Polymer

A polymer is a large molecule or a macromolecule which essentially is a combination of many subunits. Polymers may be naturally found in plants and animals (natural polymers) or may be man-made (synthetic polymers). Different polymers have a number of unique physical and chemical properties, due to which they find usage in everyday life.

Classification of Polymers based on the Source of Availability

Natural Polymers:

They occur naturally and are found in plants and animals. For example, proteins, starch, cellulose, and rubber. To add up, we also have biodegradable polymers called biopolymers.

Semi-synthetic Polymers:

They are derived from naturally occurring polymers and undergo further chemical modification. For example, cellulose nitrate, and cellulose acetate.

Synthetic Polymers:

These are man-made polymers. Plastic is the most common and widely used synthetic polymer. It is used in industries and various dairy products. For example, nylon-6, 6, polyether's etc.

Classification of Polymers based on the Structure of the Monomer Chain

Linear Polymers

The structure of polymers containing long and straight chains falls into this category. PVC, i.e. poly-vinyl chloride, is largely used for making pipes and electric cables is an example of a linear polymer.

Branched-chain Polymers

When linear chains of a polymer form branches, then such polymers are categorized as branched chain polymers. For example, Low-density polythene.

Cross-linked Polymers

They are composed of bifunctional and trifunctional monomers. They have a stronger covalent bond in comparison to other linear polymers. Bakelite and melamine are examples in this category.

Classification Based on Polymerization

- Addition Polymerization: For Example, polyethene, Teflon, Polyvinyl chloride (PVC)
- Condensation Polymerization: Example, Nylon -6, 6, perylene, polyesters.

On the basis of the type of the backbone chain, polymers can be divided into:

- Organic Polymers: Carbon backbone.
- Inorganic Polymers: Backbone constituted by elements other than carbon.

Properties of Polymers

Physical Properties

- As chain length and cross-linking increase, the tensile strength of the polymer increases.
- Polymers do not melt, and they change state from crystalline to semi-crystalline.

Chemical Properties

- Compared to conventional molecules with different side molecules, the polymer is enabled by hydrogen bonding and ionic bonding resulting in better cross-linking strength.
- Dipole-dipole bonding side chains enable the polymer for high flexibility.
- Polymers with Van der Waals forces linking chains are known to be weak but give the polymer a low melting point.

Types of Polymerization Reactions

Addition Polymerization

This is also called chain growth polymerization. In this, small monomer units join to form a giant polymer. In each step, the length of the chain increases. For example, Polymerization of ethane in the presence of Peroxides

Condensation Polymerization

In this type small molecules like H2O, CO, NH3 are eliminated during polymerization (step growth polymerization). Generally, organic compounds containing bifunctional groups such as idols, -dials, diamines, dicarboxylic acids undergo this type of polymerization reaction. For example, Preparation of nylon -6, 6.

What is Copolymerization?

In this process, two different monomers join to form a polymer. Synthetic rubbers are prepared by this polymerization. For example, BUNA – S.

How to Calculate Molecular Mass of Polymers?

There are two types of average molecular masses of Polymers:

- Number Average Molecular Masses
- Weight Average Molecular Mass

Number Average Molecular Masses:

If N_1, N_2, N_3.... are the number of macromolecular with molecular masses. M_1, M_2, M_3....., respectively then the number average molecular masses of the polymer is given by

$$\bar{M_n} = \frac{N_1M_1+N_2M_2+N_3M_3+\ldots\sum N_iM_i}{N_1+N_2+N_3+\ldots\sum N_i}$$

The number average molecular mass

$$\bar{M_n}$$

is determined by colligative properties such as Osmotic Pressure.

Weight Average Molecular Mass:

If m_1, m_2, m_3.... Are the masses of a macromolecule with molecular masses M_1, M_2, M_3..., respectively, then weight average molecular mass of the polymer is given by

$$\overline{M}_\omega = \frac{m_1M_1+m_2M_2+m_3M_3+\ldots\ldots}{m_1+m_2+m_3}$$

$$= \frac{\sum miMi}{\sum mi}$$

$$\Rightarrow \overline{M}_\omega = \frac{\sum NiMi \times Mi}{\sum NiMi}$$

$$\Rightarrow \overline{M}_\omega = \frac{\sum NiMi^2}{\sum NiMi}$$

Polydispersive index: It is the ratio of weight average molecular mass and the number average molecular mass of Polymers.

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

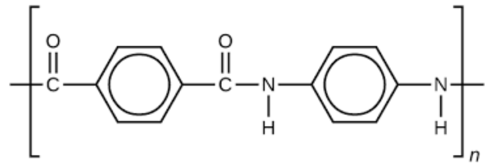
. For natural polymers, PDI = 1.

