Module: 4

Polymers and Green Fuels

Syllabus
Polymers: Introduction, Molecular weight - Number average, weight average and Numerical problems. Conducting polymers – synthesis and conducting mechanism of polyacetylene and commercial applications. Preparation, properties, and commercial applications of graphene oxide. **Green Fuels:** Introduction, construction and working of solar photovoltaic cell, advantages, and disadvantages. Generation of energy (green hydrogen) by electrolysis of water and its advantages. **Self-learning:** Regenerative fuel cells.
Course Outcomes
CO1: Identify the terms and processes involved in scientific and engineering applications
CO2: Explain the phenomena of chemistry to describe the methods of engineering processes
CO3: Solve for the problems in chemistry that are pertinent in engineering applications
CO4: Apply the basic concepts of chemistry to explain the chemical properties and processes
CO5: Analyze properties and processes associated with chemical substances in multidisciplinary situations

Polymers:

Polymers are the macromolecules [having high molecular weight] obtained by union of simple molecules called monomers.

Ex: - Polyethylene, Polystyrene, Polyvinyl chloride etc…

Monomer:-

These are the simple molecules, which combine with each other to form polymer.

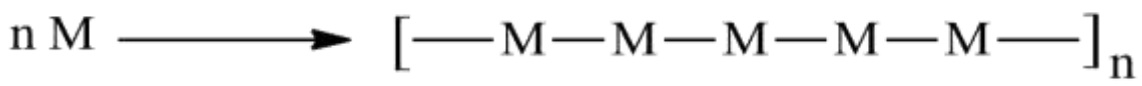
Ex: - Ethylene, Vinyl Chloride, Styrene, etc.…

Polymerization:-

The process of linking up of monomers to form polymers with (or) without the elimination of byproducts is called Polymerization.

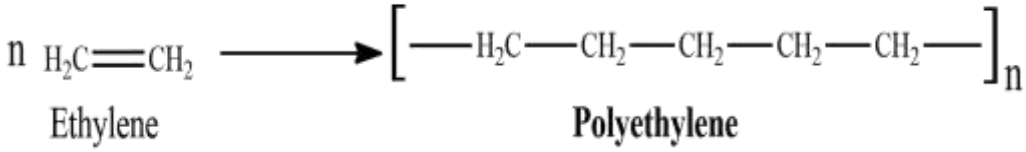
(or)

The chemical process by which the monomers are converted into polymers is called Polymerization.



Where n is the degree of Polymerization.

Ex:-



Degree of Polymerization:-

The total number of monomers present in a single chain of polymer is called as degree of polymerization.

Types of Polymerization:-

The process of polymerization is divided into two types.

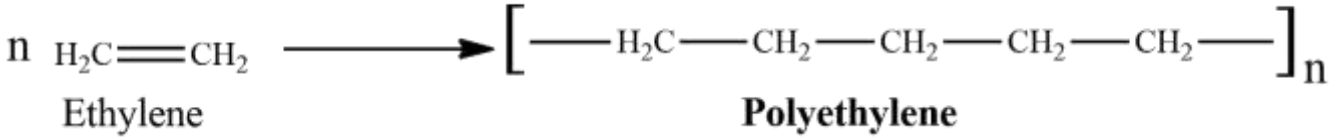
1. Addition Polymerization:-

The process in which a polymer is obtained from simple addition reaction of monomers without eliminating any simple molecule is called Addition Polymerization.

(or)

The process in which monomers united together to form a polymer without the elimination of byproduct.

Ex: - Polyethylene is obtained by addition reaction of ethylene monomer.



