UNIT-2

Battery chemistry and Corrosion

Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltages. A device which converts chemical energy to electrical energy is called Battery

* A cell contains only one anode and cathode.
* Battery contains several anodes and cathodes.

Types of Batteries These are classified into two types.

1) primary Battery / cell: In these cell the electrode and electrode reactions cannot be reversed by passing an external electrical energy. The reactions occurs only once and after use they become dead. Therefore they are not chargable

Eg: Dry cell (Leclanche), Lithium cell.

Dry cell

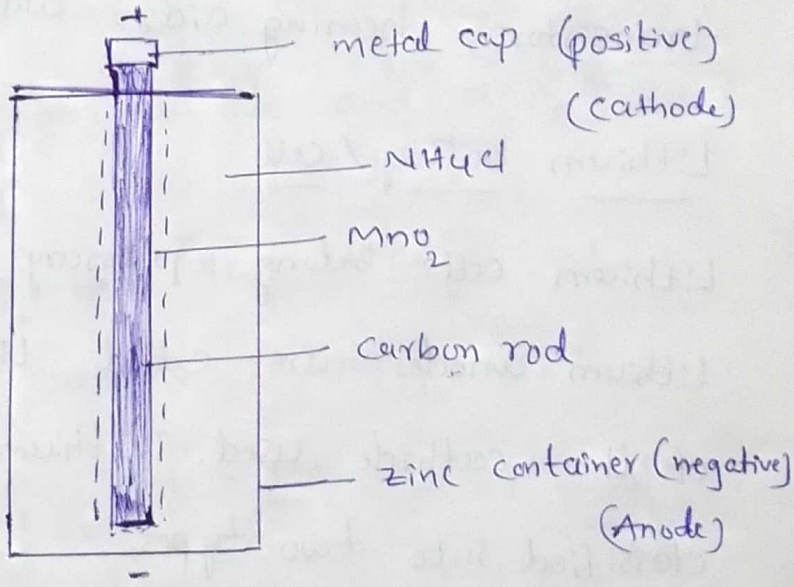
* Dry cell consists of a cylindrical zinc container which acts as anode.

→ A graphite rod placed in the centre acts as 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.



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

At cathode: $2MnO_2 + 2H_2O + 2\bar{e} \longrightarrow Mn_2O_3 + 2OH^-$ (Reduction)

The net reaction is: $Zn + 2MnO_2 + 2H_2O \longrightarrow Zn^{+2} + Mn_2O_3 + 2OH^-$

* The resulting OH^- ions react with NH_4Cl to produce NH_3 which is not liberated as gas but immediately combines with the Zn^{+2} and Cl^- ions to form a

complex salt $[Zn(NH_3)_2]Cl_2$

$$2NH_4Cl + 2OH^- \longrightarrow 2NH_3 + 2Cl^- + 2H_2O$$

$$Zn^{+2} + 2NH_3 + 2Cl^- \longrightarrow [Zn(NH_3)_2]Cl_2$$

Net reaction: $Zn + 2NH_4Cl + 2MnO_2 \longrightarrow Mn_2O_3 + [Zn(NH_3)_2]Cl_2$

Applications

* These cells have voltage ranging from 1.25 V to 1.50 V
* primary cells are used in torches, radios, transistors, hearing aids, watches. calculators etc.

Lithium battery / cell

Lithium cells belong primary cell. The cell having Lithium anodes are called Lithium cells. irrespective of the cathode used. Lithium cells can be classified into two types.

1) Lithium cells with solid cathode
2) Lithium cells with liquid cathode.

Lithium cells with solid cathode.

The cell consists of a Lithium anode, MnO_2 acts as cathode. and a mixture of propylene carbonate and 1,2 dimethoxy ethane which acts as electrolyte

Applications (Liquid cathode)

* These cells are used for military and space applications.
* These cells are also used in medical devices such as neuro-stimulators, drug delivery systems.

Secondary battery / cell

In these cells the electrode reactions can be reversed by passing an external electrical energy Therefore they can be recharged by passing electric current and used again and again these are also called storage cells.

Eg: Lead acid storage cell, Ni-cd cell, Lithium ion cell.

Lead acid storage battery / cell

A lead acid storage cell is a secondary cell. which can operate both as a electrochemical cell. and electrolytic cell.

construction * A lead acid storage cell consists of pb (lead) Anode and pbO_2 (leadoxide) Cathode.

* A number of pb plates are connected in parallel and a number of PbO_2 plates are also connected in parallel.
* Various plates are seperated from the adjecent one by insulators like rubber (or) wood.
* The entire combination is then dipped in dil H_2SO_4, which acts as an electrolyte.

Working At Anode: Lead is oxidised to form a lead ions.

$$Pb \longrightarrow Pb^{+2} + 2\bar{e}$$

* Pb^{+2} ions combines with SO_4^{-2} ions to produce $PbSO_4$

$$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4 \downarrow$$

At cathode: The two electrons released at anode flows to the PbO_2 electrode and causes reduction of PbO_2 to produce Pb^{+2} which finally combine with SO_4^{-2} to produce $PbSO_4$ (at cathode)

$$PbO_2 + 4H^+ + 2\bar{e} \longrightarrow Pb^{+2} + 2H_2O$$

$$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4 \downarrow$$

Overall reaction

$$Pb + PbO_2 + 4H^+ + 2SO_4^{-2} \longrightarrow 2PbSO_4 + 2H_2O + \text{Energy}.$$

Charging: During charging of the battery an external EMF greater than 2 volts is passed, so that the cell reactions are reversed as shown below.

Cathode: $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{-2}$

Anode: $PbSO_4 + 2H_2O + Energy \longrightarrow PbO_2 + 4H^+ + SO_4^{-2} + 2e^-$

Net reaction: $2PbSO_4 + 2H_2O + Energy \longrightarrow Pb + PbO_2 + 2H_2SO_4$.

