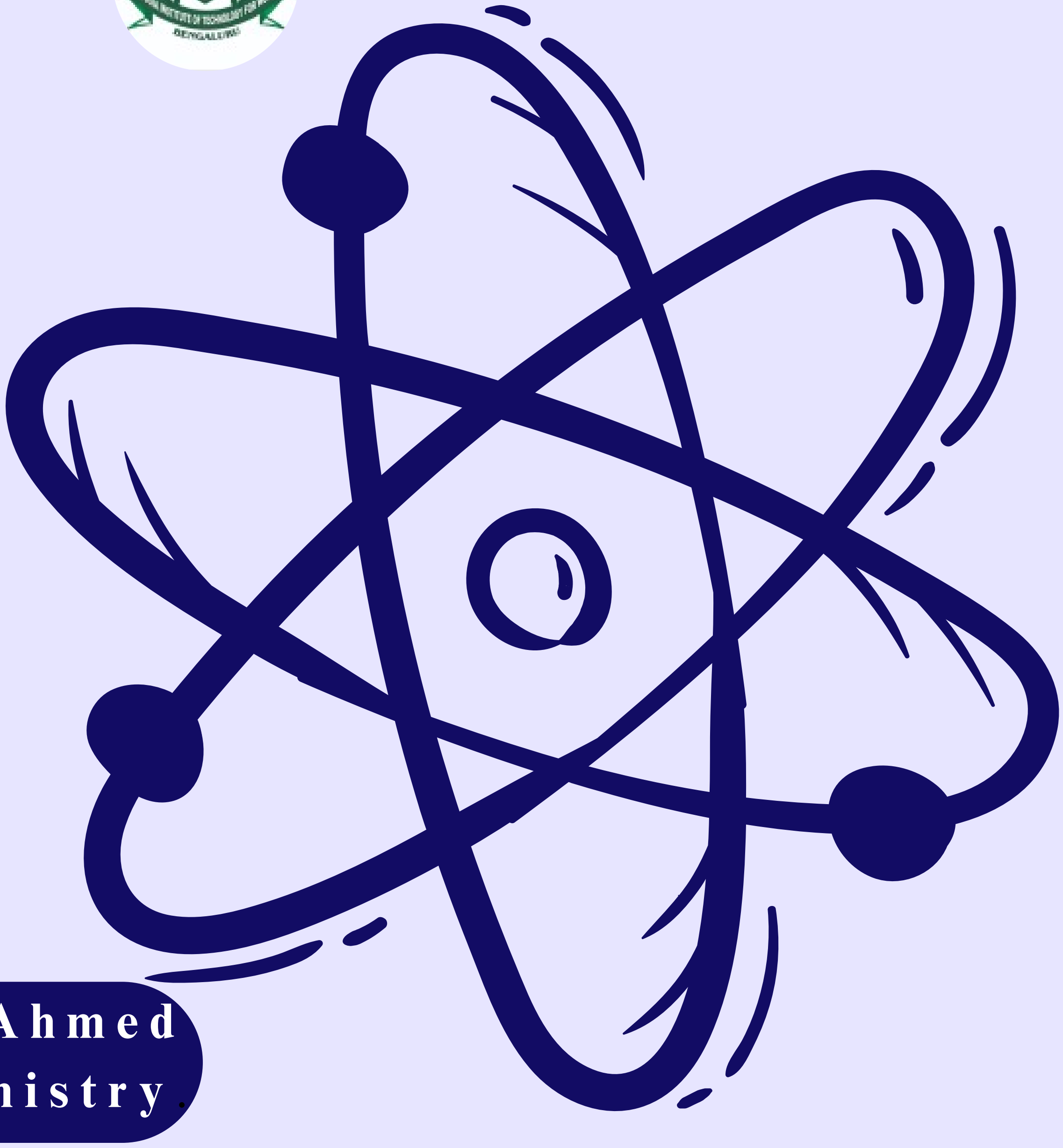
APPLIED CHEMISTRY FOR CSE STREAM

STUDY MATERIALS



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Module–I: Sensors and Energy Systems

Sl/ No.	Topics	Durations
1	Sensors: Introduction - Definition and terminologies of Transducer,Actuators and Sensors. Working principle and any four applications of Electrochemical sensors,	1 hr
2.	Working principle and any four applications of Conductometric sensors (conductometry), and Optical sensors (colorimetry),	1hr.
3	Electrochemical Sensor for the measurement of Dissolved Oxygen (DO); With brief introduction to different sensors, explain the principle, experimental procedure with electrode reactions.	1hr.
4	Electrochemical Sensor for pharmaceuticals; example-Diclofenac, and hydrocarbons; example-1-hydroxypyrene (explain with electrochemical oxidation reactions)	1hr.
5	Electrochemical gas sensors for SOx and NOx; Working principle with electrode reactions	1hr.
6	Disposable sensors (DS); Definition, advantages of DS over Classical sensors. Detection of biomolecules; Example-Ascorbic acid (AA) explain with Oxidation of AA to Dehydroascorbic acid, Pesticides; example Glyphosate (explain with electrochemical oxidation)	1hr.
7	Energy Systems: Introduction to batteries, construction, working and applications of Lithium-ion and Sodium-ion batteries	1hr.
8	Quantum Dot Sensitized Solar Cells (QDSSC's)- Principle, Properties and Applications (any four).	1hr.

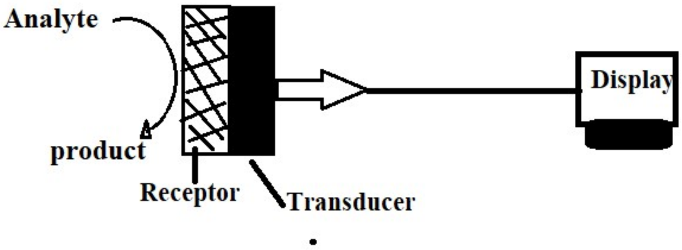
Module–I: Sensors and Energy Systems

Q1.Define the following terms
i) Sensors ii) transducers and iii)Actuators

Definition of Sensors, transducers and Actuators is enough

A sensor is a device that detects and responds to some type of input from the physical environment.

For example: heat, light, sound, weight, attraction etc are the physical stimulus/input detected by sensors



The main basic components of sensors are

1. **Receptor**:it is a biological or chemical recognition element which is capable of interacting with analyte. It produces a signal corresponds to interaction in the form of change in colour, potential, current, conductivity etc.
2. **Transducer**:transducer convert signal produce by the receptor during interaction into readable value or measurable form of physical quantities
3. **Electrical signal and display:** The electronic system analyses the signal produce by transducer, amplify and convert analog to digital form. Thees signals displayed on the screen as numerical, graphs, images etc.
4. **Actuator**: **Actuator is a device that converts electrical signals into physical input such as display, force and motion.**

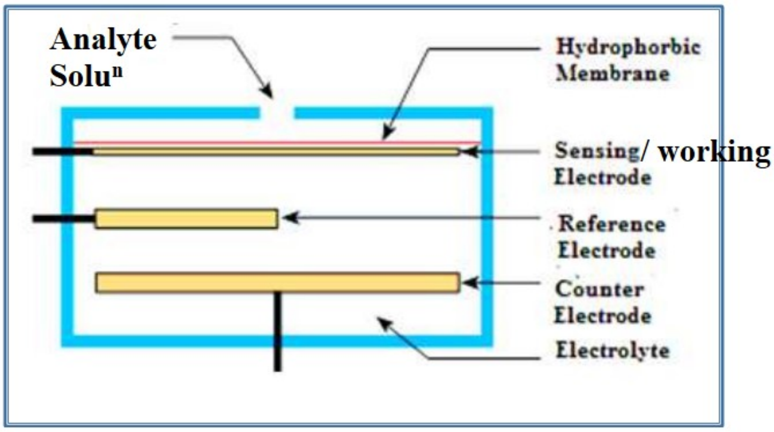
(It acts as an output device and is connected at the output of a system. It takes the input from the data provided by the sensor and gives output to the environment.)

Ex: Alarm, LED, Displays, Electric Motors. Heaters, Electro pneumatic actuator, Electro- hydraulic actuator, Magnetic actuator etc.)

Electrochemical Sensors

Q2.What are electrochemical Sensors? Explain the working principle of electrochemical sensors

Electrochemical sensor: A device that transforms chemical information obtained by chemical reaction into an analytical useful signals known as electrochemical sensors. In most electrochemical sensors;



Working Principle

1.Diffusion of the analyte to the electrode/electrolyte interface (in the liquid form)

2. Adsorption onto the electrode surface

3. Electrochemical reaction with electron transfer

4. Desorption of the product

5. Diffusion of the products away from the reaction zone to the bulk of electrolyte

6.The current that is produced from the reaction is monitored and used to calculate the important data such as concentrations from the sample

Types of Electrochemical sensors

1.Potentiometric (measure voltage)

2.Amperometric (measure current)

3.Conductometric (measure conductivity)

4. Thermometric (Measure the heat)

5. Optical sensors (Measure the light intensity)

Applications

1. Electrochemical sensors used for the detection of blood glucose
2. Electrochemical sensors are used for pH measurements
3. Used to detect pesticides
4. Used in the detection of hydrocarbon pollutants
5. Optical sensors are used to measure the concentration of coloured analyte
6. Electrochemical sensors can also used to detect dissolved oxygen, SOx NOx etc.

Q3. Discuss briefly the working principle and applications conductometric sensors.

Working principle:

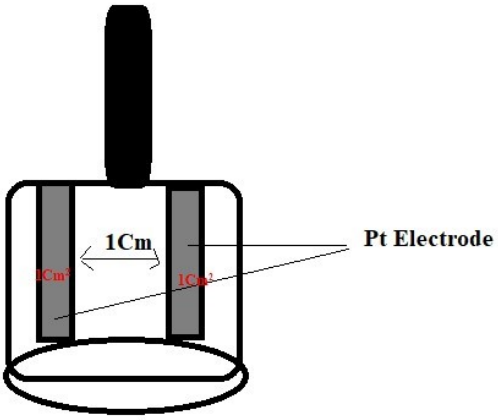
In conductometric sensors, determination of the concentration of analyte is based on measurement of change in electrolytic conductance of solution.

Conductance of solution is based on

1. the concentration (number) of ions in solution

2. Mobility of each type of ion in solution. Mobility of ions depends on its size,smaller the size higher is the mobility and higher is the elctrolytic conductance.

Electrode used in conductivity sensors is called conductiity cell which consisting of two platinum electrodes with unit area of cross section and unit distance between them. Volume between two electrodes is 1 cm^{3}and conductance of 1 cm^3 solution is called specific conductance(k).



Conductometric Sensor

k =1/R x l/a

There will be a change in specific conductance of solution when their is a change in number of ions or type of ions. The change is measured using conductivity cell.

Applications:

1) Monitoring the quality of human drinking water.
2) Monitoring the quality of industrial water.
3) Battery electrolyte density monitoring.
4) Monitoring of the marine environment.
5) It is used to estimate the acid, base and their mixture

Optical Sensors (colorimetry)

Q4. Explain the working principle and applications of Optical Sensors

Optical sensors are electronic components designed to detect and convert incident light rays into electrical signals.

Example: Colorimetric Sensors

Principle: When a sample solution is interacted with a light of suitable wavelength, certain quantity of light is absorbed by the analyte solution and it is observed by a sensor and transducer converts intensity of absorbed light into electrical signal. The change in intensity at certain wavelength within visible(400–800mm) range can be determined using special instrument known as colorimetric sensors.

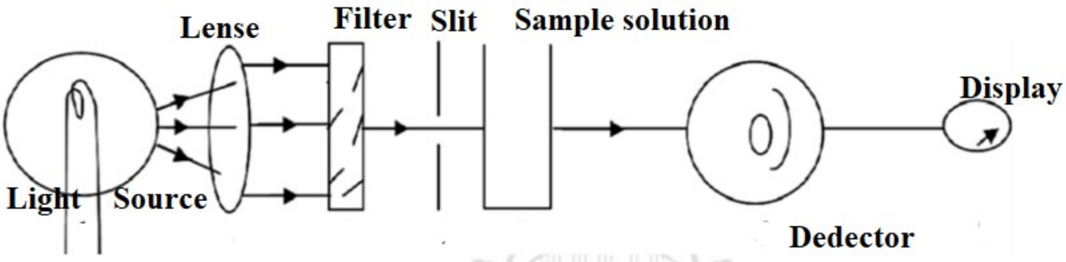


Fig. Components of Colourimetric Sensors

The main component of colorimetric sensor are as shown in fig. Simple optical sensor are used to determine to concentration of species in coloured solution based on the measurement of absorbance of transmitted light by posing through the coloured solution.This analysis governed by Beer's Lambert law.