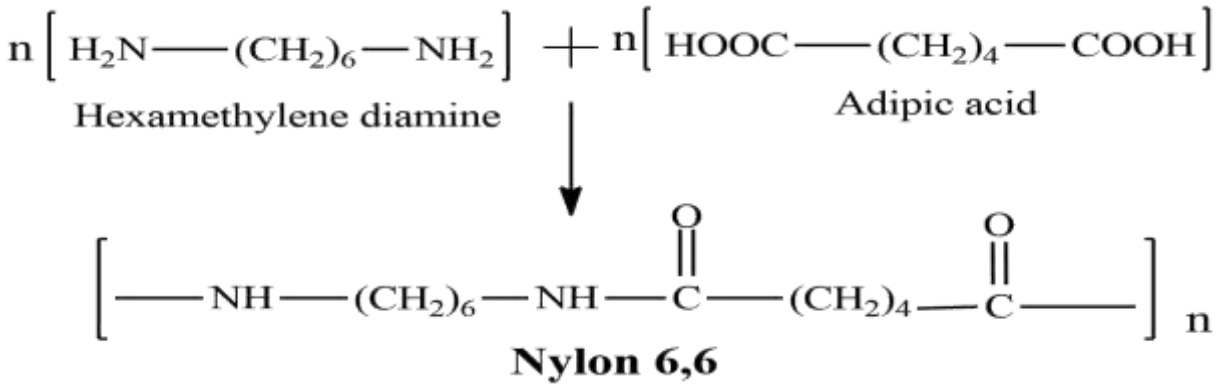
2. Condensation Polymerization:-

The process in which a polymer is obtained by condensation reaction of monomers with the elimination of simple byproducts is called as condensation polymerization.

(or)

The process in which monomers are united to form a polymer with a continuous elimination of byproducts.

Ex: - Nylon-6, 6 is obtained by condensation polymerization of Hexamethylene diamine and adipic acid.



Molecular weight of Polymers:-

The molecular weight of polymer depends on the number of monomer molecules in the polymer chain. The experimental measurement of molecular weight gives average molecular weight of a polymer.

Average molecular weight of a polymer is expressed as,

1. Number average molecular weight [$\bar{M}_n$]
2. Weight average molecular weight [$\bar{M}_w$]

Number average molecular weight [$\bar{M}_n$]:-

It is the mass obtained when total mass of all the molecules of a sample is divided by the total number of molecules.

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Where $M_i = Molecular\ Weight\ of\ Chain$

N_i = Number of chains of that molecular weight.

Weight average molecular weight: -

It is the mass obtained when sum of all the products of total mass of groups of molecules and their respective molecular masses is divided by total mass of all the molecules.

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Where M_i = Molecular Weight of Chain

N_i = Number of chains of that molecular weight.

Numerical on Molecular weight of Polymers:-

1. A polymer sample containing 5 molecules having molecular weight of 2000, 4 molecules having molecular weight of 3000 and 3 molecules having molecular weight of 4000. Calculate number average and weight average molecular weights.

Solution: - **1. Number average molecular weight [$\bar{M}_n$]:-**

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 \pm - - - - -}{N_1 + N_2 + N_3 \pm - - - - -}$$

$$\bar{M}_n = \frac{[5 \times 2000 + 4 \times 3000 + 3 \times 4000]}{[5 + 4 + 3]}$$

$$\bar{M}_n = 2833.3 \text{ g/mol}$$

Weight average molecular weight [$\bar{M}_W$]:-

$$\bar{M}_W = \frac{N_1(M_1)^2 + N_2(M_2)^2 + N_3(M_3)^2 + \cdots}{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}$$

$$\bar{M}_W = \frac{[(5 \times (2000)^2) + (5 \times (3000)^2) + (3 \times (4000)^2)]}{[(5 \times 2000) + (4 \times 3000) + (3 \times 4000)]}$$

$$\bar{M}_W = 3058.8 \text{ g/mol}$$

2. In a polymer sample, 20% of molecules have molecular mass 15000g/mol, 35% molecules have molecular mass 25000 g/mol and remaining molecules have molecular mass 20000 g/mol. Calculate the number and weight average molecular weights of the polymer.

3. A polymer sample contains 100,200,300 and 400 molecules having molecular mass 1000, 2000, 3000 and 4000 respectively. . Calculate the number and weight average molecular weights of the polymer.

4. A polymer sample containing 50, 100 and 150 molecules having molar mass 1000, 2000 and 3000 respectively. . Calculate the number and weight average molecular weights of polymer.

5. In a polymer sample, 20% of molecules have molecular mass 15000g/mol, 45% molecules have molecular mass 25000 g/mol and remaining molecules

have molecular mass 27000 g/mol. Calculate the number and weight average molecular weights of the polymer.

6. A polymer sample contains 200 molecules of molecular mass 2000, and 200 molecules of molecular mass 40,000 g/mol. Calculate the number and weight average molecular weights of polymer.

7. A polymer sample contains 100 molecules of molecular mass 20,000 g/mol, 300 molecules of molecular mass 3000 and 500 molecules of molecular mass 5000. Calculate the number and weight average molecular weights of polymer.

