

BGS COLLEGE OF ENGINEERING AND TECHNOLOGY

**DEPARTMENT OF APPLIED CHEMISTRY
MAHALAKSHMI, Bengaluru - 560086**



APPLIED CHEMISTRY (BCHES102/202)

**SENSORS AND ENERGY
STORAGE SYSTEMS
Module: 01**



SENSORS AND ENERGY STORAGE SYSTEMS

SENSORS: Introduction, working principle and applications of electrochemical sensors, Conductometric sensors, and Optical sensors. Sensors for the measurement of dissolved oxygen (DO). Electrochemical sensors for the pharmaceuticals, and hydrocarbons. Electrochemical gas sensors for SO_x and NO_x. 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.

MEASUREMENT DEVICES

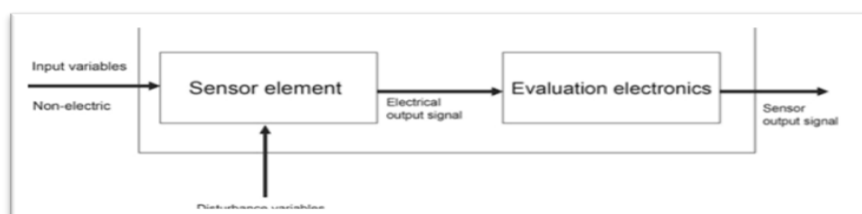
Measurement devices perform a complete measuring function, from initial detection to final indication. The important aspects of measurement system are

- a) **Sensor:** It is a device which detects or measures a physical property and record, indicates or otherwise responds to it. They are classified into two types Active sensors and Passive sensors.
- b) **Transducer:** It is a device which converts one form of energy into another form. It is a device which provides usable output response to a specific input measured which may be a physical quantity.
- c) **Actuators:** It is a device that moves or controls some mechanism. Actuators can be categorized by the energy source they require to generate motion. There are two types of actuators Rotary actuator and linear actuator.

SENSORS:

Introduction:

A device which provides a usable output in response to a specified measurand. Sensor is a device that detects and responds to some type of input from the physical environment. Input could be light, heat, motion, moisture, force, pressure, displacement, etc. It produces a proportional output signal (electrical, mechanical, magnetic, etc. The basic working principle for any kind of sensor is as shown



There are four types of sensors

1. Conductometric sensors.
2. Electrochemical sensors.
3. Thermometric sensors.
4. Optical sensors.

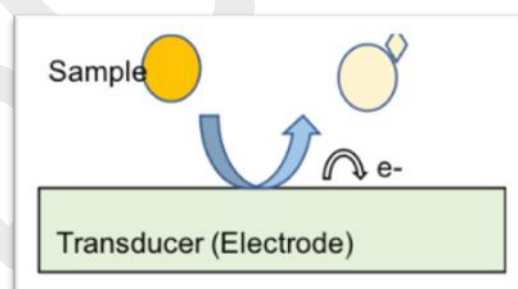
ELECTROCHEMICAL SENSORS:

Definition:

Electrochemical sensors are made up of three essential components: a receptor that binds the sample, the sample or analyte, and a transducer to convert the reaction into a measurable electrical signal. In the case of electrochemical sensors, the electrode acts as the transducer.

Electrochemical sensors:

- Electrochemical sensing always requires a closed circuit.
- Current must flow to make a measurement in most electrochemical sensors; An electrode surface is used as the site of the reaction.
- The electrode will either oxidize or reduce the analyte of interest.
- The current that is produced from the reaction is monitored and used to calculate important data such as concentrations from the sample.



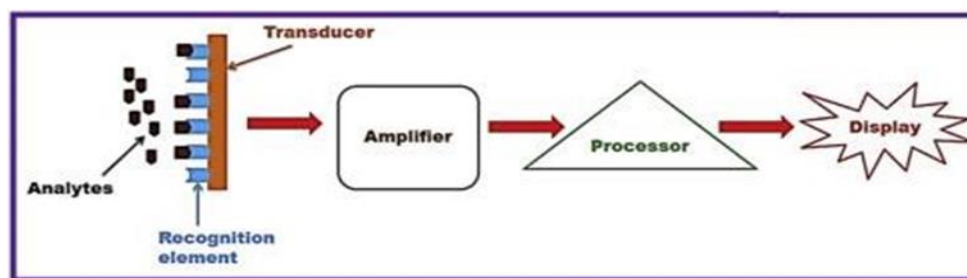
Working principle:

The fundamental concept in the detection of analytes by electrochemical. Sensors involves the measurement of electric current generated by chemical reactions in the electrochemical system.

- The reactions which occur at the interface of the surface of an electrode between the recognition element, and the target/binding analyte generate an electrical

double layer and thus this potential is measured after transforming these chemical reactions into this measurable electrochemical signal by a recognition element, and a transducer of the sensor.

- 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.



Application Electrochemical sensors:

- Electrochemical sensors are considered attractive tools to determine important molecules or biomarkers 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.

CONDUCTOMETRIC SENSORS:

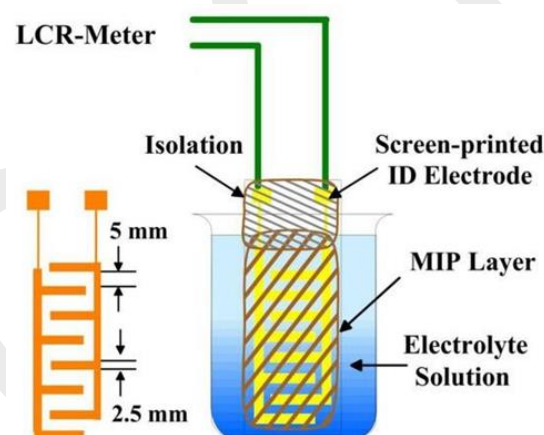
Conductometric detection is based on measurement of specific conductance of an analyte and is preferable because it can be applied for detection of both electroactive and electro inactive species. The conductivity electrodes can either be in contact with the solution or insulated using a thin layer. Conductivity detection is mostly associated with capillary electrophoresis (CE).

In contact-mode conductivity measurement, the electrodes are in direct contact with the sample. Although better contact with sample results in good sensitivity and lesser response time, it is accompanied with the increased risk of degradation of electrodes and contamination of sample.

Working of conductometric sensor:

Fabrication and Surface Modification of Electrodes

- Interdigital electrodes (IDE) were screen-printed on a glass substrate (microscope slide) to fabricate an interdigital transducer (IDT).
- Screen-printed interdigitated gold electrode-based sensor systems have been used for variety of analytes
- The desired structure of interdigital electrodes was fabricated on the substrate via screen printing with commercial gold paste.
- The electrode structure was designed by photo lithography.
- All organic components present in gold paste were removed by heating at 500 °C for 4hr. The advantage of this procedure is based on the robustness of the gold layers.
- The pattern and dimensions of the IDEs structure on transducer surface is shown in Figure 1



- IDT was fabricated by screen printing IDE of gold on glass substrate. IDT was coated with sensitive layer and LCR meter was used to measure resistance of sensitive layer by placing it in glass cell filled with electrolyte solution.

Application of conductometric sensor

- Aptamer Technology for the Detection of Foodborne Pathogens and Toxins
- Advanced Nanoparticle-Based Biosensors for Diagnosing Foodborne Pathogens
- Microfluidic electrochemical devices for pollution analysis.
- It is used for DNA Detection.

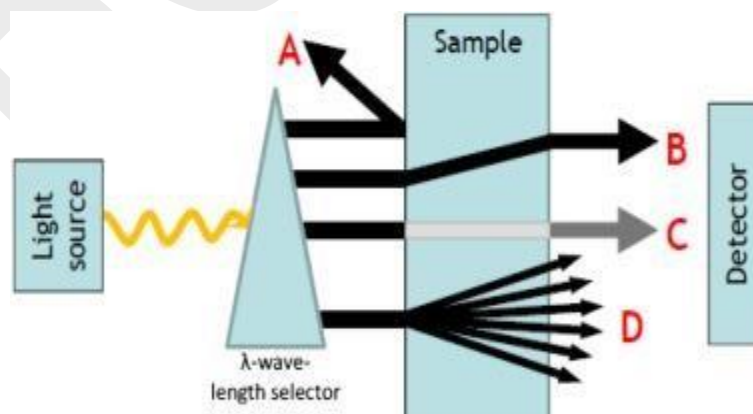
OPTICAL SENSORS:

Definition:

- Optical sensors have two basic methods, to obtain sensor data from target molecules that are label-based and label-free methods.
- Optical devices use special transducers like SPR (Surface plasmon resonance), interferometers, gratings, and refractometers.
- Optical sensors are divided into several subclasses such as resonance, dispersion, reflection, refraction, phosphorescence, infrared absorption, Raman scattering, fluorescence, and chemiluminescence.

Optical Sensors working principle

- Optical sensors use visible or ultraviolet light to interrogate sensors for analysis. Optical sensors can be represented in general terms as a wavelength-selectable light source, the sensor material itself interacting with analytes, and a light detector (**Fig. 1**).
- What the detector monitors varies by technique (e.g., refractive index, scattering, diffraction, absorbance, reflectance, photoluminescence, chemiluminescence, etc.), can cover different regions of the electromagnetic spectrum, and can allow measurement of multiple properties.
- **Colorimetry** (i.e., quantitative measurement of absorbance or reflectance spectra) is, of course, one of the oldest of analytical techniques, and colorimetric sensors stretch back even before the beginnings of chemistry.



- Colorimetric detection is a fairly simple technique, and the advent of universal digital imaging has given it new and exciting possibilities.

Application of Optical Sensors

- Application of these optical sensors ranges from computers to motion detectors. For optical sensors to work effectively, they must be the correct type for the application, so that they maintain their sensitivity to the property they measure.
- Optical sensors are integral parts of many common devices, including computers, copy machines (xerox) and light fixtures that turn on automatically in the dark.
- And some of the common applications include alarm systems, synchro for photographic flashes and systems that can detect the presence of objects.

SENSORS FOR THE MEASUREMENT OF DISSOLVED OXYGEN USING

1. ELECTROCHEMICAL SENSORS:

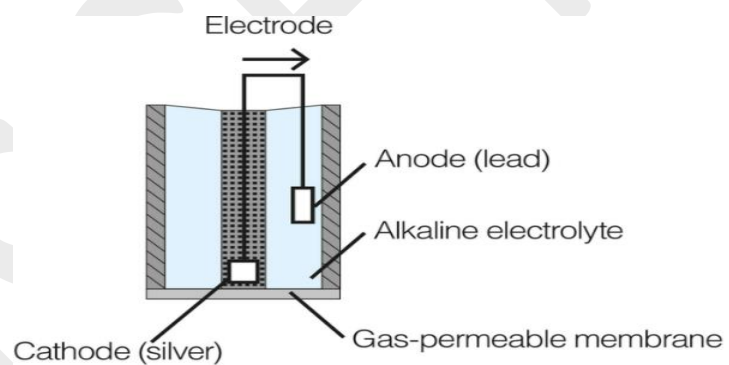
Electrochemical DO sensors, also known as amperometry or Clark-type sensors, measure dissolved oxygen concentration in water based on electrical current produced. Polarographic and galvanic are type of electrochemical DO sensors.

Example: Galvanic DO sensor.

Schematic Representation:

Components

- Cathode.
- Anode.
- Electrolyte.
- Membrane.



The cathode and anode are dissimilar metals (they differ in their SEP values). 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 the dissimilar metals causes them to self-polarize with the electrons travelling internally from the anode to the cathode. For this reason, galvanic DO sensor does not require any warm-up time. The cathode (e.g., Ag or another noble metal) accepts electrons from the anode via an internal circuit and passes them on to the oxygen molecules. It does not interfere in the reaction. Thus, the anode (e.g., Zn, Pb or another active metal) is oxidised and the oxygen is reduced at the surface of 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.

Working principle:

When 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.

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

Cathode (Ag) – oxygen reduction reaction: $\text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-$

Overall reaction: $\text{O}_2 + 2\text{Pb} + 2\text{H}_2\text{O} \rightarrow 2\text{Pb}(\text{OH})_2$

The current produced is proportional to oxygen consumed and thus to the partial pressure of oxygen in the sample.

The white solid, $\text{Pb}(\text{OH})_2$ that is produced by these reactions is precipitated out into the electrolyte solution. It neither coats the anode nor consumes the electrolyte, and thus does not affect the sensor's performance until the quantity becomes excessive. If this happens, it may interfere with the ions ability to carry current.

As galvanic DO sensor is self-polarizing, the anode is continuously consumed even when the sensor is not in use. When there is no measurement for a long period, the DO tip should be disconnected and stored according to the manual.

2. OPTICAL SENSOR:

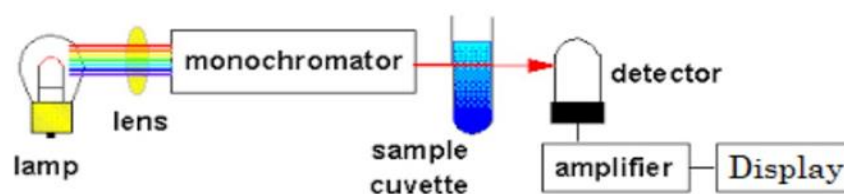
Interaction of electromagnetic radiation with matter forms the basis of a broad range of analytical methods commonly known as spectrochemical methods of analysis. Commonly, electromagnetic radiation in the ultraviolet-visible-infrared domains is used for analytical purposes. A broad range of chemical sensors have been developed on the ground of interaction of the sensing element with electromagnetic radiation. Sensors based on the transduction of interaction of electromagnetic radiation with the chemical species are called as optical sensors.

Optical transduction can be based on emission, absorption, reflectance and scattering of light by the analyte. The optical signal arises from the interaction of the

analyte with an incident radiation. The interaction could result in absorption, emission, scattering, or reflection of light.

The type of interaction depends on the wavelength of the probing radiation and on the structure of the molecules in the analyte. The intensity of the radiation emanating from the analyte carries information on the concentration of the analyte. It is measured by the optoelectronic instrumentation. In a simple optical sensor used to measure absorption of light, main components used are a light source, a wavelength selector, a photodetector, and a display of the output.

In modern optical sensors, optical components such as a lens, optical couplers, and connectors are used for coupling light into optical fibres and solid-state optoelectronic components. This has enabled the development of commercial portable optical sensor systems. Simple optical sensors are used to determine the concentration of coloured chemical species in solution. They are based on measurement of absorbance of transmittance of light of particular wavelength by coloured chemical species in the solution. They are governed by Beer-Lamberts law.



Schematic representation of a simple optical sensor

Applications of optical sensors:

- Optical sensors can be used in the determination of any chemical species which can interact with electromagnetic radiation.
- Optical sensors have been developed for a number of different types of chemical and biochemical molecules and ions. For example, ions in solution (e.g., pH, metal ions, and anions), gases (e.g., CO₂, O₂, NH₃, SO₂, NO₂, NO, etc.), vapours (e.g., moisture, volatile organic compounds, etc.), and molecules (e.g., glucose, pesticides, DNA, bacteria, etc.) can be determined using optical sensors.
- Optical sensors find important and varied uses in environmental, biotechnological, food, pharmaceutical, medical, and related applications.

- Optical fibre based (bio)sensors are used in screening of drugs, detection of food-borne pathogens, detection of explosives and environmental monitoring.

3. CONDUCTOMETRIC SENSORS:

Conductometric sensor is considered as a type of electrochemical sensor, even though it is not used to measure electrochemical change.

An electrochemical sensor measures the electrochemical processes (redox reactions) at the surface of electrodes. But, a conductometric sensor is based on measurements of physical properties of a homogeneous bulk solution like electrolytic conductance by aqueous electrolyte solutions.

In conductometric sensor, determination of the concentration of analyte is based on measurement of changes that occur in electrolyte solution. Here the electrodes are just used to measure change in electrolytic conduction of an electrolyte and they do not provide surface for any reaction. Therefore, their surface is generally not modified.

Conductance of a solution is based on:

- The concentration (number) of ions contributing to conductivity of solution.
- Mobility of each type of ion. Mobility of an ion depends on its size. Smaller the size higher is mobility and higher is electrolytic conductance.

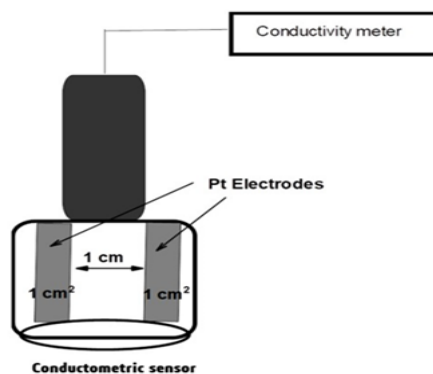
Electrode used in conductivity sensor is called as conductivity cell. It is used to measure the change in electrolytic conductance of the solution during replacement of ions of a particular conductivity by ions of different conductivity. It is made of two platinum foils with unit cross sectional area and unit distance between them. Volume between two electrodes is $A \text{ cm}^3$.

Conductance of unit volume of the solution is called as specific conductance. There will be change in specific conductance of solution when there is change in number of ions or type of ion. This change is measured using conductivity cell.

Specific conductance (\mathbf{K}) is given by, $\mathbf{K} = \frac{1}{R} \times \frac{1}{A}$

where l/A is known as cell constant and 'R' is the resistance of the solution.

The conductivity cell is dipped in the electrolytic solution taken in a beaker and it is connected to a conductance measuring device called as conductivity meter.



Applications of Conductometric sensors:

- Conductometric sensor can be used to monitor any chemical which can change the electrolytic conductance of solution on chemical reaction.
- It is used to estimate acids, bases and their mixtures in a sample.
- It is used to check the number of ionic impurities in water samples.
- It is used in measuring acidity or alkalinity of sea water and fresh water.
- Conductometric biosensors are used in biomedicine, environment monitoring, bio technology and agriculture related applications.

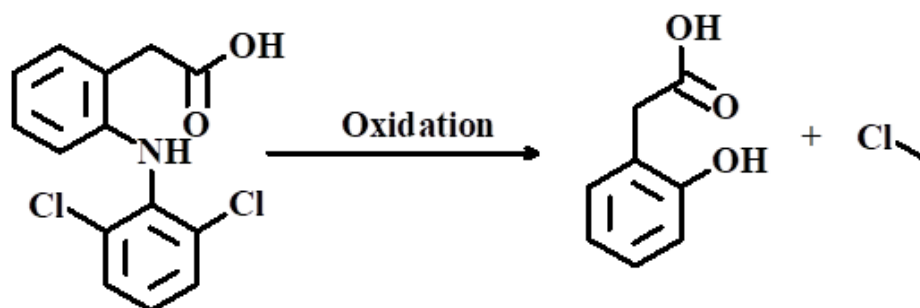
Electrochemical sensors for the pharmaceuticals and hydrocarbons:

Pharmaceuticals:

Pharmaceuticals are basically organic compounds, which are used extensively by human beings as a solution for various health issues. After usage they are excreted or washed off their hosts and enter into the environment through effluents of waste water. Even though use of pharmaceuticals for various health conditions are well understood and documented, there is limited knowledge about their unintended effects in the environment. Majority of these are complex organic molecules with lower biodegradability. Therefore, it is necessary to use sensors for the detection of pharmaceuticals to monitor their concentration and know their toxic effects. Several electrochemical sensors are available for the detection of pharmaceuticals in lower concentration. These sensors are fast, low-cost, and sensitive and use disposable strips. These sensors can be used for on-the-spot analysis. One example is the electrochemical Sensor used for detection of Diclofenac.

Electrochemical sensor for detection of diclofenac:

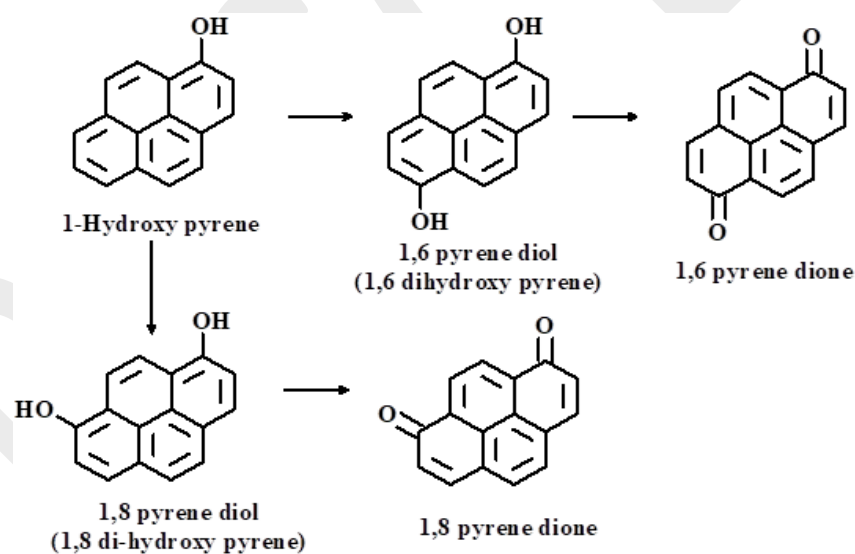
Diclofenac with chemical name 2-(2-((2,6-dichlorophenyl) amino) phenyl) acetic acid, is one of the most frequently prescribed non-steroidal anti-inflammatory drugs (NSAID) with antipyretic and analgesic effects. It is safe in prescribed dose, but may cause adverse effects at higher doses. Due to wide usage and poor biodegradability, it can have serious effects on the ecosystem. Electrochemical sensor can be used to detect diclofenac in lower concentrations. In the electrochemical sensor used to detect diclofenac, the sensing (working) electrode is graphite carbon coated with Multi walled carbon nanotubes (MWCNT) and gold nanoparticles. In the detection, along with sensing electrode, counter electrode and reference electrodes are used. When the sample containing diclofenac is put in the sensor, the following oxidation reaction of diclofenac occurs on the surface of the sensing electrode. The change in potential of the reaction gives the concentration of diclofenac.



ELECTROCHEMICAL SENSORS FOR HYDROCARBON:

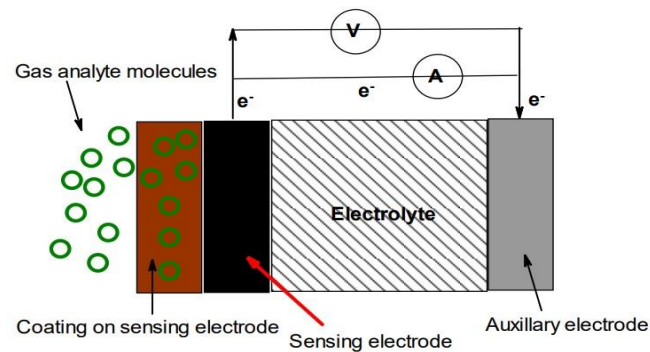
Among the dangerous hydrocarbon pollutants, polycyclic aromatic hydrocarbons (PAHs) are widely found in the air, water, soil, and food. PAHs are known carcinogenic and mutagenic compounds. They can enter the human body mainly through respiration, and diet. Detection of PAHs is essential to monitor their toxicity and carcinogenic risk. After entering the body, some PAHs are metabolized into hydroxyl PAHs (OH-PAHs), which are excreted with urine. 1-hydroxypyrene is a commonly found hydroxyl PAH in urine sample. Therefore, concentration of 1-hydroxypyrene is used as a biomarker to evaluate PAH exposure levels in the human body. Its concentration in urine, quantitatively reflect the extent of recent exposure to PAHs. Conventional methods used for estimation of 1-hydroxypyrene like HPLC-MS, GC-MS, and LC-MS/MS use large, expensive, and difficult to operate instruments. It also requires more time for laborious

sample pre-treatment and analysis. Therefore, electrochemical sensors are being developed for detection of 1-hydroxy pyrene in urine sample. These sensors are fast, low-cost, and sensitive and use disposable strips. These sensors can be used for on-the-spot analysis. In the electrochemical sensor used to detect 1-hydroxypyrene, the sensing (working) electrode is graphite carbon coated with chromium containing metal Organic framework (Cr-MOF) and graphene oxide. This material has excellent chemical and hydrothermal stability, a large surface area, large pore windows, and numerous unsaturated chromium sites, making it suitable sensing material for electrochemical sensors. The 1-hydroxypyrene structure contains electrochemically active hydroxyl groups, which can be oxidized by the anode active material. This is used for electrochemical detection. In the detection, along with sensing electrode, counter electrode and reference electrodes are used. When the sample containing 1-hydroxy pyrene is put in the sensor, the following oxidation reaction of 1-hydroxypyrene occurs on the surface of the sensing electrode. Concentration of 1-hydroxypyrene is determined from the change in potential of the reaction.



