

MODULE -I
ELECTROCHEMISTRY AND CORROSION

ELECTROCHEMISTRY

Definition:

Electro chemistry is a branch of chemistry which deals with the transformation of electrical energy into chemical energy or chemical into electrical energy.

Concept of electrochemistry:

Electrical Conduction:

The substances are divided into 4 types depending upon their capability of flow of electrons.

Conductors:

The Substances which allows electricity to pass through them are called conductors.

Ex: - Metals, metal sulphides, acids, alkalis, salt sol. and fused salts

The electrical conductors are of two types.

1. Metallic or Electronic conductors.

2. Electrolytic conductors

i) **Non-conductors:** The substances which do not allow electricity are called non-conductors.

Example: Pure water, dry wood, rubber, paper, non-metals etc.

ii) **Semi-conductors:** The substances which partially conduct electricity are called semi- conductors. The conducting properties of semi-conducting properties are increased by the addition of certain impurities called “dopping”.

Example: ‘si’ and addition of V group elements like ‘p’ ‘si’ produces n-type semi- conductor. On addition of iii group element like ‘B’, Al, ‘si’ produces p-type of semi-conductor.

Electro chemical cell (or) Galvanic cell:

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

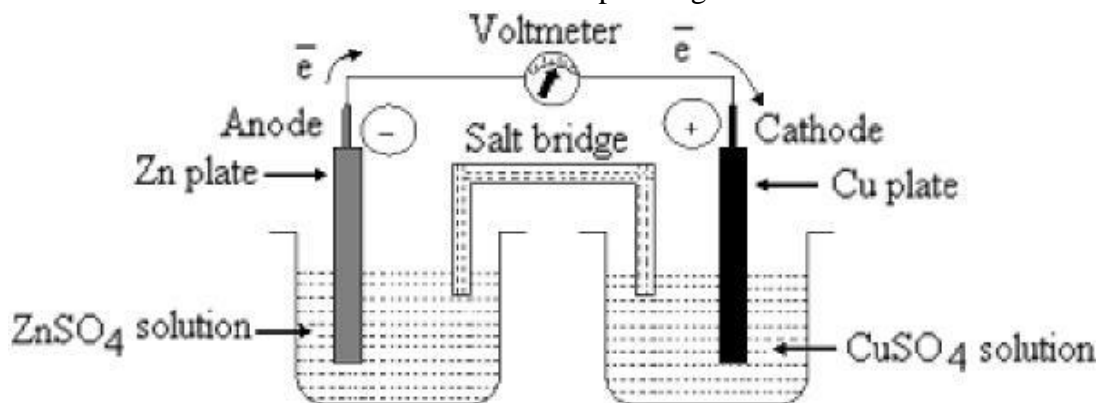
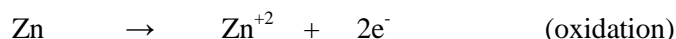


Fig1.1.1 Galvanic cell

This cell is made up of two half cells. One is oxidation or anodic half cell. The other is reduction or cathodic half-cell. The first half cell consists of 'Zn' electrode dipped in ZnSO₄ solution and second half cell consists of 'Cu' electrode dipped in CuSO₄ solution. Both the half cells are connected externally by metallic conductor. And internally by 'salt bridge' salt bridge is a U- tube containing concentrated solution of KCl or NH₄ NO₃ in agar-agar gel contained porous pot. It provides electrical contact between two solutions.

The following reactions take place in the cell.

At Anode:



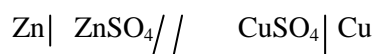
At cathode:



The movement of electrons from Zinc to copper produces a current in the circuit.

The overall cell reaction is: $\text{Zn} + \text{Cu}^{+2} \longleftrightarrow \text{Zn}^{+2} + \text{Cu}$

The galvanic cell can be represented by



The passage of electrons from one electrode to other causes the potential difference between them which is called E.M.F. The E.M.F. of the galvanic cell is 1.10V

EMF

The difference of potential which causes flow of electrons from an electrode of higher potential to an electrode of lower potential is called Electro motive force (EMF) of the cell.

The E.M.F of galvanic cell is calculated by the reduction half – cell potentials using to following ex.

$$E_{\text{cell}} = E(\text{right}) - E(\text{left})$$

$$E_{\text{cell}} = \text{EMF of the cell.}$$

E right =Reduction potential of right hand side electrode.

Eleft =Oxidation potential of left hand side electrode.

Applications of EMF measurement:-

1. Potentiometric titrations can be carried out.
2. Transport number of ions can be determined.
3. P^H can be measured.

4. Hydrolysis constant can be determined.
5. Solubility of sparingly soluble salts can be found.

Differences between Galvanic cell and Electrolytic cell.

Galvanic cell / Electrochemical cell	Electrolytic cell
<ol style="list-style-type: none"> 1. In this cell, chemical energy is converted in to electrical energy. 2. In this cell anode is -ve electrode and cathode is +ve electrode. 3. Salt bridge is required. 4. This process is reversible and spontaneous. 5. EMF of the cell is +ve. 	<ol style="list-style-type: none"> 1. In this cell electrical energy is converted in to chemical energy. 2. In this cell anode is +ve electrode and cathode is -ve electrode. 3. Salt bridge is not required. 4. This process is irreversible and not spontaneous. 5. EMF of the cell is -ve.

Single electrode potential: (E)

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 atom and its corresponding ion called the electrode potential. There is a dynamic equilibrium between the metal and metal ion and the potential diff. between the two is called electrode potential. It is measured in volts.

Standard electrode potential: (E^0)



The potential exhibited by single at unit concentration of its metal ion at 25^0C is called standard electrode potential (E^0) (If it is Gas electrode to maintain pressure at 1atm).