Uses of Polymers

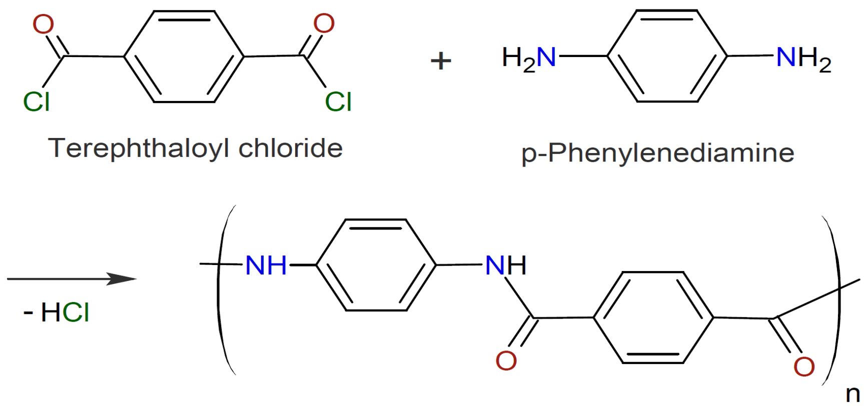
- Polypropene finds usage in a broad range of industries such as textiles, packaging, stationery, plastics, aircraft, construction, rope, toys, etc.
- Polystyrene is one of the most common plastic actively used in the packaging industry. Bottles, toys, containers, trays, disposable glasses and plates, tv cabinets and lids are some of the daily-used products made up of polystyrene. It is also used as an insulator.
- The most important use of polyvinyl chloride is the manufacture of sewage pipes. It is also used as an insulator in electric cables.
- Polyvinyl chloride is used in clothing and furniture and has recently become popular for the construction of doors and windows as well. It is also used in vinyl flooring.
- Urea-formaldehyde resins are used for making adhesives, moulds, laminated sheets, unbreakable containers, etc.
- Glyptal is used for making paints, coatings, and lacquers.
- Bakelite is used for making electrical switches, kitchen products, toys, jewelry, firearms, insulators, computer discs, etc.

Kevlar

Kevlar is the commercial name for the poly(p-phenylene terephthalamide). It was first developed as a replacement for steel in radial tyres. It is an extremely strong and light substance.



Kevlar is a polyamide, it is prepared by condensation polymerization of terephthaloyl chloride and 1,4-diaminobenzene. And HCl removed as a byproduct.



Poly(p-phenylene terephthalamide) (Kevlar)

All the monomers connect in a trans-conformation, meaning that very long straight chains are formed, making an almost fiber and allowing it such a wide range of uses.

The strength of Kevlar comes from its unusually regular internal structure; this has implications for the H-bonding which occurs between the electron dense oxygen atom and the electron deficient Hydrogen. The all trans configuration giving long straight chains means that the hydrogen bonding can occur very regularly to form a very strong lattice.

Properties:

1. It is a highly rigid polymer.
2. It has high heat stability.
3. It has high tensile strength due to extensive H-bonding.
4. Extreme chemical inertness.
5. It is a thermosetting polymer.
6. It is very resistant to impact and abrasion damage.
7. Compressive properties are relatively poor.

Application:

1. It may be used as a substitute for teflon in some non-stick frying pans.
2. It is used as an inner lining for some bicycle tyres to prevent punctures.
3. It is used for fire wicks due to its excellent heat resistance.
4. It is used for motorcycle safety clothing, especially in the areas featuring padding such as shoulders and elbows.
5. It is even used in sails for high performance racing boats.
6. It is also used to make modern drum heads that hold up withstanding high impact.
7. Used in bulletproof vests.
8. Used in aerospace and aircraft industries.

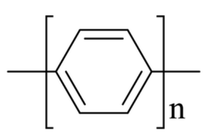
Disadvantage:

1. Kevlar fibers are non-biodegradable and unsustainable to the environment.

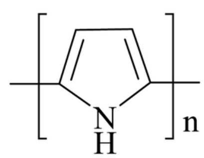
Conducting Polymer

Organic polymers that conduct electricity are known as Conducting polymers. They are also known as Intrinsically conducting polymers (ICPs).

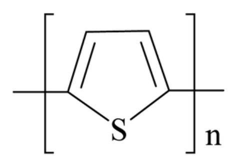
They have alternating single and double bonds along the polymer backbone (conjugated bonds) or that are composed of aromatic rings such as phenylene, naphthalene, anthracene, pyrrole and thiophene which are connected through carbon carbon single bonds.



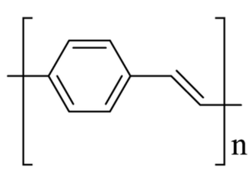
poly(p-phenylene)



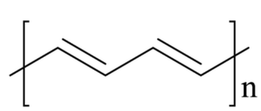
Polypyrrol



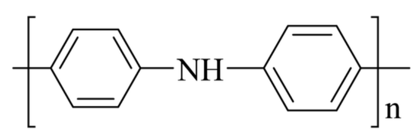
Polythiophene



poly(p-phynylene vinylene)



