Polymers

Polymers are the high molecular weight compounds obtained by repeated union of simple molecules.

A polymer is defined as a macromolecule formed by the repeated combination of several simple molecules (Monomers) through covalent bonds.

Examples: Polyethylene, nylon, PVC, Teflon, polyester, bakelite, etc.

Monomers

Monomer is defined as a simple molecule with two or more binding sites through which it forms covalent linkages with other monomer molecules to form the macromolecule.

Examples: Alkenes, vinyl chloride, adipic acid, glycerol

Polymerization, any process in which relatively small molecules, called monomers, combine chemically to produce a very large chainlike or network molecule, called a polymer.

The transformation of ethene to polythene and interaction of hexamethylene diamine and adipic acid leading to the formation of Nylon 6, 6 are examples of two different types of polymerization reactions.

Degree of polymerization (DP): - The no of repeating units or monomer units in the chain of a polymer is called degree of polymerization (DP) . The molecular weight of an addition polymer is the product of the molecular weight of the repeating unit and the degree of polymerization (DP).

$$DP = \frac{Molecular\ weight\ of\ the\ polymer}{Molecular\ weight\ of\ the\ monomer}$$

Molecular weight of a polymer. It is defined as sum of the atomic weight of each of the atoms in the molecules, which is present in the polymer

The molecular weight of any polymer is one of the important parameters as it links directly to the physical properties of polymers. In general, higher the molecular weight, tougher is the polymer.

During the formation of polymers, different polymers have different degrees of polymerization i.e, they have different chain lengths. Thus, molecular masses of individual macromolecules in a particular sample of polymer are different. Hence an average value of the molecular mass is taken. There are two ways through which average molecular masses can be calculated.

Different molecular weights

1. Number average molecular mass ($\bar{M}n$)
2. Weight average molecular weight ($\bar{M}w$)

Number Average Molecular weight ($\bar{M}n$)

Number average molecular mass is the mass obtained when total mass of all the molecules of a sample is divided by the total number of molecules.

For example, in particular polymer sample suppose N_1, N_2, N_3, so on molecules have molecular mass M_1 ,M_2 ,M_3, so on

Then total mass of all the molecules $=N_1M_1 + N_2M_2 + N_3M_3 + \ldots\ldots$

Total number of all the molecules $= N_1 + N_2 + N_3 + \ldots\ldots$

$$\overline{Mn} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + ...}{N1 + N2 + N3 + ...}$$

$$\overline{Mn} = \frac{\sum NiMi}{\sum Ni}$$

Weight average molecular weight: Weight –average molecular mass is the mass obtained when sum of the products of total mass of groups of molecules and their respective molecular masses is divided by the total mass of all the molecules.

For example, in particular polymer sample suppose N_1, N2, N_3, so on molecules have molecular mass M_1, M2, M3, so on

Then total mass of all the molecules $=N_1M_1 + N_2M_2 + N_3M_3 + \ldots\ldots$

Total number of all the molecules $= N_1 + N_2 + N_3 + \ldots\ldots$

Product total mass of all the molecules with their respective molecular mass $= N_1M_1{*}M_1 + N_2M_2{*}M_2 + N_3M_3{*}M_3 + \ldots\ldots$

$$\overline{M_w} = \frac{N_1 M_1^{\,2} + N_2 M_2^{\,2} + N_3 M_3^{\,2} + ...}{N_1 M_1 + N_2 M_2 + N_3 M_3 + ...}$$

$$\overline{Mw} = \frac{\sum Ni\, Mi^2}{\sum Ni\, Mi}$$

Poly Dispersity index [PDI]: Index of polydispersity or PDI is used as a measure of molecular weight distribution and is defined as

$$\text{PDI} = \frac{\overline{Mw}}{\overline{Mn}}$$

If PDI =1 polymer is mono disperse & Homogeneous.

PDI >1 polymer is poly disperse & less Homogeneous.

Example 1. In a sample of a polymer, 100 molecules have molecular mass 10^3 g/mol, 250 molecules have molecular mass 10^4 g/mol, and 300 molecules have molecular mass 10^5 g /mol, calculate the number average and weight average molecular mass of the polymer, Calculate PDI and comment on it.