Eg: E of $\text{Cu}^{+2} / \text{Cu} = E^0$ when concentration of Cu^{+2} is 1M. E^0 value of single electrode is determined experimentally by combining the single electrode with standard hydrogen electrode.

Electrochemical series:

- The arrangement of elements in order of decreasing standard reduction potential values is called electrochemical series. It is also called activity series.
- Standard reduction potential value shows whether the position of the equilibrium lies to the left or right of the hydrogen equilibrium.

- Elements that lose electrons more easily have lower (-ve) reduction potentials and those which accept electrons more easily have higher (+ve) reduction potential.
- Standard Hydrogen Electrode ($E^0=0$) has middle position in electrochemical series.
- Electrodes above hydrogen electrode are reduction electrodes, and those below are oxidation electrodes.
- In EMF series elements having higher (+ve) reduction potential are placed at the top.
- In EMF series elements having lower (-ve) reduction potentials are placed at the bottom.
- Metal at the bottom is the most active metal.
- Non-metal at the top is the most active non-metal.

 <p>Stronger oxidizing agent</p>	$F_2(g) + 2e^- \longrightarrow 2F(aq)$	2.87	 <p>Weaker reducing agent</p>
	$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	1.23	
	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	-0.13	
	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	-0.26	
	$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	-0.40	
	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	-0.45	
<p>Weaker oxidizing agent</p>	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	-0.76	<p>Stronger reducing agent</p>
	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	-0.83	
	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	-1.66	
	$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	-2.37	
	$Na^+(aq) + e^- \longrightarrow Na(s)$	-2.71	
	$Li^+(aq) + e^- \longrightarrow Li(s)$	-3.04	

➤ APPLICATIONS OF ELECTROCHEMICAL SERIES:

- To predict relative oxidation or reduction of various electrodes.

Reduction potential (also known as redox potential, oxidation/reduction potential, or E_h) measures the tendency of a chemical species to acquire electrons and thereby be reduced. Reduction potential is measured in volts (V)

or millivolts (mV). Each species has its own intrinsic reduction potential. The more positive the potential, the greater the species' affinity for electrons, or the more the species tends to be reduced.

➤ **To predict whether metal reacts with acid to give hydrogen.**

The reaction between a tiny amount of hydrogen and oxygen in the air produces a characteristic 'pop' sound and this serves as test for the presence of hydrogen.

➤ **To calculate standard EMF of electrochemical cell.**

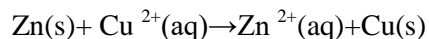
The electromotive force of a cell or EMF of a cell is the maximum potential difference between two electrodes of a cell. It can also be defined as the net voltage between the oxidation and reduction half-reactions. The EMF of a cell is mainly used to determine whether an electrochemical cell is galvanic or not.

➤ **To predict the spontaneity of a reaction.**

A spontaneous reaction is a reaction that favors the formation of products at the conditions under which the reaction is occurring. Combustion reactions, such as this fire, are spontaneous reactions. Once the reaction begins, it continues on its own until one of the reactants (fuel or oxygen) is gone.

➤ **To predict metal displacement.**

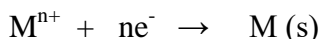
A metal can displace metal ions listed the activity series, For example, zinc is more active than copper and is able to displace copper ions from solution



Nernst Equation:

It tells us the effect of electrolyte concentration on electrode potential

Consider a general electrode reaction



For this electrode reaction, free energy change (ΔG) can be calculated provided standard free energy change (ΔG^0)

Gas constant (R), temperature (T), activity of product and activity of reactant are known using the following equation. $\Delta G = \Delta G^0 + RT \ln (a_{\text{product}} / a_{\text{reactant}})$

Since $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$

Hence

$E = E^0 - \frac{2.303 RT}{nF} \log (a_{\text{product}} / a_{\text{reactant}})$

This is Nernst equation where

E = Electrode potential

E^0 = Standard electrode potential

F = faraday of electricity (96500 C)

T = temperature at 298k

R = Gas constant ($8.314 \text{ k}^{-1} \text{ mol}^{-1}$)

a = activity

at 298k putting the value of F = faraday of electricity (96500 C) and R = Gas constant ($8.314 \text{ k}^{-1} \text{ mol}^{-1}$) we get

$$E = E^0 - 0.0591/n \log (a_{\text{product}} / a_{\text{reactant}})$$

In dilute solutions, activities may be replaced by molar concentrations terms,

$$E = E^0 - 0.0591 / n \log ([M(s)] / [M^{n+}_{(aq)}])$$

For pure solid ($[M(s)] = 1$

$$E = E^0 - 0.0591 / n \log (1 / [M^{n+}_{(aq)}])$$

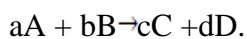
$$E = E^0 + 0.0591 / n \log [M^{n+}_{(aq)}]$$

The above equation is Nernst equation for the electrode at 298 k

Nernst studied the theoretical relationship between electrode reaction and the corresponding cell

e.m.f. This relationship generally Known as Nernst equation.

Consider a galvanic cell



Where a,b,c,d represents no. of moles respectively at

equilibrium.

$$E = E^0 - \frac{2.303 RT}{nF} \log \left(\frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

Thus Nernst equation is applicable for the determination of Emf of cell

Similarly, for the cell reaction.

$$E = E^0 - \frac{2.303 RT}{nF} \log \left(\frac{[Zn^{+2}(1M)]}{[Cu^{+2}(1M)]} \right)$$

Reference Electrode:

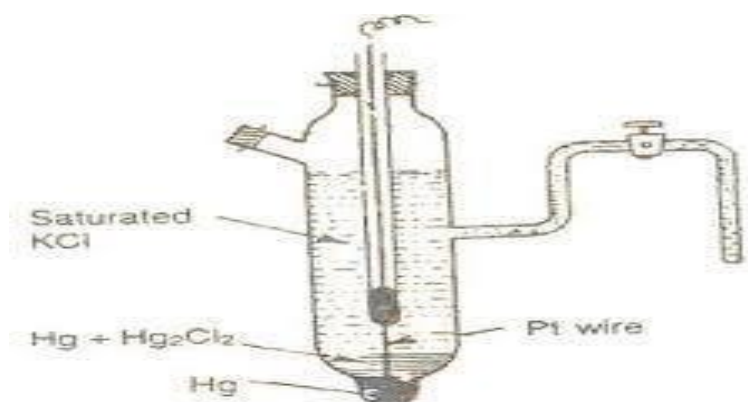
Because of the inconveniences in the usage of Hydrogen electrode like maintenance of accurate pressure, inconvenience in handling gas secondary electrodes were developed.

