

Electro Chemistry and Applications

Electrochemistry is the study of **production of electricity from spontaneous redox chemical energy** and the **use of electrical energy in non spontaneous chemical reaction**

Electrode Potential: The electrode potential is defined as **the tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions.**

Oxidation Potential: It is a tendency of giving or losing electrons of an electrode.

Reduction Potential: It is a tendency of gaining electrons of an electrode.

Standard Electrode Potential: "The electrode potential of a given electrode measured at **298K** and concentration of electrolyte is **1M** then potential of that electrode is said to be Standard Electrode Potential".

Electro Chemical Series : The arrangement of metals according to the electrode potential values in ascending order is called Electro Chemical series or Galvanic series. The hydrogen electrode is taken as having zero electrode potential: $\text{Li} < \text{Mg} < \text{Pb} < \text{Zn} < \text{Fe} < \text{Sn} < \text{H} < \text{Cu} < \text{Ag} < \text{Au}$.

Reference electrodes: The electrode of standard potential, with which we can compare the potentials of another electrodes is called as "Reference Electrode".

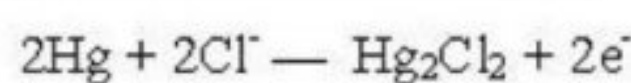
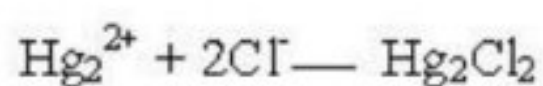
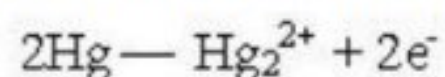
examples of reference electrodes: Standard hydrogen electrode(SHE), Calomel electrode

CALOMEL ELECTRODE:

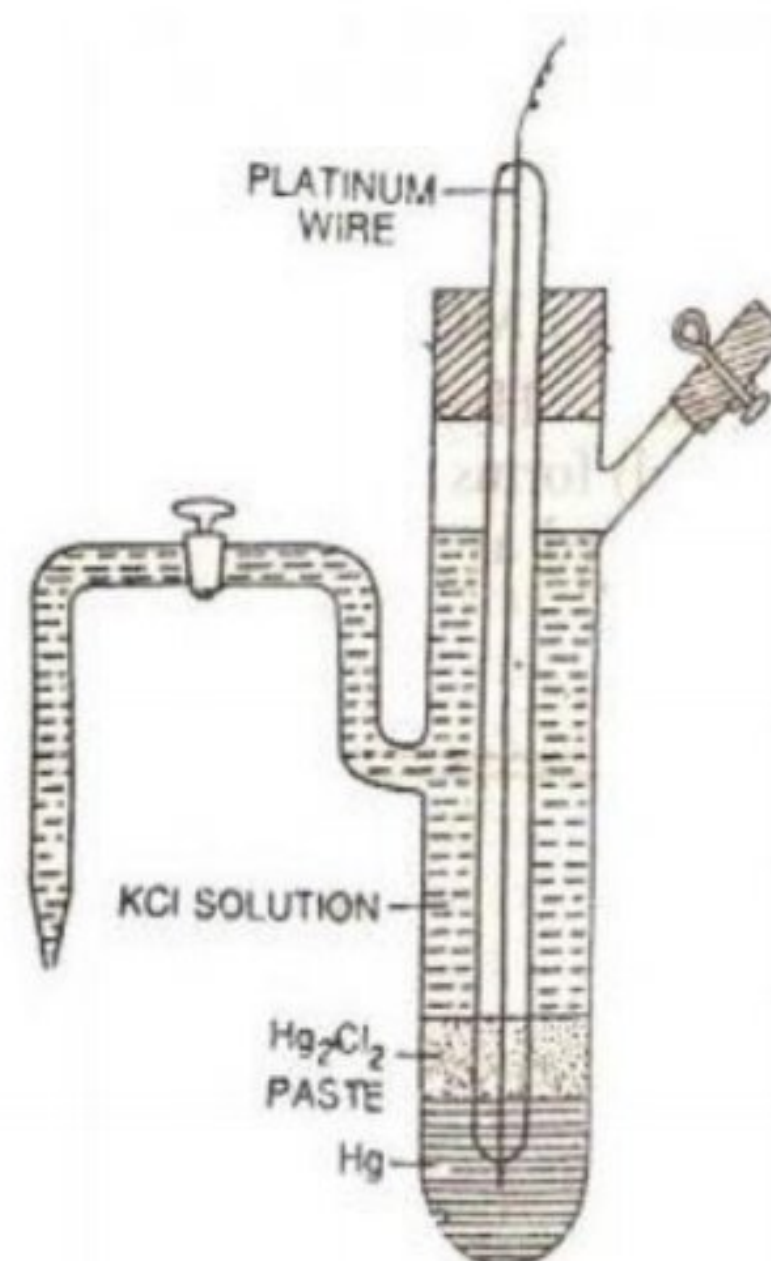
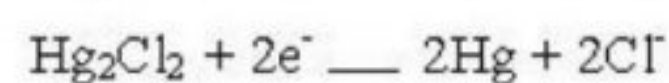
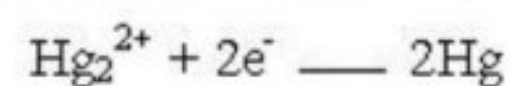
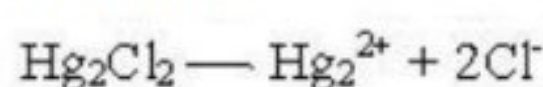
Calomel electrode is called as Mercury -Mercurous chloride electrode. The potential of the calomel electrode depends on KCl solution used. The reduction potential of various KCl solution at 25°C , $0.1\text{ N KCl} = 0.335$ then the calomel electrode is called *Decinormal calomel electrode*. $1\text{ N KCl} = 0.2810$ then the calomel electrode is called *Normal calomel electrode*. $\text{Sat. KCl} = 0.2422$ then calomel electrode is called *Saturated calomel electrode*.

The electrode reactions are represented as follows:

Calomel as anode:



As Cathode:



If Calomel electrode is connected to Zinc metal then Calomel electrode acts as cathode then the electrode potential of the cell is

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

$$E^0_{\text{cell}} = E^0_{\text{SCE}} - E^0_{\text{Zn}^{+2}/\text{Zn}}$$

$$E^0_{\text{Zn}^{+2}/\text{Zn}} = E^0_{\text{SCE}} - E^0_{\text{cell}}$$

$$E^0_{\text{Zn}^{+2}/\text{Zn}} = 0.2422 - E^0_{\text{cell}}$$

If Calomel electrode is connected to Copper metal then Calomel electrode acts as anode then the electrode potential of the cell is

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

$$E^0_{\text{cell}} = E^0_{\text{Cu}^{+2}/\text{Cu}} - E^0_{\text{SCE}}$$

$$E^0_{\text{Cu}^{+2}/\text{Cu}} = E^0_{\text{cell}} + E^0_{\text{SCE}}$$

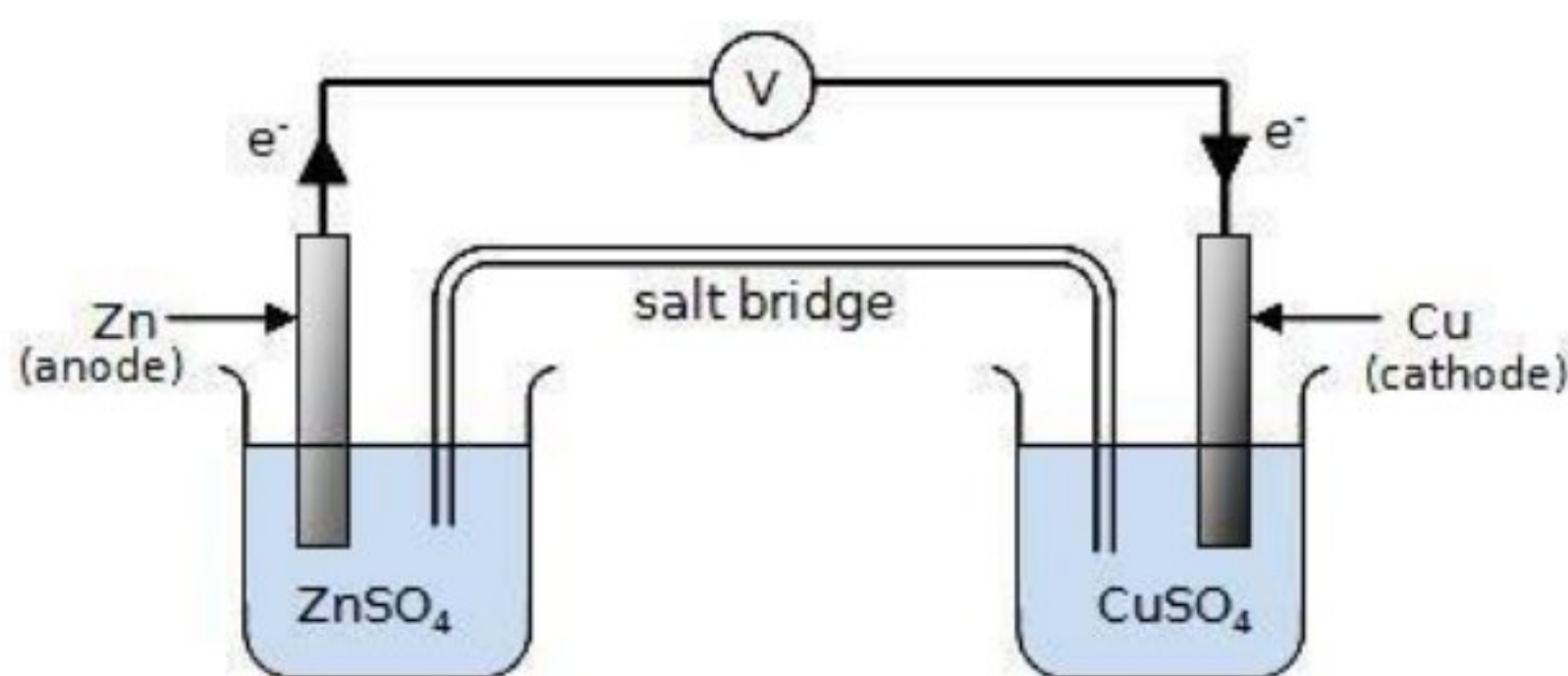
$$E^0_{\text{Cu}^{+2}/\text{Cu}} = E^0_{\text{cell}} + 0.2422.$$