Polyacetylyne



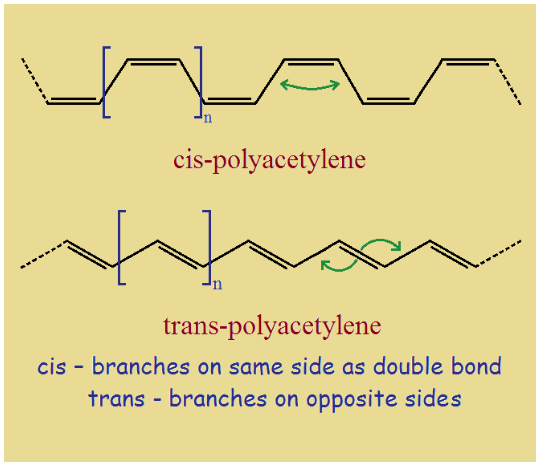
Polyaniline

The conjugated organic polymers in their pure state are either insulators or conductors. The π-electrons are normally localized and do not take part in conductivity. But these electrons delocalize on doping and conduct electricity. When an electron is removed from the valence band by oxidation is called p-doping. And an electron added to the conductivity band by reduction is called n-doping.

Polyacetylene $(C_2H_2)_n$

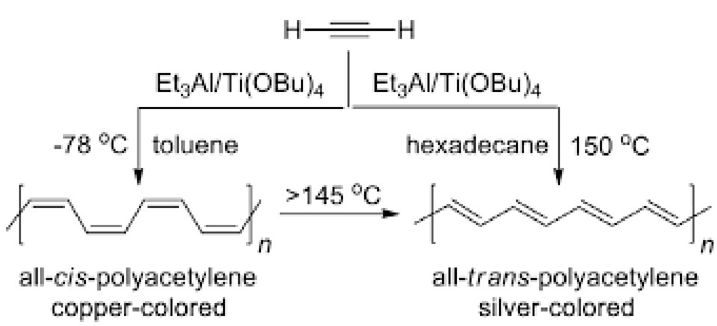
Polyacetylene consists of a long chain of carbon atoms with alternating single and double bonds between them, each carbon carrying one hydrogen atom.

A copper colored film of cis-polyacetylene and silvery film of trans-polyacetylene conductivities 10^{-8} - 10^{-7} Sm-1 and 10^{-3} - 10^{-2} respectively.



Synthesis: When acetylene gas is bubbled through heptane/toluene solvent containing the Zeigler-Natta catalyst, polyacetylene solid is formed at the gas-liquid interface.

Cis- & trans- polyacetylene can be achieved by changing the temperature at which the reaction is conducted.



Mechanism of Polyacetylene;

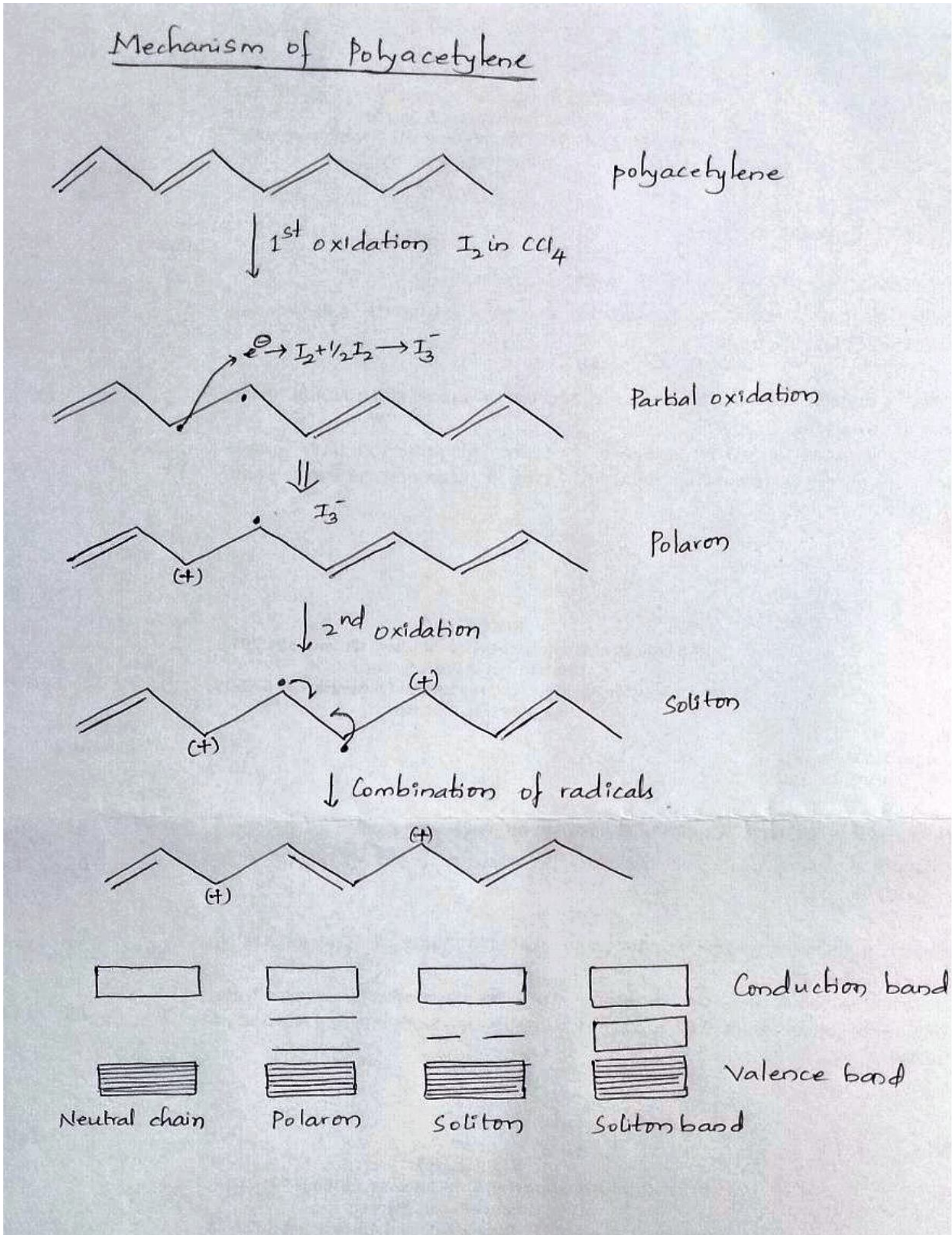
Conductivity of pure acetylene is about 4.4 x 10-5 S/cm. Upon doping with an oxidizing agent like iodine, the conductivity increases to about 400S/cm.