Standard calomel electrode (SCE):

The calomel electrode consists of a glass tube having two side tubes. A small quantity of pure mercury is placed at the bottom of the vessel and is covered with a paste of Hg and Hg_2Cl_2 . KCl solution of known concentration is filled through side tube, Shown on the right side of the vessel. The KCl sol. is filled in the left side tube which helps to make a connection through a salt bridge with the other electrode, which potential has to be determined.

A 'pt' wire is sealed into a glass tube as shown in the fig which is in contact with Hg.

When the cell is set up it is immersed in the given solution. The concentration of KCl. The electrode potentials of calomel electrode of different concentrations at 25°C are



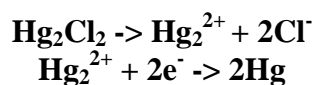
Standard calomel electrode

0.1 N KCl / Hg_2Cl_2 (s) / Hg, pt \rightarrow 0.33v

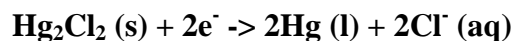
1N KCl / Hg_2Cl_2 (s) / Hg, pt \rightarrow 0.28v

Saturated KCl / Hg_2Cl_2 (s) / Hg, pt \rightarrow 0.24v

The corresponding electrode reaction is



Net cell reaction is



Merits :

- Concentration of Cl^- remains constant.
- Potential of electrode remains constant with temperature.
- Ease of oxidation-reduction reactions.
- Construction is simple and easy to maintain.
- Inexpensive.
- pH can be measured by combining with hydrogen or quinhydrone or glass electrodes.

Demerits :

- Solubility of KCl is sensitive.
- KCl has to be replaced from time to time.
- Mercury is toxic and poses health hazards.

NUMERICAL PROBLEMS:

1. Calculate the E.M.F of voltaic cell $\text{Fe} | \text{Fe}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}$.

Given the Electrode potentials of copper and iron are 0.34 volt and -0.44

volt respectively.

Formula: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

$$= 0.34 \text{ V} - (-0.44 \text{ V})$$

$$= 0.34 \text{ V} + 0.44 \text{ V}$$

$$E_{\text{cell}} = 0.78 \text{ V}$$

2. Calculate the EMF of a cell if the reduction potentials of the cell are

-0.763V and 0.337V.

Formula: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

$$= 0.337 \text{ V} - (-0.763 \text{ V})$$

$$= 0.337 \text{ V} + 0.763 \text{ V}$$

$$E_{\text{cell}} = 1.1 \text{ V}$$

3. Calculate the electrode potential of the copper wire dipped in 0.1 M CuSO_4 solution at 25°C . The standard electrode potential of copper is 0.34V.

$$E^0_{\text{cell}} = 0.34 \text{ V}$$

Formula: $E = E^0 - \frac{0.0591}{n} \log \left(\frac{1}{[M^{n+}_{(\text{aq})}]} \right)$

$$E = E^0 - \frac{0.0591}{2} \log \left(\frac{1}{0.1} \right)$$

$$= 0.34 - 0.03$$

$$E = 0.31 \text{ V}$$

4. Calculate the electrode potential of the zinc rod dipped in 0.1M ZnSO_4 solution at 25°C . The standard reduction electrode potential of zinc is -0.76 V.

$$E^0_{\text{cell}} = -0.76 \text{ V}$$

Formula: $E = E^0 - \frac{0.0591}{n} \log \left(\frac{1}{[M^{n+}_{(\text{aq})}]} \right)$

$$E = E^0 - \frac{0.0591}{2} \log \left(\frac{1}{0.1} \right)$$

$$= -0.76 - 0.03$$

$$E = -0.79 \text{ V}$$

5. The standard reduction potentials of Zn^{+2}/Zn and Cu^{+2}/Cu are -0.76V

and +0.34 V respectively. What is the e.m.f of the cell? $\text{Zn(s)}/\text{Zn}^{+2} (0.05\text{M}) // \text{Cu}^{+2} (0.005\text{M}) | \text{Cu(s)}$

$$E^0_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ V}, \quad E^0_{\text{Cu}^{+2}/\text{Cu}} = +0.34 \text{ V}$$