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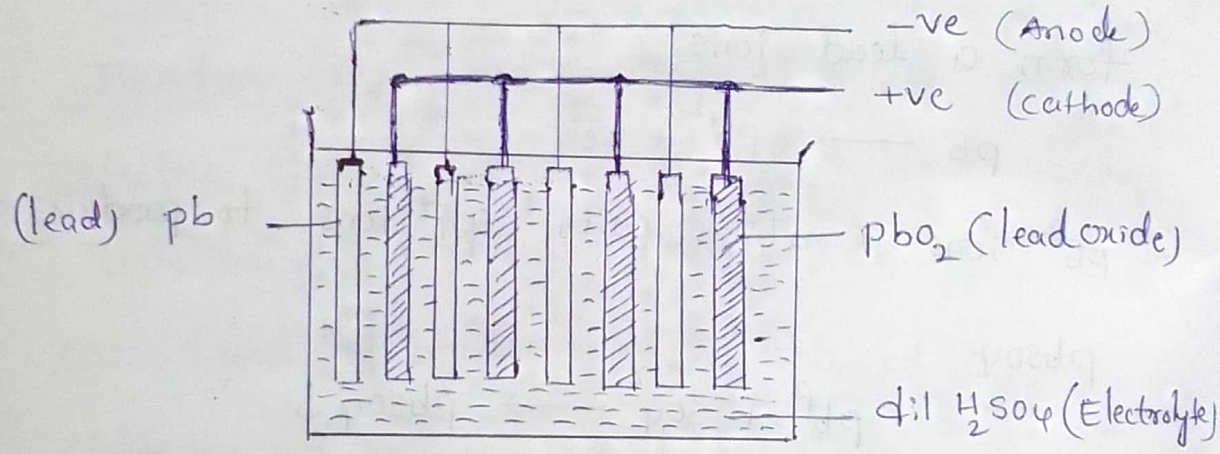


Applications of lead storage cell

The lead storage cells are used to supply current for electrical vehicles, gas engine ignition in telephone exchanges, electric trains, mines, laboratories, hospitals, automobiles and power-stations.

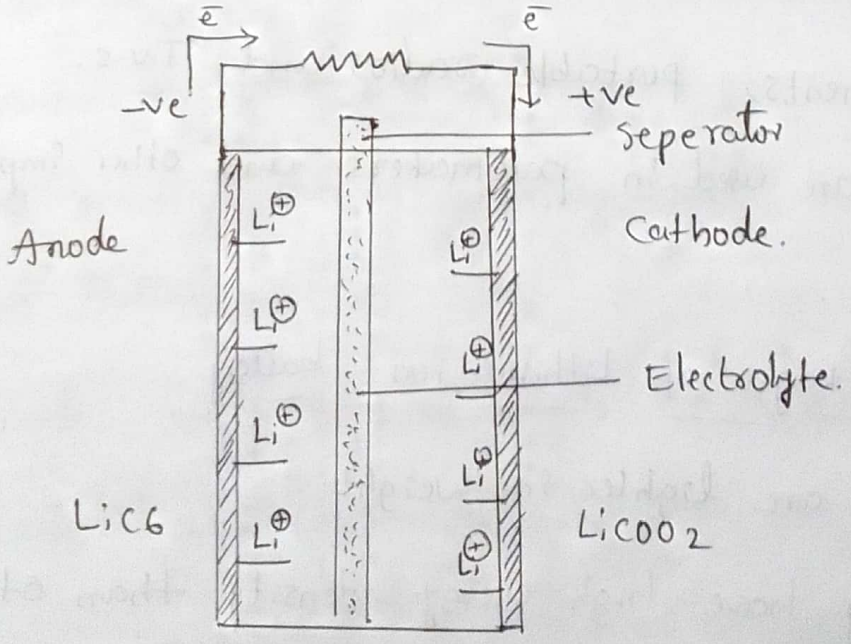
Advantages of lead storage cells

* It produces very high current.
* It is made easily.
* It has relatively constant potential i.e 12 volts.
* The electrolyte density signals its state of change.

Lithium ion battery

This battery consists of Lithium graphite (LiC_6) which is anode and Lithium cobalt oxide ($LiCoO_2$) which is cathode and the electrolyte made from either non aqueous lithium hexafluorophosphate ($LiPF_6$) of Lithium perchlorate ($LiClO_4$) Both anode and cathode are intercalated materials. The Chemistry of the Lithium ioncell is given by the following equations.

process i) Discharging



Anode: $xLiC_6 \longrightarrow xC_6 + xLi^+ + xe^-$

cathode: $Li_{1-x}CoO_2 + xLi^+ + xe^- \longrightarrow Li_xCoO_2$

overall reaction:- $xLiC_6 + Li_{1-x}CoO_2 \longrightarrow xC_6 + Li_xCoO_2$

Charging

cathode: $Li_xCoO_2 \longrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$

Anode: $xC_6 + xLi^+ + xe^- \longrightarrow xLiC_6$

overall reaction: $Li_xCoO_2 + xC_6 \longrightarrow Li_{1-x}CoO_2 + xLiC_6$

Applications of Lithium ion battery

* They are used in laptop, computers, mobile phones.
* They are used in cameras and calculators.
* They are used in telecommunication equipments instruments, portable radios and T.V.s.
* They are used in pacemakers and other implantable device.

Advantages of Lithium ion battery

* They are lighter in weight.
* They have high energy density than other rechargable batteries.

→ They produce high voltage as compared to other batteries.

* No liquid electrolyte, therefore no leakage problems.

→ They show more resistance to overcharge therefore more safe.

* Show fast charge and discharge rate.

Disadvantages

→ They are expensive

* They are not available in standard cell types.

Nickel- cadmium cell / Ni- cd cell

It is a rechargable Secondary cell. It consists of cadmium as the negative electrode (Anode) and $NiO(OH)$ as the positive electrode (cathode). potassium hydroxide (KOH) is used as an electrolyte The cell reaction during charging and discharging are as follows.

Anode: $Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$

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

Net reaction: $2NiO(OH) + Cd + 2H_2O \longrightarrow Cd(OH)_2 + 2Ni(OH)_2$

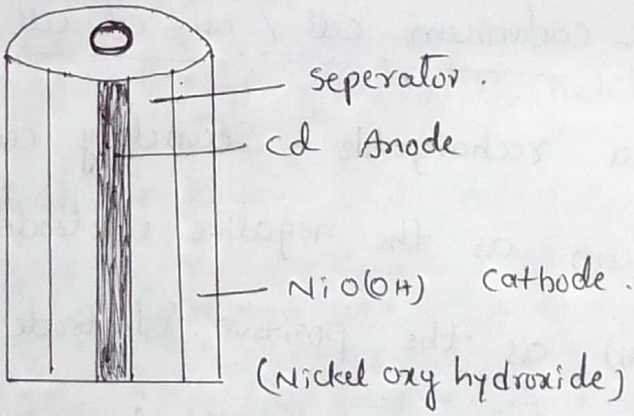
Charging

Applications of Ni-cd Batteries

* The Ni-cd batteries are used for aircraft and diesel engine starting, lighting of trains, emergency power supply and for many military applications.

Advantages of Ni-cd batteries

* They have long shelf life without any maintanance.
* These batteries are suitable to very high rate discharge and low temperature operations.
* It is smaller and lighter.



