**COURSE TITLE-APPLIED CHEMISTRY FOR COMPUTER SCIENCE AND ENGINEERING STREAM**
**COURSE CODE-BCHES102/202**

# MODULE 1
# SENSORS AND ENERGY SYSTEMS

**SYLLABUS**

**Sensors**: Introduction, working, principle and applications of Conductometric sensors, Electrochemical sensors, and Optical sensors (colorimetry). Sensors for the measurement of dissolved oxygen (DO). Electrochemical sensors for the pharmaceuticals. Electrochemical gas sensors for SOx and NOx. Disposable sensors in the detection of biomolecules and pesticides.

**Energy Systems:** Introduction to batteries, construction, working and applications of Lithium ion and Sodium ion batteries. Quantum Dot Sensitized Solar Cells (QDSSC's) - Principle, Properties and Applications.

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## SENSORS



A sensor is a device that measures or detects a physical quantity, such as temperature, pressure, humidity, light, sound, motion, or position. Sensors are used to convert the physical quantity into an electrical signal that can be processed by a computer or other electronic system.

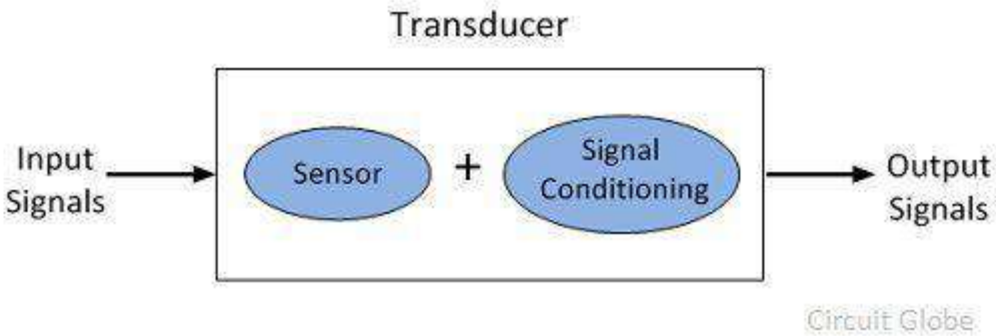
Sensors are found in a wide range of applications, from industrial automation and control to consumer electronics and healthcare. For example, sensors are used in automobiles to monitor engine performance, in smartphones to detect user input and orientation, and in medical devices to monitor vital signs.

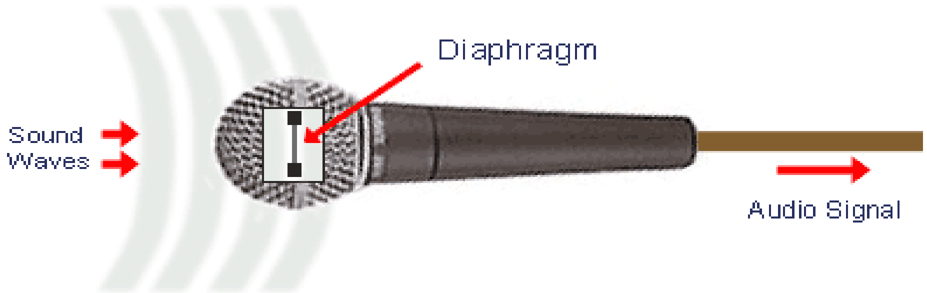
**Sensors: Sensors are electronic devices that detect and measure physical/chemical phenomena into an electrical signal**.

Physical/Chemical phenomena: Temperature, pressure, motion, light, or sound/ concentration.

Eg.microphone- It is a sensor that converts sound energy to an electrical signal that can be amplified, transmitted, recorded, and reproduced.

**Components of sensors**




- **Sensor** - observe and acquire information(input)
- **Transducer**- Converts one form of energy into another form
- **An actuator**- Converts electrical energy into mechanical energy(output)

**Measurement process for the instrumentation model**

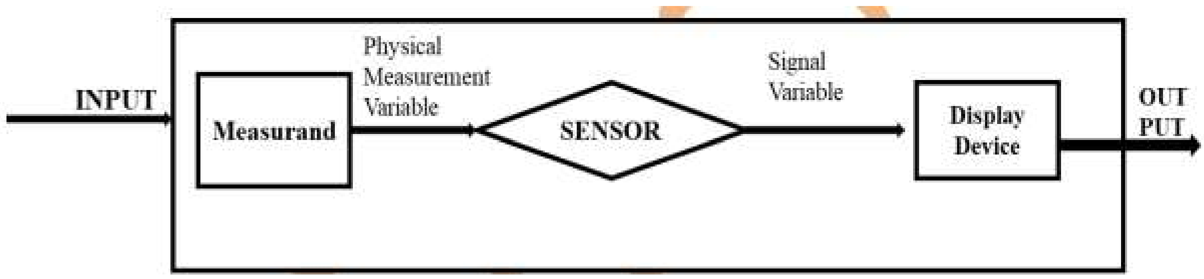
▪ Sensor input- The physical value or measurand (X) is observed by the sensor device.

▪ Sensor output – The sensor generates a signal variable (S) output which is normally electrical.

▪ Signalconditioning- The signal is transmitted and conditioned if needed (amplified, converted, filtered, etc.)

▪ Display of measurement – the measurement is then displayed by the output device.






**CONDUCTOMETRIC SENSORS**:

Conductometric sensors are chemical sensors that measure changes in electrical conductivity when a specific analyte interacts between the electrodes.

**Principle:**

The conductometric sensor is composed of two electrodes coated with a highly sensitive material that responds to a specific analyte. When the analyte of interest meets the electrode coating, it binds to the surface, causing a change in the electrical properties of the sensor. The change in conductivity is measured and correlated with the concentration of the analyte in the sample. The final output is a quantitative measure of the concentration of the analyte.

Electrolyte solution conducts current by the migration of ions under the influence of an electric field.

$$E = I\,R$$

Where; I → current, R→ Resistance

Ohm's law states that the current' I ' flow through conductor is directly proportional to the applied potential, E and inversely to the resistance R of conductor. The reciprocal of resistance is called the conductance.

The resistance of homogenous material of uniform cross-section with an area of ' a' sq.cm and length 'l' cm is given by

$$R = Ᵽ . l/a$$

Where Ᵽ → Specific resistance, l→ length, a → area cross- section

**Specific conductance** of an electrolyte solution is the conductance of the solution present between two parallel electrodes of $1cm^3$ area of cross-section and 1cm apart.

$$K = 1/R \times l/a$$

Where l/a is known as the cell constant

'R' is the resistance of solution



**Instrumentation and procedure**

The instrument used for measurement of conductance is called conductometer.

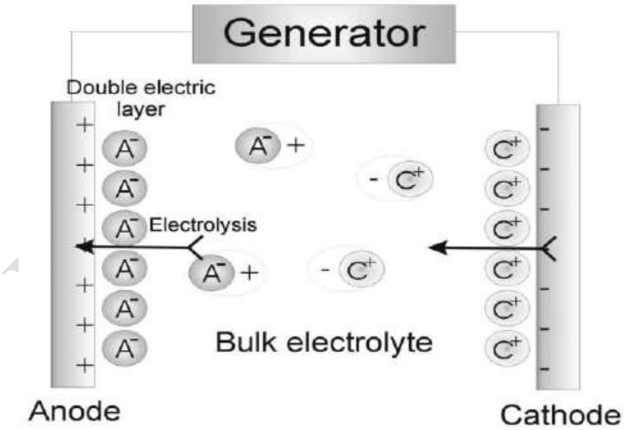
It consists of,

- Current source :AC source
- Conductivity cell : Made pyrex or quartz fitted with two Platinum electrodes
- Electrodes : Thin plates of Pt. each of unit area of cross-section placed unit distance a part

The electrodes are dipped in the electrolyte solution taken in a beaker and It is connected to a conductance measuring device. The titrant is added from a burette and solution is stirred. The conductance is measured after the addition of the titrant at intervals of 0.5 ml. The electrical conductivity of a solution of an electrolyte is measured by determining the resistance of the solution between two flat or cylindrical electrodes separated by a fixed distance .


**Working**

The conductivity is result of dissociation an electrolyte, into ions. The migration of the ions is induced by an electrical field. When a potential difference is applied to the electrode, there is an electrical field within the electrolyte, so the positively charged ions move towards cathode and negatively charged ions are move towards anode. (Figure). Thus, the current in the electrolyte is caused by the ion movement towards the electrodes where the ions are neutralized and isolated as neutral atoms (or molecules). This chemical change is recognized by working electrode and transducers converts this chemical change into electrical signal.




**Applications:**

- Monitoring of water quality
- Detection of gas and vapor
- Analysis of biochemical compounds
- Measurement of ionic strength and pH levels in solutions
- Food and beverage industry

## ELECTROCHEMICAL SENSORS

Electrochemical sensors are devices that detect and measure the concentration of a target analyte by converting a chemical reaction into an electrical signal.

In Electrochemical sensors the electrode or a set of electrodes is used as transducer element.

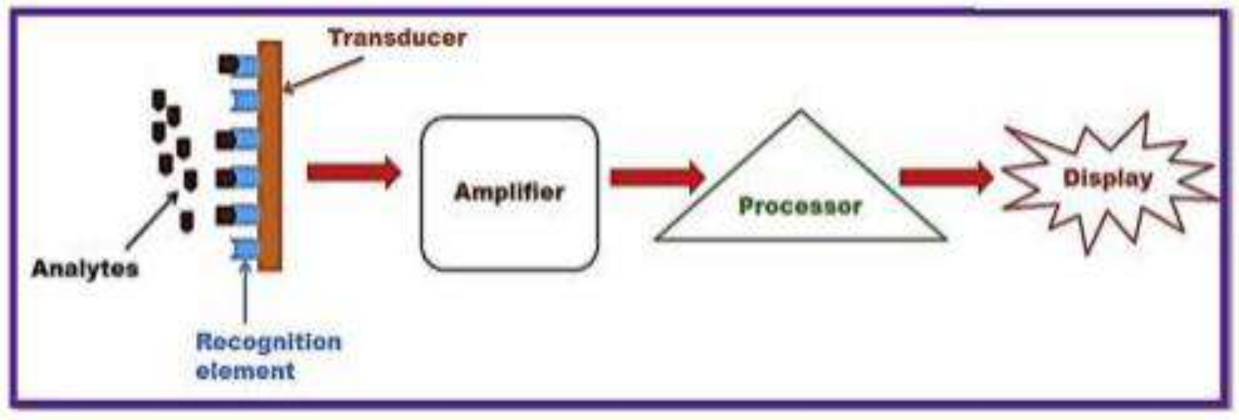
Electrochemical sensors divided into several types based on their mechanism of operation and the type of reaction involved.

- Potentiometric (measure voltage)
- Amperometric (measure current)
- Conductometric (measure conductivity)

**Working principle**

An electrochemical sensor mainly consists of two main components,

1. Chemical recognition system responsible for recognizing the analyte species
2. A transducer that converts chemical interactions into electrical signals that could be detected ,amplified and displayed easily by modern electrical instruments.




Electrochemical sensor's working mechanism involves the interaction of the target analyte material with the electrode surface and bringing the desired change as a consequence to a redox reaction, which generates an electrical signal that can be transformed to explore the nature of the analyte species.

Electrode surface can be remarkably transformed by the process of functionalization by the attachment of biomolecules such as peptides, and antigen/antibody that functions as the specific chemical recognition element.

**Applications**

- Electrochemical sensors are considered attractive tools to determine important molecules or biomarkers (BP,temp.) that are used for the diagnosis of diseases and disorders.
- They are used for the monitoring of toxic levels of different substances in food quality and environmental control.

- The biosensor application areas of these sensors extend to medical and biomedical applications, process control, bioreactors, quality control, agriculture, bacterial and viral diagnosis, industrial wastewater control.
- The oxygen sensors are used to determine dissolved oxygen in boiler water and to monitor dissolved oxygen concentrations in hydrogen fuel cell..
- Used in water analysis and environmental monitoring.
- Used in soil parameter analysis and in agricultural applications

**OPTICAL SENSORS**

Optical sensors are devices that use light and converts in to electric signals for detecting and measuring physical or chemical properties of a sample.

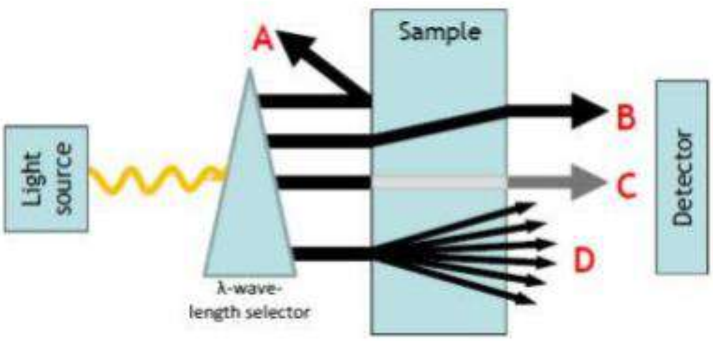
Example: (photometric) Colorimetric Sensors

**Working Principle:**

Optical sensors use visible ,IR and ultraviolet light to interrogate sensors for analysis.

- sample solution is interacted with a light of suitable wavelength,
- May results in absorption, emission, scattering and reflection of light.
- is it is observed by a sensor and transducer converts intensity of absorbed light into electrical signal
- The intensity of the radiation gives the information on the concentration of the analyte.
- Hence Optical sensors are used to determine the concentration of coloured solution. It is based on the measurement of absorbance of the coloured solution at particular wavelength. It is governed by Beer-Lambertz law

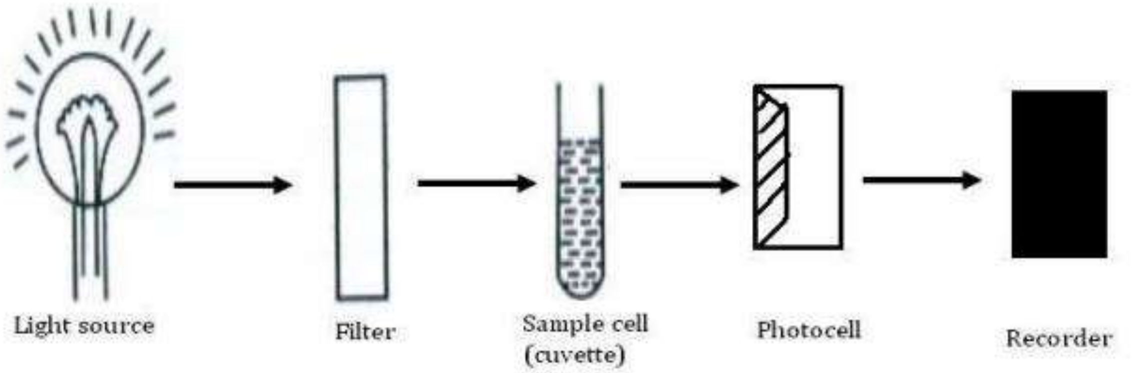





**Optical sensors working (Colorimetric Sensors)**

- A monochromatic light is pass through analyte at particular wavelength.
- A part of light is absorbed by the analyte.

- The absorbance depends on the concentration of the solution and the path length of the light through the solution.
- The photocell converts emitted light into electrical signal
- These signals are recorded and displayed.



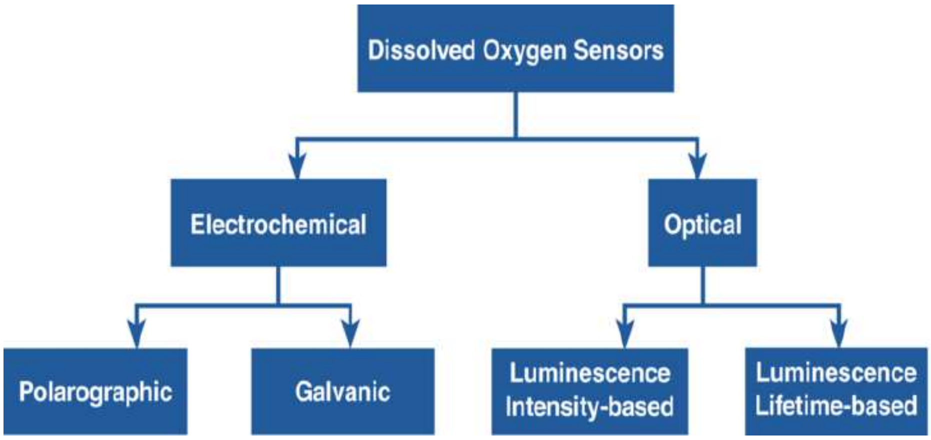

1. **Source**: tungsten bulb or lamp is used as a light source.
2. **Filter:** It is a device to provide desired wavelength range
3. **Sample cell:** sample is hold in glass cell.
4. **Photocell**: Converts the emitted light into electrical signal.
5. **Recorder:** to record the signal and display the same.



**Applications:**

- Optical sensors are integral parts of many common devices, including computers, copy machines (xerox) and light fixtures that turn on automatically in the dark.
- Medical diagnostics: Colorimetric sensors are used to detect the presence of biomolecules, such as glucose, cholesterol, and haemoglobin, in bodily fluids such as blood and urine.
- Security and defence
- Food safety testing

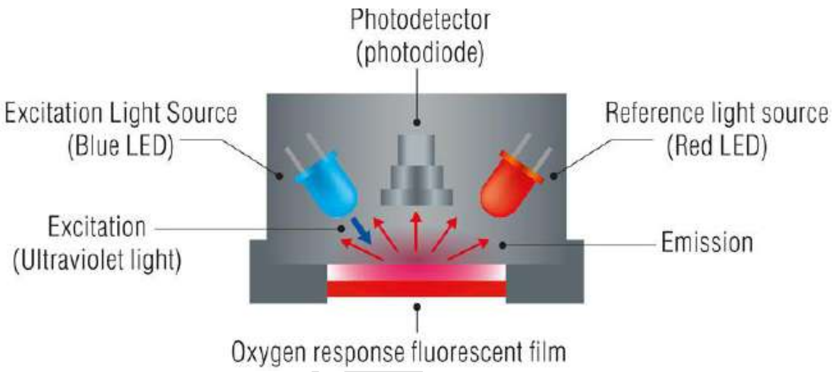
**DIFFERENT TYPES OF DISSOLVED OXYGEN SENSORS**



There are two types of DO sensors

1. **Optical Sensors** -Optical DO sensors, popularly known as luminescent DO sensors (LDO) but some are called fluorescent sensors, measure dissolved oxygen concentration in water based on the quenching of luminescence in the presence of oxygen
2. **Electrochemical Sensors** - Electrochemical DO sensors, also known as amperometric or Clark-type sensors, measure dissolved oxygen concentration in water based on electrical current produced. Polarographic and galvanic are types of electrochemical DO sensors

**Optical sensors for DO measurements.**




**Components:**

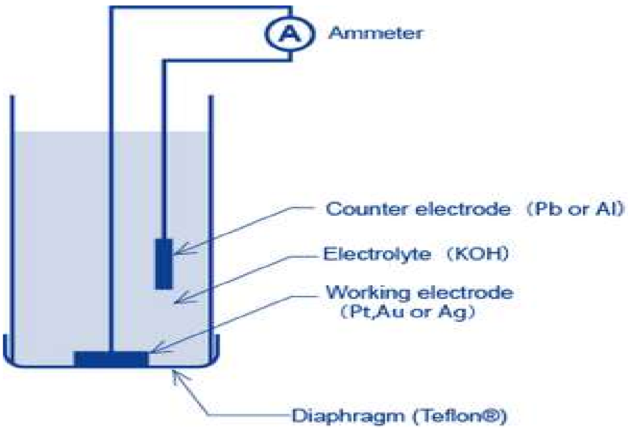
1. Light-emitting diodes (LEDs)
2. Photodetector
3. Luminescent dye
4. Membrane

**Working:** When the dye is exposed to light, it moves to excited state and return to ground state by emitting light with known intensity. When the DO crosses the semi permeable membrane and interacts with the dye, it reduces the intensity of the light emitted by dye. The intensity of the emitted light inversely proportional to the DO concentration. This intensity of light is measured using photo detector.

## ELECTROCHEMICAL SENSOR FOR THE MEASUREMENT OF DISSOLVED OXYGEN (DO)

**In electrochemical sensors components,**

- **Anode:** Zn, Pb or any other active metal
- **Cathode:** Working electrode-Ag
- **Electrolyte:** KOH, NaOH or any other inert electrolyte
- **Membrane:** Teflon




**Working:**

- The cathode and anode are dissimilar metals (different electropotentials). In order to reduce oxygen without an external applied potential, the difference in potential between the anode and the cathode should be at least 0.5V. (When placed in an electrolyte solution, the potential between dissimilar metals causes them to self-polarize with the electrons travelling internally from the anode to the cathode)
- Both the cathode and anode are submerged in an electrolyte (e.g., NaOH, NaCl, or another inert electrolyte) and enclosed in a cap fitted with thin hydrophobic, oxygen-permeable membrane.
- Galvanic DO sensor is immersed in water sample, oxygen that diffuses across the oxygen-permeable membrane at a rate proportional to the pressure of oxygen in the water is reduced and consumed at the cathode.
- This reaction produces an electrical current that is directly related to the oxygen concentration.
- This current is carried by the ions in the electrolyte and runs from the cathode to the anode
- **Reactions..**

  **Anode (Pb)** lead oxidation reaction: $2Pb \rightarrow 2Pb^{2+} + 4e^-$

  **Cathode (Ag)** oxygen reduction reaction: $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$

  **Overall reaction:** $O_2 + 2H_2O + 2Pb \rightarrow 2Pb(OH)_2$

**ELECTROCHEMICAL SENSORS FOR THE PHARMACEUTICALS**

**Electrochemical sensors for the detection of (diclofenac)**

- Pharmaceuticals are organic compounds, extensively used as solution for different health issues.

- After the usage they are excreted and enter into the environment and these are complex organic molecules with lower biodegradability.
- Hence sensors are used for the detection of pharmaceuticals to monitor their concentration and know their toxic effects.
- Electrochemical detection occurs at the interface between an analyte (diclofenac) of interest and the working electrode to which a potential is applied with respect to the reference electrode, while the corresponding current is measured.

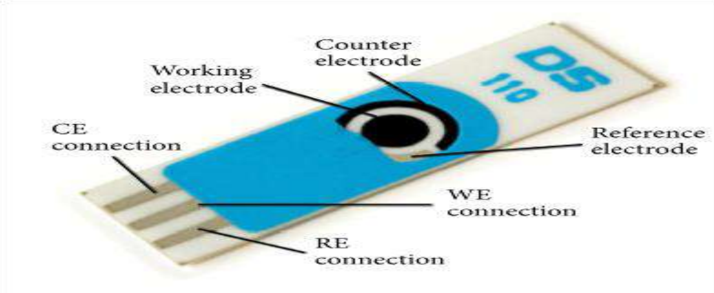
**Disposable screen printed Carbon paste electrode for diclofenac detection (Three electrode sensor)**

**Working electrode:** Carbon Paste with MWCNT or Graphene

**Counter Electrode:** Carbon Paste with MWCNT or Graphene

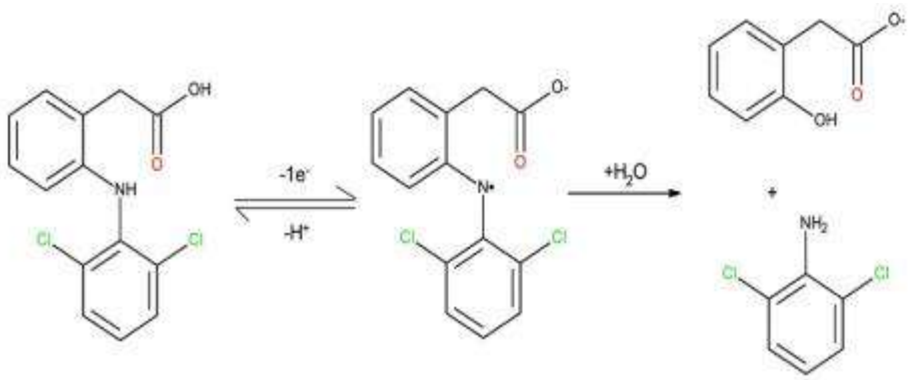
**Reference Electrode:** Ag/AgCl

**Process:** Screen Printing Technique on PVC substrate. Insulating ink was printed on the remaining PVC surface.




**Working:**

The electrochemical oxidation of DCF on carbon-based sensor at pH 7.0 is reversible reaction. Oxidation of Declofenac occurs at carbon electrode to release e-, to form radical intermediates and followed by hydrolysis of radical intermediate species. The products formed are 2,6- dichloro aniline and 2-2(-hydroxyphenyl) acetic acid. Reactions on the electrode cause the current to flow. The intensity of this current is a function of the number of oxidized / reduced molecules.




**Electrochemical sensors for the detection of Hydrocarbon: 1- Hydroxypyrene(Screen Printed Sensor)**

- Among the dangerous hydrocarbon pollutants polycyclic aromatic hydrocarbons(PAHS) are widely found in air, water, soil and food.
- PAHS are carcinogenic and mutagenic compounds
- They can enter the human body mainly through respiration and diet.
- Detection of PAHS is essential to monitor their toxicity and carcinogenic risk.

