Module 2: Energy Conversion and Storage, Corrosion

Energy conversion: Introduction, construction, working, and applications of Photo voltaic cells, methanol-oxygen fuel cell.

Storage devices: Introduction, construction and working of Li-ion battery.

Corrosion: Introduction, electrochemical corrosion of steel in concrete, types (differential metal and aeration), Stress corrosion in civil structures, corrosion control (design and selection of materials, galvanization, anodization, and sacrificial anode method).

Self-learning: Corrosion inhibitors

……

Solar Energy

The energy obtained by the sun is called solar energy. Solar energy, based on its utilization, can be of two types:

1. Director solar power
2. Indirect solar power
   1. **Director solar power:** Director solar power in walls only one step transformation into a usable form.
      Example 1) A photovoltaic cell converts solar energy to electrical energy.

      Example 2) solar thermal collector
   2. **Indirect solar power:** Indirect solar power requires more than one transformation to reach usable form.
      E.g. 1: Plants convert solar energy into chemical energy when they are burned.

      E.g. 2: Fossil fuels are obtained from plants which produce heat energy that can later be burned as fuel to generate electricity.

      E.g. 3: Ocean thermal energy production uses the thermal gradient that is present across the ocean depths to generate power.

Advantages of Indirect Solar Power

- Solar power is pollution-free
- Low operating costs
- Facilities can operate with little maintenance
- High public acceptance and excellent safety
- Solar power is economical, except the initial setup

Disadvantages of indirect solar power

- Sunlight is diffuse source
- High installation costs
- Energy can be produced only during the day.

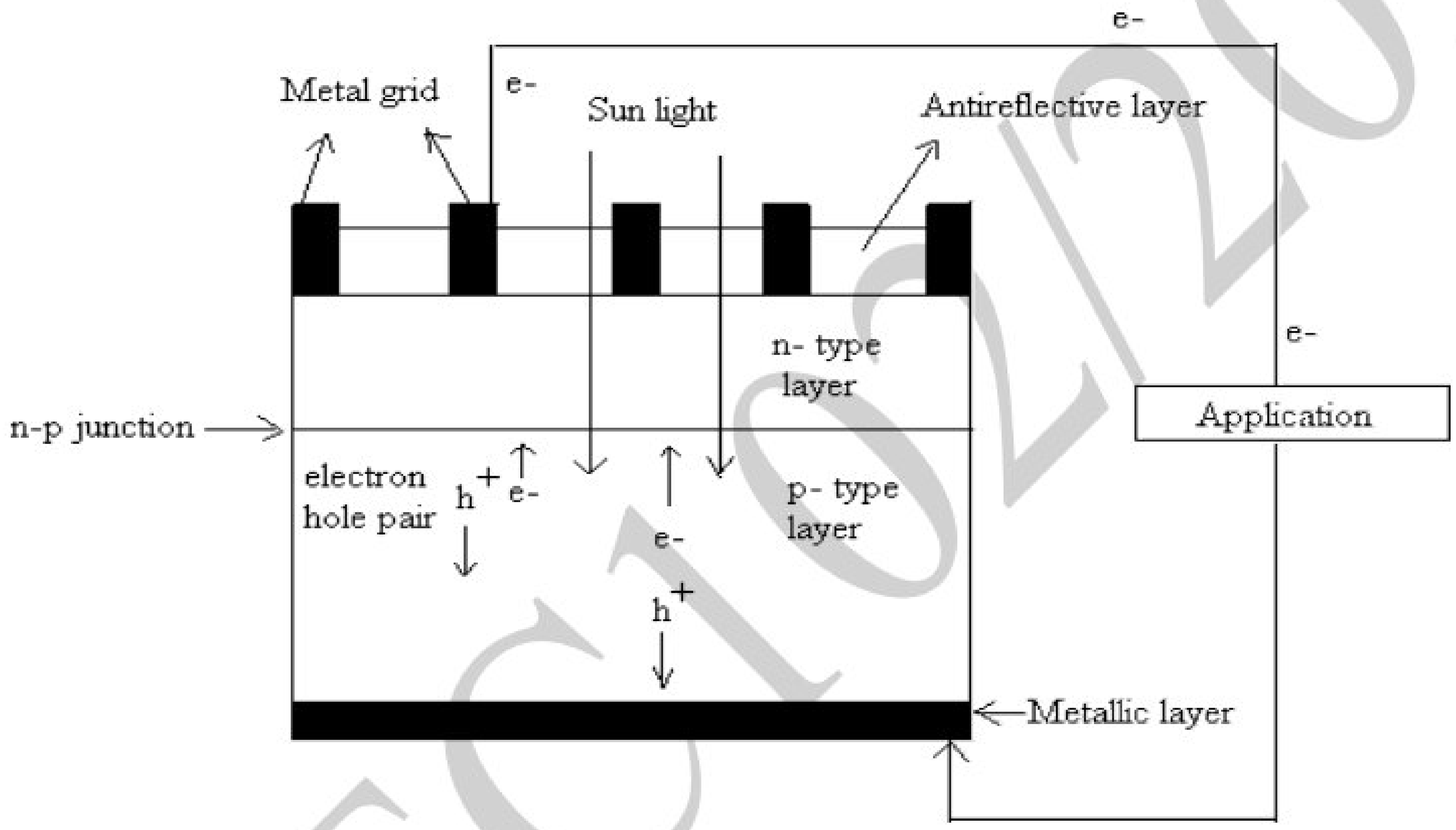
Construction and working of a photo voltaic cell

- A photovoltaic cell consists of 'n' type semiconductor at the top and 'p' type semiconductor at the bottom. Hence, the p-n junction is formed between the two.

- A metallic grid above the diode forms one of the electrical contacts and allows the light to fall on the semiconductor.
- An anti-reflexive layer made up of titanium dioxide present between the metallic grid increases the transformation of sunlight into semiconductors.
- Another metallic layer is present at the back of the semiconductor, which forms another electrical contact.

Working

When electromagnetic radiation falls on the 'p-n' junction diode, the electron pair hole is generated. Electrons move towards the 'n' type semiconductor, and the holes move towards the 'p' type semiconductor. On connecting these to ends, current flows between them to an external circuit.