When the oxidative dopant such as iodine is added it takes away an electron from the π - back bone of the polyacetylene chain and creates a positive center (hole) on one of the carbon.

The other π - electron resides on the other carbon making it a radical. The radical ion formed is called Polaron.

A dipolaron (soliton) is formed on further oxidation. Then these radicals migrate and combine to establish a backbone double bond.

As the two electrons are removed, the chain will have two positive centers (holes). The chain as a whole is neutral, but holes are mobile and when a potential is applied they migrate from one carbon to another and account for conductivity.



When a π-bond is formed, Valence and conduction band are created. Before doping, there is a sufficient energy gap between VB & CB. so the electron remains in VB and the polymer acts as an insulator. Upon doping, polarons and solitons are formed which results in the creation of new localized electronic states that fill the energy gap between VB and CB. When sufficient solitons are formed, a new mid-gap energy band is created which overlaps with the VB and CB allowing electrons to flow.

Properties:

1. Insoluble and infusible and possess high porosity.
2. Sensitive to air, moisture and sunlight.
3. Light in weight and flexible.
4. It is a polymer with a band gap of 1.5eV.
5. It is a semiconductor at room temperature with conductivity of 10^{-8} $ohm^{-1}cm^{-1}$ for cis and 10^{-3} $ohm^{-1}cm^{-1}$ for trans.
6. It becomes an organic metal (metallic type of conductor) when doped with electrons like I_2, SbF_5 or AsF_5 with conductivity of 10^5 $ohm^{-1}cm^{-1}$.

Applications:

1. They are used as electrode material for rechargeable batteries.
2. They are used in light emitting diodes.
3. They are used in display devices.
4. They are used as conductive tracks on printed circuit boards.
5. They are used in information storage devices.
6. They are used as humidity sensors, gas sensors, radiation sensors.
7. They are used in electrochemical display windows.
8. They are used in fuel cells as electrocatalytic materials.
9. They are used as membranes for gas separation.

Graphene oxide

A single sheet of carbon atoms taken out of graphite is called graphene. It is a 2D nanosheet with thickness equal to a single carbon atom. When oxygen containing functional groups like epoxides, carbonyl, carboxyl and hydroxyl groups are added to the graphene layer, then the resulting material is graphene oxide.

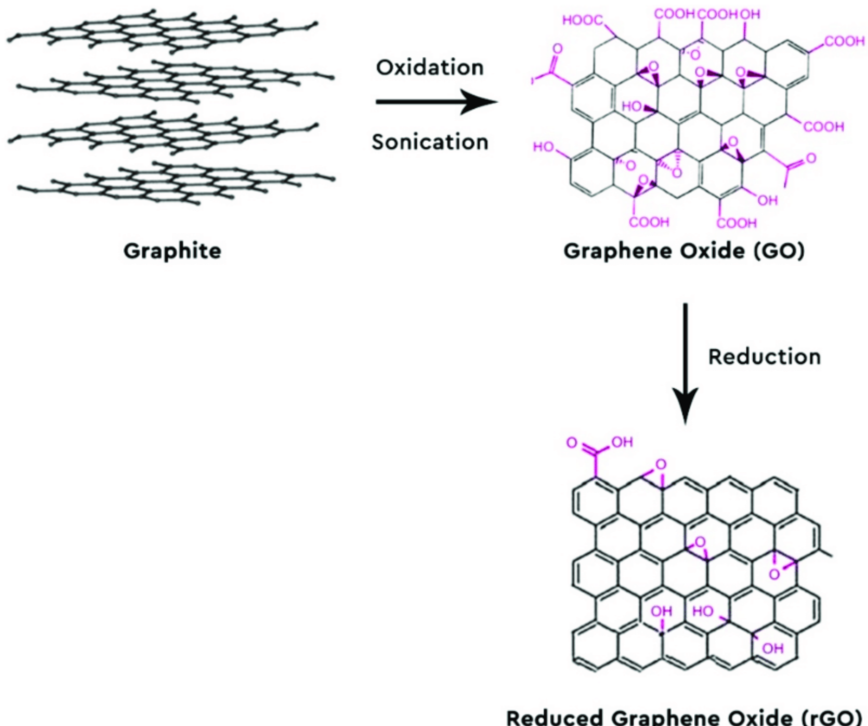
Preparation of Graphene Oxide (GO)

GO is an oxidized derivative graphite. It is obtained from cheap and abundantly available graphite by controlled oxidation. There are several methods available for the preparation of graphene oxide. Different oxidizing agents are used in each method.

