2. Electrochemical cell and corrosion

20-09-19 Friday

Conductor: The substance which allow flow of or passes of electricity.

Ex: Metals, alloys, aqueous solution of acids and bases.

1) **Metallic conductors (electric conductors)**: The substance which allow flow or passes of electricity is due to metallic conductors.

Ex: Metals, alloys...

2) **Electrolytic conductors (electrolytes)**: The substance which allow flow or passes of electricity in aqueous state or fused state.

Ex: Aqueous solution of acids and bases.

3) **Insulators**: The substance which does not allow passage of current or electricity.

Ex: Wood, paper, plastic, rubber, ...

4) **Non-electrolytes**:

5) **Specific conductance (K)**: Resistance is directly proportional to length and inversly proportional to area of cross section.

$$R \propto \frac{l}{a}$$

$$R = \rho \frac{l}{a}$$

Where, R is resistance in ohm's

l is length in cm.

a is area of cross section in cm^2.

ρ is specific resistance

Specific resistance is defined as the resistance between two opposite faces of cm^3 of that substance.

$$\rho = \frac{Ra}{l}$$

units: $\rho = \frac{ohm\ cm^2}{cm} = ohm\ cm.$

Specific conductance: Reciprocal of specific resistance is known as specific conductance.

$$K \propto \frac{1}{\rho}$$

units: $K = \frac{1}{ohm\ cm} = ohm^{-1} cm^{-1}$ $\quad (\because ohm^{-1} = mho = S)$.

$= mho\ cm^{-1}$

$= S\ cm^{-1}$.

Equivalent conductance (λ_{eq}): Equivalent conductance is defined as specific conductance is multiplied by volume in ~~ml~~ ml containing 1gm equivalent of the electrolyte.

$$\Lambda_{eq} = K \cdot V_{(in\ ml)}$$

In terms of normality,

$$\lambda_{eq} = K \cdot \frac{1000}{N}$$

$N = \frac{Wt}{G.M.W} \times \frac{1000}{V}$

$N = 1 \times \frac{1000}{V}$

$V = \frac{1000}{N}$.

units:

$$\lambda_{eq} = \frac{ohm^{-1}. cm^{-1}. cm^3}{equivalent}$$

$$= ohm^{-1}. cm^2. eq^{-1}.$$

21-09-19
Saturday

Molar Conductance (λ_m): Molar conductance is defined as specific conductance multiplied by the volume in ml containing of 1g.m.wt. of the electrolyte.

$$\lambda_m = K \cdot V_{(in\ ml)}$$

$\left(\because M = \frac{Wt}{G.M.W} \times \frac{1000}{V_{(in\ ml)}}\right.$

$\left.M = \frac{1000}{V} \Rightarrow V = \frac{1000}{M}\right)$

In terms of normality:

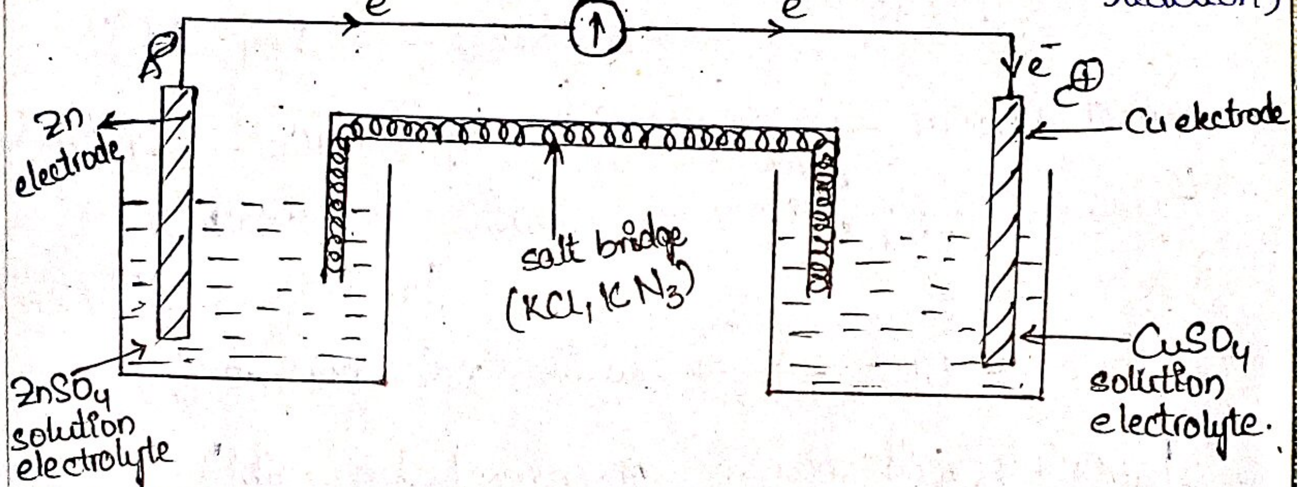
$$\lambda_m = K \cdot \frac{1000}{M}$$

Units: $\lambda_m = \frac{ohm^{-1}.cm^{-1}.cm^3}{mol}$

$= ohm^{-1}.cm^2.mol^{-1}$

Galvanic cell (or) electrochemical cell (or) voltaic cell:

Chemical energy ⟶ Electrical energy (spontaneous redox reaction)



Cell Reactions:

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

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

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

Cell Representation:

$^{\ominus}Zn / ZnSO_{4\,(1M)} // CuSO_{4\,(1M)} / Cu^{\oplus}$

Emf value + 1.09 volts.

Convention in representation of Galvanic cell:

Left hand side:

$Zn / ZnSO_4 (1M)$ $\quad$ $Zn : ZnSO_4 (1M)$

electrode electrolyte

Reference electrode:

$Pt, H_2 (1atm) / HCl (1M)$ $\quad$ $Pt, H_{2\,(1atm)} : HCl_{(1M)}$

Right hand side:

$CuSO_4(1M)/Cu$ $CuSO_4(1M) : Cu$

Cell Reaction:

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

Representation:

$Zn/ZnSO_4(1M)//CuSO_4(1M)/Cu^{\oplus}$ Emf $= 1.09V$

Reversible and Irreversible cells:

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu \longrightarrow Emf + 1.09V$$

Exact $+1.09V \longrightarrow$ reaction stop $(Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu)$

(Extra emf apply), above $+1.09V \longrightarrow$ reaction is reversible
$(Cu + Zn^{+2} \rightarrow Cu^{+2} + Zn)$

below $+1.09V \longrightarrow$ reaction not going on

Reversible cell can be measured by gibb's free energy.

$$\Delta G = -nEF$$

above relation satisfies that cell is reversible

above relation can't be satisfies that cell is irreversible.

Irreversible cell:

$$Zn + 2H^{\oplus} \xrightarrow{Ag} Zn^{+2} + H_2 \text{ (irreversible)}$$

** Standard single electrode potential (E°):

Potential executed by single electrode at unit conc. of concern metal or non-metal at 25°C called single electrode potential (E°).

$$Zn/ZnSO_4(1M)//CuSO_4(1M)/Cu$$

← half cell → ← half cell →

oxd^n (anode) red^n (cathode)

$$E_{cell} = E_{anode} + E_{cathode}$$

Left - hand side :

Electrode : oxidation electrode.

Potential : oxidation potential or potential of left hand side; SOP(loss of e's).

Right - hand side :

Electrode : reduction ~~re~~ electrode.

Potential : reduction potential or potential of right hand side; (S.RP) (gain of e's)

$$SRP = - SOP.$$

$$E_{cell} = E_{oxd^n} + E_{red^n}$$

(or)

$$E_{cell} = E_L + E_R$$

(or)

$$E_{cell} = E_R - E_L$$

Direction of spontaneous:

(1) $E_{cell} > 0$; cell reaction is left to right.

(2) $E_{cell} < 0$; cell reaction is right to ~~cell~~ left.

(3) E_{cell} is +ve; ΔG is negative, cell is spontaneous (or) feasible.

Measure of Standard electrode potential:

Direct measurement can't be possible.

Depends upon (1) conc. of the ions in solution.
(2) tendency of ions.
(3) temperature.

* Single electrode is taken as anode,

$$E_{cell} = E_R - E_L$$
$$= E_R - E^\circ \quad (\because E_L = E^\circ)$$

* Single electrode is taken as cathode,

$$E_{cell} = E_R - E_L$$
$$= E^\circ - E_L \quad (\because E_R = E^\circ).$$

Electrochemical ~~cells~~ **series**: When the elements are arranged in the increasing order of their standard reduction potential values on the basis of normal hydrogen electro-de, these series are called electrochemical series.

	Electrode metal (or) non-metal	Standard reduction potential in volts
oxidation reducing agents	Li	−3.03
	K	−2.92
	Ca	−2.87
	Na	−2.71
	Mg	−2.37
	Al	−1.66
	Zn	−0.76
	Fe	−0.44
	Pb	−0.13
	hydrogen	0.00
Reduction oxidising agents	Cu	+0.34
	Ag	+0.8
	Pt	+0.86
	Au	+1.69
	F_2	+2.87

Information from Electrochemical Series:

* **Relative ease of oxd^n and red^n:**

$$Zn \longrightarrow Zn^{+2} + 2e^{\ominus} \text{ (oxd}^n\text{)}$$

$$Ag^{+} + e^{\ominus} \longrightarrow Ag \text{ (red}^n\text{)}$$

* **Replacement tendency:**

$$Zn + FeSO_4 \longrightarrow ZnSO_4 + Fe \ (\checkmark)$$

$$Cu + FeSO_4 \not\longrightarrow CuSO_4 + Fe \ (X)$$

*To liberate H_2 from acid:

$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$ (✓)

$Cu + 2HCl \xrightarrow{\times} CuCl_2 + H_2$ (x)

*To predict spontaneously of reaction:

$^{\ominus}Zn/ZnSO_4(1M)//CuSO_4(1M)/Cu^{\oplus}$ Emf = +1.09 volts (spontaneous)

$Ag/AgNO_3(1M)//CuSO_4(1M)/Cu$ Emf = −0.46 volts (feasible).