Conducting Polymers:-

"An organic polymers with highly delocalized pi-electron system having electrical conductance of the order of a conductor" is called Conducting polymer. **(or)**

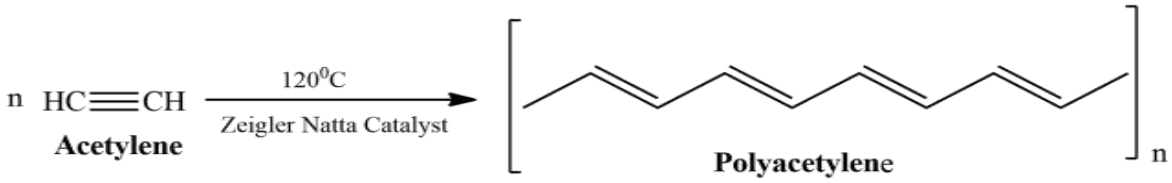
"Polymeric materials that exhibit bulk electric conductivity" are called Conducting polymers.

Ex: - Polyacetylene conductivity – 10^{-3} to 1 .7X10^{5} s/cm.

Polyaniline – 30 to 200 s/cm.

Synthesis of Polyacetylene: -

It was synthesized by using Acetylene monomer in the presence of catalyst.



Conducting Mechanism of Polyacetylene: -

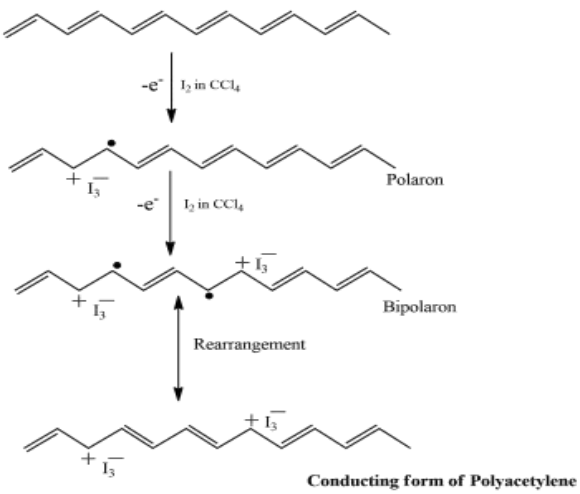
The conducting polymers are synthesized by doping, in which charged species are introduced in organic polymers having pi-back bone.

1. Oxidative doping (p-doping)
2. Reductive doping (n-doping)

1. Oxidative doping (p-doping):

In this process, pi-back bone of a polymer is partially oxidized using a suitable oxidizing agent. This creates positively charged sites on polymer back bone, which are current carriers for conduction.

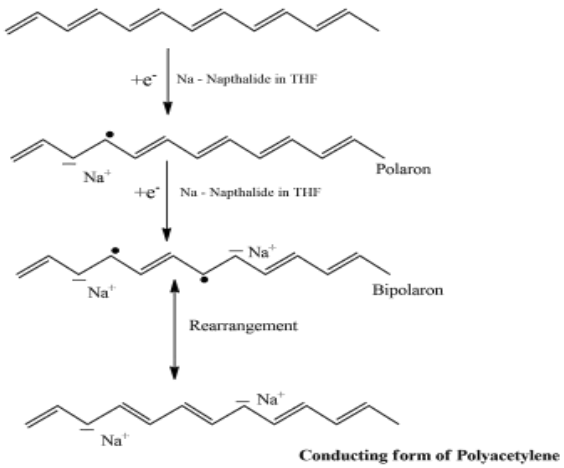
The oxidizing agents used in p-doping are iodine vapor, iodine in CCl_4, HBF_4, perchloric acid and benzoquinone.



2. Reductive doping (n-doping):

In n-doping, pi-back bone of a polymer is partially reduced by a suitable reducing agent. This creates negatively charged sites on polymer backbone. These negatively charged sites are responsible for the conduction.

The most commonly used reducing agent for partial reduction of polymer back bone is solution of sodium naphthalide in tetra hydro furan.



<u>Commercial Applications</u>: -

- Fabrication of organic thin transistors.
- Non-volatile memory devices based on organic transistors.
- Development of novel conjugated polymers for photovoltaic device applications.
- Fabrication of organic photovoltaic cells.
- Fabrication of organic light-emitting devices (OLED).
- Ferroelectric polymers for thin film devices.
- Gene Sensors.
- Printed electronics.
- Conducting polymer actuators and Micropumps.
- Responsive membranes/Hybrid Plastics.
- An antistatic material.