Applications of Optical Sensors:

1. Optical Sensors are used to determine any chemical species which cal interact with electromagnetic radiation.
2. Optical Sensors are used in motion detection in security systems.
3. They are used in devices like xerox machines and light fixtures that automatically turn lightson in the dark.
4. Optical sensors are used in alarm systems and photographic flashes.
5. Optical sensors have been widely used in the biomedical field, in optical heart-rate monitor etc.

Q5. With a neat sketch explain the measurement of dissolved oxygen by using electrochemical sensors (Amperometric sensors)

Or

Q5. What are elcerochmical sensors? Explain the applications of elcerochmical sensors in the measurement of Dissolved Oxygen (DO)

Electrochemical Sensors:

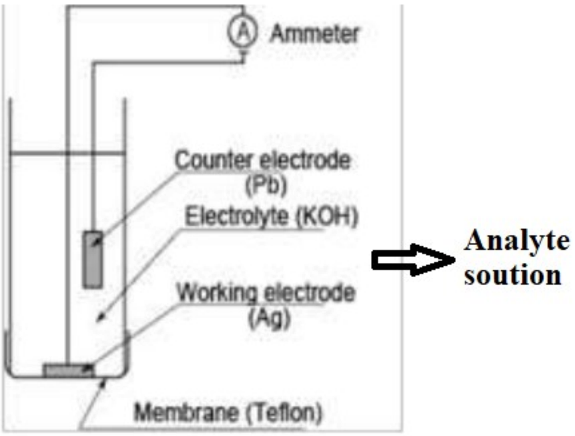


Fig:1.9 Galvanic Sensor for DO measurement

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

Working:

The difference in potential between the anode and the cathode should be at least 0.5V.

When electrode is dipped in water to measure DO, anode undergoes oxidation liberating electrons

$2Pb \rightarrow 2Pb^{2+} 4e^-$

At cathode, DO undergo reduction. Ag cathode is inert, it only passes electrons to oxygen for reduction.

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

Overall reaction is

$$2Pb + O_2 + 2H_2O \rightarrow 2Pb(OH)_2$$

The current produced by the reduction of oxygen at cathode is proportional to the oxygen in the water sample

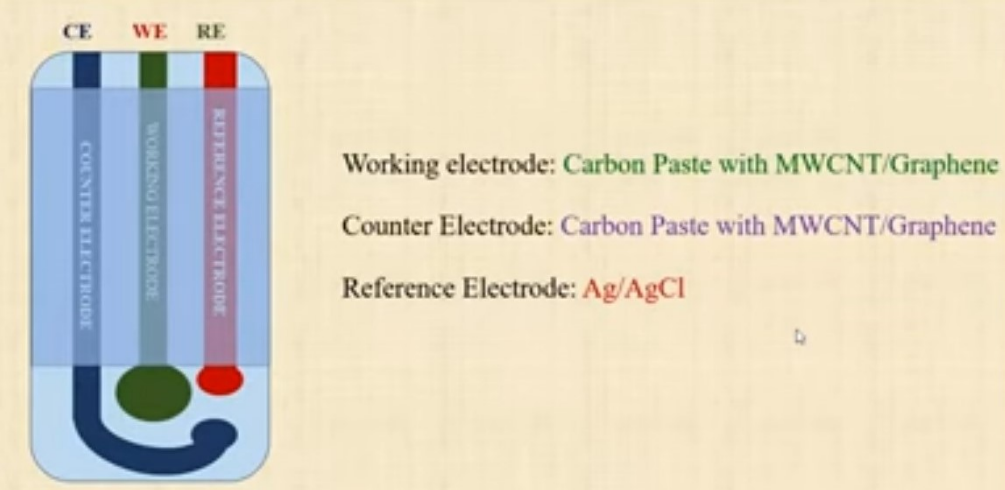
Electrochemical Sensor for pharmaceuticals-Diclofenac

(Diclofenac (DCF), 2-(2-((2,6-dichlorophenyl) amino) phenyl) acetic acid, is one of the most frequently prescribed non-steroidal anti-inflammatory drugs, widely used in the treatment of acute muscle pain and inflammation.

Consuming overdose of diclofenac can cause adverse effects in the human body due to its poor biodegradation.Hence It is very important to develop analytical tool for detection of diclofenac.)

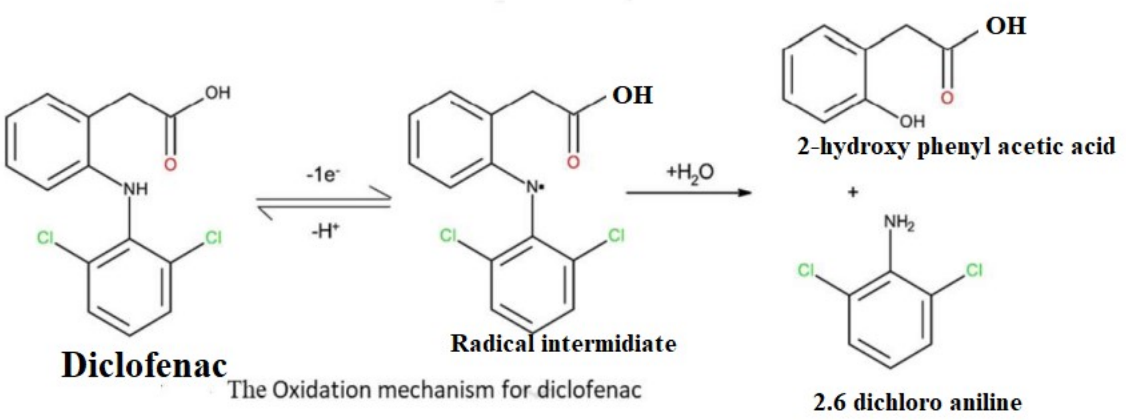
6.Describe the application of Electrochemical sensors for the detection of pharmaceuticals taking Diclofinac is an exmple

Electrochemical sensor are popularly used as one of the fast and cheapest analytical tool for the detection of Diclofenac. Electrochemical sensors contains a three elctrode system such as sensing electrode,counter electrode and reference electrode as shown in Fig.



All the electrodes is screen printed on plastic strip. When the sample containing diclofenac is put on the sensor,oxidation of diclofenac occurs on the surface of the sensing electrode. The change in potential of the reaction gives the concentration of diclofenac.

The following oxidation reaction occurs on the surface of the sensing electrode



The Oxidation mechanism for diclofenac

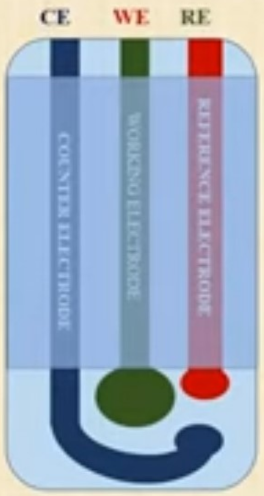
Electrochemical sensor for the detection of hydrocarbon (1-hydroxypyrene)

(Detection of hydrocarbon pollutants, mainly polycyclic aromatic hydrocarbons (PAHs) is essential to monitor their toxicity and carcinogenic risk.After entering the body, some PAH’s are metabolized into 1- Hydroxypyrene which is commonly found in urine.)

7.Describe the application of electrochemical sensor for the detection of hydrocarbon taking 1-hydroxypyrene as an example

Working

The electrochemical sensor used to detect hydrocarbon taking 1-hydroxypyrene consisting of Working electrode(Sensing), counter electrode and reference electrode as shown in fig.



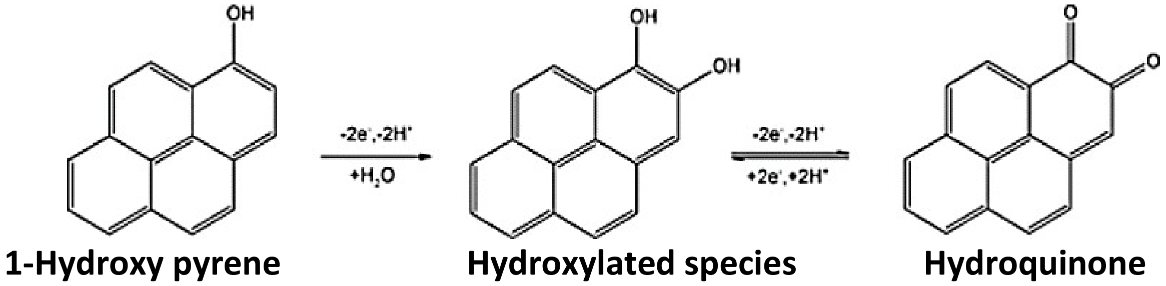
Working electrode: Carbon coated with Cr-MOF/ graphene Oxide

Counter Electrode: Pt

Reference Electrode: Ag/AgCl

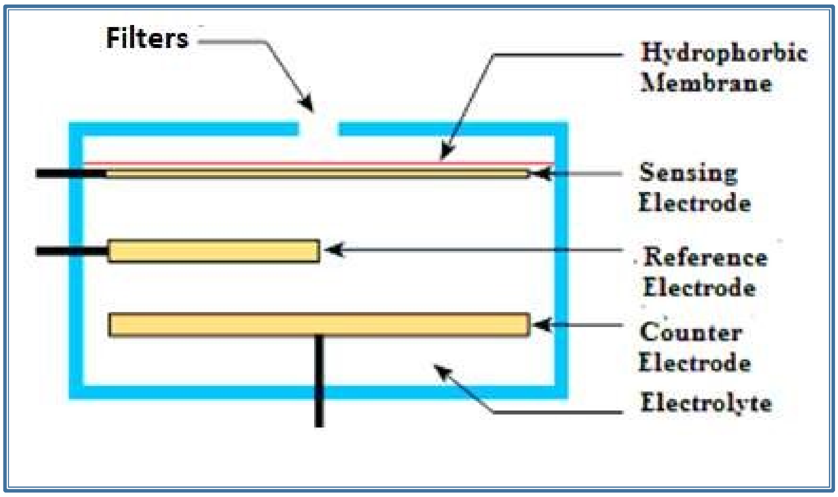
MOF-Metal Organic Frame work

When the sample containing 1- Hydroxypyrene is put in the sensor, oxidation of 1-Hydroxypyrene occurs on the surface of the sensing electrode. The change in potential of the reaction gives the concentration of 1- Hydroxypyrene.



Electrochemical Gas Sensors

Electrochemical gas sensors are gas detectors used for measuring the concentration of a target gas by oxidizing or reducing the gas at an electrode and measuring the resulting current which proportional to the gas concentration.



Filters: Used to prevent unwanted contaminants, mainly particulate matter

Membrane: A gas-permeable membrane is used to regulate the gas flow into the sensors. It allows only analyte gas to pass and prevent the leakage of the electrolyte.

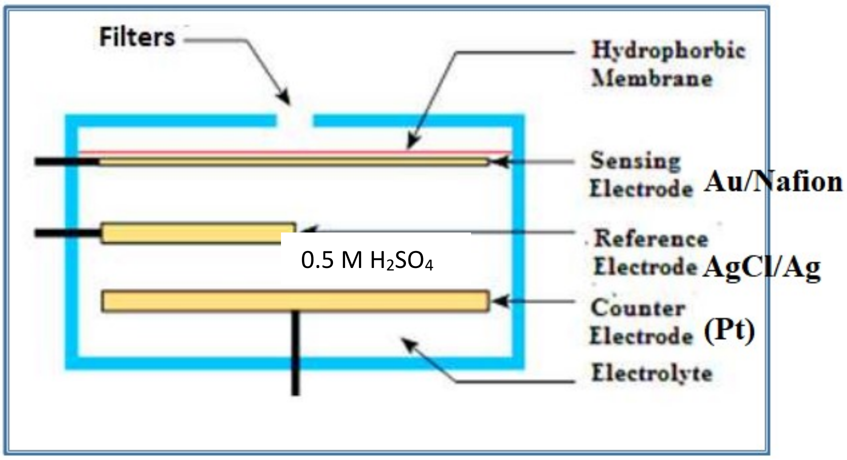
Electrodes: two or three electrodes are used on the requirement. Working or sensing, counter and reference electrode.

Electrolyte: Electrolyte should be ionic conductor and chemically stable. Main role is , it transport charge within the sensor, contact all electrodes effectively and solubilise the reactant and product for efficient transport

Q.8 What are electrochemical gas sensors? Explain how electrochemica gas sensors are used to determine of SOx and NOx in air

Sensors for SOX:

The sensors contains two or three electrode system as shown in fig



Working:

- The diffusion of gas analyte through filter, membrane and then finally through electrolyte on to the surface of sensing electrode.
- Adsorption of analyte gas molecules on the surface of sensing electrode.
- Oxidation of analyte on the surface of sensing electrode, liberating electrons.
- Desorption of product from the electrode surface.
- □ Diffusion of the products away from the reaction zone to bulk of electrolyte.

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

Sensors for NO_2:

The sensors contain two or three electrodes.

Sensing electrode: Au, Pt/Nafion.