Applications:

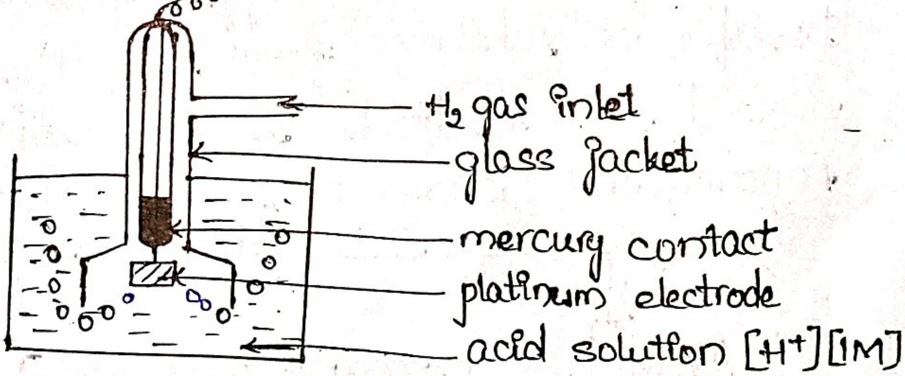
(1) Relative ease of oxdⁿ and redⁿ.
(2) Replacement tendency.
(3) To liberate H_2 from acid.
(4) To predict spontaneously of reaction.
(5) To predict nernest equation.

Reference Electrode: An electrode whose electrode potential is known is called reference electrode.

Normal Hydrogen Electrode (NHE) (or) Standard Hydrogen Electrode (SHE):

Standard Hydrogen Electrode is a primary reference electrode.

Construction:



Anode: $Pt, H_2(1atm)/HCl(1M)$ (oxdⁿ)

Cathode: $HCl(1M)/Pt, H_2(1atm)$. (redⁿ).

24-09-19 Tuesday

Cell reaction:

Anode: $H_2 \longrightarrow 2H^{\oplus} + 2e^{\ominus}$

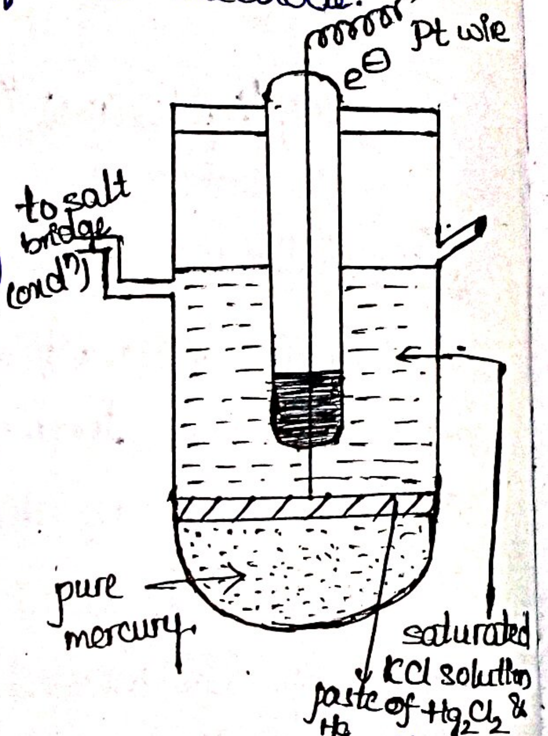
Cathode: $2H^{\oplus} + 2e^{\ominus} \longrightarrow H_2$

$H_2 \rightleftharpoons 2H^{\oplus} + 2e^{\ominus}$ Emf = 0.00 V.

Calomel Electrode: Secondary reference electrode.

Construction:

$Hg_2Cl_2, Hg / KCl$ solution



Anode:

$2Hg_{(l)} \longrightarrow Hg_2^{2+} + 2e^{\ominus}$ (oxdn)

$Hg_2^{2+} + 2Cl^{\ominus} \longrightarrow Hg_2Cl_{2(s)}$

$2Hg_{(l)} + 2Cl^{-} \longrightarrow Hg_2Cl_{2(s)} + 2e^{\ominus}$

$Hg_2Cl_{2(s)} \longrightarrow Hg_2^{2+} + 2Cl^{\ominus}$

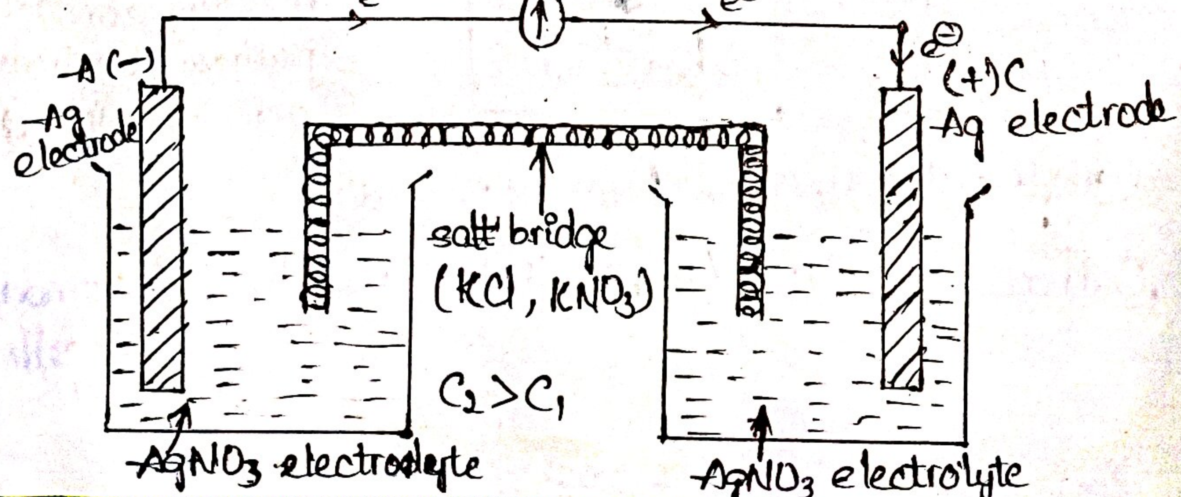
$Hg_2^{2+} + 2e^{\ominus} \longrightarrow 2Hg_{(l)}$ (redn)

$Hg_2Cl_{2(s)} \longrightarrow 2Hg_{(l)} + 2Cl^{\ominus}$ Emf = +0.2415 volts

0.1M KCl solution $\longrightarrow$ Emf = +0.338 volts

1M KCl solution $\longrightarrow$ Emf = +0.28 volts

Concentration cell: Concentration cell is depth cell in which electrical energy is produced by the depth transfer of substance from solution of higher concentrat- around one electrode to a solution of lower concentration around another electrode.



$$E = E^0 + \frac{0.0591}{n}\log C$$

$$E_{cell} = E_{right} - E_{left}$$

$$E_{left} = E^0 + \frac{0.0591}{n}\log C_1$$

$$E_{right} = E^0 + \frac{0.0591}{n}\log C_2$$

Cell reaction:

Anode: $Ag_{(C_1)} \longrightarrow Ag^+ + e^\ominus$ (oxd^n)

Cathode: $Ag^+ + e^\ominus \longrightarrow Ag_{(C_2)}$ (red^n)

Net reaction: $Ag_{(C_1)} \longrightarrow Ag_{(C_2)}$

$$E_{cell} = E^0 + \frac{0.0591}{n}\log C_2 - E^0 + \frac{0.0591}{n}\log C_1$$

$$= \frac{0.0591}{n}(\log C_2 - \log C_1)$$

$$\therefore E_{cell} = \frac{0.0591}{n}\log\left(\frac{C_2}{C_1}\right).$$

Applications:

1, To determine sparingly solubility of $BaSO_4$.

2, To determine valency of mercury ($Hg_2^{2+} \longrightarrow$ valency of 2)

* **Battery or Cell:**

A combination of several electrochemical cells which are connected in series and can be used as source of direct electric current of at a constant voltage is called Battery.

i, **Primary battery or Primary cell:** Primary cell is irreversable cell. After usage of battery, then become dead.

Ex: Dry cell, mercury cell.

ii, **Secondary battery or Secondary cell:** Secondary cell is reversable cell or rechargable cell. These cells are used again and again.

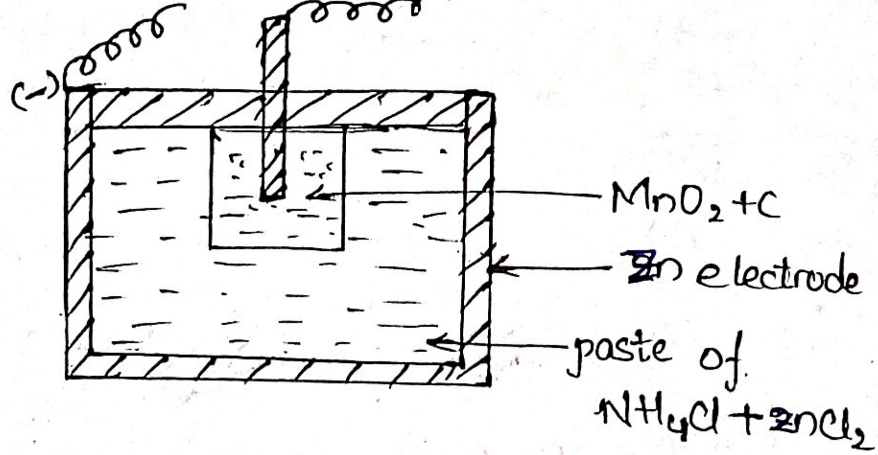
Ex: Ni-Cd, cell, lead storage cell.

Dry cell or Lach lanche cell :

Anode : zinc

Cathode : graphite ($MnO_2 + C$)

electrolyte : paste of $NH_4Cl + ZnCl_2$.



Cell reactions:

Anode : $Zn_{(s)} \longrightarrow Zn^{+2} + 2e^{\ominus}$ (oxd^n)

Cathode : $MnO_2 + \overset{\oplus}{N}H_4 + e^{\ominus} \longrightarrow MnO(OH) + NH_3$

NH_3 is not liberated as gas, NH_3 combines with Zn^{+2} to form complex. cell potential is + 1.5 volts.

Disadvantages :

1) Current is gone, the product is will be build up on the electrode which cause drop in voltage.