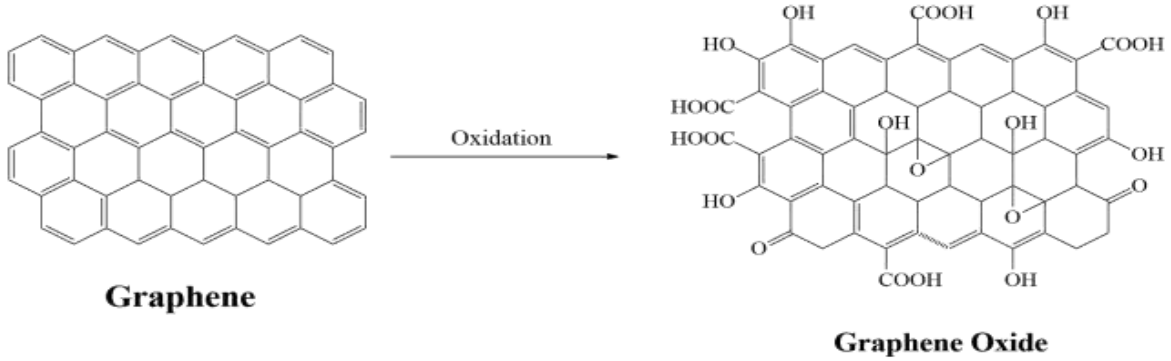
Graphene Oxide: -

Graphene is an allotrope of carbon made of a single layer carbon atoms that are bonded together in a repeating pattern of hexagons.

Graphene oxide is an oxidized form of graphene. It is obtained by treating graphene with strong oxidizers and acids.

Preparation of Graphene Oxide: - (Hummer's Method)

- Take graphene (2gm) and Sodium Nitrate ($NaNO_3$) (2gm) were combined with H_2SO_4 (90ml) and stirred for 30 min in an ice bath.
- For the resulting mixture add $KMnO_4$ (10gm) and the solution was then ultrasonicated at 50°C for 2h.
- Then add deionized water (200ml) and H_2O_2 (12ml) slowly to the above solution, then the resulting solution was wash with HCl (300ml 10%).
- The obtained product was dried gives graphene oxide powder.
- The obtained graphene oxide powder was further subjected to reduction by treating with sodium borohydride gives reduced graphene oxide.



Graphene

Graphene Oxide

Properties of Graphene Oxide: -

- High thermal conductivity.
- High electrical conductivity.
- High elasticity and flexibility.
- High hardness.
- High resistance....
- Ionizing radiation is not affected.
- Able to generate electricity by exposure to sunlight.
- Transparent material.

Commercial Applications of Graphene Oxide: -

- Electronic devices.
- Energy storage devices.
- Bio- sensors.
- Biomedical applications.
- Super capacitors.
- Membranes, catalysts, and water purification.

Polymer Composites:-

A combination of two (or) more distinct components to form a new class of material referred to as composite materials, when one of the components is a polymer; the resulting composite is called a Polymer Composite.

Polymer composites are generally made of two components. Namely

1. Matrix: - It is usually a thermoset material such as epoxy resin (or) a polyamide and it holds the fibers together.
2. Fiber: - It is embedded in the matrix in order to make the matrix stronger.

Synthesis, Properties and Applications of Kevlar:-

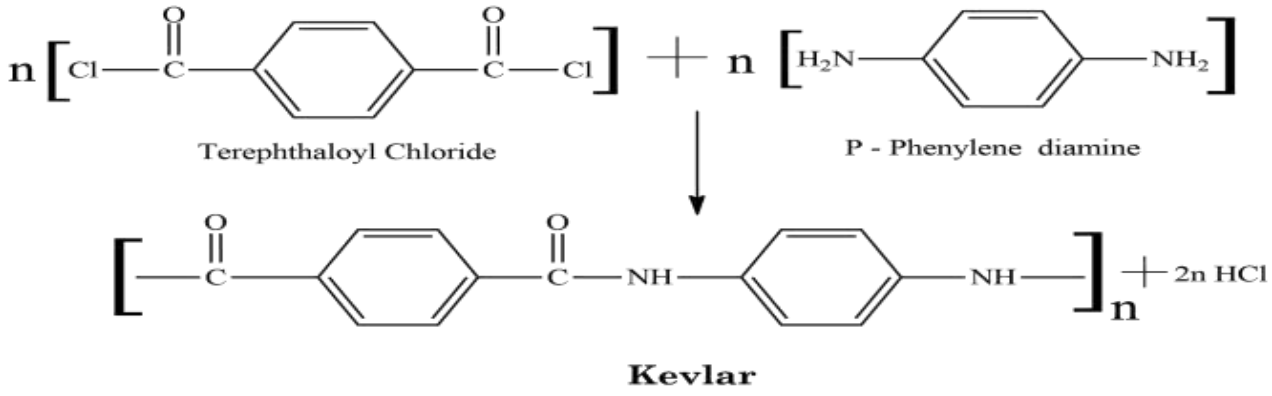
Kevlar: - Kevlar is an aromatic Polyamide. [aramide].