Hummers method:

- In this method graphite is subjected to reaction with an anhydrous mixture of conc. H_2SO_4, $NaNO_3$ and $KMNO_4$. The oxidation reaction completed within 2 hours at room temperature below 45^0C.
- Interlayer distance between adjacent layers in graphite is 0.335nm.
- Graphite is hydrophobic and its layers cannot be easily exfolited. But, in GO interlayer distance between adjacent layers increases to 0.625 nm after introducing epoxides, alcohols, ketones, carbonyl and carboxylic groups.

- The oxygenated functionalities are weaker than the Van Der Waals interactions between the layers of graphite oxides and make GO more hydrophilic.
- Hydrolysis of GO in the presence of polar solvent dimethylformamide (DMF) and sonication results in complete exfoliation in water, yielding individual GO sheets.



Graphene

Properties of GO

❖ The structure and chemical composition of GO can be fine tuned by varying degrees of oxidation and reduction. Completely oxidized GO is a yellow solid.

❖ GO is more hydrophilic due to the presence of polar functional groups. It can be dispersed in water and other polar solvents.

❖ GO exhibits tunable electrical and optical properties. Reduction of GO increases its electrical conductivity. The band gap of GO can be varied from 0.5 to 2.2 eV depending on the synthesis procedure and post synthesis reduction procedure. GO can be transformed from insulator to semiconductor.

❖ GO exhibits giant optical nonlinearity.

❖ GO exhibits a high specific area and is highly effective in desalination of water and removal of toxic heavy metals from water.

❖ GO is bio compatible and can be functionalized easily.

Application of GO

★ Used in energy storage devices, transparent conducting electrodes, photodetectors, LEDs, all optical switching and fast optical communication.

★ Used for the large-scale production of graphene by chemical reduction.

★ GO membranes can be used for cost-effective water purification.

★ Used as sensors, biosensors, effective components for medical application, including transparent devices, implants.

CHEMICAL FUEL

Definition of a chemical fuel: A chemical fuel is a substance, which produces a significant amount of heat energy and light energy when burnt in air or oxygen.

Classification of chemical fuels: Chemical fuels are classified as primary and secondary fuels.

Classification of fuels with examples

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

Primary fuels: It is the one which is natural and doesn't require any chemical processing before utilization. Ex: wood, coal, crude petroleum and natural gas.

Secondary fuels: They are produced from naturally occurring substances by Subjecting to treatments, which alter their chemical composition and improve their calorific value.

Ex: Coke, gas-LPG, Diesel, Petrol, Kerosene

Hydrocarbon fuels: Fuels which contain hydrogen, carbon, are called hydrocarbon fuels. Ex: Petrol, diesel, kerosene.

Green Fuels:

Renewable fuels which are actively produced from renewable sources and mainly make use of elements such as hydrocarbons.

Green fuels that are newly introduced in the present market.sustainable ways are to be initiated in order to safeguard the exploitation of non-renewable energy sources that occurred over the years. It is a revolutionary step for the coming up generation.

Solar Energy

Introduction: Light striking certain substances causes the surface of the material to emit electrons. It is as if light somehow kicks electrons right out of atoms. Light striking other substances causes the material to accept electrons. It is the combination of these two substances that can be made use of to cause electrons to flow through a conductor. This is the so-called photo-electric effect.

Photovoltaic means sunlight converted into a flow of electrons (electricity). Photovoltaic devices, or solar cells, are like generators that work in sunlight. They make electricity without waste, noise or pollution. They produce electricity without combustion. A solar cell is a solid state device in which there are no moving parts (except for photons and electrons) so nothing wears out. The fuel is "photons". These can be thought of as "packets of sunlight" that carry a phenomenal amount of energy to earth at a prodigious rate. The Solar Panels of today make use of this abundant energy by using silicon crystals with small amounts of impurity added. This process of adding minute amounts of different elements into an otherwise pure crystal is called "doping". By having two thin layers of doped material bonded against one another, an electric current can be induced when exposed to light.