Applications

1. For producing electricity using solar power plants
2. To provide electricity to satellite
3. Remote sensing techniques from space using satellite with objectives
4. To provide reliable weather monitoring and forecasting by monitoring the climatic factors

Fuel cells:

Introduction: The electrochemical conversion of the free energy change of a redox reaction into electrical energy is the working principle of any type of cell. The electrode reaction of a primary battery is irreversible, and the cell produces EMF as long as the active material is present in the cell.

Conventional Batteries	Fuel cells
1. Batteries are energy storage device. 2. Secondary batteries need charging. 3. The reactance and products from an internal part of batteries 4. Waste product in a battery may be harmful that is less eco-friendly.	1. Fuel cells are energy conversion devices. 2. Fuel cells do not need charging. 3. Reactance is continuously supplied, and the products are continuously removed. 4. More eco friendly

Fuel cells:

A fuel cell is defined as a galvanic cell in which chemical energy is converted into electrical energy.

The Fuel cell can be represented as follows Fuel electrode/electrolyte/electrode/oxidant.

In a fuel cell

At anode: the fuel undergoes oxidation
Fuel $\Rightarrow$ oxidized product + ne^-

At cathode: the oxidant gets reduced.

Oxidant + ne^- $\Rightarrow$ reduced product

Advantages of a fuel cell

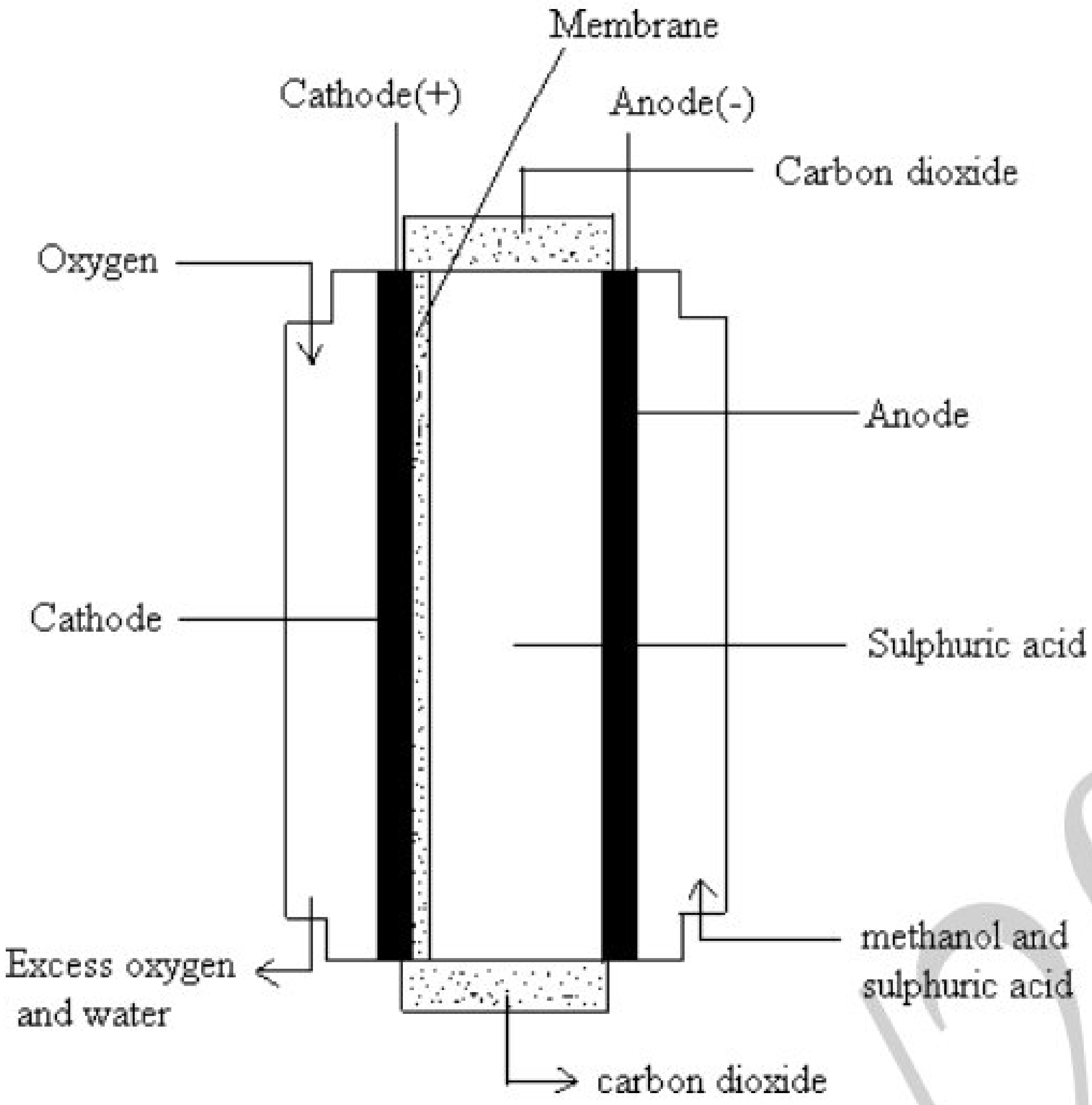
1) They offer high energy conversion
2) Energy as long as fuel and oxidants are supplied
3) Silent operation
4) They are ecofriendly
5) No need of charging

Methanol – Oxygen Fuel Cell

Methanol is one of the most electroactive organic fuels in the low-temperature range. It is mainly because:

- It has low carbon content.
- It possesses a readily oxidisable OH group and
- It has high solubility in aqueous electrolytes

Methanol containing some sulphuric acid (concentration 3.7M) is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber, and sulphuric acid (which is the electrolyte) is placed in the central compartment. Both electrodes are made of platinum. A membrane is placed adjacent to the cathode on the inner side to minimize the diffusion of methanol into the cathode thereby reducing the concentration of methanol near the cathode. In the absence of a membrane methanol diffuses through the electrolyte into the cathode and undergoes oxidation.



The electrode reactions are,

$$\text{At anode:}\quad CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6\,e^-$$

$$\text{At cathode:}\quad 3/2\ O_2 + 6H^+ + 6\,e^- \longrightarrow 3\ H_2O$$

$$\text{Net cell reaction is:}\quad CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + H_2O$$

Advantages

1. Stable at all atmospheric conditions.
2. CO_2 produced by the reaction can be easily removed.
3. Easy handling
4. Methanol has low carbon content.
5. Readily oxidizable OH group.
6. Low-cost liquid fuel.