ELECTROCHEMICAL GAS SENSOR

Electrochemical gas sensor is used in monitoring of concentration of gaseous analytes. They are used mainly to monitor the concentration of air pollutants, detection of leakage of chemicals in industries, and in defence, military and space applications. Schematic representation of a typical gas sensor is given below.



Construction of an electrochemical gas sensor

The following are the main components of an electrochemical sensor:

1. **Filter:** The filter is used to prevent unwanted contaminants, mainly particulate matter from entering in to sensor.
2. **Membrane:** A gas-permeable membrane is used to regulate the gas flow into the sensor. Its selectivity allows only the analyte gas to pass and also acts as a barrier to prevent leakage of the electrolyte from the interior of the sensor. Hydrophobic porous membranes are used with aqueous electrolytes. These pores are not wetted by the aqueous solution but allow the transport of dissolved gases to the electrode–electrolyte interface. The sensitivity and response time of the sensor mainly depends on the nature of membrane, its pore size and thickness.
3. **Electrodes:** Two or three electrode system is used based on the requirement. Working or sensing electrode, counter electrode, and reference electrodes are used.
4. **Electrolyte:** Electrolyte used should be a good ionic conductor, and chemically and physically stable under operation conditions of sensor. Main role of the electrolyte is to transport charge within the sensor, contact all electrodes effectively, and solubilize the reactants and products for efficient transport.

Working principle of an electrochemical gas sensor:

The following steps are involved in the working of a typical electrochemical gas sensor:

1. The diffusion of gas analyte through filter, membrane and then finally through electrolyte on to the surface of sensing Electrode.
2. Adsorption of analyte gas molecule on the surface of sensing electrode.

3. Oxidation of analyte on the surface of sensing electrode, liberating electrons. Transfer of liberated electrons from anode to cathode through external circuit. The surface of sensing electrode is the active part of the electrode. It is modified by coating with appropriate catalysts which can selectively interact with analyte gas and carry out its chemical change.
4. Desorption of the products from the electrode surface.
5. Diffusion of the products away from the reaction zone to the bulk of electrolyte or gas phase.

ELECTROCHEMICAL GAS SENSORS FOR SO_x and NO_x:

SENSORS OF SO_x:

- Sulphur oxides, SO₂ released from thermal power stations and other industrial plants, are gases harmful to the environment.
- It is very important to detect and control the concentrations of SO_x in industrial processes. The methods usually used to detect SO_x are chemical and electrochemical, but these methods cannot be used in situ or in constant operation.
- Recently, SO_x sensors utilizing a solid electrolyte such as K₂SO₄ [1], Na₂SO₄ [2], LiSO₄ [3], Ag₂SO₄ [4], Nasicon [5], Na-flAl₂O₃ [6] and Ag-fl-Al₂O₃ [7] have been widely studied, because this type of sensor has its own advantages:
- Continuous quantitative measurement; high selectivity and sensitivity; easy operation and fast response; simple construction and low price.

Sensing mechanism

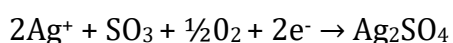
The sensor was composed of the following electrochemical cell:

Ag/ Ag-p-Alumina/ Pt, SO₃, SO₂, O₂

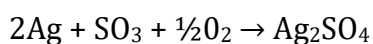
The anode reaction



The cathode reaction



The total reaction was



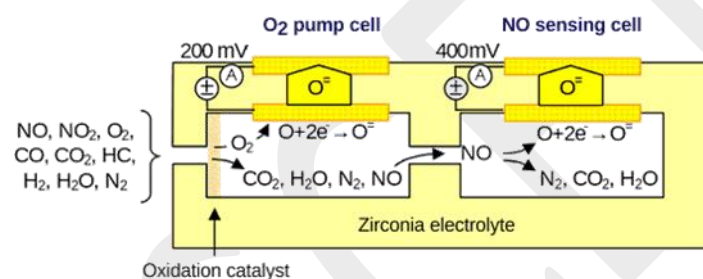
Where SO₃ was produced by the reaction can be checked by sensor.

Application

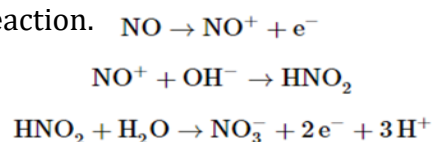
1. It is used in thermal power plant.
2. It is used in chemical industries to detect sulphur dioxide emission level

SENSORS OF NO_x:

Automotive NO_x sensors are primarily of the amperometry type, with two or three electrochemical cells in adjacent chambers. The first cell electrochemically pumps oxygen out of the sample so it does not interfere with the NO_x adsorber and Selective Catalytic Reduction (SCR) after treatment. Commercial NO_x sensors for automotive applications are primarily YSZ electrochemical sensors of the amperometry type. The schematic representation of an amperometry NO_x sensor is as shown.



The oxygen in the first cell is reduced and the resulting Oxide ions are pumped through the zirconia electrolyte by applying a bias of approximately -200mV to -400mV. The pumping current is proportional to the oxygen concentration. The remaining gases diffuse into the second cell where a reducing catalyst causes NO_x to decompose into Nitrogen and oxygen gas. As with the first cell, a bias of -400mV applied to the electrode dissociated the resulting oxygen which is then pumped out of the cell; the pumping current of the second cell is proportional to the amount of oxygen from the NO_x decomposition. An additional electrochemical cell can be used as a Nernstian Lambda sensor to help control the NO_x sensing cell. The direct electro oxidation of NO in solutions follows a 3-step reaction.



All hydrocarbons and CO in the exhaust gas should be oxidised before the NO_x sensing cell to avoid interference. Also, any nitrogen dioxide in the sample should be converted

to NO prior to NO_x sensing to ensure the sensor output is proportional to the amount of NO_x.

Disposable sensors (ds) in the detection of biomolecules and pesticides.

Definition: Disposable sensors are low cost and easy to use sensing devices intended for short term or rapid single point measurements. They transduce physical, chemical or biological changes in their environment to an analytical signal.

Disposable electrodes in the detection of biomolecules.

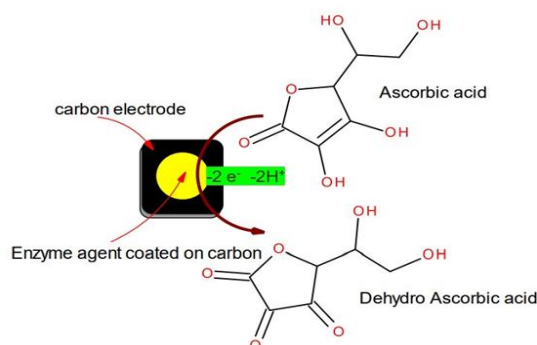
Monitoring of levels of biomolecules like carbohydrates, proteins, lipids, nucleic acids, enzymes, hormones, etc. is very essential to maintain a healthy body. Because, any deficiency or excess of these molecules may result biological disorders such as Alzheimer's disease, Parkinson's diseases, diabetes, heart attack, pregnancy complications, osteoporosis, etc resulting in decreased average life-span of the humans. Several types of disposable biosensors have been developed for continuous monitoring of these bio analytes. Disposable, pre-activated screen-printing electrodes have been developed for on spot analysis of glucose, ascorbic acid, uric acid, creatinine, lactic acid and dopamine in human blood samples.

Detection of Ascorbic acid:

Chemical name of Vitamin-C, a water-soluble vitamin is Ascorbic acid. It is an antioxidant essential for life and aids in protecting the body against oxidative stress. It is abundantly available in fruits, and vegetables. Its content varies from source to source. Thus, the electrochemical biosensors which can detect ascorbic acid in various samples in lower concentration are developed. These sensors are fast, low-cost, and sensitive and use disposable strips. These sensors can be used for on-the-spot analysis.

In the disposable strip, active materials of the sensing electrode, counter electrode and reference electrode are printed on the disposable paper strip using Screen Printing Technology. Active material coated on sensing electrode must be capable of oxidizing ascorbic acid on its surface. Several active materials are available for ascorbic acid oxidation. The ascorbate oxidase enzyme immobilized on a screen-printed carbon electrode with poly (ethylene glycol) and diglycerol ether as a crosslinking agent can be used as sensing (working) electrode in ascorbic acid disposable biosensor. It oxidizes

ascorbic acid in to dehydroascorbic acid. Concentration of ascorbic acid is determined from the change in potential of the oxidation process.

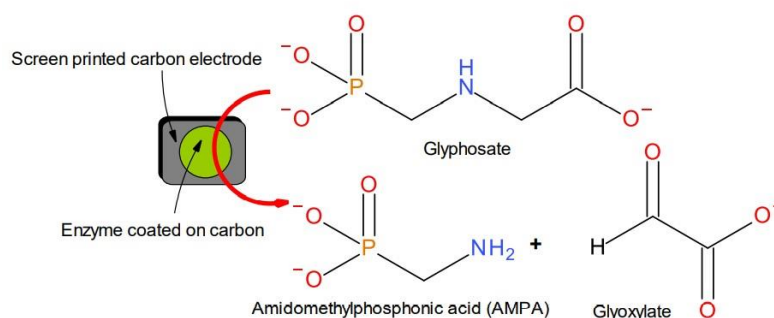


Disposable electrodes in the detection of pesticides:

With the development of science and technology, to improve yield and protect crops, farmers have started using several pesticides. These synthetic chemical pesticides are supposed to be used in very low concentration of ppm/ppb level. But, due to lack of proper knowledge they are often used in large quantities without caution. This has resulted in accumulation of pesticides in soil as well in agricultural produces. Pesticides can induce a number of diseases such as asthma, diabetes, birth defects, reproductive dysfunction, etc. Therefore, monitoring the level of pesticides in soil, water and cultivated agro-products is one of the best ways to detect the abuse of pesticides. Enzyme modified screen printed disposable paper strip electrodes are playing an important role in the detection of pesticides. These electrodes are coated with enzymes. Pesticides interact with the immobilized enzymes and leads to the formation of electroactive species. This results in decreased enzyme activity which can be measured quantitatively.

Detection of Glyphosate:

Glyphosate [N-(phosphonomethyl)glycine] is an organophosphorus pesticide. It is extensively used as herbicide in agriculture. Its residues are present in large amounts in agricultural products and entering in to ecosystem in large quantity. Glyphosate is classified as a potential carcinogen to humans. Therefore, there is a need to develop a rapid, reliable, and sensitive approach for analysing glyphosate in environmental samples.



Various analytical methods based on electrochemical biosensors have been designed and used for glyphosate determination. Glycine oxidase can catalyse the oxidative deamination of various amines and cleave the C-N bond in glyphosate. The glycine oxidase enzyme immobilized on a screen-printed carbon electrode can be used as sensing (working) electrode in glyphosate disposable biosensor. It oxidizes glyphosate into amidomethyl phosphonic acid (AMPA) and glyoxylate. Concentration of glyphosate is determined from the change in potential of the oxidation process.

Advantages of Disposable sensors over classical sensors:

Disposable sensors are,

1. They are portable with the capability of on-the-spot analysis.
2. They are economical, easy to use.
3. They require very less amount of sample to work with.

Classical sensors are,

1. Narrow or limited temperature range as they are too sensitive to temperature, hence they typically are internally temperature compensated.
2. Short and limited shelf life of six months to one year, depending on the activity.
3. Cross-sensitivity of other gases, as other gases can interfere which may lead to false readings.
4. The greater the exposure to a target the shorter the life span.

ENERGY STORAGE SYSTEMS

Battery: A battery is a cell or a series of cells connected together used as source of electrical energy.

Classification of battery: Batteries are classified into three types.

a) **Primary Batteries:** The batteries which cannot be recharged are called primary batteries or primary cells.

Example: Zn -air battery & Dry cell

b) **Secondary Batteries:** The batteries which can be recharged by passing current in opposite direction are called secondary cells or secondary batteries or rechargeable cells. A secondary cell can undergo large number of discharging and charging cycle.

Example: Ni-metal hydride battery & Li-ion battery

c) **Reserve Batteries:** The batteries which can be stored in an active state and made ready for use by activating them prior to the applications are called as reserve batteries. The key components of the batteries such as electrolyte are separated from the battery. The electrolyte is filled before its usage.

Example: Li- V_2O_5 battery.

CONSTRUCTION AND WORKING OF LI-ION BATTERIES

Anode: Lithium intercalated graphite (LiC_6)

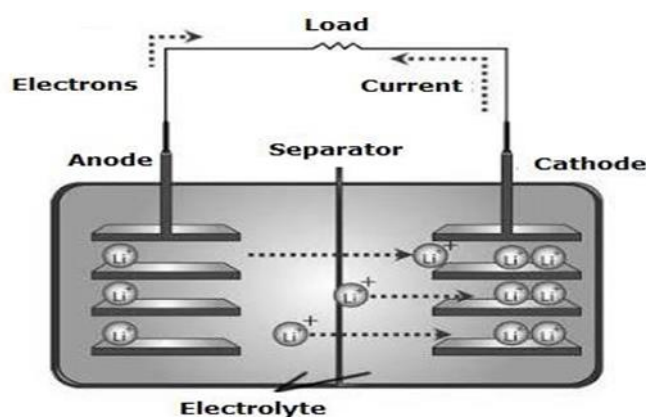
Cathode: Lithium cobalt oxide ($Li_{0.5}CoO_2$)

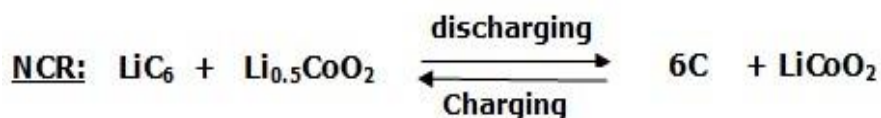
Electrolyte: Lithium salt like $LiPF_6$ (lithium hexafluoro phosphate) dissolved in a mixture of ethylene carbonate and diethyl carbonate.

Separator: Fine porous polymer film.

Representation: LiC_6 | $LiPF_6$ dissolved in organic solvents | $Li_{0.5}CoO_2$

Cell potential: 4.1V

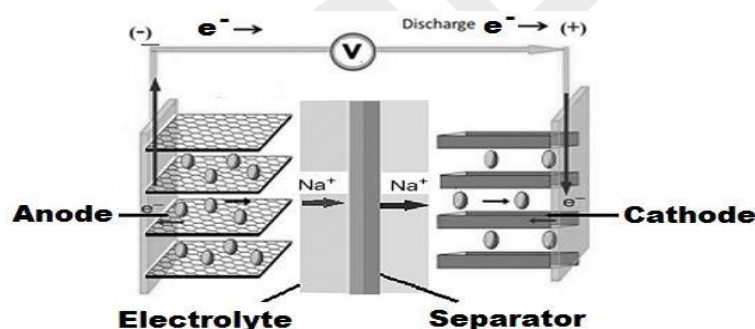


Cell reactions during discharge:

Applications: It is used in cellular telephones, digital cameras, portable game machines, medical applications such as emergency lighting, etc.

CONSTRUCTION AND WORKING OF Na- ION BATTERIES

The main advantage of Na-ion batteries comes from the natural abundance and lower cost of sodium compared with lithium.

Construction:

Anode: Sodium ions absorbed on surface of hard carbon (Na_xC_6)

Cathode: Sodium transition metal oxides ($\text{Na}_{1-x}\text{MO}_2$), where M = Fe, Ni, Mn, Co, etc.

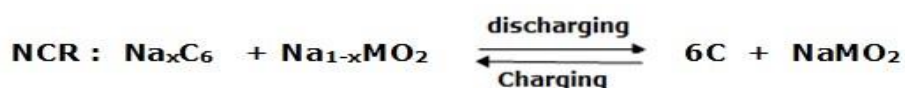
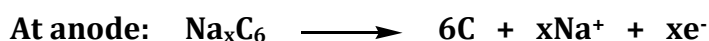
Electrolyte: Sodium salts such as NaPF_6 and NaClO_4 are used together with small amounts of mixed organic carbonate solvents like ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC).

Separator: Fine porous polymer film.

Representation: $\text{Na}_x\text{C}_6 \mid \text{NaPF}_6 \text{ dissolved in mixed organic solvents} \mid \text{Na}_{1-x}\text{MO}_2$

Cell potential: 3.8V

Type: Secondary Battery

Working: Cell reactions during discharge:

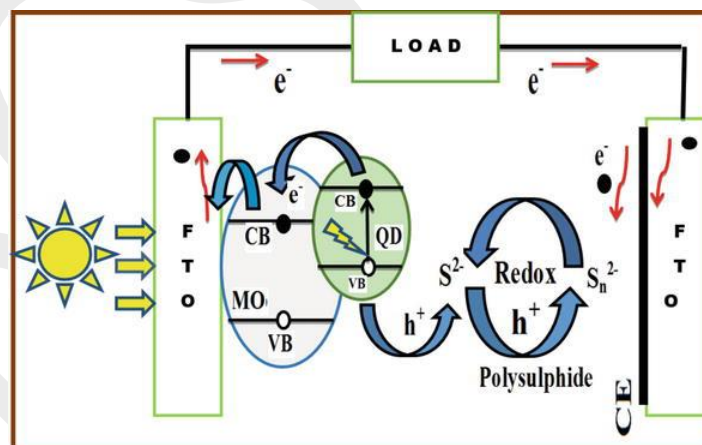
Applications: It is used in electric vehicles and power tools.

QUANTUM DOTS SENSITIZED SOLAR CELLS (QDSSC's)

Quantum dots sensitized solar cells re excitonic solar cells, the basic idea behind the emergence of third-generation photovoltaics is to design solar cells with efficiency that exceeds the limit. QDs with their unique characteristics are widely used to improve the efficiencies of QDSSC. They are the structures having properties such as size-dependent optical band gap, high molar extinction coefficients, high intrinsic dipole moments, which give rise to good charge separations and also the multiple charge carriers. Quantum dots are a special class of semiconductors, which are nanocrystals, composed of materials from II-VI, III-V, or IV-VI groups. The energy band gap increases with decrease in size of the quantum dot. The structure and working principle of QD sensitized solar cell is almost identical to dye sensitized cells.

Structure:

QDSSC consists of three essential components, namely photoanode, electrolyte containing redox couple and counter electrode. The schematic representation of QDSSC including the electron transfer processes is as shown.



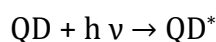
Working Principle of QDSSC:

When the light is incident on the solar cell through a transparent conducting oxide, photons are absorbed to generate excitons. As the band positions between the Conduction Band of the Photoelectrode and the CB of QD is greater than the binding energy of the exciton, then it gets separated at the Metal Oxide (MO) / QD interface into electrons and holes. The electrons move into the CB of MP to reach the transparent

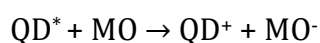
Conducting Oxide (TCO) surface before it reaches the band. In the other way, the electrolyte reduces the reductant species (Re), i.e., hole created in the QD. The Re turns into Oxidant species (Ox) after losing electron to the hole, which diffuses toward the Counter Electrode (CE) to receive an electron coming from the external circuit. With the hole reduction, the QD is ready to absorb another photon for the creation of an exciton.

Thus, a photovoltaic effect converting light into electricity does useful work in the external load. The constant photo conversion process is continual till the light is incident on the active area of the solar cell. The photovoltaic processes discussed above are summarized as,

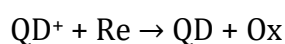
Formation of exciton due to absorption of photon



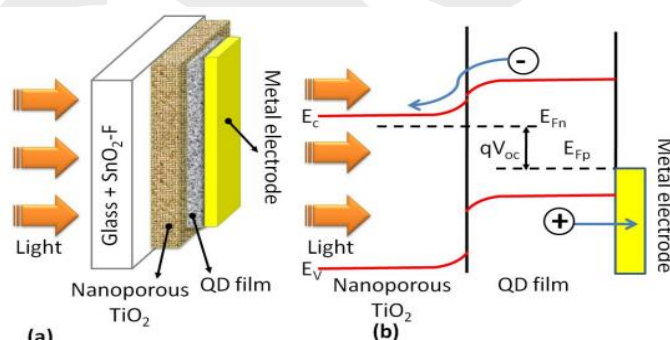
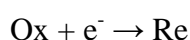
Electron transfer from QD to MO



Charged QD getting reduced to neutral QD



Reduction of oxidant from e^- supplied by CE



Properties:

1. They have the potential to increase the maximum attainable thermodynamic conversion efficiency of solar photon conversion up to about 66% by utilizing photogenerated carriers to produce higher photo voltages or higher photocurrents.
2. QDSSC's have different reaction temperatures and they are best and efficient when the temperature is 180C.

Advantages of Quantum dot solar cells

The following are the benefits of quantum dot solar cells.

- They have a favourable power to weight ratio with high efficiency.
- Their power consumption is low.
- There is an increase of electrical performance at low production costs.
- Their use is versatile and can be used in windows, not just rooftops.

Disadvantages of QDSC

- There are some disadvantages of QDSC. Cadmium selenide-based quantum dot solar cells are highly toxic in nature and require a very stable polymer shell.
- Cadmium and selenium ions which are used in the core of quantum dots are known to be cytotoxic.

Quantum dots solar cell applications

- Biological labelling,
- Imaging, and detection and as efficient fluorescence resonance energy transfer donors.
- It is used as light-emitting diodes
- It is used as photoconductors and photodetectors.
- It is used as photovoltaic.
- It is used in biomedicine and environment.
- It is used in catalysis and others.

BGS COLLEGE OF ENGINEERING AND TECHNOLOGY

DEPARTMENT OF APPLIED CHEMISTRY
MAHALAKSHMI, Bengaluru - 560086



APPLIED CHEMISTRY (BCHE102/202)

Module: 02
Materials for Memory
and Display Systems



MATERIALS FOR MEMORY AND DISPLAY SYSTEMS

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 Systems: Photoactive and electroactive 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), Light emitting electrochemical cells.

Self-learning: *Properties and functions of Silicon (Si), Germanium (Ge), Copper (Cu), Aluminium (Al), and Brominated flame retardants in computers.*

MEMORY DEVICES

Memory device: A memory device is a piece of hardware used to store data. Most electronic devices such as computers, mobile phones, tablets, etc all have a storage device that stores data and /or programs.

Basic Concepts of Electronic Memory:

An electronic memory device is a form of semiconductor storage which is fast in response and compact in size and can be read and written when coupled with a central processing unit (CPU, a processor). In conventional silicon-based electronic memory, data are stored based on the amount of charge stored in the memory cells. Organic/polymer electronic memory stores data in an entirely different way, for instance, based on different electrical conductivity states (ON and OFF states) in response to an applied electric field. Organic/polymer electronic memory is likely to be an alternative or at least a supplementary technology to conventional semiconductor electronic memory.

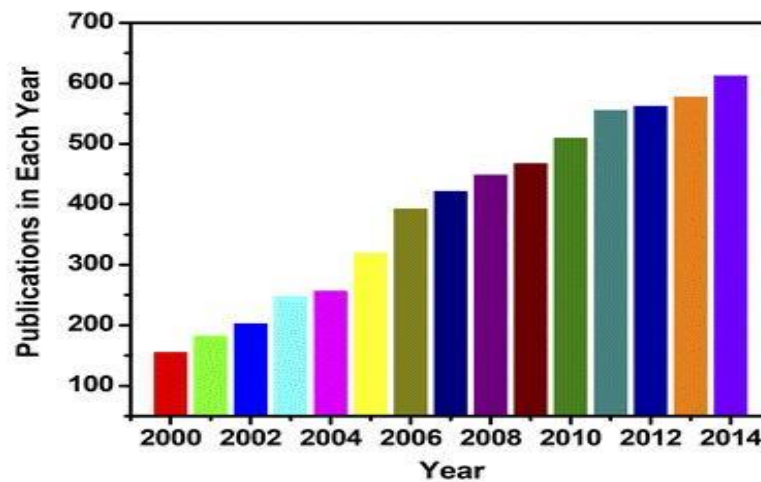
History of Organic/Polymer Electronic Memory Devices

Different forms of storage, based on various natural phenomena, have been reported since the 1940s. In the 1960s, there was a great interest in the electrical properties of amorphous semiconductors and disordered structures, arising from their

unusual electrical properties which also make them promising materials for device applications.