No of Molecules(N)	Molecular Mass(M) g/mol
N_1= 100	$M_1 = 10^3$
N_2=250	$M_2 = 10^4$
N_3= 300	$M_3 = 10^5$

Number average molecular mass (**M̄**n) is given by:

$$\overline{Mn} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + ...}{N1 + N2 + N3 + ...}$$

$$\bar{\mathbf{M}}\text{n} = \frac{100*10^3 + 250*10^4 + 300*10^5}{100+250+300} = 50153 \text{ g/mol}$$

Weight average molecular mass **($\bar{\mathbf{M}}$w**) is given by:

$$\overline{M_W} = \frac{N_1 M_1^{\ 2} + N_2 M_2^{\ 2} + N_3 M_3^{\ 2} + ...}{N_1 M_1 + N_2 M_2 + N_3 M_3 + ...}$$

$$\bar{\mathbf{M}}\text{w} = \frac{100*)*(10^3)*(10^3) + 250*(10^4)*(10^4) + 300*(10^5)*(10^5)}{100*10^3 + 250*10^4 + 300*10^5} = 92794 \text{ g/mol}$$

$$\text{PDI} = \frac{\overline{Mw}}{\overline{Mn}} = \frac{92794}{50153} = 1.85$$

PDI >1 , the given polymer is less homogeneous and poly disperse in nature

3. A polymer sample contains 1, 2, 3 and 4 molecules having molecular weights10^5, $2*10^5$, $3*10^5$ and $4*10^5$, respectively. Calculate the number average and weight average molecular weight of the polymer.

No of Molecules(N)	Molecular Mass(M) g/mol
$N_1 = 1$	$M_1 = 10^5$
$N_2 = 2$	$M_2 = 2*10^5$
$N_3 = 3$	$M_3 = 3*10^5$
$N_4 = 4$	$M_4 = 4*10^5$

Number average molecular mass ($\bar{\mathbf{M}}$n) is given by:

$$\bar{\mathbf{M}}\text{n} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_{3} + N_{14} M_4}{N_1 + N_2 + N_3 + N_4}$$

$$\bar{\mathbf{M}}\text{n} = \frac{\mathbf{1*(1*10^5) + 2*(2*10^5) + 3*(3*10^5) + 4*(4*10^5)}}{\mathbf{1+2+3+4}}$$

$$\bar{\mathbf{M}}\text{n} = \frac{\mathbf{30*10^5}}{\mathbf{10}} \qquad \boxed{\bar{\mathbf{M}}\text{n} = 3.0 * 10^5\ g/mol}$$

$$\bar{\mathbf{M}}\text{w} = \frac{(1*\mathbf{10^5})*(1*\mathbf{10^5}) + \mathbf{2*(2*10^5)*(2*10^5) + 3*(3*10^5)*(3*10^5) + 4*(4*10^5)*(4*10^5)}}{\mathbf{1*(1*10^5) + 2*(2*10^5) + 3*(3*10^5) + 4*(4*10^5)}}$$

$$\bar{M}w = \frac{(1+8+27+64) * 10^{10}}{(1+4+9+16) * 10^5}$$

$$\bar{M}w = 3.3 * 10^5 \text{g/mol}$$

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

Solution. It is given that,

N_1 =20 & M_1 = 15000g/mol,

N_2 =35 & M_1 = 25000g/mol,

N_3 =45 & M_1 = 20000 g/mol.

The number average molecular mass of the polymer is given by

$$\overline{Mn} = \frac{\sum NiMi}{\sum Ni} = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N1 + N2 + N3...}$$

$$= \frac{20X\,15000 + 35X\,25000 + 45\,X\,20000}{20+35+45} = 20750\ g/mol$$

The weight average molecular mass of the polymer is given by

$$\overline{Mw} = \frac{\sum Ni\,Mi^2}{\sum Ni\,Mi}$$

$$\overline{M_w} = \frac{N_1 M_1{}^2 + N_2 M_2{}^2 + N_3 M_3{}^2}{N_1 M_1 + N_2 M_2 + N_3 M_3}$$

$$\overline{M_w} = \frac{20X\,(15000)^2 + 35X\,(25000)^2 + 45X\,(20000)^2}{20X15000 + 35X\,25000 + 45\,X\,20000} = 21385\,g/mol$$

Poly dispersity index, PDI $= \frac{\overline{Mw}}{\overline{\overline{Mn}}} = \frac{21385}{20750} = 1.03$

PDI >1 ,the given polymer is less homogeneous and

Conducting polymers

Conductive polymers are polyconjugated organic polymers that conduct electricity because of their conjugated π-bonds. Such compounds can have either metallic conductivity or can be semiconductors. In pure form, conducting polymers have low electrical conductivity and behaves like an insulator or as a semiconductor. These polymers can be converted to polymer salts having electrical conductivities comparable to that of metals by treating with suitable oxidizing or reducing agents. These types of doped polymers having high electrical conductivities are called as synthetic metals. The electrical conductivities of undoped conjugated polymers have the range in the order of 10^{-10} S/cm from those of the typical insulators and in the range of 10^{-5} S/cm from those of the semiconductors.