**Working electrode: PAMAM/Cr-MOF/GO (Composite)**

**Counter Electrode:** PAMAM/Cr-MOF/GO

**Reference Electrode**: Ag/AgCl

Operating Voltage: +0.7 to −0.5 V

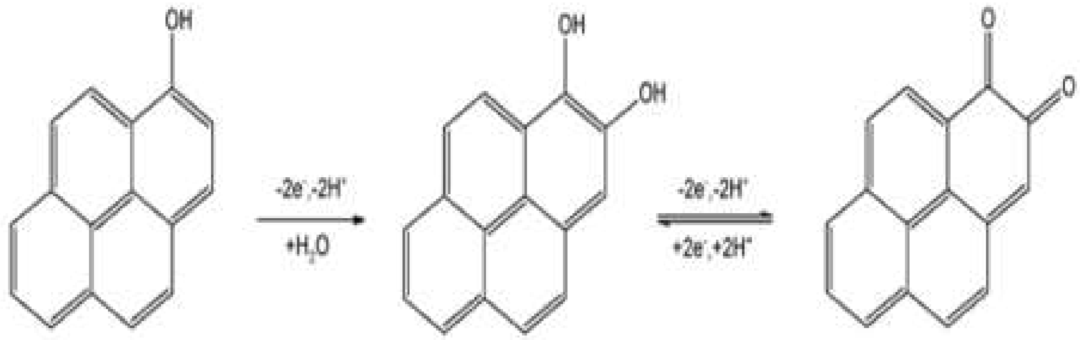
Where ,PAMAM: Dendrimer polyamidoamine

Cr-MOF: Chromium-centered metal–organic framework GO: Graphene Oxide

**Working**

When this electrode is used to detect the sample containing 1-Hydroxypyrene (water sample) the following changes takes place.

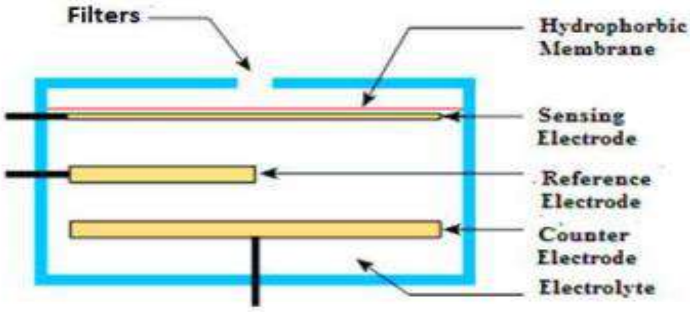
- A sample containing 1-hydroxy pyrene is put in the sensor and suitable voltage is applied.
- 1-hydroxy pyrene undergoes electrochemical oxidation at the surface of electrode and yield hydroxylated species and then hydroquinone by losing 2e−and 2H+ .
- Reactions on the electrode cause the current to flow.
- Current produced is directly proportional to the concentration 1- Hydroxypyrene.




**ELECTROCHEMICAL GAS SENSORS**

- Electrochemical gas sensors are used to measure the concentration of gases like NO2, NO and SO2.
- Electrochemical gas sensor interacts with a gas to measure its concentration and each gas has a unique voltage; the electric field at which it is ionized.
- Sensor identifies gases by measuring these voltages.

**Electrochemical gas sensor-components**




- **Filters:** Used to prevent unwanted contaminants, mainly particulate matter
- **Membrane:** A gas-permeable membrane is used to regulate the gas flow into the sensors. It allows only analyte gas to pass and prevent the leakage of the electrolyte.
- **Electrodes:** two or three electrodes are used on the requirement.

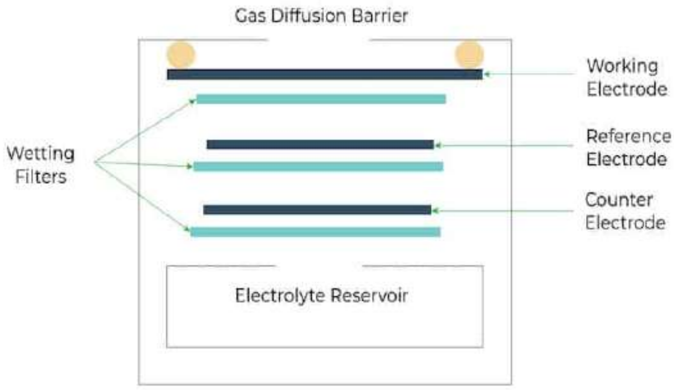
  **Working or sensing-** is made from a noble metal, such as platinum or gold, and its surface is coated with suitable receptor (chemically modified surface). Hence it selectively facilitate the reduction or oxidation of the analyte gas molecules.

  **counter and reference electrode.**
- **Electrolyte:** Electrolyte should be ionic conductor and chemically stable. Main role is , it transport.

**Working**

- Gas that comes in contact with the sensor first passes through filter and then diffuses through a hydrophobic barrier, and finally reaches the electrode surface.
- Adsorption of analyte gas molecule on the surface of sensing electrode.
- A suitable voltage is applied to the sensing electrode and that makes the sensor specific to the target gas.
- The analyte gas reacts at the surface of the sensing electrode involving either an oxidation or reduction mechanism.
- Current proportional to the gas concentration flows between the anode and the cathode is measured
- Current produced is directly proportional to the analyte gas.

**Electrochemical gas sensors for Sox**




**Construction**

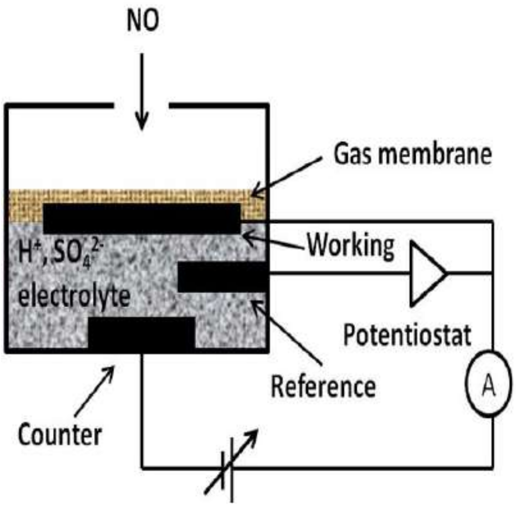
- working electrode- coated with electrocatalyst such as Gold/ Nafion, which facilitates the oxidation of SO2 to H2SO4.
- Reference electrode- Ag/AgCl
- Counter electrode -Platinum wire
- Electrolyte - 0.5 M H2SO4

**Working**

- The diffusion of gas analyte through filter, membrane and then finally through electrolyte on to the surface of sensing electrode.
- Adsorption of analyte gas molecules on the surface of sensing electrode.
- SO2 undergoes oxidation when suitable voltage is applied to produce H2SO4 and generates an electrical current proportional to its concentration in the sample
- The following oxidation reaction occurs on sensing electrode.

$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$

**Electrochemical gas sensors for NOx**




**Sensors for NO2:**

**Construction**

- working electrode- coated with electrocatalyst such as Gold/ Nafion, which facilitates the reduction of $NO_2$ to NO
- Reference electrode- Ag/AgCl
- Counter electrode -Platinum wire
- Electrolyte - 10 M $H_2SO_4$

**Working**

- The diffusion of $NO_2$gas through filter, membrane and then finally through electrolyte on to the surface of sensing electrode.
- Adsorption of analyte gas molecules on the surface of sensing electrode.
- NO2 undergoes reduction when suitable voltage is applied to produceNO and generates an electrical current proportional to its concentration in the sample
- The following reduction reaction occurs on sensing electrode.

  $NO_2 + 2H^+ + 2e^- \rightarrow NO + H_2O$ (NO2 + e- → NO)$^-$

**Sensors for NO:**

**Construction**

- working electrode- coated with electrocatalyst such as Gold/ Nafion, which facilitates the oxidation of NO to $HNO_3$.
- Reference electrode- Ag/AgCl
- Counter electrode -Platinum wire

- Electrolyte – 0.5 M $H_2SO_4$

**Working**

- The diffusion of NO gas through filter, membrane and then finally through electrolyte on to the surface of sensing electrode.
- Adsorption of analyte gas molecules on the surface of sensing electrode.
- NO undergoes oxidation to produce HNO3 when suitable voltage is applied and generates an electrical current proportional to its concentration in the sample
- The following reduction reaction occurs on sensing electrode.

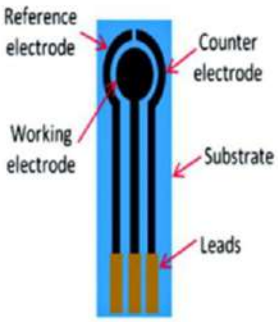
  $NO(g) + 2H_2O \rightarrow HNO_3 + 3H^+ + 3e^-$

**DISPOSABLE SENSORS:**

**Disposable sensors- Portable sensors used for on-spot analysis using disposable strip with receptor and electrode printed on it is called disposable sensor.**

Advantages of disposable sensors:

- Disposable sensors are biodegradable and sustainable
- They have a short duration of analysis and fast response times.
- It provides digitized chemical and biological information.
- Prevents the contamination of samples




The disposable sensors are a type of paper over which receptor and electrodes are printed.
Electrodes reference, working and counter electrode and receptor is printed on a single platform as shown in the fig. These electrodes are called screen-printed electrode and are main components of disposable sensors.

**DETECTION OF ASCORBIC ACID USING DISPOSABLE ELECTROCHEMICAL SENSOR**

L-Ascorbic acid (AA) or adsorbate, commonly known as vitamin C, is an important water-soluble vitamin derived from green vegetables, fruits, and other dietary supplements. AA improves the immune system. It enables collagen synthesis, which is needed to maintain healthy bones, teeth, skins, cartilages, enhances antibody levels and acts as an antioxidant; reduces necrosis.

At the same time Abnormal AA levels in bodily fluids have been reported to cause cancer, cardiovascular diseases, and Alzheimer's and Parkinson's diseases. Extended use of AA could cause urinary oxalate calculus, increase infertility in a woman, and affect embryo development. Excessive AA use has been reported to cause diarrhoea, nausea, vomiting, headache, insomnia, gastric irritation, renal problems, loss of food taste, and vomiting.

**Disposable Screen-Printed Carbon Electrodes Sensor (CNT With Gold Nanoparticles) For Biomolecule**

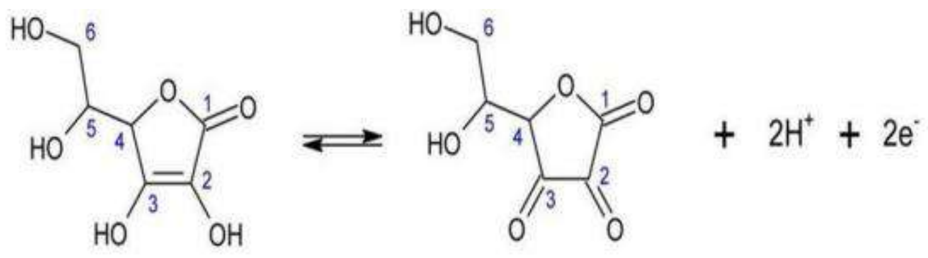
**Detection- Ascorbic acid**

- SPE sensor consists of three electrodes, working electrode, auxiliary or counter electrode, and reference electrode.
- All electrodes have been manufactured by Silk screen printing technology with conductive material ink on a plastic polyester (PET) sheet.
- The active surfaces of the counter electrode and working electrode have been printed with a conductive ink of C (MWCNT) and modified with gold nanoparticles.
- Active surface of the reference electrode has been printed with an Ag/AgCl ink

**Working**

- The electrochemical sensor can catalyze the **two-electron electro catalytic oxidation** and **hydrogen dissociation of AA** to L-dehydroascorbic
- The number of electrons released is proportional to the concentration of AA in the sample
- The electric current or voltage produced is proportional to the concentration of the ascorbic acid.





**DETECTION OF PESTICIDE SUCH AS GLYPHOSATE BY ELECTROCHEMICAL OXIDATION METHOD**

One of the most commonly used pesticides is glyphosate. Glyphosate has the ability to attach to the soil colloids and degraded by the soil microorganisms. As glyphosate led to the appearance of resistant species, the pesticide was used more intensively. As a consequence of the heavy use of glyphosate, residues of this compound are increasingly observed in food and water. Recent studies reported a direct link between glyphosate and chronic effects such as tetrogenic, tumorigenic.

**Electrochemical Sensor for Glyphosate Detection**

- The sensor is a silicon- based chip comprising of three-electrode system. It is fabricated by electro deposition technique.
- Working Electrode: A gold electrode of 4 mm diameter coated with 200nm thickness gold nanoparticles
- Counter electrode: A gold electrode of 4 mm diameter coated with 20nm thickness gold nanoparticles
- Reference Electrode: $Ag/AgCl/Cl^-$
- Electrolytes are added to increase the conductivity of the solution and minimizes the resistance between the working and counter electrode.

**Working:**

- The electrochemical detection is based on the oxidation of Glyphosate on gold working electrode.
- A potential of 0.78V is applied on working electrode, there is a interaction between analyte and electrode surface.
- Glyphosate oxidizes on the working electrode brings a change in current in the electrolyte medium.
- The change in the current is a measure of concentration of Glyphosate.

**At the anode(working electrode):** Glyphosate (Gly) + $H_2O \rightarrow$ Oxidised Gly $+2H^+ + 2e^-$

**At the cathode: (counter electrode):** $2H^+ + 2e^- \rightarrow H_2$

# ENERGY SYSTEMS

**Battery** -is a device that consists of two or more galvanic cells connected in series or parallel or both which converts chemical energy into electrical energy through redox reactions.

Example: Zn-Air battery, lead acid battery, lithium batteries, etc.

Batteries can thus generate power and can act as portable sources of electrical energy.

Batteries are classified as Primary, Secondary and Reserve batteries:

**1)Primary batteries**:

- In primary batteries, the chemical energy is converted into electrical energy as long as the chemical components are active.
- These are not rechargeable as the chemical reactions which occur within the primary batteries are irreversible and once discharged have no further electrical use.
- Ex: Zn-$MnO_2$ battery and Li-$MnO_2$ battery.

**2)Secondary batteries**:

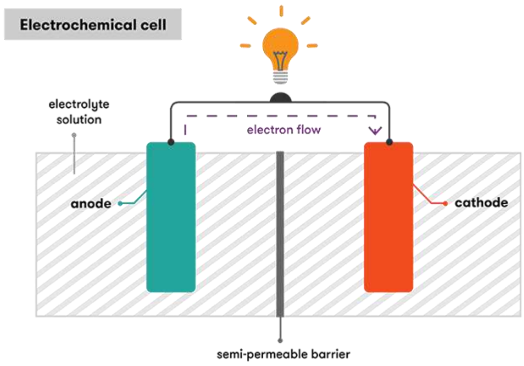
- Secondary batteries are rechargeable as the cell reactions are reversible.
- After discharge, secondary batteries can be recharged electrically to their original condition by passing current through them in the direction opposite to that of discharge current.
- The electrical energy is stored in them in the form of chemical energy and hence these are also called storage cells
- Ex: Lead storage battery , nickel-cadmium battery, Lithium ion battery etc**.**

**3) Reserve batteries:**

- Reserve batteries are a battery in which a key component is separated from rest of the components prior to activation.
- The activation involves adding electrolyte or any other cell component. Electrolyte is the component that is usually isolated to prevent the reaction with cell components and also to prevent self discharge.
- The battery has long-term storage capacity as chemical reaction (self discharge) during storage is prevented. Reserve batteries are primarily used to deliver high power for relatively short period of time after activation.
- Ex: Magnesium-water activated batteries, (Mg-AgCl, Mg-CuCl), Zn-$Ag_2O$ battery etc.

**COMPONENTS OF BATTERY**

Cells are comprised of 4 essential components.




1. **Anode:** is the negative that releases electrons to the external circuit

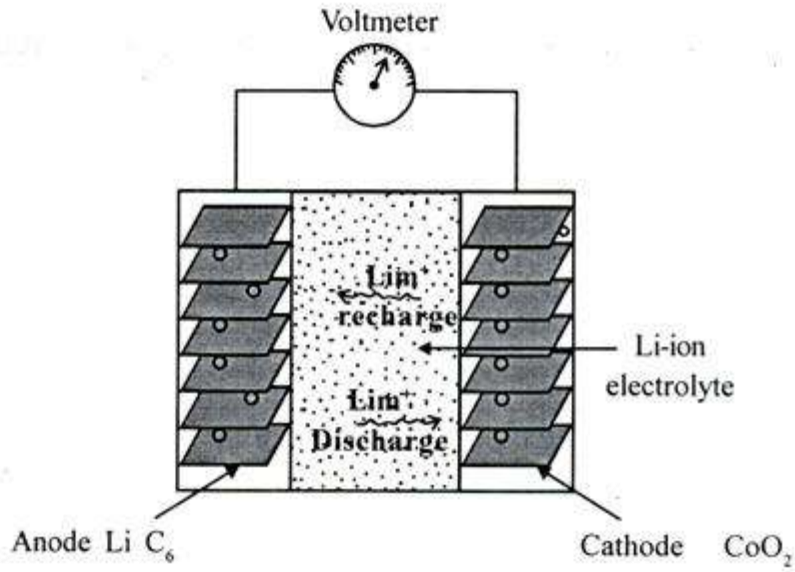
   $M \rightarrow M^{n+} + ne^{-}$

2. **Cathode:** is the positive that acquires electrons from the external circuit

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

3. **Electrolyte:** is the medium that provides the ion transport mechanism between the cathode and anode of a cell. Electrolytes are often thought of as liquids with dissolved salts, acids, or alkalis that are required for ionic conduction.
4. **Separator:** Separates anode and cathode made up of cellulose, polymer etc. This prevents short circuiting.

**LITHIUM ION BATTERY**




**Definition:** The batteries in which lithium ions are used instead of lithium metal and movement of lithium ion through electrolyte takes place from one electrode to another electrode are called lithium ion batteries.

**Construction:**

**Anode:** Lithiated carbon or graphite and a binder coated on a copper foil.

**Cathode:** Lithiated transition metal oxide like $LiCoO_2$ mixed with a conductor and binder and coated in an Aluminium foil.

**Electrolyte:** A lithium salt in an organic solvent. This electrolyte effectively **transport** Li+ ion to cathode during discharge of battery.

**Separator:** micro porous polythene

The voltage of LIB is about 3.6-3.7 V

**Working principle:**

***Discharge reactions***: During discharge, Li ions are dissociated from anode and migrate through the electrolyte to cathode.

At anode: $LiC_6 \rightarrow C_6 + Li^+ + e^-$

At cathode: $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

-----------------------------------------------------------------

Overall reaction: $LiC_6 + CoO_2 \rightarrow LiCoO_2 + C_6$

-----------------------------------------------------------------

***Recharge reactions***: During charging an external electrical power source applies a higher voltage than that produce by the battery, forcing the current to pass in reverse direction. Lithium ions then migrate from cathode to anode, where they become embed in the porous electrode material in a process known as intercalation.

$$LiCoO_2 + C_6 \rightarrow LiC_6 + CoO_2$$

**Applications of lithium ion battery**: They are used in

- cardiac pacemakers, laptops, cell phones, portable LCD, TV.
- Electric vehicles.
- Renewable Energy storage systems.
- Defence and Aerospace applications



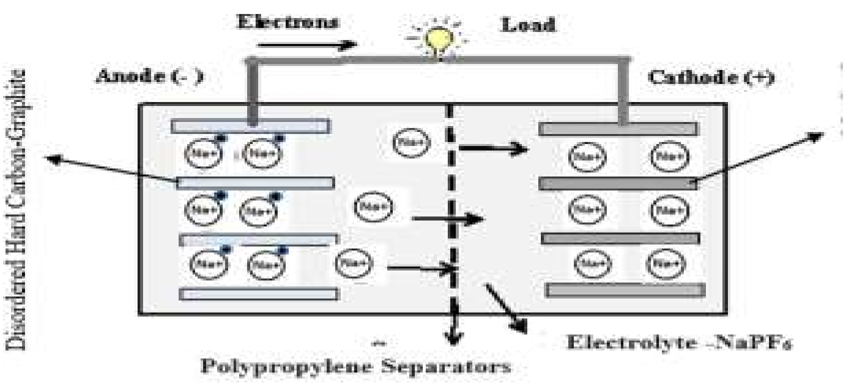
**SODIUM ION BATTERY**

The **sodium-ion battery** (**NIB** or **SIB**) is a type of rechargeable battery that uses sodium ions ($Na^+$) as its charge carriers. Recently, sodium-ion batteries (SIBs) have been reconsidered with the aim of providing a lower-cost alternative that is less susceptible to resource and supply risks..

**Construction**

Its working principle and cell construction are almost identical with those of lithium-ion battery (LIB) types, but replace lithium with sodium.

**Mechanism of Discharging**



**Anode :** Hard carbon (can not be converted to graphite) has the ability to absorb Sodium.

**Cathode:** layered Sodium transition metal oxide -$NaMO_2$ (where M = Fe, Ni, Mn, Co etc)

**Separator:** Porous polymer film.

**Electrolyte:** uses non-aqueous electrolytes -Organic carbonate solvent-based electrolytes like Propylene carbonate (PC): Ethylene carbonate (EC) containing sodium salts such as $NaPF_6$, $NaN(SO_2CF_3)_2$, and $NaClO_4$ are used together with small amounts of additives to stabilize the anode and cathode during cycling.

**Working principle:**

The NaCoO2 cathode is initially brought into the Na-ion cell in the discharged state, and the cell is activated by charging first to form the Na intercalated anode and Na deintercalated cathode in the fully charged cell.

**Discharge reactions**:

During the battery discharge, the sodium ion with positive charge moves towards cathode through electrlyte and intercalates with metal oxide and generate electric current.

At anode: $NaC_6 \rightarrow C_6 + Na^+ + e^-$

At cathode: $CoO_2 + Na^+ + e^- \rightarrow NaCoO_2$

---

Overall reaction: $NaC_6 + CoO_2 \rightarrow NaCoO_2 + C_6$

---

**Recharge reactions**: During charging an external electrical power source applies a higher voltage than that produce by the battery, forcing the current to pass in reverse direction. Na ions then migrate from cathode to anode, where they become embed in the porous electrode material in a process known as intercalation

$$NaCoO_2 + C_6 \rightarrow NaC_6 + CoO_2$$

**Applications:**

- NIB used in power tools and uninterruptible power supply (UPS) applications in the telecommunications sector.
- NIBs used in numerous stationary energy storage applications (NIB have low cost.)
- Large scale grid storage applications and used in large -scale storage of renewable energy.
- NIBs are an excellent fit with the SLI application in vehicles (by providing the specified power across the same temperature range but with lighter batteries. SLI batteries are inexpensive and operate across a broad temperature range).

**Advantages of SIBs**

- natural abundance of sodium
- low cost
- less environmental impact
- better cycle life, and better cycling stability
- nonflammable

**Dis advantages of sodium ion battery.**

- Large ionic size Na+ which require more power to keep energy flowing.
- It takes seven days to charge in case you forget to charge it.
- Lower operating voltage.

## QUANTUM DOT SENSITIZED SOLAR CELLS (QDSSC)

**QDSSC is a solar cell design that uses quantum dots as the light absorbing photovoltaic material and thus converts solar energy into electrical energy.**

- Quantum dots are special class of semiconductors and are nano crystals.
- The energy band gap increases with decrease in size of quantum dots.
- The adjustable band gap of quantum dots allows the construction of nano structured solar cell, that is able to harvest maximum amount of solar spectrum.
- QDSSCs how potential to become alternative to presently using silicon based solar cells this is due to unique property of QDs, like wide tunable band gap.

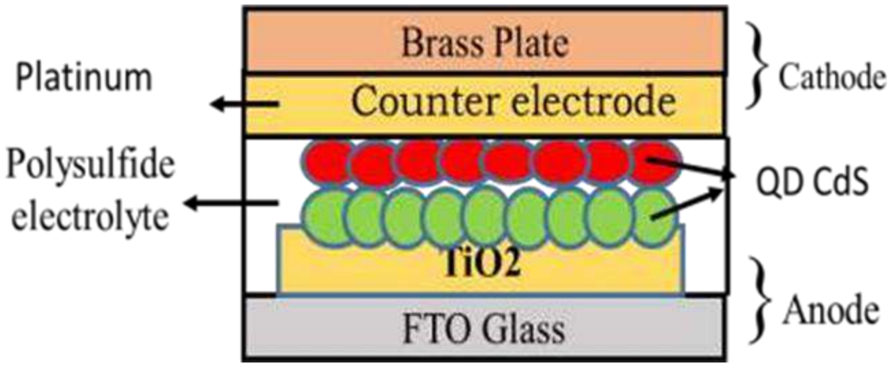


**Properties:**

- **High efficiency**: QDSSCs can achieve high conversion efficiencies due to their ability to absorb a broader range of the solar spectrum compared to conventional solar cells.
- **Size tunability:** The optical and electronic properties of QDs can be tuned by adjusting their size, making them highly versatile for use in various applications.
- **Low cost:** QDSSCs are relatively low-cost to produce compared to other types of solar cells, which makes them attractive for large-scale commercialization.
- High multiple electron generation

## PRINCIPLE, CONSTRUCTION AND WORKING OF QDSSC

**Principle:** QDSSCs work based on the principle of the photovoltaic effect, which is the generation of electrical energy from light. The QDs used here are semiconducting materials that absorb light energy and generate electrons, which are then collected to produce an electric current.

