known as concentration cell.



⇒ $C_2 > C_1$

operator: In which electrodes are same and electrons are also same but concentrations are different c_1 and c_2. In which $c_2 > c_1$.

At anode: $Ag_{(c_1)} \longrightarrow Ag^{+1}_{(c_1)} + 1e^-$ (oxidation)

At cathode: $Ag^{+1}_{(c_2)} + 1e^- \longrightarrow Ag_{(c_2)}$ (reduction)

net reaction:

$$Ag(c_1) \longrightarrow Ag^{+1}_{(c_1)} + \cancel{1e^-}$$

$$Ag^{+1}_{(c_2)} + \cancel{1e^-} \longrightarrow Ag(c_2)$$

$$\overline{Ag(c_1) + Ag^{+1}_{(c_2)} \longrightarrow Ag^{+1}_{(c_1)} + Ag_{(c_2)}}$$

According to "nernest equation"

$$\Longrightarrow EMF = E^\circ + \frac{0.0592}{n} \log(k)$$

$$\Longrightarrow EMF = E_R - E_L$$

Cell representation: $Ag(c_1) / AgNO_3(c_1) // AgNO_3(c_2) / Ag_{(c_2)}$

$$E_R = E^\circ + \frac{0.0592}{n} \log(c_2)$$

$$E_L = E^\circ + \frac{0.0592}{n} \log(c_1)$$

$$EMF = E_R - E_L$$

$$= \cancel{E^\circ} + \frac{0.0592}{n} \log(c_2) - \cancel{E^\circ} - \frac{0.0592}{n} \log(c_1)$$

$$= \frac{0.0592}{n} \left[\log(c_2) - \log(c_1)\right]$$

$$\boxed{EMF = \frac{0.0592}{n} \log\left(\frac{c_2}{c_1}\right)}$$

Battery : A device which converts chemical energy into electrical energy is known as battery. Battery principle is same to electrochemical cell.

The batteries are two types ~~p~~, they are

1. Primary battery
2. Secondary battery

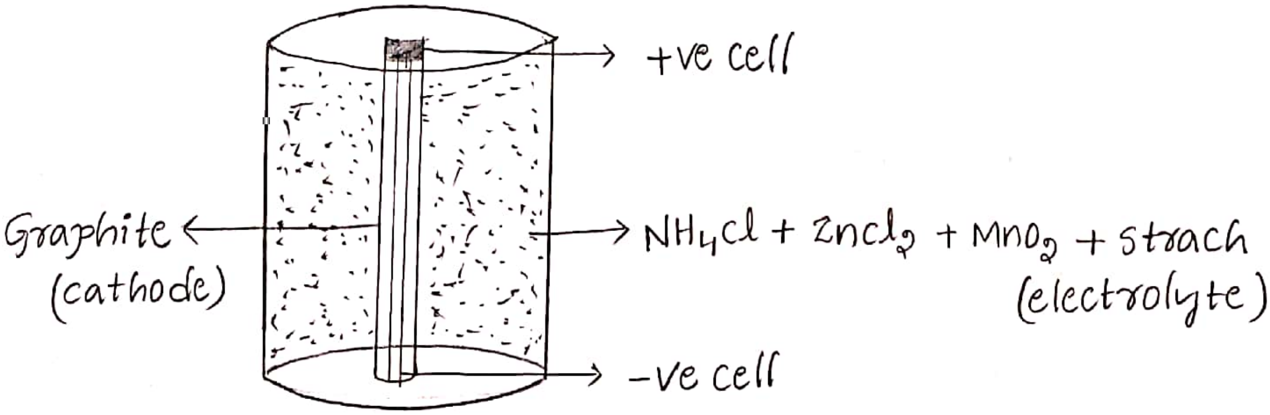
1. **Primary battery:** The starting stage of batteries (or) non-rechargable batteries is known as primary batteries

ex: dry cell Lechlance cell, zinc air cell

2. **Secondary battery:** Present using batteries (or) rechargable batteries is known as secondary batteries.

ex: nickel - cadmium cell, nickel metal hydride cell

Dry cell (or) Lechlanche cells:



Zinc can acts as anode undergoes oxidation. Graphite rod acts as cathode but it does not undergoes reduction reaction because of it is a non-metallic element.

The mixture of NH_4Cl, $ZnCl_2$, MnO_2 and small amount of starch powder acts as electrolyte which undergoes reduction reaction.

At anode: $Zn \longrightarrow Zn^{+2} + 2e^-$ (oxidation)

At cathode: $2NH_4^+ + 2MnO_2 + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$ (reduction)

Net Reaction:

$$Zn \longrightarrow Zn^{+2} + 2e^-$$

$$2NH_4^+ + 2MnO_2 + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$$

$$Zn + 2NH_4^+ + 2MnO_2 \longrightarrow Zn^{+2} + Mn_2O_3 + 2NH_3 + H_2O \; (1.6V)$$

Advantages:

1. It is low price.
2. It given 1.5 volt of voltage.
3. These are nontoxic batteries.

uses: It is used in electronic devices like calculator radios, wall locks, vacmens ..etc.

Nickel cadmium cells (Ni-CD):

It is an example of example of secondary cell (or) battery. In this cell cadium metal acts as anode undergoes oxidation and nickel oxi hydroxide

$NiO(OH)_2$ acts as cathode undergoes reduction and alkaline Potassium hydroxide (KOH) acts as electrolyte.

The power out for these batteries is 1.4V

At anode: $Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$ (oxidation)

At cathode: $2NiO(OH)_2 + 2H_2O + 2e^- \longrightarrow 2Ni(OH)_2 + 2OH^-$ (reduction)

Net reaction: $Cd + \cancel{2OH^-} \longrightarrow Cd(OH)_2 + \cancel{2e^-}$

$$2NiO(OH)_2 + 2H_2O + \cancel{2e^-} \longrightarrow 2Ni(OH)_2 + \cancel{2OH^-}$$

$$Cd + 2NiO(OH)_2 + 2H_2O \longrightarrow Cd(OH)_2 + 2Ni(OH)_2 \quad [1.4V]$$

uses:

1. These are used in medical applications.
2. These are used in research equipment.
3. These are used in high quality Lab equipments.

Nickel-metal hydrides cell ($Ni-MH_2$):

In this cell MH_2 acts as anode undergoes oxidation and nickel oxihydroxide [$NiO(OH)_2$] acts as cathode undergoes reduction and electrolyte solution is alkaline KOH solution. These batteries are recharging power is 1.2V

At anode: $MH + OH^- \longrightarrow M + H_2O + 1e^-$ (oxidation)

At cathode: $NiO(OH) + H_2O + 1e^- \longrightarrow Ni(OH)_2 + OH^-$ (reduction) net reaction:

$$MH + OH^- \longrightarrow M + H_2O + 1e^-$$

$$NiO(OH) + H_2O + 1e^- \longrightarrow Ni(OH)_2 + OH^-$$

$$MH + NiO(OH) \longrightarrow M + Ni(OH)_2 \quad (1.2V)$$

uses:

1. It is used in electronic devices like computers.
2. It also used in electrical vehicles.

Lithium ion cell ($Li-MnO_2$ cell): In this cell Lithium metal acts as anode and undergoes oxidation and MnO_2 acts as cathode undergoes reduction and Lithium metal is organic solvent in electrolyte.