(2) Electrolyte is acidic, zinc mental dissolves slowly then cell will rundown slowly.

Ni-cd cell :

Anode : Cadmium.

Cathode : Paste of $NiO(OH)$ (Nickel oxy hydroxide).

Electrolyte : KOH solution

Cell Reactions :

Anode : $Cd_{(s)} + 2\overset{\ominus}{O}H_{(aq)} \longrightarrow Cd(OH)_2 + 2e^{\ominus}_{(s)}$

Cathode : $NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^{\ominus} \longrightarrow 2Ni(OH)_2 + 2\overset{\ominus}{O}H_{(aq)}$

net reaction : $Cd_{(s)} + NiO(OH)_{(s)} + 2H_2O_{(l)} \longrightarrow Cd(OH)_2 + 2Ni(OH)_{2(s)}$.

which is reversable (formation of $Cd(OH)_2$ and $Ni(OH)_2$ deposits on concent electrode.

Cell potential is +1.4 volts.

Types: (1) Packed plate Ni-cd cell.
(2) Sintered plate Ni-cd cell.

Advantages:

(1) High range discharge and low temperature operation.

(2) Long self without any maintaince.

Applications:

(1) Aircraft application.

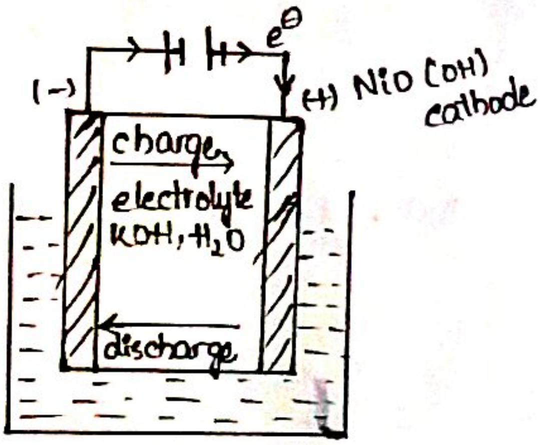
(2) Emergency power supply.

(3) Train lights.

(4) Diesel engines.

(5) Military applications.

25-09-19
Wednesday.



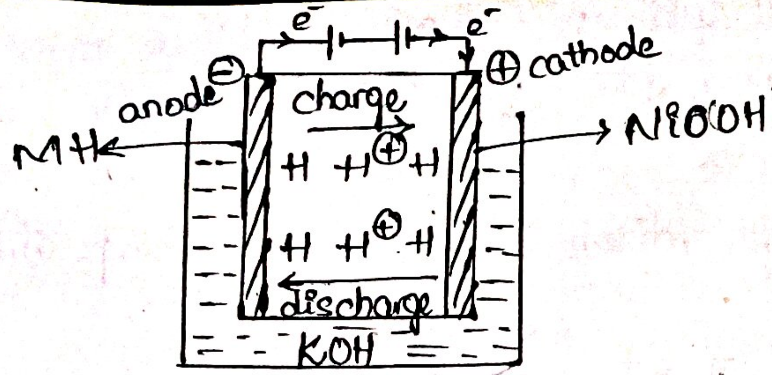
NiMH (Nickel Metal hydride) cell:

1986 "stanford ovshinsky"

anode : MH

cathode : NiO (OH)

electrolyte : KOH solution



Reactions:

Anode: $MH_{(s)} + OH^{\ominus} \rightleftharpoons M_{(s)} + H_2O_{(l)} + e^{\ominus}$ (oxdn)

Cathode: $NiO(OH)_{(s)} + H_2O_{(l)} + e^{\ominus} \rightleftharpoons Ni(OH)_{2(s)} + OH^{\ominus}$ (redn)

Net reaction $MH_{(s)} + NiO(OH)_{(s)} \rightleftharpoons M_{(s)} + Ni(OH)_{2(s)}$

cell potential is +1.2 volts.

Advantages:

1) Ecofriendly.

2) More cycle life.

3) Safety during accidents.

4) Wide temp operator

5) Low cost.

Disadvantages:

Low potential, causes corosion on electrodes.

Applications:

1) Electrical razors.

2) Tooth brushes.

3) Cameras.

4) Mobile phones

5) Automatic drives

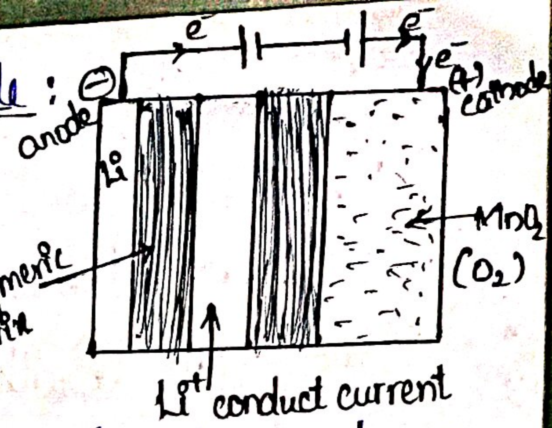
6) Medical instrument.

Lithium cell (primary cell):

1) Lithium cell with solid cathode.

2) Lithium cell with ~~b~~ liquid cathode.

(1) Lithium cell with solid cathode :



anode : lithium.

cathode : MnO_2 and Ce (3 volts)

H_2O absorbing nature

improve efficiency.

electrolyte : Mixture of propylene carbonate and 1,2-dimethoxy ~~methane~~ (solid (or) liquid)

Cell Ractions :

Anode : $Li \longrightarrow Li^+ + e^\ominus$ (oxd^n)

Cathode : $Li^+ + MnO_2 + e^\ominus \longrightarrow LiMnO_2$ (red^n)

Net reaction : $Li + MnO_2 \longrightarrow LiMnO_2$

Applications :

1, Cylindrical cell - automatic cameras.

2, Coin cell - calculators, watches.

(2) Lithium cell with liquid cathode :

Anode : Lithium Ex: (lithium sulphur dioxide $Li-SO_2$).

Cathode : Sulphur dioxide

Electrolyte : Covalent (Cosolvent) is used either acrylonitrate and

$Li + 2SO_2 \rightarrow LiS_2O_4$ propylene carbonate) (or)

Mixture of two and 50% of volume of O_2.

2, Lithium thionyl chloride ($Li-SOCl_2$) :

Anode : Lithium

Cathode : Carbon (non-woven glass separation).

active cathode : $SOCl_2$.

Electrolyte : $SOCl_2$.

Cell Reactions :

Anode : $4Li \longrightarrow 4Li^\oplus + 4e^\ominus$ (oxd^n)

Cathode : $4Li^\oplus + 4e^\ominus + 2SOCl_2 \longrightarrow 4LiCl + SO_2 + S$ (red^n)

Net reaction : $4Li + 2SOCl_2 \longrightarrow 4LiCl + SO_2 + S$

Applications:

(1) Li–$SOCl_2$ used in electronic circuit boards.

(2) These are used in military and aircraft applications.

(3) Used as Neura stimulators, drop delivery system.

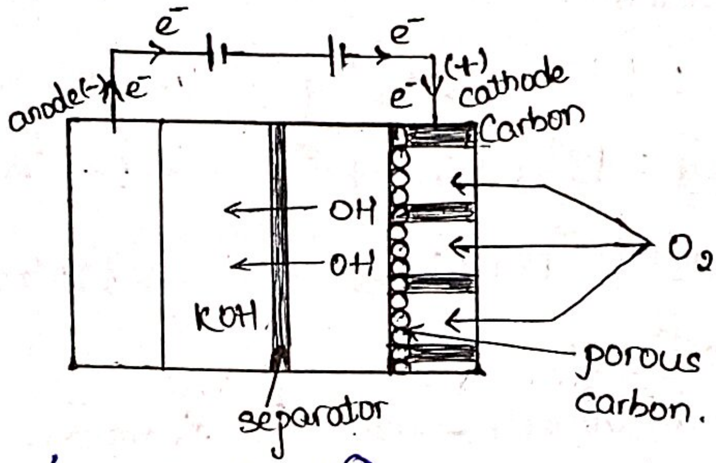
26-07-19 Thursday

Zinc – Air Battery:

Anode: Zinc.

Cathode: Carbon surrounded with oxygen.

Electrolyte: KOH solution.



Granuated $^{\ominus}Zn / 6M\ KOH / Air / \overset{\oplus}{C}$

Cell Reactions:

Anode: $2Zn \longrightarrow 2Zn^{+2} + 2e^{\ominus}$ (oxdn)

$2Zn^{+2} + 8\overset{\ominus}{OH} \longrightarrow \underset{\text{zincate (complex)}}{[Zn(OH)_4]^{-2}}$ $E^\circ = -1.25V$

$2[Zn(OH)_4]^{-2} \longrightarrow 2ZnO + 2H_2O + 4\overset{\ominus}{OH}$

Cathode: $O_2 + 2H_2O + 4e^{\ominus} \longrightarrow 4\overset{\ominus}{OH}$ (redn) $E^\circ = +0.4V$

net reaction $2Zn + O_2 \longrightarrow 2ZnO$ $(E^\circ = +0.4 - (-1.25)$
$= 1.65$ volts)

Theoritical value is +1.65 Volts

Which is reduced to 1.35 – 1.4 volts (due to zincate).

Drawback: Internal losses due to low potential.

Nernest equation:

(1) Concentration of Ions in solution.

(2) Tendency of ions.

(3) Temperature.

Let us consider reduction reactions at cathode.

$M^{n+} + ne^{\ominus} \longrightarrow M$ (gain of $e^{\ominus}$)

$\Delta G = \Delta G^{\circ} + RT \ln K$ (ΔG° = standard free energy 298 K, 1M conc.

$K = [M] / [M^{n+}]$ ΔG = free energy, K = constant)

$K = \frac{1}{[M^{n+}]}$ for $[M] = 1$ M conc. R = real gas constant

T = temperature

$\Delta G = \Delta G^{\circ} + 2.303 RT \log_{10} \left[\frac{1}{[M^{n+}]}\right]$

$\Delta G = -nEF$, $\Delta G^{\circ} = -nE^{\circ}F$ ($\because F = 96500$)

$-nEF = -nE^{\circ}F + 2.303 RT \log_{10} \left[\frac{1}{[M^{n+}]}\right]$

$E = E^{\circ} - \frac{2.303 RT}{nF} \log_{10} \left[\frac{1}{[M^{n+}]}\right]$

$E = E^{\circ} + \frac{2.303 RT}{nF} \log [M^{n+}] \longrightarrow$ for reduction.