Electrochemical Cell or Galvanic cell or Voltaic cell or Daniel cell

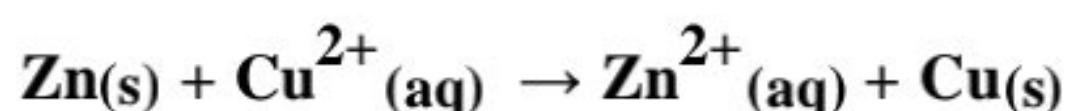
An electrochemical cell is device **which produces electrical energy by performing a spontaneous redox reaction.**

Galvanic cell consists of two half cells with corresponding electrode and electrolyte. Each of cells conducts one of the redox reactions.

Generally, at anode oxidation and at cathode reduction takes place.



The following redox reaction occurs in Daniel cell



This reaction is a combination of two half reactions whose addition gives the overall cell

reaction: At Anode (-ve electrode): $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (Oxidation reaction)

At Cathode (+ve electrode): $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$ (Reduction reaction)

Overall Redox reaction: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$

Representation of the electrochemical cell : $\text{Zn} ; \text{Zn}^{+2}(\text{M}) // \text{Cu}^{+2}(\text{M}) ; \text{Cu}$

Battery:

Battery is a device which stores and converted the chemical energy into electrical energy, and it is also called as storage battery. Generally, in battery number of electrochemical cells is connected in series.

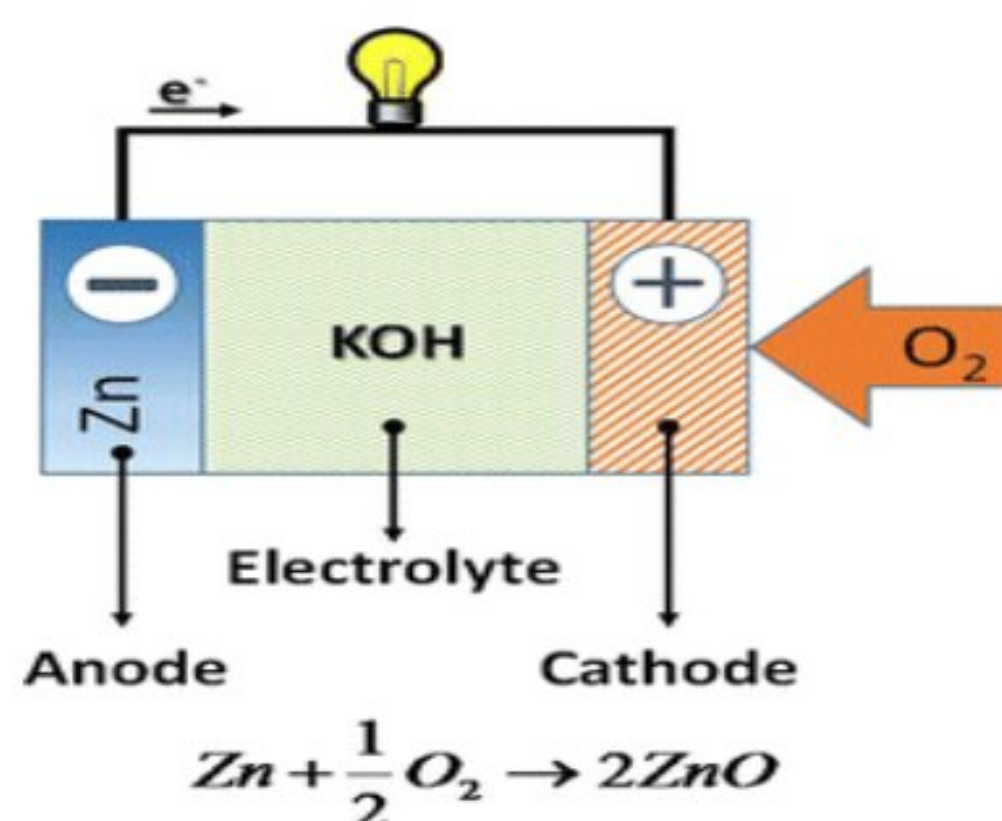
Batteries are classified as follows,

- I) Primary battery ii) Secondary battery iii) Fuel battery or Flow battery

Primary battery: Primary battery is a cell in which the cell reaction is not reversible. They are not rechargeable. They are use and throw type. Example: Dry cell, Zinc-Air cell etc.

Zinc – Air Battery:

Zn-Air batteries: zinc air cells are composed of three parts zinc metal as anode, an air electrode as cathode which is divided into a gas diffusion layer and a catalytic active layer and a separator.



Reactions :

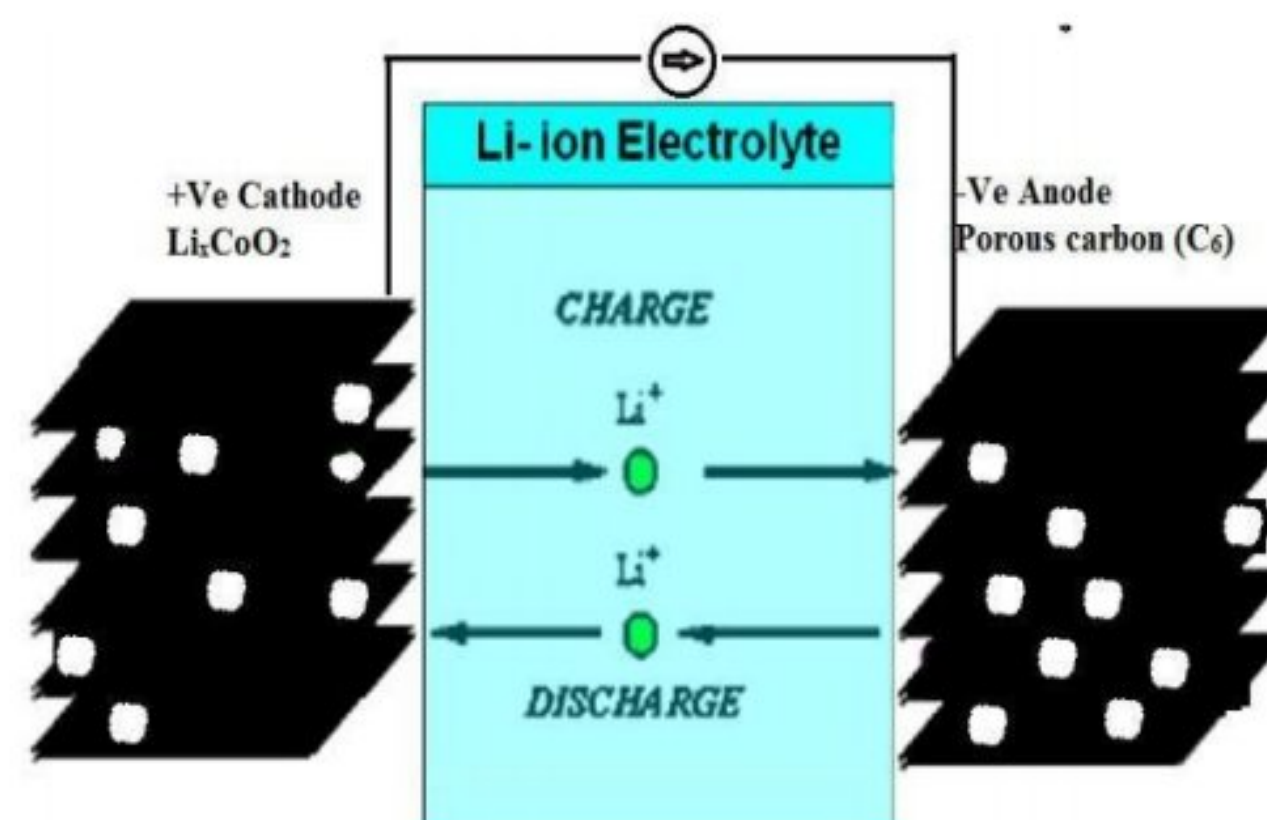


Applications : The main advantage of the Zn–air system as very high energy density and it is used in military, civil, and underwater power systems, backup power sources for telecommunication systems, and portable power supplies.

Secondary battery: Secondary battery is a cell in which the cell reaction is reversible. They are rechargeable cells. Once the battery gets exhausted, it can be recharged. Example: Nickel-Cadmium cell, Lead-acid cell, etc.