Thus, organic polymers having electrical conductance of the order of conductors are now called as conducting polymers.

Synthesis of conducting polymer

An organic polymer can be converted into a conducting polymer if it has

a) Linear Structure
b) Extensive conjugation in polymeric back bone (pi-bond)

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

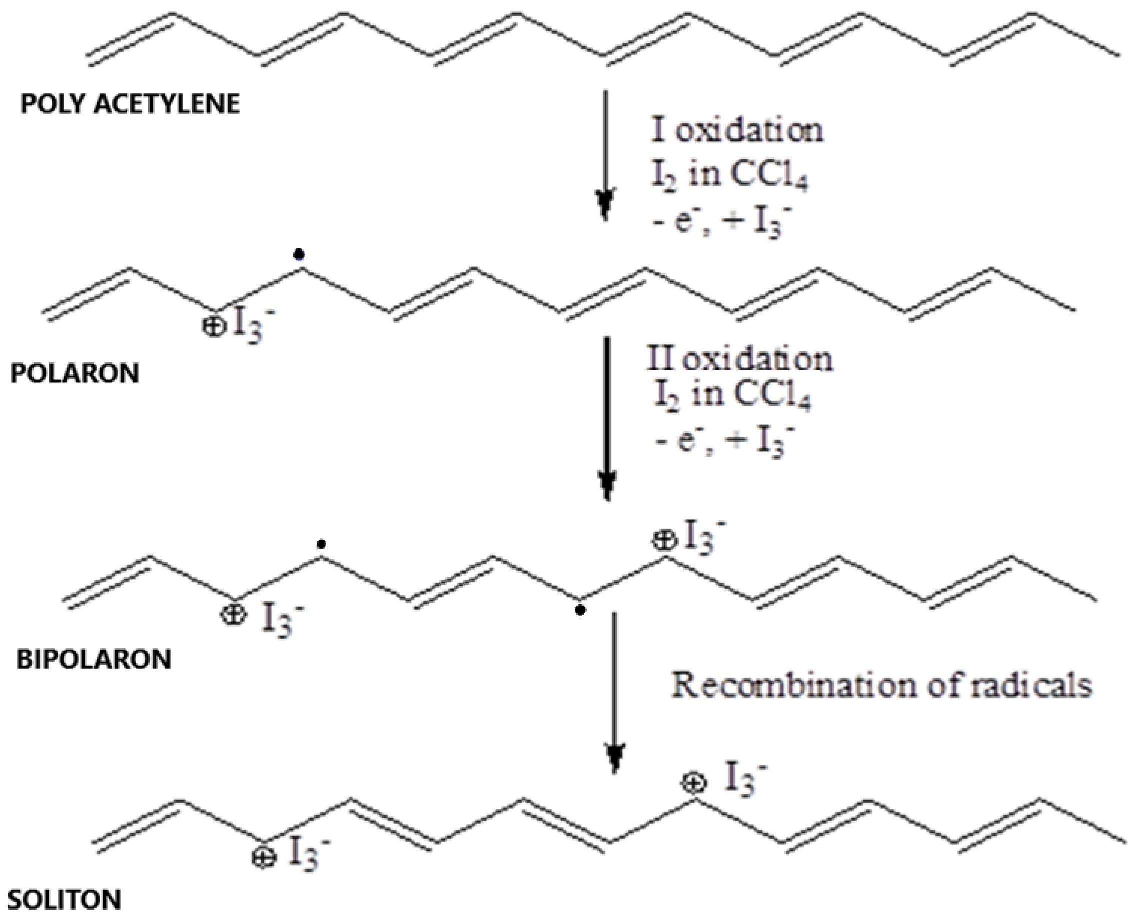
1. Oxidative doping (p-doping)
2. Reductive doping (n-doping)
3. Protonic acid doping (p-doping)

1. Oxidative doping (p-doping):

In this process, an appropriate oxidizing agent is added to bring partial oxidation of polymer pi-backbone. Thus, positively charged sites are generated on the polymer backbone and facilitates the movement of charge carriers in the chain. Most commonly used oxidative doping or p-doping agents are iodine vapor, iodine in CCl_4, HBF_4, perchloric acid and benzoquinone.