$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$ (red^n) $\left[\because R = 8.314 \text{ KJ}^{-1} \text{Mole}^{-1},\ T = 298 \text{ K},\ F = 96500 \text{ coulombs}\right]$

$E = E^{\circ} - \frac{0.0591}{n} \log [M^{n+}]$ (oxd^n)

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

Fuel + $O_2 \longrightarrow$ Comb + heat
substance which react with O_2 to give combustion with heat.

- Galvanic cell,

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

$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$

01-10-19 Tuesday

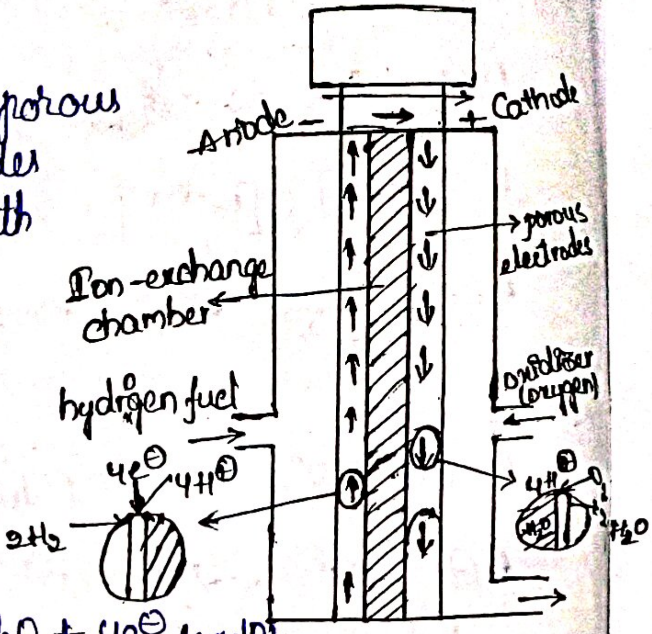
Fuel Cell: Fuel cell is a electro chemical cell which converts chemical energy contain in an easily available fuel oxidant system into electrical energy.

Characteristics of fuel cell:

1. High efficiency.
2. Low noise level.
3. Free from vibration, heat transfer and thermal pollution.

(4) Wide range of temperature operats.

Hydrogen-Oxygen Fuel cell:



Electrodes (Anode, Cathode): Two porous electrodes (made of graphite impregnated with finely divided Pt or a 75/25 alloy of Pb with Ag (or) Ni

Electrolyte: 25% KOH

Cell reactions:

Anode: $2H_{2(g)} + 4OH^{\ominus}_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^{\ominus}$ (oxdn)

Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^{\ominus} \rightarrow 4OH^{\ominus}$ (redn)

net reaction $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ Emf = +1.23 volts

Applications:

1) These are used as energy source in space vehicles, submarines and military applications.
2) Space crafts produce water is a valuable fresh water source for astronauts.

Advantages of fuel cell:

1) Energy conversion is very high (75-82)
2) Formation of water is a drinking water source for astronauts
3) Themal and noise pollutions are very low.
4) Maintance cost is low.

Limitations

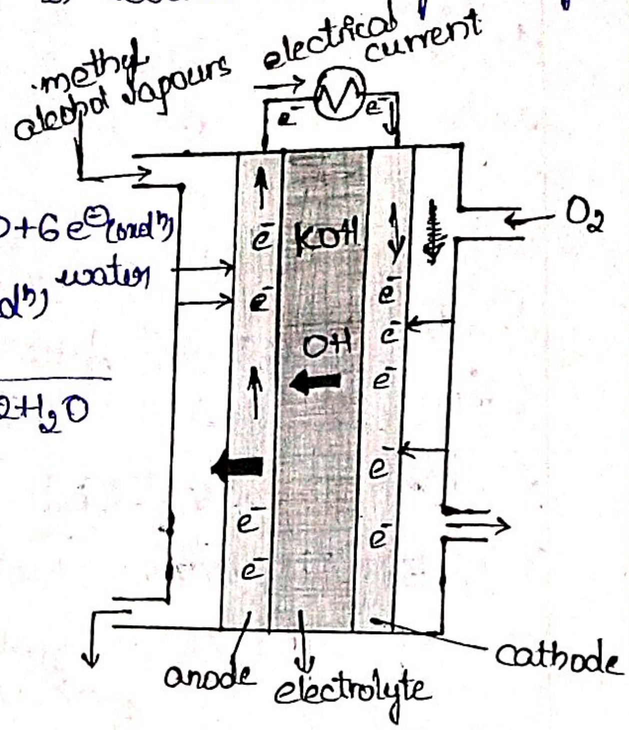
1) Lack time of fuel cells is not accurately known.
2) Initial cost is very high.
3) Distribution of hydrogen is not proper.

Methyl alcohol - Oxygen alkaline fuel cell:

Anode: Porous nickel which is impregated with Pt catalys

Cathode: Porous nickel which is coated with Ag catalyst.
Electrolyte: KOH solution.

Chemical reactions:



Anode: $CH_3OH + 6OH^{\ominus} \rightarrow CO_2 + 5H_2O + 6e^{\ominus}$ (oxdⁿ)

Cathode: $3/2\, O_2 + 3H_2O + 6e^{\ominus} \rightarrow 6\overset{\ominus}{O}H$ (redⁿ)

net reaction $CH_3OH + 3/2\, O_2 \longrightarrow CO_2 + 2H_2O$

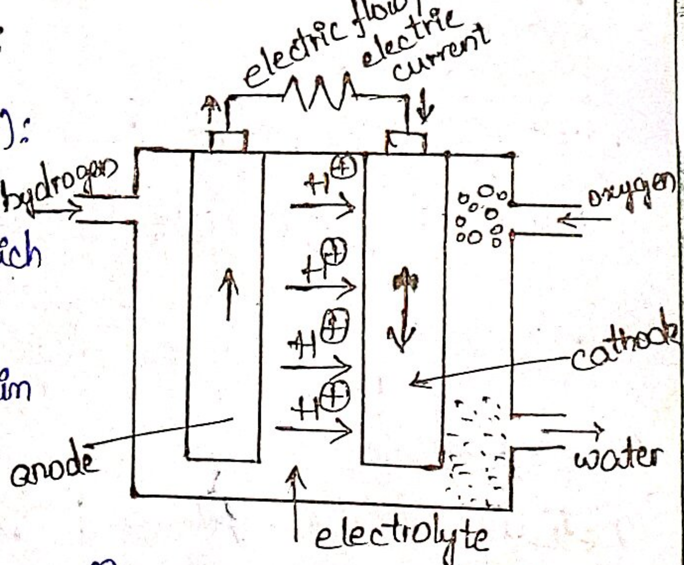
Advantages:

1) Easy to transport.
2) Excellent fuel.
3) Less risk to aquatic plants, animals, human beings,
4) 0 emission is obtained, these cells are eco-friendly.

Applications:

1) Methyl alcohol oxygen is a fuel for fuel cell motor vehicles like NECAR-5 in Japan, USA....

Phosphoric acid fuel cell:



Electrodes (Anode, Cathode):
Two electrodes made up of carbon paper (or) graphite which is coated with Pt catalyst

Electrolyte: Phosphoric acid in silicon carbide matrix

Cell Reactions:

Anode: $2H_2 \longrightarrow 4H^{\oplus} + 4e^{\ominus}$ (oxdⁿ)

Cathode: $O_2 + 4H^{\oplus} + 4e^{\ominus} \longrightarrow 2H_2O$ (redⁿ)

net reaction $2H_2 + O_2 \longrightarrow 2H_2O$.

Applications:

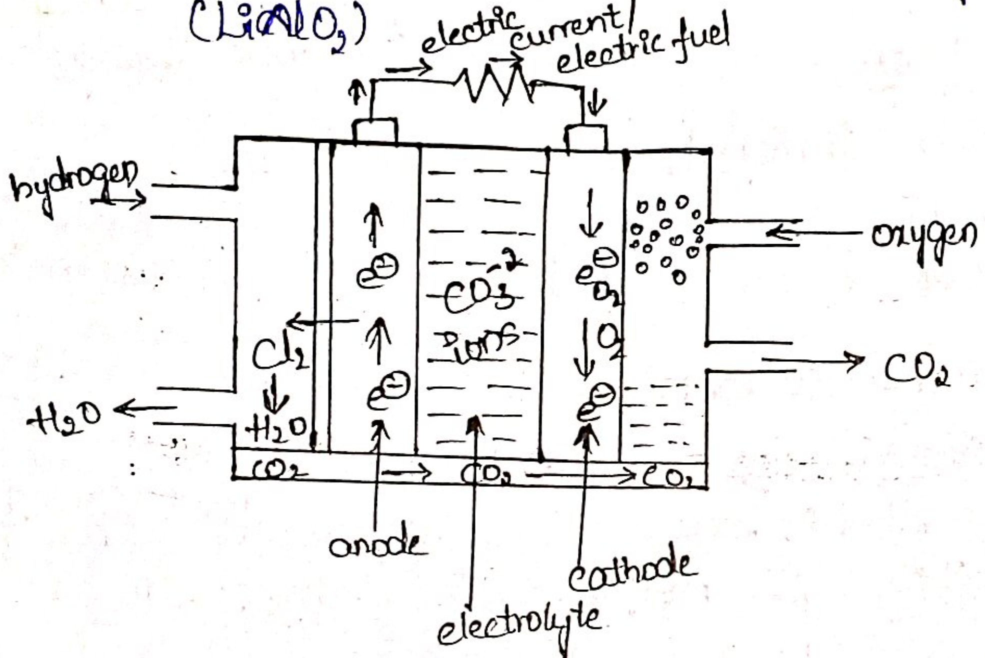
1. These are used for stationary power generations with output 100 KW to 400 KW.
2. These are used for buses.
3. In India, DRDO as developed PBAFC.