The power output for this cell is [1.3V]

At anode: $Li \longrightarrow Li^{+1} + 1e^-$ (oxidation)

At cathode: $MnO_2 + Li^{+1} + 1e^- \longrightarrow Li-MnO_2$ (reduction)

Net reaction: $Li \longrightarrow \cancel{Li^{+1}} \cancel{+1e^-}$

$$MnO_2 + \cancel{Li^{+1}} \cancel{+1e^-} \longrightarrow Li-MnO_2$$

$$Li + MnO_2 \longrightarrow Li-MnO_2 \quad (1.3V)$$

Applications:

1. These are used in automatic cameras.
2. Conic types of lithium cells are used in rist watches and calculators.

Zinc air cells: In the type of primary cell, the cell of zinc metal acts as anode undergoes oxidation and porous carbon plate acts as cathode undergoes reduction and alkaline KOH acts as electrolyte.

At anode: $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$ (Oxidation)

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

Net reaction:

$$
\begin{array}{l}
Zn + \cancel{2OH^-} \longrightarrow ZnO + \cancel{H_2O} + \cancel{2e^-} \\
\frac{1}{2}O_2 + \cancel{H_2O} + \cancel{2e^-} \longrightarrow \cancel{2OH^-} \\
\hline
Zn + \frac{1}{2}O_2 \longrightarrow ZnO \quad (1.5V) \\
\hline
\end{array}
$$

⇒ The power output for this cell is – 1.5V

Applications:

1. These are used in milaitary voice transmitters.
2. It is also used in electronic pagers.

Fuel cells:

A fuel cell is an electrochemical cell which converts chemical energy into electrical energy by using fuel in the presence of oxygen and hydrogen gases respectively.

The basic principles of fuel cells are identical to those of the electro- chemical cells.

The fuel and the oxidising agents are continuously and seperately supplied to the electrodes of cell, at which they undergo reactions. Fuel cells are capable of supplying current as long as the reactants are supplied.

∴ Fuel cells are characterised by

1. high energy efficiency.
2. Low noice Level
3. no thermal pollution

Hydrogen - oxygen fuel cells (H_2-O_2) :

In this fuel cell, 2 porous graphite electrodes coated with platinum particles acts as anode and cathode. The electrolyte solution is 2.5% of KOH solution means 2.5g KOH present in 100ml of water.

At anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$ (oxidation)

At cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (reduction)

net reaction:

$$
\begin{aligned}
2H_2 + \cancel{4OH^-} &\longrightarrow 4H_2O + \cancel{4e^-} \\
O_2 + 2H_2O + \cancel{4e^-} &\longrightarrow \cancel{4OH^-} \\
\hline
2H_2 + O_2 &\longrightarrow 2H_2O \quad (1.23V)
\end{aligned}
$$

⟹ The power output is 1.23V

Applications :

1. As an auxiliary energy source in space vehicle, submarines... ..etc.
2. Because of light weight, these are preferred for space craft. and product H_2O is a valuable fresh water for astronauts.

Advantages :

1. Energy conversion is very high.
2. Noise & thermal pollution are low.

3. Maintanance cost is Low.

4. Product H_2O, is a drinking water source for astronouts.

Limitations:

1. The lifetime of fuel cell is not accurately known.
2. This initial cost is high.

Methyl alcohol oxygen fuel cell (CH_3OH-O_2): [alkaline fuel cell]

Materials: 2 porous nickel plate, one porous nickel plate is coated imprignated with platinum particle which acts as anode, another porous nickel plate is coated with silver particles acts as cathode. The electrolyte solution is saturated KOH solution.

At anode:

$$CH_3OH + 6OH^- \longrightarrow CO_2 + 5H_2O + 6e^- \text{ (oxidation)}$$

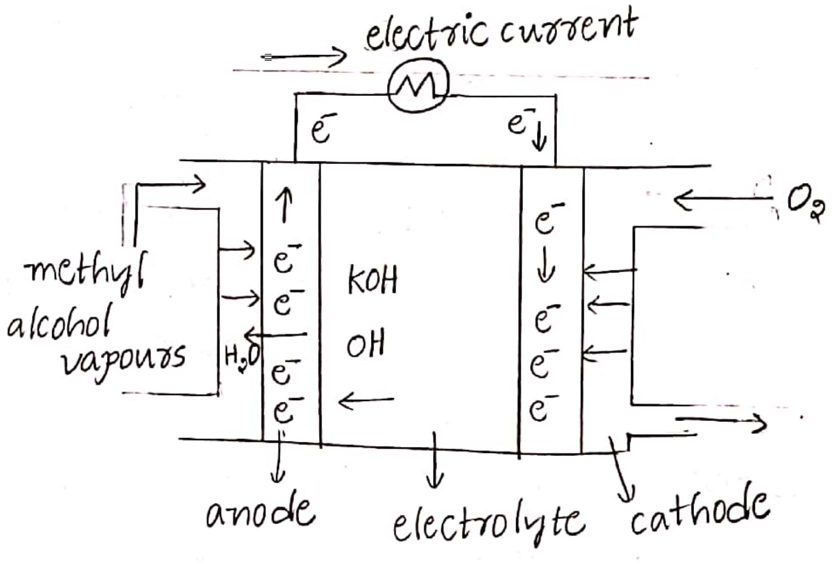
At cathode: $\frac{3}{2}O_2 + 3H_2O + 6e^- \longrightarrow 6OH^-$ (reduction)

net reaction:

$$CH_3OH + \cancel{6OH^-} \longrightarrow CO_2 + 5H_2O + \cancel{6e^-}$$

$$\frac{3}{2}O_2 + 3H_2O + \cancel{6e^-} \longrightarrow \cancel{6OH^-}$$

$$CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O$$



Advantages:

1. These cells are stable at all environmental conditions.
2. Easy to transport.
3. Less risk to aquatic plants, animals ...etc.
4. Because methanol possess lower inflamability limit than gasoline it posses less fire risk than gasoline.
5. B'co₂ of high hydrogen concentration in methanol it is an excellent fuel.

Phosphoric Acid fuel cells (PAFC):

In phosphoric acid fuel cell, 2 porous carbon plates coated with platinum particles acts as anode & cathode. The electrolyte solution is a mixture of phosphoric acid & silica carbide matrix (SiC_2) The power output is 100 - 400 kw. power output is very high due to it is strong acid acts as a electrolyte.