Mechanism of conduction:

- The removal of an electron from the polymer pi-back bone using a suitable oxidizing agents leads to the formation of delocalized radical ion called polaron.
- A second oxidation of a chain containing polaron followed by radical recombination yields two charge carriers on each chain.
- The positive charges sites on the polymer chains are compensated by anions I_3^- formed by the oxidizing agent during doping.
- The delocalized positive charges on the polymer chain are mobile, not the dopant anions.
- Thus, these delocalized positive charges are current carriers for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction.
- On doping polyacetylene using iodine in CCl_4, for partial oxidation, the conductivity increases from 10-5 $S.cm^{-1}$ to 10^3-10^5 $S.cm^{-1}$.



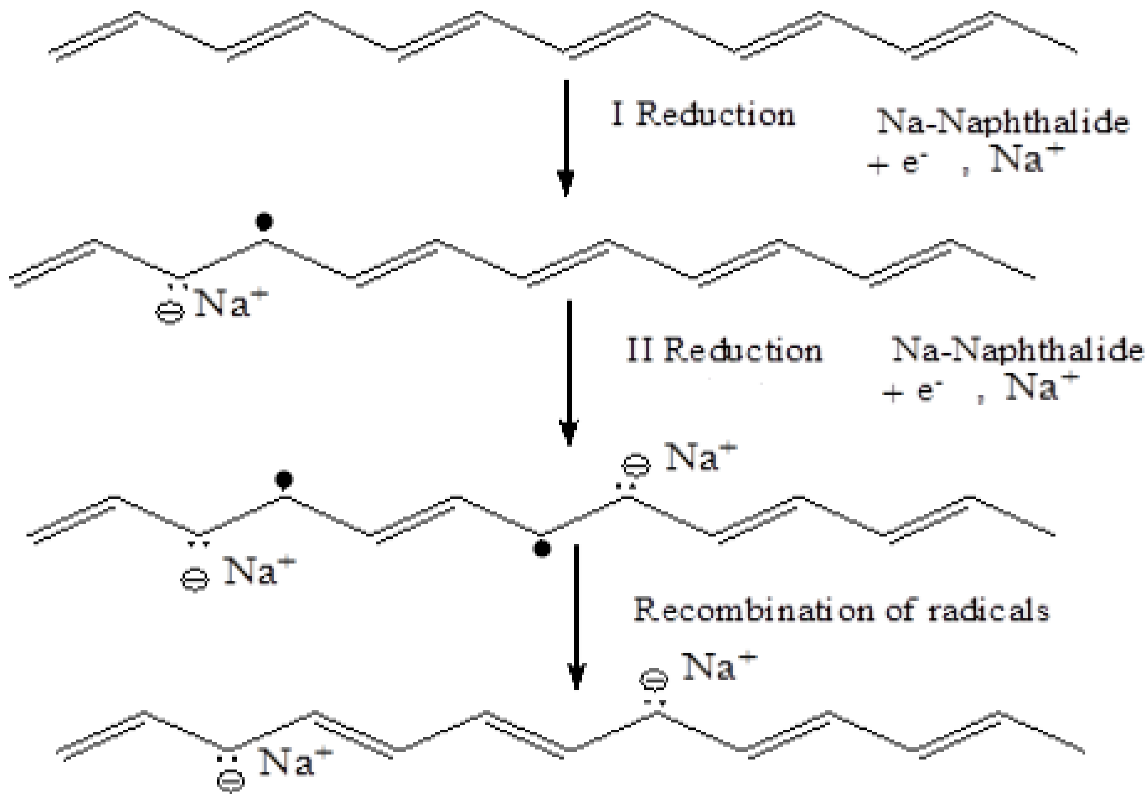
Reactions of p- doping of polyacetylene

2. **Reductive doping (n-doping)**:

In reductive doping technique, pi-backbone of a polymer is partially reduced by a suitable reducing agent. This facilitates the formation of negative charged sites on the pi-backbone and are responsible for conduction. The most commonly used reducing agents are: sodium napthalide in tetra hydro furan.