Applications

1. It is used in military applications and in large scale power production.
2. It's also used in fuel cell vehicles and space shuttles.
3. It is ideal for powering smaller vehicles such as forklift etc.

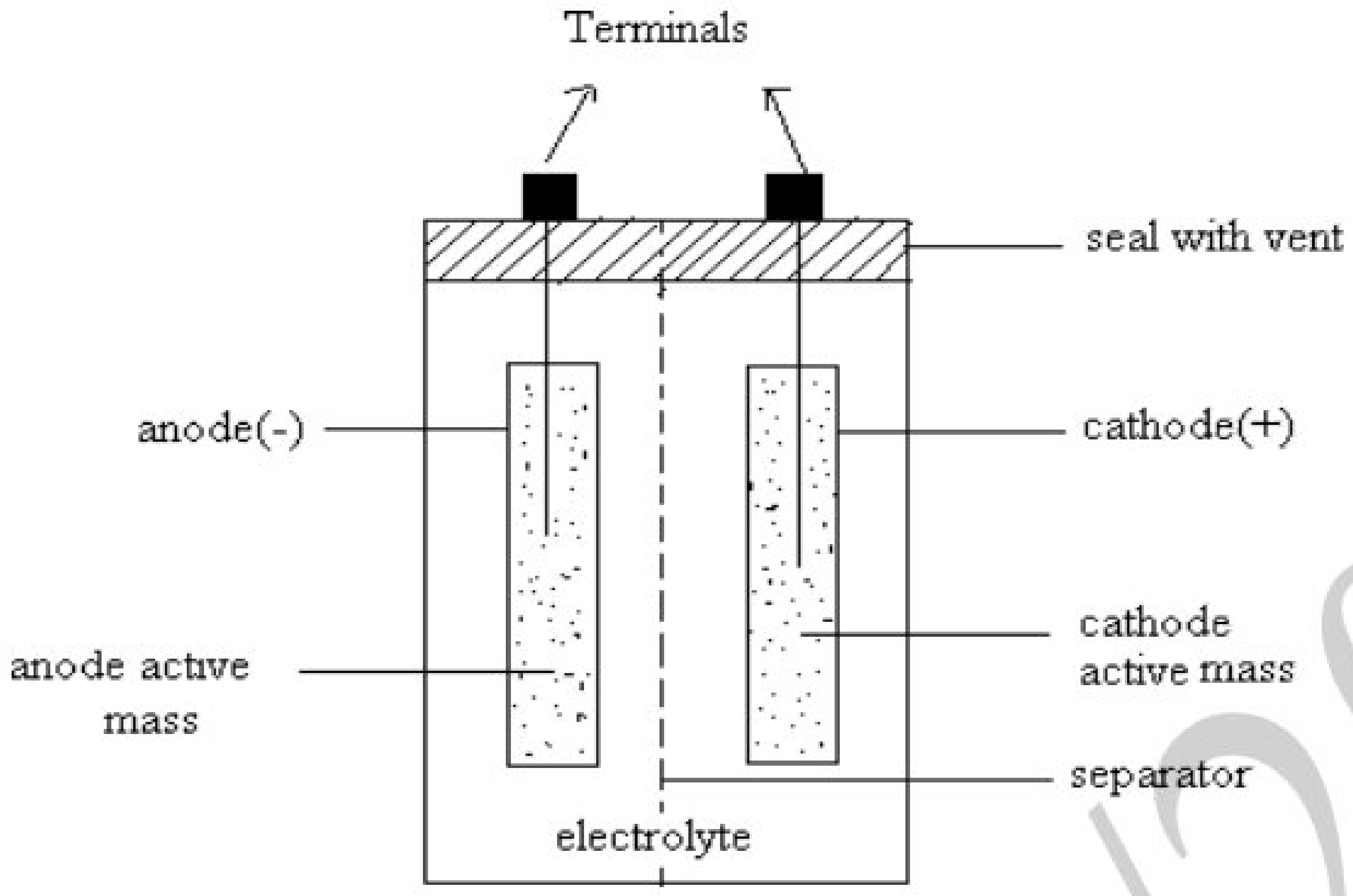
Storage Devices

Battery is a device consisting of two or more galvanic cells connected in series or parallel or both, that store chemical energy in the form of active materials and on demand convert it into electrical energy through electrochemical redox reaction.

Batteries generate power and acts as portable sources of electrical energy. Batteries are used in calculators, digital watches, pacemakers for heart, hearing aids, portable computers, digital cameras, car engines, emergency lighting, electroplating, industrial, military and space applications.

Basic concepts

The basic electrochemical unit in a battery is a galvanic cell. The components of such a cell are shown in the fig.



The principal components of a battery are

The anode or negative electrode – it gives electrons to the external circuit by undergoing oxidation during electrochemical reaction.

The cathode or positive electrode – it accepts electrons from the external circuit and reduction of the active species occurs.

The electrolyte – an ionic conductor. The electrolyte (active mass in the anode and cathode compartments) is commonly a solution of an acid, alkali or salt having high ionic conductivity. Solid electrolytes having ionic conductivity at the operating temperature of the cell are also used.

The separator – the material that electronically separates the anode and cathode in a battery to prevent internal short-circuit is referred to as a separator. It is permeable to the electrolyte to maintain the desired ionic conductivity. Thus the main function of the separator is to transport ions from the anode compartment to the cathode compartment and vice versa.

Eg: fibrous forms of regenerated cellulose, vinyl polymers and polyolefin's, cellophane and nafion membranes.

Classification of batteries

Batteries are classified as

a) Primary (irreversible) batteries

b) Secondary (reversible) batteries

c) Reserve batteries

a) Primary batteries: In primary batteries the cell reaction is not completely reversible. They are also referred to as irreversible batteries. These are not rechargeable and once discharged after that it has no further electrical use.