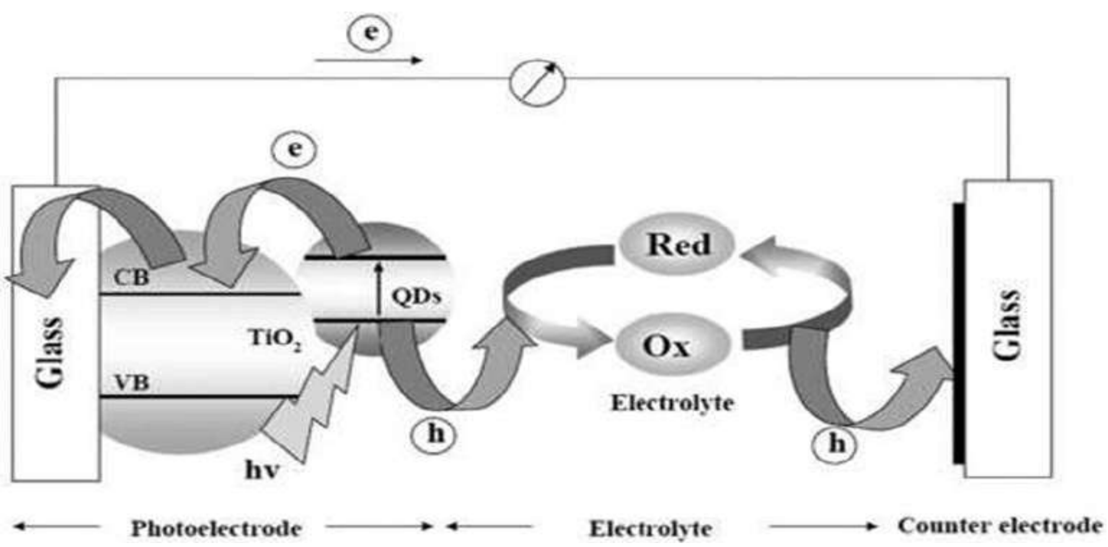



**Construction**

- **Working Electrode(photoanode)**: Fluorinated Tin Oxide(FTO) substrate is taken and coated with semiconducting TiO2. TiO2 is coated with quantum dots such as CdS(Cadmium Sulfide). TiO2 act as electron conductors (or acceptors) and transport layers. CdS facilitates the charge separation.
- **Sensitizer:** CdS is a sensitizer, it is a Quantum dot nano crystal made of semiconductor materials.
- **Counter Electrode(cathode):** A platinum and carbon based materials are coated on a brass substrate. Counter electrode is acting as cathode (it transfers electrons from external circuit to electrolyte and catalyze the reduction reaction of the oxidized electrolyte at the electrolyte/ counter electrode interface.)
- **Electrolyte**: Polysulfide is used as electrolyte (($S^{2-}/S_x^{2-}$) It is a redox electrolyte . Redox electrolyte significantly influence both stability and efficiency of QDSSC. It is a medium which transfer charges between counter electrode and photo anode for the regeneration of oxidized quantum dots.



**Working**



1.Upon light absorption QDs is excited from ground state to higher energy state.

$$QDs + h\nu \longrightarrow QDs^{*}$$

2.Absorption results in generation of electron-hole pair in the form of exciton.

$$QDs^{*} \longrightarrow QDs\ (e^{-*} + h^{+*})\ \text{(free carriers)}$$

3.The excited electron of QD are injected into the conduction band of TiO2.

$$QDs\ (e^{-*} + h^{+*}) + TiO2 \longrightarrow TiO2\ (e^{-*}) + QDs\ (h^{+*})$$

4.The electrons penetrate through nano crystalline TiO2 film to the back contact of the conducting substrate and flow through an external circuit to the counter electrode.

$$TiO2\ (e^{-*}) + CE \longrightarrow TiO2 + CE\ (e^{-*}) + Electrical\ energy$$

5. The oxidized form of the sensitizer (QD) are finally regenerated by the reduced component of the redox couple in the electrolyte.

$$QDs(^{h+*}) + S^{2-} \rightarrow QDs + S_x^{2-}$$

6.At the counter electrode the oxidized $Sx^{2-}$ component of the redox diffuse to counter electrode and accepts electron from it and reduced to $S^{2-}$

$$S_x^{2-} + e^{-}\ (C.E) \rightarrow S^{2-} + (C.E)$$

**Applications:**

- **Portable devices**: QDSSCs can be used to power portable electronic devices.
- **Building-integrated photovoltaic's (BIPV)**: QDSSCs can be integrated into the windows and walls of buildings to generate electricity.
- **Military applications:** Due to their light weight, flexibility, and ability to operate in low light conditions.
- **Space applications**: QDSSCs could be used to power space vehicles and satellites

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**Important questions**

1. Explain the working principle of conductometric sensors and Optical sensors.
2. Explain the working principle of Electrochemical Sensors and mention its applications.

3. What are electrochemical sensors? Explain its application in the measurement of dissolved oxygen(DO).
4. Explain about detection of Diclofinac and Hydrocarbons (PAH's) with electrochemical sensors.
5. Describe the applications of Electrochemical gas sensors in sensing $SO_x$ and $NO_x$.
6. What are sensors? Explain the detection of Ascorbic acid and Glyphosate using sensors.
7. Write a note on Disposable sensors?Explain its advantages over classical sensors.
8. Describe the construction ,working and applications of Lithium –ion batteries and mention any four applications.
9. Describe the construction ,working and applications of Sodium –ion batteries and mention any four applications.
10. What are batteries?Explain the working principle,properties and applications of Quantum Dot sensitized solar cells.
11. What are QDSCC's?Explain the working principle,properties and applications of Quantum Dot sensitized solar cells.

**MODULE 2**

## MATERIALS FOR MEMORY AND DISPLAY SYSTEM

**SYLLABUS**

**Memory Devices:** Introduction, Basic concepts of electronic memory, History of organic/polymer electronic memory devices, Classification of electronic memory devices, types of organic memory devices (organic molecules, polymeric materials, organic inorganic hybrid materials).

**Display system:** Photo active and electro active materials, Nanomaterials and organic materials used in optoelectronic devices. Liquid crystals (LC's) - Introduction, classification, properties and application in Liquid Crystal Displays (LCD's). Properties and application of Organic Light Emitting Diodes (OLED's) and Quantum Light Emitting Diodes (QLED's).

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## MEMORY DEVICES

**Definition**.

A memory device is a piece of hardware used to store data.

Example: CD, DVD, USB and external hard disc.

**Basic Concepts of Electronic Memory**

An electronic memory device is a form of semiconductor storage system which is fast in response and compact in size. A semiconductor storage system which can be read and written when coupled with a central processing unit (CPU, processor).

The basic goal of a memory device is to provide a means for storing and accessing binary digital data sequences of "1's" and "0's".

Electronic memory device consists of

1. Two electrodes

2. Switching layer between two electrodes -The layer is operated from High Resistance State (HRS) to Low Resistance State (LRS) under an external electric voltage. The HRS can be regarded as "0" bit in data storage (OFF). The switching from HRS to the Low Resistance State (LRS) is equivalent to"0" to "1" binary conversion (ON). If a single material (used in making memory device) provides

more than two resistance states (bistable), the storage capacity of a single memory increases exponentially.

**Classification of Electrical (electronic) Memory Devices:** Electronic memory devices can be divided into 4 types depending the type of material it is made of.

1. Transistor-Type Electronic Memory Devices

2. Capacitor-Type Electronic Memory Devices

3. Resistor-Type Electronic Memory Devices

4. Charge Transfer Type Electronic Memory Devices

**1.Transistor-Type Electronic Memory**

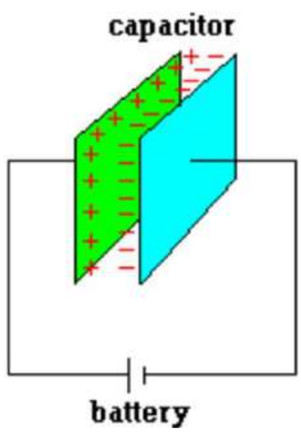
Transistors are made from silicon, a semiconductor. It is converted to p-type and n-type

semiconductor by doping trivalent and pentavalent impurities.

A transistor is a miniature electronic component that can work either as an amplifier or a switch. A computer memory chip consists of billions of transistors; each transistor is working as a switch, which can be switched ON or OFF. Each transistor can be in two different states and store two different numbers, ZERO and ONE. Since chip is made of billions of such transistors and can store billions of Zeros and ones, and almost every number and letter can be stored.



2.Capacitor-Type Electronic Memory

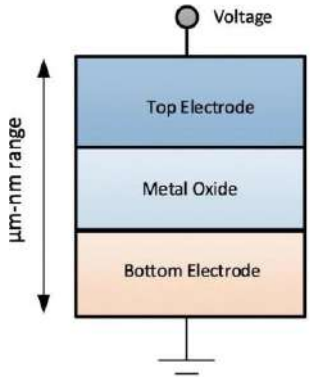



A capacitor consists of two metal plates which are capable of storing an electric charge. It is used to store data. It is like a battery that holds data based on energy. If the capacitor is charged, it holds the binary numeral, “1” and holds “0” when the cell is discharged.

If the parallel plates of a capacitor are separated by dielectric layer,

charges dissipate slowly and memory would be volatile. On the other hand, if the medium between the electrodes is ferroelectric in nature, can maintain permanent electric polarization that can be repeatedly switched between two stable states (bistable) by an external electric field. Thus, memory based on ferroelectric capacitors (FeRAM) is non- volatile memory.

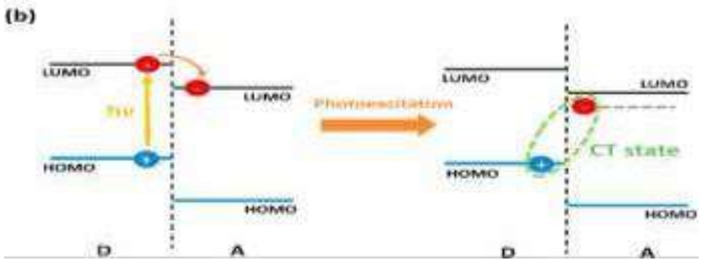
### 3.**Resistor-Type Electronic Memory**




Memory devices containing switchable resistive materials are classified as resistor-type memory, or resistive random access memory (RRAM). Resistor-type electronic memory usually has a simple structure, having a metal-insulator-metal structure generally referred to as MIM structure. The structure comprises of an insulating layer (I) sandwiched between the two metal (M) electrodes and supported on a substrate (glass, silicon wafer, plastic or metal foil). Initially, the device is under high resistance state or "OFF" and logically "0"state, when resistance changed or under external applied field changes to low resistance state or "ON" logical value "1".

### 4.Charge Transfer Effects Type Electronic Memory

A charge transfer (CT) complex is defined as an electron donor– acceptor (D–A) complex, characterized by an electronic transition to an excited state in which a partial transfer of charge occurs from the donor moiety to the acceptor moiety. The conductivity of a CT complex is dependent on the ionic binding between the D–A components.

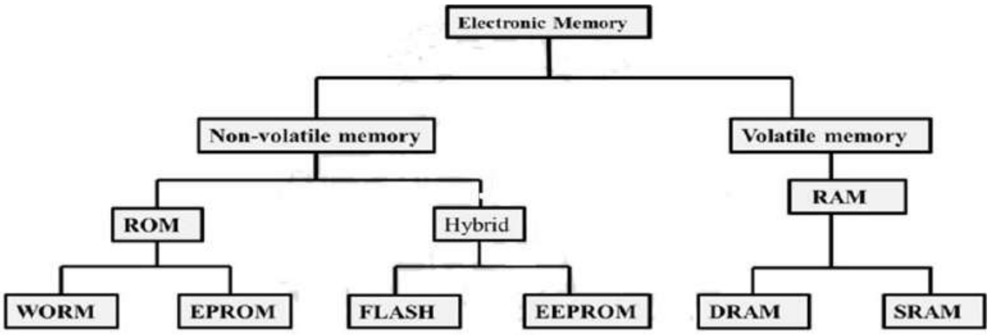



**Classification of electronic memory based on storage type of the device:**

Electronic memory can be divided into two primary categories: volatile and non-volatile memory.

**Non-volatile memory:** Non-volatile memory (NVM) or non-volatile storage is a type of memory that can retain stored information even after power is removed.

**Volatile Memory:** Volatile memory is a type of memory that maintains its data only while the device is powered. If the power is interrupted for any reason, the data is lost.




**Further it is divided as shown below:**

**ROM: Read Only Memory**

- ROM is a non-volatile memory.
- Information stored in ROM is permanent.
- Information and programs stored on it, we can only read.
- Information and programs are stored on ROM in binary format.
- It is used in the start-up process of the computer.

**WORM (Write Once Read Many times)**

Describes a data storage device in which information once written, cannot be modified. This write protection affords the assurance that the data cannot be tampered with once it is written to the device, excluding the possibility of data loss from human error, computer bugs, or malware.

**EPROM (Erasable programmable read-only memory)**

EPROM also called EROM is a type of PROM but it can be reprogrammed. The data stored in EPROM can be erased and reprogrammed again by ultraviolet light. Reprogrammed of it is limited. Before the era of EEPROM and flash memory, EPROM was used in micro controllers.

**HYBRID MEMORIES**

These can be read and written as desired, like RAM, but maintain their contents without electrical power, just like ROM. It is a Non-Volatile memory.

**FLASH**

It is an electronic non-volatile computer memory storage medium that can be electrically erased and reprogrammed. Flash memory is a non-volatile memory chip used for storage and for transferring data between a personal computer (PC) and digital devices.

**EEPROM (Electrically Erasable Programmable Read-Only Memory)**

Electronically erasable programmable read only memory, is a standalone memory storage device such as a USB drive. It is a type of data memory device using an electronic device to erase or write digital data.

**RAM: (Random Access Memory)**

It is a computer's short-term memory. It can be read and changed in any order, typically used to store working data and machine code.

RAMs consist of ferromagnetic particles embedded in a polymer matrix having a high dielectric constant. One of the most common RAMs is called iron ball paint, which contains tiny metal- coated spheres suspended in an epoxy-based paint. The spheres are coated with ferrite or carbonyl iron.

**DRAM (Dynamic Random Access Memory)**

It is a type of semiconductor memory that is typically used for the data or program code needed by a computer processor to function. All DRAM chips manufactured to date use capacitors containing electrodes made of doped silicon or polysilicon and dielectric films of silicon dioxide and/or silicon nitride.

**SRAM (Static Random Access Memory)**

It is a type of RAM that holds data in a static form, that is, as long as the memory has power. SRAM: It is made up of metal-oxide-semiconductor field-effect transistors (MOSFETs).

**ORGANIC MEMORY DEVICES**

Organic electronic memory device stores data based on different electrical conductivity states (ON and OFF states) in response to an applied electric field.

- The advantages of organic and polymer electronic memory include
- good processability,
- molecular design through chemical synthesis,
- simple device structure,
- miniaturized dimensions,
- low-cost,
- low-power operation,
- multiple state properties,

**Types of organic memory devices**

Organic memory device stores data based on different electrical conductivity states (ON and OFF states) in response to an applied electric field.

There are three types of organic memory devices

1. Organic molecular memory devices
2. Polymeric molecules
3. Organic-Inorganic hybrid materials

**1.Organic Molecular memory devices:**

If organic molecular material used to store the data is calledorganic–based memory device. Organic electronic memory devices based on organic molecules were first reported in several acene derivatives including naphthalene, anthracene, tetracene, pentacene, perylene, p-quarterphenyl and p-quinquephenyl.



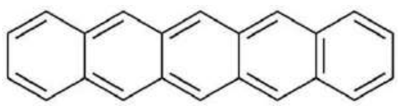
**Organic molecules**

**The p-Type Organic Semiconductor Material "Pentacene"**

An Organic molecule with $\pi$ conjugated system and possesses holes as major charge carrier is called p-type semiconductor.

**Ex: Pentacene**

- These molecules show bistable states when external field is applied i.e. ON and OFF state.
- It is linearly fused aromatic compound with five benzene rings.
- It can be obtained in crystal and thin film form.
- It shows good hole mobility, hence it behaves as a p-type semiconductor.



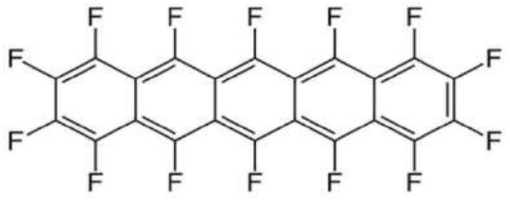
Pentacene

**The n-type organic semiconducting material Perfluoropentacene**

An Organic molecule with π conjugated system with electron withdrawing substituent groups and possess electrons as major charge carrier is called n- type semiconductor

**Ex.Perfluoropentacene**

When all the hydrogen atom of pentacene is replaced by Fluorine atoms, it formed Perfluoropentacene. Basically Fluorine is electron withdrawing nature. Hence it converts this molecules into n-type semiconductor.



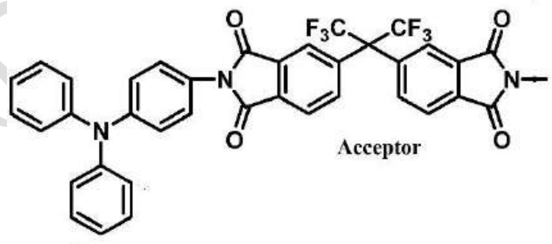

**Perfluoropentacene**

2.Polymeric Molecules

Polymer used for organic memory device is **Polyimide (PI)** with Donor-Triphenylamine and Acceptor- phthalimide.

**Donor: Triphenyl Amine group (TPA)**

**Acceptor: Phthalimide group**




This polymer has high thermal stability and mechanical strength. The donors and acceptors of PIs contribute to the electronic transition based on an induced charge transfer (CT) effect under an applied electric field.

- When an electric field more than threshold energy is applied, the electrons of the HOMO (TPA unit) is excited to LUMO.
- The energy of LUMOof donor and acceptor are similar an therefore, after excitation the electron transferred to LUMO(acceptor), generating a CT state.
- This permitsthe generation of holes in the HOMO,produces the open channel for the charge carriers to migrate through.

Therefore, Field-induced charge transfer from triphenylamine to phthalimide exhibit the switching behavior (bistable states ON/OFF).

# DISPLAY SYSTEM

A system through which information is conveyed to people through visual means.

## Photoactive and electro active organic materials

Photoactive and electroactive organic materials are the semiconductors composed of π-electron systems. Organic semiconductors used in electronic and optoelectronic devices are called as electroactive and Photoactive materials.

## Photoactive Process:

- Absorption and emission of light radiation in the wavelength region from ultraviolet tonear infrared.
- Photogeneration of charge carriers (photons of light creates electron-hole pair in the semiconductor)
- Transport of charge carriers (Charge carriers are particles or holes that freely move withina material and carry an electric charge)

## Electroactive Process

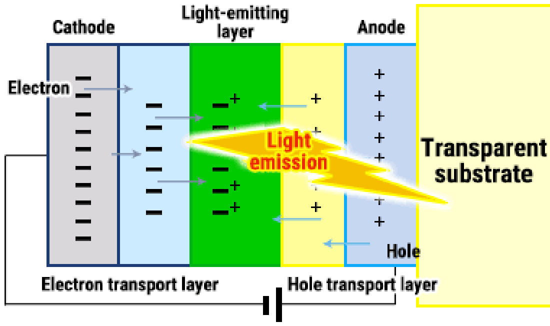
Injection of charge carriers from the electrode

- The process whereby light is emitted at the junction of N- and P-type semiconductors when an external electric source is applied to drive the electrons and the holes into the junction
- Transport of Charge carriers

## Working Principle

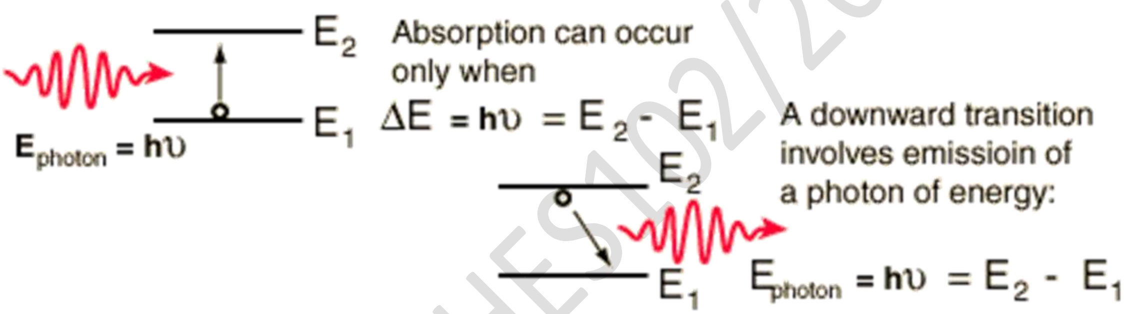
Photoactive and electroactive material absorb and emit light in the UV to IR region. Display system (OLED) consisting of photoactive and electroactive material absorb light and allows an electron to jump from HOMO of a Donor to LUMO of an Acceptor. This phenomenon generate and transport charge carriers

When electrons move from cathode, anode allows movement of holes towards light emitting layer under an applied field. Electron-hole pairs are created at the Light- Emitting-Layer and energy is released due to recombination. This energy is sufficient to excite an electron from HOMO to LUMO in the light emitting layer made of photoactive and electroactive materials. There is a re-emission of light while electron is returning to HOMO level. This light is extracted by a transparent substrate placed adjacent to either of the electrode.




## Optoelectronic Devices

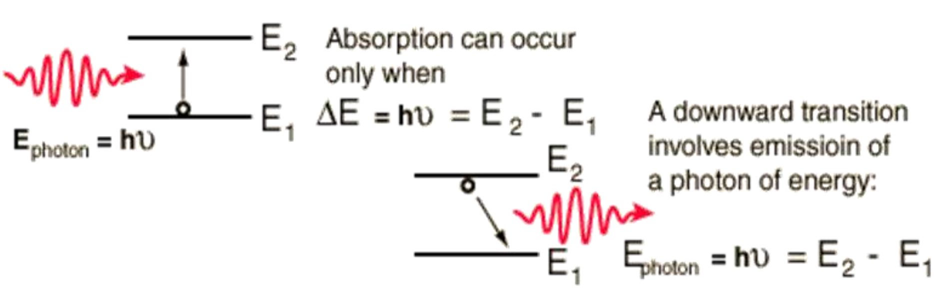
A hardware device that converts electrical energy into light and light into energy through semiconductors






## Optoelectronic Process

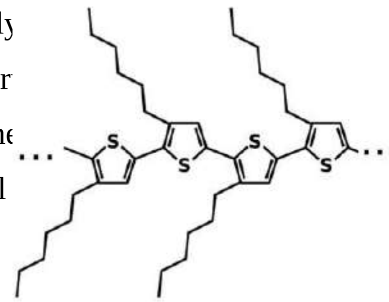
If the photon(or applied electrical field) has an energy larger than the energy a gap, the photon will be absorbed by the semiconductor, exciting an electron from the valence band into the conduction band, where it is free to move. A free hole is left behind in the valence band. When the excited electron is returning to valence band, extra photon energy is emitted in the form a light . This principle is used in Optoelectronic devices.



## Materials for Optoelectronic devices

### Organic materials for Optoelectronic devices [Light absorbing materials –Polythiophenes](P3HT)

Polythiophenes are an important class of conjugated poly environmentally and thermally stable material. Chemical str of P3HT Poly (3-hexylthiophene) is a polymer with che formula $(C_{10}H_{14}S)_n$. It is a Polythiophenes with a short alkyl on each repeat unit.



Highly ordered (P3HT) are composed of closely packed, p–p stacked (p–p distance of 0.33nm) fully extended chains which are oriented perpendicular to the substrate

**Properties:**

1. P3HT is a semiconducting polymer with high stability and exhibits conductivity due to holes therefore considered as p-type semiconductor.
2. Poly-3-hexylthiophene (P3HT) has great capability as light-absorbing materials in organic electronic devices.
3. P3HT has a crystalline structure and good charge-transport properties required for Optoelectronics.
4. P3HT has a direct-allowed optical transition with a fundamental energy gap of 2.14eV.
5. Fundamental band gap of P3HT is 490nm visible region, corresponding to $\pi \rightarrow \pi^*$ transition, giving electron-hole pair.
6. P3HT indicates that an increase in the conductivity is associated with an increase in the degreeof crystallinity.

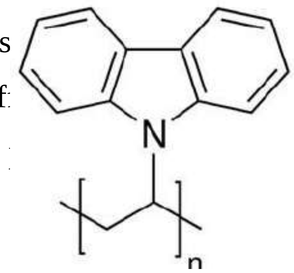


**Applications:**

1. P3HT-ITO forms a p-n junction permits the charge carriers to move in opposite direction and hence, used in Photovoltaic devices.
2. It can be used as a positive electrode in Lithium batteries.
3. Used in the construction of Organic Solar Cells.
4. Manufacture of smart windows.
5. Used in the fabrication new types of memory devices.