Mechanism of conduction:

- The addition of an electron to the polymer back bone by using a reducing agent generates a radical ion polaron.
- A second reduction of chain containing polaron, followed by the recombination of radicals yields two charged (-ve) carriers on each chain.
- These charge sites on the polymer chains are compensated by cations (Na^+ ions) formed by the reducing agent.



Reactions of n- doping of polyacetylene

Applications of Polyacetylene

1. Doped polyacetylene offers a particularly high electrical conductivity therefore it can be used in electric wiring or electrode material in lightweight rechargeable batteries.
2. Tri-iodide oxidized polyacetylene can be used as a sensor to measure glucose concentration.

Graphene

Graphene is an allotrope of carbon, where carbons are arranged in a single layer. These carbon atoms are organized in a honeycomb lattice with a two dimensional arrangement. The C-C distance in a single graphene sheet is 0.142nm. Graphene exhibits unique properties such as zero bandgap, remarkable electron mobility at room temperature, high thermal conductivity and stiffness, large surface area, impermeability to gases. Graphene has been used in many applications, which include energy storage devices like super capacitors and lithium-ion batteries, gas detection and conducting electrodes.

Graphene Oxide (GO)

Graphene oxide is a product of graphene obtained by oxidizing graphene. It has a single monomolecular layer containing oxygen functionalities such as carboxyl, carbonyl, epoxide, or hydroxyl groups. These added functionalities expand the separation between the layers and make the material hydrophilic.

Preparation of graphene oxide by a hummer's method

Graphite flakes (2 g) and NaNO3 (2 g) were mixed in 50 mL of H_2 SO_4 (98%) in a 1000 mL volumetric flask kept under at ice bath (0-5°C) with continuous stirring.

The mixture was stirred for 2 hrs, KMnO4 (6 g) was added to the suspension very slowly. The rate of addition was carefully controlled to keep the reaction temperature lower than 15°C.

The ice bath was then removed, and the mixture was stirred at 35°C until it became pasty brownish and kept under stirring for 2 days.

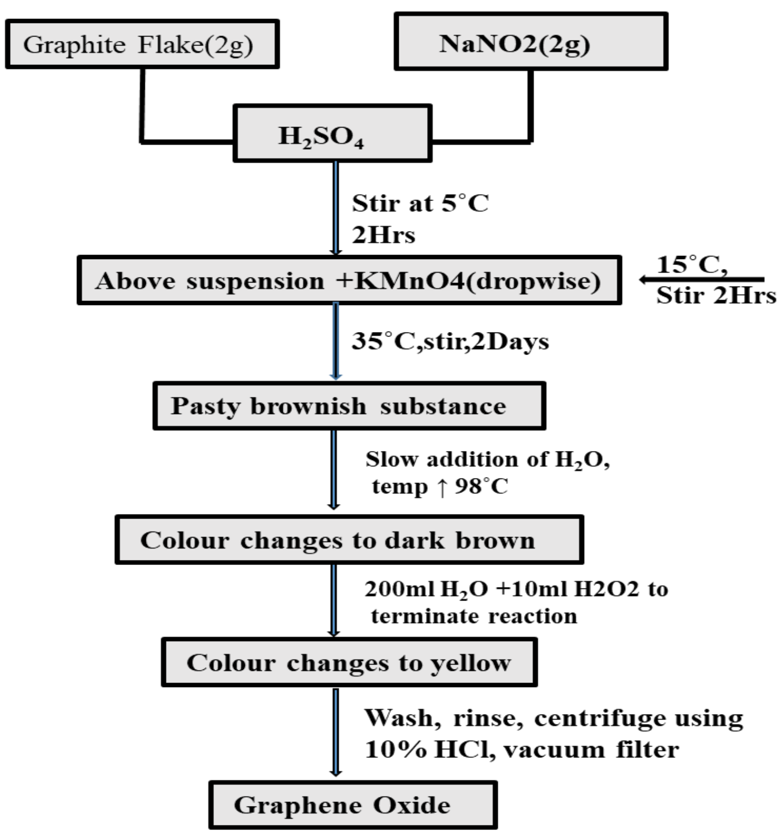
It is then diluted with slow addition of 100 ml water. The reaction temperature was rapidly increased to 98°C with effervescence, and the color changed to brown color.

Further this solution was diluted by adding additional 200 ml of water stirred continuously.

The solution is finally treated with 10 ml H2O2 to terminate the reaction by appearance of yellow color.