Zn-air battery

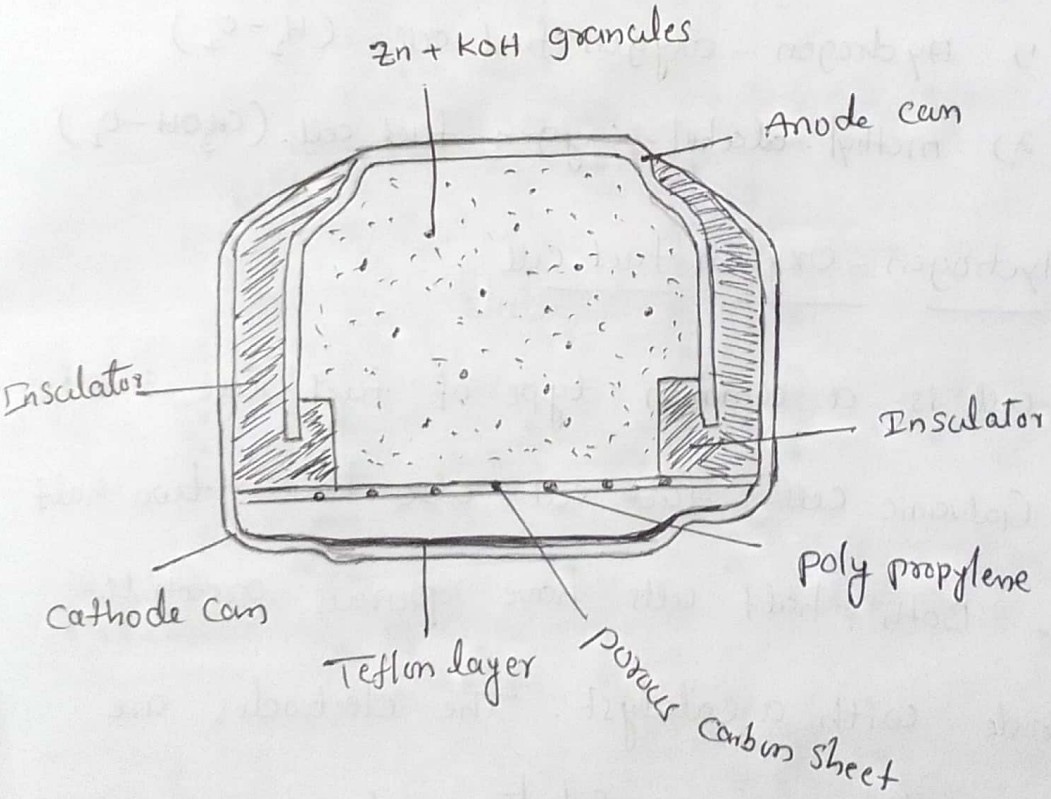
* It consists of nickel-plated steel cans acting as anode and cathode. The anodic can contain the zinc powder and electrolyte in the form of granules with a gelling agent. The cathode active material is carbon sheet impregnated

with MnO_2 with multiple air holes punched at the bottom to provide air access to the cathode. The sheet is laminated with teflon layer on one side. The anodic and cathodic compartments are seperated by polypropylene.

Anode: $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$

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

Net reaction $Zn + \frac{1}{2}O_2 \longrightarrow ZnO$.



Applications of Zn-air battery

* It is used in hearing aids.
* It is used in telecommunication devices such as

wireless headsets,

→ It is used in medical devices such as patient monitor, recorder, nurve and muscle stimulators,

Fuel cells

Fuel cell is an electro chemical cell which converts the chemical energy of the fuels directly into electricity without combustion. It converts the energy of the fuel directly into electricity.

Fuel + oxygen ⟶ oxidation products + Electricity.

Eg: 1) Hydrogen - oxygen fuel cell. (H_2-O_2)

2) methyl - alcohol - oxygen fuel cell. (CH_3OH-O_2)

1) Hydrogen - oxygen fuel cell

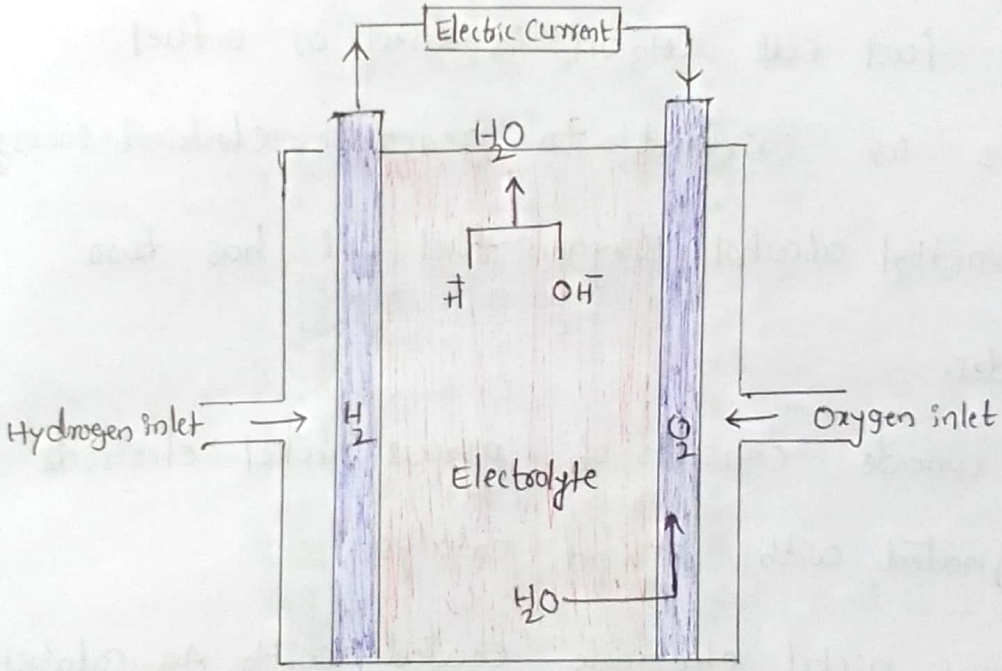
This cell is a common type of fuel cell similar to Galvanic cell. fuel cell also have two half cells. Both half cells have porous graphite electrode with a catalyst. The electrodes are placed in the aqueous solution of NaOH (or) KOH which acts as an electrolyte. Hydrogen and oxygen are supplied at anode and cathode

respectively at about 50 atmospheric pressure, the gases diffuse at respective electrodes. The two half cell reactions are as follows.

At Anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

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

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



Applications of Hydrogen - Oxygen fuel cell

* They are used as auxillary energy source in space vehicles, submarine or military vehicles.
* Because of the light weight these fuel cells are prefered for space craft and product H_2O is a

valuable fresh water source for astronauts.

Advantages

* The energy conversion is very high.
* Noise and thermal pollution is low.
* The maintanance cost is low for these fuels.

Methyl alcohol - oxygen fuel cell

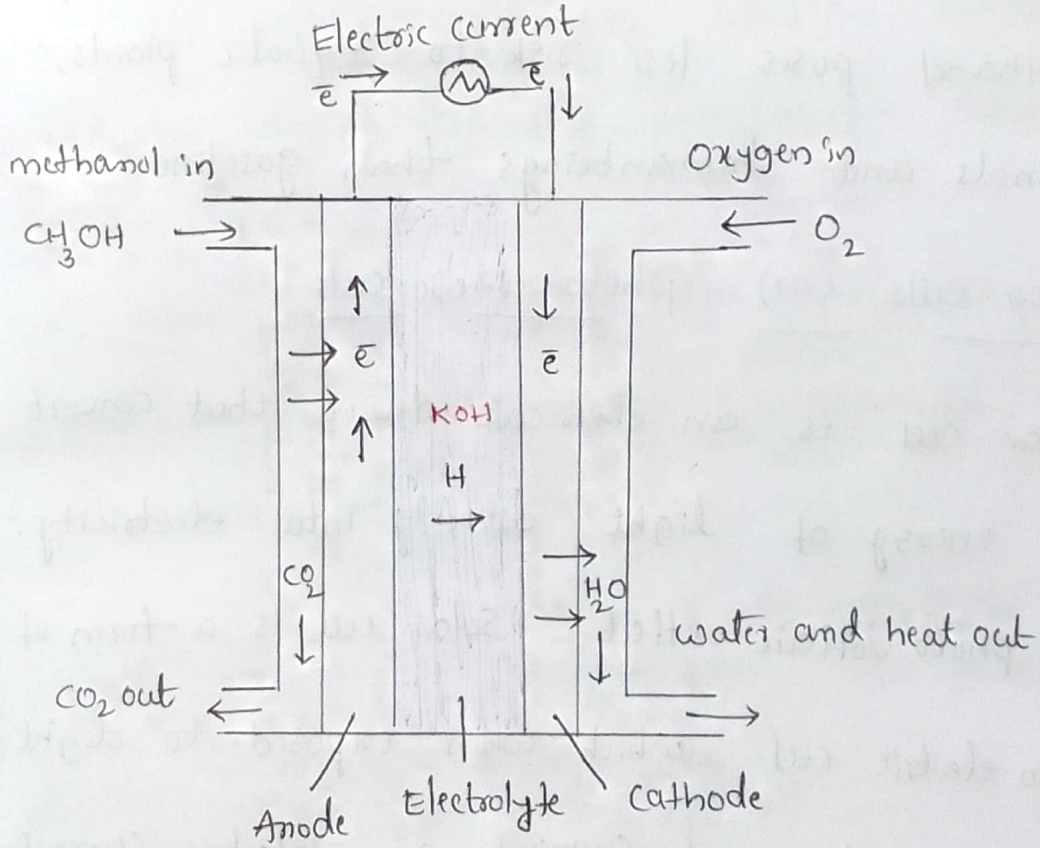
* In this fuel cell CH_3OH is used as a fuel and O_2 as oxidant to generate electrical energy.
* The methyl alcohol oxygen fuel cell has two electrodes.
* The anode consists of porous nickel electrode impregnated with pt/pd catalyst.
* porous nickel electrode coated with Ag-catalyst constitute cathode of the cell.
* The electrolyte KOH is taken in between the two electrodes.
* methanol and O_2 are sent continously into their respective electrodes.

→ The electrical energy produced with the continous replenishment of the fuel CH_3OH at the anode.

At Anode: $CH_3OH + 6OH^- \longrightarrow CO_2 + 5H_2O + 6e^-$

At cathode: $3/2\,O_2 + 3H_2O + 6e^- \longrightarrow 6OH^-$

overall reaction: $CH_3OH + 3/2\,O_2 \longrightarrow CO_2 + 2H_2O$.



Applications of methyl alcohol - Oxygen fuel cell

→ The major application of methyl alcohol - oxygen fuel cells is a fuel for cell motor vehicles like NECAR - 5 in Japan USA etc.

Advantages

* Methanol fuel cells are reasonably stable at all environmental conditions.
* Easy to transport.
* Because of high hydrogen concentration in methanol it is an excellent fuel.
* Methanol poses less risk to aquatic plants, animals and humanbeings than gasoline.

Solar cells (or) photovoltaic cells

A solar cell is an electrical device that convert the energy of light directly into electricity. by photovoltaic effect. Solar cell is a form of photo electric cell which when exposed to light can generate and support an electric current without being attached to any external voltage source.

Applications of Solar cells

* The main application of solar cells is to generate large scale or small scale electricity from sun light.
* Solar panels can be used for solar street lighting, home lighting systems.
* Solar cells are majority used in electronic industry for calculators, components, solar flash light etc
* Solar power not only helps preserving the environment but also agood economic renewable energy source.

Corrosion

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

* The metal undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides etc.

Eg: i) Rusting of iron:- When iron is caposed to the atmasphere conditions a layer of reddish scale and powder of Fe_3O_4 is formed.

$$\text{Metal} \underset{\text{metallurgy - Reduction}}{\overset{\text{Corrosion - Oxidation}}{\rightleftharpoons}} \text{Metallic Compound + Energy}$$

Causes of Corrosion

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

Effects of corrosion

* Wastage of metal in the form of its compounds.
* The valuable metallic properties like conductivity

ductility etc are lost due to corrosion.

* Life span and efficiency of metallic parts of machinery and fabrications is reduced.

Types of corrosion

There are two types of corrosions, they are

1) Dry corrosion (or) Chemical corrosion
2) Wet corrosion (or) electro chemical corrosion.

1) Dry corrosion: (or) Chemical corrosion:

The direct chemical action of environment on the surface of metal in the absence of moisture is known as dry corrosion.

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

Eg: i) Silver material undergo chemical corrosion by atmospheric H_2S gas.

ii) Iron metal undergo chemical corrosion by HCl gas.

There are three types of chemical corrosion

i) oxidation corrosion

2) Corrosion by other gases

3) Liquid metal corrosion.

1) Oxidation corrosion

The direct action of oxygen at low (or) high temperature on surface of metal in absence of moisture is known as oxidation corrosion.

* All metals are oxidised at high temperature except Au, Ag, Pt
* Alkali metals and Alkaline earth metals are oxidised at low temperature.