1. During 1968-70, bistable electrical conductivity and resistivity phenomenon was observed in Pb/polydivinyl benzene, tetracene, phthalocyanines and polystyrene polymer materials. All these materials showed bistable switching and memory switching effects. But the performance was not satisfactory for practical applications.
2. In 1980s, two stable ferroelectric polarization states were discovered in polymers. Thin films of ferroelectric polymer materials can be repeatedly switched between two stable and are capable of exhibiting non-volatile memory effects. But they required very high operating voltage of 30 V.
3. In 1995, ferroelectric polymer films as thin as 1 nm were fabricated. These required just 1 V to switch between two states. Since, then Polymer ferroelectric random-access memory (FeRAM) was developed as a promising memory technology.
4. In 2001, an organic field-effect transistors (OFETs) memory device was demonstrated using a sexithiophene oligomer as the conductor and a ferroelectric organic polymer material as gate insulator.
5. In 2003, a WORM type memory device was developed consisting of a thin film p-i-n silicon diode and a mixture of two conductive polymers, poly(ethylene dioxythiophene and poly(styrene sulfonic acid).
6. In 2004, ultrathin film organic materials were discovered with multilevel conductivity states. Poly[2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene polymer showed one low- and three high-conducting states. All four accessible states have associated memory effects for data-storage applications. To achieve ultrahigh density memory devices, organic materials with multilevel stable states are highly desirable.
7. Devices demonstrating multistability where more than two conducting states can be programmed into a single switching element will dramatically increase the amount of data stored per area or volume. Further progress in the development of multilevel organic polymer memory has been made in recent years.

The International Technology Roadmap for Semiconductors (ITRS) has identified polymer memory as an emerging memory technology since the year 2005.



CLASSIFICATION OF ELECTRONIC MEMORY DEVICES

According to the device structure, electronic memory devices can be divided into four primary categories: transistor-type, capacitor-type, resistor-type and charge transfer-type.

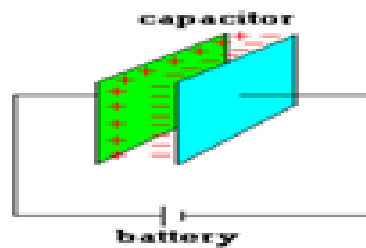
1. Transistor-type

Transistors are made from silicon, a semiconductor. It is converted to p-type and n-type semiconductor by doping trivalent and pentavalent impurities. Transistors are made using p-type and n-type semiconductor. 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 DEVICE

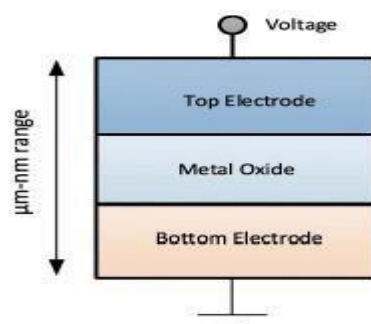
Capacitors have two parallel plate electrodes and charges are stored in these electrodes under an applied electric field. Data can be stored in these devices based on different charge stored in the cell. Charges stored in the cell maintain electric polarization that can be switched between two stable states by an external electric

field. Organic and polymeric ferroelectric materials can be used in capacitor-type electronic memory device.



3. RESISTOR-TYPE ELECTRONIC MEMORY DEVICE

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 TYPE ELECTRONIC MEMORY DEVICE

This type of electronic device is based on the Charge Transfer Effects of a charge transfer complex. A charge transfer (CT) complex consists of two parts, one electron donor and other an electron acceptor. It is also called as a donor-acceptor (D-A) complex. The conductivity of a CT complex is dependent on the ionic binding between the D-A components. In CT complex, a partial transfer of charges occurs from donor part to the acceptor part. This results in difference in conductivity. CT complexes exhibit bistable states due to difference in conductivity. This behavior is used to design molecular electronic devices.

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.

TYPES OF ORGANIC MEMORY MATERIALS

There are three classes of materials which can exhibit bistable states and are used in organic memory devices. They are:

- 1) Organic molecules,
- 2) Polymeric materials,
- 3) Organic-inorganic hybrid materials.

Under each category, lot of different types of molecules exhibiting memory effect are available. Few of them are described here:

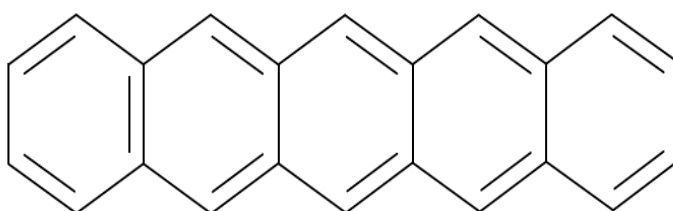
1) Organic molecules -Small organic molecules containing both an electron donor and an electron acceptor are an important type of material for organic electronic memory devices.

a) The p Type Organic Semiconductor Material "Pentacene"

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

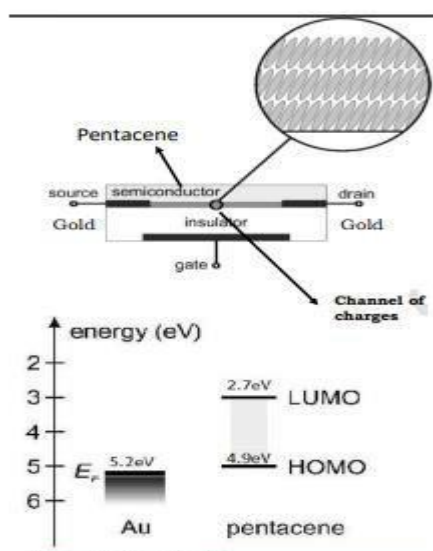
Example: Pentacene

Pentacene is a linear aromatic hydrocarbon formed by the fusion of five benzene rings. The extended π -system allows the continuous delocalization of π -electrons and there is a lateral overlapping of pi-electrons between the molecules.



Pentacene

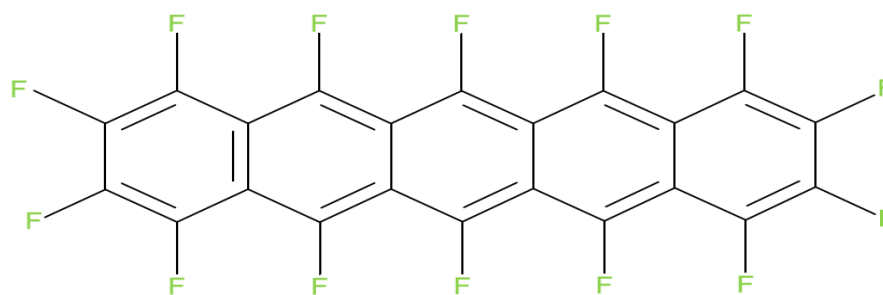
To show that Pentacene is a p-Type semiconductor.



Consider OTFT (Optical Thin Film Transistor) as shown above. Source and drain were made of gold and semiconductor was Pentacene. When a Positive voltage is applied to the gate negative charges are induced at the source electrode (Au). Since, Fermi level of gold is a way from LUMO of Pentacene, electron flow cannot take place. When a negative voltage is applied to the gate holes are injected from source to semiconductor because Fermi level energy of gold is close to energy of HOMO of Pentacene. A conducting channel is formed at the insulator and semiconductor interface and allows the movement of charge carriers holes from source to drain when secondary voltage is applied. Therefore, Pentacene is considered as p-type semiconductor.

b) 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. When a p-type semiconductor Pentacene is modified with electronegative fluorine atoms to lower the Lowest Unoccupied Molecular Orbital (LUMO) energy levels of materials for electron injection and transport. The HOMO-LUMO gaps of perfluorinated pentacene are smaller than those of the corresponding Pentacene.



Perfluoropentacene

To show that Perfluoropentacene is a n-Type semiconductor.

Consider OTFT (Optical Thin Film Transistor) as shown above. Source and drain were made of gold and semiconductor was Perfluoropentacene. The HOMO-LUMO gaps are 2.07eV for pentacene and 1.95eV for perfluoropentacene. When a Positive voltage is applied to the gate negative charges are induced at the source electrode (Au). The source and drain electrodes inject electrons in its LUMO level. This charge forms a conducting channel at the insulator and semiconductor interface and allows the charge carriers electron from source to drain. Therefore, Perfluoropentacene is considered as n-type semiconductor.

2) Polymer molecules

Polymeric material for Organic memory device

A volatile memory is a type of memory which cannot sustain the two distinct electronic states without an external electronic power supply, that is, the written data will disappear. A non-volatile memory can sustain the two distinct states without the power supply, that is, the written data will not disappear when an external electronic power supply is removed. Understanding the relationship between the chemical structure and memory properties is a subject of utmost importance in the development of polymer memory materials. One such polymer used for organic memory device is Polyimide with Donor-Triphenyl amine and Acceptor-phthalimide.

Donor: Triphenyl Amine group (TPA) Acceptor: Phthalimide group

Hexa fluoro isopropylidene (6F): Increases the solubility of PI

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 LUMO of donor and acceptor are similar and therefore, after excitation the electron transferred to LUMO (acceptor), generating a CT state. This permits the generation of holes in the HOMO, which produces the open channel for the charge carriers to migrate through. Therefore, Field-induced charge transfer from triphenyl amine to phthalimide exhibit the switching behavior (bistable states ON/OFF). This device exhibits dynamic random-access memory (DRAM) behavior with an ON/OFF current ratio of upto 10^5 .

3) Organic-inorganic hybrid materials

Generally, organic-inorganic hybrid materials are composed of organic layers containing inorganic materials. Inorganic materials used are allotropes of carbon like fullerenes, carbon nanotubes, graphene and metal nanoparticles, semiconductor nanoparticles and inorganic quantum dots (QDs).

1) Organic-Carbon Allotrope Hybrid Materials

Polymers containing electron donors, such as thiophene, fluorene, carbazole and aniline derivatives can be combined with Fullerenes to obtain a charge transfer hybrid material with donor-acceptor ability and electrical bistable states. Fullerenes exhibit high electron-withdrawing ability and can capture up to six electrons. They are used in WORM memory effect devices.

2) Organic-Inorganic Nanocomposites

These are the hybrid electronic memory devices in which organic polymer with appropriate functional group is clubbed with metal nanoparticles, quantum dots and metal oxide nanoparticles. An example is a composite of 8-hydroxyquinoline-containing polymer with gold nanoparticle sandwiched between two metal electrodes. Bistable electronic transition states are observed when an electric field is applied due to charge transfer between the Au nanoparticles and 8-hydroxyquinoline.

DISPLAY SYSTEMS

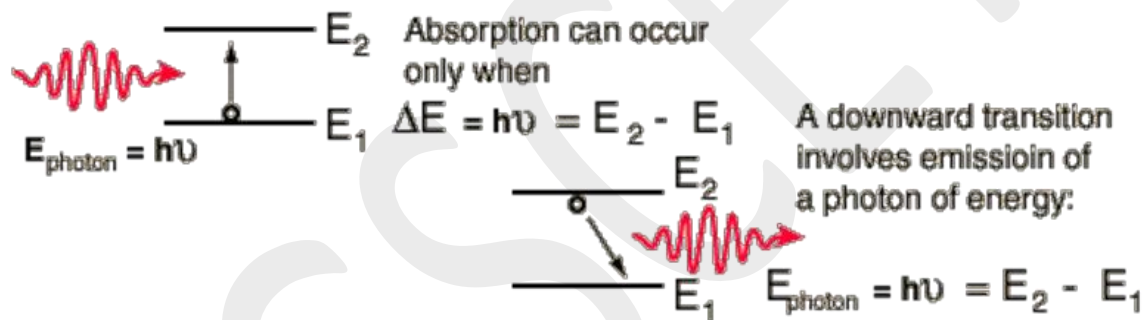
Display: Display is an output device used to present visual information.

Optoelectronics

Optoelectronics is the communication between optics and electronics, which includes the study, design and manufacture of a hardware device that converts electrical energy into light and light into energy through semiconductors.

Optoelectronic devices: A hardware device that converts electrical energy into light and light into energy through semiconductors.

Optoelectronic devices are primarily transducers i.e., they can convert one energy form to another. They can also detect light and transform light signals to electrical signals for processing by a computer.



Optoelectronic devices are special types of semiconductor devices that are able to convert light energy to electrical energy or electrical energy to light energy. If the photon 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.

Photoactive and electro active organic materials:

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

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 generates and transport charge carriers.

In an OLED device, the light-emitting layer is excited by the recombination energy of electrons from the cathode and holes from the anode, and then the light-emitting layer emits light when returning to the ground state. One of the electrodes consists of transparent material in order to extract light from the light emitting layer.

NANOMATERIALS USED IN OPTOELECTRONIC DEVICES

Nanomaterials: Nanomaterials are those materials whose characteristic length lies with in nanometer range (1-100nm). The properties of nanomaterials 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 Nanocrystals in electronics and optoelectronics fields.

Special properties of Silicon Nano crystals for optoelectronics

1. Silicon Nanocrystal has wider bandgap energy due to quantum confinement.
2. Si NCs shows higher light emission property (Photoluminescence)
3. SiNCs exhibit quantum yield of more than 60%.
4. Si-NCs exhibit tunable electronic structure
5. Larger surface area-volume ratio.

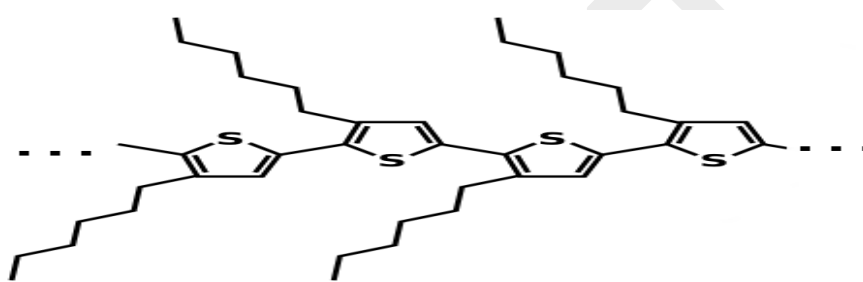
Applications:

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

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

Polythiophenes are an important class of conjugated polymers, environmentally and thermally stable material. Chemical structure of P3HT Poly(3-hexylthiophene) is a polymer with chemical formula $(C_{10}H_{14}S)_n$. It is a polythiophene with a short alkyl group 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.



structure of P3HT Poly(3-hexylthiophene)

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) have 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 bandgap of P3HT is 490nm visible region, corresponding to $\pi \rightarrow \pi^*$ transition, giving electron-hole pair.
6. P3HT indicate that an increase in the conductivity is associated with an increase in the degree of Crystallinity.

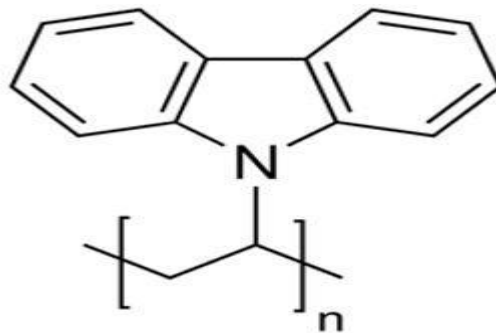
Applications:

- P3HT-ITO forms a p-n junction permit the charge carriers to move in opposite direction and hence, used in Photovoltaic devices.
- It can be used as a positive electrode in Lithium batteries.
- Used in the construction of Organic Solar Cells.

- Manufacture of smart windows.
- Used in the fabrication new types of memory devices.

Light emitting material-Poly [9-vinyl carbazole] (PVK)]

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



Structure of poly(9-vinylcarbazole) (PVK) Applications

- PVK has been commonly used in OLEDs, light harvesting applications, photo refractive polymer composites and memory devices.
- Used in the fabrication of light-emitting diodes and laser printers.
- Used in the fabrication of organic solarcells when combined with TiO₂ on glass substrate.
- Used in the fabrication of solarcells when combined with Perovskite materials.
- PVK-Perovskite junction is used in Light-Emitting Diodes with Enhanced Efficiency and Stability.

LIQUID CRYSTAL DISPLAYS

The **liquid crystals** are a unique state of matter between solid(crystalline)and liquid(isotropic)phases.

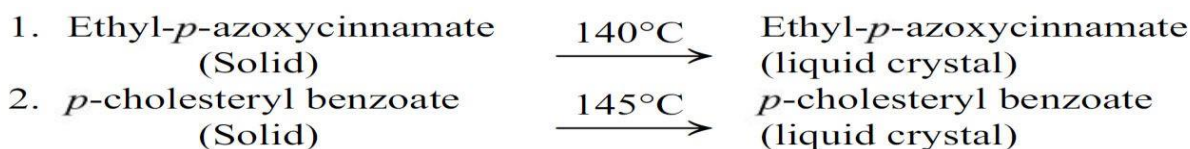
Classification of Liquid crystal

Liquid crystals are classified into two main categories, namely,

1. Thermotropic Liquid Crystals
2. Lyotropic Liquid Crystals

1) Thermotropic Liquid Crystals:

A liquid crystal is said to be thermotropic if molecules orientation is dependent on the temperature. By increasing the temperature, the increase in energy and there by movement of constituent molecules, will induce phase changes.



Thermotropic liquid crystals may be further classified as:

- Nematic liquid crystals
- Chiral Nematic liquid crystals
- Smectic liquid crystals
- Discotic Liquid Crystalline Phase

1. Nematic liquid crystals (or thread-like liquid crystals)

The molecules move either sideways or up and down. Since the molecules are oriented in one direction, they exhibit anisotropy. In this case, the molecules are readily aligned in the same direction in the presence of electric and magnetic fields. The alignment of molecules is temperature sensitive – as the temperature is increased, the degree of orientation of the nematic crystals decreases and they change into isotropic liquids.

Examples: *p*-azoxy phenetole, anisaldazine.

2. Chiral (Twisted) Nematic liquid crystals

In chiral nematic or twisted nematic liquid crystals (TNLC) all the molecules are roughly parallel to one another, the molecules in the chiral nematic phase arrange themselves to form a helical configuration.

Examples: cholesteryl formate, cholesteryl myristate, and cholesteryl benzoate.



Nematic phase

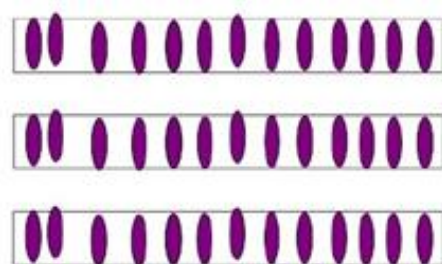


Helical pattern of Chiral nematic phase

3. Smectic liquid crystals

Substances that form smectic phases are soap-like (in Greek, smectos means soap). In smectic liquid crystals, there is a small amount of orientational order and also a small amount of positional order. The molecules are arranged in regularly spaced layers (positional order). Within the layer they tend to point along the director (orientational order).

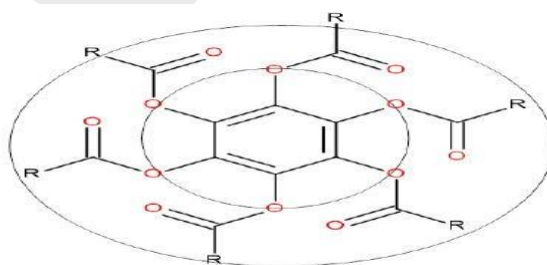
Examples: 4-cyanobenzylidene-4-n-octyloxyaniline.



Layered arrangement in smectic phases

4. Discotic Liquid Crystalline Phase

Molecules with a disk- or plate-like structure demonstrate the liquid crystal phase. These are known as columnar or discotic liquid crystals. In the centre region, these molecules have stiff structures like benzene and triphenylene. Because there is orientational order but no positional order in the simplest discotic phase, it is often referred to as the discotic nematic phase.

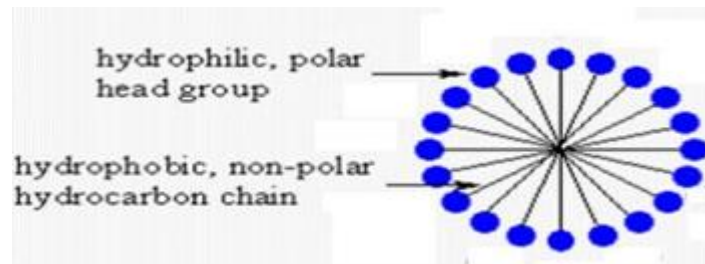


Benzene-hexa-n-alkanoates showing Discotic mesophase

2. Lyotropic Liquid Crystals

The orientational behavior of lyotropic crystals is a function of concentration and solvent. These molecules are amphiphilic—they have both hydrophilic and hydrophobic ends in their molecules. The hydrophilic end is attracted towards

water, whereas the hydrophobic end is water repellent and attracted towards non-polar solvents. At low concentrations, these molecules are randomly oriented but as the concentration increases, the molecules start arranging themselves. Cell membranes and cell walls are examples of lyotropic liquid crystals. Soaps and detergents form lyotropic crystals when they combine with water.



Properties of liquid crystals

1. They exhibit optical anisotropy which is defined as the difference between refractive index parallel to the director and refractive index perpendicular to the director. These two properties are important for the electro-optic effects in liquid crystals.
2. The intermolecular forces are rather weak and can be perturbed by an applied electric field.
3. Because the molecules are polar, they interact with an electric field, which causes them to change their orientation slightly.
4. Liquid Crystal can flow like a liquid, due to loss of positional order.
5. Liquid crystal is optically birefringent, due to its orientation order.
6. Liquid crystals, like all other kinds of matter, exhibits thermal expansion (Thermal Imaging).

APPLICATIONS OF LIQUID CRYSTALS IN DISPLAY SYSTEMS

Liquid crystal displays operate at low voltages (a few volts) and consume less power as compared to other display and hence are used in various fields, including electronics, optics, displays, sensors, and medicine. Some of the major applications of liquid crystals are:

1. Watches, calculators, mobile telephones, laptop computers and related electronic gadgets.
2. Indicators in automobile dashboards, airplane cockpits, traffic signals, advertisement boards and petrol pump indicators.

3. Blood pressure instruments, digital thermometers, and TV channel indicators.
4. pH meters, conductometers, colorimeters, potentiometers, and other analytical instruments.

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 into light via an organic emitter”.

Properties of Organic Light Emitting Diodes (OLED's)

1. OLED devices have solid and planar structure. Therefore, OLED display panels are very thin, flat and lightweight.
2. OLED devices have self-emission property and hence their devices have high contrast ratios and wide viewing angles, which are very significant factors for displays.
3. The response time of OLEDs is as fast as micro- or nanosecond order. Therefore, OLED displays can produce sharp moving images.
4. OLEDs have a wide viewing angle, which means that the image quality is maintained even when viewed from different angles.
5. OLEDs are energy efficient, as they do not require a back light like traditional LCD displays, resulting in lower power consumption.
6. OLEDs are self-emissive, which means that they do not require a separate light source, resulting in a thinner display.
7. OLEDs have a long lifespan, as they do not contain a back light that can degrade over time, resulting in a longer-lasting display.

Application of Organic Light Emitting Diodes (OLED's)

1. OLED displays are used in televisions, monitors, smartphones, and other electronic devices.
2. OLEDs can also be used as a source of lighting in various applications, including automotive lighting, street lighting, and architectural lighting.
3. The thin and flexible nature of OLEDs makes them suitable for use in wearable devices, such as smart watches and fitness trackers.
4. OLEDs can be used in automotive applications, such as dashboard displays, and interior lighting.
5. OLEDs can be used in medical applications, such as in surgical lighting and medical imaging.

6. They offer bright and highly accurate lighting options that can help improve medical procedures and diagnosis.

QUANTUM LIGHT EMITTING DIODES (QD-LEDS)

Quantum dot light emitting diodes are a form of light emitting technology and consist of nano- scale crystals that can provide an alternative for applications such as display technology". The structure of QD-LED is like the fundamental design of OLED. But the difference is that the light emitting is from the QDs, such as cadmium selenide (CdSe) nanocrystals.