At anode: $2H_2 \longrightarrow 4H^+ + 4e^-$ (oxidation)

At cathode: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ (reduction)

net reaction:

$$2H_2 \longrightarrow \cancel{4H^+} + \cancel{4e^-}$$

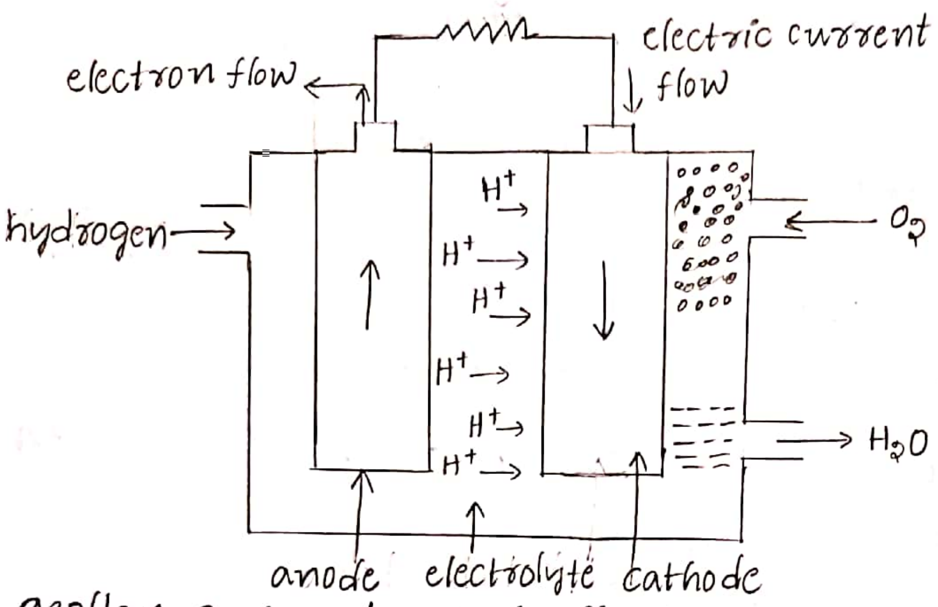
$$O_2 + \cancel{4H^+} + \cancel{4e^-} \longrightarrow 2H_2O$$

$$2H_2 + O_2 \longrightarrow 2H_2O \ (100 - 400Kw)$$

Applications:

1. Phosphoric acid fuel cells are used for stationary power generation with output 100kw to 400kw

2. used for Large vehicles as buses.



Molten carbonate fuel cells (MCFC): In this fuel cell, one porous nickel plate is imprignated with platinum particles acts as anode, another porous nickel plate is coated with Lithinated nickel oxide acts as cathode. The electrolyte solution is sodium Potassium carbonate and ciramic cell ($LiAlO_2$).

At anode: $H_2 + CO_3^{-2} \longrightarrow H_2O + CO_2 + 2e^-$ (oxidation)

At cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \longrightarrow CO_3^{-2}$ (reduction)

Net reaction:

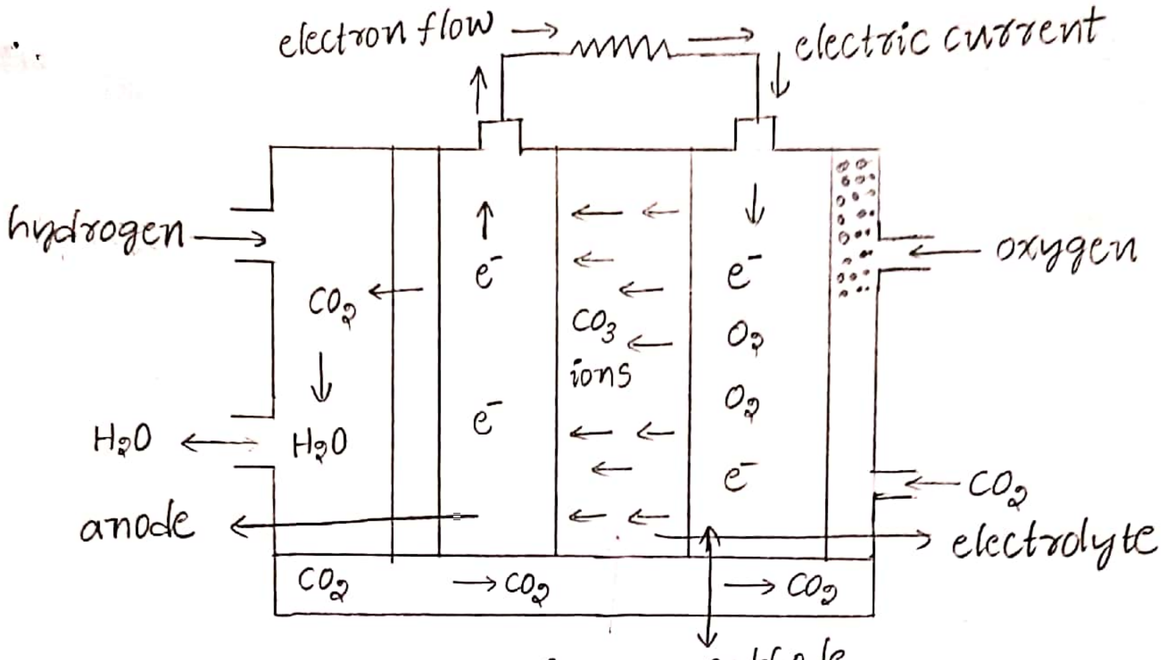
$$H_2 + \cancel{CO_3^{-2}} \longrightarrow H_2O + \cancel{CO_2} + \cancel{2e^-}$$

$$\frac{1}{2}O_2 + \cancel{CO_2} + \cancel{2e^-} \longrightarrow \cancel{CO_3^{-2}}$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

Applications:

Molten carbonate fuel cells are used in many industries to produce electric power via steam turbines.



corrosion

Corrosion: The process of destruction (or) deteriation of metals quantity by the action of environment is known as corrosion

ex: 1. Iron form reddish brown colour precipitate in its surface is known as rusting of iron $[Fe_2O_3 \cdot x \cdot H_2O]$.

2. copper forms greenish colour layer in its surface is known as rusting of copper (Cu_2O)

Theories of corrosion:

1. Acid – theorey corrosion: The metals interacts with atmosphere gases like carbon dioxide, water vapour and oxygen gas to form metallic carbonic acids. Furthur ;carbonic acid generates corrosion to the metal.

ex: $Fe + H_2O + 2CO_2 + \frac{1}{2}O_2 \longrightarrow Fe(HCO_3)_2$

Iron carbonic acid.

Dry theory (or) Direct chemical attack theorey of corrosion:

Dry corrosion

- oxidation corrosion
- corrosion with other gases
- Liquid metal corrosion

1. oxidation corrosion: Metals reacts with dry atmospheric oxygen to form a metal oxide layer on it's surface.

At anode: $M \longrightarrow M^{+n} + ne^-$ (oxidation)

At cathode: $\frac{1}{2}O_2 + ne^- \longrightarrow O^{-2}$ (reduction)

$$M + \frac{1}{2}O_2 \longrightarrow M^{+n} + O^{-2} \longrightarrow \underbrace{M_2O_3}_{}$$

metal oxide layer

Nature of M_2O Layer:

1. Stable, non-porous: If the M_2O Layer is stable and non-porous which is protective and acts as a barier between metal and environment, that means M_2O layer prevents the further corrosic of metal.

ex: copper, aluminium

2. unstable M_2O Layer:

If the M_2O Layer is unstable then it is immediately decomposer does not takes place oxygen. In this metal corrosion does not take place.

ex: gold, platinum

3. **volatile nature:** If the metal oxide Layer is volatile in nature rapid corrosion takes place.

ex: MO

4. **stable porous:** If the M_2O 8 Layer is stable and porous which increase the further corrosion of the metal.

ex: chromium

2. **Corrosion with other gases:** In this concept metals interacts with other gases like chlorine, flourine, CO_2, sulphur dioxide, NOX to form protective and non-protective Layer.

ex: $2Ag + Cl_2 \longrightarrow 2AgCl$ (protective)

$Sn + Cl_2 \longrightarrow SnCl_2$ (non-protective)

In above two example silver metal interacts with chlorine gas to form protective layer but interacts with stanum metal to form non-protective Layer.