Electrolyte: 10 M H_2SO_4

Counter Electrode: Ag/Pt

Working:

- The diffusion of gas analyte through filter, membrane and then finally through electrolyte on to the surface of sensing electrode.
- Adsorption of analyte gas molecules on the surface of sensing electrode.
- Oxidation of analyte on the surface of sensing electrode, liberating electrons.
- Desorption of product from the electrode surface.
- Diffusion of the products away from the reaction zone to bulk of electrolyte.

$$\mathbf{NO_2 + 2H^+ + 2e^- \rightarrow NO + 2H_2O}$$

Sensors for NO:

The sensors contain two or three electrodes.

Sensing electrode: Au/Nafion

Electrolyte: $NaNO_2$/0.5M H_2SO_4

Counter Electrode: Pt

Working:

- The diffusion of gas analyte through filter, membrane and then finally through electrolyte on to the surface of sensing electrode.
- Adsorption of analyte gas molecules on the surface of sensing electrode.
- Oxidation of analyte on the surface of sensing electrode, liberating electrons.
- Desorption of product from the electrode surface.
- Diffusion of the products away from the reaction zone to bulk of electrolyte.

$$\mathbf{NO + 2H_2O \rightarrow NO_3^{2-} + 4H^+ + 3e^-}$$

Disposable sensors

Disposable sensors are low-cost and easy-to-use sensing devices designed for short-term or rapid single-point measurements.

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

Examples: Blood glucose test strips sensor, Pregnancy test strip sensors, Drug and alcoholtest strips sensors, Pulse oximeters, Insulin pump sensors.

Q9. What are disposable sensors? Mention the advantages of disposable sensors

Disposable sensors are low-cost and easy-to-use sensing devices designed for short-term or rapid single-point measurements.

Examples: Blood glucose test strips sensor, Pregnancy test strip sensors, Drug and alcoholtest strips sensors, Pulse oximeters, Insulin pump sensors.

Advantages of disposable sensors:

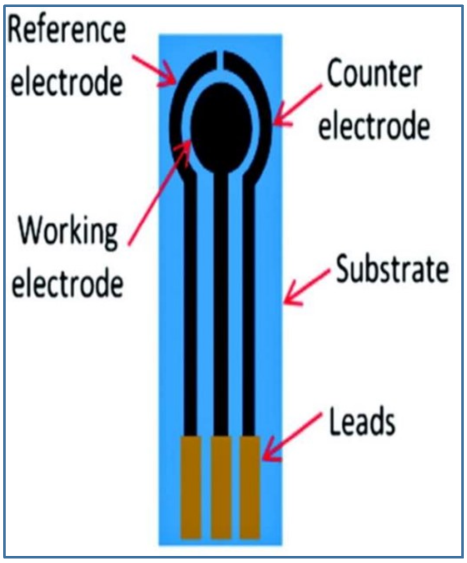
1. Inexpensive, sustainable or biodegradable materials
2. Short duration of analysis and fast response time and low cost
3. Simple to use (or) it offers automated handling of samples with minimal user interaction
4. These are miniature portable instruments, gives accurate results in accordance with international qualities standards
5. It is compact with few components.

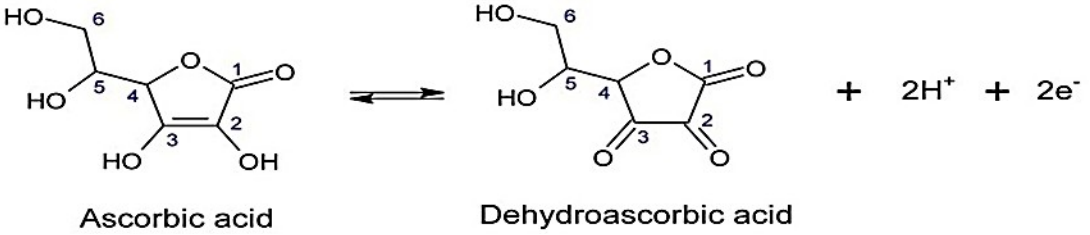
Q10.What are disposable sensors? Explain the detection of ascorbic acid using disposable sensors

Disposable sensors are low-cost and easy-to-use sensing devices designed for short-term or rapid single-point measurements.

Examples: Blood glucose test strips sensor, Pregnancy test strip sensors, Drug and alcoholtest strips sensors, Pulse oximeters, Insulin pump sensors.

In disposable sensor the active materials of working electrode, counter electrode, and reference are printed on paper or plastic strips using screen printing technology.Active material coated on sensing electrode must be capable of oxidizing ascorbic acid on its surface in to dehydroascorbic acid.The overall oxidation of ascorbic acid involves the transfer of two electrons and two protons to form dehydroascorbic acid. The sensor generates electrical signal proportional toconcentration of ascorbic acid.



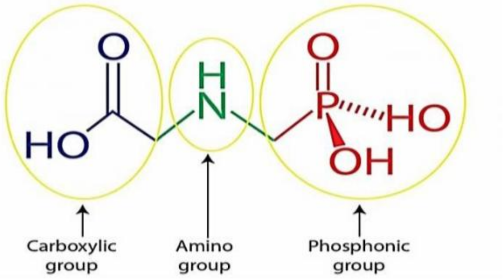


Disposable sensors for the detection of pesticides such as Glyphosate by Electrochemical oxidation

(In order to achieve improved cultivation, farmers started to use pesticide instead of using organic manures. These pesticides should only be used in minimal amounts otherwise these have direct impact on the soil as well as agro products.

Continuous usage of these pesticides makes soil and un cultivable and poor-quality vegetablesand fruits cause a significant effect on human health like asthma, diabetes, birth defects, reproductive dysfunction etc.

Glyphosate is the most commonly used pesticide)



Q11.Explain the detection of pesticides such as Glyphosate usisng disposable sensor

The sensor made of Si based strip on which electrodes are printed

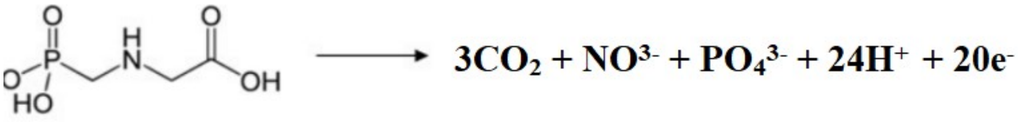
Working electrode: Gold coated with gold nano particles

Counter elctrode: Gold coated with gold nano particles

Eference electrode: Ag/AgCl

Working

The electrochemical detection is based on the oxidation of Glyphosate on working electrode.During the interaction of analyte and electrode surface,glyphosate oxidizes on the working electrode brings a change in current in the electrolyte medium. The change in the current is a measure of concentration of Glyphosate.



Glyphosate

Energy System

Devices which store energy are referred as ***energy storage system,*** *Battery is an electrochemical device which stores electrical energy in the form of chemical energy.*

Batteries:

Batteries are the assembly of two or more same type of Galvanic cells or Voltaic cells connected in series to produce more voltage.

For examples, a 12 volts lead storage battery consists of 6 Galvanic cells, each one produced 2 volts and hence the total voltage is 12volts.

Classification of battery

Primary batteries: These batteries cannot be rechargeable

Example: Dry cell. Zn-air battery

Secondary batteries: These batteries can be rechargeable

Example: Lead acid battery, Ni-MH battery, Li ion battery

Reserve batteries: The high energy batteries in which active materials are isolated from battery

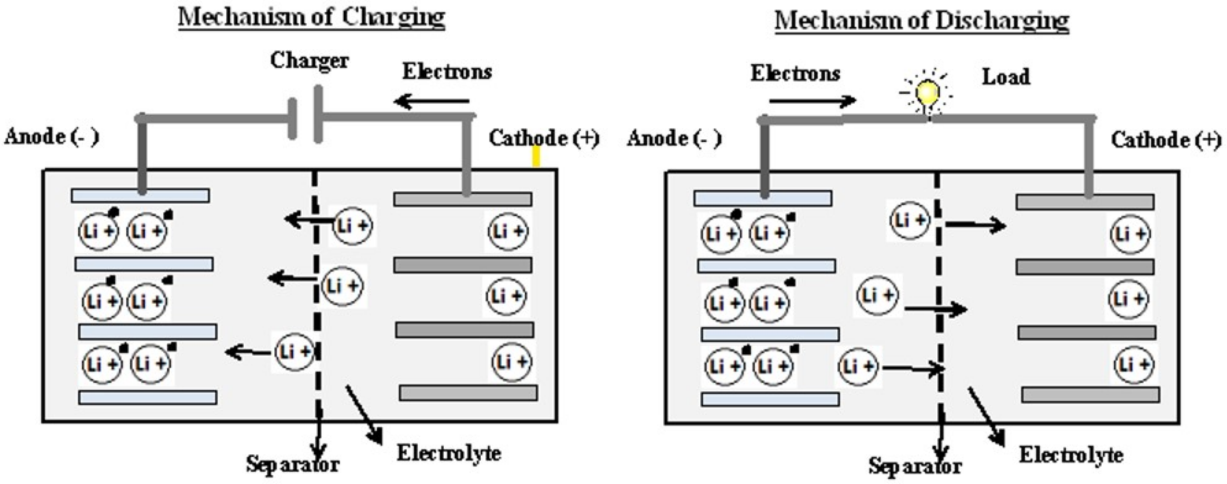
due to their high reactivity and are brought into contact whenever high energy is required for

application are called reserve batteries.

Example: Magnesium- water activated batteries, zinc-silver oxide batteries, etc.

Q12.What are batteries?Explain the construction, working and applications of Li-ion Battery

Li – Ion Battery (Construction, working and applications)



Li-ion battery is a rechargeable battery consists of

Anode: finely divided graphite or carbon in which lithium ions are intercalated, and it is coated on metal foil.

Cathode lthiated transition metal oxide such as ($LiCoO_2$/$LiNiO_2$/ $LiMn_2O_4$) mixed with a conductor, binder and coated on another metal foil.

Electrolyte: is a lithium salt such as $LiPF_6$(lithium hexafluorophosphate), $LiAsF_6$, $LiClO_4$(lithium perchlorate) $LiBF_4$ (lithium tetrafluoroborate) dissolved in ethylene carbonate or diethyl carbonate organic solvent

Electrode reactions

At anode $LixC_6 \rightarrow x\ Li^+ + xe^- + 6C$

At cathode: $Li_{(1-X)}CoO_2 + xLi^+ + x\ e- \rightarrow LiCoO_2$

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$$Li_{(1-X)}\ CoO_2 + LixC_6 \rightleftharpoons LiCoO_2 + 6C$$

With discharge, the Co is oxidized from Co^{3+} to Co^{4+}. The reverse process (reduction) occurs when the battery is being charged

Advantages

1. The output voltage is good, is about 4.1 Volts
2. The energy density is about 250wh/L
3. Good cycle life (1200 cycles)
4. Less sensitive to high temperatures
5. The efficiency is 99%)

Applications

The Li-ion batteries are used in portable telephones, computers, camcorders, LCD TV Portable CD player, cellular phones, electric vehicle such as electric cycle, electric cars, electric Scooters etc.

Q13.What are batteries?Explain the construction, working and applications of Na-ion Battery

Sodium ion battery- Introduction: Sodium ion battery is a type of rechargeable battery in which sodium ions are used as charge carrier. Since battery grade sodium salts are cheaper and most abundant than the Li, the sodium ion battery much cheaper when compare to Li-ion battery.

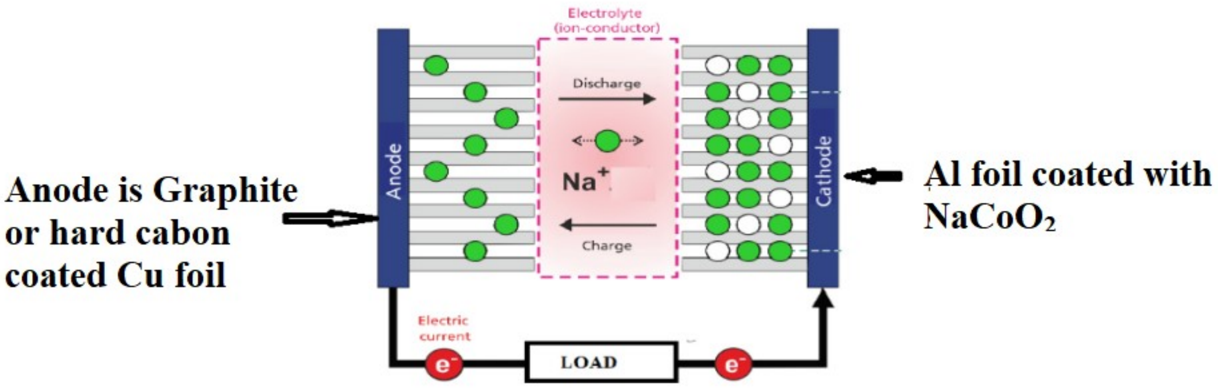
Sodium-ion battery consisting of

Anode; Sodium mixed hard carbon electrode

Cathode: Sodium mixed metal oxide($Na-MO_2$) cathode where M= Co, Mn, Cr,Ni, Fe etc

Electrolyte: electrolyte used is a sodium salt like NaPF6 dissolved in binary organic solvent mixture such as Ethylene carbonate or dimethyl carbonate

Separator: The electrodes are separated by some porous material which allow ionic flow between them and are immersed in an electrolyte.