**Light emitting material-Poly [9-vinylcarbazole] (PVK)]**

Poly(N-vinyl carbazole) (PVK)is one of the highly process polymers as hole conducting material and therefore used as an ef hole transport material to prepare highly efficient and stable heterojunction perovskite solar cells.



**Structure of poly (9-vinylcarbazole)**

**Properties of PVK**

- It is a semiconducting polymer and an electron acceptor converts ultra-violet (UV) light into electricity.
- PVK has a band gap of 3.4 eV, optical absorption edge stating at 350 nm capable of absorbing Ultra-Violet light.
- The PVK film is hydrophobic, thermally stable with a relatively high glass transition temperature (Tg) of 200 °C
- The PVK solution also showed good wettability, and provide uniform thin films on glass/ITO substrates.



**Applications:**

1. PVK has been commonly used in OLEDs, light harvesting applications.
2. Used in the fabrication of light-emitting diodes and laser printers.
3. Used in the fabrication of organic solar cells when combined with TIO on glass substrate.
4. Used in the fabrication of solar cells when combined with Perovskite materials.

**Nano materials (Silicon Nano crystals) for Optoelectronic devices**

Any substance in which at least one dimensions is less than 100nm is called nano materials.

The properties of nano materials are different from bulk materials due to:

1. Quantum Confinement effect
2. Increased surface area to volume ratio

The improved electronic properties yielded for nanostructured silicon in comparison to its bulk, which led the use of Silicon Nano crystals in electronics and optoelectronics fields.

**Properties**

1. Silicon Nanocrystal has wider band gap energy due to quantum confinement.
2. Si-NCs shows higher light emission property (Photoluminescence)
3. Si-NCs exhibit quantum yield of more than 60%.
4. Si-NCs exhibit tunable electronic structure

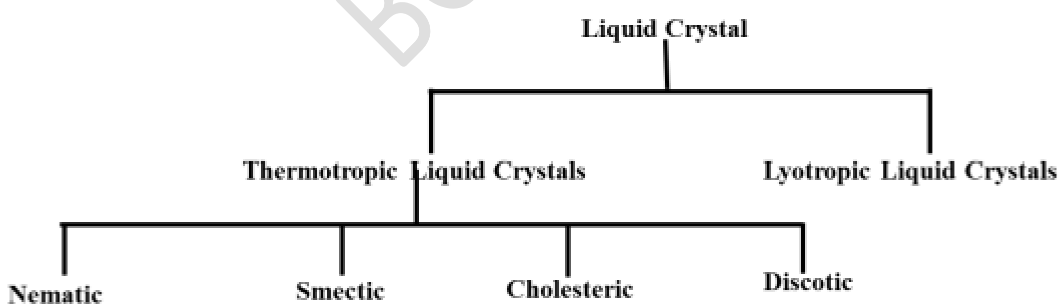
**Applications:**

1. Si-NCs are used in neuromorphic computing and down-shifting in photovoltaics
2. Si-NCs are used in the construction of novel solar cells, photo detectors and optoelectronic synaptic devices.

## LIQUID CRYSTALS

A distinct state of a matter in which degree of molecular ordering is intermediate between the ordered crystalline state and completely disordered liquid state.


**Classification:**




Liquid crystals are classified into two types

Thermotropic liquid crystals

Lyotropic liquid crystals

**1) Thermotropic liquid crystals (TLC):** The compounds which exhibit liquid crystal behaviorwith variation of temperature are called thermotropic liquid crystals.

Ex: 1) Cholesteryl Benzoate: (145.5°C & 178.5°C)

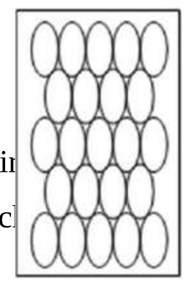

**2)** P-Azoxy Anisole: (118°C & 135°C)

**Types of Thermotropic liquid crystals:**

There are four types

a) Nematic Liquid Crystals (NLC)
b) Chiral Liquid Crystals or Cholesteric Liquid Crystals (CLC)
c) Smectic Liquid Crystals (SLC)
d) Columnar Liquid Crystals or Discotic Liquid Crystals (DLC)

**a)Nematic Liquid Crystals (NLC)**

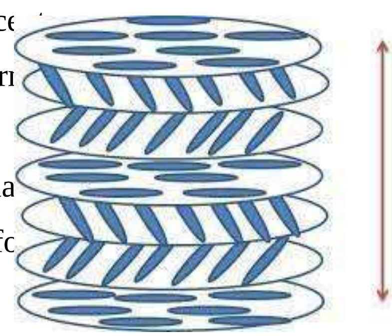


1. These are formed by the compounds that are optically inactive.
2. The molecules have elongated shape and are oriented parallel to thedir
3. These molecules possess intermolecular force of the attraction suc they stay parallel to one another to form nematic liquid crystals.

Ex: a) P-Azoxy Anisole (PAA)

b) P-Azoxy Phenetole

**b.Chiral Liquid Crystals or Cholesteric Liquid Crystals**



1. These are formed by optically active compounds having chiralce
2. Hence molecules acquire spontaneous twist about an axis norı molecular direction.
3. The twist may be right or left depending on molecular conforma
4. Molecules in successive layers are slightly twisted and fc

Ex: a) Cholesteryl benzoate

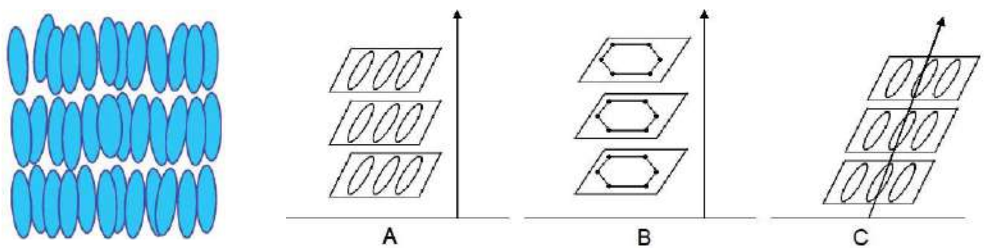
b) Cholesteryl formate etc.

**c. Smectic Liquid Crystals (SLC):**

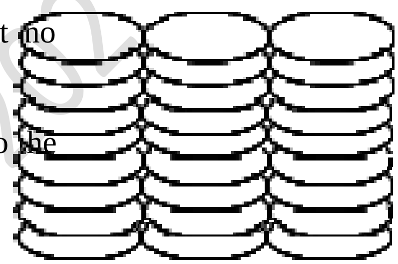
1. These liquid crystals have small amount of positional order and orientational order.
2. If the director is perpendicular to the plane, it is called smectic A. These are least ordered of the

orthogonal smectic phases. The molecules are arranged in columns.

3. If the director is perpendicular to the plane and molecules are arranged in hexagonal order, it is called smectic B.
4. If the director makes an angle other than 90°, it is called smectic C.




**d. Columnar Liquid Crystals or Discotic Liquid Crystals (DLC)**



1. In these liquid crystals, there is an orientation order but no positional order.
2. There is a random motion of the molecules perpendicular to the plane.
3. The molecules orient themselves along the director.
4. The molecules tend to position themselves in columns.
5. The columns are arranged in hexagonal lattice.



**2) Lyotropic Liquid Crystals:** Some of the compounds transformed into liquid crystal phase when mixed with another substance or solvent by the variation of concentration of the compound are called lyotropic liquid crystals

Ex: 1) Soap water mixture

2) Phospholipid water mixture

**Properties**

- Liquid crystal can flow like a liquid, due to loss of positional order
- These are elongated and have some degree of rigidity
- They have less orientational order
- Transition from crystalline solids to liquid crystals caused by a change of temperature.
- The intermolecular forces are rather weak and can be perturbed by an applied electric field.

- They interact with an electric field, which causes them to change their orientation slightly.

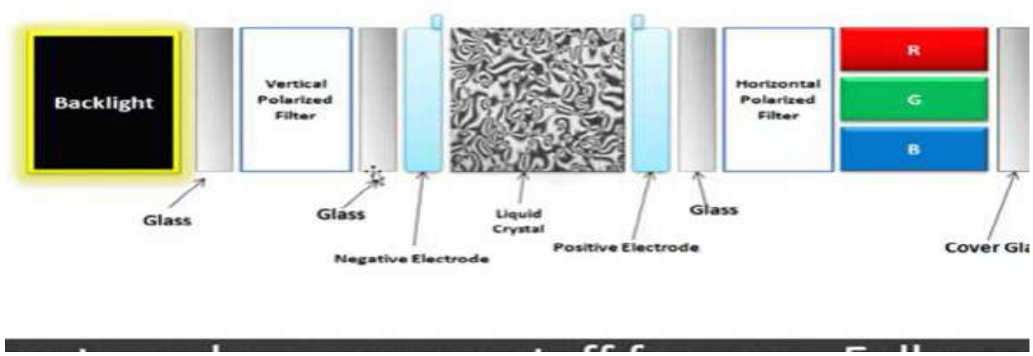
**Applications of liquid crystals:**

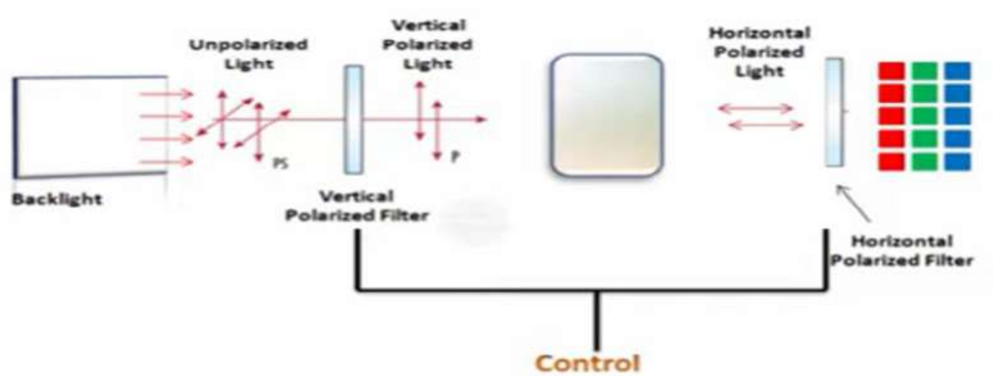
1. The liquid crystal layer in LCDs allows for the display of images and text through the use of electrical currents that control the orientation of the crystals.
2. Liquid crystals are used in watches, calculators, mobile telephones, laptops, computers etc.
3. These are used in blood pressure instrument, digital thermometers and TV Chanel indicators.
4. These are used in potentiometer, conductometer, Colorimeter etc.

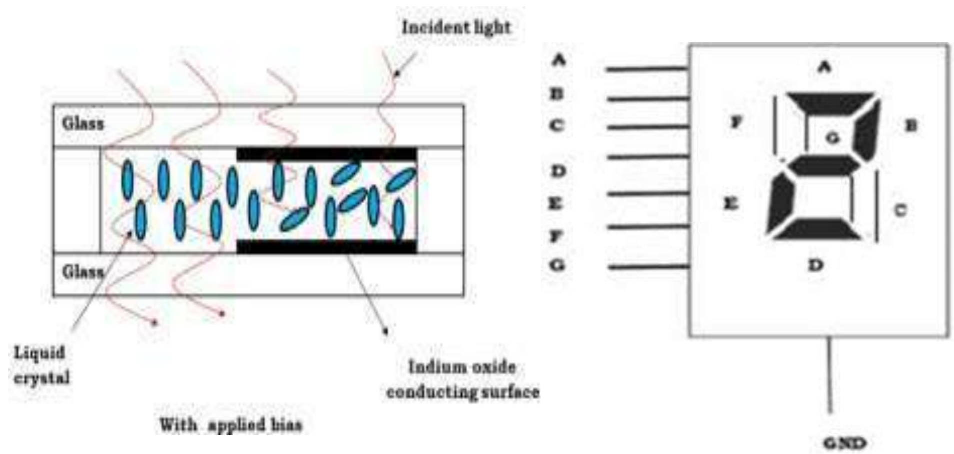
**Application of Liquid Crystal in Display System (LCD):**

**Working principle:**

Liquid-crystal displays (LCDs) consist of multiple layers. Light produced by a back light source (light-emitting diode) passes through polarizers color filters, and a liquid-crystal layer to produce an image.






- The basic working principle of LCD is blocking of light.
- When the external light passes from one polarizer to the next polarizer, the liquid crystal rotates the light angle by 90°, hence polarized light aligns itself so that the image is produced in the screen.
- The display panel is composed of backlight source , two polarizers , a mirrored surface.
- A thin film of the liquid crystal is placed between two glass sheets.
- The indium oxide conducting surface is a transparent layer which is placed on both the sides of the sealed thick layer of liquid crystal. In the absence of applied voltage, the liquid crystal molecules are precisely aligned.
- When the external bias is applied the molecular arrangement is disturbed
- This results in the polarized light from the first polarizer not being rotated by 90°completely to align with second polarizer.
- The second polarizer blocks the passing of light and causes the segment of the panel to appear black and the other area looks clear.

**For Example,**

In the segment arrangement, the conducting segment looks dark and the other segment looks clear. To display number 2 the segments A,B,G,E,D are energized.

The LCD can display images in colour by using filters that absorb different colours of light. First, a white light-emitting diode shines light toward the front of the display. The pixels actually consist of three sub pixels, one for each color—red, blue, and green. These sub pixels are made up of a liquid-crystal layer and the appropriate color filter sandwiched between two polarizing light filters. Transistor arrays switch the structural states of the liquid crystals to control whether or not a sub pixel gets lit up, which in turn produces all the colors in an image.

**Organic Light Emitting Diodes (OLED's)**

OLEDs are thin film devices consisting of a stack of organic layers sandwiched between two electrodes. OLEDs operate by converting electrical current in to light via an organic emitter.

OLED is an electroluminescent device that uses organic molecules as a source of light emission. Light is emitted by organic material when an external field is applied across it.

**Properties:**

Some of the key properties of Organic Light Emitting Diodes (OLEDs) include:

1. **Thinness and flexibility:** OLEDs are very thin and flexible, which makes them suitable foruse in curved or flexible displays.
2. **High contrast:** OLEDs have a high contrast ratio, which means that they can produce deep blacks and bright whites, resulting in images with vivid and rich colours.
3. **Fast response time:** OLEDs have a fast response time, which means that they can switch onand off quickly, resulting in smooth and seamless motion in video content.
4. **Wide viewing angle:** OLEDs have a wide viewing angle, which means that the image quality is maintained even when viewed from different angles.
5. **Energy efficiency:** OLEDs are energy efficient as they do not require a back light liketraditional LCD displays, resulting in lower power consumption.

**Applications**

1.OLED displays are commonly used in televisions, monitors, smartphones, and other electronic devices.

2.OLED displays can be used in advertising displays, such as digital billboards and signage, to produce high-quality and eye-catching visuals.

3.OLEDs can also be used as a source of lighting in various applications, including automotive lighting, street lighting

4. OLEDs can also be architectural lighting.

## Quantum Light Emitting Diodes (QLED's)

QLED is an electroluminescent device that uses quantum dots (QD's) as a source of light emission that can convert light energy into electrical energy or vice-versa.

(Quantum dot light emitting diodes are a form of light emitting devices consisting of nano-scale crystals that can convert light energy into electrical energy or vice-versa.)

**Properties:**

1. **Accurate and vibrant colours**: QLEDs are capable of producing highly accurate and vibrant colours due to their use of quantum dots, which emit light of a specific colour when they are excited by a light source or an electrical current.
2. **Energy-efficient**: QLEDs are more energy-efficient than traditional LCD displays becausethey do not require as much back lighting.
3. **High contrast**: QLED displays have high contrast ratios, which means that the difference between the darkest and brightest areas of the display is greater, resulting in more detailed and life like images.
4. **Long life span**: QLEDs have a longer life span than traditional LCD displays because they do not suffer from the same issue soft back light burnout or colour fading over time.
5. **Fast response times**: QLED displays have fast response times, which mean that they can display fast-moving images without motion blur or ghosting.
6. **Flexibility**: QLEDs can be made on flexible substrates, which allows for the creation of flexible displays that can be bent or curved.

**Applications**

1.QLED displays are commonly used in televisions, monitors, smartphones, and other electronic devices.

2.QLEDs can also be used as a source of lighting in various applications, including automotive lighting, street lighting, and architectural lighting.

3.QLEDs can be used in medical imaging applications, such as in MRI machines, to produce high-resolution and accurate images.

4.QLED displays can be used in advertising displays, such as digital billboards and signage, to produce high-quality and eye-catching visuals.

**Important questions**

1. What are Memory Devices? Explain the Classification of electronic memory devices with examples
2. Explain the types of organic memory devices by taking p- type and n-type semiconducting materials.
3. Discuss the use of Polyimide Polymeric material for Organic memory device.
4. Define Optoelectronic device. Explain the working principle of Optoelectronic device.
5. Define photoactive and electroactive materials and write their working principle in display system
6. What are nanomaterials? Explain any four properties and applications of Polythiophenes (P3HT) suitable for optoelectronic devices.
7. Write the properties and applications of Silicon Nano Crystals for Optoelectronic devices Properties of Silicon Nanocrystals for optoelectronics
8. Explain the classification of liquid crystals. Mention any four properties and applications of liquid crystals.
9. Discuss the working of Liquid Crystal Display.
10. Explain any four properties and applications of Light emitting materials - Poly[9-vinylcarbazole] (PVK)] suitable for optoelectronic devices.
11. What is OLED? Mention any four properties and applications of OLED.
12. What is QLED? Mention any four properties and applications of QLED.

# MODULE 3
# CORROSION AND ELECTRODE SYSTEM

**SYLLABUS**

**Corrosion Chemistry**: Introduction, electrochemical theory of corrosion, types of corrosion-differential metal and differential aeration. Corrosion control - galvanization, anodization and sacrificial anode method. Corrosion Penetration Rate (CPR) - Introduction and numerical problem.

**Electrode System**: Introduction, types of electrodes. Ion selective electrode – definition, construction, working and applications of glass electrode. Determination of pH using glass electrode. Reference electrode- Introduction, calomel electrode–construction, working and applications of calomel electrode. Concentration cell–Definition, construction and Numerical problems.

**Analytical Techniques:** Introduction, principle and instrumentation of Conductometry; its application in the estimation of weak acid. Potentiometry; its application in the estimation of iron.

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## CORROSION

### INTRODUCTION

**Corrosion** is a natural process that converts a refined metal into a more chemically stable oxide. It is the gradual deterioration of materials (usually a metal) by chemical or electrochemical reaction with their environment.

**Definition**

A process of deterioration or destruction of metal / alloy from its surface through an unwanted chemical or electrochemical attack by its environment is called corrosion.

Ex:

- Formation of a layer of reddish scale of hydrated ferric oxide on the surface of iron is called rusting of iron when Fe is exposed to moist air.
- Formation of green film of basic carbonate($CuCO_3 + Cu(OH)_2$) on the surface of copper,when it is exposed to moist air containing carbon dioxide.

**Cause of corrosion:**

- The combined state of metals(ore) has low energy and is stable
- The extracted metal through metallurgy process has higher energy and hence highly unstable
- Hence metals has the natural tendency to react with the environment to become stable that is how corrosion occurs.

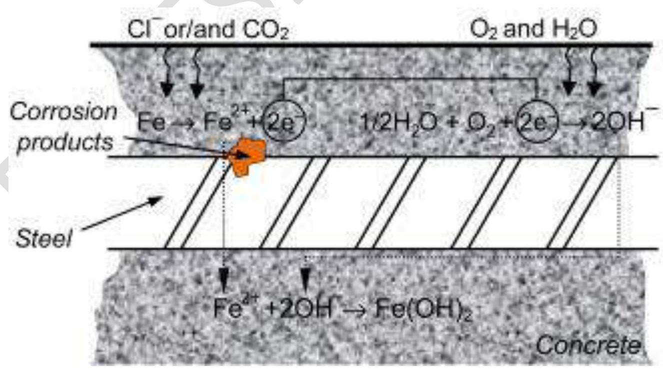
**Effects of Corrosion/global loss**

- Loss of metals/equipment
- The corrosion of steel reinforcing bars in concrete can occur without being noticed. It can cause the failure of a section of highway, damage to buildings, bridges, parking structures, and the collapse of electrical towers, etc., resulting in significant economic loss and jeopardizing public safety.
- Corrosion that occurs in major industrial plants, such as chemical processing plants or electrical power plants, is perhaps the most dangerous.
- Corrosion can cause severe failures in boiler tanks, pressure basins, blades of motors/turbines, harmful/aggressive chemical containers, airplane parts, automotive routing devices, and bridges.

## ELECTROCHEMICAL THEORY OF CORROSION

When a metal, such as iron/steel bar in concrete, is exposed to the environment, according to electrochemical theory the following electrochemical changes occur gradually.

- Anodic and cathodic areas are formed resulting in minute galvanic cells
- Oxidation (corrosion )takes place at the anodic area and electrons are liberated.
- The electrons released at the anodic area migrate to the cathodic area and reduction takes place.




**Step I: Reaction at anodic area**

Metal Fe dissolves to give $Fe^{+2}$ ions and electrons

$$Fe \rightarrow Fe^{+2} + 2e^- \quad \textbf{(oxidation reaction)}$$

**Step II: Reaction at cathodic area**

Electrons released at the cathodic area are conducted to the cathode and are responsible for various cathodic reactions.

1. ***In the presence of oxygen***: oxygen in the environment dissolves in the moisture

a. In acidic medium, $H^+$ ions reduced to $H_2O$

$4H^+ + 4e^- + O_2 \rightarrow 2H_2O$

b. In neutral or slightly alkaline medium, dissolved oxygen reduced to hydroxyl ions.

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Both the reactions involve absorption oxygen.

***2. In the absence of oxygen:***

a. In acidic medium, $H^+$ ions reduced to hydrogen gas

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

b. In neutral or slightly basic medium, moisture reduced to hydroxyl ions hydrogen gas

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

Both the reactions involve evolution of hydrogen gas.

**Step III: Formation of $Fe(OH)_2$**

Smaller $Fe^{+2}$ ions diffuses faster than the larger $OH^-$ ions to the cathodic area through the moisture and converted into $Fe(OH)_2$. Hence, the corrosion current flows between the anodic and cathodic areas through conducting media (metal).

$Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2$

**Step IV: Formation of Rust**

a. In the presence of excessive amount of oxygen, $Fe(OH)_2$ is converted into yellow rust (hydrated ferric oxide), $Fe_2O_3.3H_2O$.

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 2[Fe_2O_3.3H_2O]$ (yellow rust)

b. In the limited amount of DO, $Fe(OH)_2$ is converted into black rust (ferrouos ferric oxide), $Fe_3O_4.3H_2O$.

$3Fe(OH)_2 + \frac{1}{2} O_2 \rightarrow Fe_3O_4.3H_2O$ (black rust)



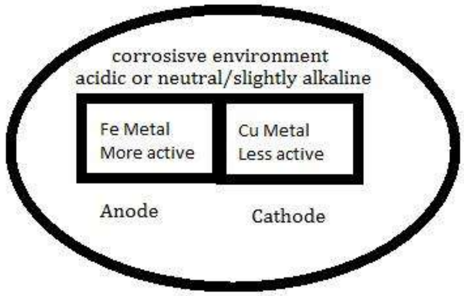
## TYPES OF CORROSION

### 1.Differential metal corrosion/Galvanic corrosion

**Definition** :Galvanic corrosion is a type of corrosion caused when two dissimilar metals are in contact with each other in a corrosive environment.

- The metal with lower reduction potential undergoes oxidation that acts as anode whereas the metal with higher reduction potential undergoes reduction acts as cathode and it is free from corrosion.
- The potential difference between the two metals is the cause for corrosion, higher the difference faster is the rate of corrosion.

Let us consider a bimetallic sample of iron and copper




- The standard electrode potential of Fe is – 0.44 V which is less than that of Cu whose standard electrode potential is 0.34 V
- Hence in this case iron acts as anode and undergoes corrosion whereas copper acts as cathode and remains un attacked.

The following are the reactions which occur during differential metal corrosion when Fe is in contact with Cu

**At anode**

$Fe \rightarrow Fe^{2+} + 2e^-$

**At cathode** either hydrogen evolution or oxygen absorption

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

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

**Examples**

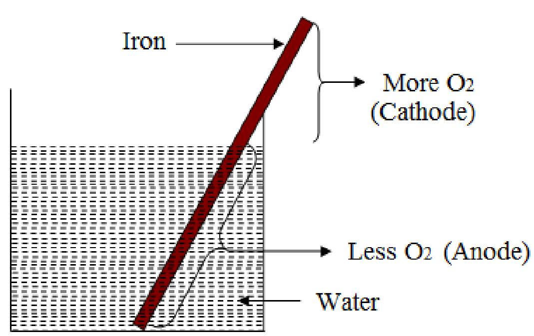
(i) Steel screws in copper sheet

(ii) Lead-tin solder around copper wire

(iii) Buried iron pipeline connected to Zinc bar.