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

$$= 0.34 \text{ V} - (-0.76 \text{ V}), = 0.34 \text{ V} + 0.76 \text{ V} = 1.1 \text{ V}$$

$$\text{Formula: } E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n} \log \left(\frac{[\text{Zn}^{+2}(1\text{M})]}{[\text{Cu}^{+2}(1\text{M})]} \right)$$

$$E_{\text{cell}} = 1.1 - 0.0591/2 \log ([\text{Zn}^{+2}(0.05\text{M})/\text{Cu}^{+2}(0.005\text{M})])$$

$$E_{\text{cell}} = 1.1 - 0.0591 / 2 \log (0.05 / 0.005)$$

$$E_{\text{cell}} = 1.07 \text{ V}$$

6. Write the overall cell reaction for $\text{Zn(s)}/\text{Zn}^{2+}(0.2\text{M})//\text{Ag}^{+2}(0.002 \text{ M})/\text{Ag(s)}$

and Calculate the emf of the cell at 25°C . The standard emf of the cell is

1.54 V.

$$E^{\circ} \text{ cell} = 1.54 \text{ V}$$

$$\text{Formula: } E_{\text{cell}} = E^{\circ} \text{ cell} - 2.303 RT / nF \log ([\text{Zn}^{+2}(1\text{M})/\text{Ag}^{+2}(1\text{M})])$$

$$E_{\text{cell}} = E^{\circ} \text{ cell} - 2.303 RT / nF \log ([\text{Zn}^{+2}(0.2\text{M})/\text{Ag}^{+2}(0.002\text{M})])$$

$$E_{\text{cell}} = 1.54 \text{ V} - 0.0591 / 2 \log (0.2 / 0.002)$$

$$E_{\text{cell}} = 1.4809 \text{ V}$$

Batteries:

When two or more electrochemical cells are electrically interconnected, each of which containing two electrodes and an electrolyte is called a Battery.

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

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

Eg: Leclanche cell, Dry cell.

Secondary Batteries: - These are rechargeable and are meant for multi cycle use. After every use the electrochemical reaction could be reversed by external application fades or lost due to leakage or internal short circuit.

Eg: Lead-acid cell, Ni-cd cell.

Differences between Primary and secondary batteries:

Primary cells	Secondary cells
<ol style="list-style-type: none">1. These are non-rechargeable and meant for a single use and to be discarded after use.2. Cell reaction is not reversible.3. Cannot be rechargeable.4. Less expensive.5. Can be used as long as the materials are active in their composition. Eg: Leclanche cell, 'Li' Cells.	<ol style="list-style-type: none">1. These are rechargeable and meant for multi cycle use.2. Cell reaction can be reversed.3. Can be rechargeable.4. Expensive.5. Can be used again and again by recharging the cell. Eg; Lead- acid cell, Ni-cd cells.

Primary Batteries:

Dry cell (Leclanche cell):

Anode: Zinc

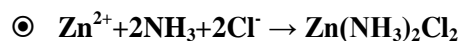
Cathode: Graphite rod

Electrolyte: paste of NH_4Cl and ZnCl_2

Emf: 1.5V.

Dry cell consists of a cylindrical Zinc container which acts as an anode. A graphite rod displaced in the center. The graphite rod does not touch the base and it acts as a cathode. The graphite rod is surrounded by powdered MnO_2 and carbon. The remaining Space in between cathode and anode is filled with a paste of NH_4Cl and ZnCl_2 . The graphite rod is fitted with a Metal cap and the cylinder is sealed at the top with a pitch.

The reactions takes place in the cell are:

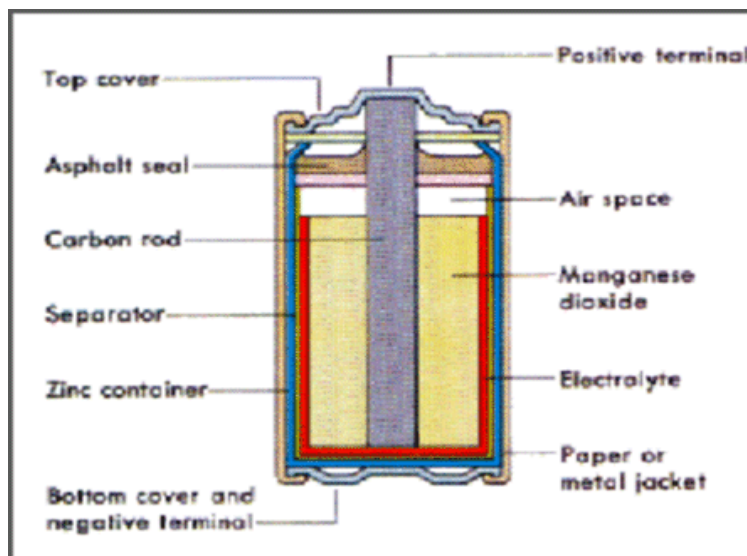


Diaminedichlorozinc



MnO_2 acts as depolarizer.

The EMF of the cell is about 1.2-1.5 volts.



Dry Cell

Lithium Cell:

- Lithium Cell (also known as coin cell) is a primary battery which cannot be recharged.



In solid cathode Lithium Cell

- Lithium metal acts as anode,
- Manganese Dioxide solid acts as cathode,
- Lithium salt dissolved in non-aqueous solvent (Acetonitrile) medium acts as electrolyte.
- **At anode:** $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$
- **At cathode:** $\text{MnO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{MnO}_2(\text{Li})$
- **Cell Reaction:** $\text{Li} + \text{MnO}_2 \rightarrow \text{MnO}_2(\text{Li})$
- MnO_2 is reduced to trivalent state from tetravalent state by Lithium.
- EMF of the cell is 3 V .

In liquid cathode Lithium Cell

- Lithium metal acts as anode,
- Thionyl Chloride liquid acts as cathode,
- Lithium salt dissolved in non-aqueous solvent (Thionyl Chloride) medium acts as electrolyte.
- **At anode:** $4\text{Li} \rightarrow 4\text{Li}^+ + 4\text{e}^-$
- **At cathode:** $2\text{SOCl}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow 4\text{LiCl} + \text{S} + \text{SO}_2$
- **Cell Reaction:** $4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{S} + \text{SO}_2$
- EMF of the cell is 3.5 V .

Advantages of Lithium Cell:

- Exhibit voltages up to 4V.
- High output energy.
- Operating temperature range is -50 °C to 70 °C.
- Long life time.
- Good conductivity.
- Wide usage.
- Coin size (typically 20 mm in diameter and 1.6–4 mm thick).