Anode is Graphite or hard cabon coated Cu foil

Al foil coated with $NaCoO_2$

At anode : $Na_xC_6 \rightarrow xNa^+ + 6C + x\ e^-$

At cathode: $Na(1-x)CoO_2 + x\ e^- + xNa^+ \rightarrow Na\text{-}CoO_2$

During charging, this process is reverse

The output voltage of sodium ion battery has been reported as 3.0V and able to maintain 115Ah/Kg capacity even after 50 charge/discharge cycles

Advantages:

- Rechargeable sodium ion battery for energy storage
- Easier to recycle
- Low market prize
- Capable of working at room temperature
- Good efficient
- Good Cycle life (more than 3000 cycles)

Disadvantages:

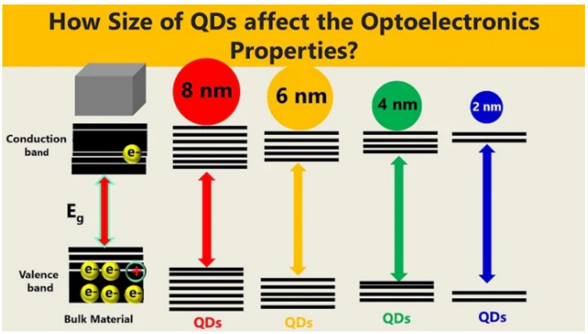
- Due to large size of Na^+ which require more power to keep energy flowing.
- It takes several day to recharge
- Lower operating voltage
- Lower energy density (130-160 Wh/L)

Applications: 1.Used in cellular phones and laptop
2.In electric Vehicles and power tools

Quantum dot sensitized solar cell (QDSSC's)

(Quantum dots are nanometer-sized semiconductor particle having specific optical and electronic properties that differ from those of larger particles.They emits light at a specific wavelengths if energy is applied to them.)

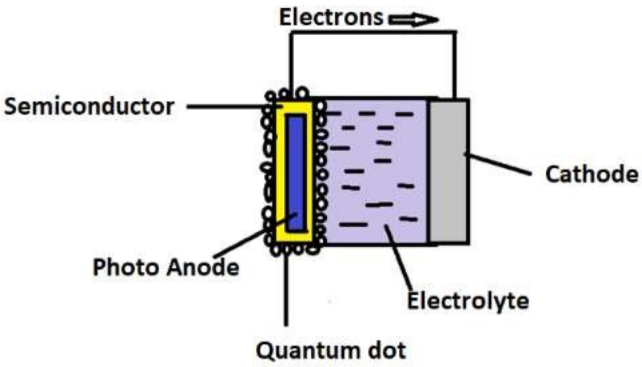
Ex: CdSc,ZnS, CdSc +ZnS



Q.14 What are Quantum Dot Sensitized Solar Cells (QDSSC's)? Explain the working Principle, Properties and Applications.

A semiconductor device which convert sunlight into direct current is called solar cell or PV cell.

A quantum dot solar cell (QDSC) is a solar cell in which **quantum dots are used as the light absorbing photovoltaic material**.



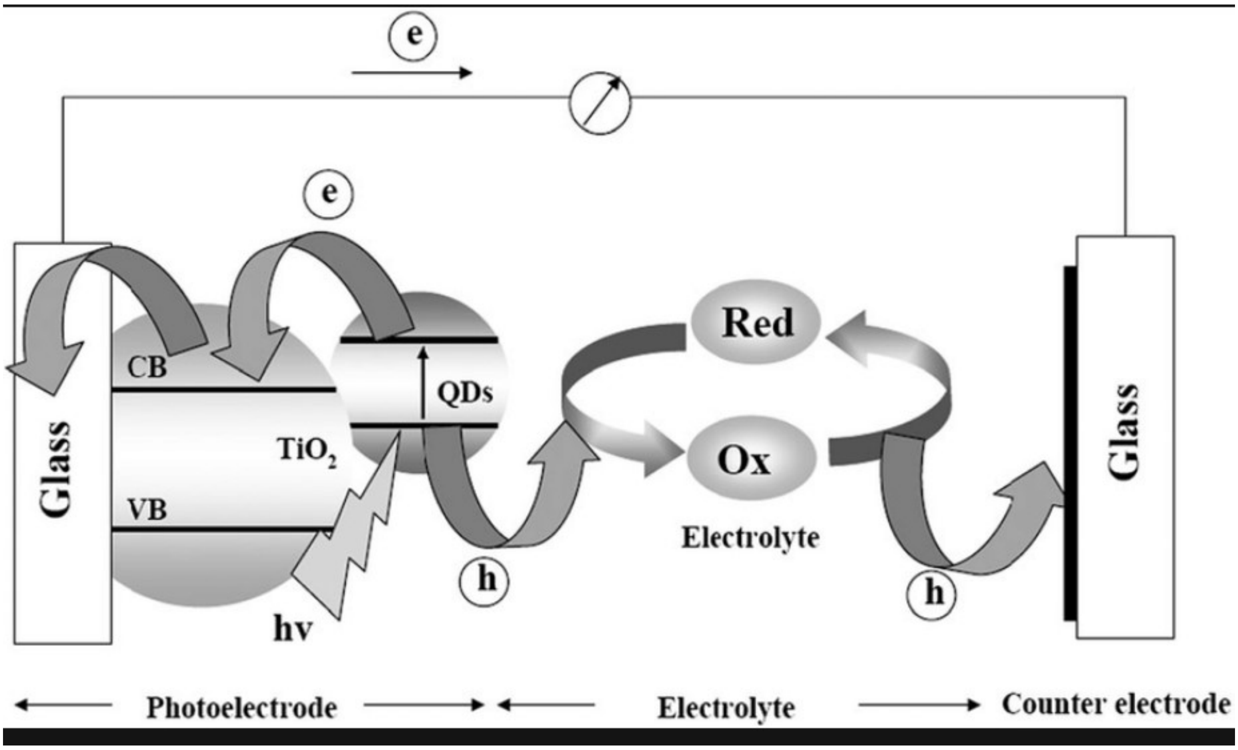
Construction:

Photo Anode: It is conducting glass over which semiconductor is coated (TiO2). Outer layer of photoanode is coated with quantum dots (QDs).

Electrolyte: Photo anode is contact with redox electrolyte. It is hole conductor.

Polysulphide is used as electrolyte.

Cathode Electrode: It is used to regenerate electrolyte and complete the circuit.



Working:

1. QDs are exposed to sunlight.

2. QDs absorb solar energy, electrons move from valence band to conduction band. These electrons are transferred to semiconductor, leaving behind holes on the surface of QD's

3. Electrolyte take up the holes from the surface of QD's and get reduced.

$S^{2-}+2h^{+} \rightarrow S$

4. Electrons flows from anode to cathode through external circuit.

5. At cathode, electrolyte is regenerated taking up electrons from cathode.

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

Properties of QDSSC's

1. Quantum dots has narrow bandgap.

2. It exhibits tunable bandgap.

3. Strong light absorption and

4. High multiple electron generation.

Application

1. QDSSC is mainly used to harness solar energy.It is cheap and renewable energy source to meet our energy requirement.

Note: The contents with in the bracket is only information not for examination

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MODULE 2: MATERIALS FOR MEMORY AND DISPLAY SYSTEM

MEMORY MATERIALS

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

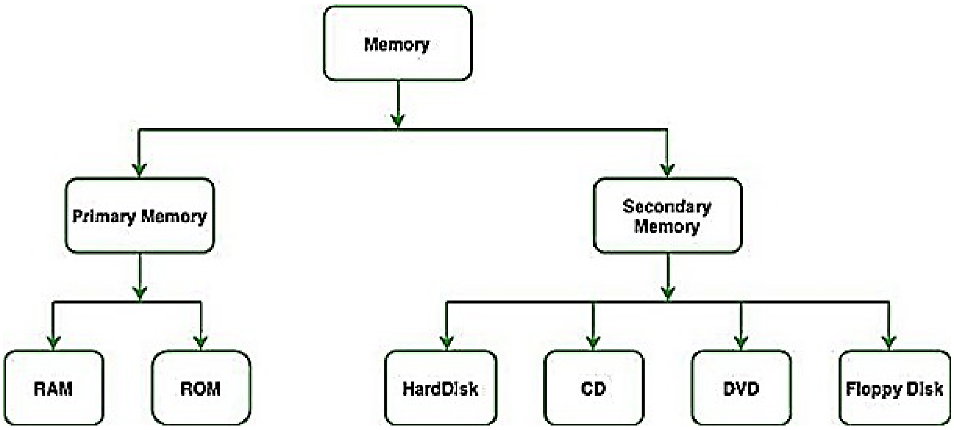
Example: CD, DVD, USB and external hard disc.

There are two basic types of memory:

1. Primary/main memory
2. External/secondary memory

1. Primary Memory: Primary memory is the internal memory of the computer and can be directly accessed by the processor is a volatile memory. The memory capacity of the primary memory is limited. Ex: Random Access Memory (RAM), Static RAM (SRAM), Dynamic RAM (DRAM), Read-Only memory (ROM) etc.

2. **Secondary Memory:** Secondary memory is not directly accessible by the processor. It is a non-volatile memory so the data is retained even in the event of power failure. It can store large amounts of data when compared to main memory. It is slower than the primary memory. Secondary memory is also cheaper than primary memory. Ex: Hard disk drives (HDD), Solid-state drive (SSD), CD-ROM - Compact Disc &DVD, USB Flash Drive, SD Card, etc.



Basic Concepts of Electronic Memory

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

1.The individual memory cells, must posses at least two stable state. The data are stored based on the amount of charge stored in the memory cells.memory cells exhibit two charge states which are coded as ‘0’ and ‘1’. These state is also referred to as ON (1) state and OFF (0) state.

2. These state must be stable for a appropriate period for the data storage

3. They can be shift from one state to another state when an external electric field is applied. This is called as writing process.

4. The states can be distinguished by applying a further external signal.this is called as the reading state

Q1.What are memory devices?Briefly explain the classifications of memory device

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

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

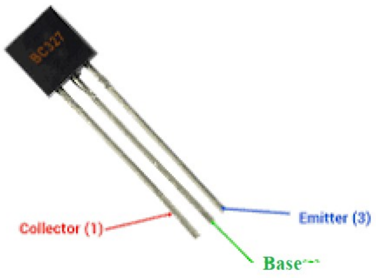
Classification of Memory Devices:

1. Transistor-Type Electronic Memory
2. Capacitor-Type Electronic Memory
3. Resistor-Type Electronic Memory
4. Charge Transfer Effects

1. Transistor-Type Electronic Memory:

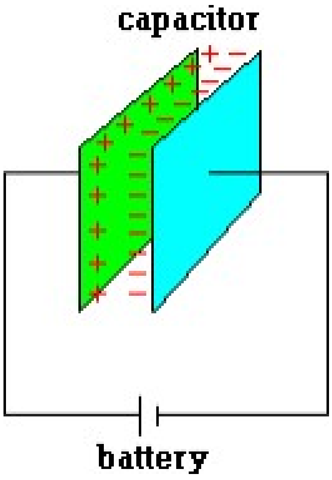
A transistor is a miniature electronic component that can work either as an amplifier or a switch. A computer memory chip consists of billions of transistors, each transistor is working as a switch, which can be switched ON or OFF. Each transistor can be in two different states and store two different 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.

Ex: DRAM



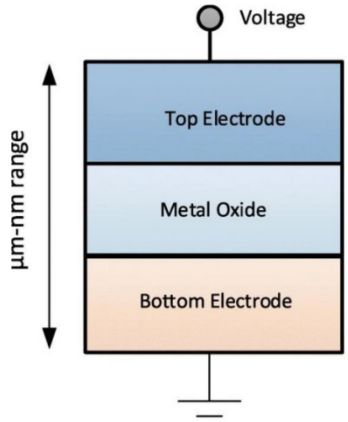
2. Capacitor-Type Electronic Memory

Capacitor have two parallel plate electrodes and charges are stored in these electrode under an applied electric field. It is like a battery that holds data based on energy.If the capacitor is charged, it holds the binary numerical,”1” and holds “0’when the cell is discharged.