Lithium ion battery:

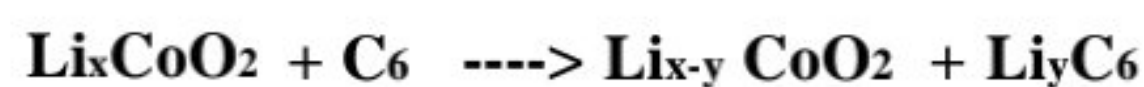
- It is a rechargeable battery in which lithium ions move from one electrode to other electrode during charging and discharging process.
- It works on intercalation mechanism.
- Li-ion batteries use an **intercalated lithium compound as cathode** material, and the porous carbon as anode (negative electrode).
- **Anodes:** Hard Carbons (LiC_6), Graphite (C_6)
- **Cathodes:** LiCoO_2
- **Separator:** Fine porous polymer film.
- **Electrolytes:** Non aqueous lithium salts such LiPF_6 , LiBF_4 in an organic solvent.



During discharge, lithium ions (Li^+) carry the current and moves from the negative (Anode) to the positive (Cathode) electrode, through the non-aqueous electrolyte. **(DAC)**

During charging the Li^+ ions migrate from the positive (Cathode) to the negative (Anode) electrode. **(CCA)**

Charging:



Discharging:



Thus charging and discharging cycle is simply migration of Li^+ ions from electrode to another with flow of electrons through the external circuit

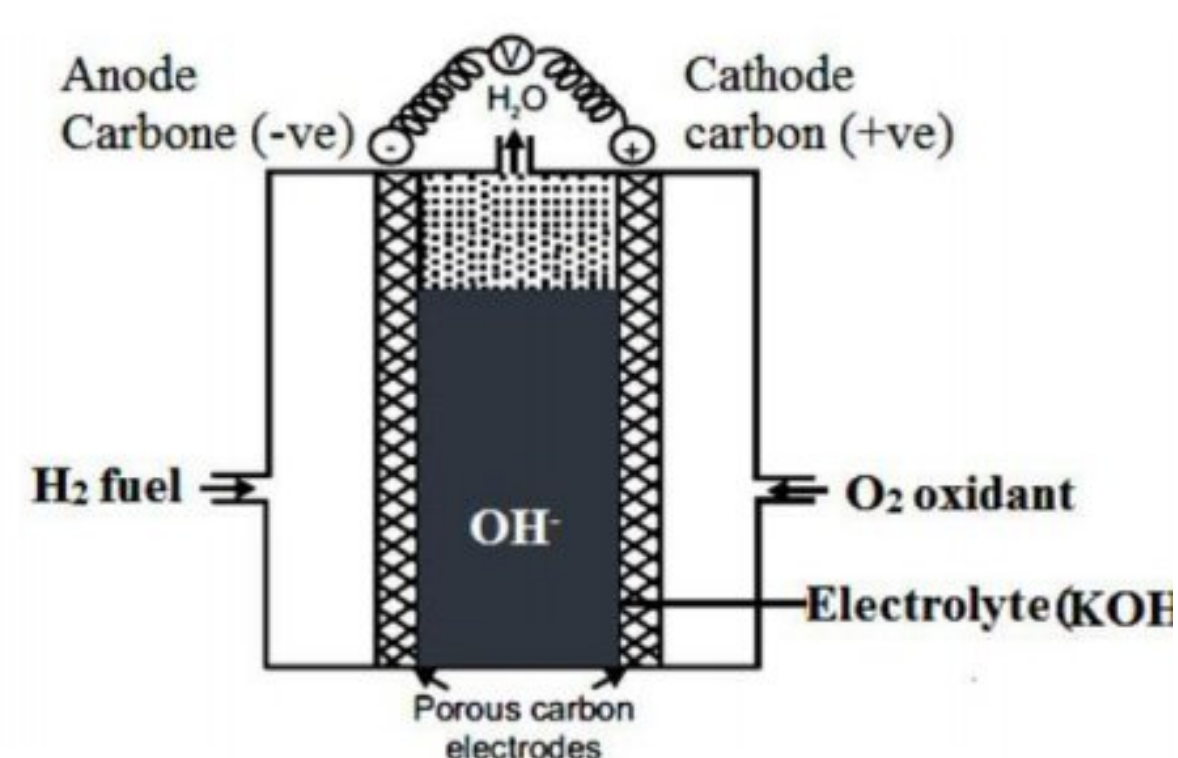
Applications: Because of the excellent voltage control they are used in electronic devices and circuit boards, military and space applications, medical devices such as simulators, drug delivery systems Etc.....

Flow or Fuel battery: Flow battery is an electrochemical cell that converts the fuel energy into electrical energy. Here fuel and oxidants continuously supply to the cell, so it never exhausted. Example: Hydrogen-oxygen cell, Methanol-oxygen cell, etc.

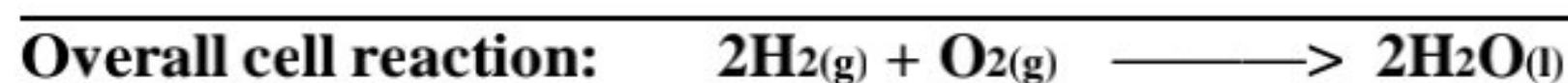
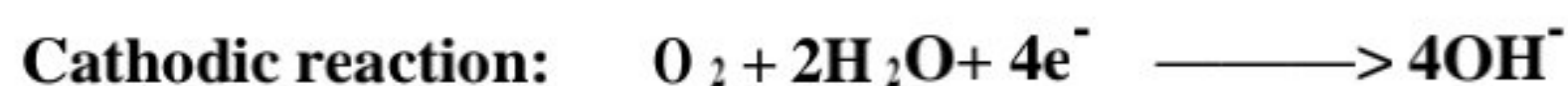
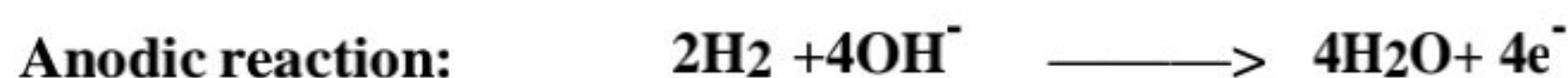
H₂ –O₂ Fuel cell (Green fuel cell):

A typical example of pollution free cell is H₂–O₂ fuel cell in which the **fuel is hydrogen** and the **oxidizer is oxygen gas**.

It doesn't produce any pollutant gases during production of electricity; hence it is called as green fuel cell.



Construction and working: Hydrogen–oxygen fuel cell consists of two porous carbon electrodes coated with small amount of catalysts (Pt, Pd, Ag). KOH or NaOH solution as the electrolyte. During working, Hydrogen (the fuel) is bubbled through the anode compartment, where it is oxidized. The oxygen (oxidizer) is bubbled through the cathode compartment, where it is reduced the following cell reactions occur.



From the above cell reactions, hydrogen molecules are oxidized to water. When a large number of fuel cells are connected in series, it is called fuel battery.

Advantages of fuel cells:

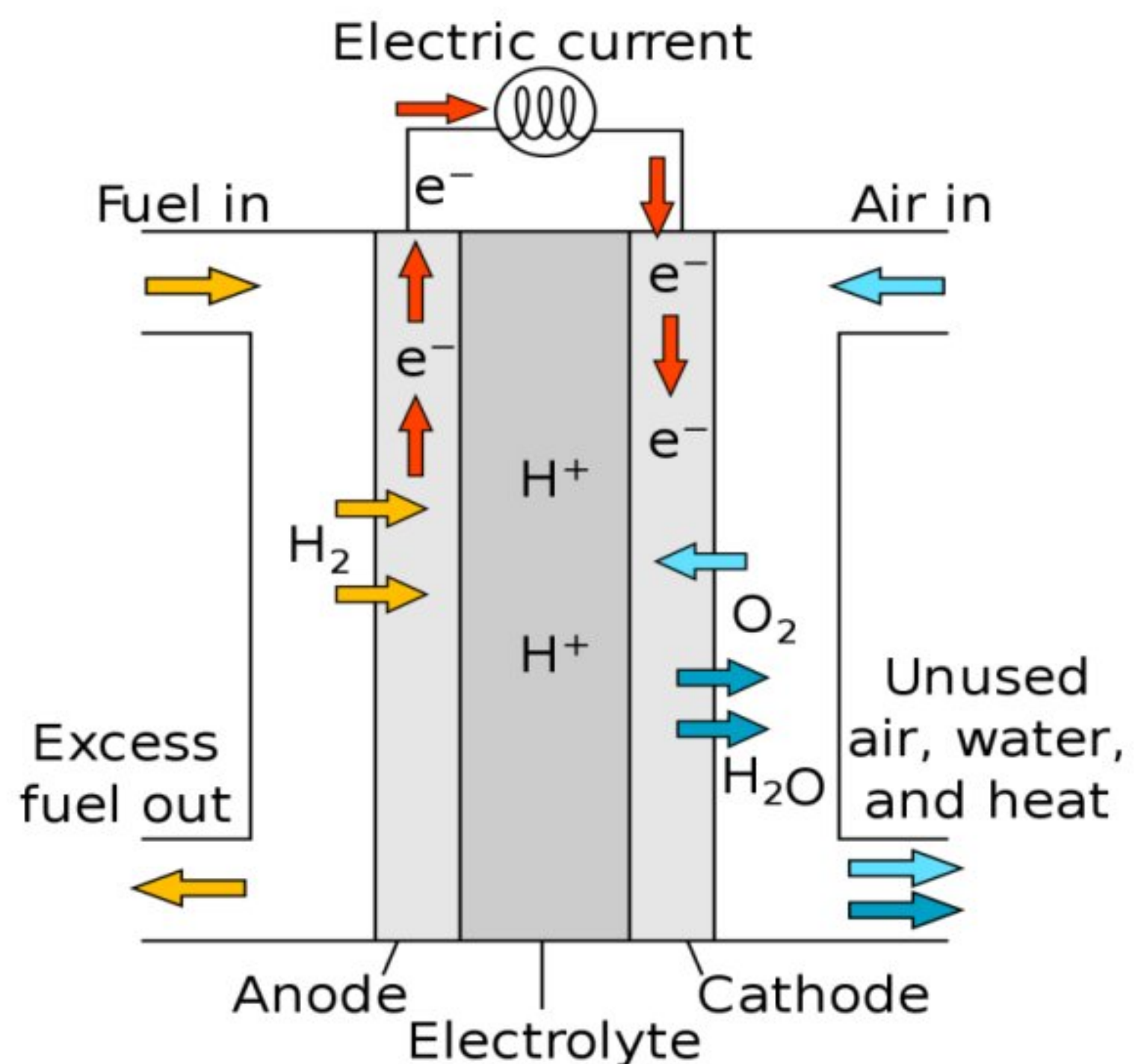
1. Fuel cells are efficient and take less time for operation.
2. No harmful chemicals are produced in fuel cells.