Properties of QLED

1. QD-LEDs are capable of producing highly accurate and vibrant colors due to their use of quantum dots, which emit light of a specific color when they are excited by a light source or an electrical current.
2. QD-LEDs are more energy-efficient than traditional LCD displays because they do not require as much back lighting.
3. QD-LED 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. QD-LEDs have a longer lifespan than traditional LCD displays because they do not suffer from the same issues of back light burn out or color fading over time.
5. QD-LEDs displays have fast response times, which mean that they can display fast-moving images without motion blur or ghosting.
6. QD-LEDs can be made on flexible substrates, which allows for the creation of flexible displays that can be bent or curved.

Applications of QD-LED

- 1) QD-LED displays are commonly used in televisions, monitors, smartphones, and other electronic devices. They offer superior image quality and color accuracy compared to traditional LCD displays.
- 2) QD-LEDs can also be used as a source of lighting invarious applications, including automotive lighting, street lighting, and architectural lighting. They offer energy-efficient and highly customizable lighting options.

- 3) QD-LEDs can be used in medical imaging applications, such as in MRI machines, to produce high-resolution and accurate images.
- 4) QD-LED displays are suitable for use in virtual and augmented reality applications due to their ability to produce vibrant and accurate colors, which can enhance the immersive experience.
- 5) QD-LED displays can be used in advertising displays, such as digital billboards and signage, to produce high-quality and eye-catching visuals.

Light-emitting electrochemical cell

Light-emitting electrochemical cells (LEC) are solid-state lighting devices that convert electric current to light within electroluminescent organic semiconductors.

- LECs are best known for their simple architecture and easy, low-cost fabrication techniques.
- The key feature of their fabrication is the use of air stable electrodes and a single active layer consisting of mobile ions that enable efficient charge injection and transport processes within LEC devices.
- LEC devices can be operated at low voltages with high efficiencies, contributing to their widespread interest.

Applications

- Electroluminescent inks and stickers
- Used as light emitting materials.

BGS COLLEGE OF ENGINEERING & TECHNOLOGY

**DEPARTMENT OF APPLIED CHEMISTRY
MAHALAKSHMI, Bengaluru - 560086**



APPLIED CHEMISTRY (BCHE102/202)

**CORROSION AND
ELECTRODE SYSTEM
MODULE-03**



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.

CORROSION

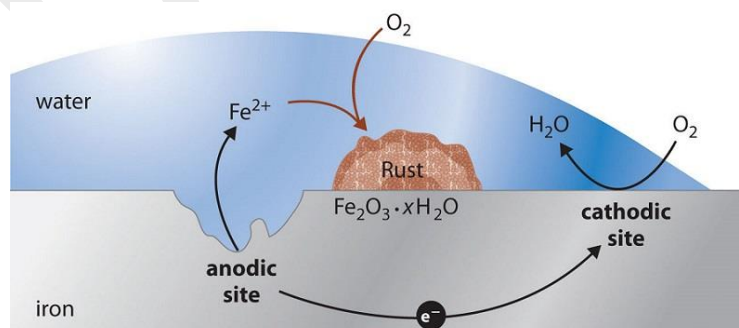
Corrosion:

It is defined as the destruction and consequent loss of metals due to chemical or electrochemical attack on its surface by the surrounding environment.

Electrochemical theory of corrosion:

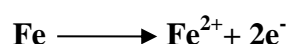
According to electrochemical theory, corrosion of metals occurs due to the following changes, when they are exposed to the environment.

1. A large number of minute galvanic cells are formed which acts as anodic and cathodic areas
2. At anode the metal undergoes oxidation and electrons are liberated which migrates towards cathodic region.
3. Oxygen of the atmosphere undergoes reduction at cathodic area in the presence of moisture forming hydroxide ions.



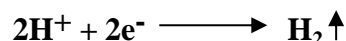
Corrosion Reaction:

1. **Anodic Reaction:** At anode the metal undergoes oxidation and liberating electrons.

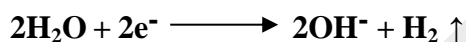


2. **Cathodic Reactions:** At cathode, reduction occurs due to the consumption of electrons generated at the anode. The different cathodic reactions are:

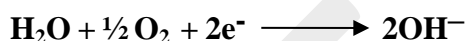
- **In acidic medium:** If the metal surface is exposed to acidic medium, in the absence of air, then hydrogen ions are reduced to hydrogen gas.



- **In alkaline and deaerated medium:** If the metal surface is exposed to only moisture under alkaline medium, in the absence of air, then water is reduced to OH^- ions and H_2 .



- **In neutral and aerated medium:** If the metal surface is exposed to moisture and air, under neutral medium, then oxygen is reduced to OH^- ions.

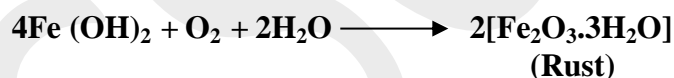


3. **Formation of rust:**

- The Fe^{2+} ions formed at anode move towards cathode and OH^- ions formed at cathode move towards anode. As Fe^{2+} ions diffuse faster than OH^- ions, they meet near the cathode forming ferrous hydroxide.



- Ferrous hydroxide further reacts with O_2 and H_2O forming *reddish brown hydrated ferric oxide (rust)*.



Factors influencing the rate of corrosion:

a) **Nature of the corrosion product:**

If the corrosion product is **insoluble, stable, uniform and nonporous**, it acts as a barrier (protective film) between the fresh metal surface and surrounding corrosion environment and preventing the further corrosion.

Example: Al, Cr & Ti

If the corrosion product is **soluble, unstable, non-uniform and porous**, do not form protective film. In such cases, the fresh metal surface is continuously exposed to the surrounding corrosion environment and corrosion of the metal takes place continuously.

Example: Zn, Fe & Mg.

b) **The ratio of anodic to cathodic area:**

If the anodic area is smaller and cathodic area is larger (i.e., the ratio of anodic to cathodic area is small), the electrons liberated at the anode, are rapidly consumed at the cathodic area. This makes the anodic reaction to take place at a faster rate, thus increasing the rate of oxidation and corrosion.

Example: Coating of tin on iron.

If the anodic area is larger and cathodic area is smaller (i.e., the ratio of anodic to cathodic area is large), the consumption of electrons liberated at the anode will be slower at cathode area and therefore rate of oxidation at anode decreases and corrosion rate also decreases.

Example: Coating of zinc on iron.

Nature of surrounding medium

c) pH:

Acidic medium is generally more corrosive than alkaline and neutral medium. Lower the pH of the medium (below 3), severe corrosion occurs even in the absence of air due to

- Continuous evolution of hydrogen at the cathode facilitating anodic oxidation of the metal.
- Dissolution of the corrosion product (oxide layer) in acidic medium exposing fresh metal surface for corrosion.

If the pH is above 10, corrosion practically stops due to the formation of a protective coating. Between pH 3 and 10 corrosion occurs only in the presence of oxygen.

d) Temperature:

In general, increase in temperature increases rate of corrosion. This is due to

- Increase in temperature increases the conductance of the aqueous medium since ions gain kinetic energy & move faster. Therefore, rate of corrosion increases.
- An increase in temperature decreases the passivity of metals & leads to corrosion of passive metals such as Al, Cr etc.
- Increase in temperature, increases the solubility of corrosion product in the medium and breaks the protective film that might exist on the surface. Therefore, rate of corrosion increases.

e) Conductivity:

Presence of conducting species in the atmosphere increases the rate of corrosion. This is because, higher the conductivity of the medium, faster the ions can migrate between anodic and cathodic regions of the corrosion cell, in turn faster will be the exchange of electrons at the electrode surfaces. *Therefore, corrosion problem is more in the sea water than in fresh water.*

Types of Corrosion

1. Differential metal corrosion:

This is also known as galvanic corrosion. It occurs when two dissimilar metals are in contact with each other in a corrosive conducting medium. The metal with lower standard reduction potential acts as anode and gets oxidized and suffers from corrosion. The metal with higher standard reduction potential acts as cathode and do not suffer from corrosion.

Example (a): Consider a bimetallic sample of iron and copper in **fig (a)**. Iron (-0.44V) is placed above copper (+0.34V) in the electrochemical series. Therefore, iron acts as anode and undergoes corrosion, whereas copper acts as cathode and remains unaffected.

At anode: $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$

At cathode: $\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2\text{e}^- \longrightarrow 2\text{OH}^-$

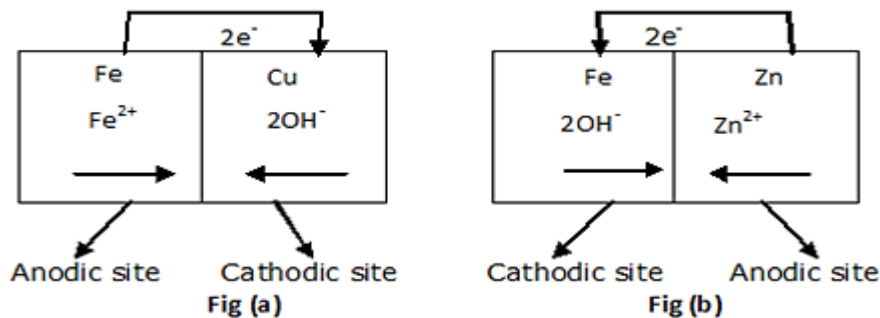
$\text{Fe}^{2+} + 2\text{OH}^- \longrightarrow \text{Fe}(\text{OH})_2$

Example (b): Consider a bimetallic sample of iron and zinc in **fig (b)**. Zinc (-0.76V) is placed above iron (-0.44V) in the electrochemical series. Therefore, zinc acts as anode and undergoes corrosion, whereas iron acts as cathode and remains unaffected.

At anode: $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$

At cathode: $\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2\text{e}^- \longrightarrow 2\text{OH}^-$

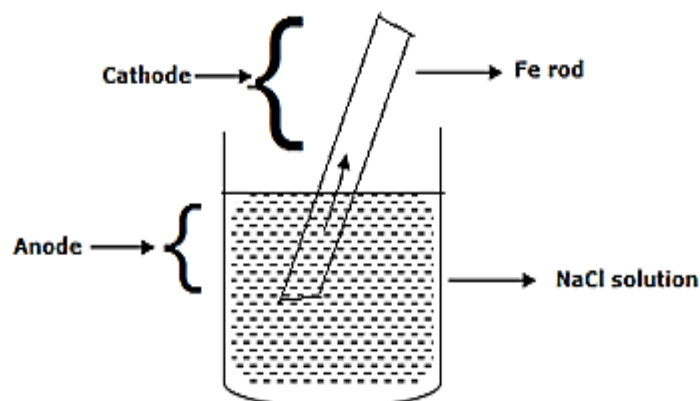
$\text{Zn}^{2+} + 2\text{OH}^- \longrightarrow \text{Zn}(\text{OH})_2$



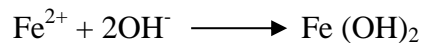
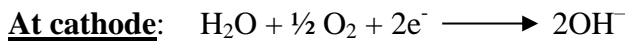
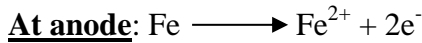
2. Differential aeration corrosion:

Differential aeration corrosion occurs when two different parts of the same metal are exposed to two different air concentration or oxygen concentration. Since cathodic reaction requires O₂, the part of the metal exposed to more air acts as cathode and part of the metal less aerated acts as anode. So, a difference in potential is created which causes flow of electrons between two differentially aerated areas of the same metal. Consequently, poorly aerated region undergoes corrosion.

Example (i):



Consider a pure iron rod which is partially immersed in an aerated solution of NaCl. Since cathodic reaction requires O_2 , the part of the iron rod exposed to air always acts as cathode. The portion of the iron rod immersed in NaCl is act as an anode. Hence, electrons flow from bottom to top of the rod. The reactions involved are as follows:

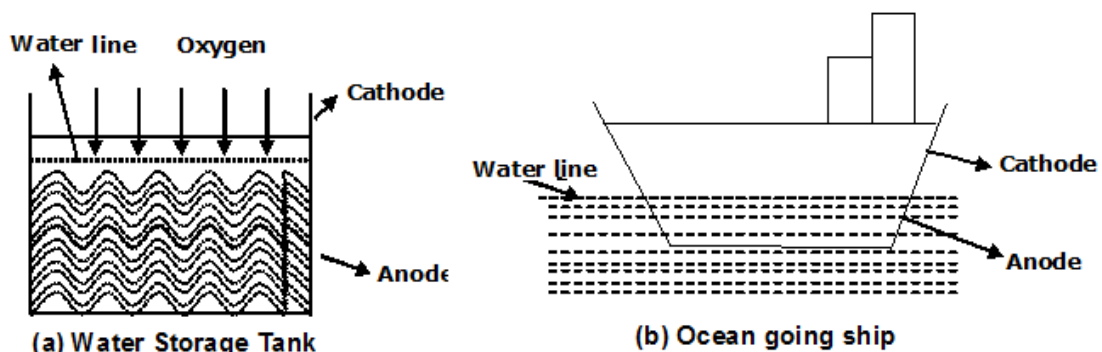


- ii) Window rods inside the frame corrode more than the exposed region.
- iii) Paper pins inside the paper get corroded and the other part is free from corrosion.

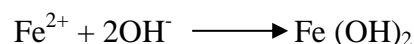
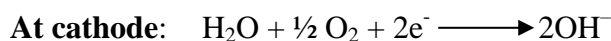
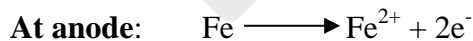
i) Water line corrosion:

This type of corrosion is an example of differential aeration corrosion. This is observed in

- a) **Water Storage Tank** - in which water is stored for a long period.
- b) **Ocean going ship** - hulls of ships which float for long periods in the sea water. Corrosion of a metal just below the water line (water level) is referred to as water line corrosion. The part of the metal below the waterline being less oxygenated acts as anode and undergoes corrosion. The part of the metal above the waterline which is more oxygenated acts as cathode and it is unaffected. Intense corrosion occurs at the anode and reduction of oxygen occurs near the waterline. Hence it is called water line corrosion.



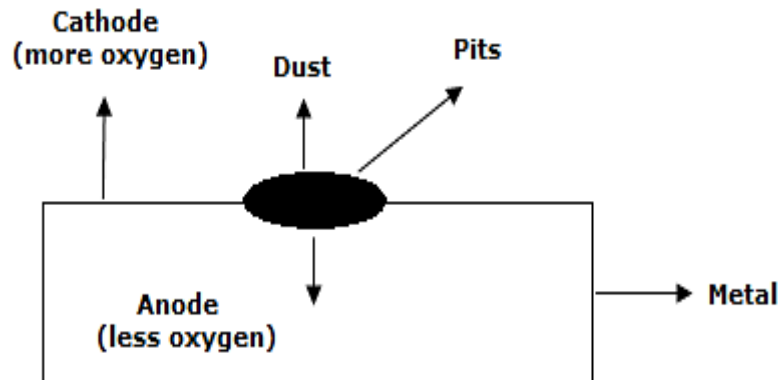
The reactions involved are as follows:



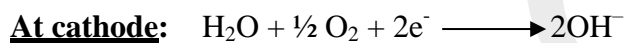
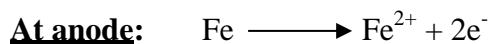
ii) Pitting corrosion:

This type of corrosion is an example of differential aeration corrosion. Pitting corrosion is a localized and accelerated corrosion resulting in the formation of pit or cavity. Pitting corrosion results when extraneous matter such as sand, dust particles, etc. are get deposited on a metal surface. The metal portion below the extraneous matter will not be well

oxygenated compared to the other metal surface. Hence the covered metal surface acts as anode and uncovered metal surface acts as cathode. In presence of a moisture, corrosion starts below the extraneous matter. This causes pits or cavities in the metal. Hence it is called pitting corrosion. Once a pit is formed the rate of corrosion increases. This is because of the formation of small anodic area.



The reactions involved are as follows:



Example: (1) Less aerated part of the machinery.
(2) Less aerated parts of barbed wire.

Corrosion Control methods

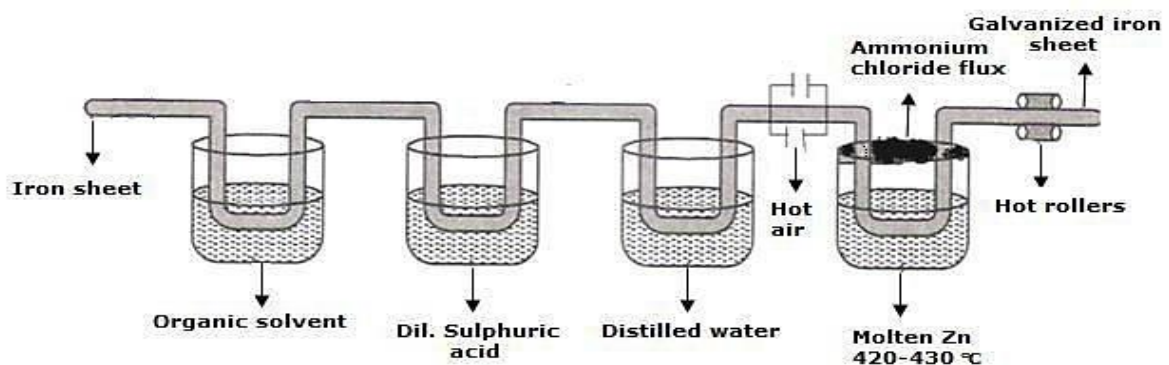
Metallic coating:

Deposition of a protective metal over the surface of a base metal is called metallic coating.

Anodic Coating: Anodic coatings are produced by coating a base metal with more active metals (having lower electrode potential) which are anodic to the base metal.

Galvanization is an example of anodic metal coating. Coating of Zn over iron as base metal is called galvanization. Galvanization is carried out by hot dipping method.

The process involves the following steps:



Galvanization

1. The iron metal surface is first washed with organic solvents (benzene or toluene, etc.) to remove oil, grease, etc.
2. Rust and other deposits are removed by washing with dilute sulphuric acid.
3. Finally, it is washed well with distilled water and dried using hot air.
4. The cleaned & dried iron metal is then dipped in bath of hot molten Zn at 420 – 430 °C and the surface of the bath is kept covered with ammonium chloride as a flux to prevent the oxidation of molten zinc. Ammonium chloride will also act as adherent for Zn coating.
5. When the iron metal is taken out, the excess Zn on the surface is removed by passing through a pair of hot rollers, which wipes out excess of Zn coating and produces a thin coating.

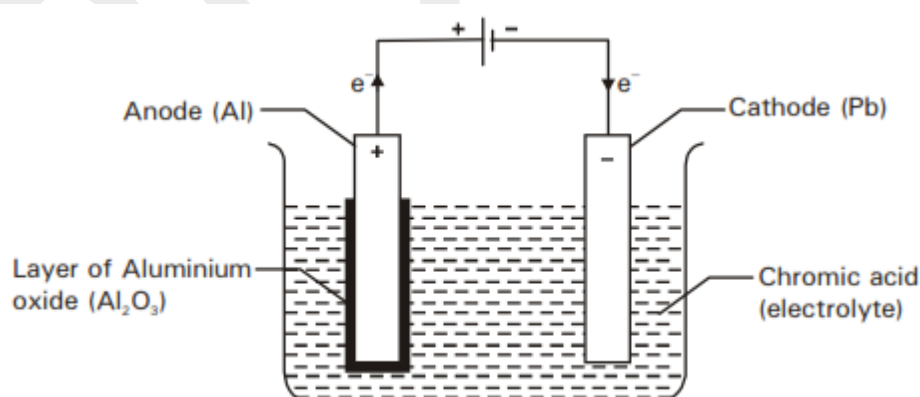
Applications:

1. Galvanized iron pipes are used for supplying potable water for domestic purpose.
2. Galvanized iron drums are used to preserve variety of chemicals, drugs and organic solvents.
3. Zinc gets dissolved in dilute acids to form highly toxic compounds. Hence, galvanized utensils are not used for storage of food products.

Anodizing:

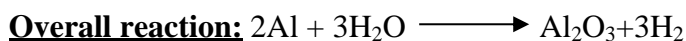
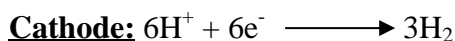
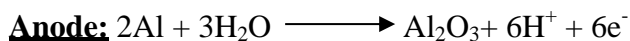
Anodizing is a process of developing an oxide layer on the surface of metal by anodic oxidation in an electrolytic cell. Metals such as Al, Ti, Mg, V and Zr are anodized in the presence of electrolyte like chromic acid, sulphuric acid, oxalic acid or boric acid, by electrochemical oxidation. This method is not applicable to ferrous and its alloys.

The process anodization of aluminium:



1. The Al article to be anodized is first de-greased with organic solvents and polished to get clean surface. It is used as anode.
2. Pb is generally used as cathode.

- Both the electrodes are dipped in the 5-10% chromic acid electrolytic solution. The electrolysis is carried out by passing D.C voltage of 40V at 35-40 °C.
- A thin oxide layer of aluminium (Al_2O_3) of 5-20 nm thickness is formed on the anode. This oxide layer is slightly porous.



- The strength of oxide layer formed is increased by dipping in boiling water. This treatment changes the porous surface into a sealed surface by forming monohydrate of aluminium oxide ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$).

Application:

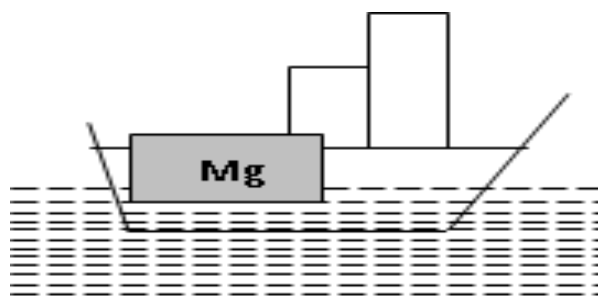
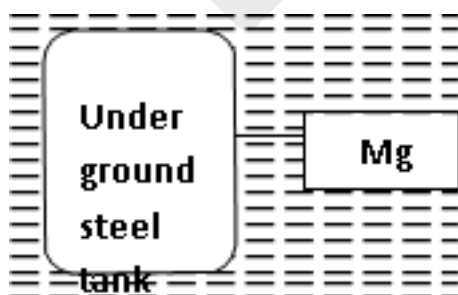
- Anodized aluminium is used in manufacture of pressure cookers, aircrafts & window frames.
- Anodized aluminium is used in office partitions.

Cathodic protection:

The principle involved in this method is to force the metal to be protected to behave as cathode, there by corrosion does not occur. This phenomenon is known as cathodic protection. There are two methods.

a) Sacrificial anode method:

- In this method, base metal is converted into cathode by connecting it to more active metals.
- These active metal acts as auxiliary anodes. Zn, Mg and Al are the common auxiliary anodes used in this method.
- The anodic metal being more reactive undergo corrosion and gives the electrons to the base metal and forces it to act as cathode, which remains unaffected.
- The sacrificial anodes have to be replaced from time to time after complete corrosion.
- Since the anodic metals are sacrificed to protect the base metal, the method is known as sacrificial anode method.



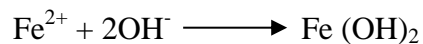
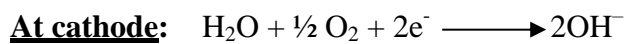
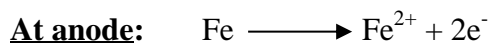
Application:

- It is used for protecting underground steel tanks with Mg blocks.

2. Mg bars are fixed to the sides of ocean-going ships to act as sacrificial anodes.
3. It is used for protecting buried iron pipe lines with Mg blocks.

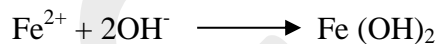
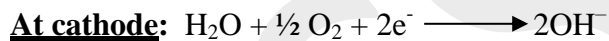
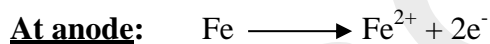
a) The presence of dust particles on iron surface for a long period.

This is due to pitting corrosion. Pitting corrosion results when small particles of dust are get deposited on a metal. The portion covered by the dust will not be well oxygenated compared to the exposed surface. Hence the covered surface becomes anodic with respect to the surface exposed. In presence of a moisture corrosion starts below the dust part. This causes pits or cavities in the metal. The reactions involved are as follows:



b) Steel pipe connected to copper plumbing.