EX: FE-RAM

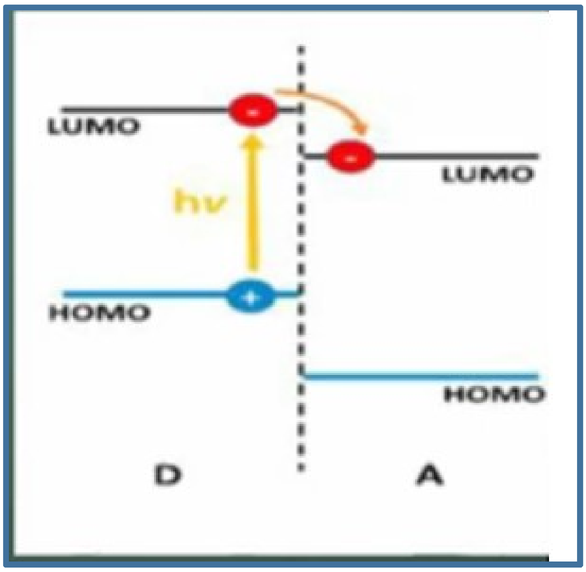
Resistor-Type Electronic Memory Memory devices containing switchable resistive materials are classified as resistor-type memory, or resistive random access memory (RRAM). Resistor-type electronic memory usually has a simple structure, having a metal-insulator-metal structure generally referred to as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



EX:Programmable RAM

Charge Transfer Effects

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



HOMO-Highest occupied Molecular orbital-highest energy orbital with one or two electrons

LUMO- Lower occupied molecular orbital-lowest energy orbital with no eectron

History of organic/polymer electronic memory devices

If organic/polymer molecular material used to store the data is called Organic/polymer based memory device

Working of organic/polymeric memory devices

- They exhibit two electrical stable state known as electrical bi stability.

- They shift from one state (ON state) to other state (OFF state) when electric field is applied
- Information is stored and retrieved by encoding and decoding of these two states

Therefore chemical material store information due to change in properties under applied electric field.

Hence in electronic semiconducting device data is stored in two charge state which are coded as ‘0’ & ‘1’ where as in Organic/polymer semiconducting device,data is stored intwo different conductivity state

Advantages

1) Dimension of the device can be decrease
2) Data storage capacity is increased by large volume
3) Device structure is very simple
4) Cost of production is less
5) Power consumption is low

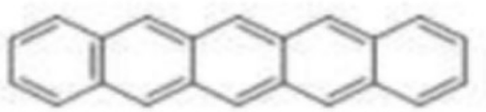
2.Explain the types of organic memory devices by taking p- type and n-type semiconducting materials.

Organic electronic memory devices are made up of organic semiconductors and stores data based on different electrical conductivity states (ON and OFF states) in response to an applied electric field.

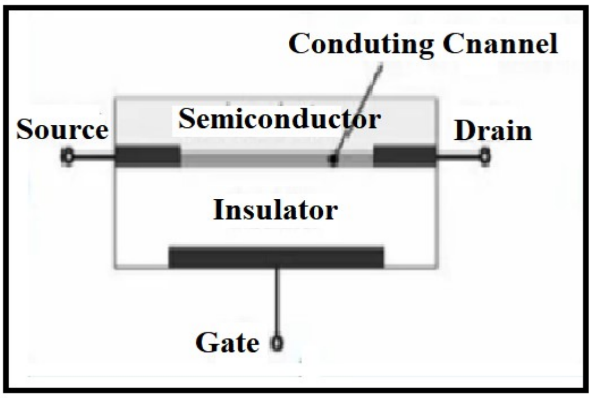
The p-Type Organic Semiconductor Material “Pentacene”

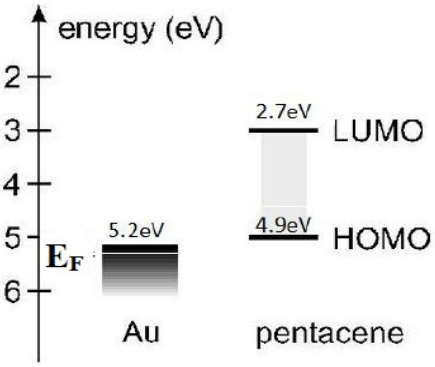
An Organic molecule with π conjugated system and possesses holes as major charge carrier is called p-type semiconductor.

Ex: Pentacene



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



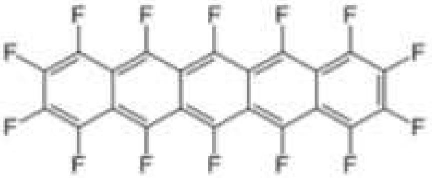


Working Principle

When a positive voltage was applied between gate and source, it was found no flow of electrons to drain due to higher energy gap between the Fermi level of gold (source) and LUMO of Pentacene.

On the other hand, when a negative voltage is applied between the drain and source, **holes** are induced at source. This permits a channel of charges (holes) to drain through semiconductor and insulator interface when a secondary voltage is applied. The flow of charges causes a change in the electrical properties of the pentacene layer, such as a change in its resistance or capacitance. This change can be used to represent a bit of information, such as a 0 or 1.

The n-type organic semiconducting material Perfluoropentacene



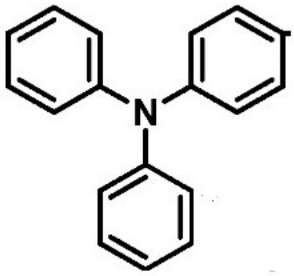
When all the hydrogen atom of pentacene is replaced by Fluorine atoms, it formed Perfluoropentacene. Basically Fluorine is electron withdrawing nature. Hence it convert this molecules into n-type semiconductor.

When a positive voltage is applied between source and drain, **electrons** are induced in the source (gold).This permits the channel of charges to drain through semiconductor-insulator interface as the bandgap between Fermi level of gold (source) LUMO energy of Perfluoropentacene is 1.95ev which is lesser than LUMO energy of Pentacene. Therefore, it is n-type semiconductor.

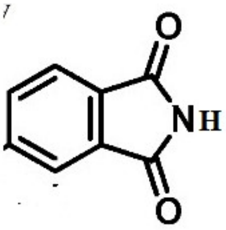
Q3.Discuss the use of Polyimide Polymeric material for Organic memory device.

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

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

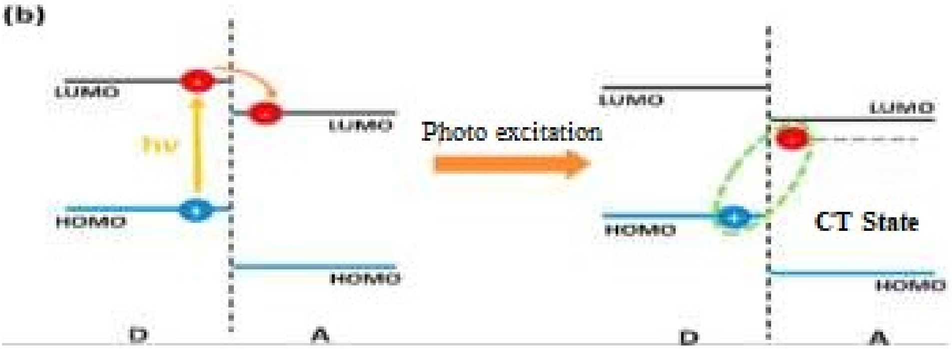


Triphenyl amine (Donor)



Phthalimide (acceptor)

1. When an electric field more than threshold energy is applied, the electrons of the HOMO (TPA unit) is excited to LUMO.
2. The energy of LUMO of donor and acceptor are similar and therefore, after excitation the electron transferred to LUMO (acceptor), generating a CT state.
3. This permits the generation of holes in the HOMO, which produces the open channel for the charge carriers to migrate through.
4. Therefore, Field-induced charge transfer from Triphenylamine to Phthalimide exhibit the switching behavior (bistable states ON/OFF)



Display System

” A display system is the combination of hardware and software output components that shows visual information, such as text, images or videos”.

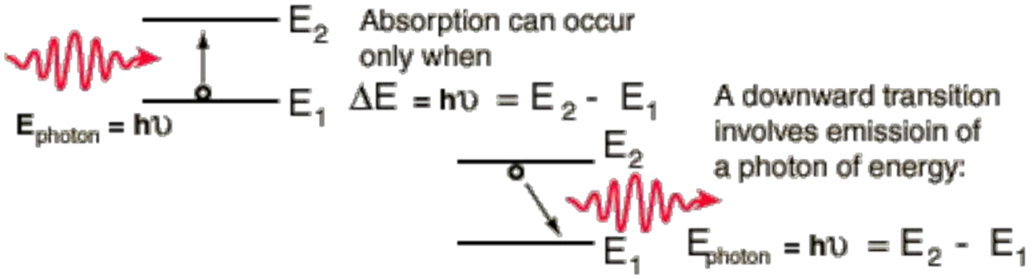
6.Define Optoelectronic device. Explain the working principle of Optoelectronic device.

A hardware device that converts electrical energy into light and light into eletric energy through semiconductors is called Optoelectronic device. Optoelectronic devices are primarily transducers i.e. they can convert one energy form to another.

For example: QLED, OLED,OPV’S etc

Working principle

If the photon has an energy greater than band gap energy is incident on semiconductor, the electron of semiconductor excited from valence band to conduction band leaving behind a free hole 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 electroactive organic materials

“Organic materials which exhibit electro-optical properties similar or superior to Inorganic semiconducting materials are used in optoelectronic devices is known as Photoactive and electroactive devices”

Q4.What are photoactive and electroactive materials and write their role in optoelectronic devices.

"Organic materials which exhibit electro-optical properties similar or superior to Inorganic semiconducting materials are used in optoelectronic devices is known as Photoactive and electroactive devices"

Photoactive materials absorb the light and convert into electrical signals.

Ex: Photo sensors, Pv cells etc.

On the other hand, **Electroactive materials** change their physical properties such as shape,size and refractive index in response to electric field.

Ex: Electroluminescent display such as watches, calculator etc.

Working Principle:

1. Absorption and emission of light radiation in the wavelength region from ultraviolet to near infrared.
2. Photogeneration of charge carriers.
3. Transport of charge carriers .
4. Injection of charge carriers from the electrode

Advantages

1. Light weight and flexible
2. Easily synthesized by chemical method.
3. Production cost is less
4. Used in thin-film flexible devices
5. Properties can be fine-tuned by structure modification

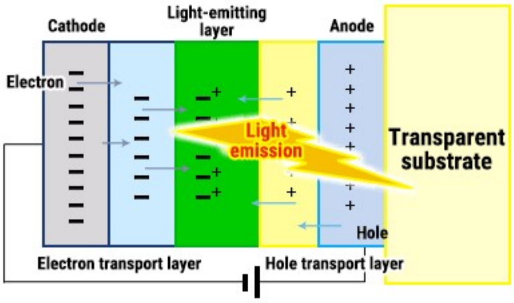
Q5.What are photoactive and electroactive materials and explain their working principle in display system

"Organic materials which exhibit electro-optical properties similar or superior to Inorganic semiconducting materials are used in optoelectronic devices is known as Photoactive and electroactive devices"

Working Principle

Photoactive and electroactive material absorb and emit light in the UV to IR region. Display system (OLED) consisting of an electrodes in which photoactive and electroactive material is sandwich between anode and cathode as shown in fig. When electrons move from cathode, anode allows movement of holes towards light emitting layer under an applied field. Electron-hole pairs are created at the Light emitting layer and energy is released due to recombination. This energy is sufficient to excite an electron from HOMO to LUMO in the light emitting layer.

There is a re-emission of light while electron is returning to HOMO level. This light is extracted by a transparent substrate placed adjacent to either of the electrode.



Nanomaterials

“Any substance in which at least one dimension is less than 100nm is called nanomaterials”.

6.What are nanomaterials? Write the properties and applications of Silicon Nanocrystals for Optoelectronic devices

Properties of Silicon Nanocrystals for optoelectronics

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

Applications:

1. Si NCs are used in neuromorphic computing and down-shifting in photovoltaics
2. Si NCs are used in the construction of novel solar cells, photodetectors and optoelectronic synaptic devices.
3. Also used in gas sensors, bio sensors, and environmental sensors

Organic Nanoparticles:

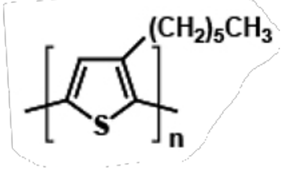
“Organic nanoparticles are nanoparticles that are made from carbon-based molecules”.

Like inorganic immaterialness, organic Nanomaterials shows unique size dependent physical and chemical properties, for example, optical, magnetic, catalytic, thermodynamic and electrochemical. In fact, organic nanomaterials have been projected as active components in optoelectronic devices. These are used in various fields like biopolymer, drug delivery, molecular nanotechnology, and food nanotechnology. Examples of organic nanoparticles include lipids, proteins, and sugars.