3. It is used as auxiliary energy source in space vehicles, submarines etc.
4. It is used in producing drinking water for astronauts in the space.

Limitations:

- 1) The life time of the fuel cells are not accurately known.
- 2) Their initial cost is high.

Polymer Electrolyte Membrane Fuel Cell : Polymer electrolyte membrane (PEMFC) fuel cells is also called proton exchange membrane fuel cells.



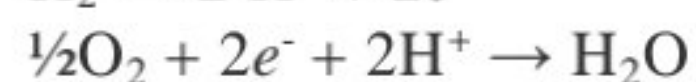
Carbon Materials used for Polymer Electrolyte Fuel Cells, Hydrogen supplied to the anode side is oxidized, and produced H^+ moves through the membrane to the cathode side. This H^+ is used in the reaction in which water is formed by the reduction of oxygen supplied to the cathode side.

Reactions:

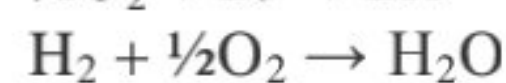
Anodic reaction:



Cathodic reaction:



Overall reaction:



Advantages:

Deliver high power density, low weight and volume when compared with other fuel cells.

Electro Chemical Sensors :

Sensor is a device which is able to detect in physical or chemical quantity of a sample and provides information continuously in discrete steps in the form of an electrical signal is termed as a sensor.

Electrochemical sensors are the most versatile and highly developed chemical sensors. They are divided into three types

1. Potentiometric sensors (measure voltage)
2. Amperometric sensors (measure Current)
3. Conductometric sensors (measure conductivity)

Applications:

1. Water quality can be measured by Amperometric sensors
2. These sensors are used in gas analysis in diverse areas, such as food industry, beverage industry to detect explosive materials and toxic gases such as NO₂, SO₂, CO₂, H₂S etc.
3. These sensors are used to determine the concentrations of ionic chemical content in blood, urine and other biological samples.
4. These sensors are used to determine the trace level of concentrations of pesticides, fertilizers, drugs and pharmaceuticals etc,

Potentiometric Sensors:

The sensor that measures potential difference

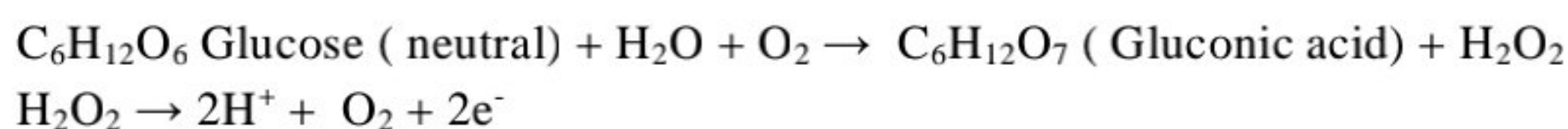
Between working electrode and reference electrode.

Glass electrode is used as working electrode.

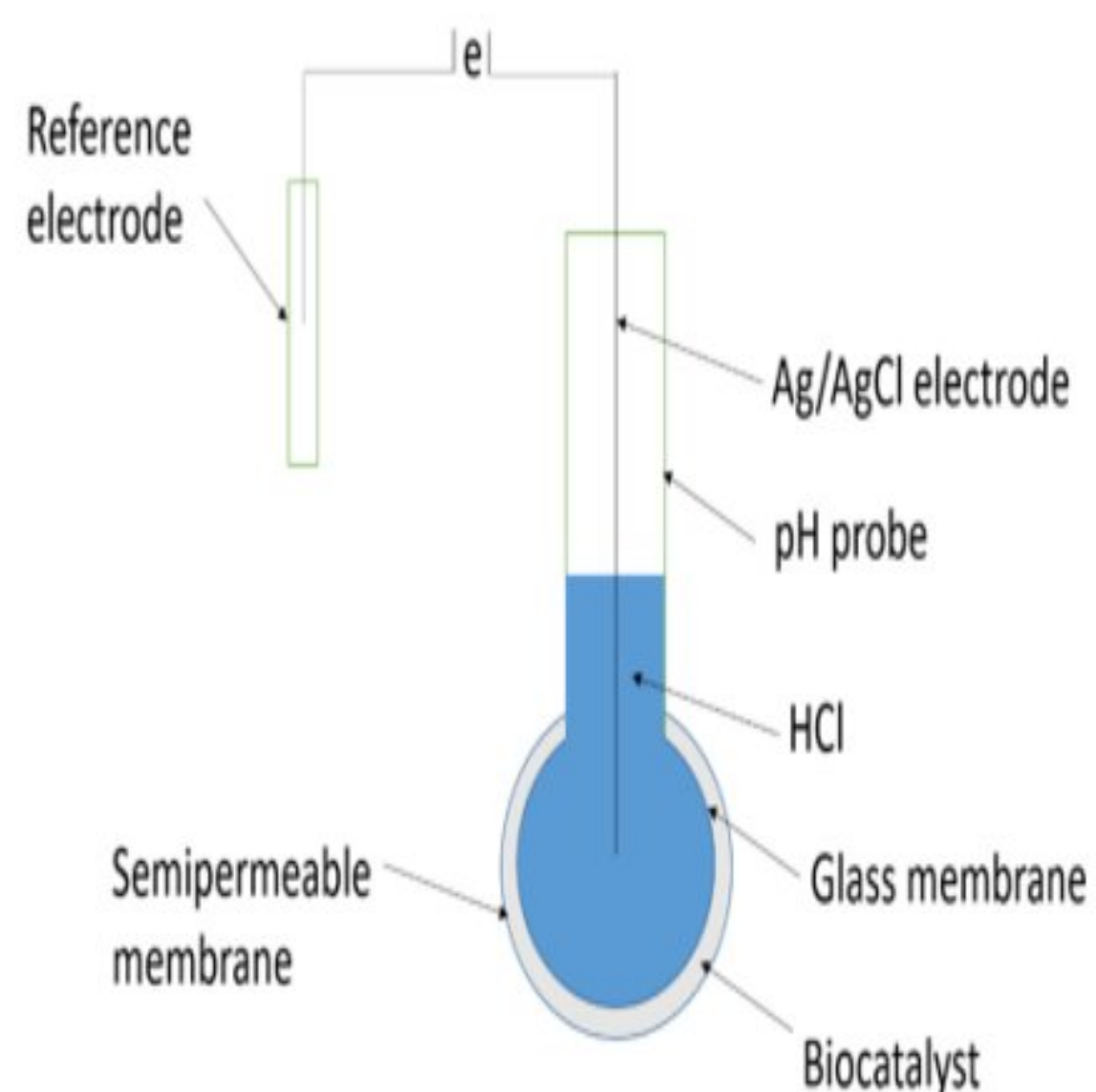
Glass electrode is a type of ion selective electrode that only identifies H⁺ ions in the solution.

Potential of the glass electrode will change accordingly to concentration of H⁺ ions in the solution.

Analysis of Glucose level in Blood:



The released H⁺ ions come in contact with the glass electrode then there is a potential change developed across the membrane and produces an electrical signal in the cell that indicates the level of glucose in blood sample.



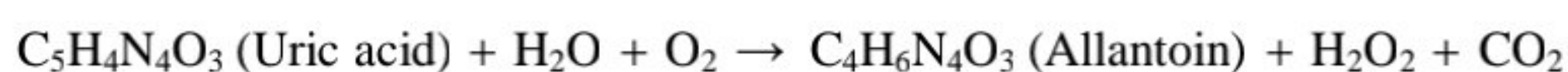
Amperometric Sensors:

The sensor that measures flow of current in between working electrode and reference electrode.