This is due to galvanic corrosion. Iron or steel is placed above copper in the electrochemical series. Therefore, iron acts as anode and undergoes corrosion, whereas copper acts as cathode and remains unaffected. The reactions involved are as follows:



Corrosion Penetration Rate (CPR):

Corrosion Penetration Rate (CPR) is defined as: *The speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment.*

$$\text{CPR} = \frac{KW}{\rho At}$$

W = Weight loss, mg

ρ = density of specimen, g/cm³

A = area of specimen, sq. in.

t = exposure time, hr

K is constant depends on unit used, when K = 534 the unit **mpy** will be used.

When K = 87.6, the unit **mm/yr.** will be used.

CPR < 20 mil/yr. or about 0.5 mm/yr. is acceptable

CPR Units	K Value	Units			
		W	ρ	A	t
mpy	534	mg	g/cm ³	in. ²	h
mm/yr	87.6	mg	g/cm ³	cm ²	h

NUMERICAL PROBLEMS

Problem 1: 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 in² and that approximately 2.6 kg had corroded away during the 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 the steel is 7.9 g/cm³.

Solution: Given: CPR= 200 mpy, W= 2.6 kg, A= 10 in², $\rho = 7.9 \text{ g/cm}^3$

$$\text{CPR} = \frac{KW}{\rho At}$$

$$200 = \frac{534 \times 2.6}{7.9 \times 10 \times t} \times 10^6 \quad [1\text{kg} = 10^6 \text{ mg}]$$

$$t = \frac{534 \times 2.6}{7.9 \times 10 \times 200} \times 10^6$$

$$t = \frac{87,893}{8760} \text{ hrs}$$

$$= \text{approx. 10 years.} \quad [1\text{yr} = 24 \text{ hr} \times 365 \text{ days} = 8760 \text{ hrs}]$$

Problem 2: A metal iron plate was found in a vessel containing acidic media, it was estimated that the original area was 20 inch² that approximately 1.2 kg had corroded. Assuming a corrosion penetration rate of 400mpy for this iron in acidic, calculate time in years, density of iron 7.87g/ cm³.

Solution:

$$A = 20\text{in}^2 \quad W = 1.2\text{kg} = 1.2 \times 10^6\text{mg} \quad \text{CPR}=400\text{mpy} \quad \rho = 7.87\text{g/cm}^3$$

$$\text{CPR} = \frac{KW}{\rho At}$$

$$400 = \frac{534 \times 1.2 \times 10^6}{7.87 \times 20 \times t}$$

$$t = \frac{534 \times 1.2 \times 10^6}{7.87 \times 20 \times 400}$$

$$t = \frac{640.8 \times 10^6}{62,960} = 10,177.89 \text{ hrs} \quad [1\text{yr} = 24 \text{ hr} \times 365 \text{ days} = 8760 \text{ hrs}]$$

$$t = \frac{10,177.89}{8,760} = 1.16\text{yrs}$$

Problem 3: A thick steel sheet of area 400cm^2 is exposed to air near the ocean. After a one-year period it was found to experience a weight loss of 375g due to corrosion. To what rate of corrosion, in both mpy and mm/yr., does this correspond? The density of the steel is 7.9g/cm^3 .

$$\text{Solution: } A = 400 \times 0.155 = 62 \text{ in}^2 \quad 1 \text{ cm}^2 = 0.155 \text{ in}^2$$

$$\text{CPR} = \frac{KW}{\rho At}$$

$$\text{CPR} = \frac{534 \times 375}{7.9 \times 62 \times 365 \times 24} \times 10^3 = 46.7 \text{ mpy.}$$

$$\text{CPR} = \frac{87.6 \times 375}{7.9 \times 400 \times 365 \times 24} \times 10^3 = 1.19 \text{ mm/yr.}$$

Problem 4: A thick metal plate of area 40 in^2 has corroded in ocean belt. If the corrosion rate is 295mpy. Calculate its density if the weight lost due to corrosion is 5.8kg after 2 years.

Solution:

$$\text{CPR} = \frac{KW}{\rho At}$$

$$295 = \frac{534 \times 5.8}{\rho \times 40 \times 2 \times 365 \times 24} \times 10^6$$

$$\rho = \frac{534 \times 5.8}{295 \times 40 \times 2 \times 365 \times 24} \times 10^6 = 14.98 \text{ g/cm}^3$$

Problem 5: A metal bar of area 25in^2 has been left inside an ocean belt for 4 years. If the corrosion penetration rate is 45.8 mpy. Calculate the weight lost, if density of the metal is 7.9g/cm^3 .

Solution:

$$\text{CPR} = \frac{KW}{\rho At}$$

$$45.8 = \frac{534 \times W}{7.9 \times 25 \times 4 \times 365 \times 24}$$

$$W = \frac{45.8 \times 7.9 \times 25 \times 4 \times 365 \times 24}{534} = 593547 \text{ mg} = 0.593 \text{ kg}$$

Problem 6: Calculate the CPR of the metal in mm/yr. whose area exposed in sea water for 12 years is 123cm^2 . Density of the metal was found to be 12.4g/cm^3 and weight lost by the metal is 3kg.

Solution:

$$\text{CPR} = \frac{KW}{\rho At}$$

$$\text{CPR} = \frac{87.6 \times 3}{12.4 \times 123 \times 12 \times 365 \times 24} \times 10^6 = 1.639 \text{ mm/yr.}$$

Problem 7: Determine the area of the metal if its density 14.92 g/cm^3 has lost 8.1kg in 3years at a CPR 295mpy.

Solution:

$$\text{CPR} = \frac{KW}{\rho At}$$

$$295 = \frac{534 \times 8.1}{14.92 \times A \times 3 \times 365 \times 24} \times 10^6$$

$$A = \frac{534 \times 8.1}{14.92 \times 295 \times 3 \times 365 \times 24} \times 10^6 = 37.39 \text{ in}^2$$

Problem 8: A sheet of carbon steel one meter wide by three meters long has lost 40g to corrosion over the past six months. Convert that mass loss to a penetration rate of the steel in mm units and mpy units. What would be the corrosion rate? (Carbon steel density= 7.8 g/cm^3)

Solution:

$$W = 40\text{g} = 40 \times 10^3 \text{ mg} \quad \rho = 7.8 \text{ g/cm}^3 \quad t = 6 \times 30 \times 24 \text{ hrs}$$

$$\text{CPR in mmpy: } K = 87.6 \quad A = 1\text{m} \times 3\text{m} = 3 \text{ m}^2 = 3 \times 10^4 \quad [1\text{m}=100\text{cm}]$$

$$\text{CPR} = \frac{KW}{\rho At}$$

$$\text{CPR} = \frac{87.6 \times 40 \times 10^3}{7.8 \times 3 \times 10^4 \times 6 \times 30 \times 24}$$

$$\text{CPR} = \frac{3,504}{1,01,088} \times 10^{-1} = 0.00346 \text{ mm/yr} = 3.466 \times 10^{-3} \text{ mmpy}$$

$$\text{CPR in mpy: } K=534 \quad A = 1\text{m} \times 3\text{m} = 3 \text{ m}^2 = 3 \times 1550 \text{ in}^2 \quad [1\text{m}^2=1550\text{in}^2]$$

$$\text{CPR} = \frac{KW}{\rho At}$$

$$\text{CPR} = \frac{534 \times 40 \times 10^3}{7.8 \times 3 \times 1550 \times 6 \times 30 \times 24}$$

$$\text{CPR} = \frac{21,360}{15,66,86,400} \times 10^3 = 0.1363 \text{ mpy}$$

Problem 9: Calculate the CPR in both mpy and mmpy for a thick steel sheet of area 100 in² which experiences a weight loss of 485 g after one year. (Density of steel=7.9g/cm³).

Solution:

$$W = 485\text{g} = 485 \times 10^3 \text{mg} \quad t = 24 \times 365 \quad \rho = 7.9\text{g/cm}^3$$

$$\text{CPR in mm/yr} : K = 87.6 \quad A = 100\text{in}^2 = 645\text{cm}^2 \quad [1 \text{ inch}^2 = 6.45 \text{ cm}^2]$$

$$\text{CPR} = \frac{KW}{\rho At}$$

$$\text{CPR} = \frac{87.6 \times 485 \times 10^3}{7.9 \times 645 \times 365 \times 24}$$

$$\text{CPR} = \frac{42,486 \times 10^3}{4,46,36,580} = 0.9518 \text{ mm/yr}$$

$$\text{CPR in mpy} : K = 534 \quad A = 100 \text{ in}^2$$

$$\text{CPR} = \frac{KW}{\rho At}$$

$$\text{CPR} = \frac{534 \times 485 \times 10^3}{7.9 \times 100 \times 365 \times 24}$$

$$\text{CPR} = \frac{2,58,990 \times 10^3}{69,20,400} = 37.4241 \text{ mpy}$$

Problem 10: A thickness of brass sheet of area 400 inch² is exposed to air near the ocean. After two years period it was found to experience a weight loss of 375g due to corrosion. If the density of Brass is 8.73 g/cm³. Calculate the CPR in mm/year and mpy

Solution:

$$W = 375\text{g} = 375 \times 10^3 \text{mg} \quad t = 2\text{yrs} \quad \rho = 8.73\text{g/cm}^3$$

$$\text{CPR in mm/yr} : K = 87.6 \quad A = 400 \text{ in}^2 = 400 \times 6.45 \text{ cm}^2 \quad [1 \text{ inch}^2 = 6.45 \text{ cm}^2]$$

$$\text{CPR} = \frac{KW}{\rho At}$$

$$\text{CPR} = \frac{87.6 \times 375 \times 10^3}{8.73 \times 400 \times 6.45 \times 2 \times 365 \times 24}$$

$$\text{CPR} = \frac{32850 \times 10^3}{39,46,09,968} = 0.0832 \text{ mm/yr}$$

CPR in mpy: $K = 534$

$A = 400 \text{ in}^2$

$$\text{CPR} = \frac{KW}{\rho At}$$

$$\text{CPR} = \frac{534 \times 375 \times 10^3}{8.73 \times 400 \times 2 \times 365 \times 24}$$

$$\text{CPR} = \frac{2,00,250 \times 10^3}{6,11,79,840} = 3.2731 \text{ mpy}$$

ADDITIONAL NUMERICAL PROBLEMS

Problem 11: A piece of corroded aluminium plate was found in a submerged ocean vessel; it was estimated that the original area was 64 cm^2 that approximately 350 g had corroded away during the submersion. Assuming a corrosion penetration rate of 2.4 mpy for this alloy in sea water, estimate the time in years, density of aluminium 2.7 g/cm^3 [Ans: $t = 8.44 \text{ yrs}$].

Problem 13: A metal iron plate was found in a vessel containing acidic media, it was estimated that the original area was 20 inch^2 that approximately 1.2 kg had corroded. Assuming a corrosion penetration rate of 400mpy for this iron in acidic, calculate time in years, density of iron 7.87 g/cm^3 . [t = 1.16yrs]

Problem 14: 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 35 g due to corrosion. If the density of alloy is 8.4 g/cm^3 . Calculate the CPR in mpy and mpy. [Ans: 0.064mmpy & 2.54mpy]

Electrode System

Types of electrodes:

- 1) **Metal-Metal ion electrodes:** These are the electrodes where a metal is dipped in solution containing its own ions. Eg: $\text{Cu}|\text{CuSO}_4$, $\text{Zn}|\text{ZnSO}_4$
- 2) **Gas electrodes:** These are the electrodes where gas is in contact with an inert metal like platinum dipped in an ionic solution of gas molecules. Eg: Hydrogen electrode.
- 3) **Metal–Metal insoluble salt electrodes:** These are the electrodes where a metal will be in contact with its insoluble salt. Eg: Calomel electrode ($\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{Cl}^-$), Silver-Silver chloride electrode ($\text{Ag}|\text{AgCl}|\text{Cl}^-$).
- 4) **Ion selective electrodes:** These are the electrodes which are sensitive to particular ionic species and will develop a potential when a membrane is in contact with an ionic solution. Eg: Glass electrode
- 5) **Redox electrodes:** These are the electrodes, where inert metal like Pt will be in contact with oxidized and reduced species of the same metal in solution. Eg: $\text{Pt}|\text{Fe}^{2+}, \text{Fe}^{3+}$ and $\text{Pt}|\text{Sn}^{2+}, \text{Sn}^{4+}$
- 6) **Amalgam electrodes:** An amalgam electrode is a modification of metal-metal ion electrode. These are electrodes in which metal amalgam is dipped in the solution of its own metal ions. Eg: Lead amalgam electrode ($\text{Pb-Hg}|\text{Pb}^{2+}$)

Ion selective electrodes:

These are the electrodes which are sensitive to particular ionic species and will develop a potential when a membrane is in contact with an ionic solution.

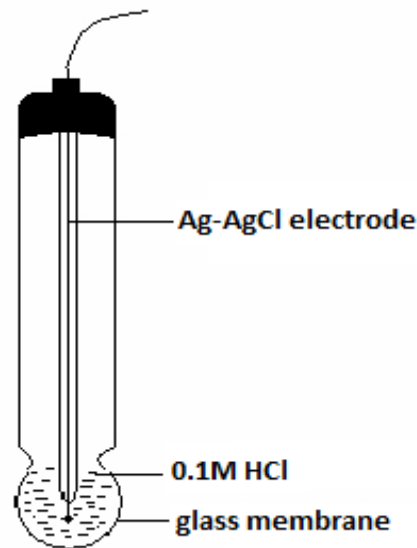
Example: Glass electrode

Glass electrode is an ion selective electrode in which a thin glass membrane is present which is permeable to H^+ ion and not to other ions in the solution.

Construction:

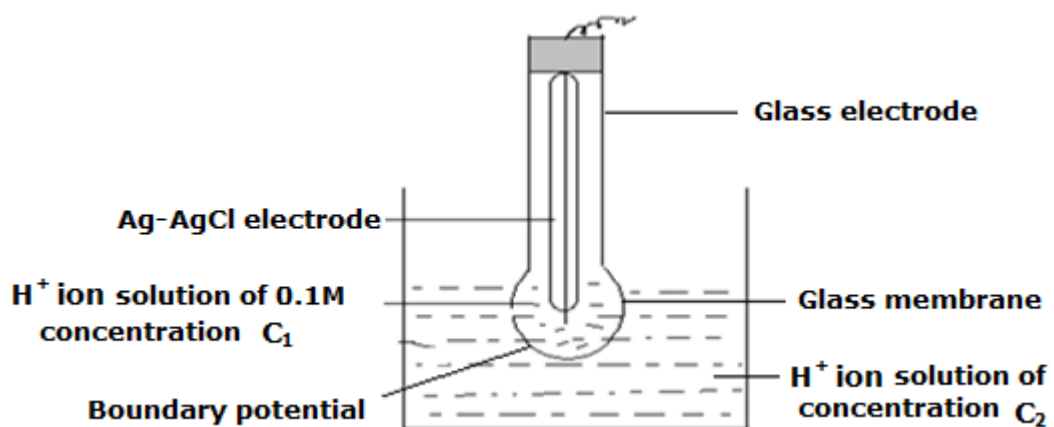
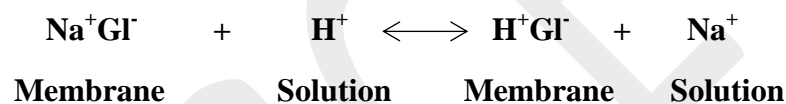
- A glass electrode consists of a thick-walled glass tube with a very thin walled glass membrane (bulb) at the bottom. Its thickness varies from 0.01-0.03 mm.
- This glass membrane made up of special glass of low melting point and high electrical conductivity. The approximate composition of this glass is 72% SiO_2 , 22% Na_2O and 6% CaO .
- This glass membrane allows only H^+ ions up to a pH range from 1 to 9.
- The glass bulb is filled with 0.1M HCl in which a silver–silver chloride electrode is dipped as an internal reference electrode which provides external electrical contact.

Representation: $\text{Ag}|\text{AgCl}|\text{HCl}(0.1\text{M})|\text{glass membrane}$



Working:

When the glass electrode is dipped in the test solution, the Na^+ ions of the glass membranes are exchanged for H^+ ions of the test solution.



When a glass electrode is placed between two H^+ ion solutions of different concentrations (C_1 and C_2), boundary potential is developed across the membrane. The boundary potential is given by the equation.

$$E_b = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$$E_b = \frac{0.0591}{n} \log C_2 - \frac{0.0591}{n} \log C_1 \quad (n=1 \text{ for } \text{H}^+ \text{ ion})$$

$$E_b = 0.0591 \log C_2 - 0.0591 \log C_1$$

$$E_b = L + 0.0591 \log C_2$$

(Where $L = -0.0591 \log C_1$, is a constant, $\because C_1 = 0.1M$)

Since C_2 is the unknown H^+ concentration, we can write

$$E_b = L + 0.0591 \log [H^+] \quad (\text{since } pH = -\log [H^+])$$

$$\boxed{E_b = L - 0.0591 pH} \dots\dots\dots(1)$$

It is found that the potential of the glass electrode (E_G) has three components:

- Boundary potential (E_b)
- Asymmetric potential (E_{assy})
- Potential of the internal reference Ag – AgCl electrodes ($E_{Ag/AgCl}$)

$$\boxed{\therefore E_G = E_b + E_{assy} + E_{Ag/AgCl}} \dots\dots\dots(2)$$

Substitute equation (1) in (2), we get

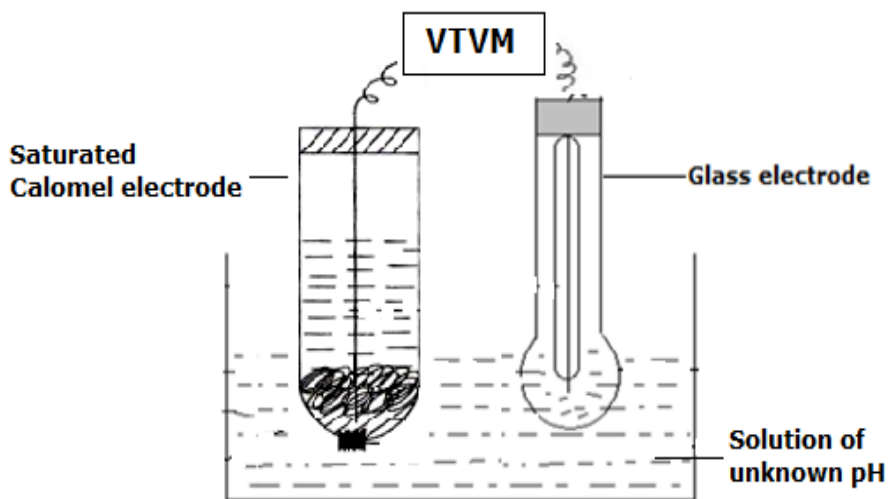
$$E_G = (L - 0.0591 pH) + E_{assy} + E_{Ag/AgCl}$$

$$\boxed{E_G = E_G^0 - 0.0591 pH}$$

Where $E_G^0 = L + E_{assy} + E_{Ag/AgCl}$. E_G^0 is the combination of three constant terms.

Determination of pH of solution using glass electrode

The cell consists of a glass electrode as indicator electrode and a saturated calomel electrode (SCE) as reference electrode, the cell is immersed in a solution whose pH is to be determined. The emf cell is measured using vacuum tube voltmeter (VTVM).



The cell assembly is represented as:

Pt|Hg|Hg₂Cl₂|KCl(sat)||solution of unknown pH| glass membrane|HCl (0.1M) |AgCl|Ag

The emf of the cell is given by

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

$$E_{\text{cell}} = E_G - E_{\text{SCE}}$$

$$E_{\text{cell}} = (E_G^0 - 0.0591 \text{ pH}) - E_{\text{SCE}} \quad (\text{Where } E_G = E_G^0 - 0.0591 \text{ pH})$$

$$p^H = \frac{E_G^0 - E_{\text{cell}} - E_{\text{SCE}}}{0.0591}$$

E_G^0 value of a glass electrode can be determined by using a solution of known pH.

Advantages and disadvantages of glass electrodes.

Advantages:

- Glass electrodes are portable and easy to operate.
- Accurate results are obtained between pH ranges 1 – 9. However, by using special glass electrodes the range can be extended to 1 – 14.
- It is not easily poisoned.
- It can be used even in presence of oxidizing and reducing agents.
- Equilibrium is rapidly achieved.
- It can be used for coloured, turbid and colloidal solutions.
- It does not require the use of any salt bridge.

Disadvantages:

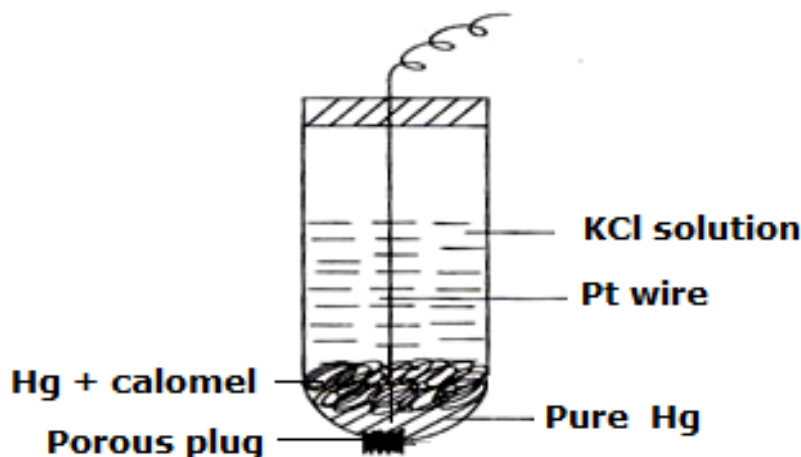
- ✓ Glass electrode cannot be used in presence of fluoride ions since they attack the glass membrane.
- ✓ Glass electrodes are very thin and fragile, should be handled with care.
- ✓ It requires special glass membrane for solutions of pH more than 9.
- ✓ Glass membrane has high internal resistance; ordinary potentiometer is not employed and hence requires vacuum tube voltmeter (VTVM). This is relatively costlier when compared to ordinary potentiometer.

Reference electrodes: These are the electrodes of constant potential which are used to determine electrode potential of other electrodes. There are two types of reference electrodes.

- ❖ Primary reference electrode. Eg: Standard hydrogen electrode.
- ❖ Secondary reference electrode. Eg: Calomel electrode, Ion selective electrode.

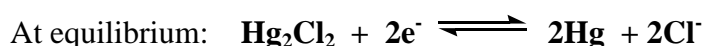
Construction and working of calomel electrode:

Construction:



- Calomel electrode is a metal-metal insoluble salt electrode and is a secondary reference electrode.
- Calomel electrode consists of a glass tube. A small amount of pure mercury is placed at the bottom of the glass tube and it is covered by a paste of Hg and calomel (mercurous chloride).
- The remaining portion of the glass tube is filled with KCl solution of known concentration (saturated, 1N or 0.1N).
- A platinum wire is dipped into the mercury and is used to provide external electrical contact. The porous plug at the bottom acts as a salt bridge.
- **Representation:** $\text{Pt}|\text{Hg}|\text{Hg}_2\text{Cl}_2|\text{KCl}(x)$ Where $x = \text{sat or } 0.1\text{N or } 1\text{N}$.

Working: Calomel Electrode can act as anode or cathode depending on the nature of the other electrode.



The electrode potential is given by

$$E_{\text{cal}} = E^0 - 0.0591 \log [\text{Cl}^-]$$

From the above equation it is clear that as the concentration of Cl^- ion increases, the electrode potential decreases.

Advantages:

- ❖ It is easy to construct and maintain.
- ❖ Its potential can remain constant and it can easily be reproduced.
- ❖ It can be used in the presence of oxidizing agents.