Q7. What are organic nanomaterials? Explain any four properties and applications of Polythiophenes (P3HT) suitable for optoelectronic devices.

“Organic nanoparticles are nanoparticles that are made from carbon-based molecules”.

Polythiophenes(P3HT) is a organic light absorbing polymer with π-conjugation. P3HT is an environmentally and thermally stable material having Chemical structure of P3HT Poly (3-hexylthiophene) with chemical formula $(C_{10}H_{14}S)n$.



The improved electronic properties yielded for nanostructured P3HT suitable for optoelectronic devices are listed as follows:

1. P3HT is a semiconducting polymer with high stability and exhibits conductivity due to holes therefore considered as p-type semiconductor.
2. 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 2.14 eV.
5. Fundamental bandgap of P3HT is 490nm visible region, corresponding to π

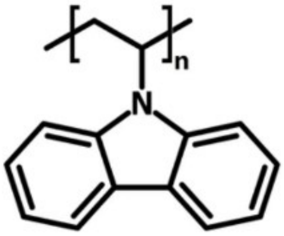
→π* transition, giving electron-hole pair.

Applications:

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

Light emitting materials - Poly(9-vinylcarbazole) (PVK)]

Ployvinyl carbozole is linear polymer obtained from the polymerization vinyl carbozole manomers. The carbozole units are responsible for extensive conjugation and semiconducting properties of the polymers.it is a commonly used a mterials in opto-electronics devices such as organic light emitting diodes (OLED's),and organic photovoltaic cell.It is a p-type semiconductor.



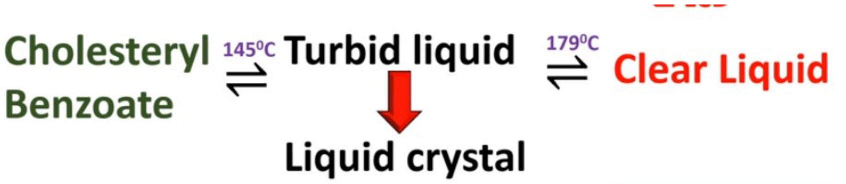
Q8.Explain any four properties and applications of Light emitting materials - Poly[9-vinylcarbazole] (PVK)] suitable for optoelectronic devices

Properties of PVK	Applications
1. It is a semiconducting polymer and an electron acceptor converts ultra-violet (UV) light into electricity. 2. PVK has a band gap of 3.4 eV, optical absorption edge stating at 350 nm capable of absorbing Ultra-Violet light. 3. The PVK film is hydrophobic, thermally stable with a relatively high glass transition temperature (T_g) of 200 °C 4. The PVK solution also showed good wettability, and provide uniform thin films on glass/ITO substrates.	1. PVK is used in OLEDs for light harvesting applications. 2. Used in the fabrication of light-emitting diodes and laser printers. 3. Used in the fabrication of organic solar cells when combined with TIO on glass substrate. 4. Used in the fabrication of solar cells when combined with Perovskite materials. 5. PVK-Perovskite junction is used in Light Emitting Diodes with Enhanced Efficiency and Stability

Display Systems: Liquid crystals (LC’s)

Liquid crystal are intermediate stat of matter between solid and pure liquids posses the properties of solids as well as liquid .

That is liquid crystal may flow like liquid, but its molecules may be oriented like crystal. Liquid crystal molecules can be aligned precisely when subjected to electric fields as like metal showing line up in presence of magnetic field. Liquid crystal allow light to pass through when the molecules are properly aligned.



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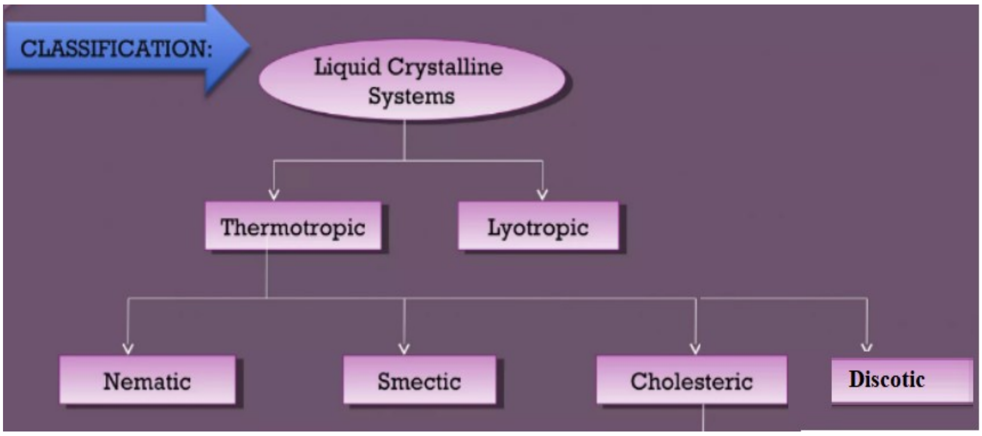
Classification



1. Thermotropic liquid crystals: They are the class of compounds, exhibit liquid crystalline behaviour on variation of temperature.

   Example: 1.Cholesteryl bezoate- 145.8-178.5^{o}C

   2. Anisaldazine - 165-180^{o}C

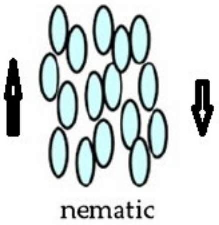
2. Lyotropic liquid crystals: Liquid crystalline phase are formed when a molecules is dissolved in suitable solvent (with specific concentration and at particular temperature)

For example: Soap (Soap + Water)

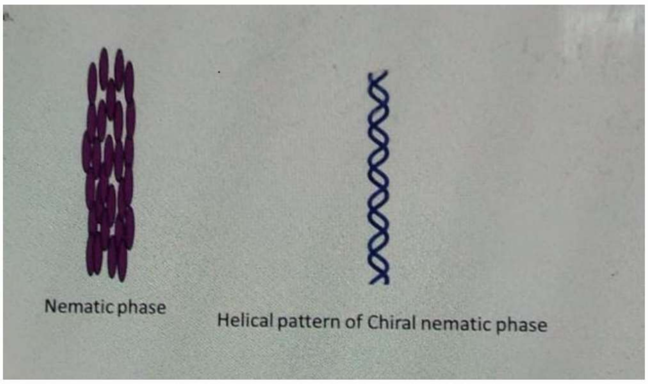
Thermometric liquid crystal have four different phases based on positional order or orientation order

1. Nematic liquid crystalline phase: They are tread like structure where the molecules moves in in both the direction and hence no positional order but only orientation order

P- Azoxy anisole (118-135^{0}C)

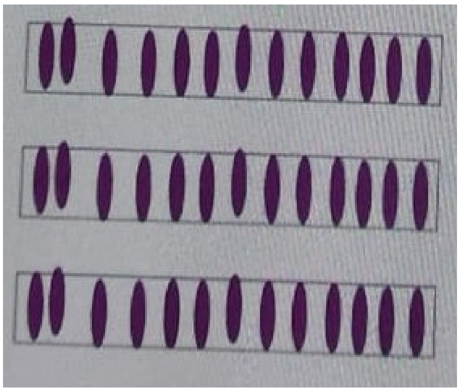


2. Cholestric liquid crystalline phase /chiral (Twisted) nematic: They also tread like structure. The molecules are having high rotational movement but no PO and OO. They are the derivatives of cholesterol



For EX:-Cholesteryl bezoate- 145.8-178.5^{o}C

3. Smectic liquid crystalline phase: They are layered structure having sliding properties and posses some PO and OO



Foe Ex-CBOOA

4-cyanobenzylidine -4-n-octyloxyaniline

Properties

1. Liquid crystal can flow like a liquid due to loss of positional order
2. LC's have optically birefingent due to its orientation order
3. LC's phase geometrically cloudy in appearance , which means that they scatter light in much same way as such as collides(milk)
4. Liquid crystals are subjected to thermal expansion .
5. Liquid crystal change color with temperature
6 Like true liquid, liquid crystal have viscosity, surface tension etc.

Applications:

1. Thermography
2. In Liquid crystal display

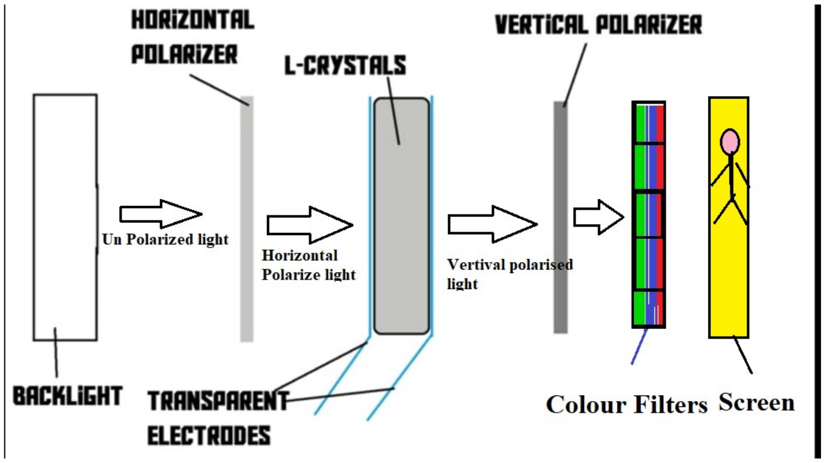
Thermography:

1. As a temperature sensors in thermometer
2. To find out point of failure in electric circuits
3. to locate blockage in veins, arteries, infection and tumors by skin Thermographs

3. Application in Liquid crystal display

Q10.Discuss the working of Liquid Crystal Display.

Liquid crystal display is a thin, flat panel display devices used for electronically displaying information such as text, images and moving pictures etc.. LCD is used in computer, monitoring, television. Instrument panels, gaming devices etc.



Working

Principal: The optical properties of liquid crystal can be manipulated by applying electric or magnetic field that changes the orientation of its molecules and there by intensity of the passing light.

In a liquid crystal display a thin film of liquid crystal usually a Nematic liquid crystal is sandwich between the two thin transparent electrodes (TFT). An arrangement has made to apply electric field across the small area of liquid crystal films known as pixels. There are two polarizing filters fixed either side of the liquid crystal and back light arrangement which will illuminate the screen as shown in fig. This white light is made pass through polarising filters to get polarized light and made fall on the liquid crystal film. The liquid crystal changes the polarization of light which is controlled by applying electric field across the pixels. The intensity of light changes across the small region and the combined effects is the image displayed on the LCD screen. To get the colour image, colour filters have been used which consisting of three pixels ie red, green and blue called as triplet

Advantages:1. It is thin and compact

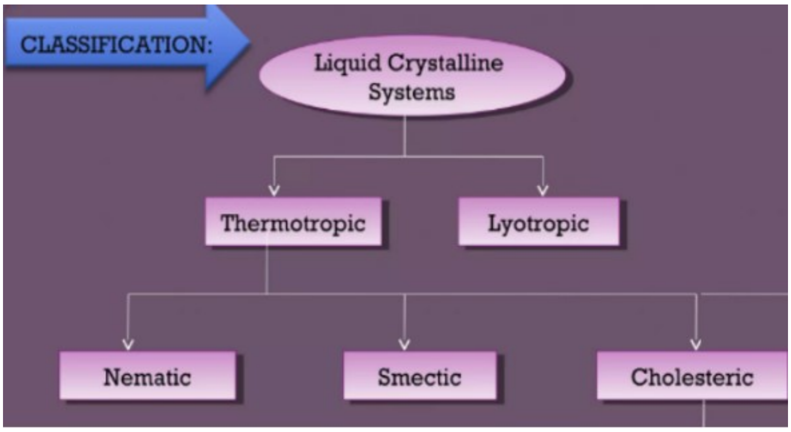
2. Less power consumption

3. Low cost

4. Low heat emission during operati**on**

Q 9. What are liquid crystals?Explain the classification of liquid crystals with examples.

Liquid crystal are intermediate stat of matter between solid and pure liquids posses the properties of solids as well as liquid .



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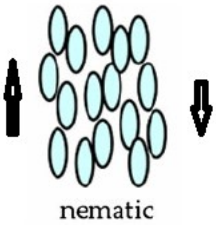

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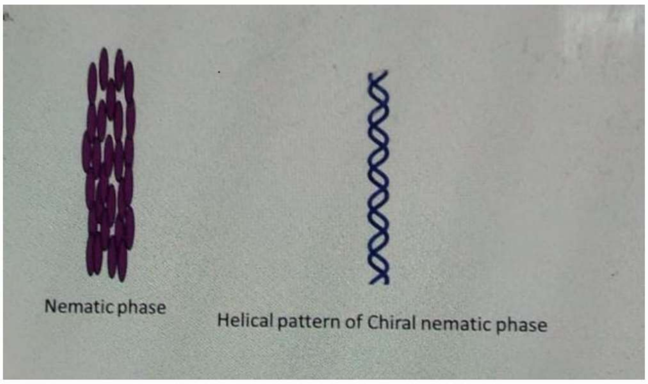

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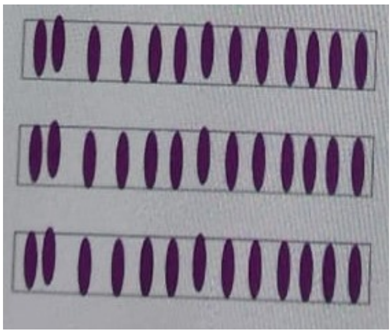

Foe Ex-CBOOA

Q10. What are LC's? Mention any four properties and applications Lc's.