Eg: Leclanche cell(Zn-MnO_2) and Li-MnO_2battery

b) **Secondary batteries:** Secondary batteries are rechargeable. The cell reactions are reversible and these are also referred to as storage or reversible batteries. After discharge secondary batteries can be recharged electrically to their original condition by passing current through them in the direction opposite to that discharge current.
Eg: Lead acid battery, Ni-Cd battery

c) **Reserve batteries:** Reserve batteries are the batteries which are stored in an inactive state and made ready for use by activating them before the application. The activation involves adding electrolyte or any other cell component. One of the components is isolated and stored separately and is filled just before it is needed. Electrolyte is the component that is usually isolated and hence the battery has long term storage capacity.
Eg: Mg water activated batteries (Mg-AgCl and Mg-CuCl), Zn- Ag_2O batteries.
Lithium-Vanadium Pentoxide battery (Li-V_2O_5)

Li- ion Battery

The three components of a lithium-ion battery are the positive and negative electrodes and electrolyte. The negative electrode of a lithium-ion cell is made of carbon (graphite). The positive electrode is a layered metal oxide such as lithium cobalt oxide or lithium manganese oxide. The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing lithium salts, such as $LiPF_6$, $LiBF_4$ or $LiClO_4$. A liquid electrolyte acts as a carrier between the positive and negative electrodes when current flows through an external circuit.

Electrode reactions

While discharging, lithium atoms present in the graphite layer are oxidized, liberating electrons and lithium ions. Electrons flow through external circuit to the cathode and lithium ion moves through the electrolyte towards cathode. At cathode lithium ions are reduced to lithium atoms and are inserted into the layered structure of metal oxide.

At Anode

$$\text{Li-C}_6 \longrightarrow \text{Li}^+ + 6\text{C} + e^-$$

At Cathode

$$\text{Li}^+ + e^- + \text{MO}_2 \longrightarrow \text{Li-MO}_2$$

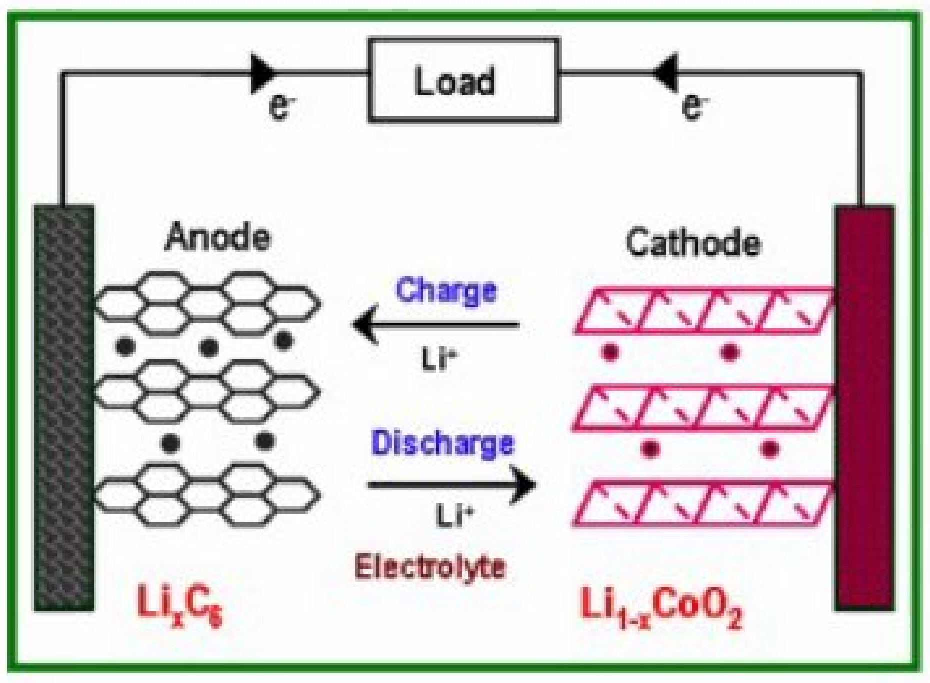
When the cell is charging, the reverse occurs. Lithium present in the layered metal oxide oxidized, liberating electrons and lithium ions. Electrons flow through external circuit to the cathode and lithium ion moves through the electrolyte towards anode.

At Anode

$$\text{Li-MO}_2 \longrightarrow \text{Li}^+ + e^- + \text{MO}_2$$

At Cathode

$$Li^+ + 6C + e^- \longrightarrow Li\text{-}C_6$$



Applications

- Used in mobile phones and smart phones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).
- Used in electric vehicles like electric cars, Pedelecs (pedal electric cycle), electric wheelchairs, radio-controlled models etc.

Corrosion

Corrosion is defined as "the destruction of metals or alloys by the surrounding environment through chemical or electrochemical changes."

The process of corrosion is the transformation of pure metal into its undesired metallic compounds. The life of a metal object gets shortened by the corrosion process.

The familiar examples of corrosion are

i. Rusting of iron – a reddish brown scale formation on iron and steel objects. It is due to the formation of hydrated ferric oxide.
ii. Green scales formed on copper vessels. It is due to the formation of basic cupric carbonate [$CuCO_3 + Cu(OH)_2$]

Ill Effects of Corrosion

- Loss of efficiency.
- Contamination of product.
- Damage of metallic equipments.
- Inability to use metallic materials.
- Appearance as when corroded material is unpleasing to the eye.
- Loss of valuable materials such as blockage of pipes, mechanical damage of underground water pipes.
- Accidents due to mechanical loss of metallic bridges, cars, aircrafts etc.
- Safety, for example, sudden failure can cause fire, explosion, release of toxic products, and construction collapse.
- Depletion of Natural Resources.
- India Losses 5.7 % GDP due to corrosion.

Chemical corrosion (Dry corrosion)

Chemical corrosion occurs due to the direct chemical reaction between the metal and the gasses present in the corrosive environment. This type of corrosion is generally observed in the absence of moisture or conducting electrolyte medium. Therefore, it is also known as dry corrosion.

Eg: Oxidation of metals or alloys on exposure to oxygen in air. Reaction of corrosive gasses such as HCl, H_2S, SO_2, Cl_2, F_2, NH_3 etc. with metal and alloy surfaces.

Electrochemical corrosion (Wet corrosion)

Electrochemical corrosion involves reactions in aqueous medium. The conducting surface of the metal undergoes an electrochemical reaction with the moisture and oxygen present in the atmosphere. This process can be explained on the basis of electrochemical theory of corrosion.