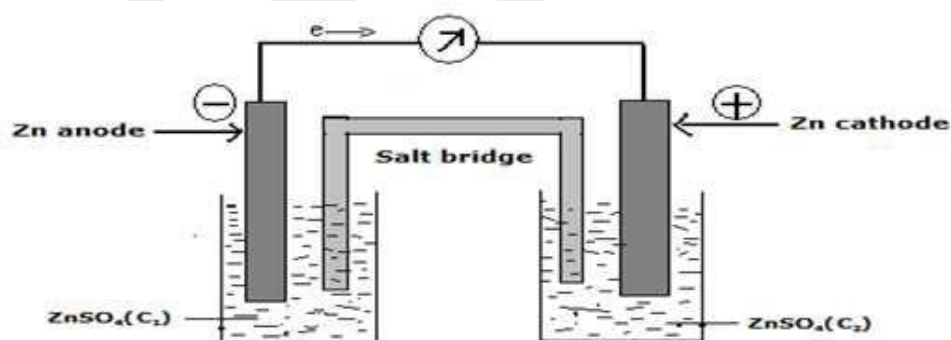
Applications:

- ❖ It is used as reference electrode in all potentiometric titrations.
- ❖ It is used as reference electrode with glass electrode in pH determination.
- ❖ It is used as a secondary reference electrode in the measurement of single electrode potential.

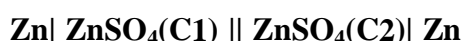
Note: At 298K, the electrode potentials are as follows.

KCl concentration	0.1N	1N	Saturated
E_{cal} (V)	0.334	0.281	0.2422

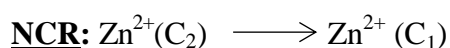
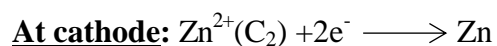
Electrolyte concentration cells: The galvanic cell in which electrode and electrolyte present in both half cells are same but only the concentration of electrolyte is different is called **electrolyte concentration cell**.

Derivation:

The above concentration cell can be represented as:



The electrode reactions are



Where C_1 and C_2 are concentrations of $ZnSO_4$ solution at anode and cathode respectively & $C_2 > C_1$

$$\text{Emf of anode is given as: } E_{\text{anode}} = E^0_{(Zn^{2+}/Zn)} + \frac{2.303RT}{nF} \log C_1 \dots\dots\dots(1)$$

$$\text{Emf of cathode is given as: } E_{\text{cathode}} = E^0_{(Zn^{2+}/Zn)} + \frac{2.303RT}{nF} \log C_2 \dots\dots\dots(2)$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \dots\dots\dots(3)$$

Substitute eqn (1) & (2) in (3),

$$E_{\text{cell}} = (E^0_{(Zn^{2+}/Zn)} + \frac{2.303RT}{nF} \log C_2) - (E^0_{(Zn^{2+}/Zn)} + \frac{2.303RT}{nF} \log C_1)$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log C_2 - \frac{2.303RT}{nF} \log C_1$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} (\log C_2 - \log C_1)$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

On substituting the values for $R = 8.314 \text{ J/K/mol}$, $T = 298\text{K}$ & $F = 96500 \text{ C}$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Numerical Problems

- [1] A concentration cell was constructed by immersing two silver electrodes in 0.02M and 2M $AgNO_3$ solutions. Write the cell representation, cell reactions and calculate the emf of the cell at 25°C .

Solution:

(i) Cell representation: $Ag|AgNO_3(0.02 \text{ M}) || AgNO_3(2\text{M})|Ag$

(ii) Electrode reactions: At anode: $Ag \longrightarrow Ag^+(0.02\text{M}) + e^-$

At cathode: $Ag^+(2\text{M}) + e^- \longrightarrow Ag$

NCR: $Ag^+(2\text{M}) \longrightarrow Ag^+(0.02\text{M})$

(iii) The emf of the concentration cell:

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$$E_{\text{cell}} = \frac{0.0591}{1} \log \frac{2}{0.02}$$

$$E_{\text{cell}} = 0.0591 \log(100)$$

$$E_{\text{cell}} = 0.0591 \times 2$$

$$E_{\text{cell}} = 0.1182 \text{ V}$$

- [2] Represent the cell formed by the coupling of two Cu electrodes immersed in CuSO₄ solutions. The concentration of cupric ions in one electrode system is 100 times more concentrated than other. Write the cell reaction and calculate the potential at 300 K.

Solution:

(i) Cell representation: Cu|CuSO₄(x M) || CuSO₄(100x M)|Cu

(ii) Electrode reactions: At anode: Cu \longrightarrow Cu²⁺(x M) + 2e⁻

At cathode: Cu²⁺(100x M) + 2e⁻ \longrightarrow Cu

NCR: Cu²⁺(100x M) \longrightarrow Cu²⁺(x M)

(iii) The emf of the concentration cell:

$$E_{\text{cell}} = \frac{2.303 RT}{nF} \log \frac{C_2}{C_1}$$

$$E_{\text{cell}} = \frac{2.303 \times 8.303 \times 300}{2 \times 96500} \log \frac{100}{1}$$

$$E_{\text{cell}} = 0.0297 \log(100)$$

$$E_{\text{cell}} = 0.0297 \times 2$$

$$E_{\text{cell}} = 0.0595 \text{ V}$$

- [3] A cell is obtained by combining two Cd electrodes immersed in cadmium sulphate solutions of 0.1M and 0.5M at 25 °C. Write the cell representation, cell reactions and calculate the emf of the concentration cell.

Solution:

(i) Cell representation: Cd|CdSO₄(0.1 M) || CdSO₄(0.5 M)|Cd

(ii) Electrode reactions: At anode: Cd \longrightarrow Cd²⁺(0.1 M) + 2e⁻

At cathode: Cd²⁺(0.5 M) + 2e⁻ \longrightarrow Cd

NCR: Cd²⁺(0.5 M) \longrightarrow Cd²⁺(0.1 M)

(iii) The emf of the concentration cell:

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$$E_{\text{cell}} = \frac{0.0591}{2} \log \frac{0.5}{0.1}$$

$$E_{\text{cell}} = 0.02955 \log(5)$$

$$E_{\text{cell}} = 0.02955 \times 0.6989$$

$$E_{\text{cell}} = 0.0207 \text{ V}$$

[4] The emf of the cell $\text{Cu} | \text{CuSO}_4(0.01 \text{ M}) || \text{CuSO}_4(x \text{ M}) | \text{Cu}$ is 0.0295V at 25°C . Find the value of x .

Solution:

The emf of the concentration cell: $E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$

$$0.0295 = \frac{0.0591}{2} \log \frac{x}{0.01}$$

$$\log \frac{x}{0.01} = 0.9983$$

$$\log(x) - \log(0.01) = 0.9983$$

$$\log(x) - (-2) = 0.9983$$

$$\log(x) + 2 = 0.9983$$

$$\log(x) = 0.9983 - 2$$

$$\log(x) = -1.0017$$

$$x = \text{antilog}(-1.0017)$$

$$\boxed{x = 0.0996 \text{ M}}$$

[5] A spontaneous galvanic cell $\text{tin} | \text{tin ion}(0.024\text{M}) || \text{tin ion}(0.064\text{M}) | \text{tin}$ develops an emf of 0.0126V at 25°C . Calculate the valency of tin.

Solution:

The emf of the concentration cell: $E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$

$$0.0126 = \frac{0.0591}{n} \log \frac{0.064}{0.024}$$

$$n = \frac{0.0591}{0.0126} \log \frac{0.064}{0.024}$$

$$n = 4.690 \times \log(2.6666)$$

$$\mathbf{n = 1.99 \approx 2} \text{ (n is the valency of tin)}$$

Analytical Techniques

Potentiometry

Potentiometry is the estimation of substances in solution by observing sudden change in potential of the cell at equivalence point.

Theory: The relation between electrode potential and metal ion concentration is given by the Nernst equation.

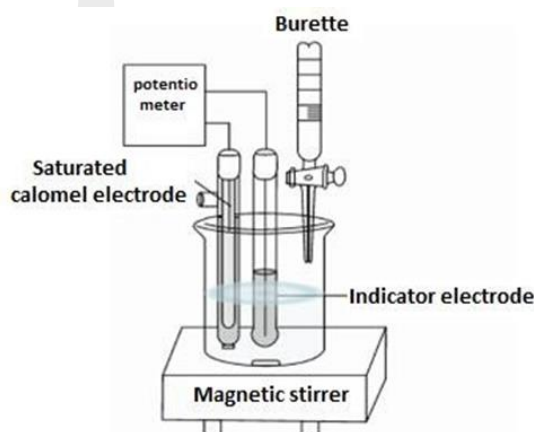
$$E = E^{\circ} + \frac{0.0591}{n} \log[M^{n+}]$$

The potential of an electrode E depends upon the concentration of the ion M^{n+} to which it is reversible.

Assume the concentration of the analyte to be $x \text{ mol/dm}^3$. Let $y \text{ mol/dm}^3$ be the volume of titrant added at a given instant. Under these conditions let z mole of the product be formed. The value of z will vary through the course of the titration since the concentration of the titrant is being continuously altered.

Initially the change in potential will be small. At the equivalence point, there will be sharp raise in the potential. Beyond the equivalence point, there will be small change in the potential. The equivalence point can be determined by plotting $\Delta E/\Delta V$ against volume of the titrant added.

Instrumentation: A potentiometer consists of a reference electrode, an indicator electrode and a device for measuring the potential. The indicator electrode responds rapidly to the changes in the potential due to the concentration changes of the analyte. A simple arrangement of potentiometric titration is shown in Figure.



A known volume of the analyte is taken in a beaker and its potential is determined by connecting the assembly to a potentiometer. The titrant is added in increments of 0.5ml and the potential is measured each time. The end point is determined by plotting change in potentials against the volume of titrant.

Applications:

1. It is used in redox titrations to estimate the concentration of analyte in the sample solution. **Example:** Estimation of FAS potentiometrically using standard $K_2Cr_2O_7$ solution.
2. It is used in precipitation titrations, which involves insoluble salt metals. **Example:** Titration of silver ion with a halide ion. Silver electrode is used as indicator electrode.

Conductometric titration

Theory: Ohm's law states that the current I (ampere) flowing through a conductor is directly proportional to the applied potential, E (volt) and inversely proportional to the resistance R (ohms) of the conductor.

$$I = \frac{E}{R}$$

The reciprocal of the resistance is called conductance. The resistance of a homogenous material of uniform cross section with an area of 'A' sq. cm and length 'l' cm is given by

$$R = \frac{\rho \times l}{A}$$

Where ρ is specific resistance or resistivity.

The reciprocal of the specific resistance is called specific conductance (κ). Specific conductance of an electrolyte solution is the conductance of the solution present between two parallel electrodes of 1cm^2 area of cross section and 1cm apart.

The specific conductance of the solution is given by

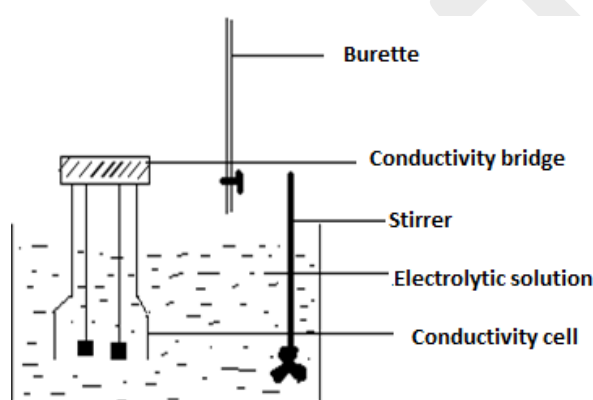
$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

l/A is known as the cell constant and R is the resistance of the solution.

Conductance measurements are used to determine the equivalence point in acid – base titrations. There is a sudden change in conductance of the solution after the equivalence point.

The equivalence point is determined graphically by plotting conductance against the volume of titrant added.

Instrumentation: A simple arrangement of conductometric titration is shown in Figure. It consists of two platinum electrodes each of unit area of cross section placed unit distance apart. The electrodes are dipped in the electrolytic solution taken in a beaker. It is connected to a conductivity bridge. The titrant is added from a burette and the solution is stirred. The conductance is measured after the addition of the titrant at intervals of 0.5 ml. The end point is determined by plotting conductance against the volume of titrant added.



Application:

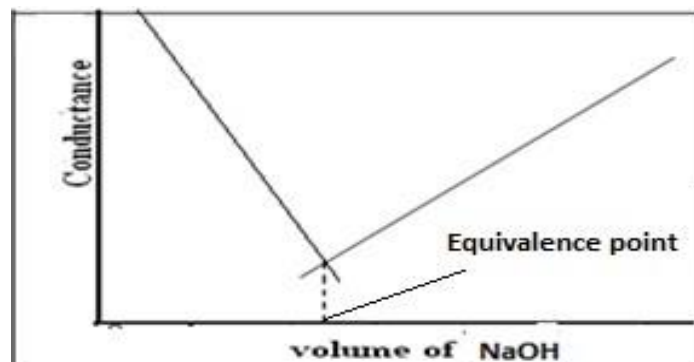
Explain the nature of conductometric graph for the following titrations

a) Strong acid with a strong base:

Consider the titration of HCl against NaOH.

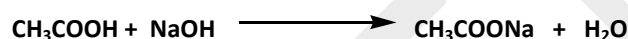


The conductance initially decreases till complete neutralization of the HCl takes place. This is due to the replacement of highly mobile H^+ ion by the Na^+ ion. After complete neutralization of the HCl, further addition of NaOH raises the conductance sharply. This is due to increase in the concentration of the OH^- ions. A plot of conductance (ohm^{-1}) against the volume of NaOH (cm^3) gives a graph as shown in Figure. The point of intersection of the curve gives the equivalence point.

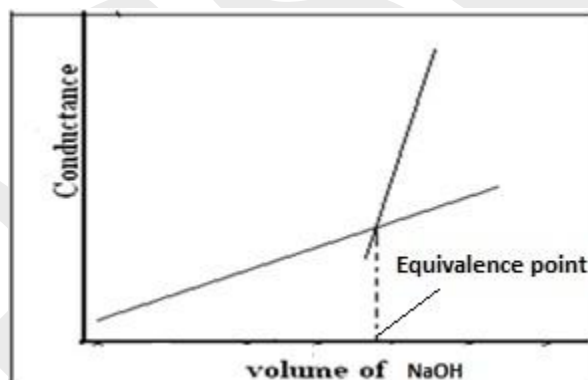


b) Weak acid with strong base:

Consider the titration of acetic acid against NaOH.



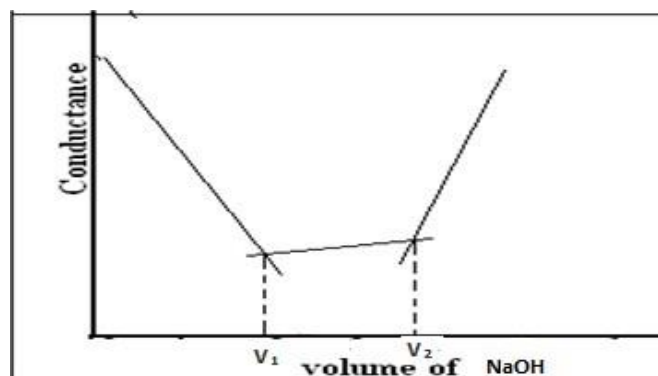
The conductance will be initially low since acetic acid is a weak electrolyte. When NaOH is added to the acetic acid, the sodium acetate formed is highly ionized and the conductance increases. After complete neutralization of the acetic acid, further addition of NaOH raises the conductance sharply. A plot of conductance (ohm^{-1}) against the volume of NaOH (cm^3) gives a graph as shown in Figure. The point of intersection of the lines gives the equivalence point.



c) Mixture of acids (strong and weak) with strong base:

Consider the titration of mixture of HCl and acetic acid against





HCl being stronger acid than CH_3COOH will get titrated first. The titration of CH_3COOH will start only after HCl is completely neutralized.

During the titration of HCl versus NaOH, the conductivity decrease due to replacement of H^+ ions with Na^+ ions. After neutralization of HCl, the neutralization of CH_3COOH will start and the conductivity increases to small extent till its neutralization is complete due to the sodium acetate formed is highly ionized. After neutralization of CH_3COOH , the conductance rapidly rises with further additions of NaOH. This is due to increase in the concentration of the OH^- ions. A plot of conductance (ohm^{-1}) against the volume of NaOH (cm^3) gives a graph as shown in Figure. The point of intersection of the lines gives the equivalence point V_1 and V_2 .

BGS COLLEGE OF ENGINEERING & TECHNOLOGY

**DEPARTMENT OF APPLIED CHEMISTRY
MAHALAKSHMI, Bengaluru - 560086**



APPLIED CHEMISTRY (BCHES102/202)

**MODULE-04
POLYMER AND
GREEN FUELS**



POLYMERS AND GREEN FUELS

Syllabus:

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

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.

POLYMER

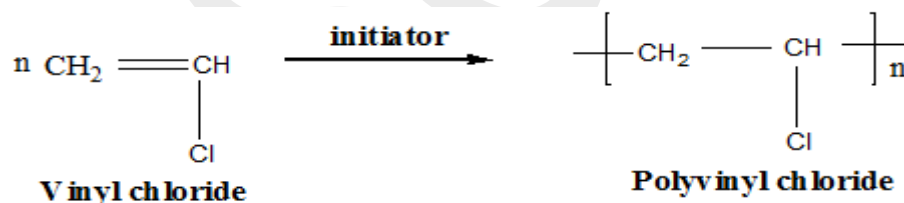
Monomers: These are simple compounds, which combine with each other to form polymers. Monomers are also called building blocks of polymers.

Ex: Vinyl chloride, ethene, propene etc.

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

Ex: Starch, Polyvinyl chloride, Polyethene, Nylon-6,6, etc.

- **Polymerization:** The process by which the monomers are transformed into a polymer is called polymerization.



- **Degree of polymerization:** The number of repeating units present in a polymer is called degree of polymerization.

Molecular mass of polymers:

Polymer properties are related to their molecular mass, size and structure. The polymer contains chains of varying lengths and hence, molecular mass is always expressed as an average. This is done in two ways.

Number - average molecular mass (\bar{M}_n):

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

If n_1, n_2, n_3, \dots are the number of molecules having molecular masses M_1, M_2, M_3, \dots respectively, then number - average molecular mass is given by

$$\overline{M}_n = \frac{n_1M_1 + n_2M_2 + n_3M_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

Mass - average molecular mass (\overline{M}_w):

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

If m_1, m_2, m_3, \dots are the masses of molecules having molecular masses M_1, M_2, M_3, \dots respectively, then mass-average molecular mass is given by

$$\overline{M}_w = \frac{m_1M_1 + m_2M_2 + m_3M_3 + \dots}{m_1 + m_2 + m_3 + \dots}$$

Where $m_1 = n_1M_1, m_2 = n_2M_2, m_3 = n_3M_3, \dots$

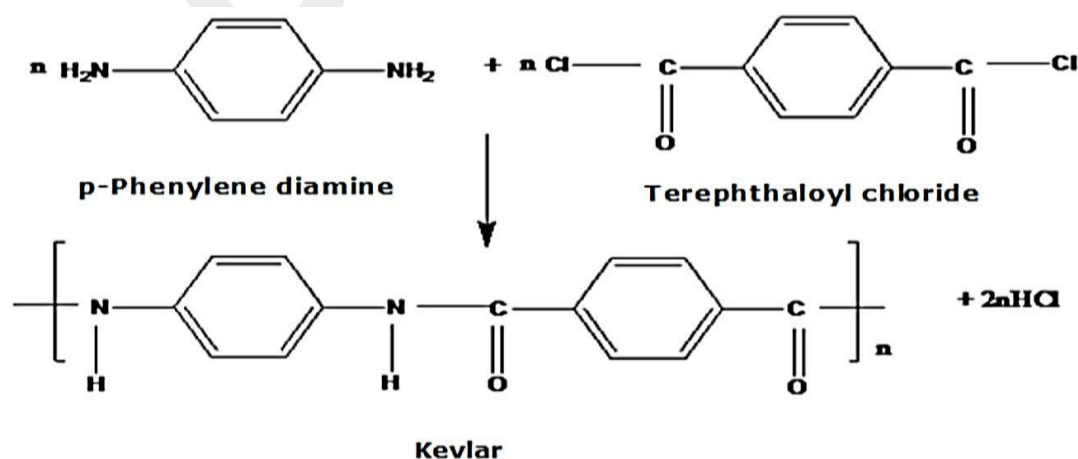
Hence, mass - average molecular mass is given by

$$\overline{M}_w = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2 + \dots}{n_1M_1 + n_2M_2 + n_3M_3 + \dots}$$

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

Kevlar:

Preparation: It is an aromatic polyamide (aramide). It is prepared from condensation polymerization of *p*-amino aniline and 1,4-benzenedicarbonyl chloride.



Properties:

1. It is very light weight.
2. It has high strength and stiffness.
3. It has very good abrasion and corrosion resistance.
4. It decomposes only at 450°C.

Applications: They are used in making

1. Boat hulls, aircraft panels and race cars fuel tanks.
2. High pressure cylinders for H₂ storage
3. Ropes, cables, fire proof protective clothing.
4. Bullet-proof vests.
5. Military helmets.
6. Vehicle tyres, lining for clutch and brake pads.

Conducting Polymers:

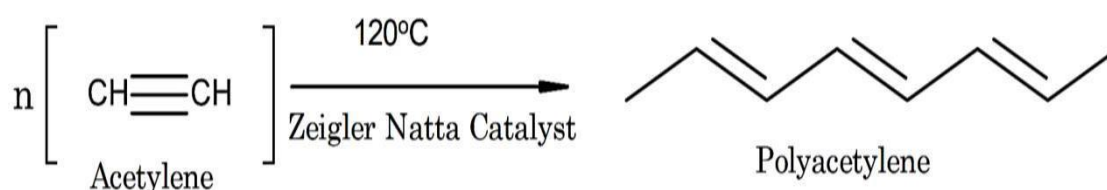
Polymers with highly delocalized pi-electron system, whose conductivity is comparable with that of conductors, are called conducting polymers. The basic requirement for organic polymer to be inherently conducting is

- They should have linear structure with relatively rigid chains.
- They should have continuous conjugation (alternative single and double bonds) through the polymer chain.

Eg: Polyacetylene, polyaniline, polypyrrole, etc.

Polyacetylene

Polyacetylene films are synthesized using the Zeigler-Natta catalyst. The catalyst tetrabutoxytitanium and triethylaluminum suspended in silicone oil through which acetylene is passed, is stirred for two hours at 120° C, and then cooled slowly to room temperature resulting in thin sheets of polyacetylene.