Uses of Lithium Cell:

- Small lithium batteries are very commonly used in small, portable electronic devices, such as PDAs, clocks, watches, camcorders, digital cameras, thermometers, calculators, personal computer BIOS (firmware), communication equipment and remote car locks.
- Used in many long-life, critical devices, such as pacemakers and other implantable electronic medical devices. These devices use specialized lithium-iodide batteries designed to last 15 or more years.

Secondary Batteries:

Lead – acid cell:

Anode: Sponge metallic lead

Cathode: Lead dioxide PbO_2

Electrolyte: Aqueous H_2SO_4 .

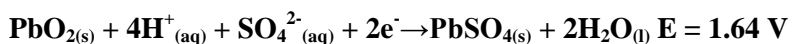
- ⊙ **Emf:** Single pair of electrodes give a potential of 2V.
- ⊙ **Storage cell** contains 6 pairs in series giving 12V.

Cell reactions:

At Anode:



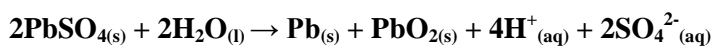
At Cathode:



Cell Reaction (Discharging):



Cell Reaction (Charging):

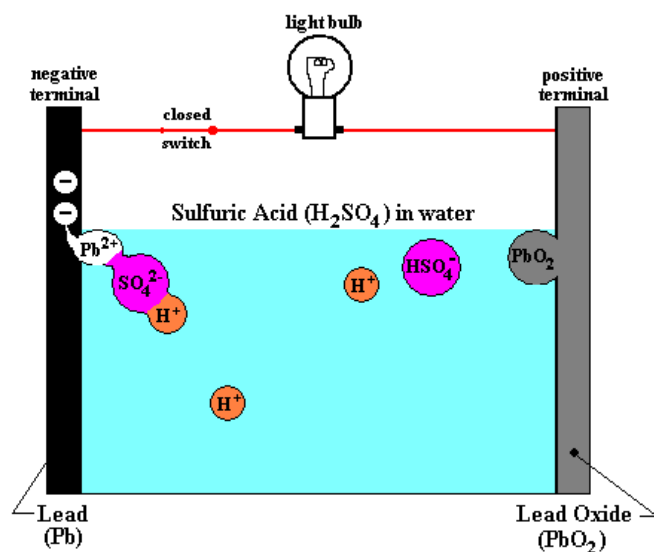


Applications:

- i. Automobile and construction equipment.
- ii. Standby system for engine batteries.

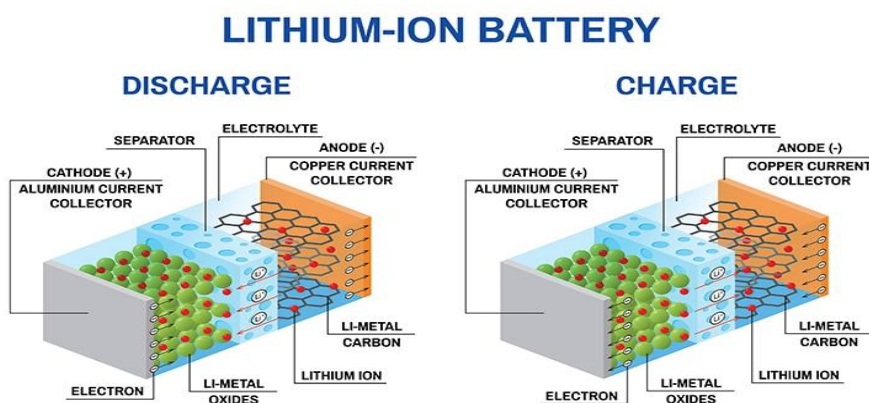
Advantages:

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



Lithium-ion battery:

- Lithium-ion cell is a secondary cell.
- It can be recharged.
- Anode is Lithium doped graphite.
- Cathode is a intercalated lithium compound such as layered lithium cobalt (III) oxide – LiCoO_2 .
- The liquid electrolyte consists of complex lithium compound such as lithium hexafluoro phosphate dissolved in an organic solvent such as dimethyl carbonate.
- Provide lightweight, high energy density power sources for variety of devices.



- **At Anode:** $\text{Li}_n\text{C} \rightarrow n\text{Li}^+ + n\text{e}^- + \text{C}$
- **At Cathode:** $\text{Li}_{1-n}\text{CoO}_2 + n\text{Li}^+ + n\text{e}^- \rightarrow \text{LiCoO}_2$
- **Cell Reaction (Discharging):** $\text{Li}_n\text{C} + \text{Li}_{1-n}\text{CoO}_2 \rightarrow \text{C} + \text{LiCoO}_2$
- **Cell Reaction (Charging):** $\text{C} + \text{LiCoO}_2 \rightarrow \text{Li}_n\text{C} + \text{Li}_{1-n}\text{CoO}_2$

Uses:

- Lithium-ion batteries are commonly used for portable electronics and electric vehicles and are growing in popularity for military and aerospace applications.
- Used in mobile phones, notebook PC's, cameras, camcorders, MP3, PDA's
- Used in power tools such as cordless drills, sanders, saws and variety of garden equipment including whipper-snippers and hedge trimmers.
- Secondary non-aqueous lithium batteries provide reliable backup power to load equipment in a network environment of telecommunications provider.

CORROSION

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

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

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

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

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

Causes of corrosion:

1. The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc.
2. During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy.
3. Hence the isolated pure metals are regarded as excited states than their corresponding ores. So metals have natural tendency to go back to their combined state (minerals/ores).

When metal is exposed to atmospheric gases, moisture, liquids etc., and the metal surface reacts and forms more thermodynamically stabled compounds.