Electrochemical theory of corrosion of steel in concrete

Steel in concrete is naturally in a passive state, which can be broken under following conditions:

1. Presence of chloride ions, which convert passive steel into active form.
2. When concrete is exposed to air, carbon dioxide in air reacts with surface of concrete, calcium hydroxide in the concrete is carbonated which lowers the pH and converts steel from passive to active.

Corrosion of iron metal in concrete as explained as follows:

i) Formation of galvanic cells. Anodic and cathodic areas are formed resulting in minute galvanic cells.

ii) At anode oxidation takes place so that metal is converted into metal ions with the liberation of electrons and move towards cathode.

iii) Oxygen of the atmosphere is reduced to OH^- ions in the presence of water (moisture) at the cathodic area.

Anodic reaction:

At the anodic area, oxidation takes place resulting in the corrosion of iron.

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

Cathodic reactions:

Electrons flow from the anodic to cathodic area and cause reduction depending on the nature of the corrosive environment. Since the metal cannot be reduced further, metal atoms at cathodic region are unaffected by the cathodic reaction. Some constituents of the corrosion medium take part in the cathodic reaction.

Most common types of cathodic reactions are either liberation of hydrogen or absorption of oxygen.

In acidic medium and in the absence of oxygen, hydrogen liberation takes place.

$$\mathbf{2H^+ + 2e^- \longrightarrow H_2\uparrow}$$

In neutral or alkaline medium and in the absence of oxygen, hydroxide ions are formed with liberation of hydrogen.

$$\mathbf{2H_2O + 2e^- \longrightarrow 2OH^- + H_2\uparrow}$$

In neutral or alkaline medium & in the presence of oxygen, hydroxide ions are formed

$$\mathbf{2H_2O + O_2 + 4e^- \longrightarrow 4OH^-}$$

The metal ions formed at the anode combine with the OH^- ions and form the insoluble $Fe(OH)_2$. In an oxidizing environment, it is oxidized to ferric oxide and the yellow rust is hydrated ferric oxide.

$$\mathbf{2Fe^{+2} + 4OH^- \longrightarrow 2Fe(OH)_2}$$

$$\mathbf{4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow \underbrace{2[Fe_2O_3 \cdot 3H_2O] + H_2}_{\text{Yellow Rust}}}$$

Types of Corrosion

1. Differential Metal Corrosion (Galvanic Corrosion)

Differential metal corrosion occurs when two dissimilar metals are in contact with each other in a corrosive conducting medium. The two metals differ in their tendencies to undergo oxidation, the one with lower electrode potential or the more active metal acts as anode and the one with higher electrode potential acts as cathode. The potential difference between the two metals is the driving force for corrosion. The anodic metal undergoes corrosion and the cathodic metal is generally unattacked.

The following reactions occur during differential metal corrosion. At the anode:

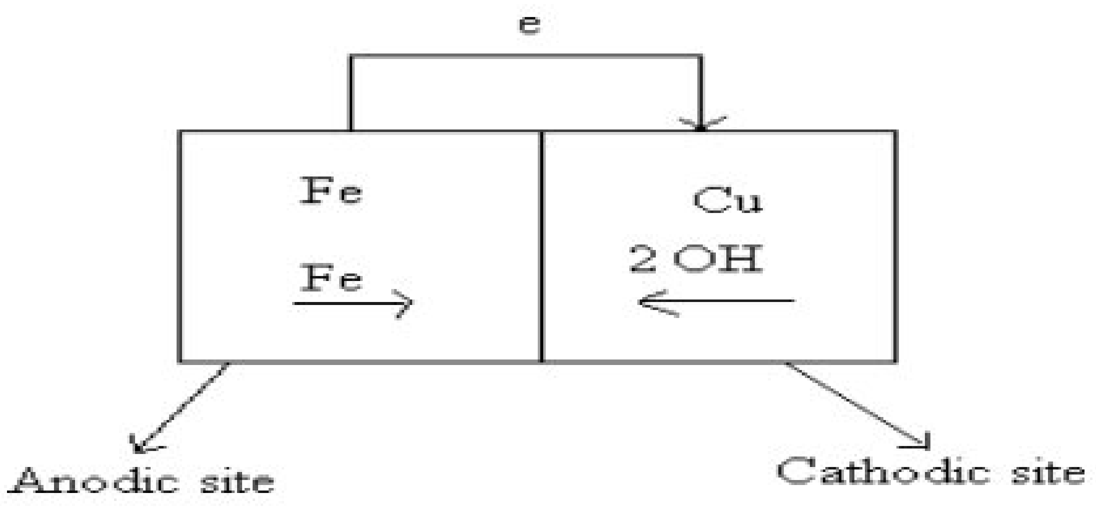
$$M \longrightarrow M^{+n} + ne^-$$

At the cathode: Depending on the nature of the corrosion environment the cathode reaction is either hydrogen evolution or oxygen absorption.

(i) $\mathbf{2H^+ + 2e^- \longrightarrow H_{2\,(g)}}$

(ii) $\mathbf{O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-}$

For example, if a piece of iron combined with copper is exposed to corrosive atmosphere. Iron acts as anode in the presence of copper (iron is placed above copper in the electrochemical series). In such case, iron undergoes corrosion and copper is unaffected.



2. Differential Aeration Corrosion

Differential aeration corrosion occurs when a metal surface is exposed to differential air concentrations or oxygen concentrations, the part of the metal exposed to higher oxygen concentration acts as cathodic region and the part of the metal exposed to lower oxygen concentration acts as anodic region. As a result the part of the metal exposed to lower oxygen concentration undergoes corrosion.

At the anode (less O_2 concentration)

$M \longrightarrow M+n + ne-$ (oxidation)

At the cathode (more O_2 concentration)

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

"Corrosion of metals is due to the formation of an oxygen concentration cell because of the uneven supply of air on the metal surface is known as differential aeration corrosion."

Examples

i. Part of the nail inside the wall which is exposed to lower oxygen concentration than the exposed part, undergoes corrosion.

ii. Window rods inside the frame suffer corrosion but not the exposed parts.