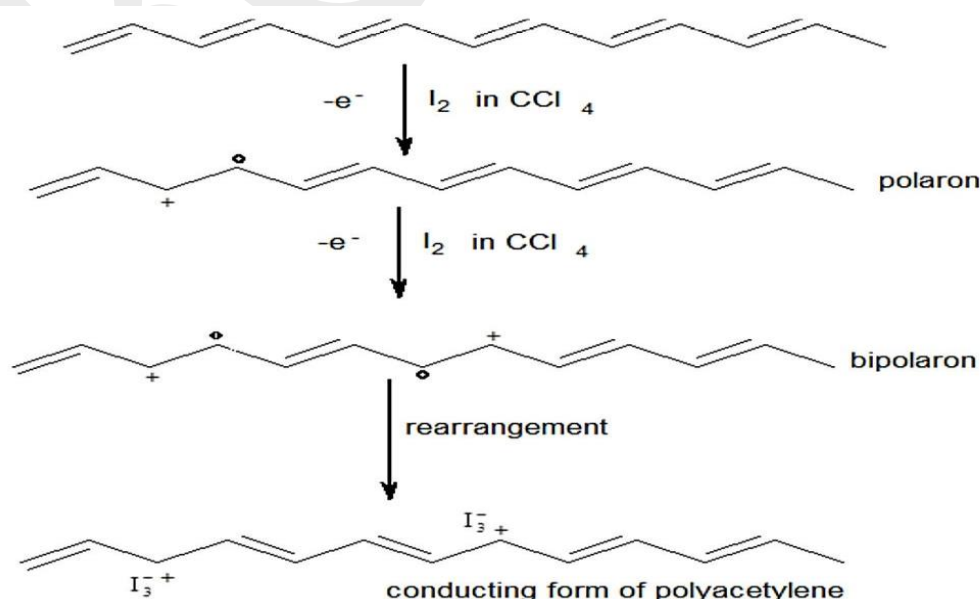


Above kind of polymers in their original form are insulators. But on suitable doping, their conductivity can be increased considerably. Doping creates charge carriers like holes or excess electrons (similar to doped silicon) and thereby, an organic polymer becomes a conductor. The important doping techniques are:

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

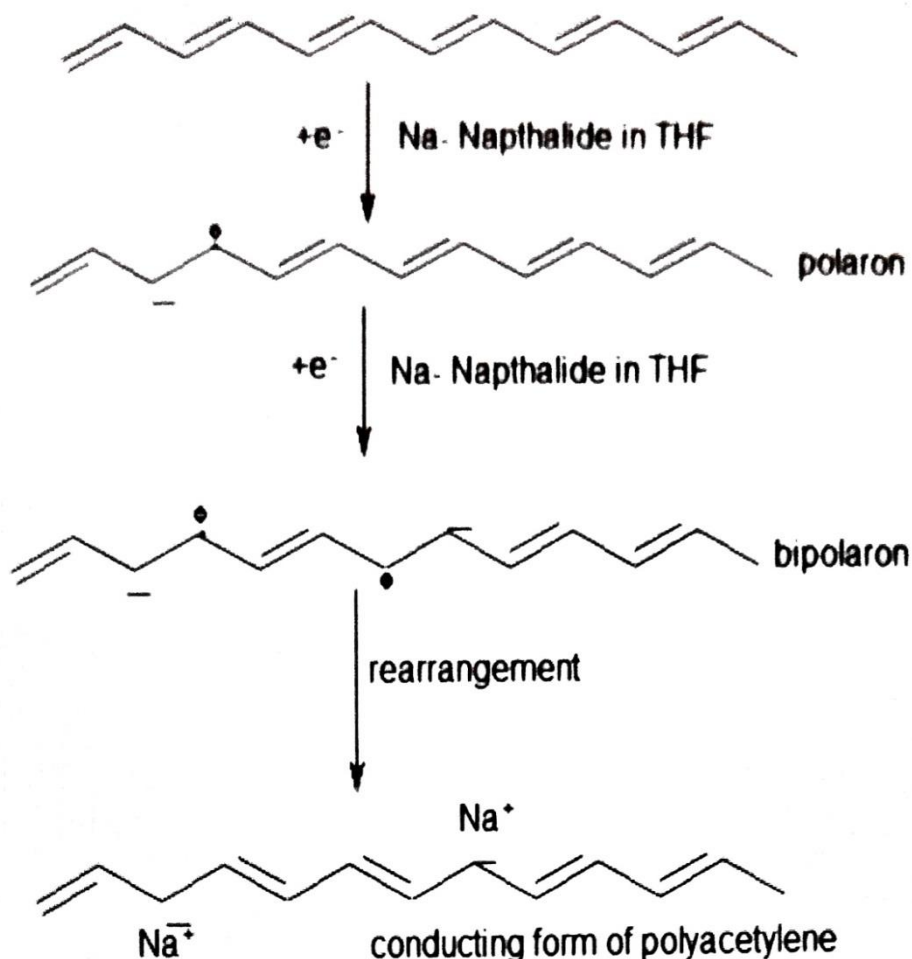
Mechanism of conduction in Polyacetylene: Oxidative doping (p-doping)

- Polyacetylene consists of carbon atoms linked by alternating single and double bonds.
- When a suitable oxidizing agent such as iodine vapour or iodine in CCl₄ or perchloric acid is added, it takes away an electron from the pi-backbone of the polyacetylene chain.
- It creates a +ve charge on one of the carbon. The other electron resides on another carbon making it a radical. So, a radical cation called polaron is formed.
- A bipolaron (soliton) is formed on second oxidation.
- These two radicals (electrons) migrate and combine to establish back one double bond.
- As two electrons are removed, the chain will have two +ve centers (holes). These positive charges are mobile and when a potential is applied, they migrate accounting for conductivity. Positive charges are compensated by I₃⁻ ions and thus the polymer is electrically neutral



Mechanism of conduction in Polyacetylene: Reductive doping (n-doping)

- Polyacetylene consists of carbon atoms linked by alternating single and double bonds.
- When a suitable reducing agent such as sodium or lithium naphthalide is added, it supplies an electron to the pi-backbone of the polyacetylene chain.
- It creates a -ve charge on one of the carbon. The other electron resides on another carbon making it a radical. So, a radical ion called polaron is formed.
- A bipolaron (soliton) is formed on second reduction.
- These two radicals (electrons) migrate and combine to establish back one double bond.
- As two electrons are added, the chain will have two -ve centers. These -ve charges are mobile and when a potential is applied, they migrate accounting for conductivity.
- Negative charges are compensated by Na^+ ions and polymer as a whole is electrically neutral. Since negative charges are the carriers of electric current, this type of doping is called as n-doping.



Applications: It is used

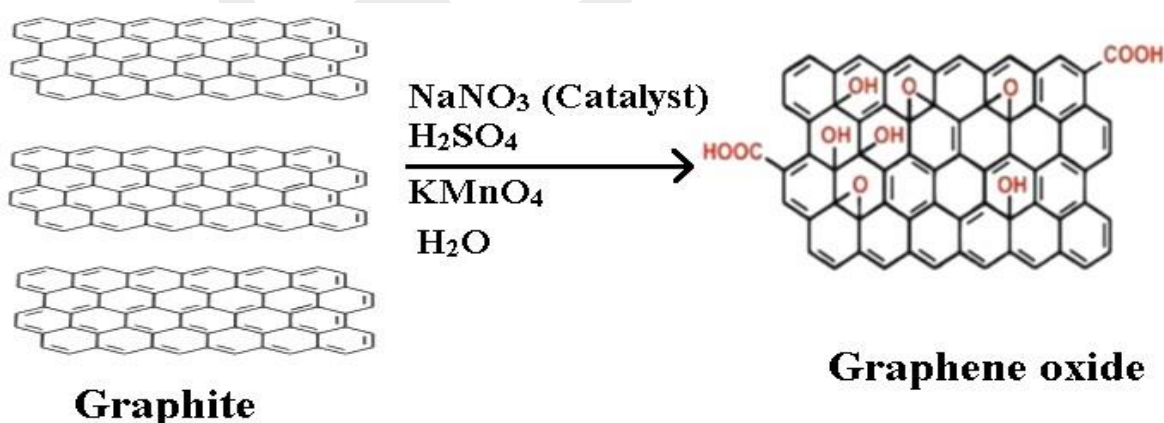
1. As electrode material for commercial rechargeable batteries. **Eg:** Lead-Acid battery.
2. For making sensors for pH, O₂, SO₂, NH₃ and glucose.
3. In telecommunications systems.
4. In electronic devices such as transistors and diodes.
5. In fuel cells as the electro catalytic materials.

Graphene Oxide

A single sheet of carbon atoms taken out of graphite is called as graphene. It is a two dimensional nanosheet with thickness equal to single carbon atom. When Oxygen containing functional groups like epoxide, carbonyl, carboxyl, and hydroxyl groups are added to graphene layer, then the resulting material is Graphene Oxide. It contains hydroxyl (-OH), alkoxy (C-O-C), carbonyl (C=O), carboxylic acid (-COOH) and other oxygen-based functional groups

Preparation of Graphene Oxide:

Graphite is subjected to reaction with an anhydrous mixture of concentrated sulfuric acid, sodium nitrate, and potassium permanganate. The oxidation reaction is completed within 2 hours at a temperature below 45 °C.



Properties:

1. It is hydrophilic due the presence of hydroxyl, alkoxy, carbonyl, carboxylic acid groups.
2. It can mix with matrix such as polymer and ceramic to improve their mechanical and electrical properties.

3. It is hygroscopic and forms a strong hydrogen bond with water molecules.
4. It has large surface area (890 m²/g), so it is more reactive.
5. It has low thermal conductivity (0.5-1 W/m/K) as compare to graphite (3000-5000W/m/K)
6. It has low electrical conductivity than graphene.

Applications:

1. Graphene oxide can be used in coating technology, as its film can be deposited on any substrate like steel, aluminium, etc., to produce an impermeable and transparent conductive film, which gives better corrosion resistance and wear resistance in dry conditions.
2. Graphene oxide papers can be used in desalination and reverse osmosis techniques to get pure water from saline water.
3. GO can be used in the biomedical fields such as drug delivery, cancer therapy, bioimaging and biosensor because of its biocompatibility nature.
4. Nanocomposite of GO and silver (Ag) ions used for bacteria detection.
5. GO is used as a biosensor for the detection of cancer cells in early stage.

GREEN FUELS

Introduction:

Green energy is any energy type that is generated from natural resources, such as sunlight, wind or water. Green energy is important for the environment as it replaces the negative effects of fossil fuels with more environmentally-friendly alternatives. The **six most common forms** are as follows: solar power, wind power, hydropower, geothermal, biomass and biofuel.

Mainly the energy sources are divided into 2 types based on sources

1. Conventional energy sources: Conventional energy sources are provided by nature but are present only in restricted quantities. Example coal, petroleum etc.
2. Non-conventional energy sources: These are non-polluting and present in abundance within the earth's atmosphere. Example sun, wind, geothermal etc.

Past and future perspective of green fuels

Green fuels are fuels produced from biomass sources through a variety of biological, thermal, and chemical processes. These products are chemically identical to petroleum gasoline, diesel, or jet fuel. The shift from use of conventional fossil fuels to green fuel is mainly because they are clean, safe and obtained from renewable sources. They release lower levels of carbon dioxide and other emissions when burnt compared to standard diesel. Green fuel production increases the demand for suitable biofuel crops, providing a boost to the agriculture industry.

Definition: Green fuels also called green hydrocarbons, biofuels, are fuel produced from biomass sources through a variety of biological and thermochemical processes.

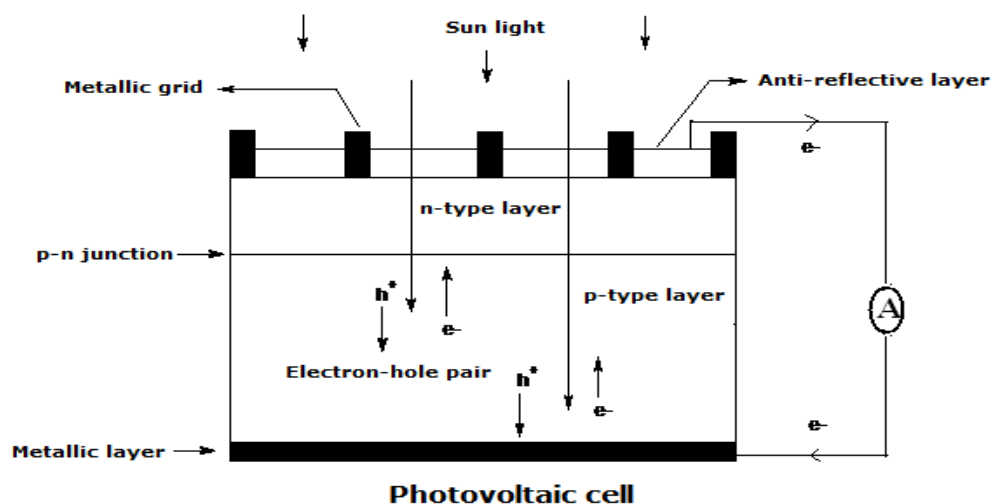
Photovoltaic Cells: When semiconductor devices are exposed to sunlight (electromagnetic radiation), electricity is generated. Such devices are called photovoltaic cells or solar cells.

Construction:

- A typical photovoltaic cell is composed of an ultra-thin wafer of phosphorus doped silicon (n -type) on top of a thicker layer of boron doped silicon (p-type).
- A p-n junction is formed when n-type and a p- type semiconductor are brought together to form a metallurgical junction. This region is called depletion region.
- Photovoltaic cell has two electrical contacts (made from Ti-Ag solder), one of which is in the form of metallic grid which allows sunlight to fall on the semiconductors between the grid lines and the other is a layer metal on the back of the photovoltaic cell, which completely covers the surface.
- An antireflective layer of silicon nitride between grid lines increases the amount of light transmitted to the photovoltaic cell.

Working:

When solar radiation falls on the p-n junction diode, electron-hole pairs are created by the absorption of the radiation. The p-n junction produces a potential gradient within the cell and electrons are drifted to and collected at the n - type end and holes are drifted to and collected at the p-type end. When the two ends are electrically connected through a conductor there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced and is available for use.

**Advantages:**

1. Solar power is unlimited and inexhaustible and free.
2. Power obtained from solar energy using photovoltaic cell is pollution free. Therefore, they are environment friendly.
3. Low operating cost (no fuel).
4. They need no recharging.
5. They operate at ambient temperature.
6. They do not corrode.
7. They have no movable parts and hence do not suffer from wear and tear.
8. Quick installation.

Disadvantages:

1. These are expensive to install.
2. Solar energy is not available throughout day and night and also not equally in all seasons and areas.
3. Solar cells produce only DC power which must be converted to the AC power.
4. Power efficiency of a commercial Si based PV cell is very low (16%).

Green hydrogen:

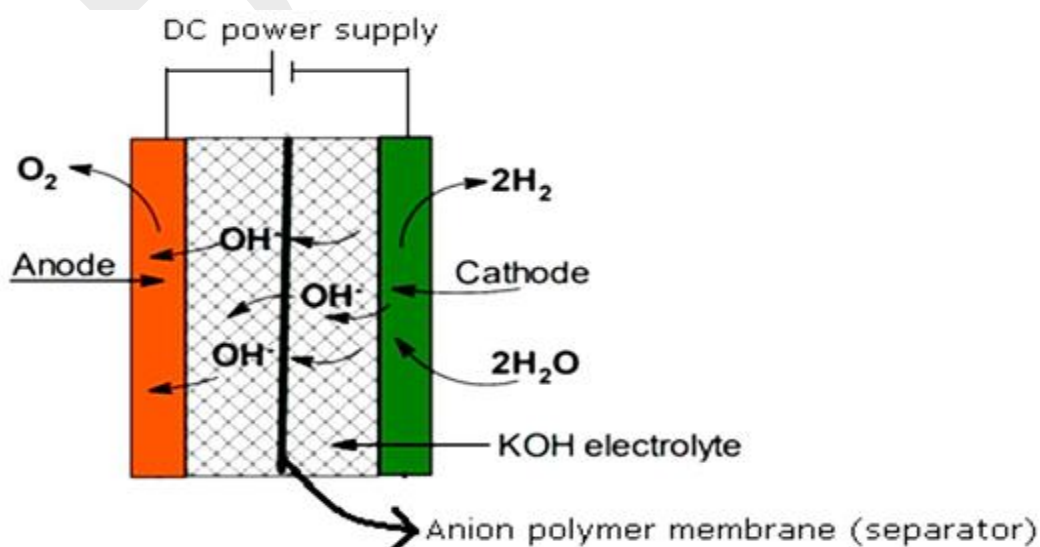
Carbon containing fuels are non-renewable and emit carbon dioxide which is the main greenhouse gas. Therefore, developing an alternative source of energy which is clean, continuous and renewable, is required to meet global energy demand. Hydrogen is the only promising alternative fuel to carbonaceous fuels.

Properties of hydrogen fuel:

1. Hydrogen is an ideal, highly efficient, renewable, clean, and sustainable energy source.
2. It is abundant from various sustainable sources (biomass or water).
3. Energy content of hydrogen is 122 kJ/g, which is 2.75 times greater than hydrocarbon fuels like petrol and Diesel.
4. The combustion product is water, which is not a pollutant.
5. It can be used as fuel in Fuel cell for production of electric current.
6. It can be used as chemical fuel and burnt directly to produce heat energy.
7. It has high storage capability, thus considered as an ideal alternative source of energy for fossil fuels.

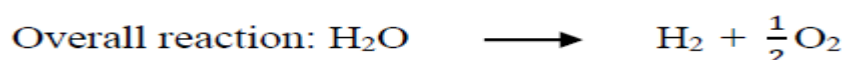
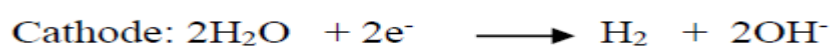
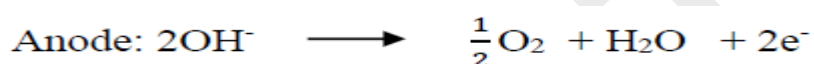
Green hydrogen by electrolysis of water (Alkaline water electrolysis)**Construction:**

1. Anode: Nickel metal particles dispersed on porous carbon
2. Cathode: Nickel metal particles coated on porous carbon
3. Electrolyte: Aqueous solution of KOH
4. Separator: Porous dense anion exchange membrane. It is a good ionic conductor for hydroxide ions and bad electronic conductor. It prevents the spontaneous recombination of H_2 and O_2 .



Working

- Water electrolysis is a non-spontaneous chemical reaction. So, DC power supply is used.
- Anode is connected to positive end and cathode is connected to negative end.
- At the cathode, water molecules are reduced by electrons to hydrogen and negatively charged hydroxide ions. Hydroxide ions migrate through KOH and through separator to the anode.
- At the anode, hydroxide ions are oxidized to oxygen and water while releasing electrons.
- Overall, a water molecule splits in to hydrogen and oxygen in the ratio of 2:1.

**Advantages:**

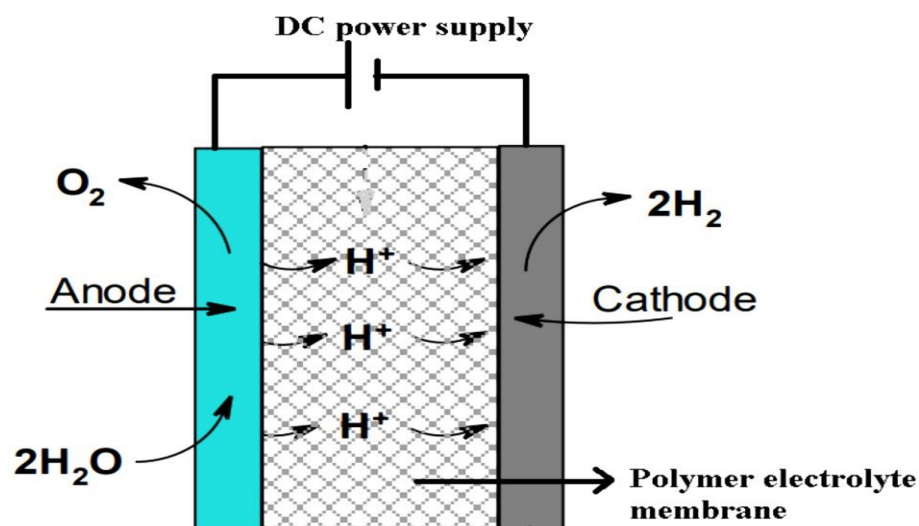
1. Alkaline water electrolysis is cheaper and simple method for hydrogen production.
2. Electrodes are made of cheaper nickel metal.
3. Pure carbon free hydrogen is obtained from this method.
4. Excess cheap current from renewable sources like solar power can be converted to hydrogen gas and stored as chemical energy.

Green hydrogen by electrolysis of water (Proton exchange membrane electrolysis)**Construction:**

Anode: Iridium metal particles dispersed on porous carbon.

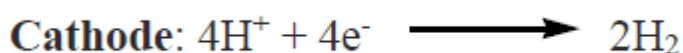
Cathode: Platinum particles coated on porous carbon.

Electrolyte/Separator: A porous solid polymer electrolyte made of chemically stable sulfonated tetrafluoroethylene-based fluoropolymer is used as an electrolyte as well as a separator. It is a good ionic conductor for protons and bad electronic conductor. It prevents the spontaneous recombination of H₂ and O₂.



Working:

- Water electrolysis is a non-spontaneous chemical reaction. So, DC power supply is used.
- Anode is connected to positive end and cathode is connected to negative end.
- Deionized water is circulated in the anodic chamber where it is oxidized liberating oxygen gas and hydrogen ions.
- Hydrogen ions migrate through the Solid Polymer Electrolyte membrane to the cathode, where they are reduced into molecular hydrogen.



Advantages:

1. Use of polymer membrane avoids use of liquid acid electrolyte. Therefore, chance of electrolyte leakage is prevented.
2. Polymer membrane is chemically stable and non-corrosive.
3. Pure carbon free hydrogen is obtained from this method.
4. Excess cheap current from renewable sources like solar power can be converted to
5. Hydrogen gas and stored as chemical energy.

BGS COLLEGE OF ENGINEERING AND TECHNOLOGY

**DEPARTMENT OF APPLIED CHEMISTRY
MAHALAKSHMI, Bengaluru - 560086**



APPLIED CHEMISTRY (BCHE102/202)

**E-WASTE
MANAGEMENT
MODULE:05**



E-WASTE MANAGEMENT

Syllabus:

Introduction, sources of e-waste, Composition, Characteristics, and Need of e-waste management. E - Waste. 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).

Self-Learning Topics: Impact of heavy metals on environment and human health.

E-WASTE

In the new world of materials, usage of electrical and electronic items has been increasing rapidly year by year. These materials have lesser life span and also used for lesser duration due to fast change in features and the capabilities. All these electric and electronic items which are discarded on completion of their use comprise e-wastes. Today's electronics gadgets, Tomorrows e-waste. India is 5th largest producer of e-waste.

All items of electronics and electrical equipment/devices and its parts that have been discarded by the uses as waste without the purpose of re-use is considered as e-waste.

SOURCES:

The main sources of e-waste are:

1. Computer peripherals: Monitor, keyboard, mouse, motherboard, laptops, CDs, etc.,
2. Household appliances: TVs, refrigerators, washing machines, radios, ovens, dish washer, etc.,
3. Industrial electronics: Sensors, medical devices, automobile devices, etc.,
4. Telecommunication devices: Telephone, cell phones, routers, pagers, fax machine, etc.,
5. Electrical devices: Switches, wires, tube lights, bulbs, pen drive, etc.,

COMPOSITION:

E-waste has become a diverse and complex nature of waste having hazardous and non-hazardous ingredients.

1. It contains about 65-67% of iron and steel and other metallic materials including costly metals like Pt, Au, Ag, and toxic metals like Pb, Hg, Cd, Cr, etc.,
2. E-waste contains about 20-22% of polymeric non-biodegradable materials including PVCs, PCBs (polychlorinated biphenyls), and brominated flame-retardant plastics.
3. E-waste also contains about 11.8-13.2% of CRT and LCD screens and other materials like glass, wood, plywood and ceramics in traces.

Toxic Materials Used In Manufacturing Electronic and Electrical Products

According to toxicity, the types of substances in e-waste can be categorized into hazardous and non-hazardous substances. Hazardous substances are toxic, and can affect the quality of the ecosystem and can have detrimental effects on human health.

These include:

- Heavy metals like Cd, Cr, Pb and Hg.
- Organic compounds like chlorofluorocarbon, polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxin furans (PCDDFs).

HEALTH HAZARDS DUE TO EXPOSURE TO E-WASTE

Toxic materials	Sources	Health hazards
Lead	Batteries, solder in printed circuit board, glass panels, gaskets & in computer monitors casing, transistors, lasers, LEDs,	<ul style="list-style-type: none"> • Cause damage to central and peripheral nervous system, blood system and kidney. • It is a neurotoxin affects badly on child brain development, IQ deficiency, circulatory system and kidney. • Long term exposure can damage reproductive system and affect nervous system of young children.

Cadmium	Rechargeable batteries, chip resistors, CRT screens, circuit boards, semiconductors, pigments,	<ul style="list-style-type: none"> • Irreversible toxic effects on kidney and lungs. • Chronic damage to kidney and soften bones. • Accumulates in kidney and liver. • Being carcinogenic causes lung cancer and Itai-Itai disease, which causes severe pain in the joints and spine. • Pulmonary damage. • Irreversible damage to neural system. • It disrupts calcium mechanism, causing hypertension and heart disease.
Mercury	Batteries in clocks and pocket calculators, switches, LCDs, PCBs,	<ul style="list-style-type: none"> • Cause chronic damage to brain. • Cause respiratory and skin disorders. • Affects the central nervous system, kidney and immune system. • It impairs foetus growth and harm the Infants through mother's milk. • It bio accumulates in fishes and affect food chain.
Chromium	Corrosion protectant in galvanised steel parts, dyes or pigments, switches, solar panels, decorator or hardener for steel casing.	<ul style="list-style-type: none"> • Inhaling hexavalent chromium can damage to liver and kidney. • Affects DNA and cause lung cancer. • Cause bronchial maladies including asthmatic bronchitis.
Beryllium	Switch boards, PCBs, circuit motherboards,	<ul style="list-style-type: none"> • It is carcinogenic in nature, causes lung cancer. • Inhalation causes chronic disease in lungs called berylliosis. • Exposure to fumes causes skin disease characterised by poor wound healing and wart like lumps.