For purification, the mixture was washed by rinsing and centrifugation with 10% HCl and then deionized (DI) water several times.

After filtration and drying under vacuum at room temperature, the graphene oxide (GO) was obtained as a powder.



Properties of Graphene Oxide

Monolayer GO (produced by modified Hummer's method) with a Young's modulus of 207.6 $\pm$ 23.4 GPa, possess very good mechanical properties. Graphene Oxide is hydrophilic, can easily disperse in organic solvents, water, and different matrixes. This is a major benefit when combining the material with polymer or ceramic matrixes to enhance their mechanical and electrical properties. Graphene oxide functions as an electrical insulator, because of the disturbance of its sp^2 bonding networks. It is important to reduce the graphene oxide so as to recover the honeycomb hexagonal lattice of graphene, in order to restore electrical conductivity.

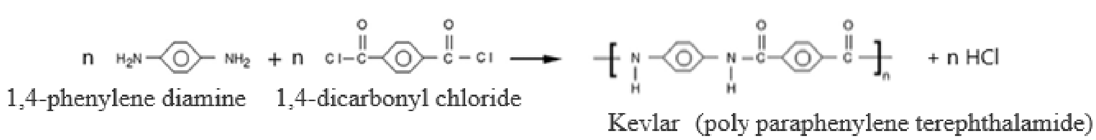
Applications of Graphene Oxide

GO have been used in nanocomposite materials, polymer composite materials, Electronics Devices energy storage devices, biosensors, biomedical applications, Water Purification, as coating material and catalysis. Graphene-based field effect transistor (FET) have been used as chemical sensors and biosensors. Go has led to its emergence as a precursor for fabricating transparent conductive films (TFCs). Functionalized GO can be used as fluorescence and photo luminescent means in cellular imaging. Chemically-altered graphene oxide disperse easily in organic solvents makes the material better suited to production of bio devices and optoelectronics, and for use in drug delivery.

Polymer Composite: A polymer composite is a material made of two or more types of polymers with different physical and chemical properties that, when combined, produce a material with characteristics different from the individual components.

Polymer composites are usually made of two components, Fiber and Matrix

Kevlar is poly paraphenylene terephthalamide (Aramide), an aromatic polyamide is prepared by the polycondensation reaction between an aromatic dichloride (1,4-dicarbonyl chloride) and aromatic diamines (1,4-phenylene diamine). In Kevlar amide groups are separated by phenylene groups.



Properties of kevlar are

1. *Kevlar is crystalline, light weight and non- flammable*
2. *Resistant to heat, impact, scratch*
3. *Withstands harsh environmental condition*
4. *Abrasion and corrosion resistant*
5. *High tensile strength*
6. *Resistant to Chemicals*

Applications

The physical properties of Kevlar make it a suitable material for many applications, such as:

1. It is used in light weight boat hulls. Aircraft panels, Race cars
2. Bullet proof vests and combat helmets
3. Reinforce material for car tyres, bicycle tyres, which reduces puncture rate
4. Marine current turbine and wind turbine
5. Ropes and cables
6. Fibre-optic cables for communication, data transmission and ignition

Green Fuels

SOLAR ENERGY

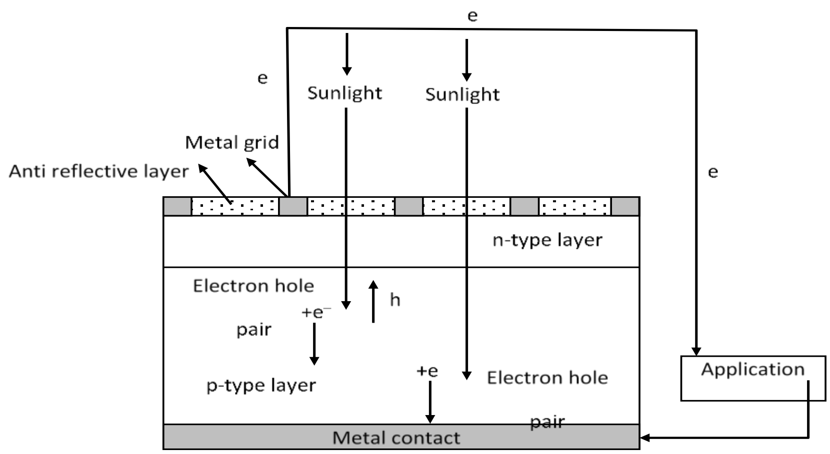
Photovoltaic Cells:

Photovoltaic cells are semiconductor device which convert solar energy into electrical energy. (Photovoltaic cell is based on the principle of photoelectric effect).