(iv) Steel pipe connected to copper plumbing

**2.Differential aeration Corrosion**

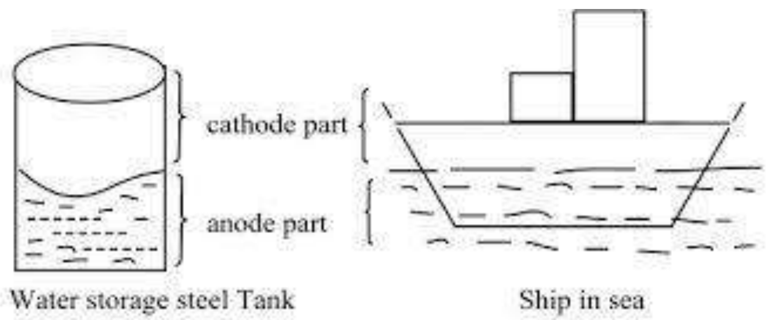



**Definition :**It is a type of corrosion occurs when a metal surface is exposed to differential air (or) oxygen concentration in a corrosive medium.

- Part of the metal exposed to lower concentration of oxygen will have lower potential and therefore acts as anode. This part undergoes corrosion.
- The other part of the metal exposed to higher concentration of oxygen acts as cathode and remains unaffected.
- ***At the anode*** (less $O_2$ concentration);  $M \rightarrow M^{n+} + n\,e^-$
- ***At the cathode*** (more $O_2$ concentration);  $H_2O + ½\,O_2 + 2e^- \rightarrow 2OH^-$

***Example:*** Waterline corrosion and pitting corrosion

**Water line corrosion**




- Waterline corrosion is a case of differential aeration corrosion that occurs in ocean going ships, water storage steel tanks , in which a portion of the metal is always under water.
- The part of the metal below the water line is less aerated while the part above the water is more aerated.
- Thus part of the metal below the water acts as anode and undergoes corrosion and part above the waterline is free from corrosion. Rusting is observed along a line just below the level of the stored water.

**At anode** $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

**At cathode** $H_2O + ½\,O_2 + 2e^- \rightarrow 2OH^-$ (reduction)

$$2Fe(OH)_2 + ½\,O_2 + H_2O \rightarrow Fe_2O_3.3H_2O \text{ (Rust)}$$

**Pitting corrosion**

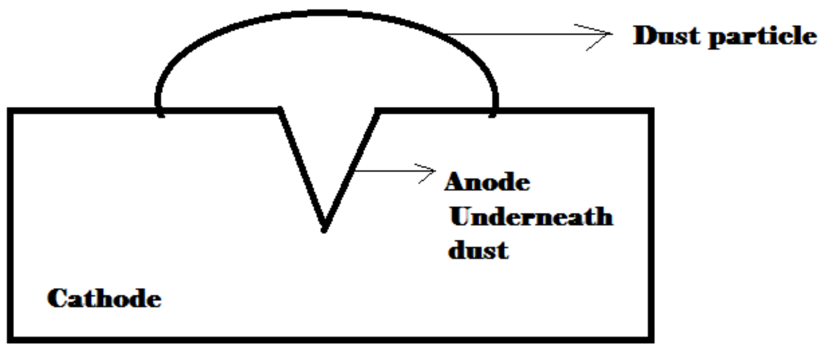
- Pitting corrosion is a localized corrosion on the small area of the metal surface resulting in the formation of pits or holes.
- The pitting corrosion is generally initiated by the deposition of sand, water drop, dust etc. or due to the breakdown of the protective film.

- The metal below the deposit is exposed to lower oxygen concentration acts as anode and the metal surrounding the deposit acts as cathode since it is exposed to higher concentration of oxygen.
- Corrosion starts under the dust resulting in a pit. The pit grows and ultimately may cause failure of the metal.

**Corrosion reactions:**

***At anode*** $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

***At cathode*** $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$ (reduction )




**CORROSION CONTROL**

Corrosion control refers to measures that are implemented in various fields to control corrosion.

The following methods are used to protect metals against corrosion:

- Proper Design and selection of materials
- By modifying environment
- Use of corrosion inhibitors
- **Protective coatings**
- **Cathodic Protection**

**Galvanization.**

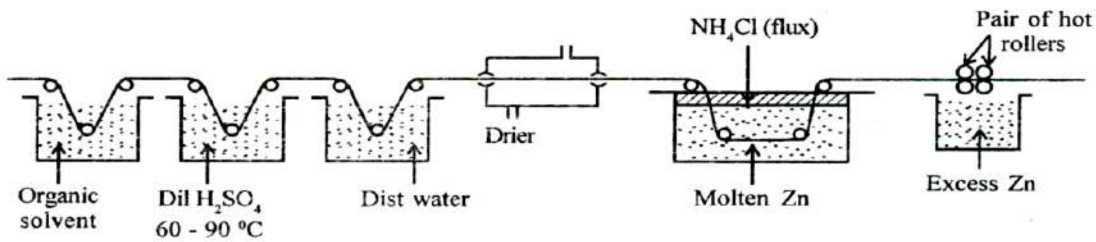
Is an example for metal coating that is deposition of a protective metal over the surface of a base metal.

***Definition:*** Galvanizing (Galvanization) is a process of coating a base metal surface with zinc metal.

Galvanization is carried out by hot dipping method. The galvanization process involves the following steps.

- The metal surface is first washed with organic solvents to remove oil and grease deposits.
- Rust and other deposits are removed by washing with dilute sulphuric acid (pickling).

- Finally the article is washed with water and air dried.
- The article is then dipped in a bath of molten zinc, maintained at 425-430$^0$C and covered with a flux of ammonium chloride to prevent the oxidation of molten zinc.
- The superfluous (excess) zinc on the surface is removed by passing through a pair of hot rollers, which wipes out excess of zinc coating and produces a thin coating.



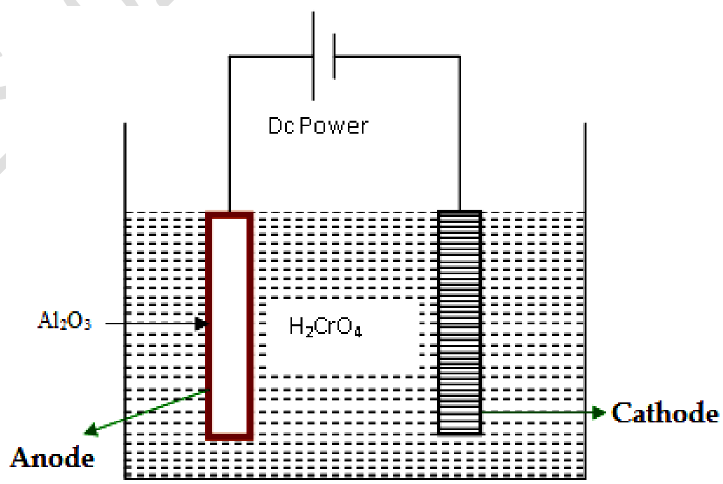

Galvanization of metal sheet

***Applications:*** Galvanization is most widely used for protection of iron from atmospheric corrosion in the form of roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc.

***Disadvantages*:** Galvanized articles are not used for preparing and storing food stuffs since zinc dissolves in dilute acids producing toxic compounds.

**Anodization**

***Anodizing:*** It involves the electrolytic oxidation of metal surface to produce a tightly adherent & durable oxide scale by passing electric current through an electrolyte to impart more protection against corrosion. Anodized coating is generally produced on non-ferrous metals like Al, Zn, Mg and their alloys.




**Anodising of Aluminium**

**Anode**: Aluminum

**Cathode:** Cu / Steel/Lead

**Electrolyte**: 5-10 % chromic acid or 10 % H2SO4

**Temperature**: 35oC

**Voltage**: 40 V

**Current density:** 100 A /m2

**Electrode reactions -At anode** (Oxidation): $2Al + 3\ H_2O \rightarrow Al_2O_3 + 6\ H^+ + 6\ e$

**At cathode** (Reduction): $6\ H^+ + 6\ e^- \rightarrow 3\ H_2$

**Overall reaction**: $2\ Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$

- The metal after pretreatment is made to act as anode and steel copper or lead acts as cathode.
- The electrolyte consists of 5-10 % chromic acid.
- The temperature of the bath is maintained at 35°C
- A current density of 100 A/m2 is applied which oxidizes the outer layer of Al to $Al_2O_3$
- An oxide layers of $Al_2O_3$ with a thickness 2-8 µm is formed.
- The outer part of the oxide film formed may be slightly porous and it is sealed by dipping in boiling water. This treatment converts porous alumina at the surface of coating into its monohydrate ($Al_2O_3.H_2O$) which occupies more volume, there-by the pores are sealed.
- For higher thickness 10% H2SO4 is used as the electrolyte

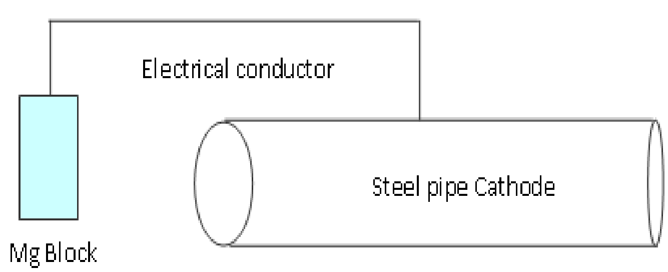
**Applications:** It is used providing attractive, highly durable exteriors, roofs, ceilings, floor, lobbies, escalators and staircases

**Cathodic Protection**

**Definition:** Cathodic protection is defined as a method of protecting a metal or alloy from corrosion by converting it completely into cathodic**.** Cathodic protection can be achieved by the following methods: (i) Sacrificial anode method (ii) Impressed current method.

**Sacrificial anode method:**

- In this method the metal to be protected from corrosion is converted into cathode by connecting into a metal which is anodic to it.
- The base metal is usually iron, copper or brass.




- Metals like Mg, Al and Zn are more active and hence are used as anodes.

- These metals being more active acts as anode undergo corrosion and supply electrons to the specimen.
- In this way the protected metals acts as cathode.
- Since anodic metals are scarified to protect the metal structure this technique is called sacrificial anode method.

Example: Mg block connected to buried oil storage tanks

**CORROSION PENETRATION RATE (CPR)**

**Definition**: The Corrosion penetration rate is the speed at which any metal or alloy deteriorates in a specific corrosive environment through chemical or electrochemical reactions.

It is also defined as the amount of weight loss per year in the thickness of metal or alloy due to corrosion.

The Corrosion penetration rate also referred as corrosion rate.

Corrosion penetration rate depends on following factors;

1. Nature of metal.
2. Nature of corrosive environment/medium.
3. Nature corrosion product.
4. Speed at which corrosion spreads in the inner portion of metal.

Following formula is used to determine CPR

$$CPR = \frac{KW}{DAT}$$

Where ,

- K-is constant
- W- Weight loss after exposure time
- D-density of metal/alloy
- A-surface area of exposed specimen
- T-exposure time in corrosive medium

**Units-**CPR expressed as **mmpy**(millimeter per year) or **mpy** (mils per year)

**Note-to remember**

| | **mmpy** | **mpy** |
|---|---|---|
| | | |

| Conversion factor |
|---|
| |

| | | |
|---|---|---|
| **K** | **87.6** | **534** |
| **W** | **mg** | **mg** |
| **D** | **$g/cm^3$** | **$g/cm^3$** |
| **A** | **$cm^2$** | **$Inch^2$** |

| |
|---|
| **$1m^2=100*100cm^2$** |
| **$1m^2=1550inch^2$** |
| **$1inch^2=6.45cm^2$** |
| **$1cm^2=0.155inch^2$** |

**PROBLEMS**

**1.A thickness of alloy sheet of area 100 $inch^2$ is exposed to air near the ocean.After 1 year period it was found to experience a weight loss of 35g due to corrosion. If the density of alloy 8.4 $g/cm^3$.Calculate CPR in mmpy and mpy.**

| Given | mmpy | mpy |
|---|---|---|
| K | 87.6 | 534 |
| W-35g | 35x1000mg | 35x1000mg |
| D-8.4 $g/cm^3$ | 8.4 $g/cm^3$ | 8.4 $g/cm^3$ |
| A-100 $inch^2$ | 100x6.45$cm^2$ | 100 $inch^2$ |
| T-1 year | 365x24 hrs | 365x24 hrs |



**Solution**

**To find mmpy**

$$\boldsymbol{CPR = \frac{KW}{DAT}}$$

= 87.6x35x1000/8.4x100x6.45x365x24

= 0.064mmpy

**To find mpy**

$$\boldsymbol{CPR = \frac{KW}{DAT}}$$

= 534x35x1000/8.4x100x365x24

= 2.54mpy

**2. A piece of corroded steel plate was found in a submerged ocean vessel. It was estimated that the original area of the plate was 10 inch$^2$ and that approximately 2.6 kg had corroded away during submersion. Assuming a corrosion penetration rate of 200 mpy for this alloy in sea water, estimate the time of submersion in years. The density of steel is 7.9 g/cm$^3$.**

$$CPR = \frac{KW}{DAT}$$

| Given |
|---|
| K =534 |
| W-2.6Kg=2.6x1000x1000mg |
| D-7.9 g/cm$^3$ |
| A-10 inch$^2$ |
| CPR =200mpy |
| T-? |

We can write

T= 534x2.6x1000x1000/7.9x10x200

T = 87873.41/365x24

**= 10.03 years**

## ELECTRODE SYSTEM

### ELECTROCHEMICAL CELL

A device which converts chemical energy into electrical energy and vice versa is known as Electrochemical cell. There are two types of electrochemical cell: galvanic and electrolytic cell.

**1. Galvanic cell** -A device which converts the chemical energy of spontaneous redox reactions into electrical energy.Eg.battery

**2. Electrolytic cell** - A device which converts electrical energy into chemical energy

### CELL TERMINOLOGY

- **Current:** The flow of electrons through a wire or any conducting medium is called current.
- **Anode** The anode is the negative that releases electrons to the external circuit and oxidizes during the electrochemical reaction.
- **Cathode** The cathode is the positive electrode that acquires electrons from the external circuit and is reduced during the electrochemical reaction.
- **Singe Electrode/Half-cell** A device consisting of a single electrode immersed in an electrolytic solution and thus developing a definite potential difference.
- **Single electrode potential or electrode potential (E):** The tendency of an electrode to lose (oxidation potential) or gain (reduction potential) electrons when it is in contact with the solution of its own ions.

  Or

  The potential developed when an electrode is in equilibrium with a solution of its own ions. It is denoted by "E".
- **Standard electrode potential ($E^0$):** The potential developed when the electrode is in equilibrium with 1M solution (1atm in case of gases) of its ions at 298K. It is denoted by '$E^0$'.

  **Ex:** $E^0_{Zn} = -0.76V$ & $E^0_{Cu} = +0.34V$
- **Electromotive force (EMF) of a cell:** The maximum potential difference between the electrodes of Galvanic cell. It is denoted by EMF or $E_{cell}$.

  $\mathbf{E_{cell} = E_{RHE} - E_{LHE}}$ or $\mathbf{E_{cell} = E_{cathode} - E_{anode}}$



## TYPES OF ELECTRODES

**1.Metal-metal ion electrode**: This type of electrode consists of a metal in contact with a solution of its own ions.

Eg: 1.Zinc in a solution of zinc sulphate.
2. Copper in a solution of copper sulphate.

**2.Metal-metal salt ion electrode**: This type of electrode consists of a metal in contact with one of its sparingly soluble salts and a solution of a soluble salt having a common anion with the sparingly soluble salt.

Eg: 1. Calomel electrode $Hg / Hg_2Cl_2 / Cl^-$
2.Silver-Silver chloride electrode $Ag / AgCl (s) / Cl^-$

**3.Gas electrode**: A gas electrode consists of a particular gas flushed around an inert electrode (Pt), which is dipped in a solution containing ions to which it is reversible.

Eg: SHE Pt / $H_2$ (1atm) / $H^+$ (1M)

**4.Oxidation-reduction electrode**: This type of electrode consists of an inert electrode (Pt or Au) immersed in a mixed solution containing both the oxidized and reduced forms of a molecule or ion.
Eg: Pt / $Fe^{2+}$: $Fe^{3+}$ Pt / $Sn^{2+}$: $Sn^{4+}$

**5.Ion selective electrode:** In ion selective electrode, a membrane is in contact with a solution, with which it can exchange ions.
Eg- Glass electrode.

**ION SELECTIVE ELECTRODE**

Ion-selective electrode is a membrane electrode which is selectively sensitive to a specific ion in a mixture and potential developed at the electrode is a function of concentration of that ion in the solution. The electrode generally consists of a membrane which is capable of exchanging the specific ions with the solution with which it is in contact. Therefore these electrodes are also referred to as membrane electrodes. Example: Glass electrode, Nitrate electrode, Fluoride electrode

| Reference electrode 2 | Solution to be analysed $[M^{n+}] = C_2$ | Internal stnadard solution $[M^{n+}] = C_1$ | Reference electrode 1 |
|---|---|---|---|

External reference electrode ⟷ Ion selective electrode



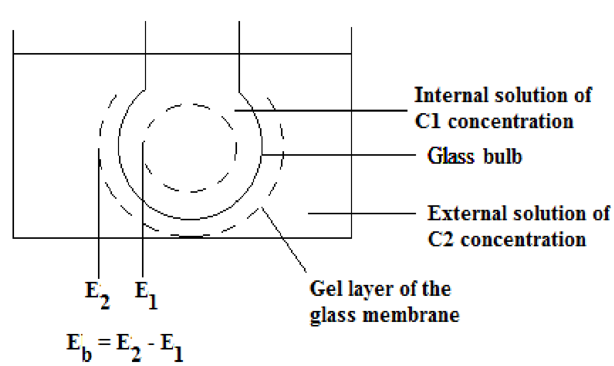
**GLASS ELECTRODE**

**Construction:** A glass electrode consists of a long glass tube with a thin walled glass bulb at one end. This glass can specifically sense hydrogen ions up to a pH of about 9. The bulb contains 0.1 M HCl and Ag/AgCl electrode (as internal reference electrode) immersed into the solution and connected by a platinum wire for electrical contact.

The electrode is represented as: Ag | AgCl (s) | HCl (0.1M)| Glass

**Working principle:**

A glass bulb containing an acid is immersed in analyte solution, a potential is developed across the glass membrane. The potential difference, $E_B$ at the interface also referred to as the ***boundary potential*** is the result of difference in potential



($E_1 – E_2$) developed across the gel layer of glass membrane between the two liquids.

The boundary potential, $E_B$ can be related to the difference in the hydrogen ion concentration of the two solutions by the relation,

$$E_B = E_2 - E_1$$

$$E_B = (E^0 + \frac{0.0591}{n}\log C_2) - (E^0 + \frac{0.0591}{n}\log C_1) \quad -----1$$

Where $C_2$ is the concentration of $H^+$ ions of acid solution inside the glass bulb and $C_1$ is the concentration of the acid solution into which the glass bulb is dipped.

$$E_B = \frac{0.0591}{n}\log[C_2] - \frac{0.0591}{n}\log[C_1] \quad -----2$$

Since concentration of $C_1$ is known,

$$E_B = \frac{0.0591}{n}\log[C_2] + \text{Constant}$$

Since $C_2$= [$H^+$] of the solution,

$$E_B = \frac{0.0591}{n}\log[H^+] + \text{Constant}$$

$$E_B = \text{Constant} - 0.0591\ \text{pH}$$

$$E_B = L - 0.0591p^H \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

Where, L is a constant, which depends primarily on the pH of the solution taken in the bulb and glass electrode assembly.

The membrane undergoes an ion exchange reaction; $Na^+$ ions on the glass are exchanged for $H^+$ ions.

The boundary potential established due to the above reaction is mainly responsible for the glass electrode potential $E_G$ is given by

$$E_G = E_B + E_{Ag/AgCl} \ldots\ldots\ldots\ldots(5)$$

From equation (1), $E_B = 0$ when $C_1 = C_2$. But in practice, it has been observed that even when $C_1 = C_2$, a small potential is developed. This is called asymmetric potential ($E_{asy}$). Hence, Equation (5) can be written as

$$E_G = E_B + E_{Ag/AgCl} + E_{asy}$$

$$E_G = L - 0.0591\ pH + E_{Ag/AgCl} + E_{asy}$$

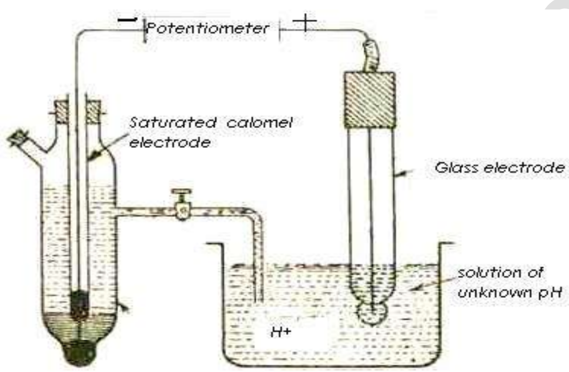
$$\mathbf{E_G = E_G^0 - 0.0591\ pH} \ldots\ldots\ldots\ldots(6)$$

Where $\mathbf{E_G^0}$ is a constant equal to $L + E_{Ag/AgCl} + E_{asy}$

**Application of Glass electrode:** Glass electrode is used to determine the pH of an unknown solution.

**Determination of pH of the solution by using glass electrode**

The glass electrode is immersed in a solution of which pH is to be determined. It is combined with a reference electrode such as a calomel electrode through a salt bridge. The cell assembly is represented as:




Calomel electrode || Solution of unknown $p^H$ |glass electrode

or

Hg | $Hg_2Cl_2$ (s) | KCl (sat.) || Solution of unknown $p^H$ |glass | HCl (0.1M) | AgCl | Ag(s)

The EMF of the above cell, $E_{cell}$ is measured using an electronic potentiometer. $E_{cell}$ measured is the difference between potential of glass electrode $E_G$ and calomel electrode ($E_{cal}$).The potential developed at the indicator glass electrode is higher than the reference calomel electrode ($E_G > E_{cal}$).

Hence, $E_{cell} = E_{cathode} - E_{anode}$

$= E_G - E_{cal}$

$E_{cell} = [E_G^0 - 0.0591\ pH] - E_{cal}$ (Since, $E_G = E_G^0 - 0.0591\ pH$)

$0.0591pH = E_G^0 - E_{CAL} - E_{CELL}$

Therefore, **pH =** $\dfrac{E_G^0 - E_{CAL} - E_{CELL}}{0.0591}$

Where, $E^0_G$ and $E_{cal}$ are constants. By substituting $E_{cell}$ value, $p^H$ of an unknown solution is calculated.

Note: $E^0_G$ value is evaluated by dipping the glass electrode in a solution of known $P^H$ and measuring EMF of the cell formed when combined with calomel electrode.

## REFERENCE ELECTRODE

Any electrode of constant and reproducible potential, used to determine the potential of other electrode is called reference electrode.

Ex: Standard hydrogen electrode — primary reference electrode

Calomel electrode — secondary reference electrode

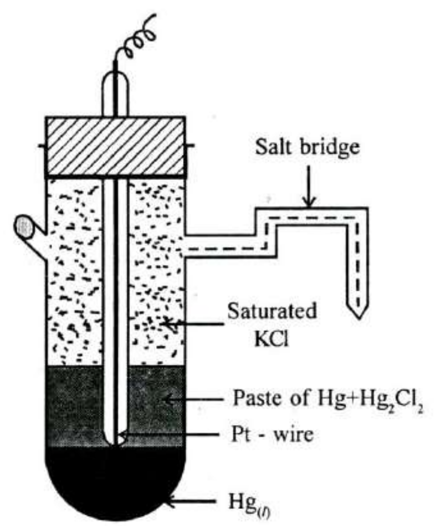
Ag-AgCl electrode — secondary reference electrode

**Construction, working and applications of calomel electrode**

**Construction*:***Calomel electrode is a metal-metal salt ion electrode. A platinum wire is sealed inside a glass tube dipped into mercury and used to provide the external electrical circuit. Mercury is placed at the bottom of glass tube. A paste of calomel ($Hg_2Cl_2$) and mercury is placed over the pool of mercury. The remaining part of the tube is filled either a saturated or standard solution of potassium chloride. The calomel electrode is represented as:

**$Hg_{(s)} | Hg_2Cl_{2(s)}$ | KCl (Sat)**






**Working principle:** Calomel electrode can act as anode or cathode depending on the nature of the other electrode of the cell. The electrode reactions are represented as follows:

**As anode:**

$2Hg \rightarrow Hg_2^{2+} + 2e^-$

$\underline{Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2}$

$2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$

**As cathode:**

$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2Cl^-$

$\underline{Hg_2^{2+} + 2e^- \rightarrow 2Hg}$

$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$

The net reversible electrode reaction is

$$\frac{1}{2} Hg_2Cl_2 + e^- \rightarrow Hg\,(l) + Cl^-\,(aq)$$

Electrode potential of calomel electrode is given by:

$$E = E^0 - 0.0591 \log [Cl^-] \text{ at } 298\text{ K}$$

Since the calomel electrode is reversible with respect to chloride ion its electrode potential depends on the concentration of KCl solution. At 298K, the electrode potentials as follows:

| KCl concentration | 0.1N | 1N | Saturated |
|---|---|---|---|
| Electrode potential (V) | 0.334 | 0.281 | 0.2422 |

**Advantages of calomel electrode (a secondary reference electrode):**

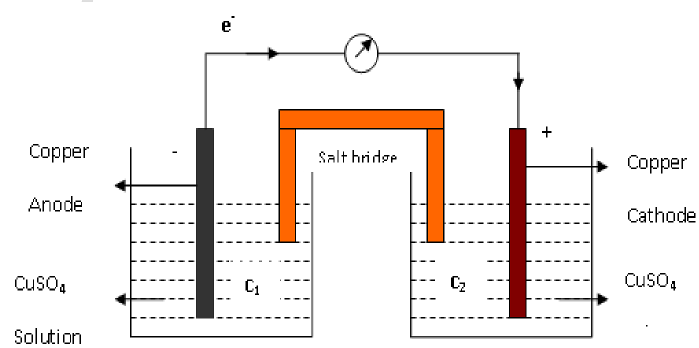
1. It is very simple in construction.
2. The potential is reproducible and stable over a long period.
3. Its electrode potential will not vary with temperature.