Barium	Electron tubes, filler of plastic and rubber, lubricant additives,	<ul style="list-style-type: none"> • Short term exposure can lead to brain swelling, muscle weakness, damage to heart, liver and spleen. • Long term exposure leads to increased blood pressure, change in heart beat rate.
Arsenic	Semiconductor, diodes, microwave oven, LEDs, solar cells.	<ul style="list-style-type: none"> • Causes various skin diseases. • Chronic damage to lung causing cancer and can be fatal. • Decreased response, as nerves are affected.
Antimony	Semiconductors, flame retardant formulations in plastics.	<ul style="list-style-type: none"> • It is toxic causing dermatitis. • Affects skin cells, respiratory tract and immune system. • Stated as possible carcinogenic by International Agency for Research on Cancer, 1989.
Brominated Flame retardants (e.g., PBDEs)	Casing, circuit board, cables, PVC cables,	<ul style="list-style-type: none"> • Combustion of halogenated case material and printed wiring boards releases toxic emissions including dioxins which can lead to severe hormonal disorders, disrupts endocrine system function in animals and human beings.
Cobalt	Insulators	<ul style="list-style-type: none"> • Accumulation leads to toxicity in liver, kidney, pancreas, heart, skeleton and skeletal muscle. • Produce tumours in animals and is likely carcinogenic as well.
Copper	Conducting wires, solenoids, coils, transistors, pigments, PCBs	<ul style="list-style-type: none"> • Short term exposure causes nausea, vomiting, diarrhoea, stomach cramps. • Accumulation causes liver damage (Wilson's disease), kidney damage and can be fatal.

Lithium	Batteries, photographic equipment,	<ul style="list-style-type: none"> • Corrosive to the eyes, skin and respiratory tracts. • Inhalation causes lung oedema.
Nickel	Alloys, batteries, relays, switches, semiconductors, pigments	<ul style="list-style-type: none"> • It is carcinogenic, causes asthma and chronic bronchitis. • Long term exposure causes lung cancer, nose cancer, larynx cancer and prostate cancer.
PCBs	Transformers, capacitors, glue, softening agent in plastics and paints,	<ul style="list-style-type: none"> • Causes number of serious non cancer health effects in animals. • Affect immune system, reproductive system, nervous system, endocrine system and other health hazards.
PVCs and Plastics	Circuit boards, cabinets, cable wires,	<ul style="list-style-type: none"> • It is carcinogenic, can harm reproductive and immune system. • Burning PVCs produces dioxins which is harmful. • BFR can leach into landfills.
CFCs	Cooling units, insulating foam	<ul style="list-style-type: none"> • It is harmful to environment, depletes ozone layer. • This results in increased incidents of skin cancer in human and genetic damage in many organisms.
Selenium	Photoelectric cells, photocopy and fax machines as pigments, LEDs	<ul style="list-style-type: none"> • Exposure to high concentrations cause selenosis, leading hair loss, nails brittleness and neurological abnormalities (such as numbness and other odd sensation in the extremities).
Americium	Medical equipment, fire detectors, active sensing element in smoke detectors,	<ul style="list-style-type: none"> • It is radioactive, causes cancer in long term exposure. • It can damage the DNA in cells. • High doses of radiation can cause Acute Radiation Syndrome (ARS) or Cutaneous Radiation Injuries (CRI).

NEED OF E-WASTE MANAGEMENT

- E-waste is not eco-friendly (E-waste is not hazardous waste as such. However, the hazardous constituents present in the e-waste render it hazardous).
- E-waste is a complex mixture of metals, polymers and ceramics. Disposing of this mixture in **landfills can cause serious environmental issues**.
- In the area of landfill sites there is mixing up of hazardous chemicals in to soil, water and air and **affect food chain**. Also, it results in loss of **metals** that quantities are **limited in the earth's crust**.
- Appropriate control over the materials used in the manufacturing process is an imperative way to trim down waste generation. By reducing both the extent of hazardous materials used and the amount of surplus raw materials during manufacturing, **the magnitude of waste and cost generated can be reduced**.

Due to these facts, proper efficient e-waste management is required for the recovery and reuse of component of e-waste.

RECYCLING AND RECOVERY OF E-WASTE

In e-waste, among various constituents, metals contribute to the significant economic value and effects are focused on extracting those metals during recycling operation.

Recovery and Recycling Technologies

The recycling of e-waste is initiated with physical or mechanical processes.

- **Dismantling and separation of components:** This involves physical removal of toxic materials and unwanted components.
- **Mechanical crushing and grinding:** To collect the fragments of metal bearing components
- **Electrical & Magnetic Separation:** The above obtained fragment is passed through electrical to separate metallic and non-metallic components and then through magnetic separator to separate ferrous metals from non-ferrous.
- **Gravity Separation:** It is used to separate the Al metals.

The most widely used chemical techniques for metal recovery are:

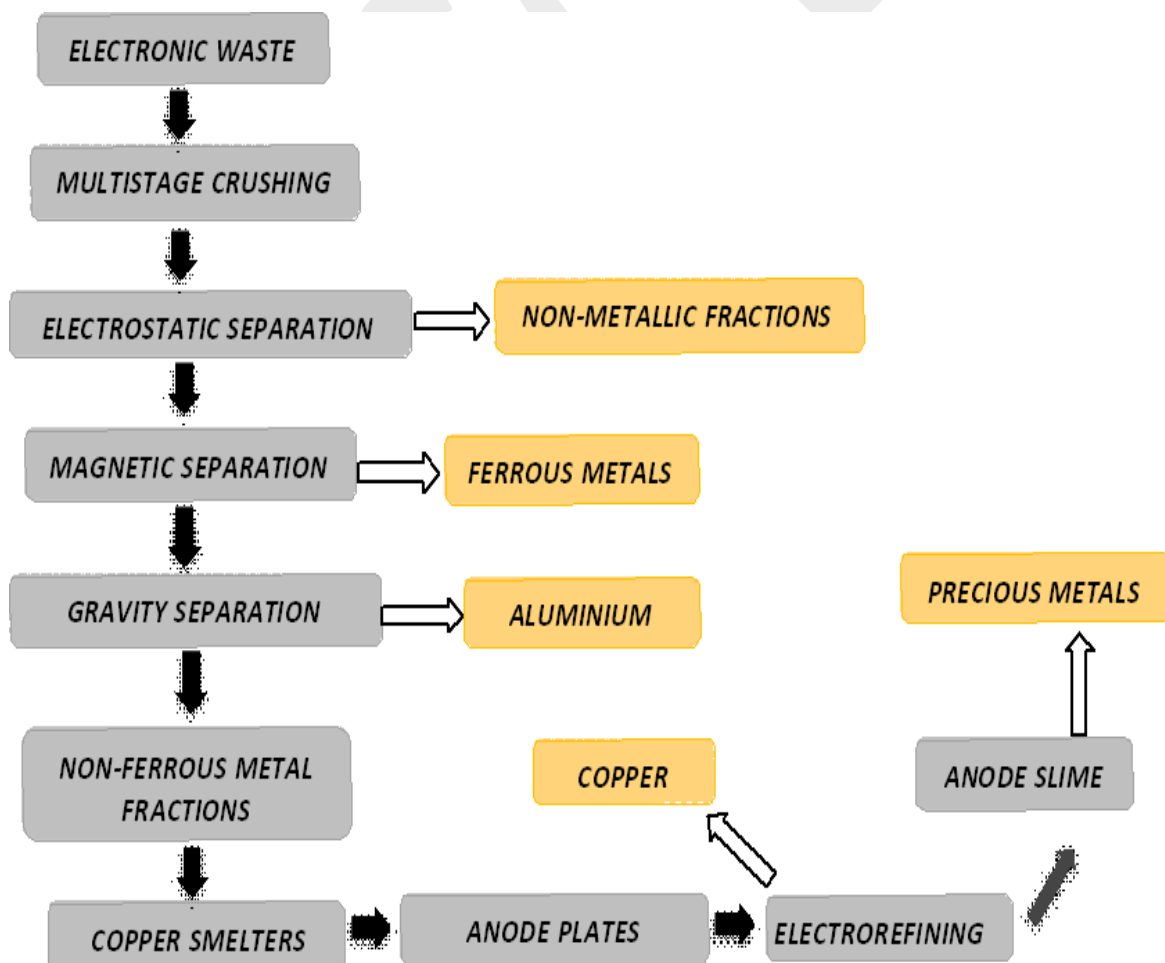
- a) Pyrometallurgical process
- b) Hydrometallurgical process

1. PYROMETALLURGICAL PROCESS:

Pyrometallurgical technology is used to extract pure non-ferrous and precious metals from e-waste. Smelting, combustion, pyrolysis and molten salt processes are the main pyrometallurgical methods employed. These methods are briefly explained below:

a) Smelting:

- The processed scrap after preliminary stage contains mainly Cu, Pb, Sn, Sb, Zn, As, Hg, Cd and precious metals as metallic constituents. This mixture is fed into the copper smelters.
- During smelting, Pb, Sn, Sb, and precious metals are collected in the copper parent phase. This is casted into anode slabs and refined by electrometallurgy.
- The anode is dissolved and 99.99% pure Cu is deposited over cathode leaving a slurry residue, called anodic slime.
- Anodic slime is rich in valuable metals like Au, Ag, Pt, Pb, Sn & Sb. These metals are recovered from slurry using hydrometallurgical techniques.



- b) Combustion of e-waste:** Here e-waste is subjected to open burning in uncontrolled manner which releases all sorts of pollutants in to atmosphere. Hence, this method is highly dangerous for the environment and also increases the health risk of the workers.
- c) Incineration of e-waste:** Here e-waste is burnt at temperature above 800°C obtained gaseous products of the first incineration are further oxidized above 1100°C. Heavy metals are collected in the bottom of furnace.
- d) Pyrolysis of e-waste:** Pyrolysis is a thermal decomposition of e-waste at higher temperature in an oxygen free environment. In the temperature range of 450 & 1100 °C low molecular products are formed and these can be used as fuel and chemical feedstock. This process releases toxic halogens into atmosphere with flue gases.
- e) Molten salt process:** In this process, the e-waste is fed in with the salt, and salt is melted at desired temperature under an inert atmosphere. Organic parts decompose in the molten salt forming carbonates and silicates and are trapped in molten salt. Halogens are converted into alkali metal halides, which remain in the molten salt. After removing molten salt, mixture containing valuable metal is further treated to obtain pure metal.

2. HYDROMETALLURGICAL PROCESS:

There are three stages in metal recovery by hydrothermal method:

- a) Pre-treatment stage (Separation)
 - b) Chemical treatment stage (Leaching)
 - c) Metal recovery stage (Recovery)
- a) Pre-treatment Stage:** This stage involves physical separation of metal components from e- waste as in pyrometallurgical process followed by smelting of the mixture.
- b) Chemical treatment stage:** Metals are made to leach into the solutions using different leaching reagents.
- i. **Cyanide Leaching:** Alkali cyanide like KCN is used as leaching agent. The precious metals like Au and Cu readily dissolves in cyanide solutions. Further, the same solution can be subjected for electroplating to obtain pure metal.
 - ii. **Acid and alkali leaching:** HNO₃, H₂SO₄ and HCl are prominent mineral acid used for leaching of target metals. A few organic acids such as ascorbic acid, citric acid and acetic acid are also used to leach light metals from spent batteries and mobile

devices. Li is leached from lithium-ion battery waste by treating with citric acid and H_2O_2 as reducing agent.

- iii. **Thiosulphate leaching:** Ammonium thiosulphate solution is used to solubilize Au, Ag, Pt and other precious metals in the form of anionic stable complexes for a wide range of pH. This reagent is safe, non-toxic, non-corrosive and metal can be recovered readily from the complex.
 - iv. **Thiourea Leaching:** Thiourea is a sulphur based organic complexing agent, that forms a cationic soluble complex with the Au and Ag present in printed circuit board recycling. Thiourea gives quick rate of leaching, less interference of ions, low cost and is environment friendly.
 - v. **Halide Leaching:** Cl^- , Br^- and I^- ions containing salt solutions can be replaced for cyanide leaching agents. They exhibit high solubility, improved redox potentials and high rate of leaching. They are cheaper selective to the target and ideal leaching agent.
- c) **Metal Recovery Stage:** In this stage pure metal is recovered from leached solution. There are varieties of methods involved to recover metal. Choice of method depends upon the nature of leached solution.
- i. **Solvent extraction:** Leached solution is treated with an organic solvent, called extractant in a separating funnel. It results in two phase system. Here metal is extracted from leached solution phase to organic phase. For example, methyl isobutyl ketone is used as an extractant for gold.
 - ii. **Electrodeposition:** In this technique, pure metal is obtained from leached solution by constructing an electrolytic cell. Pure metal same as metal to be extracted is taken as cathode and inert metal is used as anode. They are dipped in leached solution. When a current is applied, pure metal is electrodeposited on cathode. This method has the advantage of high efficiency in metal recovery at cathode. For example, Cu can be leached from PCBs with simultaneous cathodic electrodeposition from the leaching solution with 99.95% efficiency leaving the residue rich in gold metal.
 - iii. **Ion Exchange:** This is an improved method of solvent extraction. Here solvent extractants are impregnated on polymer beads (ion exchange resins). The functional group in the reagent acts as chelating group and selectively binds to metal ions. Thus, they can be used for selective recovery of the metal ion. Some

advantages of using this method are their ease to use, no loss of reagent, low cost, use even in the low concentration of metal ions and environment friendly.

- iv. Adsorption:** Metals can be recovered from leached solutions by adsorption on appropriate adsorbents. For example, adsorption of gold-thiourea complex solution on activated carbon is effective method.

EXTRACTION OF GOLD FROM E-WASTE

Gold metal has good electric conductivity and chemical stability and hence it is used for making integrated circuits of electronic devices, coating for contacts and connectors.

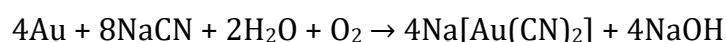
Among e-waste, PCBs are rich in metals. It contains around 35% Cu, 0.16% Ag and 0.13% Au by weight. Several techniques such as pyrometallurgy, hydrometallurgy, bio-metallurgy, microwave treatment and plasma technology are employed to recover precious metals from e-waste. Among these recoveries from hydrometallurgy method is the most economical.

Hydrometallurgical method: Extraction of gold can be done in different methods like cyanide leaching, aqua regia, bleach and hydrochloric acid mixture and so on.

Cyanide leaching: There are three stages in metal recovery by this method. They are

a) Pre-treatment Stage: E-waste is dismantled to separate various fractions like metals, ceramics, plastics, wood and paper. Techniques such as gravity separation, electrostatic separation, magnetic separation and eddy current separation are used to separate metals from other fractions.

b) Chemical Treatment Stage: Target metals are leached into the solutions by treating with appropriate chemical reagents. Cyanide leaching is the most common method used to extract gold metal. Sodium salt of 3-nitrobenzene sulfonic acid with KCN/NaCN in the presence of oxygen is used as leaching agent. A water soluble dicyanoaurate gold complex is obtained in the process.



c) Metal Recovery Stage: Metal is recovered from the leached solution by suitable method. Gold can be recovered from leaching solution by electrodeposition of dicyanoaurate gold complex. Pure metal is taken as cathode and inert anode is dipped in leached solution. When current is applied, gold is electrodeposited on cathode.

Aqua regia method: The extraction of gold in this method is pretty exactly same. There are three major steps to recover gold in this method.

Step 1: Pre-treatment stage: This step involves separating gold from circuit boards by dissolving them giving a bunch of gold and other debris. Gold is attached to a strip in circuit board. These boards basically have copper, nickel and gold coated one over the other. Here gold is separated by selectively dissolving in 3:1 mixture of HCl and H₂O₂ in the presence of oxygen. After a week the contents are filtered and washed with distilled water.

Step 2: Chemical treatment stage: The above obtained flakes of gold are treated with aqua regia (3:1 mixture of HCl & HNO₃) for about 2 hrs and occasional stirring. All the flakes are oxidised.



Obtained gold ions will react with chloride ions of HCl to give stable complex of gold called chloroaurate anion complex.



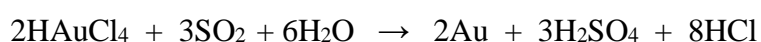
Chloroaurate anion complex in the presence of H⁺ ion gives a yellow solution of chloroauric acid, which is extremely soluble in water.

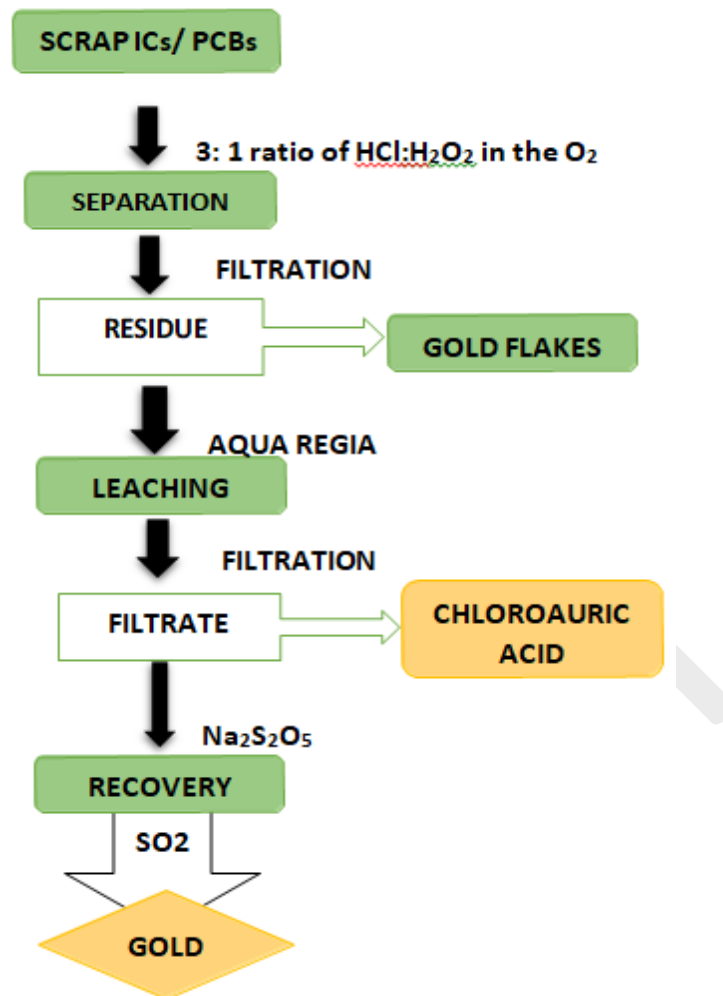


Step 3: Recovery of Gold: Yellow solution is filtered and constantly washed with distilled water to extract maximum gold solution in filtrate, sodium metabisulphite is added. When metabisulphite is reacted with above filtrate, gives sulphur dioxide as one among the products.



This SO₂ reacts with Chloroauric acid and metal gold is precipitated slowly and filtered after 2-3 days.





DIRECT RECYCLING OF E-WASTE

Another method of recycling the e-waste is by direct recycling method.

- It involves harvesting electronic components directly from e-waste without breaking them further into small components.
- Harvested materials are further processed with healing method to regenerate recycled materials.
- The regenerated materials have performance equivalent to original materials.

For example, direct recycling of lithium-ion batteries. Here, the battery is discharged first to avoid short circuiting and self-ignition of the battery and dismantled to separate anode, cathode, electrolyte and separator. These components are reassembled for reuse.

Advantages:

- It is cost effective.
- Requires less amount of energy and reagents.
- Most environment friendly methods.

Disadvantages:

- Direct regeneration of components depends on state-of-health of used electronic materials.
- Defects and impurities accumulated during usage could affect the quality of the refurbished active material.
- Also, in this method one cannot restore the initial property of pristine active materials.

ROLE OF STAKE HOLDERS IN ENVIRONMENTAL MANAGEMENT OF E- WASTE

Basically, there are four stake holders in environmental management of the e-waste.

They are;

1. Statutory government regulatory bodies.
2. Producer (Manufacturing units).
3. Recycler (Recycling units & Collections units).
4. Consumers.

1. Statutory Government Regulatory Bodies:

State Pollution Control Board/ Pollution Control Board play the vital role in management of E-waste. The main role of these statutory bodies is:

- a. To collect the green tax from producer.
- b. Responsible to levy taxes on producer (manufacturing units) in the form of penalty, when no proper recycling of e-waste is assured.
- c. Provide the incentives in the form of subsidy to recycler and collectors, when recycling of e-waste is monitored properly.
- d. To conduct the programs of awareness and trainings in the society about importance of recycling the e-waste.

- e. Prevention of e-waste, granting authorization, registration, monitoring of compliance, maintaining information on the restrictions, terms and conditions imposed on authorization, etc.,
- f. Preparation of guidelines for Environmental sound e-waste management.
- g. Recommendation of standards and specifications for processing and recycling of e- waste.
- h. Set a target for compliance to the reduction in use of hazardous substance in manufacture of electrical and electronic equipment.

2. Producers (Manufacturing units):

The main role of producers in management of e-waste is:

- a) Purchase the recycled material at fixed value and using of recycled ones during manufacturing.
- b) Setting up collection centres or offer exchange on old products individually or collectively.
- c) Financing and organizing a system to meet the costs involved in environmentally sound management of e-waste generated and accomplish this in transparent manner.
- d) Forming the group of manufactures and encourage the recycling of e-waste.
- e) Bearing the transportation cost and collection fees to ease the collection process.
- f) Obtaining an authorization from the concerned State Pollution Control Board or Centre Pollution control committee (SPCB/CPCB) in accordance with rules.
- g) Maintaining the records and produce the same during inspection.

3. Recycler (Collection units and Recycling Units):

The main roles of recycler in management of E-waste are:

- a) The accountability of recycling units is dismantling, recycling processing of e-waste materials, management of scrap materials (like incineration) and reselling of recycled materials.
- b) Establish the collections units and a group of people who can ensure return of e-product from a consumer in exchange offer or directly approach them for door-to-door collection.

- c) Collect the e-waste from the collection units, dealer or retailer.
- d) Providing incentives when proper collection of e-waste is assured by collections units.
- e) To obtain the authorization and registration from the statutory body.
- f) To ensure that no damage is caused to the environment during storage (for not more than 80-100 days), health of the workers and during transportation of e-waste.
- g) To ensure that recycling and facilities for processing are in accordance with the standards or guidelines published by CPCB from time to time.
- h) To ensure that residue generated after recycling process is disposed of in a Hazardous Waste Treatment Storage Disposal Facility.
- i) To avail all the records to the Statutory bodies during inspection.

4. Consumer:

The main roles of consumer in management of e-waste are.

- a) To ensure that e-waste generated is channelized to authorized pick-up or return service provided by the producers (exchange offers).
- b) Develop self-awareness on e-waste management and involve in awareness programs.
- c) Monitoring the society on management of e-waste and file compliance against the producers/ recyclers when e-waste is not handled with care.
- d) Setting up an NGOs with an objective of monitoring and programming the waste management.
- e) Identifying the recyclers and providing them the proper guidelines, safety-kit and subsidy. Also setting up free medical check-up occasionally.

QUESTIONS BANK

1. Mention the sources of e-waste.
2. Give the composition of e-waste.
3. Explain the pyrometallurgical method for recovery of e-waste.
4. Explain the recycling of e-waste.
5. Explain the methods involved in hydrometallurgy.
6. Explain the ill effects of toxic materials used in manufacturing electrical and electronic products.
7. Explain the hydrometallurgy method of extraction of gold from e-waste.
8. Briefly explain direct recycling method.
9. Explain the process involved in recovery of precious metals from e-waste.
10. Write a short note on the health hazards caused by
A). Lead B). Chromium C). Cadmium
11. Explain the need for e-waste management.
12. Briefly explain metal recovery stage.
13. Write a short note on smelting method.
14. Give the ill effects and sources of constituents of organic polymeric compounds present in electronic and electrical products.
15. Write a brief note on role of producers in e-waste management.
16. Write a brief note on role of statutory body in e-waste management.
17. Write a brief note on role of consumers in e-waste management.