IUPAC Name-Poly-ParaPhenylene Terephalamide.

It is a synthetic fiber stronger than steel.

Synthesis: -

It was synthesized by the reaction b/w Para-Phenylene-diamine and Terphthaloyl chloride.



Kevlar

Properties:-

- It is stronger than steel.
- It is Crystalline, very lightweight & non-flammable.
- It has very good corrosion resistance.
- It has high abrasion resistance.
- It has very good chemical resistance.
- It has excellent force & tensile strength.
- Resistance to high temperature, fire, chemical attack.

Applications:-

- Used to make some car & bicycle tyres.
- Used for making boat hulls & aerospace industry.
- Used in the manufacture of formula one racing car petrol tanks.
- Used in the manufacture of bullet-proof & bridge structures.
- It used for puncture resistant for bicycle tyres.
- In anterior part of sports shoes and its laces.
- Used in marine turbine (or) wind turbine.

Green Fuels

Fuel is defined as "A naturally occurring (or) an artificially manufactured combustible carbonaceous material, which serves particularly as a source of heat and light".

Classification of Fuels:-

On the basis of their origin fuels are classified as Primary and Secondary fuels.

1. **Primary Fuels: -** Fuels which occur naturally is called Primary fuels.

   Ex: - Wood, Coal, Petroleum, Natural gas, etc.…

2. **Secondary Fuels: -** Fuels which are derived from primary Fuels are called Secondary Fuels.

   Ex: - Charcoal, Coke, Petrol, Diesel, etc……

On the basis of Physical state fuels are classified as Solid, Liquid, Gaseous fuels.

Physical State	Primary Fuel	Secondary Fuel
Solid	Wood, Coal	Charcoal, Coke
Liquid	Petroleum	Petrol, Diesel
Gas	Natural gas	LPG

Green Fuel:-

Green fuels are liquid or gaseous fuels produced with electricity from renewables.

Ex: - Synthetic Natural Gas (SNG), Hydropower, Solar Power, Wind Power, Biomass etc.,

Solar Energy: Introduction:

Solar energy is one of the solutions for sustainable energy conversion processes. Solar radiation coming from sun is highly useful in photosynthesis and is the major energy source for ecosystem. Solar energy is non-depleting, nonpolluting and available freely & can be utilized for various applications.

Radiations from the sun constitute solar energy.

It is a clean and renewable source of energy available in abundance.

Photovoltaic Cells:-

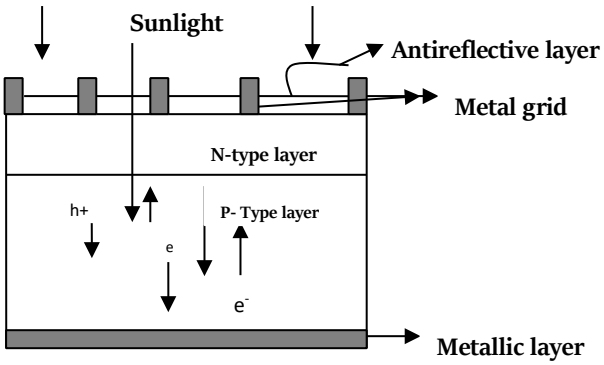
Photovoltaic cells are semiconductor device which convert solar energy into electrical energy.

Photovoltaic cells can generate electricity as long as Sun light is available.

Construction and working of Photovoltaic cells:-

Photovoltaic cell is composed of a thin mater consisting of an ultra thin layer of phosphorous doped [n-type] silicon on the top of boron doped [p-type] silicon. Hence P-n junction is formed b/w the two.