Effects of corrosion:

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

Theories of corrosion

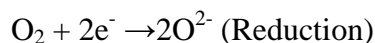
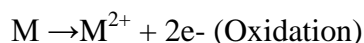
Dry corrosion or Chemical corrosion

This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses like O_2 , halogens, H_2S , SO_2 , N_2 or anhydrous inorganic liquid with the metal surface.

There are three types of chemical Corrosion:

- (1) Oxidation corrosion
- (2) Corrosion due to other gases
- (3) Liquid metal corrosion

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



Mechanism: Initially the surface of metal undergoes oxidation and the resulting metal oxide scale forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide.

i.If the metal oxide is stable, it behaves has a protective layer which prevents further Corrosion.

E.g., the oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.

ii.If the metal oxide unstable, the oxide layer formed decomposes back into metal and oxygen.

Oxidation corrosion is not possible.

E.g., Ag, Au and Pt do not undergo oxidation corrosion.

iii.If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO_3).

iv.If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This cause continuous corrosion till conversion of metal into its oxide is completed.
Ex: Alkali and alkaline earth metals (Li, Na, K, Mg etc.)

Pilling- Bedworth Rule :

When the oxide film is sufficiently porous so that the diffusion of cation M^+ and anion O^- takes place smoothly then oxidation corrosion takes place continuously.

Pilling-Bedwroth rule describe the porous and non-porous nature of metallic oxide which is formed during corrosion.

According to this rule specific ration calculated follows

Specific volume ratio = Volume of metal oxide / Volume of metal

If the specific volume ration is smaller, then oxidation corrosion will takes place. Because the oxide films will be sufficiently porous for diffusion of M^+ and O^{2-} . If the specific volume ration is more than 1 then it will be non-porous.

If the volume of the metallic oxide is equal or greater in volume to the metal surface. The metal surface is compact, non-porous-protective. For example Cu, In, Al, Ni, Cr forms oxides whose volume is greater then the

volume of the metal.

If the volume of the metallic oxide is less than the volume of the metal surface then that oxide layer is porous and non-protective. For example Alkali and alkaline earth metals – Li, Na, K and Mg.

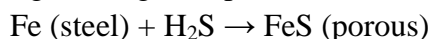
Corrosion due to other gases: This type of corrosion is due to gases like SO_2 , CO_2 , Cl_2 , H_2S , F_2 etc. In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bed worth rule.

i.If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent; non-porous does not allow the penetration of corrosive gases.



ii.If the volume of the corrosion film formed is less than the underlying metal, it forms Pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

Ex. In petroleum industry, H_2S gas at high temperature reacts with steel forming a FeS scale.



Liquid metal corrosion: This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

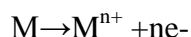
Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

Wet corrosion or electrochemical corrosion

This type of Corrosion occurs where a conducting liquid is in contact with the metal. This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.

At anodic area, oxidation reaction occurs there by destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

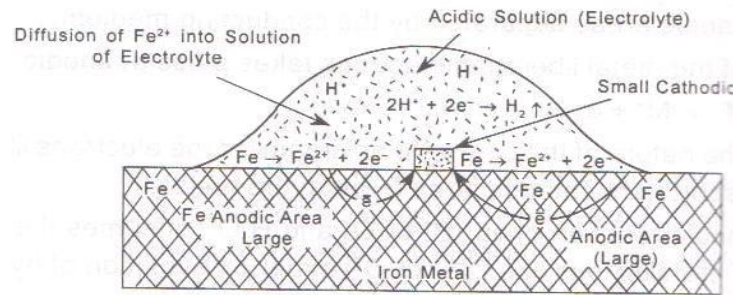
Mechanism: Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.



The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

Evolution of hydrogen: This type of corrosion occurs in acidic medium.

E.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with Liberation of electrons.



Hydrogen evolution

Anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ (Oxidation)

The electrons released flow through the metal from anode to cathode, whereas H^+ ions of acidic solution are eliminated as hydrogen gas.

Cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (Reduction)

The overall reaction is: $\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2$

This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas. The anodes are large areas, whereas cathodes are small areas.

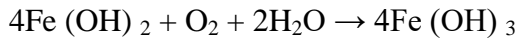
Absorption of oxygen: For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large Cathodes. The released electrons flow from anode to cathode through iron metal.

At anode: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

At cathode: $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$ (Reduction)

Overall reaction: $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$

If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.



The product called yellow rust corresponds to $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

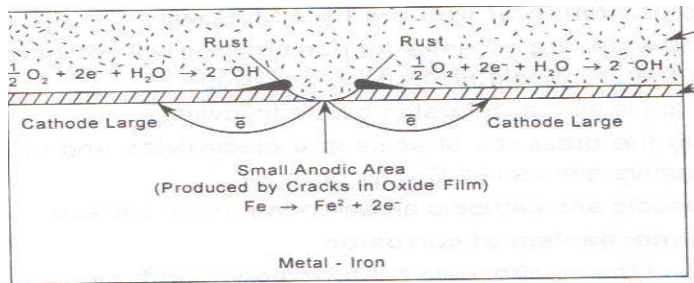


Fig.1.8.2.2 Oxygen absorption corrosion

Corrosion control methods:

Cathodic protection

The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.

There are two types of cathodic protection

- (a) Sacrificial anode method
- (b) Impressed current method.