**Applications of calomel electrode:** It is the most commonly used as secondary reference electrode for potential measurements of unknown electrodes.



**CONCENTRATION CELLS**

**Definition:** A concentration cell is a galvanic cell which generates electrical energy at the expense of chemical energy. Unlike galvanic cells, a concentration cell consists of two electrodes of same material and same electrolyte but with different concentrations.




**Construction**: Electrolyte concentration cell is a galvanic cells consisting of both anode and cathode made up of same element (metal or nonmetal) in contact with the solutions of the same electrolyte of different concentration. A typical Copper concentration cell is shown in figure. It consists of two copper electrodes, immersed in $CuSO_4$ solutions of two different concentrations. These two electrodes are externally connected by metallic wire and internally by a salt bridge. The cell can be represented as,

$$Cu \mid Cu^{2+} (C_1) \parallel Cu^{2+} (C_2) \mid Cu \quad \text{Or}$$

$$Cu_{(s)} / CuSO_4 (C_1) // CuSO_4 (C_2) / Cu_{(s)} [\text{where } C_2 > C_1]$$

**Working principle:** By convention left hand electrode is the anode and right hand electrode is cathode.

| | |
|---|---|
| At anode | $Cu \rightarrow Cu^{2+} (C_1) + 2e$ |
| At cathode | $\underline{Cu^{2+} (C_2) + 2e \rightarrow Cu}$ |
| Net cell reaction | $Cu^{2+} (C_2) \rightarrow Cu^{2+} (C_1)$ |

The net cell reaction is merely the change in concentration; as a result the current flows through the circuit.

The Nernst equation for the EMF of a concentration cell is given by the equation:

$$E_{cell} = \frac{0.0591}{n} \log\left[\frac{C_2}{C_1}\right] \text{at } 25^0;\ C_1 < C_2$$

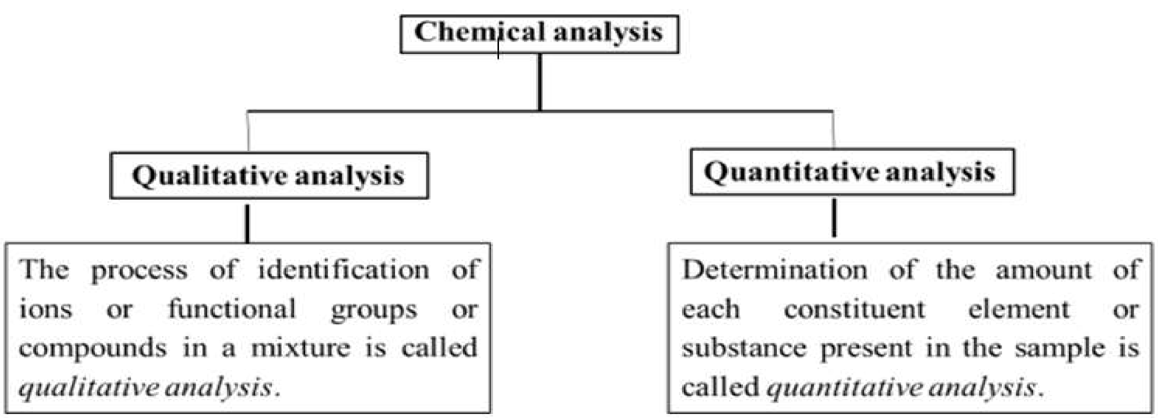
**Applications:** Used to determine the valence state of metal ions

## ANALYTICAL TECHNIQUES

### Introduction

The study of the chemical composition and structure of substances is known as chemical analysis. Chemical analysis deals with method of identification, quantification and determination of molecular structure of a substance.

**Two types of chemical analysis,**




### CONDUCTOMETRY

It is a qualitative chemical analysis in which sample concentration is determined conductometrically. Changes in electrical conductivity is measured when a specific analyte interacts between the electrodes.

Electrolytic conductance is a measure of the ability of a solution to carry an electric current. Electrolytic solutions conduct current due to migration of ions under the influence of an electric field.

Electrolytic conductivity of an electrolytic solutions depends on following factors,

- Type of ions (cations, anions, singly or doubly charged)
- Concentration of ions
- Temperature
- Mobility of ions

**Principle:**

Conductity of electrolytic solutions is similar to the metallic conductors. It obeys Ohm's law

i.e. **E = I R**

Where

- E is applied potential(volts)
- I is current(amperes)
- R is the resistance.(ohms)-

**Resistance-** Is the measure of the hindrance caused for the flow of current under the potential applied.

**Conductance** - Reciprocal of resistance. (Ease with which current flows per unit area of the conductor per unit potential applied.)

**C= 1/R or C=I/E** It is expressed in $ohm^{-1}$ or Siemen(S)

It is known that resistance of any conductor is directly proportional to the length and inversely proportional to the area of cross section of the conductor.

**R = S(l/a)**

Where

- **S is specific reistance** (is resistance offered by a conductor of unit length having unit cross section )
- l – length of the conductor
- a- area of cross section

**S = aR/l**

**Specific conductance:** is the conductance of an electrolyte solution kept between two electrodes of 1m2 cross sectional area at 1 m apart. It is conductance of a meter cube of the solution.

The specific conductance (conductivity), κ (kappa) is the reciprocal of the specific resistance.

k = 1/S or k = l/a x 1/R

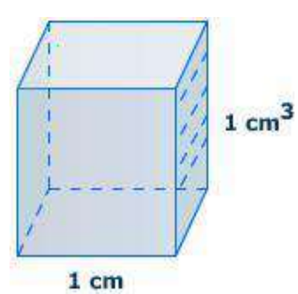
we have C =1/R

Therefore , k =l/a x C

Or C =l/a x k

Where l/a is Cell constant.

SI unit of Specific conductance **is** $\mathbf{Sm^{-2}}$






**Instrumentation and measurements**

The instrument used for measurement of conductance is called conductometer.

It consists of,

- Current source :AC source
- Conductivity cell : Made pyrex or quartz fitted with two Platinum electrodes
- Electrodes : Thin plates of Pt. each of unit area of cross-section placed unit distance a part

The electrodes are dipped in the electrolyte solution taken in a beaker and It is connected to a conductance measuring device. The titrant is added from a burette and solution is stirred. The conductance is measured after the addition of the titrant at intervals of 0.5 ml. The electrical conductivity of a solution of an electrolyte is measured by determining the resistance of the solution between two flat or cylindrical electrodes separated by a fixed distance .

**Conductometric titrations**

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

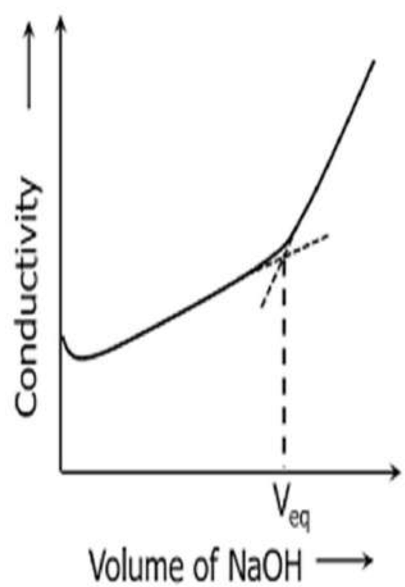


**Eg.Weak Acid with a Strong Base**

E.g. acetic acid with NaOH:

$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$

- Since the acid is weak, its conductivity is relatively low and decrease in conductance due to the replacement of H+ by Na+ and common ion effect.
- But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated $CH_3COOH$ to $CH_3COONa$ which is the strong electrolyte



- Beyond the equivalence point, conductance increases more due to the highly conducting $OH^-$ ions

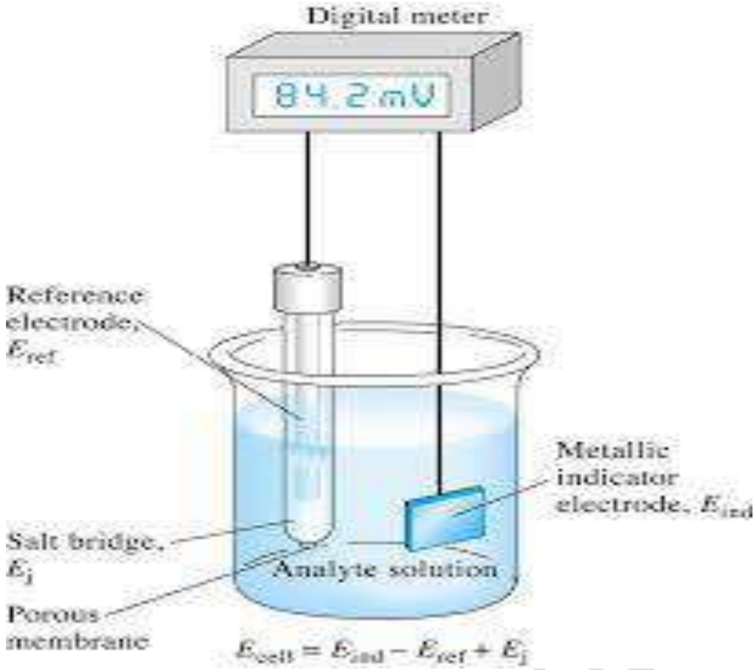
**POTENTIOMETRY**

It is a method of analysis in which the determination of concentration of an ion or substances by measuring the potential developed when a sensitive electrode is immersed in the solution of species to be determined. Potential of the electrode is a function of ratio of concentration of reduced species to the concentration of oxidized species of a specimen (metal ion or a compound).

**Potentiometric Titration in Determination of Iron:**

Determination of iron can be done using potentiometry method. It is a technique similar to direct titration of a redox reaction. No indicator is used; instead the potential is measured across the analyte, typically an electrolyte solution. Potentiometer is used to determine the difference between the potential of two electrodes. The potential of one electrode — the working or indicator electrode — responds to the analyte's activity and the other electrode — the reference electrode - has a known, fixed potential.

The typical potentiometric analytical cell has two electrodes immersed in a solution containing the analyte, whose concentration is to be measured. The reference electrode (Calomel, Ag-agCl electrodes) and indicator electrode is Pt whose response depends on the concentration of the analyte and the instrument used is modern electronic voltmeter or potentiometer.




The potential of a potentiometric electrochemical cell is

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

Where $E_{cathode}$ and $E_{anode}$ are reduction potentials for the redox reactions at the cathode and the anode. Reduction potential is calculated using the Nernst equation:

$$E = E^0 + \frac{RT}{nF} 2.303 \log \frac{[M^{n+}]}{[M]}$$

This is redox titration where Mohr's salt is a reducing agent and $K_2Cr_2O_7$ is an oxidizing agent. Titration is carried out read the potential difference. Initially the potential difference is with respect to ferric ferrous system:

$Pt_{(s)} \mid Fe^{3+}, Fe^{2+}$

Reduction reaction of this system is:

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ (aq.)

Potential developed is given by the Nernst equation shown below:

$$E_{Fe3+/Fe2+} = E^0 + 0.0592 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

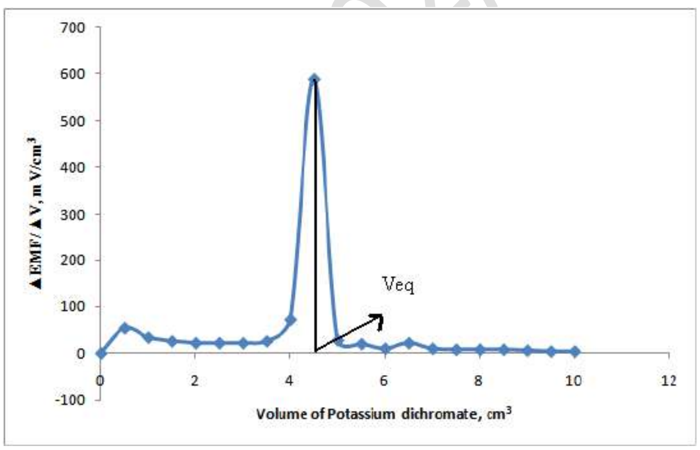
Thus potential of this electrode is determined by the ratio, $[Fe^{2+}]/[Fe^{3+}]$.The formal potential (standard potential under the specified experimental conditions) of this system is +0.68 V in 1M $H_2SO_4$ with respect to SHE (standard hydrogen electrode).

$Fe^{2+}$ ions are oxidized to $Fe^{3+}$ions, when dichromate solution is added.

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Dichromate ions are reduced to $Cr^{3+}$ ions by $Fe^{2+}$ ions. Thus the ratio,$[Fe^{2+}]/[Fe^{3+}]$ gradually decrease and hence $E_{Fe^{3+}/Fe^{2+}}$gradually increases in accordance with the Nernst equation, when dichromate is added to Mohr's salt solution. This occurs until the end point.

After the endpoint, dichromate remains in solution, because $Fe^{2+}$ ions do not exist in solution to react with it. Hence potential of the redox electrode is determined by $Cr_2O_7^{2-}/Cr^{3+}$coupleinstead of $Fe^{3+}/Fe^{2+}$couple after the end point. The formal potential of $Cr_2O_7^{2-}/Cr^{3+}$ system is about +1.3V in 1M $H_2SO_4$ w.r.to SHE. Hence a steep change in the electrode potential results at the endpoint. Then again gradual increase in the EMF.




## Applications

- It is used for all types of volumetric analysis: acid base, redox, precipitometry and complexometry.
- Used to highly colored and turbid solutions.
- For very dilute solutions
- Used when there is no availability of indicator for the titration

**Important questions**

1. What is metallic corrosion? Explain electrochemical theory of corrosion taking iron as an example.
2. Explain differential metal corrosion ?
3. Explain differential aeration corrosion with waterline and pitting corrosion examples.
4. Describe galvanizing and mention its application
5. Explain sacrificial anode method for the corrosion control
6. What is anodizing? Explain anodizing of aluminium. Mention its applications
7. Identify and explain the type of corrosion taking place in the following cases.
   i. Bolt and nut made up of two different metals in contact with each other.
   ii. Presence of dust particles on the metal surface for a long time.
   iii. Iron bolt in copper vessel is undesirable.
   iv. Ship sailing in water suffers differential aeration corrosion while the ship sunk in sea water does not.
8. What are ion selective electrodes? Explain the construction and working principle of glass electrode. Mention the advantages and disadvantages of glass electrode
9. What are reference electrodes? Describe how potential of the given electrode measured using calomel electrode.
10. What are concentration cells? Represent a cell formed by immersing two silver electrodes in silver nitrate solutions of concentration 0.01 and 0.1 M. Write the reactions and find the emf of the cell
11. Two copper rods are separately placed in copper sulphate solution of different concentrations. The concentration of copper sulphate solution in one electrode system is 100 times more than the other. Represent the cell and find the emf of the cell at 300K
12. Explain how the pH of the given solution is determined using glass electrode
13. Briefly explain the principle, instrumentation and working of potentiometry taking estimation of Iron as example.
14. Explain the application of conductometry in estimation of weak acid.
15. Explain the principle, instrumentation and working of conductometry.

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## MODULE 4- POLYMER AND GREEN FUELS

**SYLLUBUS**

**Polymers:** Introduction, Molecular weight - Number average, weight average and numerical problems. Preparation, properties and commercial applications of Kevlar. Conducting polymers– synthesis and conducting mechanism of polyacetylene and commercial applications. Preparation, properties and commercial applications of grapheme 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.

=====================================================================

# Polymers

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

Mainly there are two types of polymers:

1) Natural polymers: Rubber, resins, cellulose etc.
2) Synthetic polymers: Nylon, PVC, Bakelite etc.

**Monomer:** 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.

Ex. Ethene CH2=CH2

Hence monomers are often called as the building blocks of a polymer chain. The properties of polymers are different from that of the monomers from which they are formed. Polymers have high molecular weight (Ranging from 10,000 to 1,00,000)

**Types of Polymers**

- There are many types of polymers based on origin: natural (silk, collagen, keratin cellulose, starch, glycogen) and synthetic polymers Plastics Fibers
- Based on the type of monomer unit: homo polymer (polystyrene) and Copolymer : [A-B-A-B-A-B]- type
- **Homopolymers:** These consist of chains with identical bonding linkages toeach monomer unit. This usually implies that the polymer is made from allidentical monomer molecules. These may be represented as : -[A-A-A-A-A-A]- Homopolymers are commonly named by placing the prefix poly in frontof the constituent monomer name. For example, polystyrene is the name for the polymer made from the monomer styrene (vinylbenzene).
- Copolymers: These consist of chains with two or more linkages usually implying two or more different types of monomer units. These may be represented as : -[A-B-A-B-A-B]-

Polymers classified by mode of polymerization

- **Addition Polymers:** The monomer molecules bond to each other without the loss of any other atoms. Addition polymers from alkene monomers orsubstituted alkene monomers are the biggest groups of polymers in this class. Ring opening polymerization can occur without the loss of any smallmolecules.
- **Condensation Polymers:** Usually two different monomer combine with theloss of a small molecule, usually water. Most polyesters and polyamides (nylon) are in this class of polymers. Polyurethane Foam in graphic above.

**Polymerization:**

The chemical process by which monomers are converted into polymers is known as polymerization. To convert monomer into polymer, small quantity of chemicals known as initiators are needed. Temperature and pressure should be maintained.

$$\text{Monomer} + \text{Initiator} \xrightarrow[\text{Pres.}]{\text{Temp}} \text{Polymer}$$

$$\underset{\text{Ethylene monomer}}{nCH_2{=}CH_2} + \text{Peroxide initiator} \longrightarrow \underset{\text{Polythene}}{[CH_2\text{-}CH_2]\text{-}_n}$$

Examples for initiators: Dibenzoyl peroxide, Zieglar Natta catalyst, aliphatic azo compounds. Suitable Temperature and pressure should be maintained.

**Methods of Polymerization:**

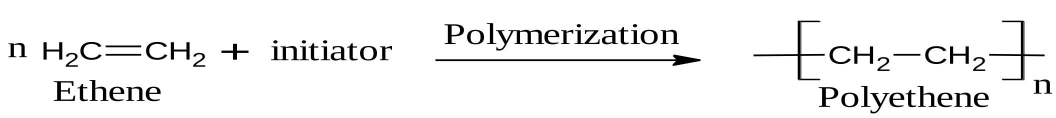
There are mainly two methods of polymerization which are classified as:

1) Addition polymerization

2) Condensation polymerization.

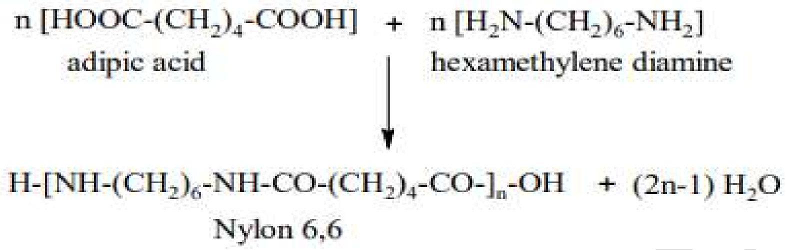
**1) Addition polymerization**: [chain growth polymers]-**Free radical polymerisation**

- An addition polymer is a polymer formed by chain addition reactions between monomers that contain a double bond without the elimination of byproduct.
- Unsaturated monomers [containing double bond or triple bond] normally undergo addition polymerization.
- Addition polymerization is initiated by initiators such as hydrogen peroxide, dibenzoyl peroxide [$C_6H_5CO\text{-}O\text{-}O\text{-}OCC_6H_5$], or Zeigler-Natta catalyst [$TiCl_4 + (C_2H_5)_3\,Al$], heat or pressure.
- Eg: Molecules of ethene can polymerize with each other under the right conditions to form the polymer called polyethylene.
- Addition process proceed through free radical mechanism. Free radical polymerization proceeds in three different steps: initiation, propagation and termination.



2. **Condensation polymerization** :[Step growth polymers]

- A polymerization reaction in which two or more monomers (similar or dissimilar) undergo intermolecular condensation with continuous elimination of byproducts such as $H_2O$, HCl, $NH_3$, alcohol etc is called condensation polymerization.
- Thus the resulting material is a copolymer. e.g. Nylon is made by the condensation of adipic acid with hexamethylene-diamine



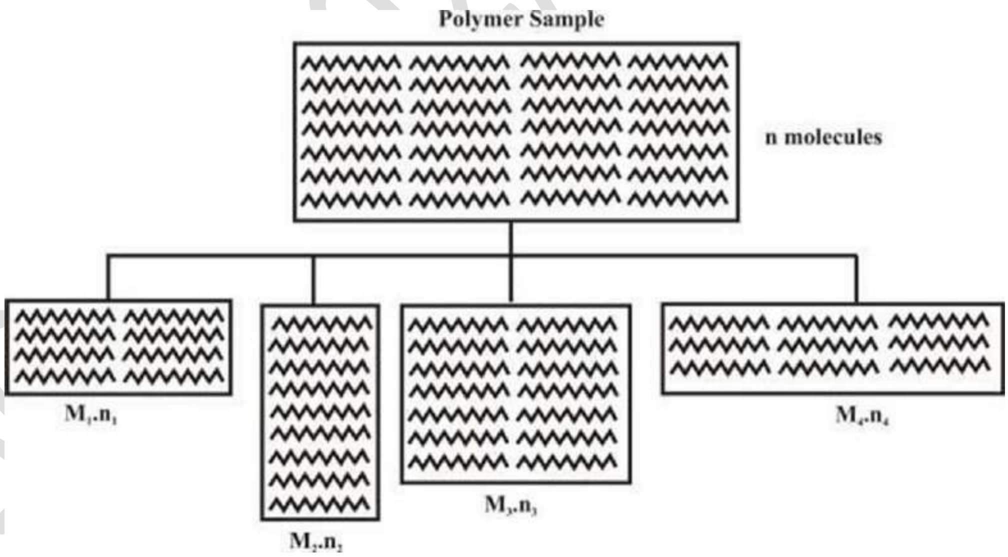

**Degree of polymerization (DP):**

Degree of polymerization is the number of repeating monomeric units present in a polymer. Degree of polymerization is related to the molecular weight of the polymer [M] by the equation,

M = m x DP (where m: Molecular weight of monomer unit)

**Molecular weight of a Polymer:**

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




As the polymers are made up of mixture of molecules having different properties, its molecular weight can be determined in two different ways :

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

**Number – average molecular mass ($\bar{M}n$):** Number average molecular weight is the mole fraction of molecules in a polymer sample. It is a way of determining the molecular mass of a polymer. It gives the average of the molecular masses of the individual macromolecules.

It is defined as total mass of all the molecules in a polymer sample divided by total number of molecules present.

$$\mathbf{M_n = \sum N_iM_i / \sum N_i}$$

$$\overline{Mn} = \frac{N_1M_1+N_2M_2+N_3M_3+\cdots}{N_1+N_2+N_3\ldots..}$$

Here, $M_n$ is the number average molecular weight, $N_i$ is the number of molecules having $M_i$ weight in the polymer sample, and $M_i$ is the weight of a particular molecule of the sample

1. **Weight average molecular weight ($\bar{M}w$):** Weight average molecular weight is the weight fraction of molecules in a polymer sample. It is another way of determining the molecular mass of a polymer. It gives the average of the molecular masses of the individual macromolecules in the polymer sample. We can find this parameter using the following equation:

$$M_w = \sum \mathbf{N_iM_i^2} / \sum \mathbf{N_iM_i}$$

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \cdots}{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}$$

Where $M_W$ is the weight average molecular weight, $N_i$ is the number of molecules of molecular mass $M_i$.

**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**.**

**Problems on Molecular weight**

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.