3. **Liquid metal corrosion:**

All the metals are solids at room temperature except of mercury. The mercury interact with ~~Layer~~ other metals to form amalgam except of iron, platinum is known Liquid metal corrosion.

⟹ This amalgum is useful in dental treatment to full fill cavity present in teeth.

wet theorey (or) electrochemical attack theory:

In electrochemical theorey metals acts as anode undergoes oxidation and environment it acts as cathode undergoes reduction reaction in two cases those are acidic environment, basic (or) neutral environment.

At anode: $M \longrightarrow M^{+n} + ne^{\ominus}$ (oxidation)

At cathode:

case-i : $2H^+ + 2e^- \longrightarrow H_2 \uparrow$ (reduction)

case-ii : $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$ (reduction)

Rusting of iron:

The iron metal interacts with basic (or) neutral environment to form yellow colour ferrous hydroxide. Immediately it loses water molecules to get reddish brown colour precipitate ~~tio~~ as a rust ($Fe_2O_3 \cdot xH_2O$)

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

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

net reaction:

$$Fe \longrightarrow Fe^{+2} + \cancel{2e^-}$$

$$\frac{1}{2}O_2 + H_2O + \cancel{2e^-} \longrightarrow 2OH^-$$

$$Fe + \frac{1}{2}O_2 + H_2O \longrightarrow Fe^{+2} + 2OH^- \longrightarrow \underbrace{Fe(OH)_2}_{\text{yellow colour}}$$

$$\Longrightarrow 2Fe(OH)_2 \xrightarrow[-H_2O]{} \underbrace{Fe_2O_3 \cdot xH_2O}_{\text{reddish brown colour.}}$$

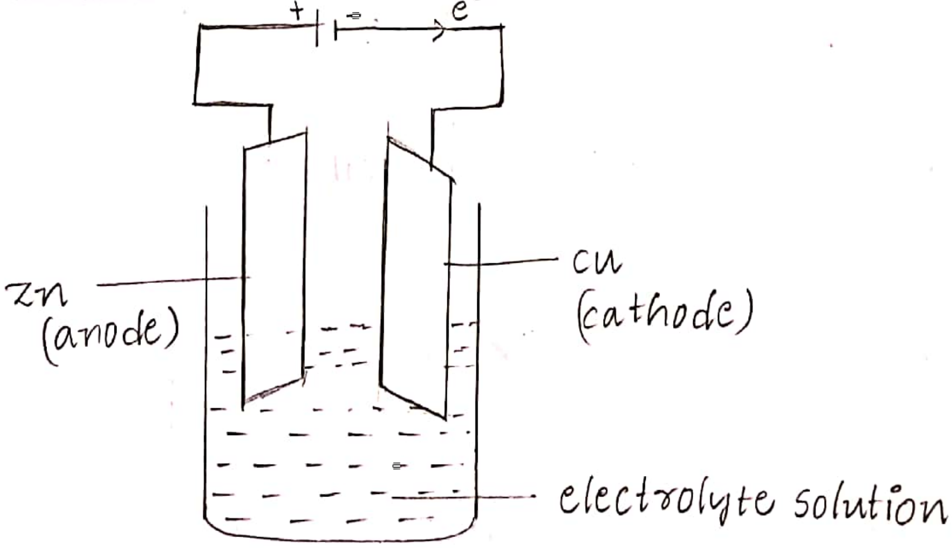
Formation of different types of cells during corrosion: ⑰

There are four types of cells.

1. Different metal corrosion.
2. Different aeration (or) concentration cell corrosion.
3. water line corrosion.
4. Stress corrosion.

1. Different metal corrosion:

Whenever two different metals placed in electrolyte solution connected with electrically. According to electrochemical series out of these two metals one metal acts as anode (zinc) undergoes corrosion, another metal acts as cathode (copper) does not undergoes corrosion is known as "different metal ~~coroco~~ corrosion"

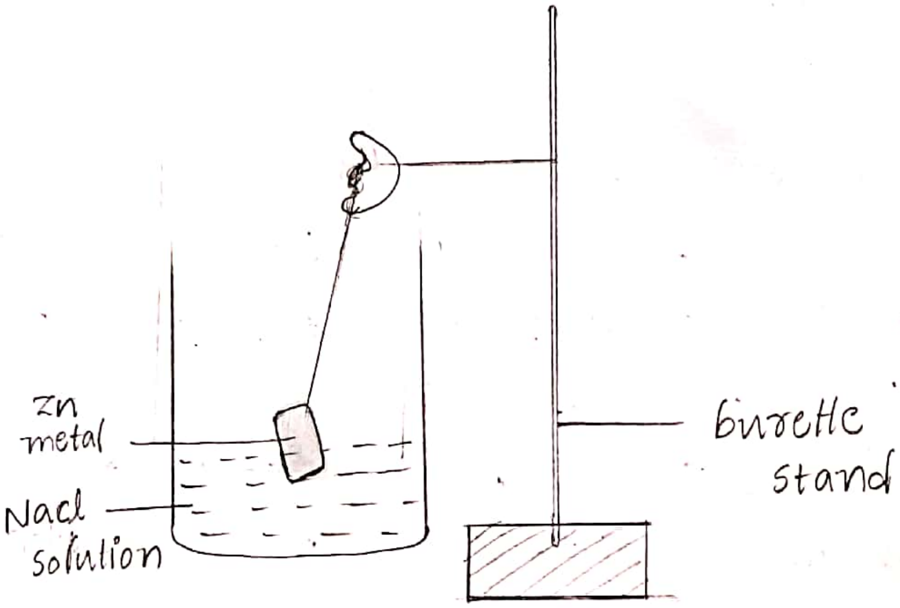


At anode: $zn \longrightarrow zn^{+2} + 2e^-$ (oxidation)

At cathode: $cu + 2e^- \longrightarrow cu$ (reduction)

2. Different aeration (or) concentration cell corrosion:

In this cell is prepared by the concentration of electrolyte solution. Zinc metal dipped in Nacl solution is partially here ~~un~~dipped portion of zinc metal acts as anode undergoes corrosion and undipped portion of zinc metal acts as cathode does not undergoes corrosion.

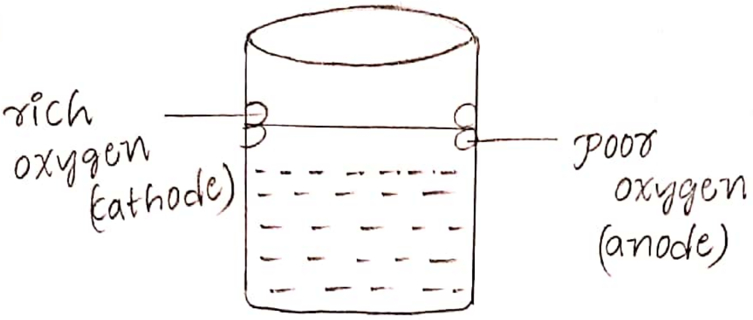


At anode: $Zn \longrightarrow Zn^{+2} + 2e^-$ (oxidation)

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

3. Water Line corrosion: In this cell is prepared by concentration of oxygen level

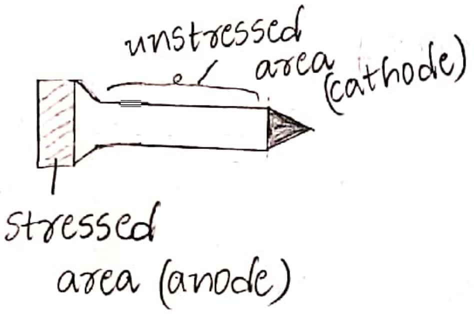
example: Take a water container which is filled with water below the water level is poor oxygenated part acts as anode undergoes corrosion and above the water level is rich oxygen part acts as cathode does-not undergoes corroison.