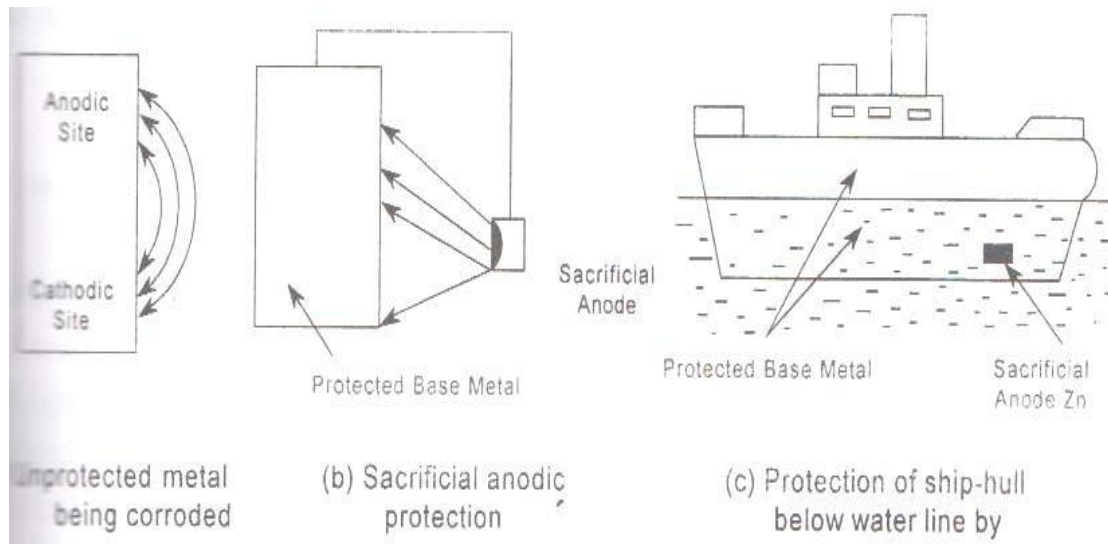
Sacrificial anode method:

In this protection method, the metallic structure to be protected (base metal) is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.

The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

Eg. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

Eg. The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.



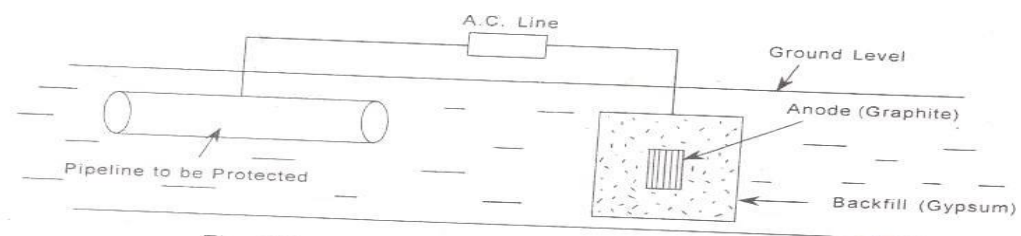
Sacrificial anode method: ship hull and underground water pipeline

Impressed current Cathodic protection:

In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.

The impressed current is slightly higher than the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.

The impressed current is taken from a battery or rectified on A.C. line. The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.



Impressed current method

Surface coatings:

These are produced by coating one metal on the surface of molten metal. The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

Metallic coatings

The surface of the base metal is coated with another metal (coating metal). Metallic coatings are broadly classified into anodic and cathodic coatings.

Anodic coating: the metal used for the surface coating is more anodic than the base metal which is to be protected.

For example, coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially.

The formation of pores and cracks over the metallic coating exposes the base metal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected.

Cathodic coating:

- Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal. They protect the base metal as they have higher corrosion resistance than the base metal due to cathodic nature.
- Cathodic coating protects the base metal only when the coating is uniform and free from pores.
- The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.

Methods of application of metallic coatings:**Hotdipping**

Hot dipping process is applicable to the metals having higher melting point than the coating metal. It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal and a flux layer.

The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

Eg. Coating of Zn, Pb, Al on iron and steel surfaces.

The most widely used hot dipping processes are galvanizing and tinning.

Galvanizing:

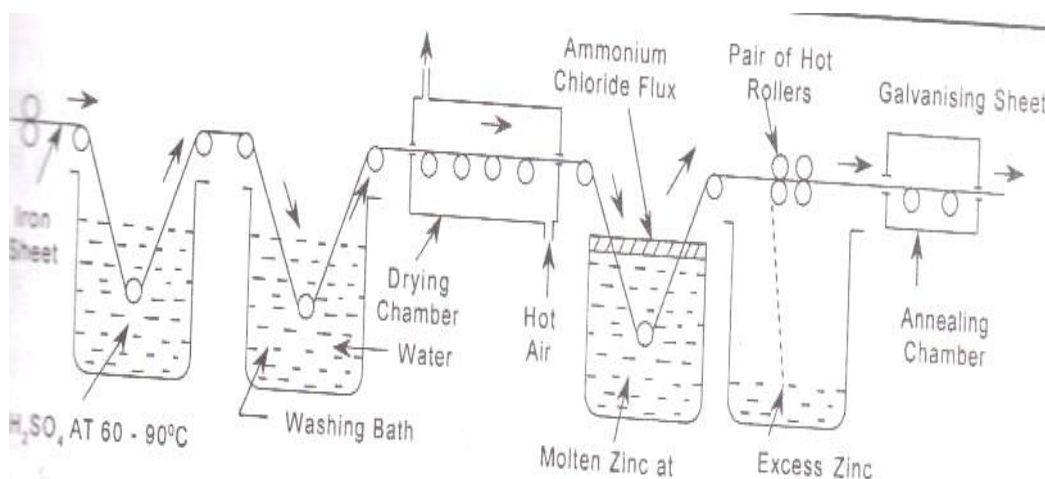
Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc.

It is the anodic protection offered by the zinc. In this process, at first iron or steel is cleaned by pickling with dilute sulphuric acid solution at a temperature range of 60-90°C for 15 to 20 minutes. Therefore, it removes scale, rust and other impurities present and then washed well in a water bath and dried.

Then after dipped in the bath containing molten zinc which is at 425-450°C. To prevent it from oxide formation, the surface of bath is covered with a ammonium chloride flux. When the iron sheet is taken out it is coated with a thin layer of zinc.