Mechanism

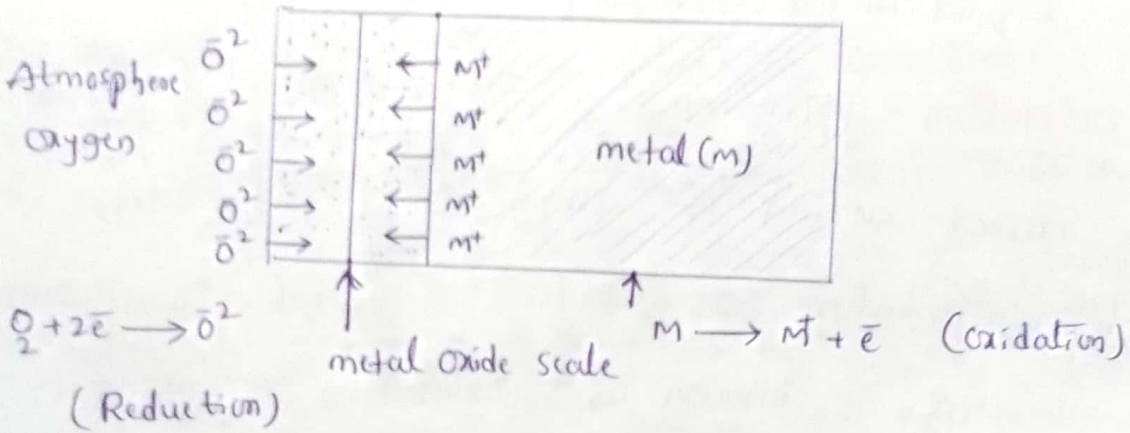
* Oxidation takes place at the surface of the metal forming metal ions M^{+2}
* Oxygen is converted to oxide ion (O^{-2}) due to the transfer of electrons from metal.
* The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.

Reactions

$$2M \longrightarrow 2M^{+2} + 2\bar{e} \quad \text{(oxidation)}$$

$$O_2 + 2\bar{e} \longrightarrow 2\bar{O}^{2} \quad \text{(Reduction)}$$

$$2M + O_2 \longrightarrow 2M^{+2} + 2\bar{O}^{2} \longrightarrow 2MO \quad \text{(metal oxide)}$$



* Initially the surface of metal undergo oxidation and the resulting metal oxide scale form a barrier which restrict further oxidation. The extend of corrosion depends upon the nature of metal oxide.

i) If metal oxide is stable:

stable metal oxide layer

metal + O_2 ⟶ metal ⟶ No corrosion

Eg: The oxide film of Al, Sn, Pb, Cu, Cr etc.

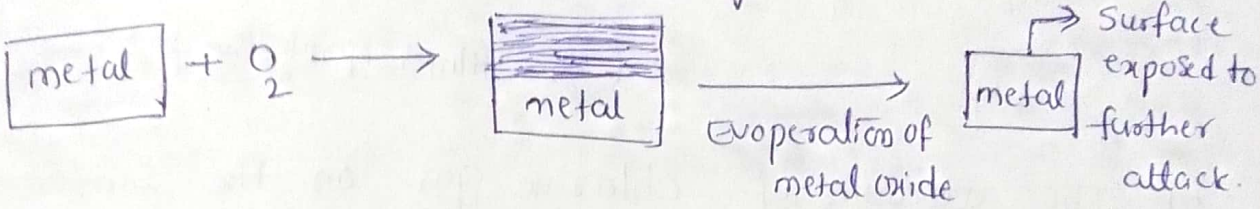
ii) If metal oxide is unstable:

unstable metal oxide layers

metal + O_2 ⟶ metal ⟶ Decomposition of metal oxide ⟶ metal + O_2

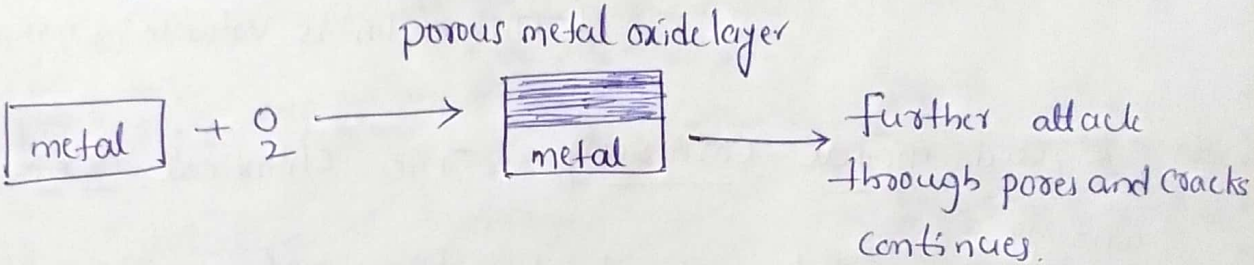
Eg: Au, Ag, Pt donot undergo oxidation corrosion.

iii) If metal oxide is volatile in nature.



Eg MoO_3 (molybdenum oxide)

iv) If the metal oxide is porous in nature



Eg: Oxide films of alkali and alkaline metals (Li, Na, K mg)

2) Corrosion by 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 extend of corrosion mainly depend on the reactivity to the gas on the metal surface.
* The nature of metal compound determins the corrosion.

Eg i) The attack of chlorine gas (Cl_2) on silver metal (Ag)

$$Cl_2 + 2Ag \longrightarrow 2AgCl$$

(This film is protective)

ii) The attache of chlorine gas on the surface of tin metal.

$$2Cl_2 + Sn \longrightarrow SnCl_2$$

(This film is volatile in nature)

3) Liquid metal corrosion The chemical action of a flowing liquid metal at high temperature on a solid metal (or) alloy produces liquid metal corrosion.

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

2) Wet corrosion (or) electro chemical corrosion

The direct chemical action of environment on the surface of metal in presence of conducting liquid with the formation of electro chemical cells.

→ In this corrosion Anodic and cathodic areas are seperated by the conducting medium.

* The oxidation of metal liberating electrons at Anodic area.

Anode:- $M \longrightarrow M^{+} + \bar{e}$ (oxidation)

* The electrons liberated at anode are transported to cathodic area through the metal.