**Solution:**

| Sl. No | No of Molecules(N) | Molecular Mass( M) g/mol |
|---|---|---|
| 1 | $N_1$= 100 | $M_1$= $10^3$ |
| 2 | $N_2$=250 | $M_2$= $10^4$ |

| | | |
|---|---|---|
| 3 | $N_3$= 300 | $M_3$= $10^5$ |

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

$$\overline{Mn} = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}{N_1 + N_2 + N_3 \ldots..}$$

$$\overline{Mn} = \frac{100 * 10^3 \ + 250 \ * 10^4 + 300 * 10^5}{100 + 250 + 300}$$

**= 50153 g/l**

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

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \cdots}{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}$$

$$\overline{Mw} = \frac{100*(10^3)*(10^3)+250*(10^4)*(10^4)+300*(10^5)*(10^5)}{100*10^3+250*10^4+300*10^5}$$

**= 92794 g/l**

**PDI** = $\frac{\overline{\boldsymbol{Mw}}}{\overline{\boldsymbol{Mn}}}$

= 92794/50153

=1.85

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

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,

| Sl No | No of Molecules(N) | Molecular Mass( M) g/mol |
|---|---|---|
| 1 | $N1$= 20 | $M1$= 15000 |
| 2 | $N2$=35 | $M2$= 25000 |
| 3 | $N3$= 45 | $M3$= 20000 |

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

$$\overline{Mn} = \frac{N_1M_1+N_2M_2+N_3M_3+\cdots}{N_1+N_2+N_3 \ldots..}$$

$$\overline{Mn} = \frac{20 * 15000 + 35 \ * 25000 + 45 * 20000}{20 + 35 + 45}$$

= **20750 g/l**

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

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \cdots}{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}$$

$$\overline{Mw} = \frac{20 * (15000)^2 + 35 * (25000)^2 + 45 * (20000)^2}{20 * 15000 + 35 * 25000 + 45 * 20000}$$

**= 21385 g/l**

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

= 21385/20750

= 1.03

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

Note: For additional problems refer class notes

## 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.

Composite materials have High strength to weight ratio -Light weight and more stronger.

**Fiber Reinforced Polymer Composite** is a composite material made of polymer matrix reinforced with fiber.

Fiber is embedded in the matrix to make the matrix stronger.

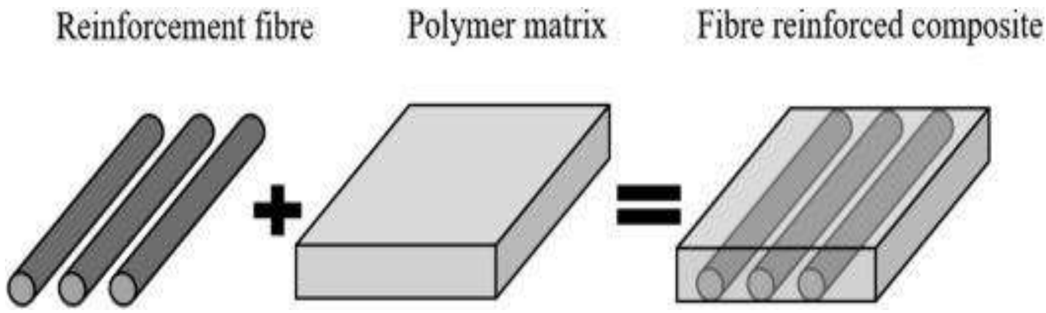
- Commonly used fibers are glass, carbon, aramid etc
- Polymer matrix – epoxy, vinyl ester, polyester, wood, asbestos etc,

**Fibers:**

Fibers are the polymer which have strong intermolecular forces between the chain. These forces are either hydrogen bonds or dipole-dipole interaction.

Example: Propylene fibre , Nylon 6,6

The commonly used reinforcements are glass, carbon and aramid (Kevlar- trade name of Du Pont Company) fibers. The glass epoxy composite is popularly known as GFRP- Glass fiber reinforced plastic, and the carbon- epoxy composite is called CFRP – Carbon fiber reinforced plastics.

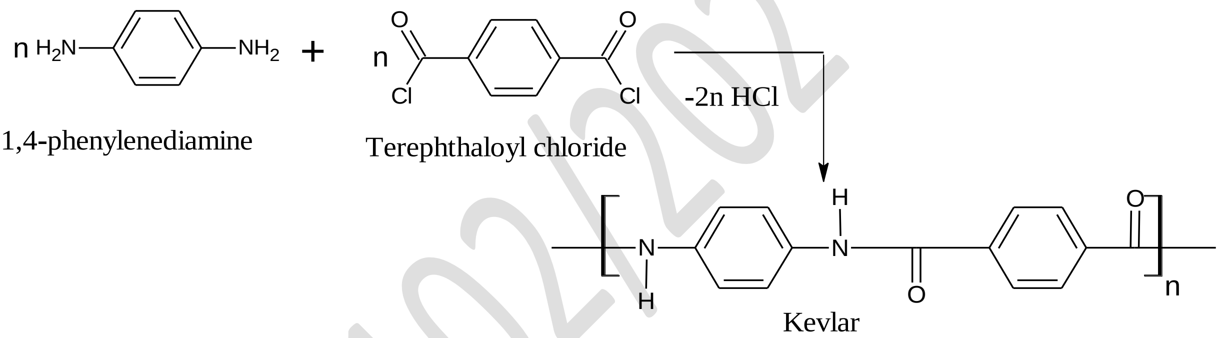



## SYNTHESIS, PROPERTIES AND APPLICATIONS OF KEVLAR FIBRE:

Kevlar is an aromatic polyamide in which all the amide groups are separated by para-phenylene groups. The Chemical composition of Kevlar is poly para phenylene terephthalamide.

Kevlar is synthesized in solution of N-methyl-pyrrolidone & calcium chloride from the monomers namely, 1,4- phenylene-diamine or (para-phenylenediamine) and terephthaloyl chloride through a condensation reaction with liberation of HCl as a byproduct.

It is the one of the fiber with sufficient tensile strength and structural rigidity to be used in advanced composites.




**Properties:**

- High tensile strength (five times stronger per unit weight than steel)
- High modulus of elasticity
- Very low elongation up to breaking point
- Low weight
- High chemical inertness
- Very low coefficient of thermal expansion
- High fracture toughness (impact resistance)
- High cut resistance
- Flame resistance

**Uses:**

- Used as reinforcement in tyre and rubber mechanical goods.
- Industrial applications are as cables, in asbestos replacements, break linings, and body armor.
- Used in plastic reinforcements for boat hulls, airplanes and bicycles.
- Kevlar is well known component of personal armor such as combat helmets, ballistic face masks etc.

- Used as inner lining for some tyres to prevent punctures.
- The Kevlar fiber is used in woven rope and in cables.
- Aramid fibers are widely used for reinforcing composite materials, often in combination with carbon fiber and glass fiber. The matrix for high performance composite is usually epoxy resin. Typical applications include bodies for F1 racing cars, helicopter rotor blades, tennis, table tennis, badminton and squash rackets, cricket bats, and hockey sticks.

## CONDUCTING POLYMERS

"**An organic polymer with highly delocalized pi-electron system having electrical conductance of the order of a conductor is called conducting polymer".**

The polymer should have the extensive conjugation of pi-bond, linear backbone chain and easily oxidizable and reduceable to become a conducting polymer. Few polymers which conduct electricity are Polyacetylene, polypyrrole, polythiophene, polyphenylene, polyaniline etc.

**Synthesis: (<u>POLYACETYLENE</u>)**

In this method polyacetylene is synthesized by using monomer gaseous acetylene in the presence of Ziegler-Natta catalyst such as Titanium isopropaxide ($Ti(OPr))_4$) and triethyl aluminium ($Al(C_2H_5)_3$). The catalyst is suspended in silicone oil through which acetylene gas is passed, is stirred for two hours at 120$^o$C. Later it is cooled slowly to room temperature resulting in thin sheets of Polyacetylene.

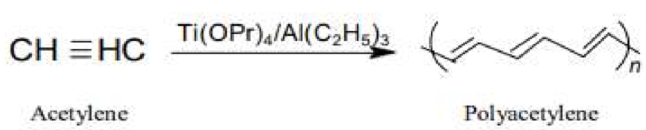
The conducting polymers are synthesized by doping in which charged species are introduced in organic polymers having pi- back bone. The important doping reactions are

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

Ex: Polyacetylene, polypyrrole, polythiophene, polyphenylene, polyaniline, etc.

### Synthesis of Polyacetylene:

In this method polyacetylene is synthesized by using monomer gaseous acetylene in the presence of Ziegler-Natta catalyst such as Titanium isopropaxide ($Ti(OPr))_4$) and triethyl aluminium ($Al(C_2H_5)_3$).




**Commercial Applications of Polyacetylene:**

1. Used in the manufacture of chemical sensors, corrosion inhibitors.
2. Used in compact electronic devices such as polymer based transistors, LEDs etc.

## MECHANISM OF CONDUCTION IN POLYACETYLENE:

Conducting polymers are generally produced by doping an oxidizing or a reducing agent intoan organic polymer with conjugated back bone consisting of pi-electron system.

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

1. Linear structure
2. Extensive conjugation in polymeric back bone (Pi-back bone)

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;

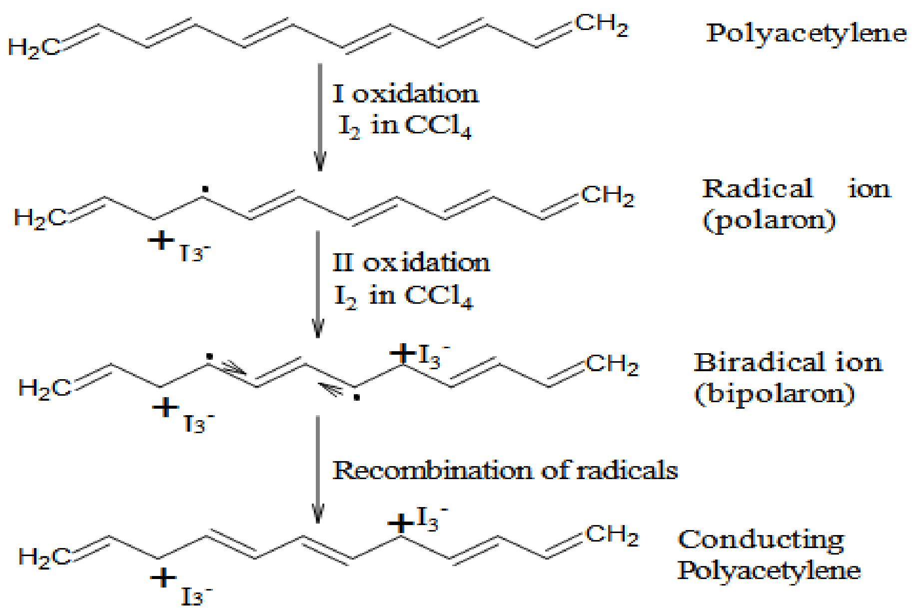
1. Oxidative doping (p-doping)
2. Reductive doping (n-doping)
3. Protonic acid doping (p-doping)

**1.Oxidative doping (p-doping)**:

- In this process, pi-back bone of a polymer is partially oxidized using a suitableoxidizing agent.
- The oxidizing agents used in p-doping are iodine vapor, iodine in $CCl_4$, $HBF_4$, perchloric acidand benzoquinone
- This creates positively charged sites on polymer back bone, which are current carriersfor conduction.

**Mechanism:**

- The removal of an electron from the polymer pi-back bone using a suitable oxidizingagents leads to the formation of delocalized radical ion called polaron.
- A second oxidation of a chain containing polaron followed by radical recombinationyields 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, the delocalized positive charges move and thus making a conductive polymer.
- On doping polyacetylene using iodine in $CCl_4$, for partial oxidation, the conductivity increases from $10^{-5}$ $S.cm^{-1}$ to $10^{3}$-$10^{5}$ $S.cm^{-1.}$

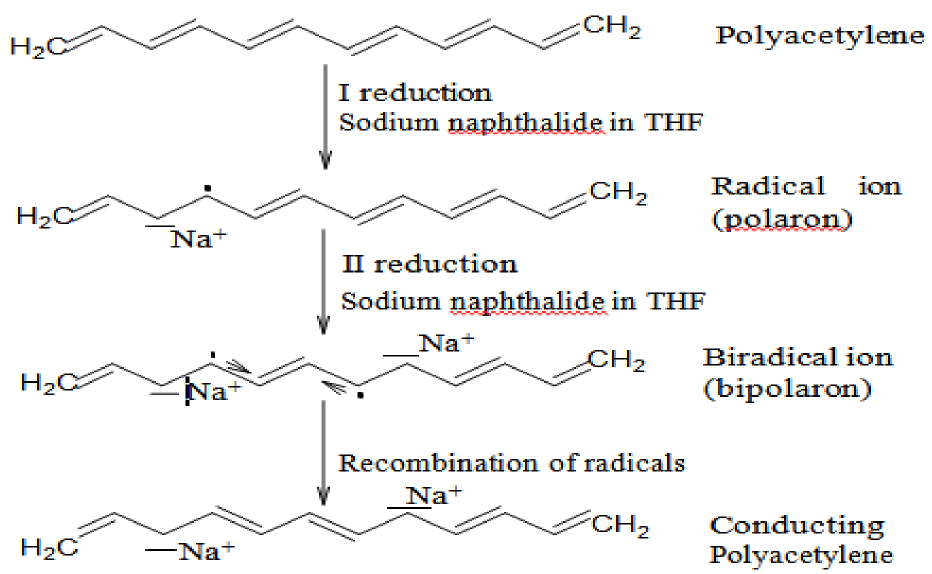



**2. Reductive doping (n-doping):**

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

**Mechanism of conduction:**

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



**Polyacetylene Applications:**

- Doped polyacetylene offers a particularly high electrical conductivity therefore it can be used in electric wiring or electrode material in lightweight rechargeable batteries.
- Tri-iodide oxidized polyacetylene can be used as a sensor to measure glucose concentration.
- Used as humidity sensor, gas sensor and radiation sensor etc.
- Used in electrochromic display window, solar cells, LED's.

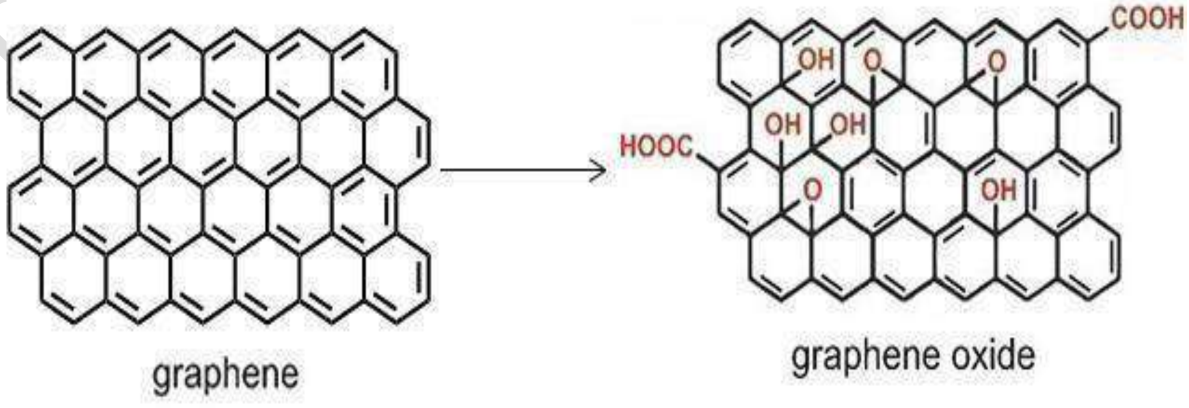
**Conducting Polymers Applications:**

- Fabrication of organic thin transistors.
- Fabrication of organic photovoltaic cells.
- Fabrication of organic light-emitting devices (OLED).
- Focused upon polymer membranes that incorporated electronically conducting polymers
- Light weight rechargeable batteries.

**GRAPHENE OXIDE:**

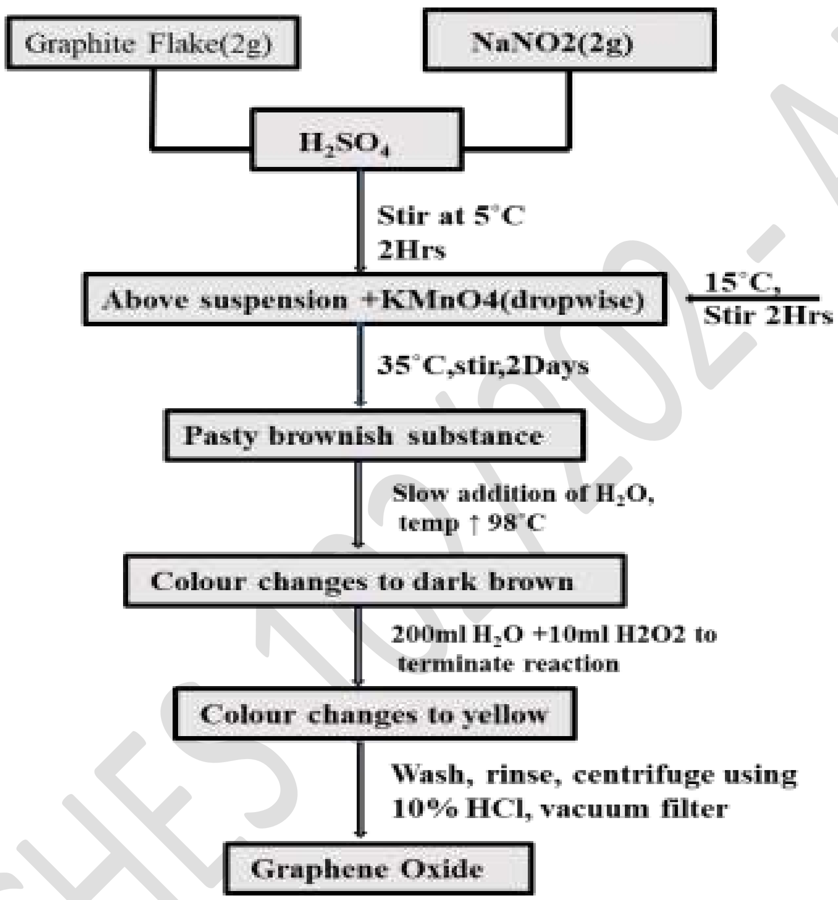
- Graphene oxide (GO) is two-dimensional material formed by the oxidation of graphene.
- It is a single-atomic-layered material, when stacked together forms graphite oxide.
- It contains hydroxyl (-OH), alkoxy (C-O-C), carbonyl (C=O), carboxylic acid (-COOH) and other oxygen-based functional groups.
- These groups are attached to both the sides of a single graphite sheet and overcome the inter-sheet van der Waals force. As a result, interlayer spacing increase causing reduction in its conductivity.
- It has been using in several applications in electronics, conductive films, electrode materials and nano composites.
- GO is hydrophilic, can easily disperse in organic solvents, water, and different matrixes.





## Preparation of graphene oxide by a hummer's method

Graphene oxide can be prepared from Hummer method from pure graphite powder. In this method graphite is subjected to reaction with anhydrous mixture of concentrated sulphuric acid, sodium nitrate and potassium permanganate. The oxidation reaction is completed within 2 hours at a temperature below 45°C. Next the hydrolysis of Graphite oxide in presence of polar solvent Dimethylformamide (DMF) and sonication results in complete exfoliation in water, yielding individual graphene oxide sheets.




- Graphite flakes (2 g) and NaNO3 (2 g) were mixed in 50 mL of H2 SO4 (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, potassium permanganate (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 of100
- 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.

- Finally, treat the solution with 10 ml $H_2O_2$ to terminate the reaction.
- For purification, the mixture was washed by rinsing and centrifugation with 10% HCl and then deionized (DI) water several times.
- After filtration, dry it in vacuum at room temperature to get powdered graphene oxide.

**Graphene Oxide properties:**

- Graphene oxide is hydrophilic in nature due to the presence of oxygen, can easily disperse in organic solvents, water, and different matrixes.
- Used to mix with matrix such as a polymer and ceramic to improve their mechanical and electrical properties.
- Graphene oxide has High elasticity and flexibility.
- Graphene oxide has more surface area, so it is more reactive.
- Thin films of Graphene oxide exhibit a high optical transparency.

**APPLICATIONS**

- Graphene oxide sheets have been used to prepare strong paper-like materials, membranes, thin films, and composite materials
- Used as membranes, catalysts and water purification technology.
- Chemically-altered graphene oxide disperse easily in organic solvents makes the materialbetter suited to production of bio devices and optoelectronics, and for use in drug delivery.
- Graphene oxide is used as electrode material in super capacitors, lithium-ion and sodium-ion batteries
- Graphene oxide sheets used as a catalyst in photocatalytic water splitting.
- Graphene oxide is used to store hydrogen.it is a good sensor for hydrogen, nitrogen dioxide and humidity.
- Graphene oxide finds uses in a wide variety of nanomedical applications including tissue engineering, cancer treatment, medical imaging, and drug delivery.

## GREEN FUELS

A fuel derived from biomass is called as green fuel. They are considered as renewable, eco-friendly, relatively less flammable compared to fossil fuel, has better lubricating properties and reduce greenhouse gases up to 65 percent. It can be manufactured from wide range of materials. Most common forms of green fuels are solar power, wind power, hydropower, biofuel such as power alcohol, biodiesel, biomass etc.

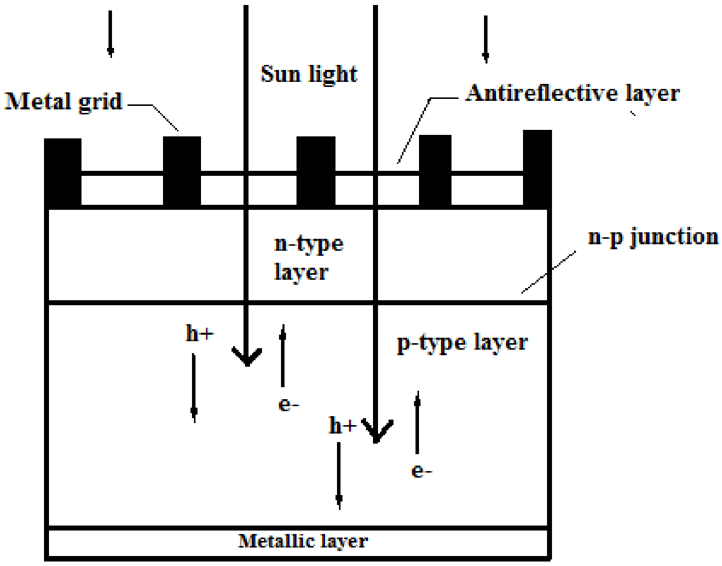
## SOLAR CELL :

Solar energy is the radiant energy due to illumination of the sun. It can be converted into various forms of energy such as thermal and electrical energies. The main advantage of using solar energy as a source of energy are that it is readily available, free of cost and eco-friendly. Solar energy alone can supply much more energy than the earth demands, but the only disadvantage that the sun does not shine all the time and not everywhere equally. Most of the other power sources like wind energy, wave energy and hydroelectricity have a common origin in sun.

**PHOTOVOLTAIC CELLS OR SOLAR CELLS :**

Definition: Photovoltaic cells are the semiconductor devices that generate direct current from sunlight. When semiconductors such as silicon are illuminated by photons (eg. from sun light), electricity is generated.

**Construction of photovoltaic cells:-**




A silicon photovoltaic cell is composed of a thin wafer of polycrystalline silicon wafer. Cell contains a very thin layer of phosphorous doped silicon (n-type) which is kept above boron doped silicon (p-type). So p-n junction is formed between these two layers. The anti-reflective layer containing silicon nitride or titanium dioxide is applied by plasma enhanced chemical vapour deposition technique, which increases the amount of light transmitted to the semiconductor.

Metallic grids are placed above P-doped silicon forms electrical contact of the diode and allows the light to fall on the semiconductor between the grid line. The other electrical contact is made using metallic layer back side of the solar cell.

**Principle:** The principle involved is the ejection of electrons from metal surface by striking with photons of solar radiation.

**Working of a photovoltaic cell:**

The solar cell is a semiconductor diode. Photovoltaic cell is based on photoelectric effect. When semiconductors such as silicon are illuminated by photons (eg. From sunlight), electricity is generated. Semiconductors have the capacity to absorb light and a part of the energy of the absorbed photons act as a charge carries electrons and holes. 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 and collected at n-type end (metal grids) and holes are drifted and collected p-type end (metal layer). When these two ends are electrically connected, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced and available for use such as lighting spinning of fans, working of motors. A silicon photovoltaic cell produces an open circuit DC volt of about 0.5 to 0.6V, The current output depends on its efficiency, size and proportional to the intensity of sunlight.

**Advantages of PV cells**::

- Energy source is vast and essentially infinite.
- Solar cells need no recharging like batteries and produce electrical energy as long as sunlight is available
- Solar cells have no movable parts and hence do not suffer from wear and tear.
- The materials used in PV cells do not corrode and serve for long duration.
- They operate at ambient temperature.
- PV cells involve no emissions, no combustion or radioactive residues for disposal.
- PV cells are environment friendly,
- low operating costs and quick installation

**Disadvantages of PV cells**:

- Poor reliability of auxiliary elements including storage
- The installation cost is high.
- PV cells generate only DC current and must be converted into AC power when used in distribution grids.
- Sun light is diffuse source, i.e , it is relatively low density energy.