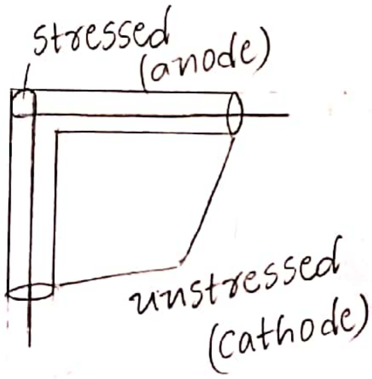


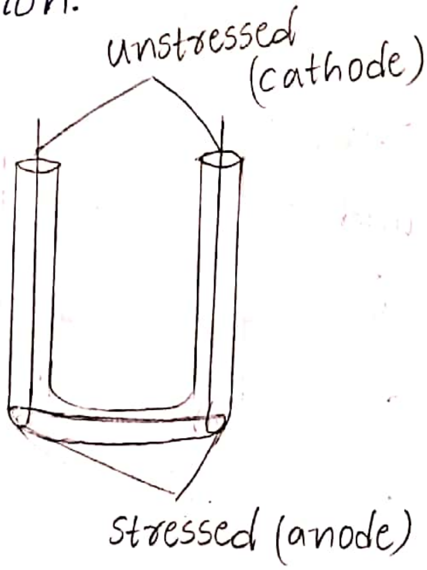
4. Stress corrosion:

Stress cells are prepared by stressing

example: In a nail, head and tail part is stressed area acts as anode undergoes corrosion. The remaining body is unstressed area acts as cathode does not undergoes corrosion.







Passivity of metals:

The process in which a metal exhibits higher corrosion resistance is called "passivity of metal."

When a stable, non-porous and higher protective M_2O layer is formed on the surface of it is called "Passivity". This metal M_2O Layer is formed a barrier between metal and environment and protective the metal form corrosion. This property is called "passivity."

Factors influencing rate of corrosion:

1. Nature of metal
2. Nature of environment

Nature of metal:

a) Physical state of metals:

The rate of corrosion is informed by grain due to stress, Smaller the size of metal greated the rate of corrosion.

b) Position of metal on galvanic series:

when two metals are in contact with electrolyte. The metal above the series acts as anode and undergoes corrosion. The metal below the series acts as cathode and does not undergoes corrosion.

c) Surface of metal: A rough surface of metal rapidly corrodes as it collects more dust. A smooth surface does not corroded easily.

d) Purity of metal: Generally pure metals does not undergoes Corrosion if impurities are added undergoes corrosion.

e) Nature of M_2O Layer:

If the M_2O Layer is stable, non-porous which protects the metals but M_2O Layer is stable, porous which increases the corrosion.

Nature of environment :

(14)

a) effect of temperature: Corrosion rate is proportional to temperature, increases the temperation rate of corrosion also increases.

b) humidity (or) moisture: Moisture in the atmosphere acts as electrolyte and causes electro chemical corrosion (or) wett corrosion.

c) Amount of oxygen in atmosphere:

oxygen in atmosphere causes differential areation types of corrosion less oxygenated part acts as anode and more oxygenated part acts as cathode. corrosion take place at anode.

d) presence of impurities in atmosphere:

Impurities like H_2S, SO_2 ... etc. present in the atmosphere metal undergoes rapidly corrosion.

e) Effects of pH: In acidic environment metal undergoes rapid corrosion.

Corrosion control:

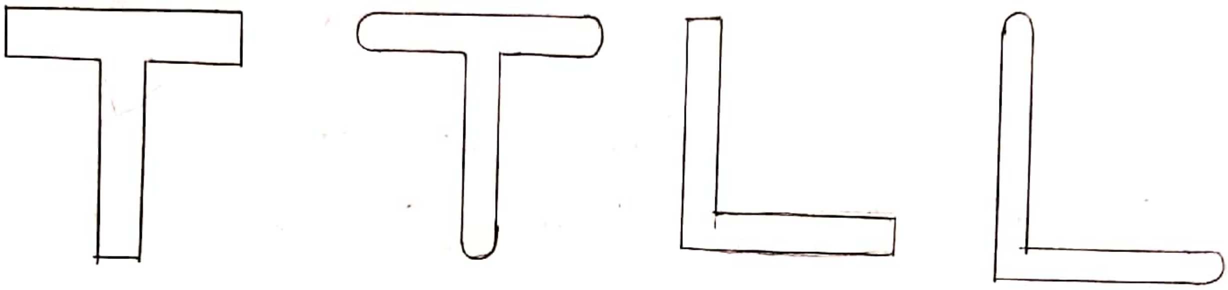
1. Proper designing:

⟹ when anode and cathode materials are used to gather then the area of anodic material is Large.

⟹ The anodic part should not be painted (or) coated because any cracks in coating causes rapid corrosion

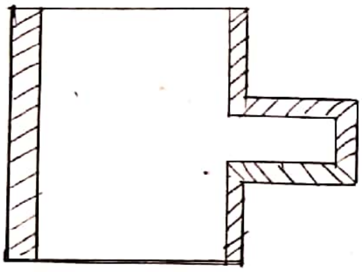
⇒ Avoiding alloys

⇒ Angles, corners, edges should be avoided in a structure.

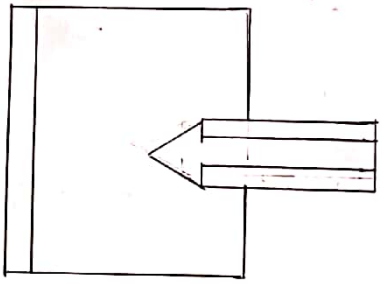


⇒ The materials should not have sharp corners and revises. They help in store of impurities.

⇒ The proper design should avoid the presence revises between the adjacent parts of the structure.