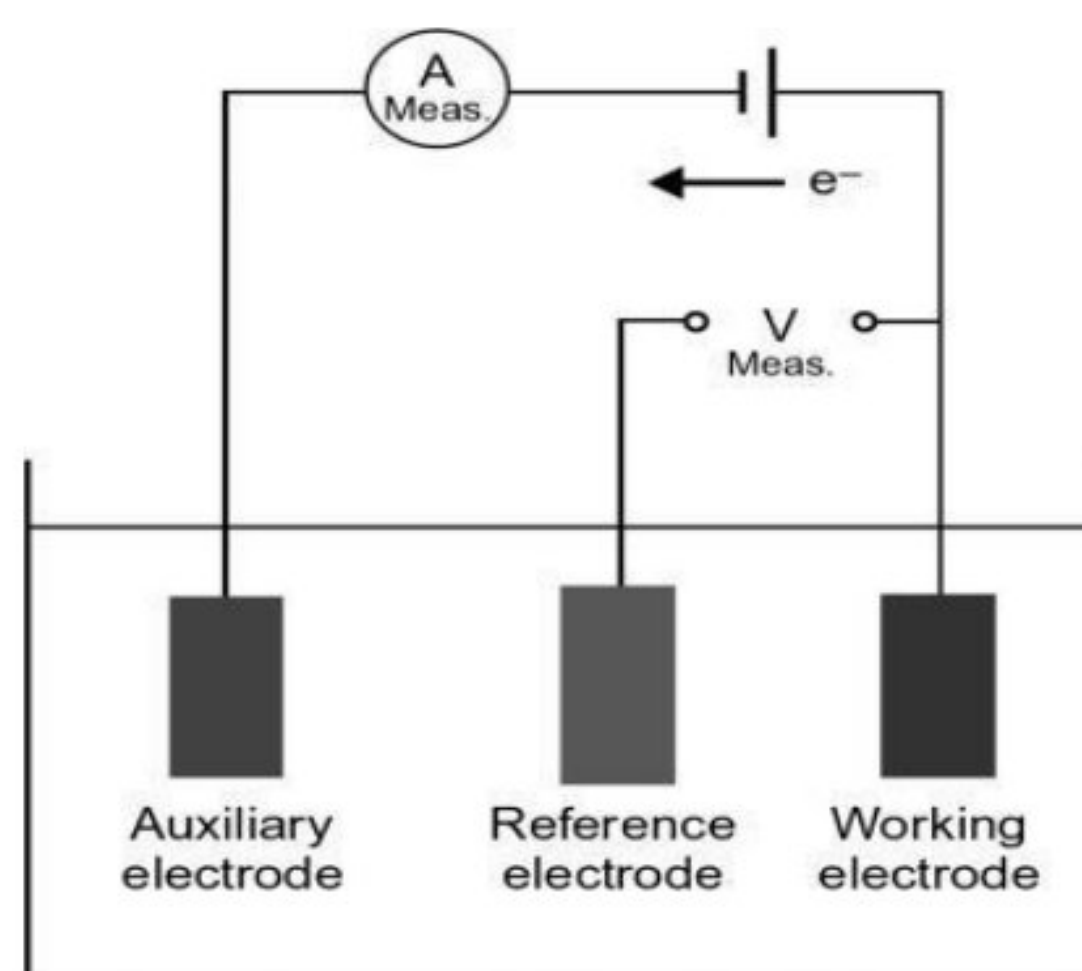
Redox reactions can be measured through amperometric sensors.

Current generated through redox reactions is identified by working electrode and gives suitable electrical signal on display.

Analysis of Uric Acid :



The released electrons moves from working electrode to reference electrode and due to flow potential of the working electrode changes and the electrode potential will be displayed on the cell that indicates the quantity of uric acid present in the urine sample.



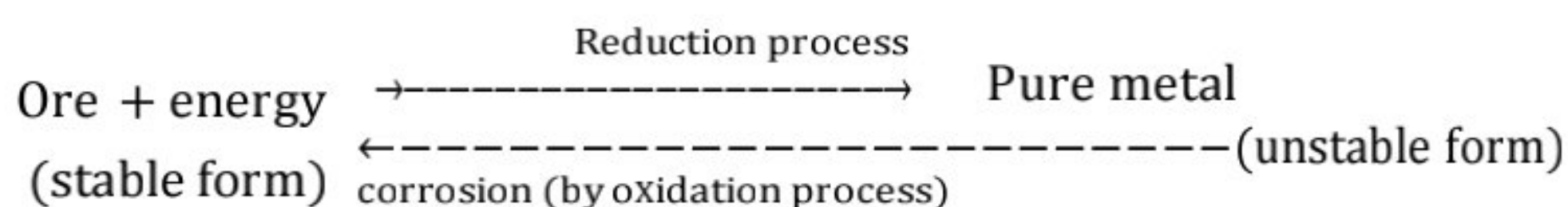
CORROSION

Corrosion:

- It is the destruction of metal by chemical reactions with the surrounding environment like gases or liquids.
- For example:
 - Rusting of iron is due to formation of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (by reacting with surrounding O_2 and water).
 - Green layer on copper is due to the formation of $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ (by reacting with CO_2 & water)
 - Blackening of silver is due to formation of silver sulfide (by reacting with surrounding H_2S)

Cause of Corrosion:

- Metal is available as a stable form of oxides, sulfides and carbonates. These are called ores of metals.
- These are changed into metals by reduction process and hence metals are in unstable form.
- That's why metals always try to get its stable form, it is known as corrosion.



Effects of corrosion:

1. Decrease in thickness of metal leads to cracks in the metal
2. Damage of structures (like bridges, cars, aero planes etc.) and loss of men and women

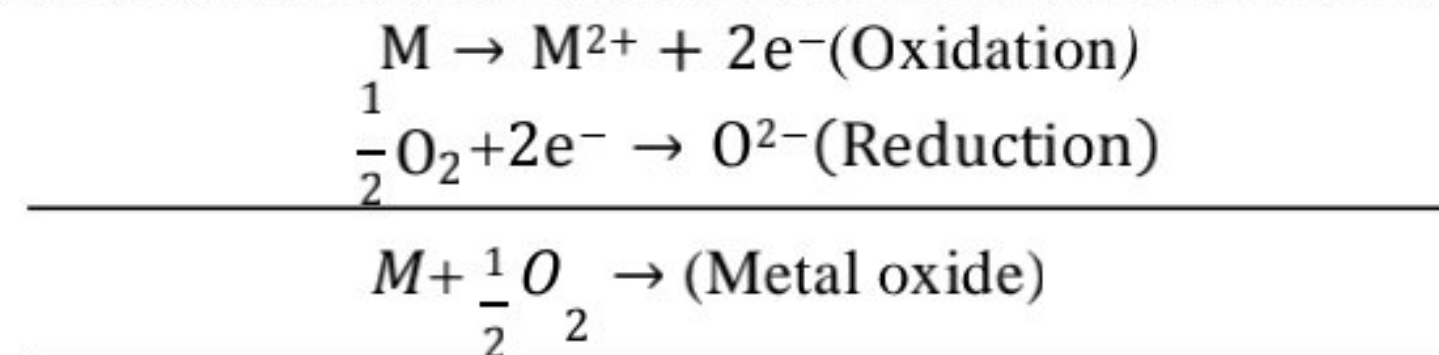
3. It makes the holes in vessels and pipes leads to leakage of liquids
4. It makes the liquid present in vessels and pipes dirty.
5. Decrease in price of new items due to bad look
6. Loss of surface properties
7. Corrosion products stops the flow of liquids, gases etc. through pipelines.

Theories of corrosion:

- There are two types of theories of corrosion
 1. Dry or chemical theory of corrosion
 2. Wet or electrochemical theory of corrosion

1. Dry or chemical theory of corrosion:

- This theory explains how corrosion takes place in the presence of dry atmospheric gases.
- In this, a chemical reaction takes place between metal and atmospheric gases like O_2 to form metal ions and electrons and these electrons react with O_2 to form oxide ion.
- The metal ion and oxide ion form metal oxide on the metal surface.



- The nature of metal oxide layer plays an important role in corrosion
- There are four types of metal oxide layers

○ **Stable metal oxide layer:**

- These metal oxide layer are stable, these do not have any holes and these do not allow the passage of oxygen through them.
- These metal oxides stick to the metal surface very strongly to stop the corrosion
- For example: Al, Cr, Cu & W.

○ **Unstable metal oxide layer:**

- This unstable oxide layer is changed back into metal & oxygen.
- This layer completely stops the corrosion
- For Example: Au & Pt.

○ **Volatile(or vaporizable)metal oxide layer:**

- This metal oxide layer is evaporated as soon as it is formed.
- It corrodes the metal very fast.
- For example: Molybdenum (Mo) & tin (Sn)

○ **Non- Protective metal oxide layer:**

- This metal oxide layers have holes and these holes allow the passage of oxygen on the metal surface through them to increase corrosion.
- For example: Alkali & Alkaline earth metals

• **Pilling bed worth rule:**

- It is used to find out whether the oxide layer is having holes (pores) or not.