Construction and working of photovoltaic cells

The Solar cells or Photovoltaic cells are made out of semiconductors which have the capacity to absorb light. When n-type and p-type semiconductor are bought together a semiconductor diode is formed. The semiconductor diode separates and collects the carriers and conducts the generated electrical current preferentially in a specific direction.

A typical silicon photovoltaic cell is composed of a thin poly crystalline silicon wafer consisting of an ultra-thin layer of phosphorus doped. (n-type) silicon on top of boron doped (p-type) silicon. Hence a p-n junction is formed. A metallic grid forms one of the electrical current contacts of the diode and allows light to fall on the semiconductor between the grid lines as shown in Fig. An antireflective layer between the grid lines increases the amount of light transmitted to the semiconductor. The cell's other electrical contacts is formed by a metallic layer on the back of the solar cell.



Photovoltaic cell

Working: PV cell works on the principle of photoelectric effect E=hγ, when light radiation falls on the p-n junction diode, electron – hole pairs are generated by the absorption of the radiation. The electrons are drifted to and collected at the n-type end and the holes are drifted to p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced.

Applications: PV can meet the need for electricity for parking meters, temporary traffic signs, emergency phones, radio transmitters, water irrigation pumps, stream-flow gauges, remote guard posts, lighting for roadways, and more.

Advantages of PVcell:

- Fuel source is vast and infinite.
- No emissions, no combustion or radioactive residues for disposal.
- Does not contribute to global warming or pollution.
- Low operating cost and high reliability.
- No moving parts and so no wear and tear.
- No recharging is required.
- They do not corrode.

Disadvantages of PV cells:

- Sunlight is relatively low density energy.
- High installation cost.
- Energy can be produced only during daytime.

Generation of energy (green hydrogen) by electrolysis of water and its advantages

Green hydrogen is defined as hydrogen produced by splitting water into hydrogen and oxygen using renewable electricity.

Electrolysis is a promising option for carbon-free hydrogen production from renewable and nuclear resources. Electrolysis is the process of using electricity to split water into hydrogen and oxygen. This reaction takes place in a unit called an electrolyzer.

Principle of water electrolysis

Water electrolysis is the process whereby water is split into hydrogen and oxygen through the application of electrical energy. Typically, a water electrolysis unit consists of an anode, a cathode separated with an electrolyte, and a power supply. The electrolyte can be made of an aqueous solution containing ions, a proton exchange membrane (PEM) or an oxygen ion exchange ceramic membrane. A direct current (DC) is applied from the negative terminal of the DC source to the cathode (seat of the reduction reaction), where the hydrogen is produced. At the anode, the electrons produced by the electrochemical reaction return to the positive terminal of the DC source. For the case of water electrolysis in an acid aqueous electrolyte, the processes that occur at the anode and the cathode are

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad E^0_{H_2O/O_2} = 1.23V \tag{1}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^0_{H^+/H_2} = 0.00V \tag{2}$$

The half reactions occurring on the cathode and anode, respectively, can be written as:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^0_{H_2O/H_2} = -0.83V \tag{3}$$

$$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \qquad E^0_{OH^-/O_2} = 0.4\ V \tag{4}$$

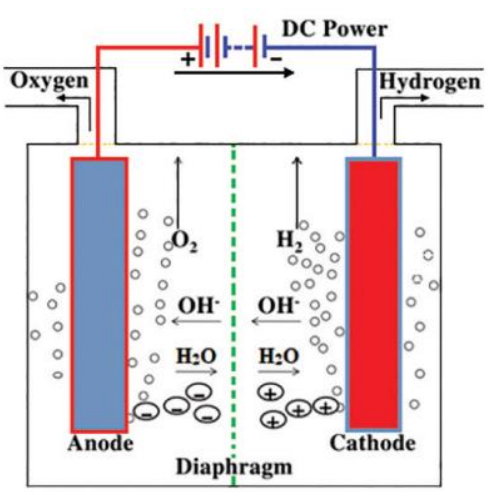
The global reaction for the two cases is:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \qquad \Delta E^0 = E^0_{H_2O/H_2} - E^0_{OH^-/O_2} = -1.23\ V \tag{5}$$