- Reduction reaction takes place at cathodic area by two ways.

i) Evalution of hydrogen

ii) Absorption of oxygen.

i) Evolution of Hydrogen gas (H_2)

This type of corrosion evolution of hydrogen occurs in acidic medium. ~~Example~~ - considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

$$Fe \longrightarrow Fe^{+2} + 2\bar{e} \quad \text{(oxidation)}$$

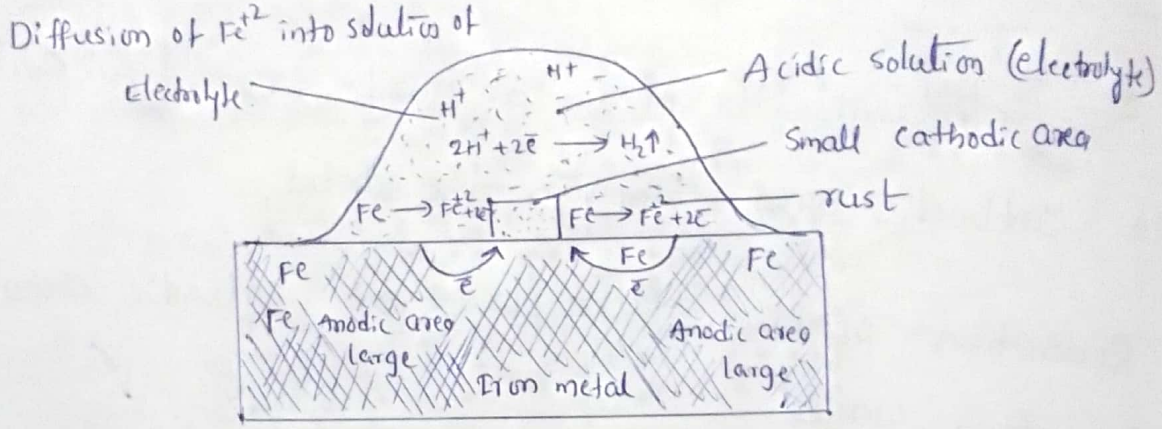
* The 2 electrons flow from anodic area to cathodic area through the metal where H^{+} ions

are available and eliminated as hydrogen gas.

$$2H^+ + 2\bar{e} \longrightarrow H_2 \uparrow \text{ (reduction)}$$

The overall reaction is

$$Fe + 2H^+ \longrightarrow Fe^{+2} + H_2 \uparrow$$



ii) Absorption of Oxygen

The rusting of iron takes place in neutral aqueous solution of electrolytes (presence of atmospheric oxygen). If the metal surface develops cracks, anodic areas are created on the surface whereas the metal parts acts as cathodes.

At Anode: $Fe \longrightarrow Fe^{+2} + 2\bar{e}$ (Oxidation)

The released electrons flow from anode to cathode through iron metal

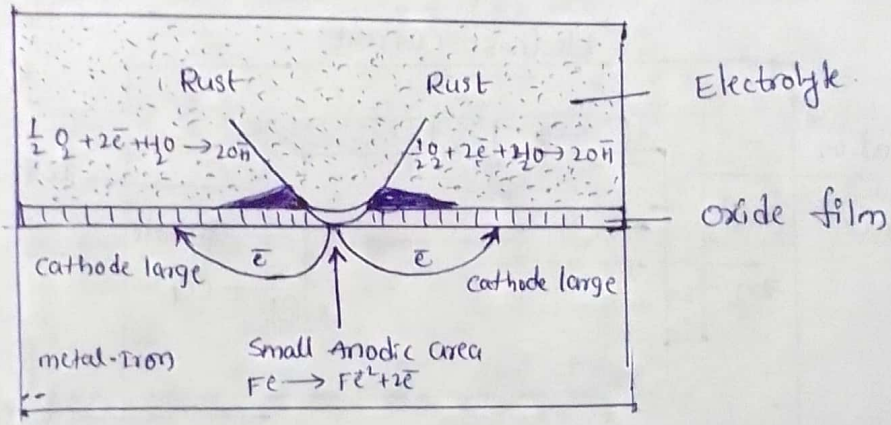
At cathode: $\frac{1}{2}O_2 + H_2O + 2\bar{e} \longrightarrow 2OH^-$ (Reduction)

* The Fe^{+2} ions and OH^- ions diffuse and form ferrous hydroxide precipitate when they meet with each other

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

* If oxygen is in excess ferrous hydroxide is easily oxidised to ferric hydroxide

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$$



Types of wet / Electro Chemical corrosion

1) Galvanic corrosion

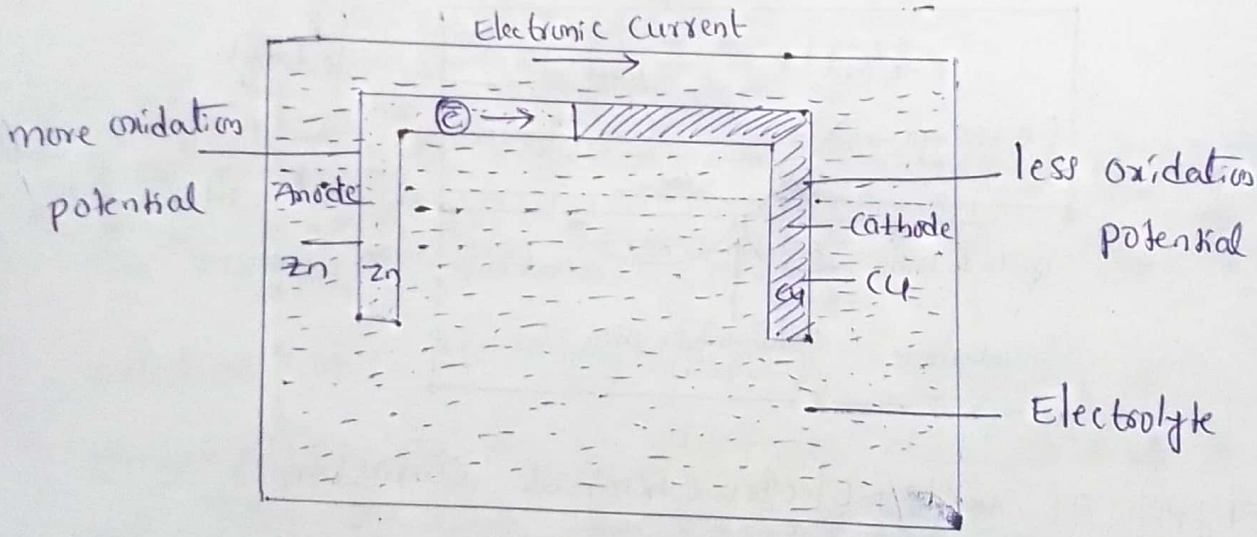
* When two dissimilar metals are connected and exposed to the corrosive atmosphere. the metal which has higher oxidation potential becomes anodic and undergoes corrosion.