$\text{Pilling Bed worth Rule} = \frac{\text{volume of metal oxide formed}}{\text{volume of metal consumed}}$

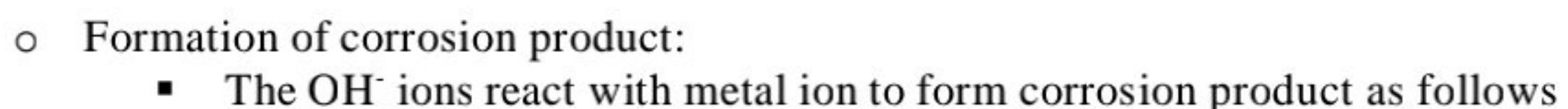
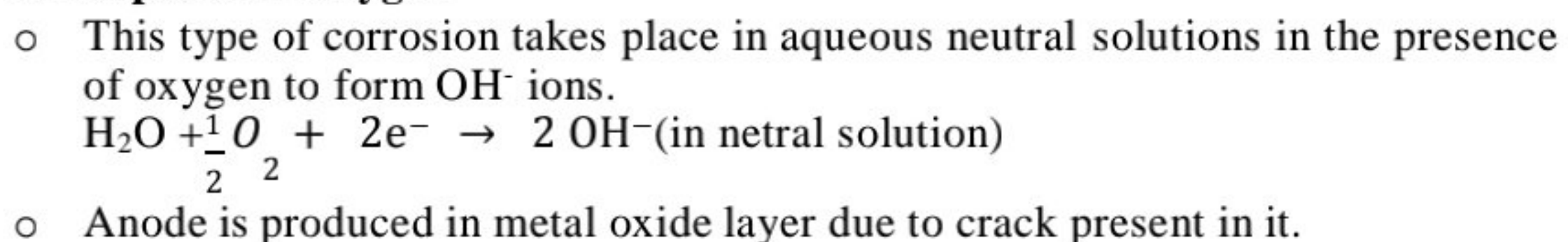
- According to this Rule

- If this ratio < 1 , then the metal oxide layer will be porous (having holes) & non-protective.

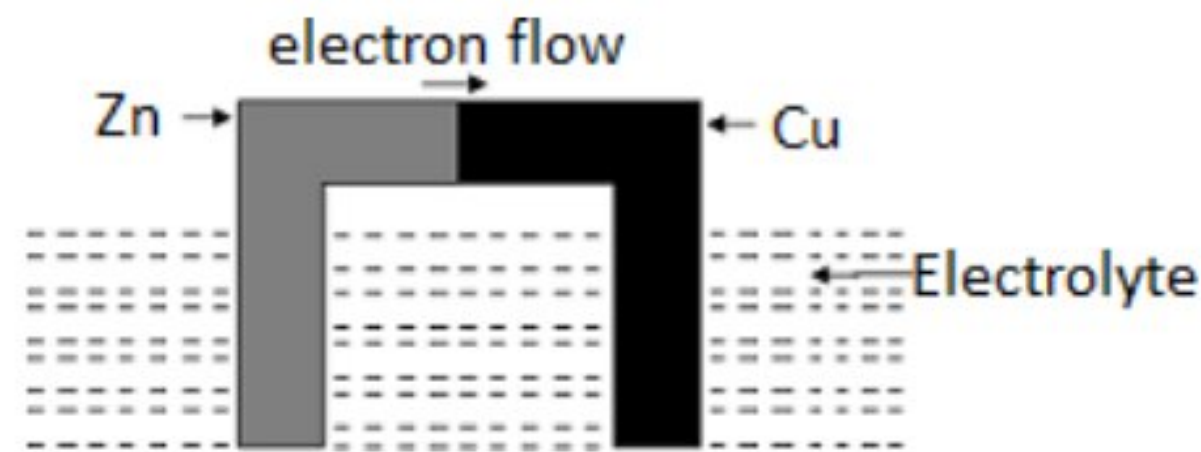
- If the ratio = 1 or >1 , then the metal oxide layer will be non-porous & Protective.
For example: Al, Cr, Cu & W

- According to this theory, the metal under goes an electrochemical reaction with moisture present in the atmosphere.
- **At anode**, oxidation of metal takes place to form metal ions and electrons and **at cathode**, the reduction takes place.
- To explain this, let us take an example of corrosion of iron.
- **At Anode:** $Fe \rightarrow Fe^{+2} + 2e^{-}$
- **At Cathode**, two types of reactions take place

- This type of corrosion takes place in both aqueous acidic and basic solutions in the absence of O_2 to release H_2 gas.
- The H^+ ions present in acidic solutions takes electrons formed at anode and release H_2 gas.
 $2H^+ + 2e^- \rightarrow H_2$ (in acidic solution)
- The water molecules present in basic solutions takes electrons formed at anode to release H_2 gas.
 $2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (in basic solution)



- When Zn and Cu metal blocks are placed side by side, Zn acts as anode and undergoes corrosion and Cu acts as cathode and gets protected from corrosion.
- The half cell reaction at Zn block is $Zn \rightarrow Zn^{2+} + 2e^-$



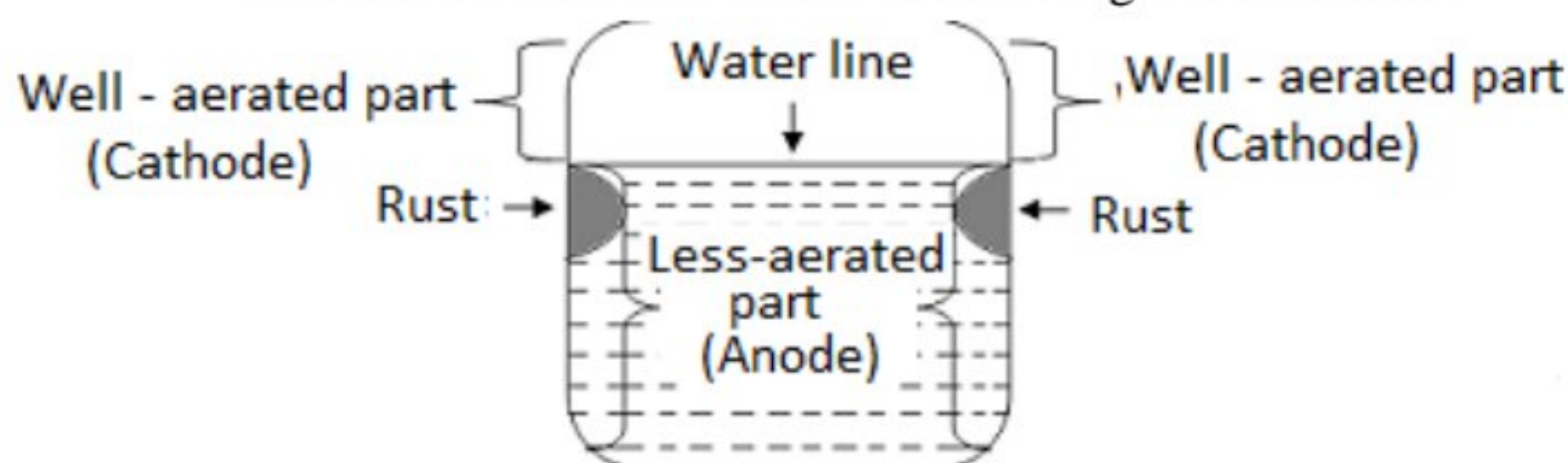
- As the difference in electrode potential between metals in contact increases, rate of corrosion increases.
- **The galvanic corrosion can be stopped by**
 - Avoiding galvanic couple
 - Selecting metals closely placed in galvanic series
 - Keeping an insulating material between two metals

Differential Aeration Corrosion:

- It takes place when a metal is exposed (or opened) to different air concentrations. It has been found that well-aerated part acts as cathode and is protected from corrosion whereas less-aerated part acts as anode and undergoes corrosion.

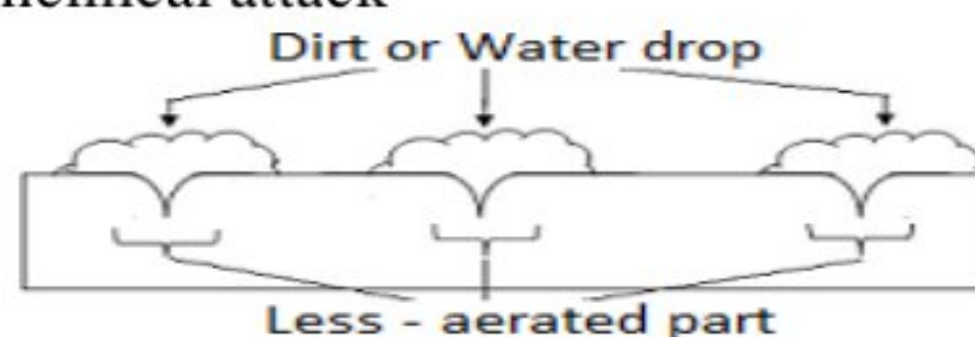
Water line Corrosion:

- When water is stored in a steel tank for a long time, it is observed that corrosion takes place just below the water line.
- The ship also suffers from water line corrosion. The bottom metallic surface under the sea water line undergoes corrosion.



Pitting corrosion:

- It is a localized form of corrosion caused by cavities, pinholes, pits and cracking in the protective layer formed on the metal surface.
- When dirt, sand, water droplet, etc. are present on the metal surface, the part of metal covered by water or other particles is less-aerated and acts as anode.
- The other metal part exposed to more air acts as cathode.
- Corrosion takes place at the part below dust and a small pit is formed.
- Cracking of protective layer may be due to
 - Surface roughness
 - Scratches
 - Sliding under load
 - chemical attack



Factors affecting the rate of corrosion:

1. Nature of metal:

- **Position of metal in galvanic (or electrochemical) series:**

- The rate of corrosion depends up on the position of metal in galvanic series.
- More the oxidation potential more the corrosion & act as anode.