Poor



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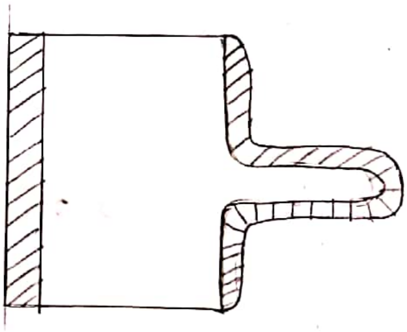

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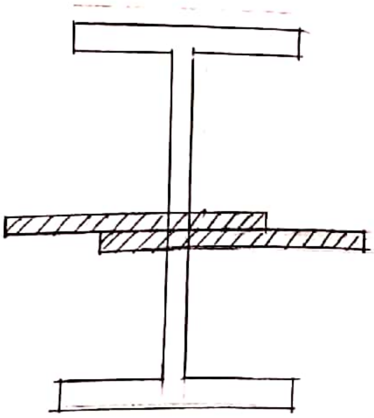

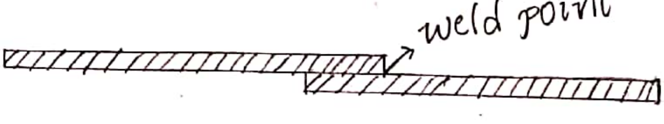

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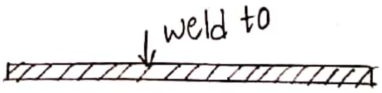
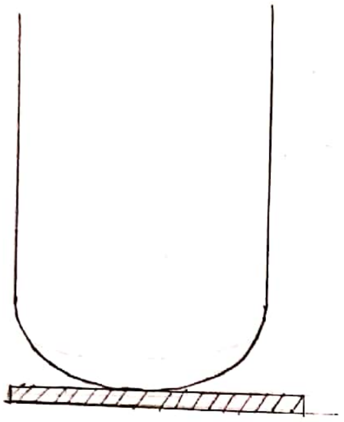
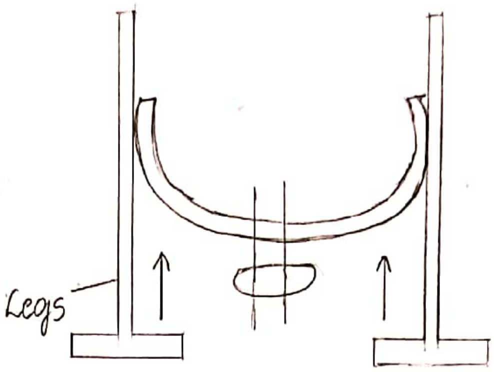


best

when ever possible the equipment should be supported is on legs free air circulation.



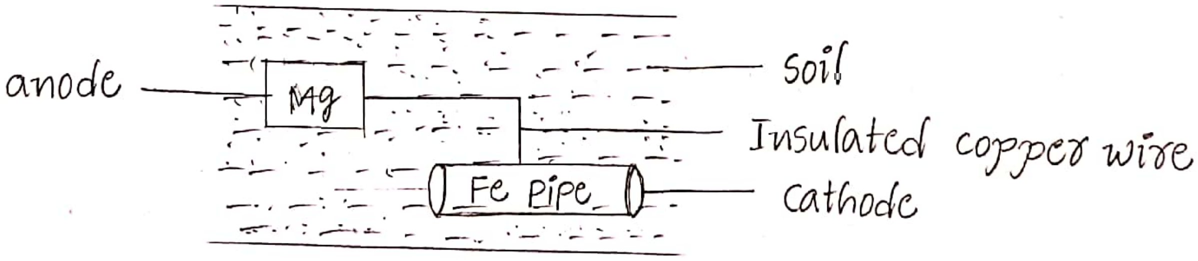


2. Cathodic protection:

The principle involved in this metal is to force the metal to be protected like a cathode they by corrosion does not occurs. It is two types

1. Sacrifical anodic protection
2. Impressed current cathode protection

1. sacrifical anodic protection:



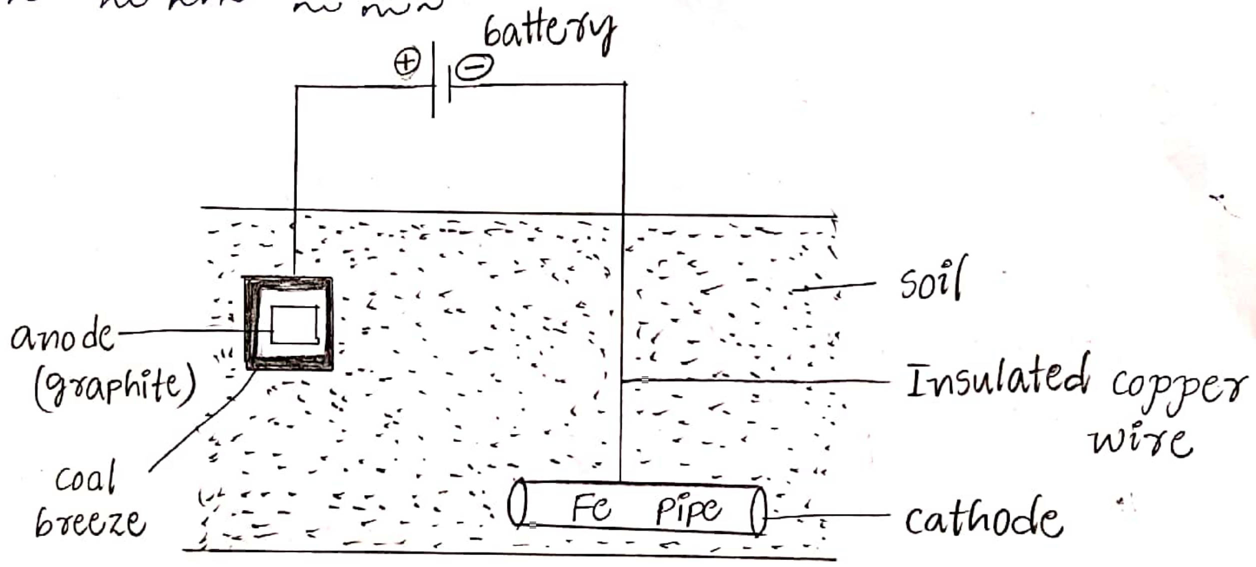
In this method a more anode metal is ~~connecte~~ connected to base metal for protection from corrosion the more anode metal itself corrode slowly, while the base is protected.

The more anode metal is called sacrifical anode. ∴ the corrode the sacrifical anode is replaced by fresh one. general all used sacrifical anode Mg-Zn, Al, ... etc.

Application:

1. To prevent corrosion of understand iron pipes, cable wires ... etc
2. To prevent corrosion of shiphulls.

2. Impressed voltage method:



In this method an impressed current is applied in opposite direction then the base metal changes from anode to cathode.

In this method the base metal is connected to negative terminal of D.C. Hence the base metal acts as cathode and protected from corrosion. The positive terminal of D.C. connected to graphite and acts as ~~cathode~~ anode undergoes corrosion. This type of protection is used in burried oil pipes, water pipes.

Applications:

1. To prevent rust formation of Laid upships.
2. To prevent rust formation in transmission line towers.

Protectective coatings:

Metallic coating: The surface of base metal is coated with an other metal is called metallic coating. It is of two types.

i) anodic coating
ii) cathodic coating

i) **anodic coating:** The base metal is coated with more anode metal is called "anode coating". Generally used anode metals are Zn, Mg, Al.

If any holes breaks (or) cracks are formed on the anode coating. A galvanic cell is formed between the coat metal and exposed part of base metal. zinc is more anodic than iron. Hence zinc acts as anode and undergoes corrosion; Fe acts as cathode and protected from corrosion.

Base metal iron is coated with more anode zinc (coated metal).

ii) **cathodic coating:** Generally used cathode (are tin (Sn). Cathode coating provide effective protection the base metal only when the Layer is continuous and does not form any hole (or) break. If any hole (or) crack are formed on the coated Layer. The base metal undergoes more corrosion.

example:

Tin coating on the surface of iron provides protection and as long as the surface of metal is covered but if any hole (or) crack fromed tin layer.