Molten carbonate fuel cell (MCFC):

Anode: Porous Nickel with 2% of Al (or) Cr (alloy).

Cathode: Porous Nickel.

Electrolyte: Sodium Potassium Carbonate by ceramic ($LiAlO_2$)



Cell Reactions:

Anode: $H_2 + CO_3^{-2} \longrightarrow H_2O + CO_2 + 2e^{\ominus}$ (oxd^n)

Cathode: $\frac{1}{2}O_2 + CO_2 + 2e^{\ominus} \longrightarrow CO_3^{-2}$ (red^n)

net reaction $H_2 + H_2O_2 \longrightarrow 2H_2O$

Applications:

1. These cells are used in many industries.
2. Electricity produced via steam turbines.

03-10-19 Thursday

Corrosion: Natural tendency of convertion of metal into mineral compounds or metal oxides with the interaction of environment is called corrosion.

Ex: (1) Rusting of iron : reddish layer on iron ($FeC_2O_3 \cdot H_2O$).
(2) Green layer on copper ($CuCO_3 + Cu(OH)_2$).
(3) Tarnishing of silver : blakish layer on silver (Ag_2S).

Causes of corrosion :

$$\underset{\text{stable}}{\text{ore}} \xrightarrow{\text{metallurgy}} \underset{\text{unstable}}{\text{metal}} \xrightarrow{\text{corrosion}} \underset{\text{stable}}{\text{corrosion product}}$$

Types of

Types of Corrosion

- dry corrosion (or) chemical corrosion
  - oxidation corrosion
  - corrosion by other gases
  - liquid metal corrosion
- wet corrosion (or) electro chemical corrosion
  - electrochemical corrosion evaluation of hydrogen & absorption of oxygen.
  - galvanic corrosion (differential metal corrosion (or) bimetallic corrosion
  - concentration corrosion cell
    - pitting corrosion
    - differential aeration (water in corrosion)
  - underground corrosion (or) soil corrosion
  - stress corrosion
  - intergranual corrosion

(1) **Dry corrosion**: Corrosion occured in presence of dry condition ($O_2, CO_2, SO_2, Cl_2, H_2S$).

(i) **Oxidation corrosion**: Corrosion in presence of oxygen.

Ex: Rusting of iron.

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3.$$

(ii) **Corrosion by other gases**: Corrosion in presence of Cl_2, SO_2, H_2S, CO_2.

(iii) **Liquid metal corrosion**: Liquid sodium is used as a coolant nuclear reactor and causes corrosion of cadmium rods.

Mechanism of corrosion:

$$M \longrightarrow M^{+} + e^{\ominus} \quad (\text{oxd}^n)$$

$$\tfrac{1}{2}O_2 + e^{\ominus} \longrightarrow O^{-2} \quad (\text{red}^n)$$

$$M + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{metal oxide}}{M^{+}O^{-2}}$$

Types of oxide films:

(1) **Protective, non-porous oxide film:**

Ex:- Al, Cu, CrW.

(2) **Unstable oxide film:**

Ex:- Ag, Au, Pt.

(3) **Volatile oxide film:**

Ex: MoO_3

(4) **Non-protective, porous oxide film:**

Ex: Alkali and Alkali earth metals.

Pilling-bed worth rule:

$$\text{Pilling-bed worth ratio} = \frac{\text{volume of metal oxide formed}}{\text{volume of metal consumed}}.$$

case-1: Ratio less than one (alkaline and alkaline earth metals) non-protective porous.

case-2: Ratio greater than one (Al, Cu, CrW).

10-10-19 Thursday

Electrochemical corrosion (or) wet corrosion :

Corrosion in presence of aqueous solution electrochemical corrosion evaluation of H_2 and absorption of O_2.

Ex: Rusting of iron.

Anodic reaction : $Fe \longrightarrow Fe^{+3} + 3e^{\ominus}$

Cathodic reaction :

Evaluation of H_2 :

$$2H^{+} + 2e^{\ominus} \longrightarrow H_2$$

Absorption of O_2 :

$$\tfrac{1}{2}O_2 + H_2O + 2e^{\ominus} \longrightarrow H_2$$

$$Fe^{+2} + 2(\overset{\ominus}{OH}) \longrightarrow Fe(OH)_2$$

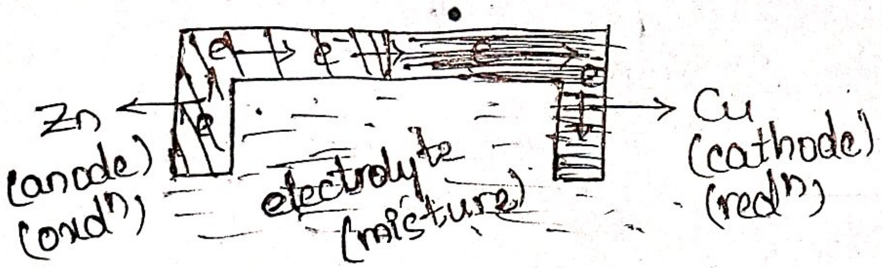
$$Fe(OH)_2 + H_2O + O_2 \longrightarrow Fe(OH)_3$$

$$4Fe(OH)_3 \longrightarrow 2(Fe_2O_3 \cdot 3H_2O)$$

Galvanic corrosion (or) Differential metal corrosion (or) Bimetallic corrosion :

Zn, Mg, Fe $\longrightarrow$ anode (oxdⁿ) higher in electrochemical series.

Cu, ~~Ag, Au~~ $\longrightarrow$ cathode (redⁿ) lower in electrochemical series.



Galvanic ~~cell~~ series (oxdⁿ potential are arranged in decreasing order of activity):

High anodic (active towards corrosion)

Mg
Mg alloys
Zn
Al
low 'c' steel
cast iron
stainless steel (active)
lead tin alloys
lead
tin
Brass
Copper
Bronze
Copper-Nickel alloys
Inconel
Silver
Stainless steel (passive)
Monel
Graphite
Gold
Titanium
Platinum

active (anodic)

nobel (cathodic)

<u>Concentration cell corrosion</u>:

* Less oxygenated part act as anode.
* More oxygenated part act as cathode.

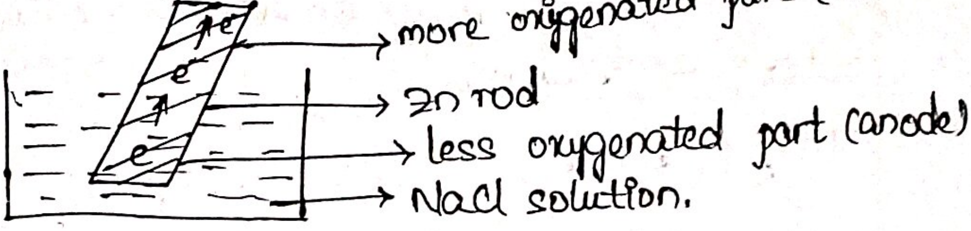
Concentration cell corrosion may arise due to

1) Difference in the conc. of metal.
2) Difference in the air/aeration.
3) Difference in the temp.
4) Inadequate agitation
5) Difference in the diffusion of metal.

19-10-19 Saturday

Differential aeration Corrosion:

1, Partial immersion of metal in solution (or) Waterline corrosion:

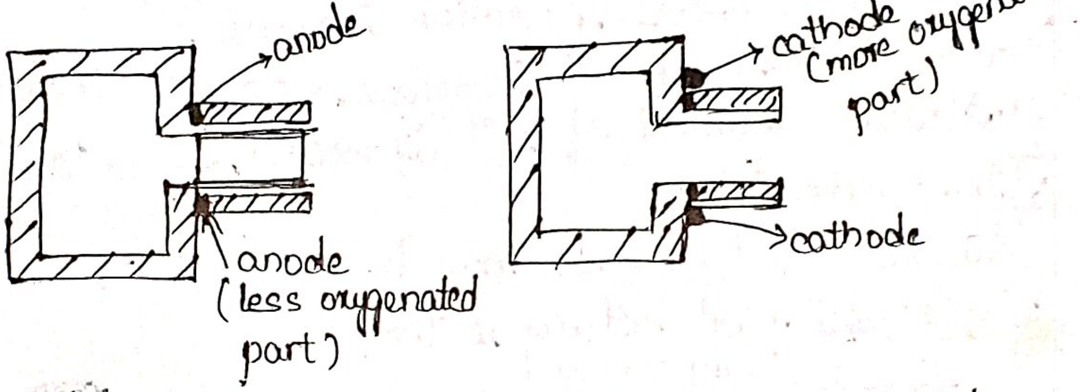


Reactions:

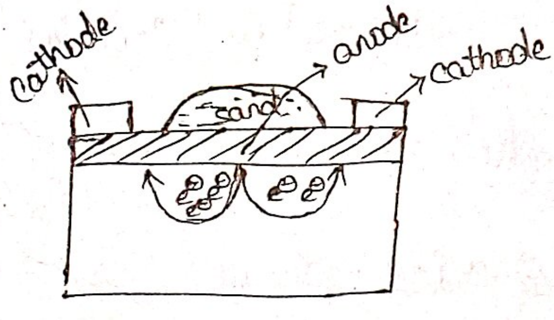
Anode: $Zn \longrightarrow Zn^{+2} + 2e^{\ominus}$ (oxd^n)

Cathode: $\frac{1}{2}O_2 + H_2O + 2e^{\ominus} \longrightarrow 2\overset{\ominus}{O}H$ (red^n)

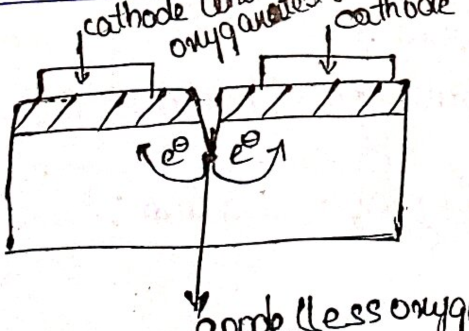
Faulty design of Equipment:



Accumulation of sand; dirt and scale on metal:



** Pitting Corrosion:



15-10-2019 Tuesday

Boiler corrosion: Hard water passed in boiler, enhance corrosion.