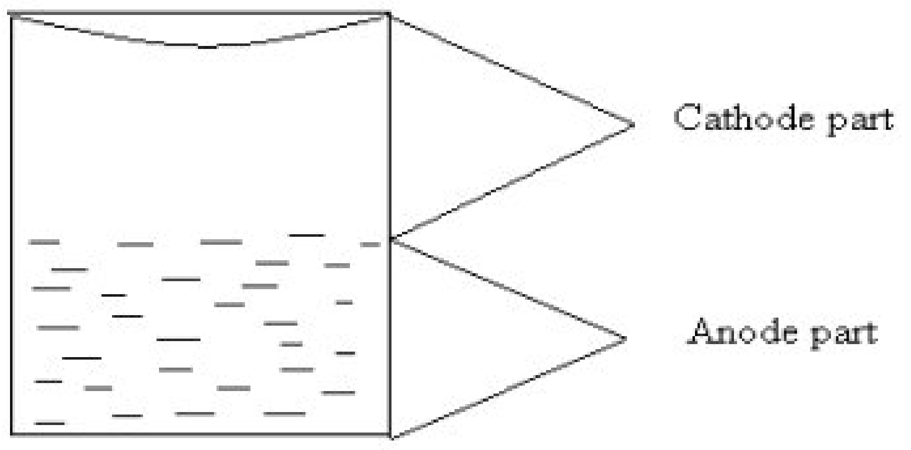
iii. Metal under dirt, dust, scale or water undergoes corrosion.

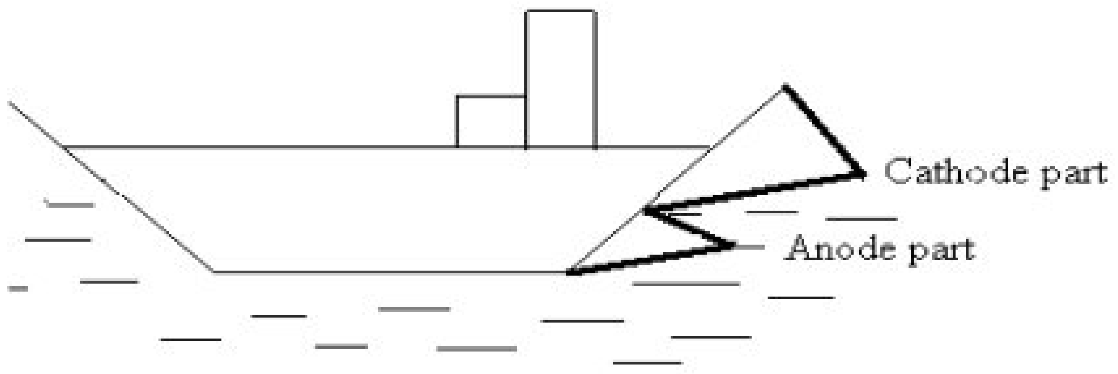
iv. Paper pins inside the paper gets corroded, and the exposed part is free from corrosion.

Water line corrosion and pitting corrosion are the two cases of differential aeration corrosion.

3. Water Line Corrosion

Water line corrosion is observed in steel water tanks, ocean going ships etc. The water line corrosion takes place due to the formation of differential oxygen concentration cells. The part of the metal below the water line is exposed only to dissolved oxygen while the part of the metal above the water is exposed to higher oxygen concentration of the atmosphere. Thus part of the metal below water acts as anode and undergoes corrosion and the part above the water line is free from corrosion.





Stress Corrosion In Civil Structure

Example: Caustic embrittlement of water boiler

- This type of corrosion is seen when the metal is under stress.
- Stress can be either applied stress or residual.
- Residual stress is from the process like welding, quenching, bending and deformation.
- Metal alloys are more susceptible than pure metals.
- Stress corrosion is dangerous because it can lead to cracking of the metal without a warning or with little warning.
- Ex: the water boilers made up of mild steel undergo corrosion at the stressed region when exposed to hot concentrated alkaline solution.
- Corrosion mechanism involves passage of alkaline impurities present in water into fine hair like crack made on the boiler.
- When water is boiled the Na_2CO_3 present in the boiler water is hydrolysed to NaOH at high temperature.

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

- NaOH thus formed reaches into the crack and reacts with Fe, forming sodium ferroate and decomposes into Fe_3O_4 and NaOH.

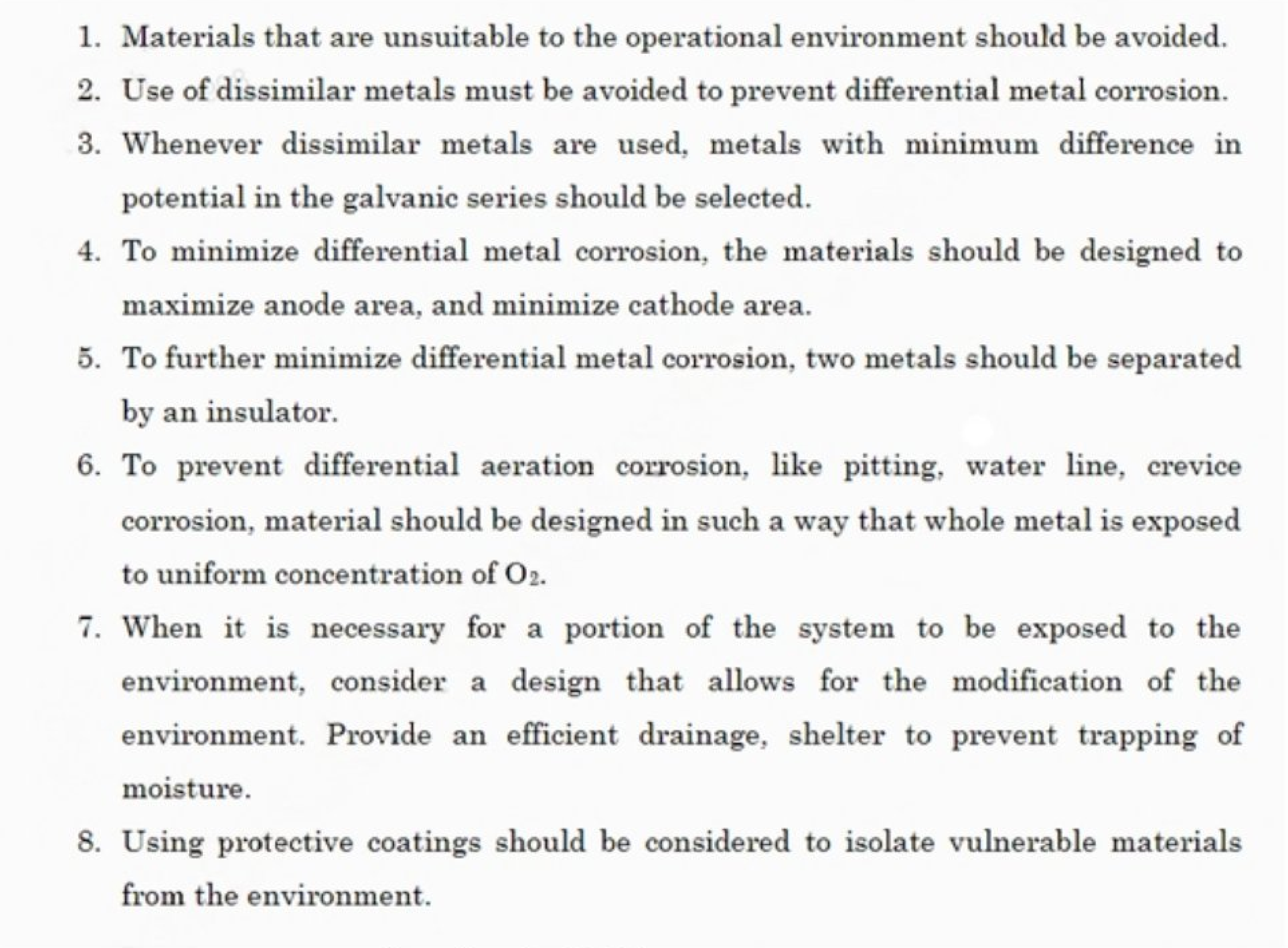
  $2\ NaOH + Fe \rightarrow Na_2FeO_2 + H_2$