- **Purity of metal:**

- The rate of corrosion depends on the purity of metal
- More the purity less the corrosion of metal as shown in the table

% Purity of metal	99.999	99.99	99.95	99.00
Corrosion rate	1	2650	5000	7200

- **Ratio of anodic area to cathodic area:**

- If $\frac{\text{Anodic area}}{\text{Cathodic area}}$ is small, corrosion is more and it means more the cathode area more corrosion.
- For example: when copper sheet having small iron pins (rivet), iron pins are corroded completely because iron pins acts as anode and copper sheet acts as cathode.

- **Nature of metal oxide layer:**

- The formation of stable metal oxide layer decreases the corrosion
- The formation of vaporizable, unstable metal oxide layer having holes increases the corrosion.

- **Physical state:**

- The rate of corrosion is affected by the physical state of a metal. As the size of crystal of metal decreases the rate of corrosion increases.

2. Nature of Environment:

- **Temperature:**

- As the temperature increases the rate of corrosion increases.

- **Humidity**(amount of water or moisture) **of air:**

- The amount of water (humidity) present in air increases corrosion. Since moisture acts as a medium.

- **Presence of impurities in atmosphere:**

- Corrosion increases if air is having waste gases like H_2S , SO_2 & CO_2 .

- **Effect of pH:**

- In acidic medium, metals are more corrosive than alkaline or neutral media.
- By increasing pH value we can control the corrosion. For example: Corrosion of Zn decreased by increasing pH to 11

- **Conductance of the soil:**

- Dry sandy soils have lower conductance as compared to soils having salts.
- Metals are corroded in soils having salts very fast than dry sandy soils.

Cathodic Protection:

- In cathodic protection, the metal to be protected from corrosion is changed into cathode by joining with some other metal that acts as anode.

- There are two types of cathodic protections

- Sacrificial anodic Protection
- Impressed Current Cathodic Protection:

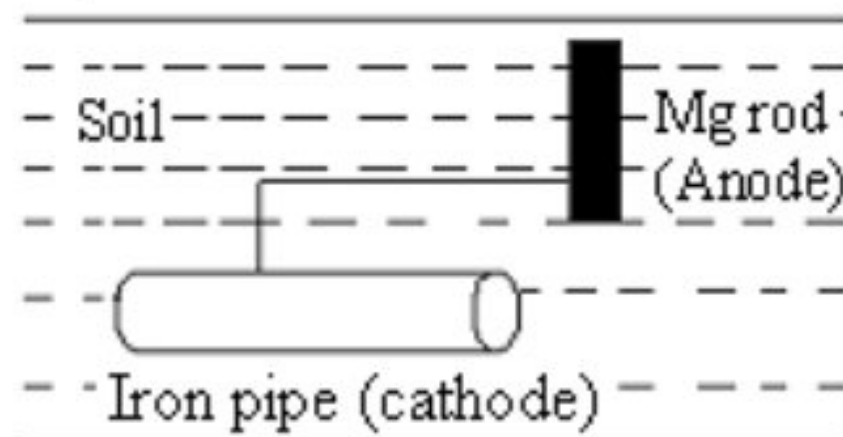
- **Sacrificial anodic Protection:**

- In this method, the metal (like iron) to be protected from corrosion is joined with a metal (like Mg) that acts as anode as shown in the diagram.

- More anodic metal (Mg) gets corroded while the metal (Fe) is protected.
- The more anodic metal used is known as **Sacrificial anode**. Since anodic metal (Mg) is sacrificed (lost) in the process of saving iron.
- The corroded sacrificial anode is replaced by a new one when used up completely.
- The Sacrificial anodes are Mg, Zn and Al.
- Cell reactions:

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

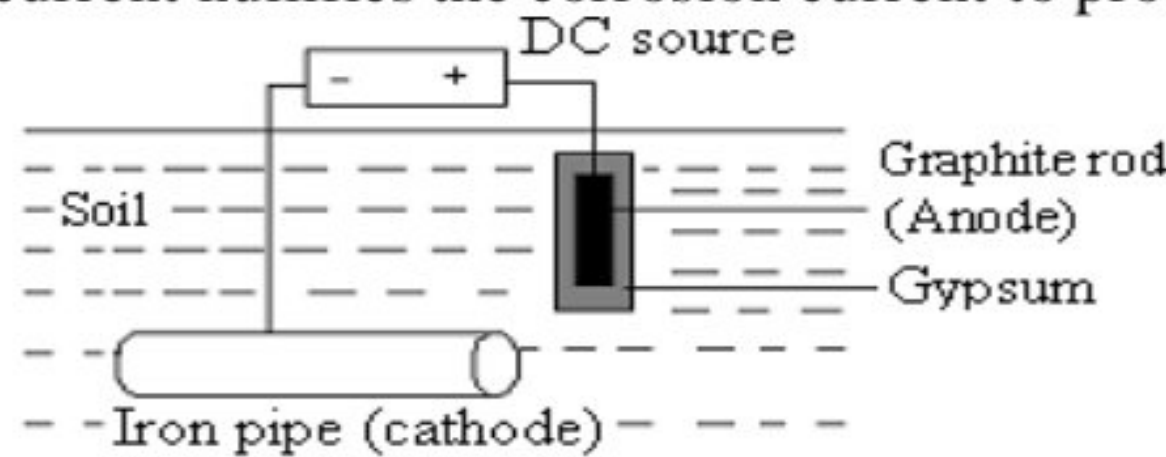
At cathode: $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$



- **Uses:**
 - This method is used to protect underground pipe lines; ships and boats moving in sea and house hold water boilers

- **Impressed Current Cathodic Protection:**

- In this method, the metal to be protected is joined to the negative terminal of the DC source.
- The positive terminal is joined to anodes like graphite, platinum.
- Gypsum is filled around graphite rod to pass electric current to the soil.
- The impressed current nullifies the corrosion current to protect the metal.



- This method is used to protect underground pipelines, underground cables, water tanks etc.

Surface coating or protective coating:

- It is a thin layer of some material on the surface of a metal
- These are put (applied) on the surface of a metal in order to stop the corrosion.
- It separates metal surface from corrosive gases, liquids and solids.
- It gives beautiful look to the metal surface and it increases the life time of a metal.
- Surface coatings are three types:

1. Metal coatings
2. Non-metal coatings
3. Organic surface coatings

- **Metal coatings:**

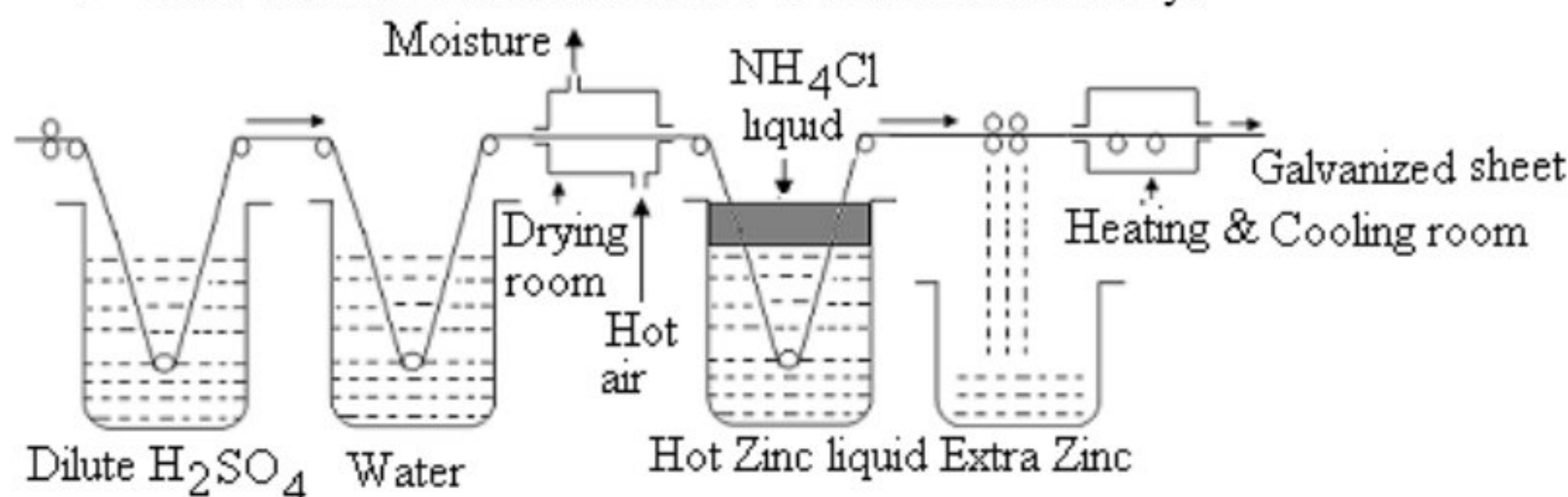
- The metal to be protected from corrosion is base metal and the metal coated on the base metal is called coating metal.
- Examples for coating metals are Zn, Sn, Ni, Cu, Cr, Al, Pb, etc.
- Metal coatings are two types
 1. Anodic coatings
 2. Cathodic coatings

Hot dipping:

- In this, the metal to be coated is put (dipped) in the hot thick (molten) liquid of the coating metal.
- Hot dipping is two type
 1. Galvanizing
 2. Tinning

- **Galvanizing:**

- It is the coating of Zn on iron, steel and copper metal sheets
- In this, iron or steel sheet is cleaned with dilute H_2SO_4 for 20 minutes at 90°C .
- The sheet is then washed well and dried.
- Then this sheet is put in a vessel having hot thick liquid of Zinc maintained at 430°C .
- The surface of the vessel having liquid Zn is kept closed with NH_4Cl liquid to stop corrosion.
- The sheet is taken out and extra Zn is removed by passing the sheet in between a pair of hot cylinders that turn round (rollers).
- Then this sheet is heated at 650°C and cooled slowly.