- A metallic grid forms one of the electrical contacts of the diode and allows light to fall on the semiconductor b/w grid lines.
- An antirefractive layer b/w the grid lines increase the amount of light transmitted to the semiconductor.
- The cells other electrical contact is formed by a metallic layer on the back of the solar cell.



Working:-

- When light radiation falls on the P-n junction diode, electrons-hole pairs are generated by the absorption of the radiation.
- The electrons are drifted and collected at n-type end and the holes are drifted and collected at the P-type end.
- When these two ends are electrically connected through a conductor, there is a flow of current b/w the two ends through the external circuit. Thus Photoelectric current is produced and available for use.

Advantages:-

- They are Environmental friendly.
- They need no recharging.
- They do not corrode.
- They operate at low temperature.
- No emission, no combustion.
- High public acceptance and excellent record.
- Low operating cost.
- No moving parts and so no wear and tear.

Disadvantages:-

- High installation cost.
- Energy can be produced only during the day time.
- Poor reliability of auxiliary elements including storage.
- Sun light is a diffuse, ie, it is relatively low density energy.

Green Hydrogen: -

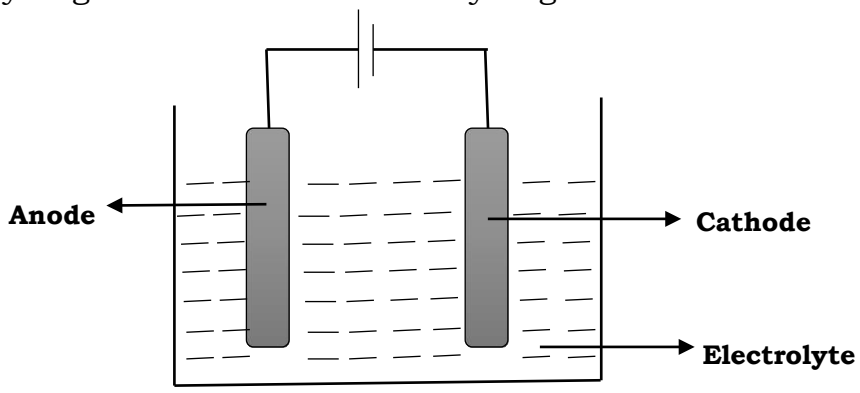
It is hydrogen produced by splitting water by electrolysis.

Electrolysis of Water: -

It is a process of splitting of water into a hydrogen and oxygen using electricity.

Process:-

- It consists two pair of platinum electrodes with water and H_2SO_4 electrolyte.
- At the anode, water is oxidized to oxygen gas and hydrogen ions.
- At the cathode, hydrogen ions are reduced to hydrogen.



Anode reaction: $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

Cathode reaction: $H^+ + 2e^- \rightarrow H_2$

Net reaction: $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2$

Properties of Hydrogen pertaining to fuel: -

- Hydrogen can be produced from renewable resources.
- Hydrogen burns with a pale-blue.
- Hydrogen is highly flammable.
- It has a high energy.
- It combines with oxygen, gives water.

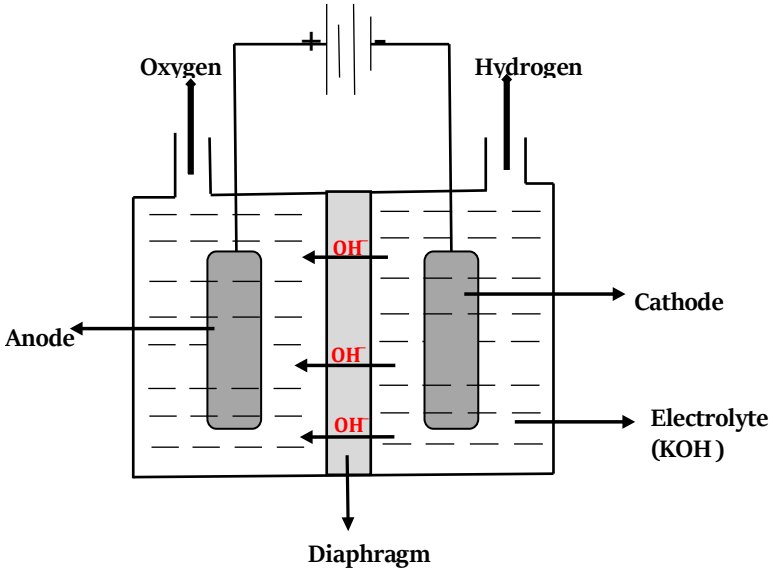
Alkaline Water Electrolysis: -

Construction: -

- It consists of two electrodes made from an inert metal such as platinum.
- The two electrodes are immersed in alkaline electrolyte solution like KOH with catalyst and connected to electrical power source.
- The electrodes are separated by using separator or diaphragm.