To remove excess zinc, it is passed through a pair of hot rollers and then it is annealed at a temperature of 450°C followed by cooling.

Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.



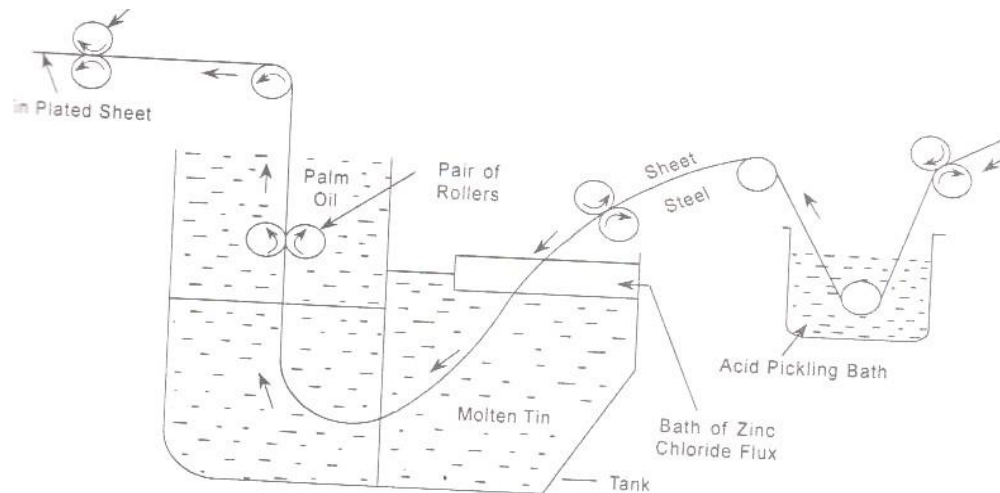
Tinning:

The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning.

Tin is a noble metal and therefore it possess more resistance to chemical attack. It is the cathodic protection offered by the tin. In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present.

A cleaned iron sheet is passed through a bath ZnCl_2 molten flux followed by molten tin and finally through a suitable vegetable oil. The ZnCl_2 flux helps the molten metal to adhere to the base metallic surface.

Palm oil protects the tin coated surface against oxidation. Tinning of mild steel plates is done mostly for the requirements of the food stuff industry.



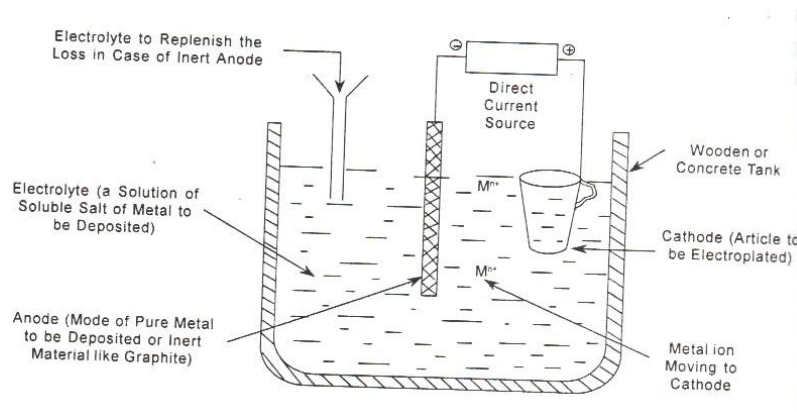
Tinning

Electroplating:

Electroplating is the process of coating metals and protects them from corrosion, wear and chemical attack.

Electroplating is the method of electro-deposition of metal by means electrolysis over surface of metals and alloys.

The base metal is first subjected to acid pickling to remove any scales, oxides etc. The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.



The two electrolytes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal. When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer. Low temperature, medium current density, low metal ion concentration conditions are maintained for better electro-plating.

Reasoning:

➤ **Why does a steel pipe in a larger copper tank corrode, causing rapid destruction?**

When two dissimilar metals are in contact with one another a voltage difference, characteristic of the two metals, is created. If the area of contact is allowed to get wet, then galvanic action can take place whereby one metal acts as the anode and the other as the cathode which then leads to migration of metal from the anode (known as the sacrificial electrode). This is precisely the effect that you have described in your question. The higher the potential difference between the metals, the faster is the corrosion.

Interestingly, a galvanic action between copper and iron manifested itself with the Statue of Liberty. The outside is copper while the inside, load-bearing structure, was cast iron separated from the copper by asbestos, an insulator. A rain leak developed over the years through the hand-held torch, thus providing electrical contact between the outer copper and the cast iron within, leading to significant galvanic corrosion that threatened the integrity of the structure. In about 1984 the internal cast iron was replaced with stainless, high-carbon steel to support the structure and prevent a catastrophe.

The stainless steel in wet contact with copper produces an acceptably low potential difference, thereby minimising any galvanic corrosion.

➤ **How is cathodic protection of iron different from its galvanization?**

In cathodic protection, the iron object is made cathode by connecting it with a more reactive metal like Mg, Zn etc. whereas in galvanisation, the iron object is protected from corrosion by coating it with zinc.

➤ **Galvanized container is not used for storage of food products, but tin coated container is used. Comment on the statement**

Galvanized containers cannot be **used for storing** acidic foodstuffs as zinc reacts with food acid forming poisonous compounds. Tin coated containers and utensils can be used for storing any food stuff as tin is non-toxic and protects metal from corrosion.

➤ **Iron does not rust if the zinc coating is broken in a galvanized iron pipe, but rusting occurs much faster if the tin coating over iron is broken.**

Iron does not rust even if the zinc coating is broken in a galvanised iron pipe but, rusting occurs much faster if the tin coating over iron is broken. ... On the other hand, tin is less electro-positive than iron. Therefore, when tin coating over iron gets broken, iron acts as anode and gets oxidised.