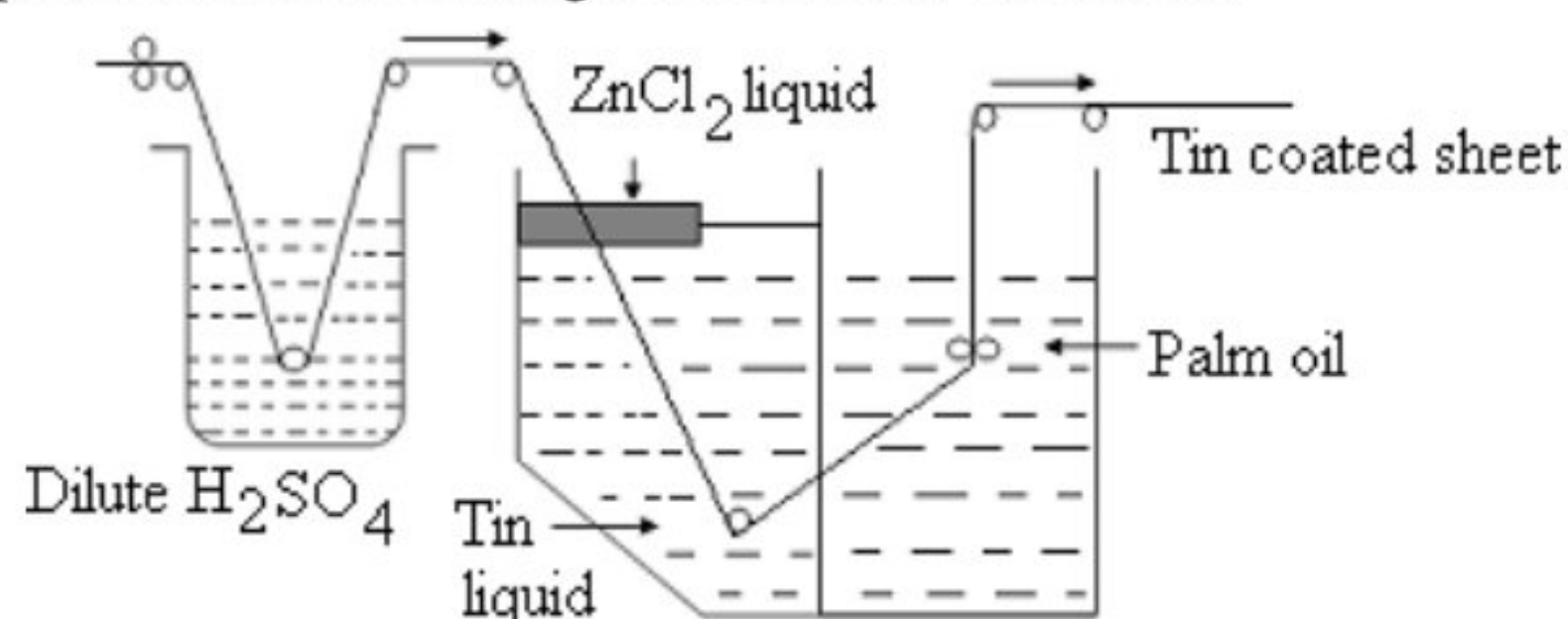


- **Applications:**

- It is used to protect iron sheets used on the top part of buildings etc., wires, pipes, nails, bolts, screws, buckets and tubes.
- Galvanized vessels cannot be used for cooking and storing food.

- **Tinning:**

- It is the coating of tin (Sn) on iron or steel, copper and brass sheets.
- In this, the iron sheet is cleaned with dilute H_2SO_4 for 20 minutes at 90°C .
- This sheet is passed through Zinc chloride liquid
- The sheet is then passed through a vessel having hot thick liquid of tin solution maintained at 240°C .
- It is then pressed between two rollers present in a vessel having palm oil to get uniform thin coating and to remove extra tin.
- Palm oil protects the tin coating surface from oxidation.



- **Applications:**

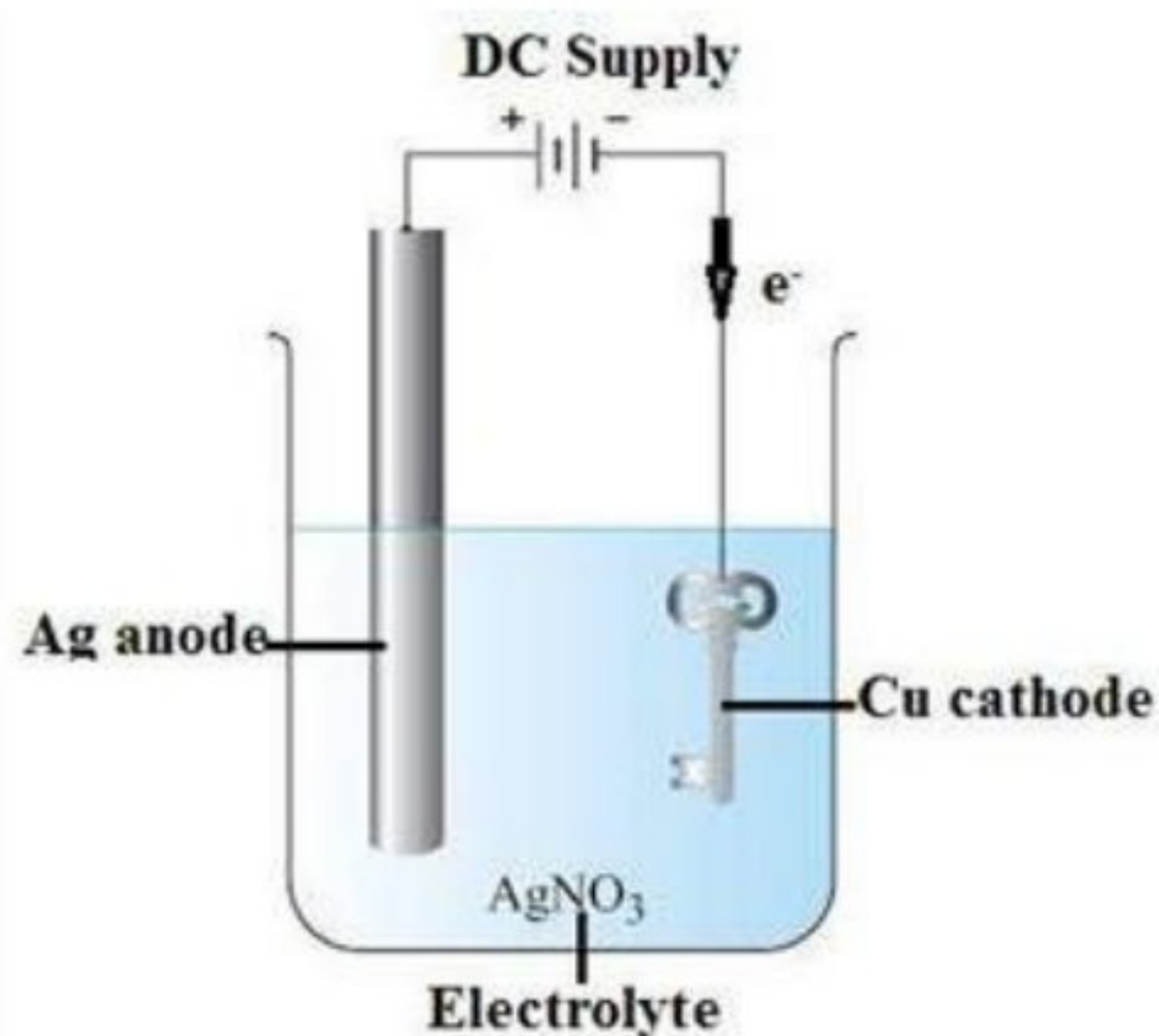
- The vessels coated with tin are used for storing and packing food.
- Copper sheets coated with tin are used for making cooking vessels.

Electroplating:

Electroplating is a process in which the coat metal is deposited on the base metal by passing a direct current through an electrolytic solution”.

Procedure:

- In this process, Base metal is made as the cathode and the coat metal is taken as the anode. A solution of the coat metal salt is taken as the electrolyte.
- The electrodes are connected to a battery and DC current is passed.
- Now electrolysis takes place and the coat metal is deposited over the base metal.
- Nature of coating depends on the current density, time, temperature and the concentration of the electrolyte.



Example:

To coat silver on copper material:

The copper material is taken as the cathode. A silver plate is taken as anode. Silver-thiocyanate solution is the electrolyte. DC power source of electricity, silver is deposited over the copper material.

At cathode reduction takes place: $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$ (deposited on Cu)

Applications:

1. Used in jewellery coating.
2. Purification of metals.
3. Changing the texture of metal surfaces.
4. Preventing corrosion
5. Facilitating conduction in circuit boards.