Eg: Zn and Cu metals are electrically connected and exposed to corrosive atmosphere (Electrolyte).

* Zn undergoes oxidation and gets corroded.
* Cu undergoes Reduction and gets protected.

Anode: $Zn \longrightarrow Zn^{+2} + 2\bar{e}$ (Oxidation)

Cathode: $Cu^{+2} + 2\bar{e} \longrightarrow Cu \downarrow$ (Reduction)



2) Waterline Corrosion (or) concentration cell Corrosion

* This type of corrosion occurs if a metal is exposed to an electrolyte of different concentrations (or) differential aeration.
- In this cell, less exposed part acts as anode

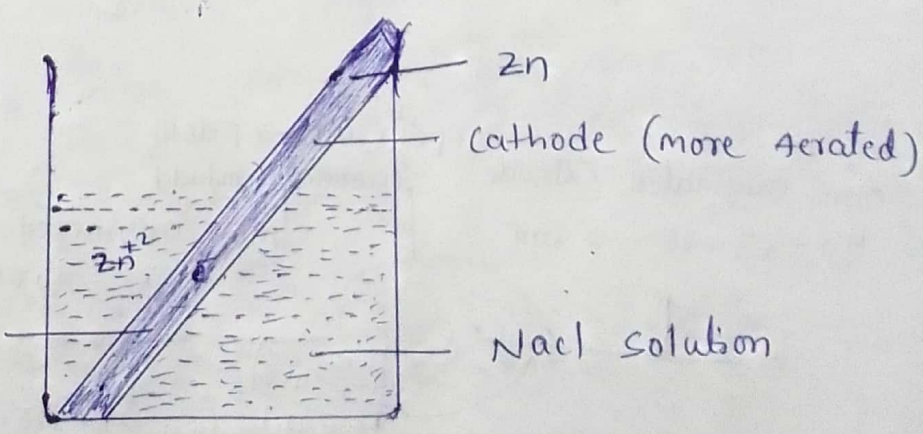
and undergoes corrosion and more exposed part acts as cathode.

Eg: If Zn metal is partially immersed in a solution of neutral sodium chloride, the part immersed in the solution has lower concentration of oxygen and hence it acts as anode and undergoes corrosion. The part above the water line acts as cathode

At Anode: $Zn \longrightarrow Zn^{+2} + 2\bar{e}$ (Oxidation)

At Cathode: $H_2O + \frac{1}{2}O_2 + 2\bar{e} \longrightarrow 2OH^-$ (Reduction)

$$Zn^{+2} + 2OH^- \longrightarrow Zn(OH)_2$$



3) Pitting Corrosion

In pitting corrosion a pit is formed when the protective coating on the metal surface

break, a micro pit (anode) formed on the metal surface.

* Once the pit is form the process of corrosion become very fast due to different amount of oxygen in contact with metal surface.

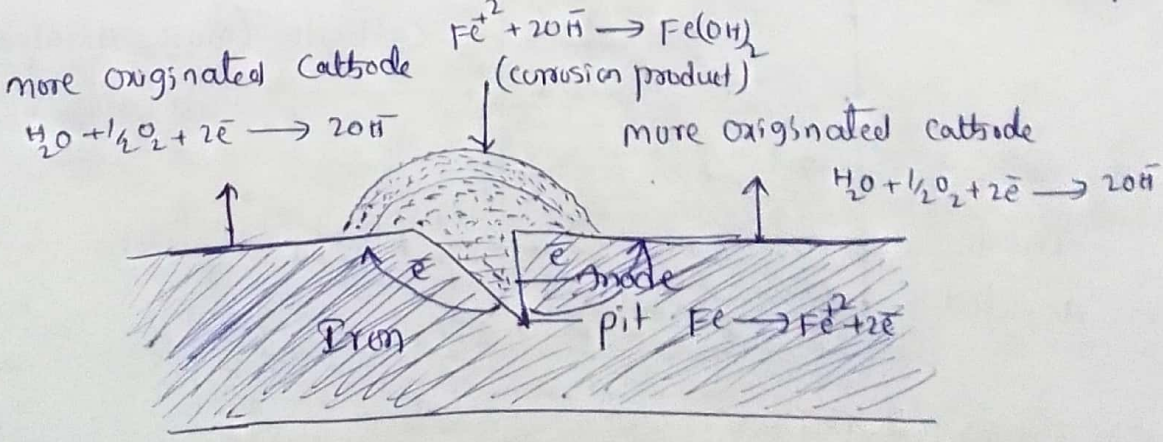
* The portion (pit) with lower concentration of oxygen become anode and the portion (with corroded.) higher concentration of oxygen becomes cathode.

Anode:- $Fe \longrightarrow Fe^{+2} + 2\bar{e}$ (Oxidation)

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

$$Fe^{+2} + 2OH^- \longrightarrow Fe(OH)_2 \xrightarrow{(O)} Fe(OH)_3$$

corrosion product



Factors affecting the rate of corrosion

The rate and extend of corrosion mainly depends on.

i) Nature of metal

ii) Nature of corroding environment.

i) Nature of metal.

1) position of metal galvanic series

metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily.

→ metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion.

2) purity of the metal

Impure metal undergo corrosion, The rate of corrosion increases with amount of impurities in the metal so pure metal is more corrosion resistance than impure metal.

3) physical state of metal

metal which small grain size have more tendencies to undergo corrosion. metal with more stress / strain also undergo corrosion easily.

4) Nature of the corrosion product.

If the corrosion product is soluble in the

in the corroding medium the corrosion rate will be faster, if the corrosion product is volatile the corrosion rate will be faster

ii) Nature of Corroding environment

1) Temperature:

The rate of corrosion reactions increases with increase in temperature.

2) presence of impurities

Atmospheric gases like CO_2, SO_2, H_2S etc increases in air and rate of corrosion also increases.

3) Effect of pH

Acidic media are more corrosion than alkaline and neutral media.

4) Humidity

The corrosion of metal is very fast in humid atmosphere than in dry atmosphere.