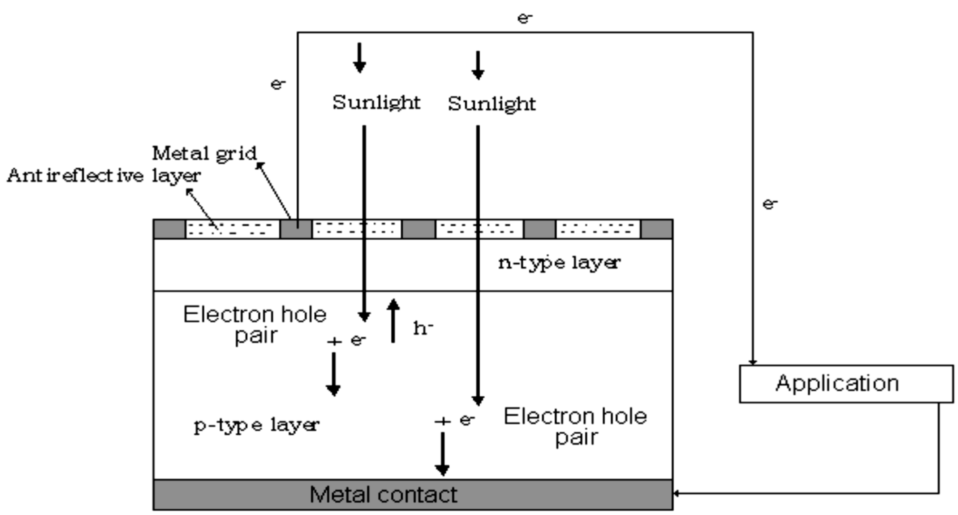
Photovoltaic Cells:

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

Solar cells: The combination of p & n types of semiconductors is called semiconductor diodes. These diodes when exposed to magnetic radiation (sunlight) electricity are generated. Such devices are called photovoltaic cells or solar cells.

Working of Photovoltaic Cell:

A typical silicon photovoltaic cell is composed of a thin wafer consisting of an ultra thin layer of phosphorous doped (n-type) silicon on top of boron doped (p-type) silicon.



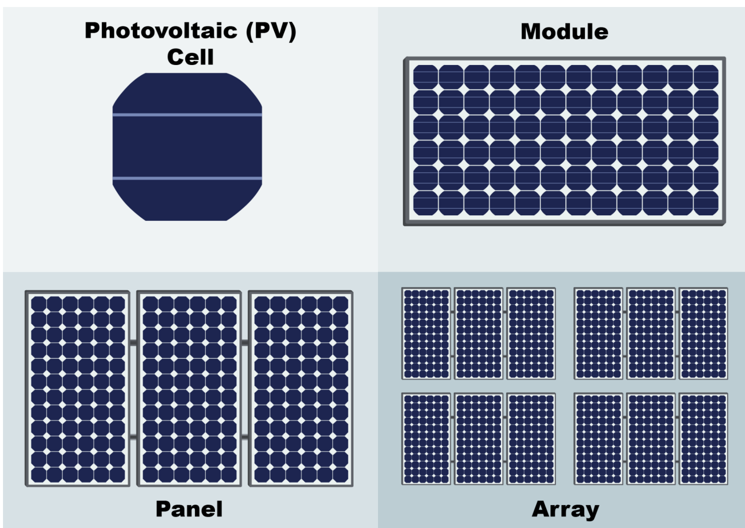
- A metallic grid forms one of the electrical contacts of the diode and allows light to fall on the semiconductor between the grid lines.
- An antireflective layer between the grid lines increases the amount of light transmitted to the semiconductor.
- The cell's other electrical contact is formed by a metallic layer on the back of the solar cell.
- 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 and collected at the 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 and available for use.

Importance of Photoelectric cell

- Photovoltaic cells provide an enormous amount of energy from the sun which is unlimited, inexhaustible and renewable.
- Photovoltaic cells can serve for both off grid and on grid application.
- Photovoltaic cells produce no pollution so it is environment friendly. Photovoltaic cell energy conversion is highly modular. This is important with respect to the development of electricity supply systems in many rural and remote areas, where grid extension is economically not feasible.
- It provides power for spacecraft and satellites.
- Photovoltaics can be used as roof integrated systems, providing power and also serving as optical shading elements for the space below and preventing overheating in the summer.
- Developments in the field of Photovoltaic cells will boost the semiconductor industry and storage battery industries.

Design:



Advantages of PV cells:

- Fuel source is vast and essentially infinite.
- No emissions, no combustion or radioactive residues for disposal. Does not contribute to global change or pollution.
- Low operating cost (no fuel).
- No moving parts and so no wear and tear.
- High reliability in modules.
- No recharging
- They do not corrode.
- Can be integrated into new or existing building structures.
- High public acceptance and excellent record.

Disadvantages of PV cells:

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

Hydrogen as Green fuel

- Hydrogen is an ideal, highly efficient, renewable, clean and sustainable energy source.
- It is abundant from various sustainable sources (biomass/water).
- Energy content of hydrogen is 122KJ/g, which is 2.75 times greater than hydrocarbon fuels like petrol and diesel. However, its volumetric density is lower than petrol and diesel.
- The combustion product is water, which is not a pollutant.
- It has high storage capability, thus considered as an ideal alternative source of energy for fossil fuels.

Drawbacks:

- Hydrogen is a colorless, odorless gas, which is extremely flammable and highly explosive. Therefore storing, handling, and transportation is very difficult.
- Cost of storing hydrogen as a compressed gas or liquid is high as it requires a lot of energy.
- Cost of development of hydrogen infrastructure is very high.
- Hydrogen is a secondary source of energy. Production of clean hydrogen from renewable sources is a major challenge.