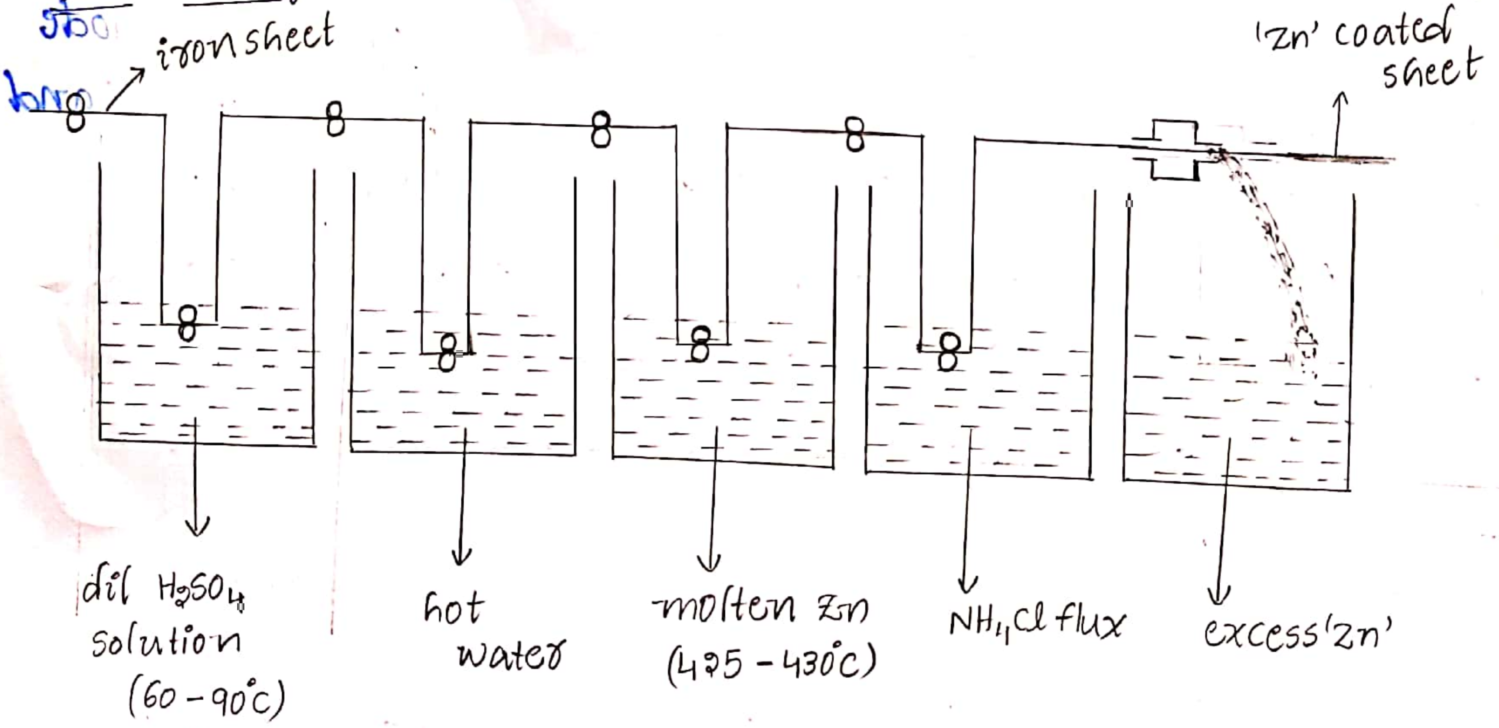
Application methods of corrosion:

1. Galvanising
2. Tinning

} "Hot dipping process"

3. Electroplating
4. Electroless plating
5. Metal cladding

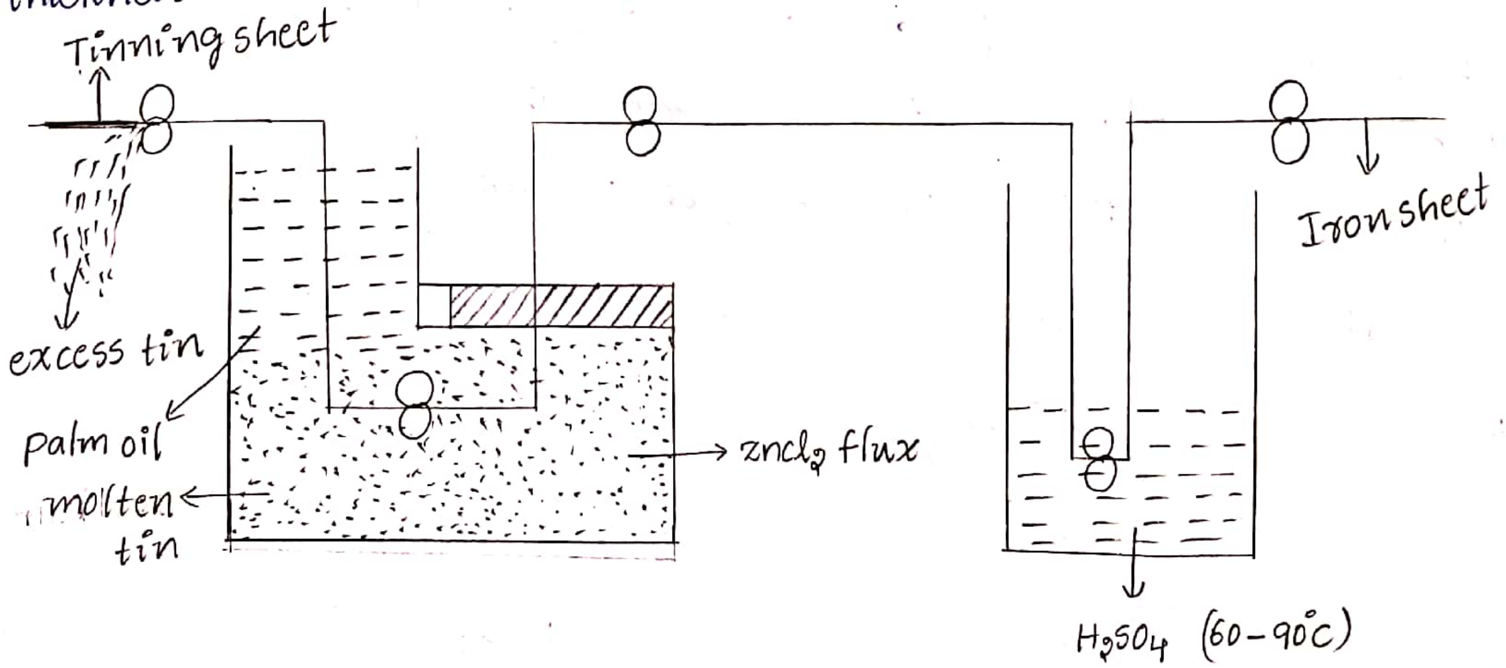
1. Galvanising:



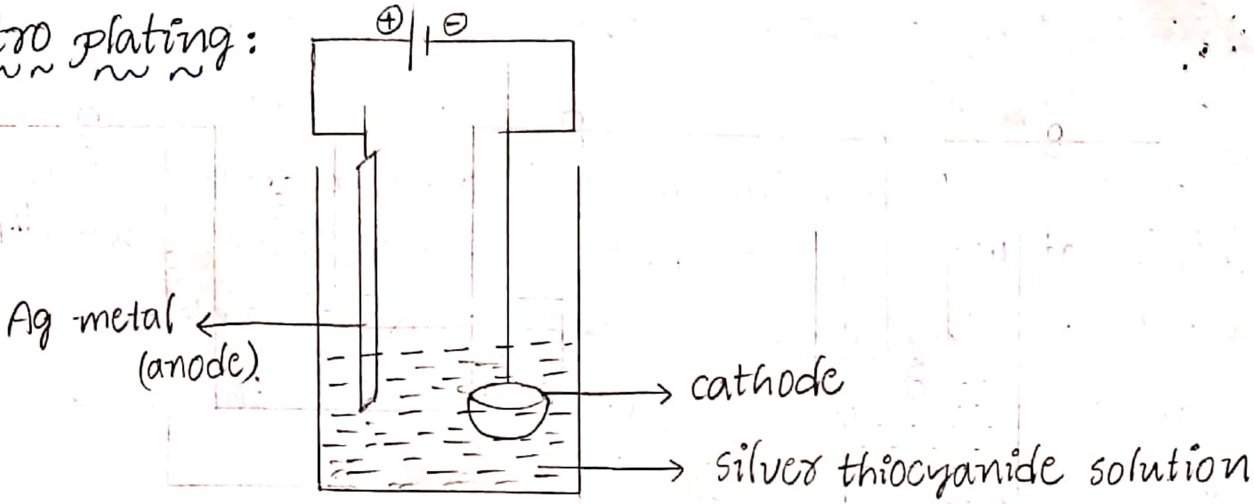
∴ Galvanising is the process. The iron sheet is coated with Zinc. The iron article is first dipped in dilute H_2SO_4 to remove rust and dust. Then, this metal is dipped in molten zinc bar maintain at 430°C. The surface of bar is covered with NH_4Cl flux. For sticking on the surface of molten 'zn'. The coated base metal is passed through. uniform ~~tic~~ thickness of coat metal. Finally we get galvanising article.

2. Tinning:

Tinning is coated tin over the iron or steel articles. The process consists in first treating steel sheet indilute sulphuric acid to remove any oxide film. After this, it is passed through a bath of zinc chloride flux. The flux helps the molten metal to add here to the metal sheet. Next, the sheet passes through a tank of molten tin and finally through a series of rollers from under neath the surface of a layer palm oil. The palm oil protects the hot tin-coated surface aganist oxidation. The rollers remove any excess of tin and produce a thin film of uniform thickness.



3. Electro plating:



Electroplating is a process in which the coated metal is deposited on the base. Metal by passing D.C through an electrolyte solution.

In this process the cleaned base metal is made as cathode to be connected negative to terminals of D.C and the coat metal is taken electrolyte. The electrodes are connected to battery and D.C. current is passed. Now electrolysis is takes place and the coast metal is deposited over the base metal.

example: The ~~coat~~ ~~s~~ coast silver on a copper spoon where spoon acts as cathode and silver acts as anode and silver thio sulphur (or) cynate is electrolyte. when the electrodes are connected D.C, Ag is deposited on the spoon.

S.NO	Name of the anode	Electrolyte solution
1.	silver	silver thio cyanide
2.	Arrum	$AuCl_2$
3.	nickel	$NiCl_2$

4.	platinum	$PtCl_2$
5.	cadmium	$CdSO_4$

Electroless plating:

A techinque of deposition of coat metal and a catalystical active surface of base metal by as suitable reducing agents without using electrical energy is known as "electroless plating."

Electroless plating process:

In this process electrons release from the oxidation of reducing agents, reduce the metal ions at catalytically active surface to metal atoms and deposited to coat metal.

Electroless plating of nickel:

1. Bathing solution (or) electrolitic bathing solution — $NiCl_2$ solution
2. Reducing agent — sodium hypophosphate
3. buffer solution — sodium acetate
4. Medium solution (or) complexing agent — sodium succinate
5. pH — 4-5
6. temperature - 93°C

at anode : $H_2PO_2^{\ominus} + H_2O \longrightarrow H_2PO_3^{\ominus} + 2H^{\oplus} + 2e^{\ominus}$ (oxidation)

at cathode: $Ni^{+2} + 2e^{-} \longrightarrow Ni$ (reduction)

Electroless plating of copper:

1. Bathing solution (or)
   electrolitic bathing solution — $CuSO_4$
2. Reducing agent — formaldehyde
3. buffer solution — Rochelle salt (Sodium potassium tatrate)
4. Medium solution (or) — EDTA solution
   complexing agent
5. pH — 11 to 12
6. Temperature — 25°C

At anode:

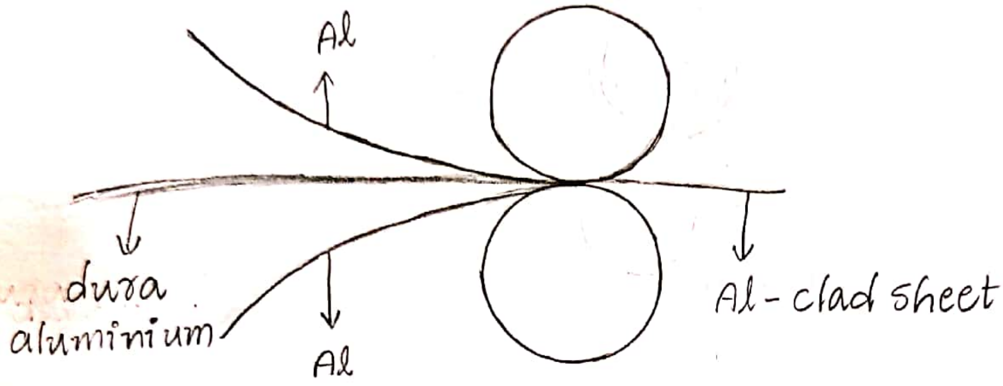
$$2HCHO + 4OH^{\ominus} \longrightarrow 2HCOO^{\ominus} + 2H_2O + H_2 + 2e^{\ominus}$$

At cathode: $Cu^{+2} + 2e^{\ominus} \longrightarrow Cu$

Metal cladding (or) Metal sandwitching:

In this process base metal is coated with two homogeneous metals to form cladding sheet like sandwitch manne.

example: Dura aluminium is coated with two 'Al' metals in the presence of electric rollers by applying temperature and pressure to form Al-clad sheet.



Paints (OR) organic coating:

Paint is a dispersion of a pigment in a medium oil paint contain the following ~~ind~~ gridients.

1. Binders: These are added to paints to hold together all the ingridients with pigments.
   ex: wax

2. Fillers: These are added to paints to reduce the cost & to improve the special property like durabilised hardness, strength
   ex: Talc, silica, gypsum.

3. Pigments: These are added to paints for different colours
   ex: carbon - black
   Zno - white.

4. Drying oil: The liquid position of paints in which the Pigment is dissolved is called medium (or) drying oil.

ex: soyabeen oil, fish oil

5. Tinners: These are added to paint to reduce the thin so that, they can easily applied on the surface.

ex: kerosene, vitamin-c

6. Plasticizers: These are added to paints to give the plasticity and flexibility to the paint.

ex: Triphenyl amine.

7. Antioxidants:

These are added to paints to prevent oxidation of paints.

8. Anti skinning: These are added to paints to prevent skinning of paints.

ex: polyhydroxy phenyl.

prepared by

Sarvepalli. VenkataRao

M.SC. BEd