Corrosion control methods

1) Cathodic protection

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

These are two types of cathodic protection.

a) Sacrificial anode method

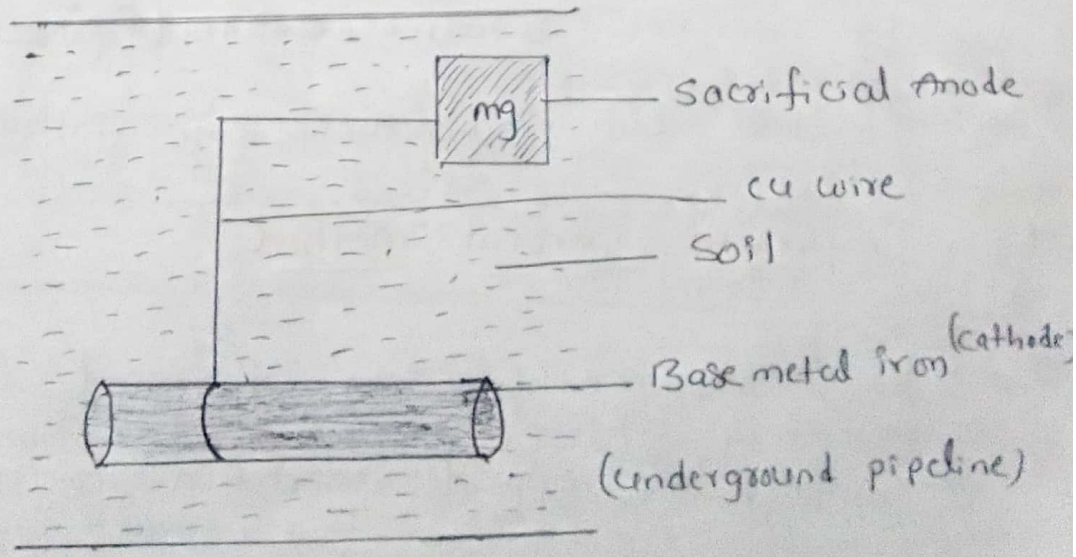
→ In this method metallic structure to be protected is connected by a wire to a more anodic metal so that all the corrosion concentrated at this more anodic metal.

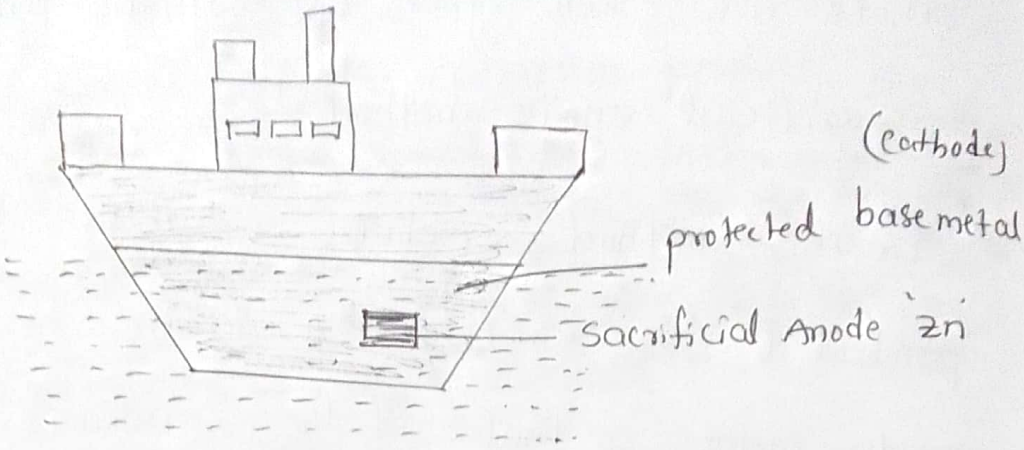
→ The more anodic metal it self gets corroded slowely while the parent stoucture is protected.

→ The more active metal so employed is called sacrificial anode.

→ Metals commonly used as sacrificial anode are mg, Al, Zn, and their Alloys.

Eg: The underground waterpipelines water tanks, and ships are protected by sacrificial anode method





Ship

Applications

The method can be applied for the protection of

1) Buried pipelines
2) underground cables
3) Buried oil and coater pipes
4) Water tanks.

Advantages

1) It is a simple method.
2) It does not require external power
3) It has low maintanance and installation cost.

b) Impressed Current method

→ In this method an impressed current is applied in opposite direction to nullify the corrosion current, and converted the

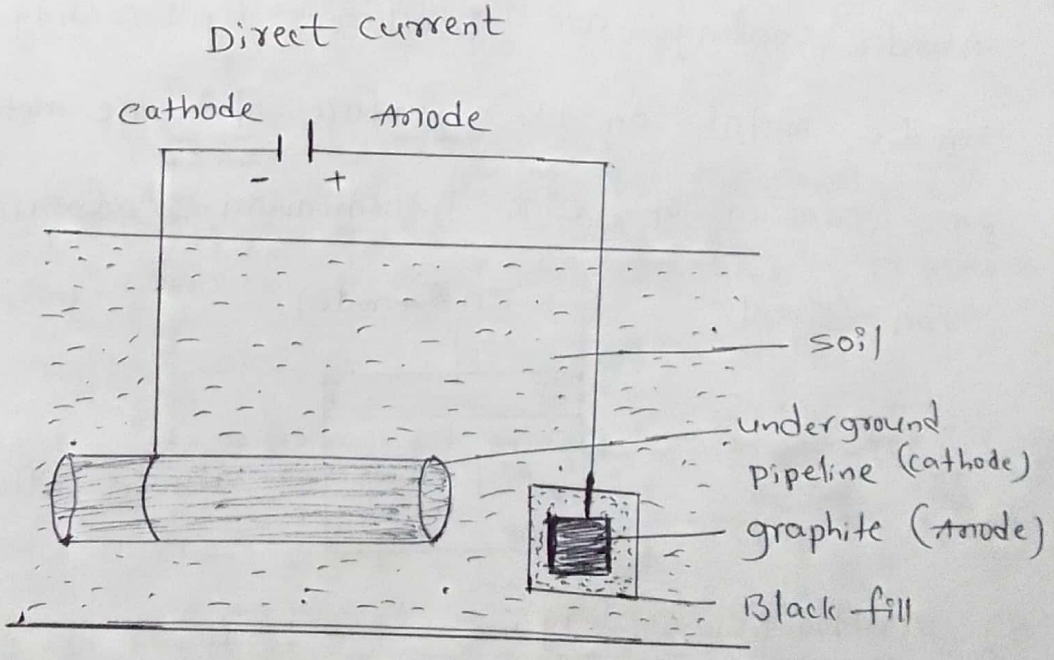
corroding metal from anode to cathode.

* This can be done by connecting negative terminal of the battery to the metallic structure to be protected.

* The positive terminal of the battery is connected to an inert anode like graphite.

* The anode is buried in a black fill containing mixture of gypsum and coke.

* The black fill provides good electrical contact to anode.



Applications

The method can be applied for the protection of

1) water tanks
2) Buried oil and water pipes.

3) Condensers, Ships

4) Transmission line towers.

Advantages

The method is mainly employed to protect large structure for long term operations.