Electrolysis of water is not a spontaneous phenomenon because the standard global reaction potential is negative. Therefore, it needs an external intervention (power source) and the global reaction can be written as:

$$H_2O + electricity \rightarrow H_2 + \frac{1}{2}O_2$$

Alkaline electrolysis: The conductivity of the solution is enhanced by the use of strong electrolytes like NaOH,KOH or NaCl that deliver ions with high mobility, such as sodium, potassium for positive ions, and hydroxide or chlorides as negative ions. The electrodes consist of non-noble metals like nickel with an electrocatalytic coating. During electrolysis, the water molecules move to the cathode by diffusion as they are consumed, and the hydroxide ions move to the anode by migration because they have an opposite charge and diffusion because they are consumed. A diaphragm separates the two anode and cathode compartments and the gases formed are thus collected: hydrogen at the cathode and oxygen at the anode.



Anode: $2OH^- \rightarrow H_2O + ½\ O_2 + 2e^-$

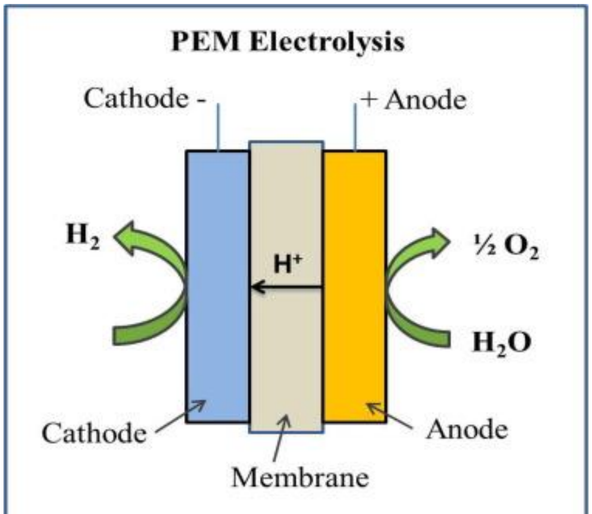
Cathode: $2\ H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Overall cell: $H_2O \rightarrow H_2 + ½\ O_2$

- Alkaline Fuel Cells (AFCs) are easy to handle, have very high electrical efficiency and are very suitable for dynamic operating modes.
- They can be built into small compact systems as well as in large power plants.
- Cheaper catalysts with respect to the platinum metal group based catalysts used for PEM water electrolysis.
- Higher durability due to an exchangeable electrolyte and lower dissolution of anodic catalyst.
- AFCs' high performance is due to the rate at which chemical reactions take place in the cell. They have also demonstrated efficiencies near 60% in space applications.
- The disadvantage of this fuel cell type is that it is easily poisoned by carbon dioxide (CO2).

PEM electrolyzer (Polymer electrolyte Membrane)

A proton-conducting perfluorinated sulfonic acid polymer as the electrolyte or Proton Exchange Membrane. Electrodes are porous, high-surface area material impregnated with an electrocatalyst, like platinum or platinum alloy is used. PEM electrolyzers are characterized by their very simple construction and their compactness. The operating principle of electrolysis of water with an electrolyte protons exchange membrane (PEM) is simple. When operating in electrolysis, the water decomposes at the anode into protons and molecular oxygen. The oxygen is evacuated by the water circulation, and the protons migrate to the cathode under the effect of the electric field. There, they are reduced to molecular H_2.



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

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

Overall cell: $2H_2O \rightarrow H_2 + \frac{1}{2} O_2$

- Advantages of PEM electrolysis is its ability to operate at high current densities. This can result in reduced operational costs, especially for systems coupled with very dynamic energy sources such as wind and solar, where sudden spikes in energy input would otherwise result in uncaptured energy.
- The polymer electrolyte allows the PEM electrolyzer to operate with a very thin membrane (~100-200 μm) while still allowing high pressures, resulting in low ohmic losses, primarily caused by the conduction of protons across the membrane (0.1 S/cm) and a compressed hydrogen output.
- The polymer electrolyte membrane, due to its solid structure, exhibits a low gas crossover rate resulting in very high product gas purity. Maintaining a high gas purity is important for storage safety and for the direct usage in a fuel cell.
- compact design, ability to operate at high current density, high efficiency, fast response, small footprint, operates under lower temperatures (20–80 °C), produces ultrapure hydrogen and also produced oxygen as a byproduct.

Limitations

- Cost of electrodes is too high and Maintenance cost is high