Production of hydrogen

Steam reforming

- ☐ Natural gas; the partial oxidation of heavy hydrocarbons or coal in presence of Ni catalyst at 900^0C.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

- ☐ Carbon monoxide produced in the process is further converted to hydrogen and carbon dioxide through water gas shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2$$

Drawback

It relies on fossil fuels.

It requires harsh conditions.

Cost of production is higher.

Pure carbon free hydrogen can be obtained by splitting of water

- ☐ *Electrolysis of water:* Splitting of water into hydrogen and oxygen by passing electric current through it.
- ☐ *Solar water splitting:* Splitting of water into hydrogen and oxygen using a photo catalyst and sunlight.

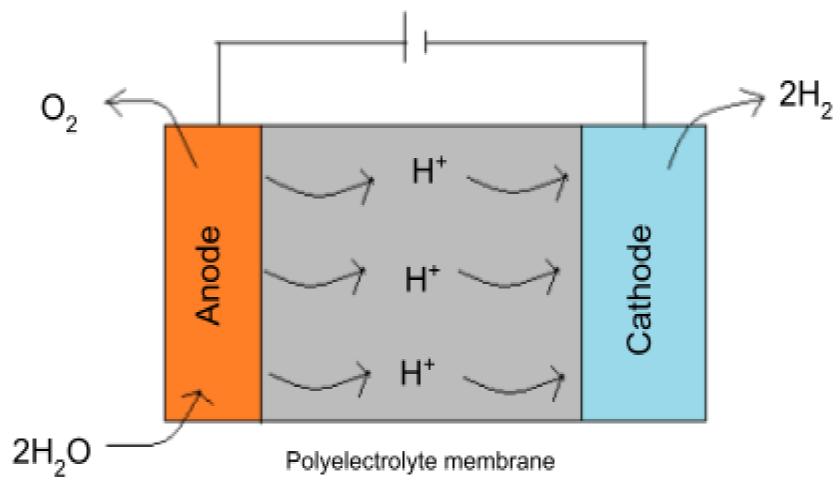
Electrolysis of water

Splitting of water into hydrogen and oxygen by passing electric current through it at room temperature is called electrolysis of water.

Water electrolysis is a non spontaneous chemical reaction. It is driven by external electricity and by applying a sufficient voltage between the two electrodes.

Two types of cells are commonly used in electrolysis of water

Polymer electrolyte membrane water electrolysis



Construction: Porous metal electrodes separated on either side of the surface of the polymer membrane are used as anode and cathode.

Anode: Iridium metal particles dispersed on porous carbon are used as electrocatalyst for oxygen evolution reaction.

Cathode: Platinum particles coated on porous carbon are used as electro catalysts for hydrogen evolution reaction.

Electrolyte/separator: A porous solid polymer electrolyte made of chemically stable sulfonated tetrafluoroethylene based fluoropolymer is used as electrolyte as well as separator.

Working:

Anode is connected to the positive end of direct current and Cathode is connected to the negative end. Deionized water is circulated in the anodic chamber where it is oxidized liberating oxygen gas and hydrogen ions.

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

Hydrogen ions migrate through the solid polymer electrolyte membrane to the cathode, where they are reduced into molecular hydrogen.

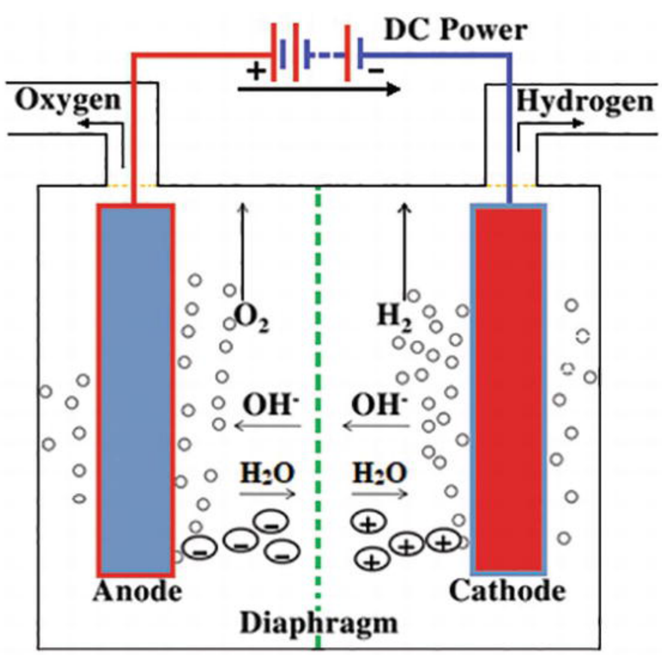
$$2H^+ + 2e^- \rightarrow H_2$$

Overall reaction, $$H_2O \rightarrow \frac{1}{2} O_2 + H_2$$

Advantages

- ❖ Use of polymer membrane avoids use of liquid acid electrolyte. Therefore, the chance of electrolyte leakage is prevented.
- ❖ Polymer membrane is chemically stable and non corrosive.
- ❖ Pure hydrogen, free of carbon which is required for hydrogen oxygen fuel cells, can be produced by electrolysis of water.
- ❖ Excess of cheap current from renewable sources like solar power can be converted into hydrogen gas and stored as chemical energy.