**Applications of Photovoltaic Cells**

- Telecommunication repeater stations/tower
- Water pumps
- Navigational aids
- Laptop computers
- Cottages and remote residences
- Parks in remote regions
- Supplying occasional power
- Satellites
- Toys, watches

## GREEN HYDROGEN

Green hydrogen is defined as hydrogen produced by splitting water into hydrogen and oxygen usingrenewable energy source instead of fossil fuels.

Hydrogen has the highest energy content per unit of mass of any chemical fuel and can be substituted hydrocarbon in a broad range of applications. It can be easily produced from water found in abundance. Hydrogen produced via electrolysis can result in zero greenhouse gas emissions.

### Hydrogen fuel is preferred over the other fossil fuels because of the following features.

- It is lightest element
- Gas of diatomic molecules having the formula H2.
- Colourless, odourless and Tasteless

- Non-metallic and non-toxic
- Highly combustible,
- Most abundant chemical substance in the universe
- Hydrogen produced via electrolysis can result in zero greenhouse gas emissions.

### Generation of green hydrogen by electrolysis of water

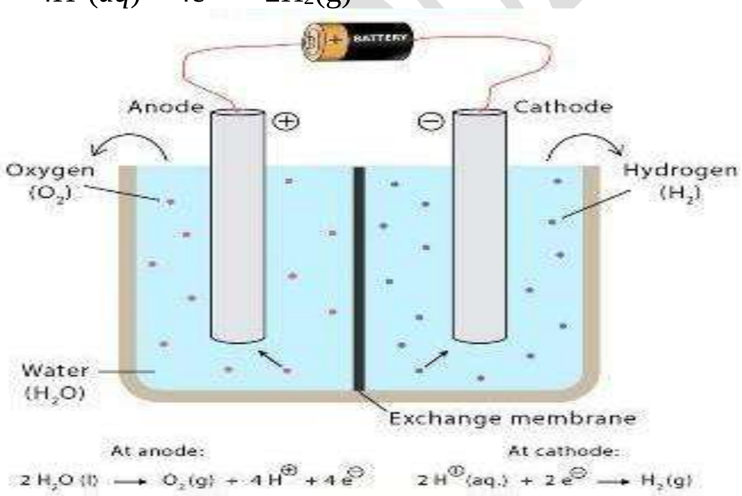
It is the process of splitting of water into oxygen and hydrogen gas by electrolysis.

- It consists of two electrodes i.e. anode and cathode.
- Both are separated by membranes.
- When electricity is passed, oxidation takes place at anode, it gives $H^+$ ions and electron, alsoliberates Oxygen gas.

$$2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e^-$$

- The $H^+$ ions move into cathodic compartment through membranes and electrons move fromanodeto cathode through external circuit.
- At cathode the $H^+$ ions accepts electrons and forms H2 gas. This liberated hydrogen gas isused as a fuel

$$4H^+(aq) + 4e^- \rightarrow 2H_2(g)$$




**Reactions**

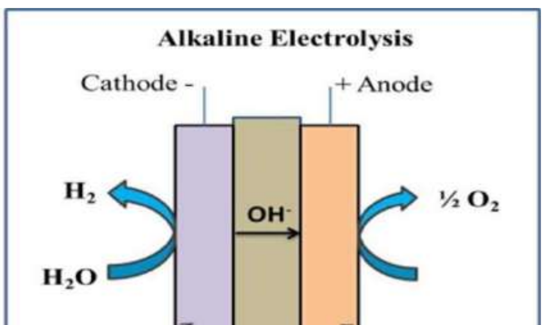
At Anode: $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) +$

$4e^-$ At Cathode : $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$

**Overall : $H_2O(l) \rightarrow 2H_2(g) + O_2(g)$**

**ALKALINE WATER ELECTROLYSIS**

- It consists of two electrodes i.e. anode and cathode.
- Both electrodes are made up of Ni based



metal, because it is more stable during the oxygen evolution.

- These electrodes are immersed in KOH solution (25-35%).
- Both electrodes are separated by porous diaphragm prevent gases crossover and allows only hydroxide ions.
- Cell voltage is 1.3 – 2 V
- When electricity is passed, at anode hydroxide ions lose electrons and forms water molecules.

Anode: $2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^-$

- At cathode, water molecules accept electrons and liberate hydrogen gas and forms hydroxide ions.

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

- These hydroxide ions move from cathode to anode through diaphragm and processcontinues.

**Anode:** $2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^-$

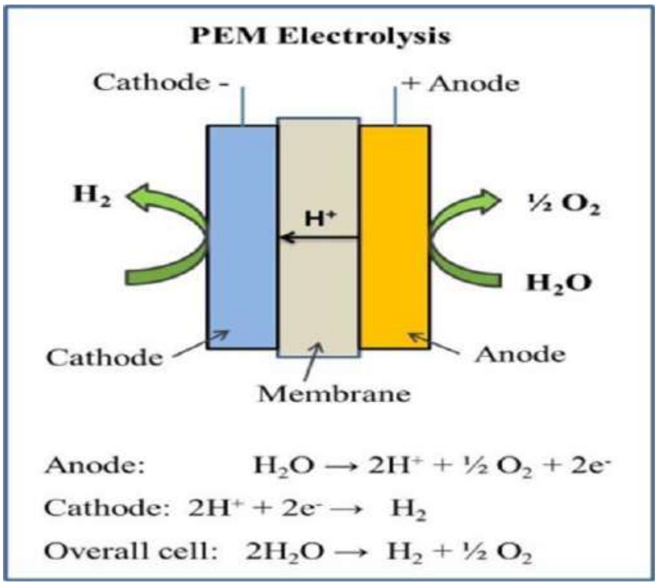
**Cathode:** $2H_2O + 2e^- \rightarrow 2H_2 + 2OH^-$

**Overall reaction** : $H_2O \rightarrow 1/2O_2 + 2H_2$

**Advantages:**

- Low cost and well established technology
- Long Stability and stacks in the megawatt range
- Non-noble catalyst

## PROTON EXCHANGE MEMBRANE ELECTROLYSIS OR POLYMER ELECTROLYTE MEMBRANE:




- In a polymer electrolyte membrane (PEM) electrolyzer, the electrolyteis a solid specially plastic material.
- PEM water electrolysis is involving the pumping of water to the anode where it is spilt into oxygen (O2), protons ($H^+$) and electrons ($e^-$).

  The electrons flow through an external circuit and the hydrogen ions selectively moves across the PEM to the cathode.
- Reactions..

  **At Anode:** $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e^-$ **At**

  **Cathode:** $4\ H^+(aq) + 4e^- \rightarrow 2H_2(g)$

  **Overall : $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$**

**Advantages**

- No corrosive and leaking electrolyte
- No acid carryover
- Minimum power requirement per unit of gas generated

**Important questions**

1. Define number average and molecular average molecular weight of polymer
2. Explain the preparation, properties and commercial applications of Kevlar.
3. Explain the synthesis of polyacetylene and mention its applications.
4. Explain the preparation, properties and commercial applications of graphene Oxide.
5. What are conducting polymers? Discuss the conduction mechanism in polyacetylene through oxidative doping technique and its uses.
6. What are green fuels? Explain the generation of hydrogen by Alkaline water Electrolysis with its advantages.
7. Explain the production of hydrogen by electrolysis.
8. Mention the significances of green fuel. Mention the properties and applications of hydrogen fuel.
9. What are green fuels? Explain the generation of hydrogen by PEM electrolysis with its advantages.
10. Explain the construction and working of photovoltaic cells. Mention the advantages and disadvantages.

# MODULE 5
# E-WASTE MANAGEMENT

**SYLLABUS**

Introduction, sources of e-waste, Composition, Characteristics, and Need of E-waste management. Toxic materials used in manufacturing electronic and electrical products; health hazards due to exposure to e-waste. Recycling and Recovery: Different approaches of recycling (separation, thermal treatments, hydrometallurgical extraction, pyrometallurgical methods, direct recycling). Extraction of gold from E-waste. Role of stake holders in environmental management of e-waste (producers, consumers, recyclers, and statutory bodies)

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## E-WASTE MANAGEMENT

Today's Electronic Gadgets, Tomorrow's E- Waste! It's no secret that E-Waste is increasing at an alarming rate with each passing day.

## What is E-Waste?

**Definition of waste.**

Waste refers to any electrical or electronic material that is not wanted or needed and is discarded or disposed of.

Electronic Waste or E-Waste describes rejected electrical or electronic devices. All items of electrical and electronic equipment and its parts that have been discarded by the user as waste without the purpose of re-use or re-cycle is called Electronic Waste.

- Any item which is considered as Electronic Waste has a Lifetime Profile which differs for different categories of Electrical and Electronic devices. Lifetime Profile includes the information about hazardous quantity present in discarded items, economic value and the effects on environment and health of people if they are not recycled appropriately.
- Electronic Waste is dismantled and sorted manually in developing countries unlike developed nations which make use of sophisticated machinery and provides PPE (Personal Protective Equipment) for the people who risk their lives in extraction of different materials from Electronic Waste

## Causes of E-Waste

The main causes of Electronic Waste are:

- Advancement in Technology.
- Changes in style fashion and status.
- End of their helpful life.
- Not taking precautions while handling them

## Sources of electronic waste (e-waste):

The main sources of electronic waste (e-waste) include:

1. Consumer electronics such as smart phones, laptops, televisions, and household appliances.
2. Office equipment such as computers, printers, copiers, and fax machines.
3. Medical equipment such as X-ray machines, monitors, and diagnostic equipment.
4. Electronic toys and games.
5. Military and government surplus equipment.
6. Obsolete technology such as outdated computer equipment and VCRs.
7. Discarded or broken electronic devices.
8. Colleges often use electronic equipment such as projectors, computer equipment, and audio-visual equipment in classrooms and laboratories.

## Composition of E-waste

The composition of electronic waste (e-waste) can vary depending on the typeof device and its components. In general, e-waste contains a mixture of materials including:

1. **Metals**: E-waste often contains valuable metals such as copper, gold, silver, and aluminum.
2. **Plastics:** Many electronic devices contain plastic components, including casings, insulation, and cables.
3. **Glass:** Electronic devices often contain glass components, such as screensand lenses.
4. **Circuit boards:** Many electronic devices contain circuit boards, which contain a mixture of metals and other materials.
5. **Batteries:** Some electronic devices contain batteries, which can contain hazardousmaterials such as lead, mercury, and cadmium.
6. **Other hazardous materials:** E-waste may also contain other hazardous materials, such as flame retardants, heavy metals, and polychlorinated biphenyls (PCBs).



## Characteristics of E-waste:

The characteristics of electronic waste (e-waste) can include:

1. **Complexity:** E-waste often contains a complex mixture of materials, making it challenging to recycle and dispose of properly.
2. **Hazardousness:** E-waste can contain hazardous materials such as heavy metals, flame retardants, and batteries, which can pose significant environmental and health risks.

3. **Volatility:** E-waste is a rapidly growing waste stream due to the increasing use of electronic devices and the limited lifespan of many electronic products.
4. **Global issue:** E-waste is a global issue, as electronic devices are manufactured, used, and discarded worldwide.
5. **Resource depletion:** The extraction of raw materials for electronic devices contributes to resource depletion, and the improper disposal of e- waste can lead to environmental contamination and waste of valuable resources.
6. **Environmental and health impacts:** Improper disposal of e-waste can lead to significant environmental and health impacts, including soil and water contamination, air pollution, and harm to human health.

## Effects of E-Waste

The effects of improper disposal of E-waste on the environment pose very real threats and dangers to the global environment at large. Improper disposal of these wastes affect the soil, air and water components of the environment.

- <u>Effects of E-Waste on Air:</u> Most common result of E-waste on air is through air pollution. Burning of e waste can release hydrocarbons within the atmosphere that pollutes the air.
- <u>E-Waste Negatively Impacts Soil:</u> E-waste can have a negative effect on the soil. As e-waste breaks down, it releases toxic heavy metals. Such heavy metals include lead, arsenic, and cadmium. When these toxins penetrate the soil, they influence the plants and trees. Thus, these toxins can enter the human food supply, which can lead to birth defects as well as a number of other health complications.
- <u>Effects of E-Waste on Water:</u> Heavy metals like mercury, lithium, lead present in electronics (found in mobile phone and computer batteries), etc., when not disposed properly, these heavy metals penetrate from soil to groundwater which then run to the surface as streams or small ponds of water.



## Define E-waste m anagement.

E-waste management refers to the processes and systems used to collect, transport, treat, and dispose of electronic waste (e-waste) in an environmentally responsible and safe manner

## Need of E- Waste Management:

E-waste management is necessary because it helps to address several environmental, health, and resource-related concerns, including:

1. **Protecting the environment:** E-waste contains toxic substances, such as lead, mercury, and cadmium that can have harmful effects on the environment causing soil, air and

water pollution and human health if not properly managed.

2. **Conserving resources:** E-waste contains valuable resources, such as metals, that can be recovered and reused through proper recycling.
3. **Reducing greenhouse gas emissions:** The production of new electronic products releases greenhouse gases, such as carbon dioxide, into the atmosphere. Proper recycling and disposal of e-waste can reduce theenvironmental impact of electronic products.
4. **Reducing land filling:** land filling of electronic waste can result in the release of toxic materials into the environment and contribute to soil and water pollution.
5. **Protecting public health:** Improper handling and disposal of e-waste can expose workers and the general public to hazardous materials and cause serious health problems.
6. **Data security:** E-waste can contain sensitive personal information and confidential business data that could be exploited if not properly managed.
7. **Economic benefits:** Proper e-waste management can create job opportunities and generate revenue from the sale of recovered materials.
8. **Rapid growth of electronics industry:** India is one of the fastest growing electronics markets in the world, leading to a growing volume of e-waste.
9. **Lack of proper disposal infrastructure:** In many parts of India, there is a lack of proper facilities and infrastructure for the disposal and management of e-waste.
10. E-waste management programs aim to promote responsible recycling and disposal of electronic waste and minimize the release of hazardous materials into the environment.



## Toxic materials used in manufacturing Electronic and Electrical products.

Electronic and electrical products can contain a variety of toxic materials,including:

1. **Lead:** Lead is a toxic heavy metal commonly used in the manufacture of batteries, computer monitors, and other electronic components.
2. **Mercury:** Mercury is used in some fluorescent lights, batteries, and otherelectronic devices.
3. **Cadmium:** Cadmium is a toxic heavy metal used in rechargeable batteries, pigments, and plastic stabilizers.
4. **Polyvinyl Chloride (PVC):** PVC is a common plastic used in electronic cables and other components. It can release toxic chemicals, such as dioxins, when burned or during disposal.

5. **Brominated flame retardants (BFRs):** BFRs are used in the manufacture of electronic products to prevent fires. However, they are toxic and can harm the environment and human health.
6. **Barium:** Barium is used in some electronic components, including cathode ray tubes.
7. **Rechargeable Batteries contains** Lithium is used in batteries, but it can be toxic if not handled properly. Cadmium, Lead, Sodium, Lithium, Nickel etc.,
8. **Chlorofluorocarbons (CFCs)** are toxic chemicals that were widely used ascoolants and solvents in electronic products, such as refrigerators, air conditioners. They cause ozone depletion.

## Health hazardous due to exposure of e waste:

Exposure to electronic waste (e-waste) can have serious health consequences,including:

1. **Poisoning:** E-waste can contain toxic substances, such as lead, cadmium, and mercury that can cause poisoning if they enter the body.
2. **Respiratory problems:** Exposure to dust and fumes generated during thedismantling and disposal of e-waste can cause respiratory problems, such as asthma and bronchitis.
3. **Neurological effects:** Exposure to toxic substances in e-waste, such as lead and mercury, can cause neurological effects, including memory loss, tumors and coordination problems.
4. **Reproductive problems:** Exposure to toxic substances in e-waste, such as cadmium, can cause reproductive problems, including infertility and birth defects.
5. **Cancer:** Exposure to carcinogenic substances, such as dioxins and polychlorinated biphenyls (PCBs), found in e-waste, can increase the risk of cancer.



## E- Waste recycling:

The process of e-waste recycling typically involves the following steps:

1. **Collection and transportation:** E-waste is collected from various sources such as households, businesses, and recycling facilities. It is then transported to a recycling plant for processing.
2. **Sorting and dismantling:** E-waste is sorted into different categoriesbased on the typeof material and the manufacturer. The recyclers then dismantle the devices to separate the valuable materials from the hazardous components.
3. **Shredding:** The e-waste is shredded into smaller pieces to make it easier to separate the different materials. The shredded pieces are then sorted into different categories based on their composition.

4. **Separation:** The valuable materials, such as metals, plastics, and glass, are separated from the other components through a series of physical and chemical processes.
5. **Processing:** The separated materials are processed to remove any impurities and contaminants, and to prepare them for reuse. For example, metals are smelted to produce pure metal alloys, while plastics are meltedand molded into new products.
6. **Disposal of hazardous waste:** The hazardous components of e-waste, such as batteries and LCDs, are properly disposed of to prevent pollution and health hazards.

## E- Waste recycling and recovery different approaches (recycling, separation and thermal treatment)

E-Waste recycling and recovery can be achieved through different approaches, including separation and thermal treatments.

**Separation:**

This involves physically separating different components of e-waste, such as metals, plastics, and circuit boards. This can be done manually or through automated processes, and the separated materials can then be processed further for recycling or disposal.

**Thermal treatments**:

E-waste thermal treatment refers to the use of high temperatures to recover valuable metals and other materials from electronic waste. This process can include incineration or other pyrometallurgical techniques, and typically involves melting down the waste to separate the metal components. The separated metals can then be recovered and reused. Thermal treatment can be an effective method for e-waste recycling.



**Hydrometallurgical extraction of E waste:**

E-waste hydrometallurgical extraction is a process used to extract valuable metals and other materials from electronic waste through chemical reactions in aqueous solutions. The process typically involves the following steps:

**Pre-treatment:** This involves the fragmentation and size reduction of electronic waste to prepare it for further processing.

1. **Leaching:** The e-waste is treated with chemical reagents in a solution to dissolve the metals and other materials, creating a leachate. Leaching is carried out by dissolving crushed e-waste in mineral acid like HCl, $H_2SO_4$, and aqua regia for leaching metals

like Zinc, Tin, Iron and Aluminium.

Cyanide based solutions are used for leaching precious metals like Copper and gold.

2. **Separation:** The leachate is then processed to separate and purify the metals and other materials, through methods such as precipitation or ion exchange.

   In **Chemical precipitation** more reactive metals displace less active metals by displacement reaction. In **Ion exchange** method using resin for adsorption with activated carbon often with higher adsorption and recovery rates.

3. **Recovery:** The extracted metals and other materials are then recovered and processed for reuse.

Hydrometallurgical extraction is a more environmentally friendly alternative to thermal treatments, as it generates less hazardous waste and can be more easily regulated to minimize environmental impact.

**Pyrometallurgical methods E-waste recycling:**

E-waste pyrometallurgical methods refer to the process of extracting valuable metals and other materials from electronic waste using high temperatures. These methods include:

1. **Smelting:** The e-waste is melted in a furnace and then separated into individual metals and other materials. Smelting is carried out at temperature of 1200°C (approximately.) Molten metal and slag are tapped from the furnace bottom
2. **Refining:** The metals from the smelted e-waste are further processed to removeimpurities and improve their quality.
3. **Incineration**: Electronic waste is burned at high temperatures to reduce its volume and recover metals.

Pyrometallurgical methods are effective at recovering valuable metals from e- waste, but they also generate hazardous byproducts and require significant energy inputs. Additionally, these methods can pose a risk to the environment and human health if not properly regulated and monitored.

**Direct recycling of e waste:**

Direct recycling of e-waste refers to the process of recovering valuable materials from electronic waste without the need for intermediate processing steps. This can include processes such as shredding, granulating, and sorting, which are used to separate the different components of e-waste, such as metals, plastics, and glass. The separated materials are then processed to extract the valuable components and prepare them for reuse.

**Advantages of direct recycling:**

Several advantages over other methods of e-waste recycling, including lower energy inputs, lower environmental impact, and the potential for higher quality end products.

By combining direct recycling with other methods, such as chemical and pyrometallurgical processing, it is possible to maximize the recovery of valuable materials from electronic waste and minimize the environmental impact of e-waste management.

## Extraction of gold from e-waste (Explain the Principle and experimental procedure):

**Principle:** The principle behind the extraction of gold from e-waste is based on the fact that gold is a relatively non-reactive metal, which allows it to be recovered from complex electronic waste matrices through a series of chemical and physical processes.

Experimental procedure:

1. **Collection and segregation of e-waste:** The first step involves collecting and segregating the e-waste into different categories, such as computer motherboards, cell phones, and other electronic devices.
2. **Physical separation:** The e-waste is physically separated into different components, such as plastics, metals, and glass.
3. **Leaching**: The metals, including gold, are leached from the e-waste using a suitable reagent, such as aqua regia (a mixture of hydrochloric acid and nitric acid), to dissolve the gold.

$$Au + HNO_3 + 4HCl \rightarrow HAuCl_4 + NO + 2H_2O$$

4. **Precipitation:** The dissolved gold is then precipitated out of the solution through the addition of a suitable reducing agent, such as sodium metabisulfite.

$$2H[AuCl4] + 3Na_2S_2O_5 + 3H_2O \rightarrow 2Au + 3SO_2 + 3Na_2SO_4 + 8HCl$$

5. **Purification:** The precipitated gold is then purified through processes such as ion exchange, electro-winning, or distillation, to remove impurities and improve its quality.
6. **Recovery**: The purified gold is then recovered for reuse.

**Advantages:**

High yield expected.

Faster extraction of gold is possible.

**Disadvantages:**

Chemicals are used.

Acid residues are not disposed of properly, which harms the environment.



## Role of stakeholders in the environmental management of e-waste:

The role of stakeholders in the environmental management of e-waste can vary depending on the stakeholder and their level of involvement.

From a **local perspective**, stakeholders in the environmental management of e- waste may include:

1. **Governments:** responsible for creating and enforcing regulations and policies to manage e-waste, as well as promoting public awareness and education about e-waste management.
2. **Manufacturers**: responsible for the design, production, and disposal of electronic products, and may be involved in the collection and recycling of e-waste.
3. **Consumers:** responsible for properly disposing of e-waste and making informedchoices about the purchase of electronic products.
4. **E-waste recyclers and processors:** responsible for the safe and responsible management of e-waste, including the collection, dismantling, and recycling of electronic waste.
5. **Environmental organizations:** responsible for advocating for sustainable and responsible e-waste management practices and raising public awareness about e-waste issues.
6. **Community groups:** responsible for organizing and participating in e- waste recycling programs and events and promoting awareness of e-wasteissues in the local community. From a global perspective, stakeholders in the environmental management of e-waste include
7. **International organizations**: such as the United Nations, World Trade Organization, and the International Telecommunication Union, that is responsible for setting global standards for e-waste management and promoting cooperation and collaboration among countries.
8. **Transnational corporations:** responsible for the design, production, and distribution of electronic products on a global scale, and have a significant impact on e-waste management practices.
9. **Global e-waste trade networks:** responsible for the transportation and processing of e-waste between countries and may impact the environmental and health outcomes of e-waste management.
10. **Governments of developed and developing countries:** responsible for creating and enforcing regulations and policies to manage e-waste, as well as promoting public awareness and education about e-waste management.
11. **Environmental organizations:** responsible for advocating for sustainable and responsible e-waste management practices and raising public awareness about e-waste issues on a global scale.
12. **International community:** including consumers, NGOs, and civil society

organizations, that can raise awareness about e-waste issues, demand responsible e-waste management practices, and push for change at the international level.

## Role of stake holders - producers, consumers, recyclers, and statutory bodies.

In the management of electronic waste (e-waste), the following stakeholders play important unique role in the management of e-waste:

1. **Producers** - are responsible for designing and producing electronic products and may also be involved in the collection and recycling of e- waste.
2. **Consumers -** play a crucial role in the responsible disposal of e-waste and making informed choices about the purchase of electronic products.
3. **Recyclers -** are responsible for safely and responsibly managing e-waste, including the collection, dismantling, and recycling of electronic waste.
4. **Statutory bodies -** such as governments, are responsible for creating and enforcing regulations and policies to manage e-waste and promoting public awareness and education about e-waste management.

**Role of stake holders in environmental management of e-waste (producers, consumers, recyclers, and statutory bodies) is listed in the below table**:



| | |
|---|---|
| Producers | Pay the e-waste recycling fee according to market share |
| Recyclers | Sorting: dismantling: treatment of e- waste |
| Waste disposers | Landfill or incineration of hazardous material & waste |
| Consumers | Submit(or sell) the e-waste to the qualified collectors |

**Important questions**

1. Discuss the sources of e-waste and explain the need for e-waste management.
2. Discuss hydrometallurgical and pyro metallurgical process of recovery of e-waste.
3. Explain the steps involved in extraction of gold from e-waste with its advantages and disadvantages.
4. Explain the pyro metallurgical recycling methods.
5. Briefly explain the various chemical methods involved in hydrometallurgy process of recovery of e-waste.
6. Summarize about the toxic materials used in electrical and electronic products and health hazardous effects of e-waste exposure.
7. Explain ill effects of toxic materials used in manufacturing electrical and electronic products.
8. Write a note on roll of stake holders for example producers,consumers,recyclers and statutory bodies.