Corrosion product $\longrightarrow$ anode

other than parts in boiler $\longrightarrow$ cathode

Caustic embrittlement:

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

enhance corrosion in iron pipe

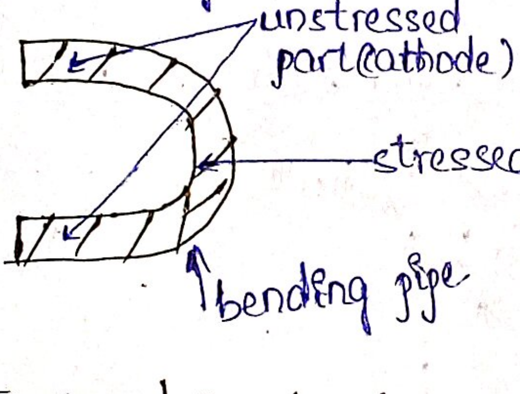
Underground corrosion:

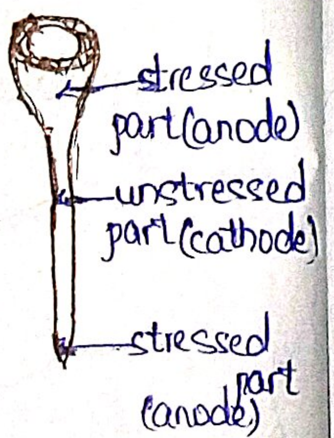
(1) Acidity of soil increases, corrosion increases.
(2) Aeration ~~inversed~~ increases, corrosion increases.
(3) Conductivity of soil increases, corrosion increases.
(4) Moisture content of soil increases, corrosion increases.

Stress corrosion:

Stressed part act as anode

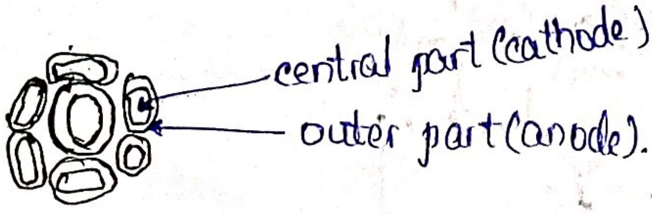
Unstressed part act as cathode.





Intergranular corrosion:

Ex:- Grains, smaller molecules.



** Factors influencing rate of corrosion:

(1) Nature of metal.
(2) Nature of corroding environment.

1. Natural of metal:

(i) Position of metal in electro-chemical series can be (or) galvanic series:

$Zn, Mg, Fe \rightarrow$ higher in electrochemical series (oxdⁿ) - enhance the corrosion

$Cu, Ag, Au \rightarrow$ lower in electrochemical series (redⁿ) - resist the corrosion

(ii) Over voltage:

ROC is slow because

Zn in 1N H_2SO_4 then gets H_2 gas and higher over voltage i.e., 0.7 volts.

If few drops of $CuSO_4$ added to above solution the deposite Cu on Zn and reduces the voltage to 0.33 volts (Cu on Zn accelerate the corrosion).

(iii) Relative ratio of anodic and cathodic parts:

$$\text{Ratio} = \frac{\text{cathodic area}}{\text{anodic area}}$$

anodic area ↑, rate ↓, corrosion ↓.

(iv) Purity of metal:

metal	% of purity	rate of corrosion
Zn	99.999	1
Zn	99.99	2650
Zn	99.95	5000.

(v) Passive character of metals:

Metals like Al, Ti, Cr, Ni $\longrightarrow$ passive character.

Ex: stainless steel $\longrightarrow$ steel contain 13 to 25% of "Cr".

(vi) Volatile nature of corroding product:

molybdenum oxide

$MoO_3 \longrightarrow$ volatile nature $\longrightarrow$ corrosion ↑

(vii) Solubility of corroding product:

Pb is soluble in $FeSO_4 \longrightarrow$ corrosion ↑

(viii) Physical state of metal:

Grains, small parts, stressed parts $\longrightarrow$ corrosion ↑

(2) Nature of corroding environment:
(i) Temperature: Temp ↑, rate of corrosion ↑
(ii) Humidity: humidity ↑, rate of corrosion ↑.
(iii) Presence of impurities in atmosphere: Imputies like H_2S, CO_2, SO_2, smoke in atmosphere increases the corrosion.
(iv) Nature of ions present in the medium:

Cu^{+2} + Fe ⟶ corrosion ↑

Cu^{+2} + silicates ⟶ corrosion ↓

(v) Conductivity of corroding medium:
dry sand soil ⟶ corrosion ↓
wet soil ⟶ corrosion ↑
(vi) Amount of oxygen in atmosphere:
Rusting of Iron: Anode: $Fe \longrightarrow Fe^{+3} + 3e^{\ominus}$ (oxdn)

Cathode: $2H^{\oplus} + 2e^{\ominus} \longrightarrow H_2$

$\frac{1}{2}O_2 + H_2O + 2e^{\ominus} \longrightarrow 2\overset{\ominus}{O}H$

$2Fe^{+2} + 4\overset{\ominus}{O}H \longrightarrow 2Fe(OH)_2 + O_2 + H_2O \longrightarrow 2Fe(OH)_3$ (or) $Fe_2O_3 \cdot 3H_2O$

(vii) Velocity of ions which flow in the medium:
Diffusion of ions ↑, rate of corrosion ↑.
(viii) Effect of pH: Acid solution have high rate of corrosion than neutral and base solution.

Control methods of corrosion:

Proper designing of equipments:
1. To avoid contact between two dissimilar methods.
2. Anodic area ↑, cathodic area ↓.
3. Position of metal in electrochemical ~~serence~~ series very closed.
4. Maitain homogenious of metals.
5. Anode must be painted.
6. Two electrodes contact between insulating materials.

Use of pure metals and alloys:
Heterogenius corrosion ↑

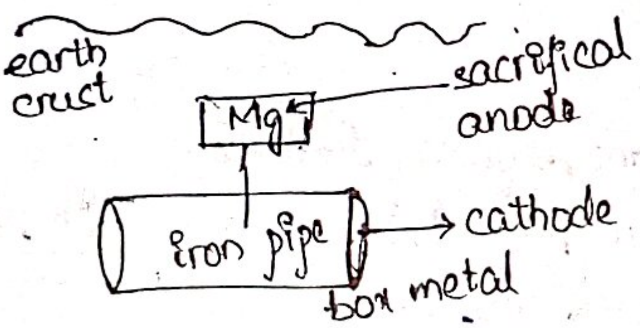
Homogenous corrosion ↓
Ex: Stainless steel ⟷ Cr (13 to 25%)

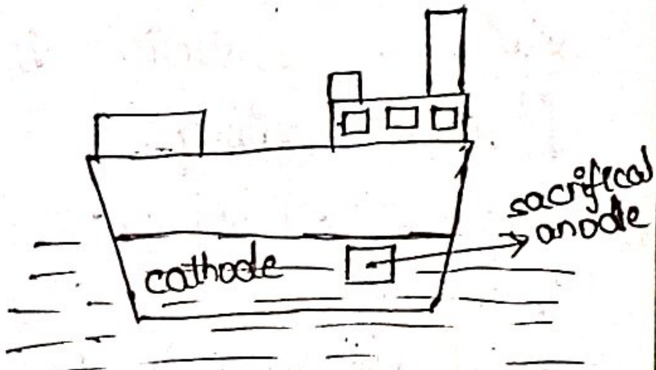
Cathodic Protection : Protection of base metal behave like a cathode i.e., cathodic protection.

(1) Sacrifical anodic protection.

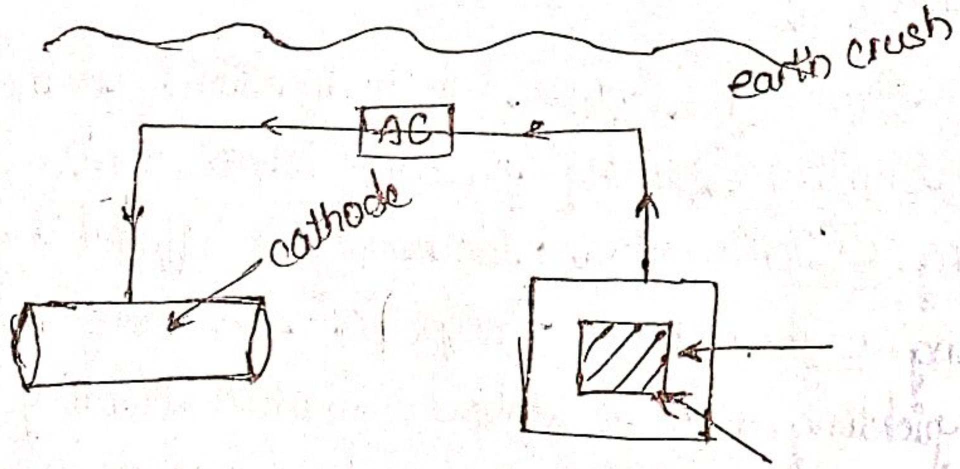
(2) Impressed current voltage method.

(1) **Sacifical anode protection** : Base metal ~~with~~ which is protected by "Mg".





(2) Impressed current voltage method : Base metal which is protected by voltage current.



Corrosion
~~Cathodic~~ inhibitors: A substance which when added in small quantities to the aqueous environment effectively decrease the corrosion of a metal is called ~~cathodic~~ corrosion inhibitors.

1) Anodic inhibitors.
2) Cathodic inhibitors.

1) Anodic inhibitors: Inhibitors avoid the corrosion on metal. Protective film on the surface of the metal; reducing the corrosion.
Ex: Chromates, phosphates, tungstates, transition metals.