Working: -

- When current is supplied, hydroxide ions are formed at the cathode by the reduction of liquid water into gaseous hydrogen.
- The liberated hydroxyl ions migrate towards anode through diaphragm, where it was oxidized into oxygen and water.



Anode reaction: $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

Cathode reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Net Reaction: $2H_2O \rightarrow O_2 + 2H_2$

Advantages:-

- It is easier, cheaper and simple method.
- Pure carbon free hydrogen is obtained from this method.
- It relatively low cost.
- It has long term Stability.
- Non Nobel catalyst are used.

Proton Exchange Membrane Electrolysis:-

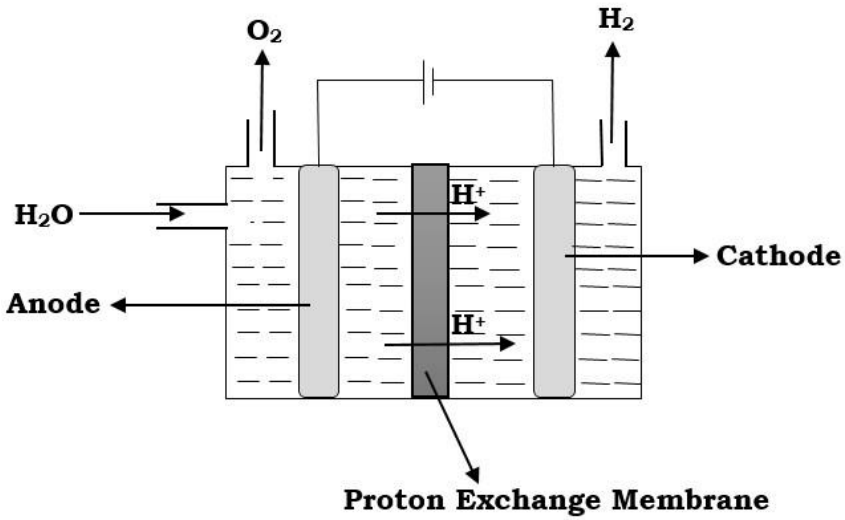
It is an electrolysis of water in a cell equipped with a proton exchange membrane.

Construction:-

- It consists of anode electrode with iridium as catalyst.
- It consists of anode electrode with platinum as catalyst.
- It consists of proton exchange membrane between anode and cathode.

Working: -

- It is carried out by pumping of water to the anode, where it is split into oxygen (O_2), protons and electron.
- The liberated protons are moved to cathode through proton exchange membrane.
- In which proton and electrons combine to produce hydrogen (H_2).



Anode Reaction: $H_2O \longrightarrow 2H^+ + 1/2\ O_2 + 2e^-$

Cathode Reaction: $2H^+ + 2e^- \longrightarrow H_2$

Net Reaction: $H_2O \longrightarrow 2H^+ + 1/2\ O_2$

Advantages: -

- High Gas Purity.
- The Proton exchange membrane is chemically stable and non-corrosive.

- Pure carbon free hydrogen is obtained from this method.
- It has compact system design.
- The proton exchange membrane separates the oxygen from hydrogen.
- It produces higher rate of hydrogen.

Important Questions: -

1. Define Conducting Polymers. Explain the Synthesis of Polyacetylene.
2. Write any five application of Conducting Polymers.
3. Describe the Conducting Mechanism of Conducting Polyacetylene.
4. Explain the Synthesis of Graphene Oxide. Mention its Properties and Applications.
5. Explain the Synthesis, Properties and Applications of Kevlar.
6. Numerical on Molecular weight of Polymers.
7. Define Solar cell. Explain Construction and Working of Photovoltaic cell.
8. Explain the generation of Hydrogen by Alkaline Electrolysis.
9. Explain the generation of Hydrogen by Proton Exchange Membrane Electrolysis.