  $3\ Na_2FeO_2 + 4\ H_2O \rightarrow Fe_3O_4 + 6NaOH + 4H_2$

- NaOH thus formed reacts with iron and causes an explosion of the boiler.
- Since NaOH (caustic soda) is the main reason for corrosion this is also called caustic embrittlement.

Corrosion Control

Design And Selection of Materials

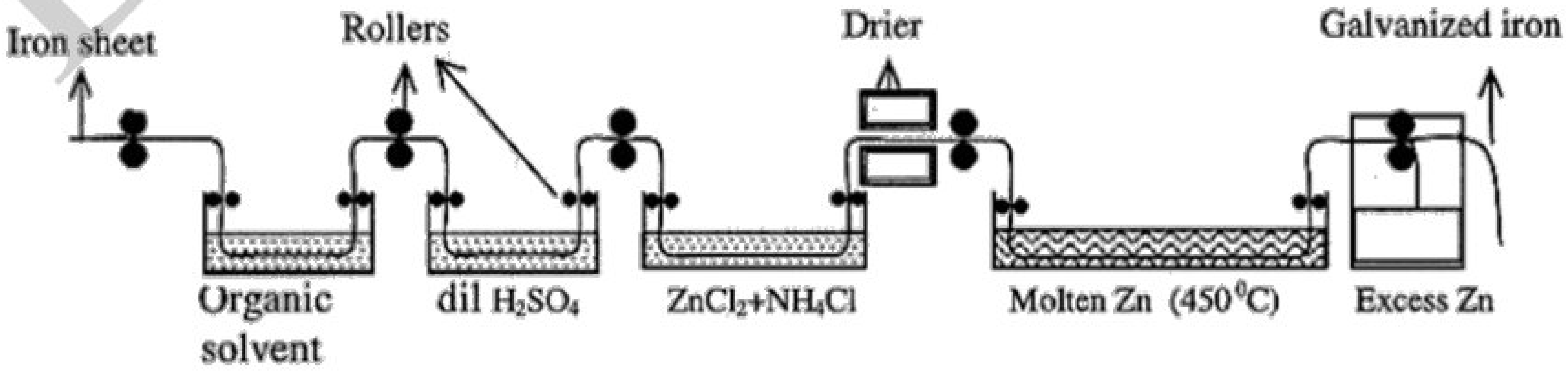


1. Materials that are unsuitable to the operational environment should be avoided.
2. Use of dissimilar metals must be avoided to prevent differential metal corrosion.
3. Whenever dissimilar metals are used, metals with minimum difference in potential in the galvanic series should be selected.
4. To minimize differential metal corrosion, the materials should be designed to maximize anode area, and minimize cathode area.
5. To further minimize differential metal corrosion, two metals should be separated by an insulator.
6. To prevent differential aeration corrosion, like pitting, water line, crevice corrosion, material should be designed in such a way that whole metal is exposed to uniform concentration of O_2.
7. When it is necessary for a portion of the system to be exposed to the environment, consider a design that allows for the modification of the environment. Provide an efficient drainage, shelter to prevent trapping of moisture.
8. Using protective coatings should be considered to isolate vulnerable materials from the environment.

Galvanization:

The coating of anodic Zn metal on iron is called galvanizing. Steps:

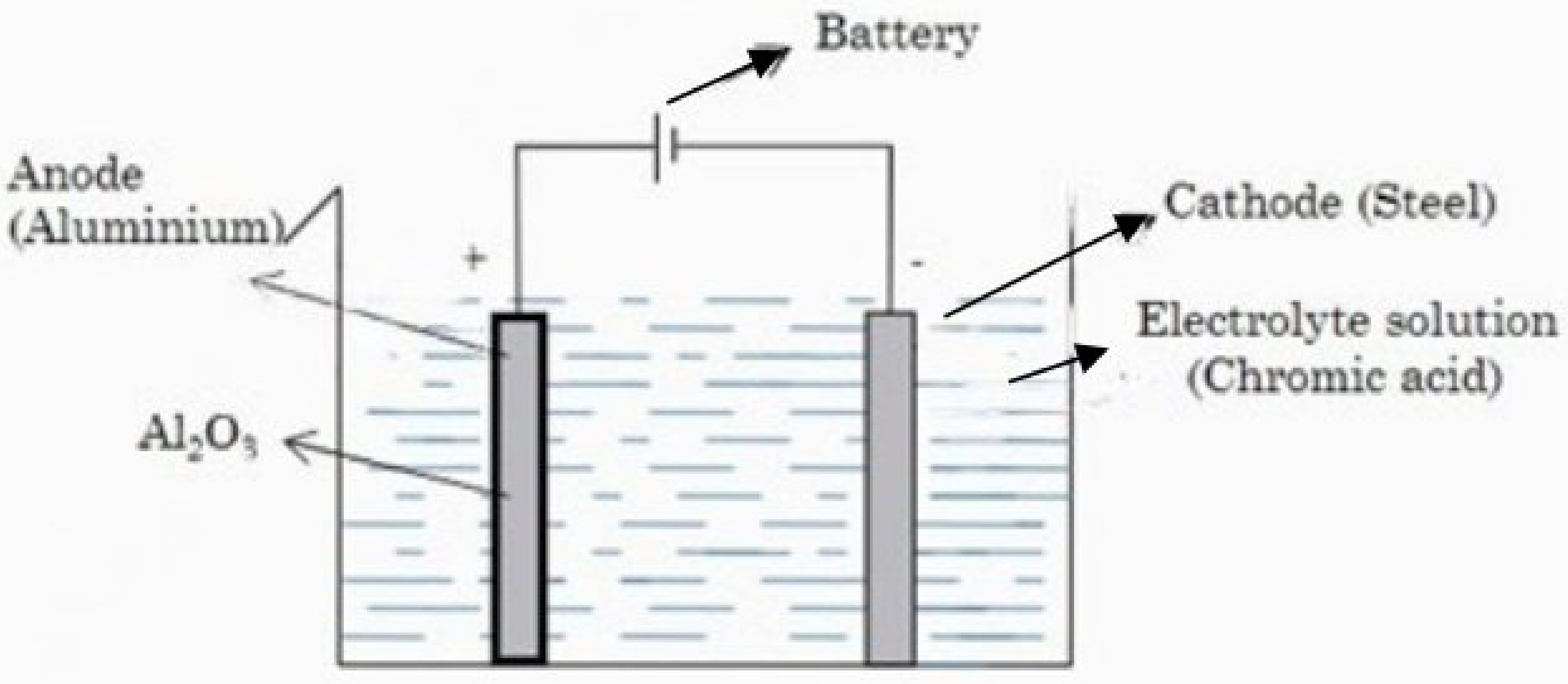
1. Iron sheet is passed through organic solvent to remove oil or grease.
2. Then it is washed with dil. H_2SO_4 to remove any rust.
3. Then it is treated with mixture of aqueous solution of $ZnCl_2$ and NH_4Cl.
4. It is dried then dipped in molten Zinc at 450°C
5. Excess zinc present on iron sheet is removed by passing through rollers.



Galvanization of iron

Anodizing

Anodizing is the process of oxidation of outer layer of metal to its metal oxide by electrolysis. Oxide layer formed over the metal itself acts as a protective layer.

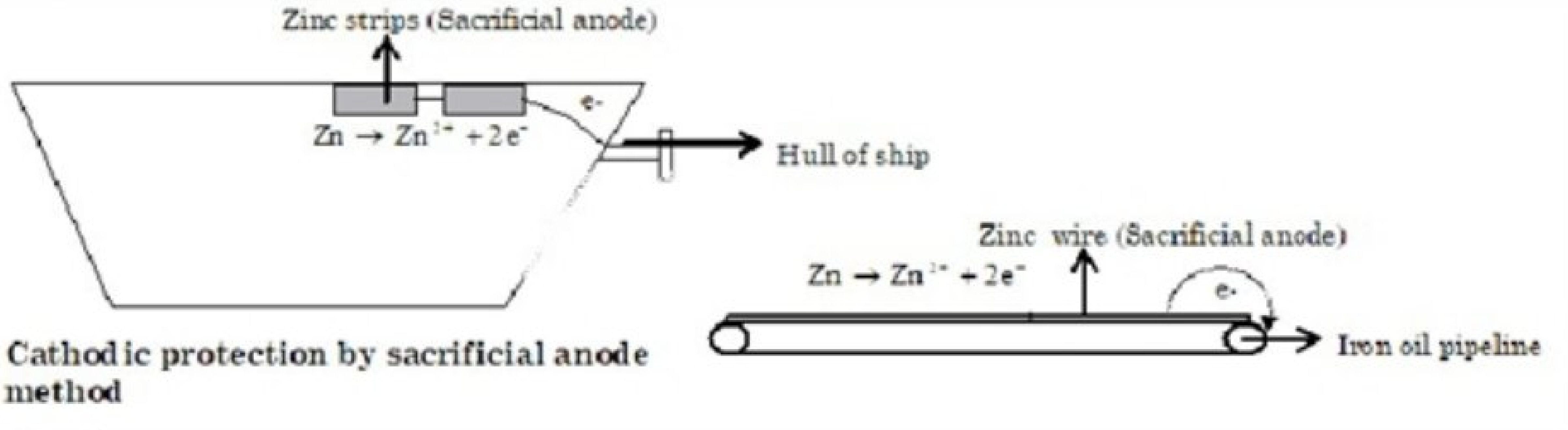


Anodizing

Before subjecting aluminium to anodization, it's surface is cleaned, degreased and polished and then it is taken as anode in an electrolytic cell. It is then immersed in an electrolyte consisting of 5-10% chromic acid. Steel or copper is taken as cathode. Temperature of the bath is maintained at 35°C. A current density of 100 or more A/m^2 is applied which oxidizes outer layer of Al to Al_2O_3 that gets deposited over the metal.

Sacrificial Anode

In **Sacrificial anode** method, metallic material to be protected is connected to a more active metal (anodic metal). Anodic metal like Zn can be employed to protect iron articles. When an anodic metal is in contact with iron specimen, a galvanic cell is set up, where anodic metal becomes anodic area and whole iron article becomes cathodic area. Anodic metal undergoes oxidation and provides electrons to the specimen and the entire specimen becomes cathodic and hence protected from corrosion. In the process, anodic metal undergoes corrosion and sacrifices itself to protect the specimen; therefore it is called as sacrificial anode. Sacrificial anodes have to be replaced in due course of time



Cathodic protection by sacrificial anode method