2) Cathodic inhibitors:

$$2H^{\oplus} + 2e^{\ominus} \longrightarrow H_2$$

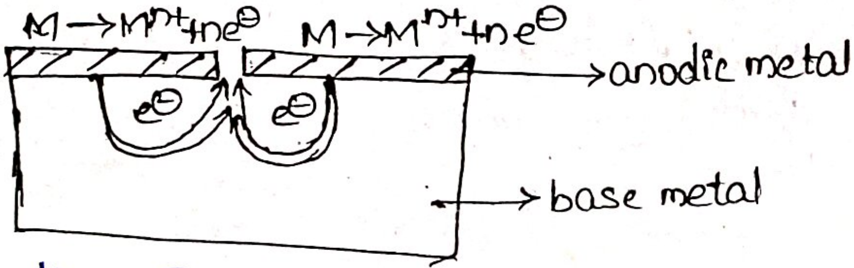
i) Diffusion of $H^{\oplus} \downarrow$
ii) Over voltage $\uparrow$
Ex: Amines, Heterocyclic compounds.

Disadvantages:
1) Base metal is protected but surrounding ion is affected by corrosion.
2) Cost of protection is high.

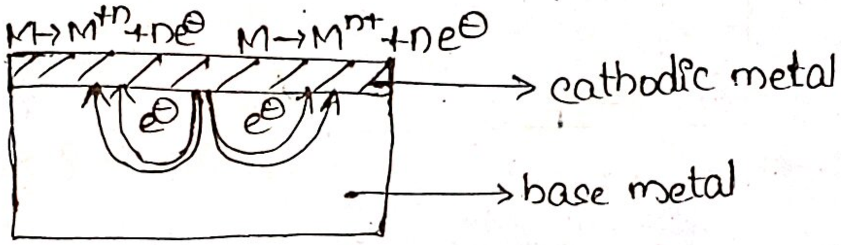
Surface coating:
Solvent cleaning: Ex: Acetone, xylene, toulene.
Alkaline cleaning: Tri sodium phosphate along with soap and rinsed with 0.1% chromic acid.
Mechanical cleaning: Loosily particles removed by brush. Sticky scales removed by sand paper. After cleaning with detergants.
Flame cleaning: Scales, dirty particles removed by flame.
Sand blasting: Sticky particles and removed sand blasting. Disadvantage: Workers are effected by silicosis disease.
Pickling and etching: Except "Al" remaining all metals follow acid pickling. Al is follow alkaline pickling.
* Acid pickling of steel $\longrightarrow$ warm H_2SO_4 and cold HCl.

Metallic coating: Base metal coated with another metal.

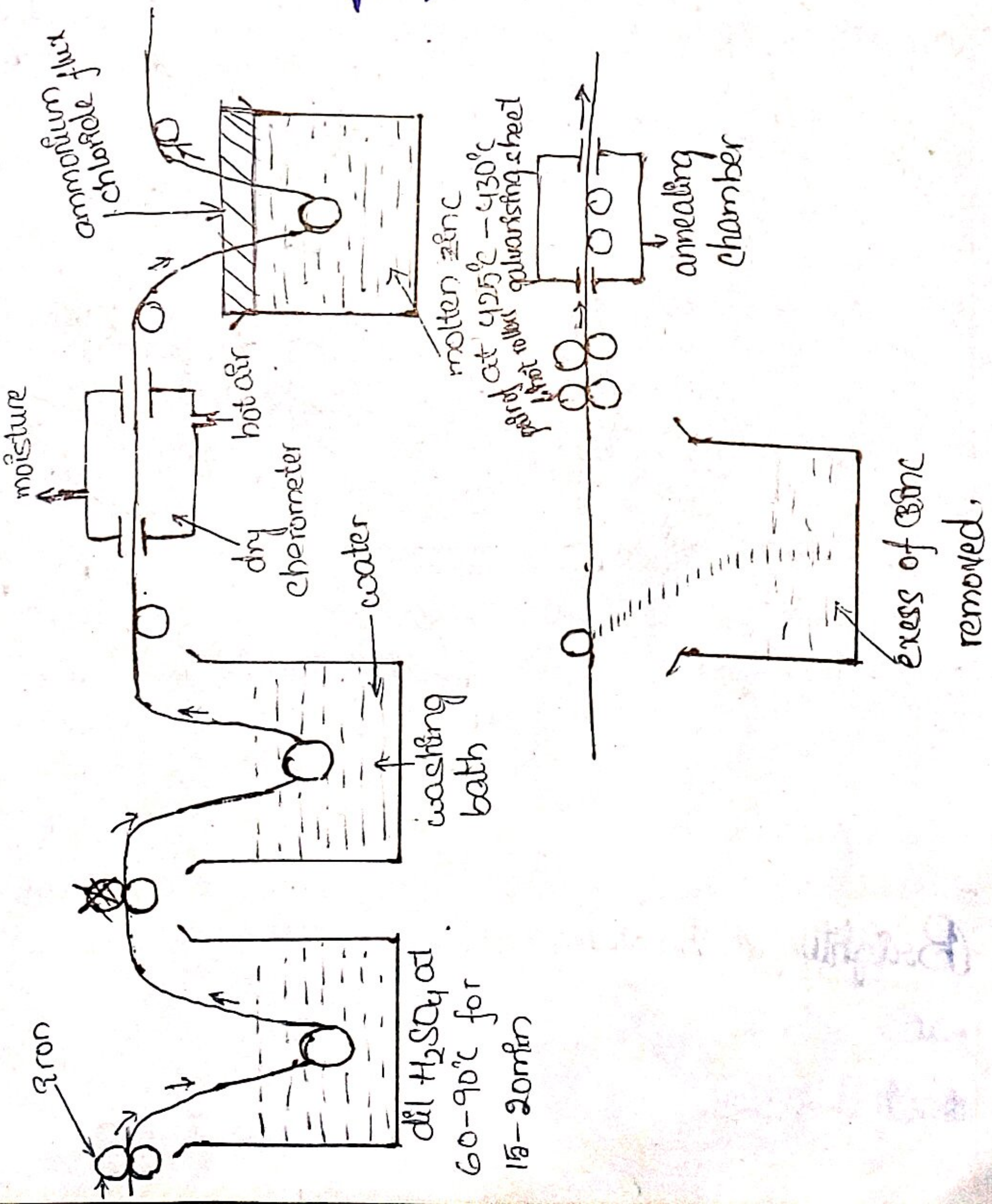
1. **Anodic coating:** Base metal is coated with anodic metal.



2. **Cathodic coating:** Base metal is coated with cathodic metal.



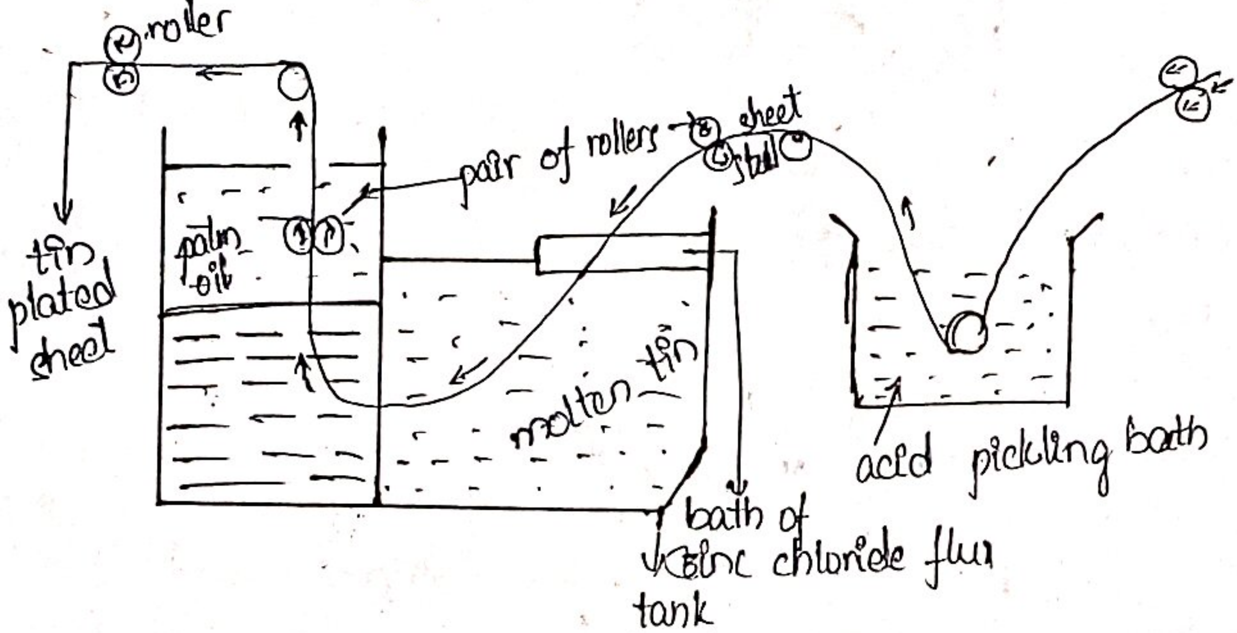
Galvanizing: ~~Co~~ Coating of zinc on iron (or) steel.



Applications: lilires, sheets, pipes, nails, bolts etc.