Alkaline water analysis



Construction: There are four components in an alkaline water electrolysis cell.

Anode: Nickel metal particles dispersed on porous carbon are used as electrocatalyst.

Cathode: Nickel metal particles coated on porous carbon are used as cathode electrocatalyst.

Electrolyte: Aqueous solution of KOH.

Separator: Porous dense anion exchange membrane is used as the separator. It is a good ionic conductor for hydroxide ions and a bad electronic conductor.

Working:

Cathode is connected to the negative end and anode is connected to positive and of direct current. Deionized water is circulated in the cathodic chamber where it is reduced, liberating hydrogen gas and hydroxide ions.

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

Hydroxide ions migrate through the electrolyte and separator membrane to the anode where they are oxidized into molecular oxygen.

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

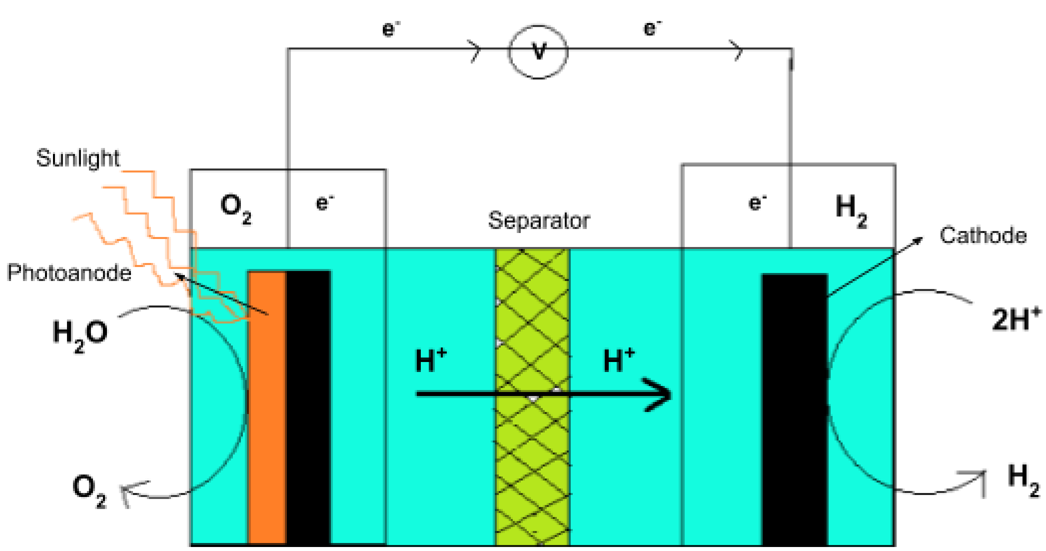
Overall reaction, $$H_2O \rightarrow \frac{1}{2}O_2 + H_2$$

Advantages

- ❖ Alkaline water electrolysis is an easier, cheaper and simple method for hydrogen production.
- ❖ Electrodes are made of cheaper nickel metal.
- ❖ Pure hydrogen, free of carbon which is required for hydrogen oxygen fuel cells, can be produced by electrolysis of water.
- ❖ Excess cheap current from renewable sources can be converted to hydrogen gas and stored as chemical energy

Photo-electrochemical-cell reaction(Photo electrocatalytic reaction)

In a photo-electrochemical- cell, the photocatalyst is deposited as a thin film on a substrate to form a photo-anode or a photoelectrode for carrying out the water splitting reaction in solution. However, an external circuit is required to direct the photogenerated electrons from the photo-anode to the cathode, where the hydrogen is produced.



Photocatalytic water splitting in a photo-electrochemical-cell mechanism basically involves 4 main steps:

The generation of electron-hole pairs from light irradiation on the photo-anode,

$$TiO_2 + h\boldsymbol{\nu} \rightarrow e^-_{Tio2} + h^+_{Tio2}$$

The oxidation of water by photo-generated holes on the photo-anode surface to produce O_2 and H^+.

$$H_2O + 2h^+ \rightarrow \frac{1}{2} O_2 + 2H^+$$

The transfer of photo-generated electrons through an external circuit to the cathode and the reduction of H^+ ions by the photogenerated electrons on the cathode surface to produce H_2.

$$2H^+ + 2\,e^- \rightarrow H_2$$

Water splitting will occur when the energetic requirements are met, where the practical potential will be much higher than the minimum required to overcome overpotential and other system losses.

Advantages:

1. Sustainable: It is an alternative fuel to traditional fossil fuel. It does not emit polluting gasses in either its production or combustion.
2. Versatile:it can replace coal due to its high capacity to generate energy.
3. Storage : it can store gas in liquid form or gas form.
4. No noise pollution.
5. More efficient than other sources of energy.

Disadvantages:

1. Safety concern: highly flammable and volatile substance.
2. Not free in nature, must be extracted.
3. Difficulty to transport: it is extremely light and low density than He.
4. Expensive