Properties

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2.Liquid crystal change color with temperature

3. Like true liquid, liquid crystal have viscosity, surface tension etc.

4. Liquid crystal can flow like a liquid due to loss of positional order

Applications

1.Thermography

2.In Liquid crystal display

3. As a temperature sensors in thermometer

4.To find out point of failure in electric circuits

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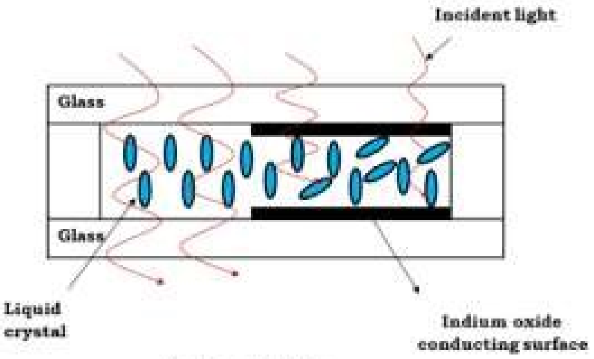
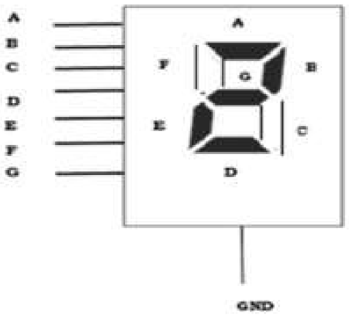
Q10.Discuss the working of Liquid Crystal Display.



With applied bias



When the external field is applied the molecular arrangement is disturbed and that area looks dark and the other area looks clear. In the segment arrangement, the conducting segment looks dark and the other segment looks clear. To display number 2 the segments A,B,G,E,D are energized, that will the number 2 in dark colour.

The LCD can display images in colour by using filters that absorb different colours.

Properties and application of Organic Light Emitting Diodes

Q11.Explain any four properties and applications of OLED

The OLED stands for Organic Light-Emitting Diode - a technology that uses LEDs in which
the light is produced by organic molecules.
OLED displays are made by placing a series of organic thin films between two conductors.
When an electrical current is applied, a bright light is emitted.

Properties : 1. self-emission &vivid colors

2. Low power consumption & wide viewing angle,

3. Ultra-thin thickness, fast response time, simple structure, Flexible

4. Low driving,voltage, high brightness

Applications:

1. OLED’s are used to crate digital display such as TV screen, computer monitors, mobile phone display etc.

2.Used to produce curved display panels, smart watches

3. OLED’s have great picture quality,brilliant color,infinite contrast, fast response rate and Wide viewing angles

4. Since OLED’s doesnot require backlight which make them to manufacture very thinner and more efficient Television

Properties and application of Quantum Light Emitting Diodes

Properties :

Q12.What is QLED? Mention any four properties and applications of QLED.

QLED’s are Quantum dots which are inorganic, durable, stable and allow for excellent colour

and brightness. Quantum dots are manufactured nanocrystals that consist of ultra-fine semiconductor materials. Quantum dots are able to emit precise coloured light because particle

sizes adjust at quantum-level velocities, resulting in accurate and efficient light emissions

1. High brightness than OLED’s
2. High efficiency with long life time
3. More flexible
4. 4.Low processing cost
5. Q LED's have great picture quality, brilliant colour, infinite contrast, fast response rate and vide viewing angles.

6.The major advantages of QLED are the natural colour, long life of the panel and reduced energy Energy consumption.

Applications:

1. QLED’s are used to develop displays of TV screen, computer monitors, mobile phone etc

2. To have more bright and natural colour images

2.Used to produce curved display panels, smart watches

3. QLED’s are used in live imaging, and medical diagnosis

4.QLEDs are also used in two critical photo medical application i.e., in wound repair and cancer treatment.

MODULE 3: Corrosion Science and Electrode System (8hr)

Blow Up Corrosion Chemistry:

Corrosion Chemistry: Introduction (ill effects, global losses), elector-chemical theory of corrosion (principle, reactions under different conditions and diagram taking iron as an example) 1hr

2.Types of corrosion: Differential metal - Definition, Principle, Process and application), Differential aeration – (Water line) – principle and explanation,1hr

3. Corrosion control – Introduction (Definition, Principle and application) galvanization, Anodization and sacrificial anode method (explain with neat diagrams and reactions wherever applicable) 1hr

4. Corrosion Penetration Rate (CPR)- Introduction - (Definition, formula and importance), Numerical problems 1hr

5. Electrode System: Introduction, types of electrodes; Ion selective electrode – definition, construction, working and applications of the glass electrode. 1hr

6. Determination of pH using glass electrode, Reference electrode: Introduction (Definition and role of reference electrode); Calomel electrode – Construction, working and applications of calomel electrode 1hr

7.Concentration cell – Definition, construction, working and Numerical problems. 1hr

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

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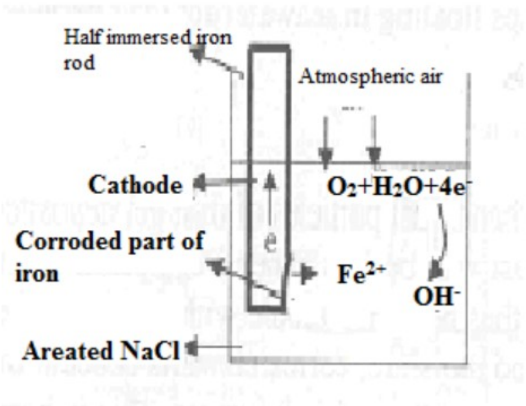
Definition: Destruction or deterioration of metal and its alloy, when it is exposed to corrosive atmosphere through chemical or electrochemical reactions is known as corrosion.

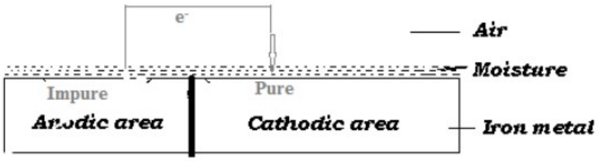
Corrosion is broadly classified into two types depends on corrosive environment

1 Dry corrosion: This type of corrosion occurs when the metal exposed to dry atmosphere in which corrosive gasses like O_2, Cl_2, SO_2 etc.attack the metal and corrosion takes place.

2. Wet corrosion: wet occurs when the metal exposed to wet atmosphere which contains moisture, acidic and alkaline impurities etc.

2. Electrochemical theory of corrosion: According to this theory when a metal is exposed to atmosphere, the number of tiny galvanic cells are formed between pure and impure part of the metal. Impure part or less aerated part of the metal will be act as anode and pure part or well aerated part become cathode.





At anode oxidation takes place where as at the cathode, reduction reaction occur.

Reactions:

At anode : $M \rightarrow M^{n+} + n e^-$

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

At Cathode:

i) If the corrosion medium is neutral and aerated

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

Ii) If the corrosion medium is neutral and deaerated

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

iii) If the corrosion medium is acidic

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

iv) Formation of corrosion product:

$2Fe_2+ + 4OH^- \rightarrow 2Fe(OH)_2$

$2Fe(OH)_2 + O_2 + (n-2)H_2O \rightarrow Fe_2O_3 . n H_2O$

4. Types of corrosion:

i) Bimetallic or differential metal corrosion:

When two dis-similar metals are in contact with each other in a corrosion environment, a galvanic cell is formed, due to the difference in their electrode potential values. Metal with lower electrode potential value act as anode and metal with higher electrode potential value act as cathode.

The rate of corrosion depends on the amount of electrons flow from anode to cathode, this intern depends on the potential difference of the two metals, larger the difference, more no of electron flow from anode to cathode and higher will be the rate of corrosion. (Fig-(a&b))

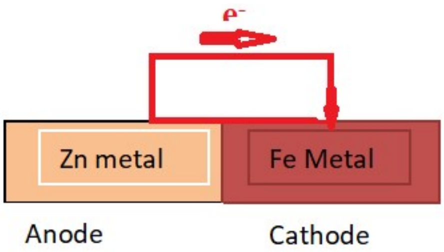


Fig. (a)

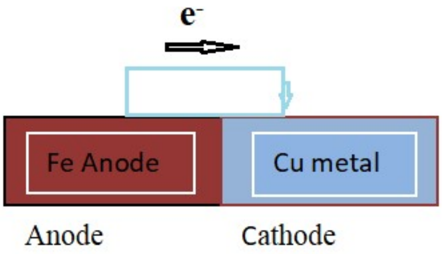


Fig. (b)

Ex;1. Fe in contact with Zn.

$$E_{cell} = E_R - E_L$$

$$= E_{Fe} - E_{Zn}$$

$$= -0.44-(-o.76v)$$

$$= 0.32V$$

In this case Zn has lower electrode potential value compare to Fe and hence Zn act as anode & Fe act as cathode, corrosion of Zn takes place. Also the potential difference between the two metals is less, hence the rate of corrosion is also less.

Ex; 2 Fe in contact with Cu

$$\text{Eemf cell} = ER - EL$$

$$= E_{Cu} - E_{Fe}$$

$$= 0.34v - (-0.44v)$$

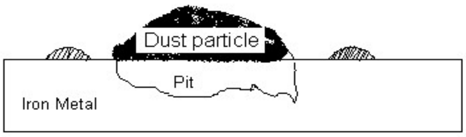
$$= 0.78v$$

In this case Fe has lower electrode potential when compare to Cu and hence Fe act as anode and Cu act as cathode, corrosion of Fe takes place. Also potential difference between the two metals is high and hence the rate of corrosion is also high.

4.2 Differential aeration corrosion.

(i) Pitting corrosion:

This type of corrosion result when a small quantity of dust get deposited on a steel surface .The portion of the metal covered by the dust is less aerated and act as anode, rest of the portion which is more aerated act as cathode. In the presence of electrolyte and moisture corrosion starts beneath the dust and which makes the formation of pit. once the pit is formed, the rate of corrosion increases, this is because of the formation of small anodic area (pit) and large cathodic area (surface). Anodic area undergoes severe corrosion resulting in the enlargement of pit.



Reaction:

At anode; Fe → $\mathbf{Fe^{2+} + 2e^-}$

At cathode; $\mathbf{O_2 + 2H_2O + 4e^- \quad 4OH^-}$

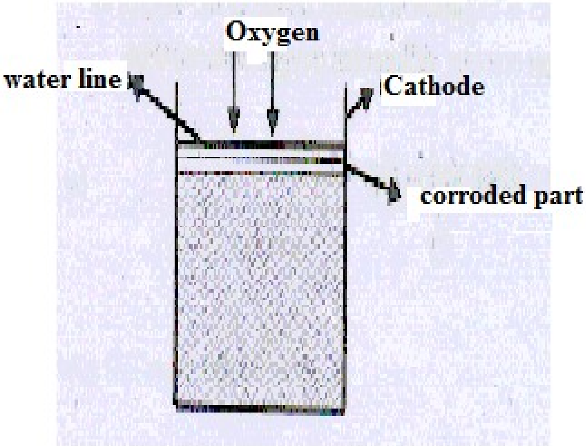
Formation of corrosion product,

$\mathbf{2Fe(OH)_2 + O_2 + (n\text{-}2)H_2O \rightarrow Fe_2O_3 .\ n\ H_2O}$

1. Part of nail inside the wall undergoes corrosion.
2. When a dirt particle sits on a metal bar, the part under the dirt undergoes corrosion.

(ii) Water line corrosion:

The water line corrosion takes place due to the formation of differential aeration The portion of the metal below the water line has least contact with air and act as anode, while the portion of the metal above the water line has more aerated with air and act as cathode. Hence, corrosion takes place below the water line. A distinct brown line is formed just below the water line due to the deposition of rust.



Reaction:

At anode ; $\mathbf{Fe \rightarrow Fe^{2+} + 2e^-}$

At cathode; $\mathbf{O_2 + 2H_2O + 4e^- \rightarrow 4OH^-}$

Formation of corrosion product,

$$\mathbf{2Fe(OH)_2 + O_2 + (n-2)H_2O \rightarrow Fe_2O_3 . n H_2O}$$

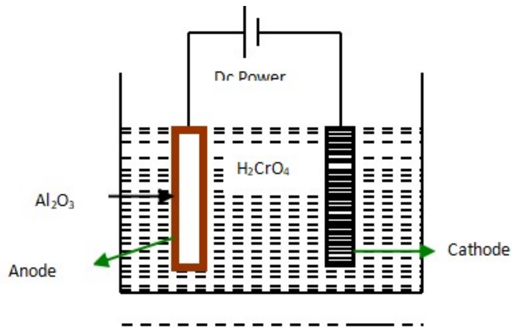
For example: Partially filled iron tank undergoes corrosion inside water.