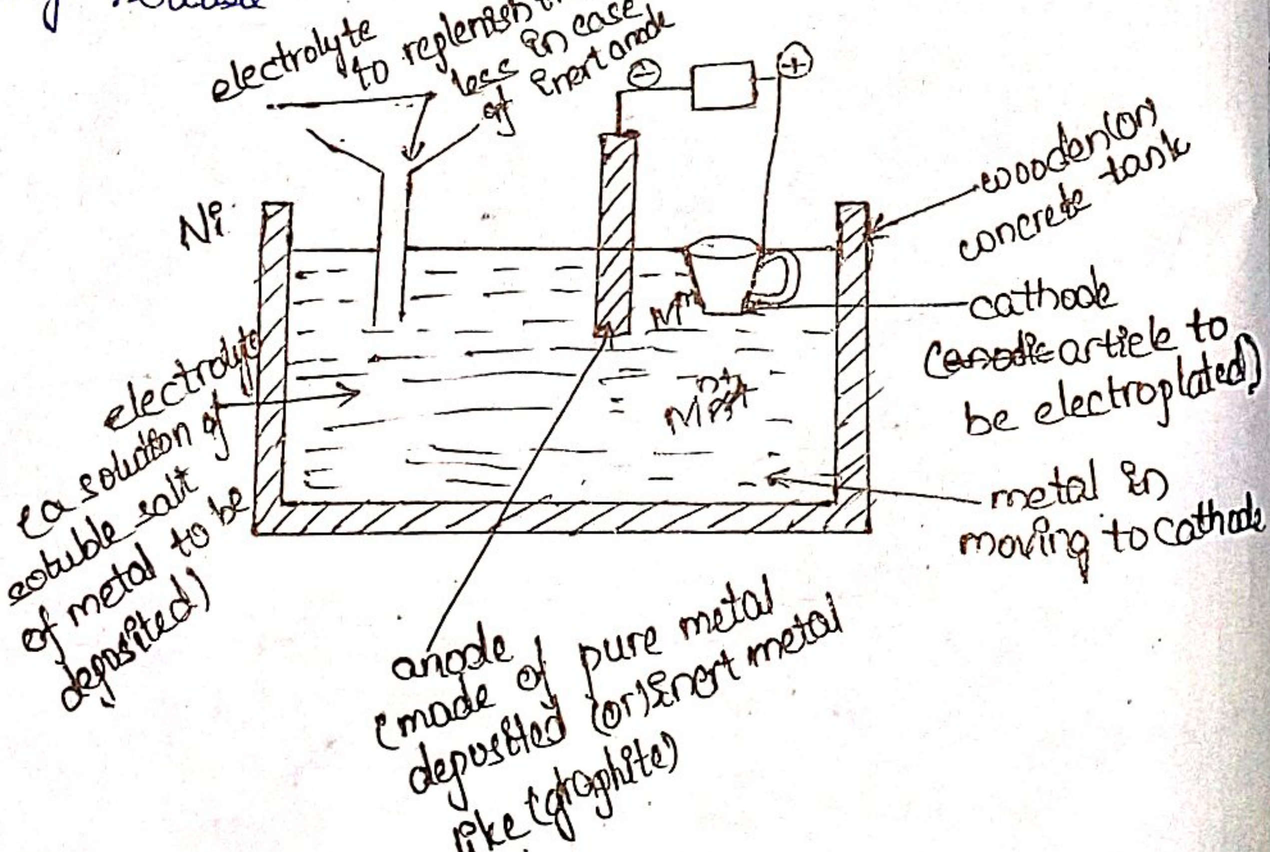
Disadvantages:- Galvanised untensils can't be used for cooking purpose. ($Zn + H_2SO_4 \longrightarrow$ poisnous).

** **Tinning**: Coating of tin on iron or steel.



Tinniring of sheet steel

- Electroplating (or) Electro deposition: Coating metal is deposited on through ~~soluble~~ ~~cont~~ solution containing soluble



Electroplating of Ni on Iron article:
Electrolyte : $NiSO_4$, $NiCl_2$, boric acid.
p^H : 4 (boric acid buffer).
Temp: 40 - 70°C
Current density : 20-30 mA/cm².
Additive added: Saccharin, Coumarin.
Anode: 99% pure Ni piece.
Cathode: Base metal article.
Applications: Used in industries to produce metallic coating.
Electroplating: Corrosion chemical resistance, hardness, surface property non-metals like plastics, wood, glass etc.

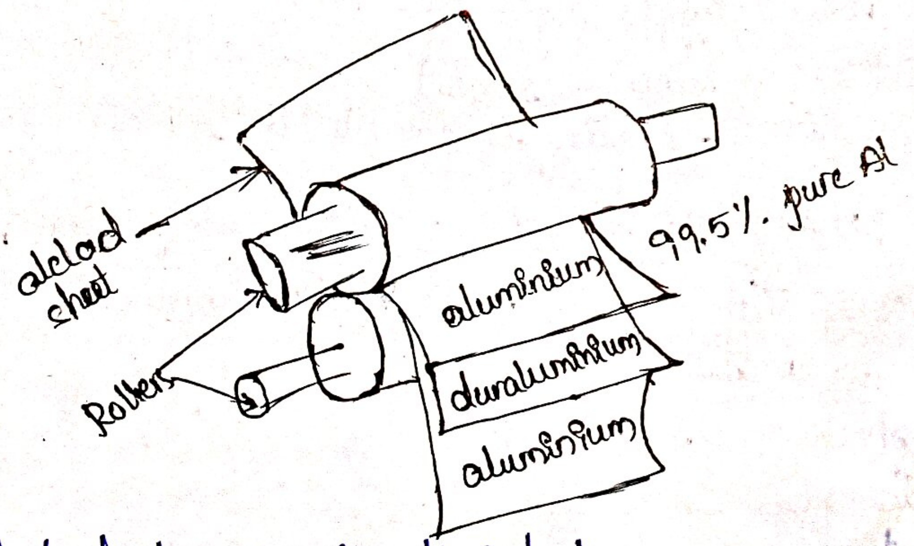
Electroless plating (or) Displacement plating (or) Immersion plating (or) Chemical reduction plating (or) Auto-catalyst plating:

Metal ions + Reducing agents ⟶ Metal deposited on the base metal surface + oxidising product

Ex: $Ni^{+2} + H_2PO_2^{\ominus} + H_2O \xrightarrow{catalyst} Ni + H_3PO_3 + 2H^{\oplus}$

(Iron) Nickel sulphate + sodium hyphosphatic ⟶ (nickel metal phosphide) deposited on base metal (iron)

Metal cladding: Metal cladding is a process by which a dense homogenous layer of coated metal is bonded permanently to the base metal on one (or) both sides.



Alclad sheet ⟶ aircraft industry
duraluminium (Al + Mg + Mn + Cu) between 99.5% pure Al.

18-10-19 Friday

Metal spraying: Base metal which is protected by spraying of another metal.

(1) Gun method.

(2) Powdered method

Cementation (or) diffusion:

(1) Sherardising → Fe is coated with Zn (350-370°C)(2-3hrs)

(2) Colorising → Fe is coated with Al (Al_2Fe_2).

(3) Chromidising → 55% Cr, 45% Al on base metal (1300-1400°C for 3hrs).

(4) Siliconising → silicon tetra chloride on base metal (silicon tetra chloride is a coating metal)

Organic coating:

Paints: Paint is a uniform ~~dispulsion~~ dispersion of finally divided solid in a liquid is called vehicle.

Constituents of Painters:

(1) Pigments

(2) Vehicle (or) drying oil (or) binder (ex: rinsed oil, castor oil)

(3) Thinners (or) solvents. (ex: kirosin, methyl alcohol).

(4) Fillers

(5) Plasticisers.

Varnishes: Varnish is a collidal dispersion of natural (or) synthetic resin in oil or ~~at~~ thinners or both.

Varnishes are 2 types:

(1) oil varnishes → resin + solvent

(2) spirit varnishes → resin is soluble in solvent.

Lacquers: Lacquer is a collidal dispersion of cellular derivative and resin in a solvent.

(1) Cellular derivatives

(2) Resin shellac

(3) Plasticisers

(4) Solvent

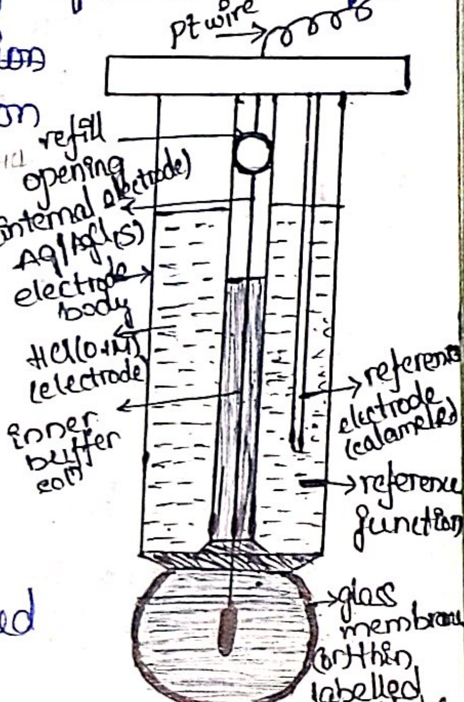
Enamels: Enamel is pigmented varnish which on drying gives ~~less~~ lusters hard and glossy film.

(1) Pigment.
(2) Vehicle (or) drying oil.
(3) Emulsifying agent.

Glass electrode: Glass electrode is also called pH electrode and belongs to ISE (Ions selective electrode) family.

Construction:

Glass electrode consists of glass tube ended with thin walled glass bulb. Buffered solution of fluorides is filled inside the electrode. AgCl-coated ~~solution~~ silver while is immersed in the solution (in place of Ag, Pt electrode in 0.1M of HCl can also be used). The membrane of the glass tube is sensitive to problems.



Principle:

When two solutions of different pH values are separated by a thin glass membrane a potential difference developed ~~by~~ between the two surfaces of the membrane. The potential difference is proportional to the difference in pH value.

The glass membrane function as ion exchange resin.

The glass electrode can be represented as ~~Ag. AgCl~~

$$Ag, AgCl / 0.1M\ HCl / glass / H^{\oplus}\ (unknown)$$

The electrode potential of the glass electrode depends upon the concentration of the $H^{\oplus}$ ions in the experimental solution and given by

$$E_g = E_g^{\circ} - 0.0591 \log [H^+]$$

$$E_g = E_g^{\circ} + 0.0591\, pH.$$

where E_g° is the standard electrode potential i.e, the of the glass electrode when the solution contains unit concentration of $H^{\oplus}$ ions (25°C).

<u>Working</u>: [To determine the pH of the given solution].

If the potential of the glass electrode is known the pH of the solution can be calculated.

To determine the value of the glass electrode (E_g).

It is combined with a reference electrode like calomel electrode. The emf of the cell is given by

$$E_{cell} = E_{calomel} - E_g$$

$$E_{cell} = E_{calomel}\ 0.2422 - (E_g^{o} + 0.0591\ pH)$$

$$pH = \frac{0.2422 - E_g^{o} - E_{cell}}{0.0591}$$

E_g^{o} value can be calculated by using a solution of known pH.

<u>Advantages</u>:

(1) It is simple and can be used easily.

(2) Equilibrium is reached quickly.

(3) The results are accurate.