Corrosion Control
1.Protective coating:
1.1Anodizing:

Process: (Anodizing of aluminum): Anodizing is applicable for non-ferrous metals such as Al, Mg Zn Etc

When aluminum metal is made anodic in an electrolytic bath contain sulphuric acid or chromic acid as an electrolyte, a thin layer of aluminium oxide (Al_2O_3) is formed on the surface. This process is called anodizing of aluminium or anodic oxidation of aluminum.

When anodized aluminium is exposed to a corrosive environment, the Al_2O_3 layer on the surface acts as a protective coating. Hence corrosion is prevented.Other metals such as Mg, Ti etc. can also be anodized.



Electrolyte	*5-10% of chromic acid*
Temperature	*35^0c*
Current Density	*10-20 mA/cm2*
Thickness of oxide layer	*2-8µm*

(Note: On anodizing, Al_2O_3 is formed on the surface as a porous layer. The layer may be made compact by sealing, which involves heating with boiling water or steam. During sealing, Al_2O_3 is converted into $Al_2O_3.H_2O$ which occupies higher volume. Therefore, the pores are sealed.)

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$$

$$6H^+ + 6e^- \rightarrow 3H_2$$

Anodized articles are used in the manufacture of Soap boxes, window frames, automobile air-craft components

3.0 Anodic metal coating:

3.1Galvanization: Coating of a metal (steel) surface with Zinc metal in the molten state is called galvanization. Galvanization is carried out by hot dipping method. It involves the following steps.

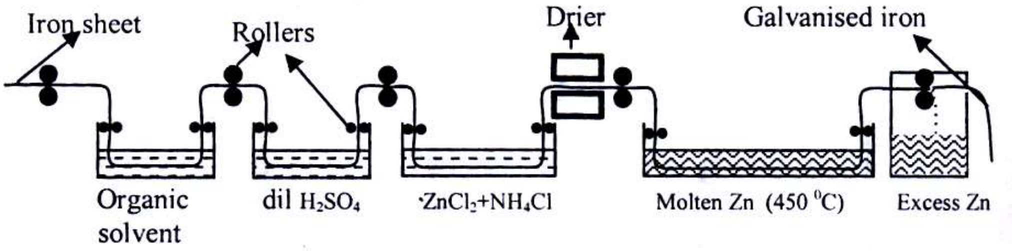
i) The metal surface is washed with organic solvents to remove organic matter on the surface.

(ii) Rust and the other deposits are removed by washing with dilute sulfuric acid ,

(iii) Finally, the article is well washed with water and air dried.

(iv)The metal is then treated with a flux of NH_4Cl and $ZnCl_2$ for improving adhesion and also to prevent the oxidation of Zinc.

(v) The article is then dipped in a bath of molten Zinc, maintained at 425-430^{o}c The excess Zinc is on the surface is removed by passing through a pair of hot rollers, which wipes out excess of Zinc coating and produces a thin coating. (Fig-3.7)



(Fig-3.7)

Applications: Galvanization is used extensively to protect iron from corrosion in the form of roofing sheets, fencing wires, barbed wires.

6. Cathodic metal coating:

6.1 Cathodic protection:

Corrosion of a specimen occurs primarily because of the flow of electrons from the anodic to cathodic regions. The anodic region undergoes corrosion where as the cathodic regions are unaffected. If electrons are supplied from the external source, then the specimen remains always cathodic and prevents the formation of galvanic cells on the surface of the metal. This type of protection is known as cathodic protection.

There are two types of cathodic protection:

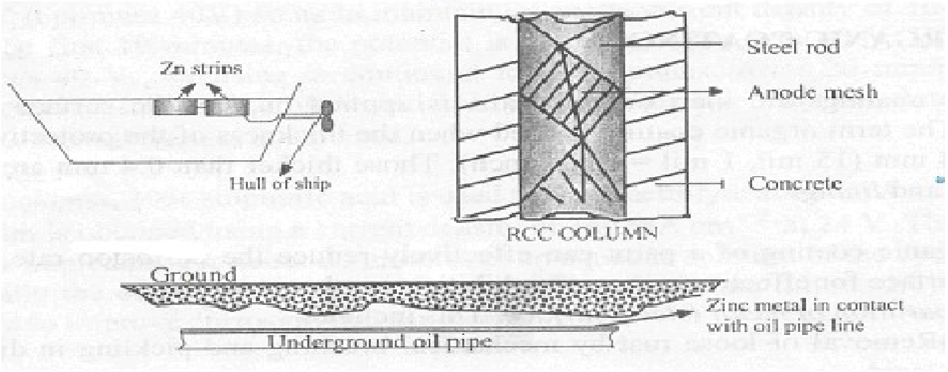
i) **Sacrificial anode method**:

ii) impressed current method

(i) Sacrificial anode method:

In sacrificial anode technique, the specimen to be protected (Fe) is connected with an external anode such as Mg, Zn and their alloys which are more active than the protected metal. The external anode provides electrons to the specimen and converting the anodic site into cathodic site. During this process the external anode get corrode itself in the course of time. The corroded external anode has to be sacrifices frequently by replacing with new piece of anode. Thereby the entire specimen gets protected from the corrosion. This type of protection is known as sacrificial anode method

For Ex: This method is used to protect buried pipelines, ship hulls, industrial water tank, steel rods, in rcc column.



Corrosion Penetration Rate (CPR): The corrosion penetration rate is expressed in terms of thickness or weight loss where the surface of the metal corrodes uniformly across an area and is defined as

“The speed at which any metal deteriorates due to a chemical reaction when it is exposed to a corrosive environment,

The rate of corrosion (R) or (CPR) is calculated using the following equation

Corrosion Penetration Rate (CPR). R $= \frac{KW}{\rho A t}$

CPR in mpy (mil/year, 1mil 0.001 inch)	**CPR in mm/year**
K= 534 **W-mg** **D or ρ=g/cm^3** **A= inch^2** **Tor t = hrs**	**K=87.6** **W= mg** **A= cm^2** **T or t= hrs.** **P or D=g/cm^3**

NOTE: **CPR** $= \frac{KW}{\rho At\ (DAT)}$

Mils penetration per year (MPY): It is a unit of measurement equal to one thousand of an inch. Mils penetration per year is used to gauge a coupon’s corrosion rate. The unit may also use to measure coating’s thickness or tolerance

(1) A steel sheet of area 100 in^2 is exposed to air near the ocean. After one year period it was found to experience a weight loss of 486 g due to corrosion . given density of steel is 7.9g/cm^3.

(a) Calculate CPR in mpy
(b) Calculate CPR in mm/year

Ans:

Given:

Weight loss after exposure time t in mg, w= 486g = 486 ×1000 mg

Density of specimen in g/cm^{3,} ρ = 7.9 g/cm^3

Exposed surface area of specimen in in^2 for mpy and Cm^2 for mm/year

A = 100 in^2 and A = 100 × 2.54^2 Cm^2 (1 inch=2.54 cm)

Time of exposure in hours t = 1 year = 365 × 24

WKT

(a) CPR in mpy =
$$\mathbf{\frac{KW}{\rho At} = \frac{534 \times 486 \times 1000}{7.9 \times 100 \times 365 \times 24} = \underline{37.50\ mpy}}$$

(b) CPR in mm/year
$$\mathbf{= \frac{KW}{\rho AT} = \frac{87.6 \times 486 \times 1000}{7.9 \times 100 \times 2.54^2 \times 365 \times 24} = 0.95 mm/yr}$$

(2) A piece of Corroded steel plate was found in a submerged ocean vessel. It was estimated that the original area of the plate was 10 in^2 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 steel is 7.9g/cm^3.

Ans:

Given A = 10 in^2

W = 2.6 kg = 2.6 ×10^3 g ×10^3 mg

CPR = 200 mpy

Density ρ = 7.9 g/ cm^3

Time of submersion in years =?

(a) CPR in mpy =
$$\mathbf{\frac{KW}{\rho AT}}$$

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

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

$$\mathbf{t = 87873.41\ hrs.}$$

$$t = \frac{87873.41}{24x365} = 10.03 \text{ years}$$

(3) A thick steel sheet of area 400 cm2 is exposed to air near the ocean. After a one year period it was found to experience a weight loss 375 g due to corrosion. To what rate of corrosion in both mpy and mm/year does this corresponds?

Ans:

Given:

Weight loss after exposure time t in mg, w= 375g = 375 ×1000 mg

Density of specimen in g/cm^3 = 7.9 g/cm^3

Exposed surface area of specimen in in^2 for mpy and Cm^2 for mm/year

A = 400 cm^2 and A = 400 / 2.54^2 in^2

Time of exposure in hours t = 1 year = 365 × 24

WKT

(a) CPR in mpy $= \frac{KW}{\rho At} = \frac{534 \times 375 \times 1000}{7.9 \times 400 / 2.54^2 \times 365 \times 24} = \underline{46.67 \text{ mpy}}$

(b) CPR in mm/year $= \frac{KW}{\rho At} = \frac{87.6 \times 375 \times 1000}{7.9 \times 400 \times 365 \times 24} = \underline{1.19 \text{ mm/yr}}$

4. A thick brass sheet of area 400inch^2 is exposed to moist air. After 1 years period it was found to experience a weight loss of 375g due to corrosion. If the density of the brass is 8.7g/cm^2 calculate the corrosion penetrating rate in mpy and mmy

(c) CPR in mpy $\frac{KW}{D\ AT} = \frac{534 \times 375 \times 1000}{8.7 \times 400 \times 365 \times 24} = \underline{6.56 \text{mpy}}$

(d) CPR in mm/year $= \frac{KW}{D\ AT} = \frac{87.6 \times 375 \times 1000}{8.7 \times 400 \times 2.54^2 \times 365 \times 24} = 0.167 \text{mmy}$

Module-3,Electrode System: **A**n electrode is a metallic conductor which conduct the electricity without any decomposition.

Types of electrode: There are four types of single electrodes

1. Metal ion metal electrode, Ex: Zn/Zn^{2+}, Ag/Ag^{+} etc.

2. Metal insoluble salt metal electrodes, Ex: Calomel and Silver chloride coated Ag electrode

3. Gas electrode, Ex: Hydrogen gas electrode

4. Ion selective Electrodes, Ex: glass electrode

5. Amalgam electrode, Ex: $Pb\text{-}Hg/Pb^{2+}$

6. Oxidation reduction Electrode, Ex: Pt/Fe^{2+}, $Fe3^{+}$ Pt/Sn^{2+}, $Sn4^{+}$

Reference Electrodes:

Reference electrodes are the standard electrode with reference to those, the potential of any electrode can be measured.

Ex: Hydrogen gas electrode, calomel electrode, silver chloride coated silver electrode etc.

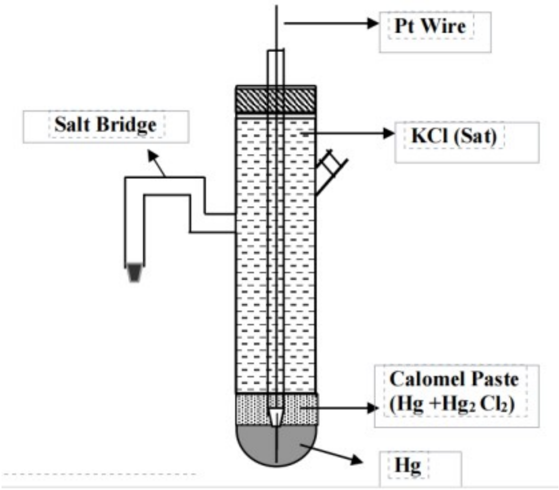
There are two types of reference electrodes

1. Primary reference electrodes; e.g standard hydrogen gas electrodes (SHE)

2. Secondary reference electrodes; e.g Calomel electrode, Ag / AgCl electrode etc.

Secondary reference Electrodes:

2) Describe the construction and working of calomel electrode**.**



Calomel electrode consists of a glass tube in which metal mercury is placed at the bottom. Above the Hg a past of Hg with Hg_2Cl_2 is taken. A saturated solution of KCl is placed over the solid mixture. Electric connection can be given by inserting a Pt. wire. This half-cell is coupled with another half-cell by using a salt bridge.

Cell representation: Pt, Hg, $Hg_2\,Cl_2$ (sat.) / KCl (sat.)//

Cell reaction: $2Hg + 2\,Cl^- \longrightarrow Hg_2Cl_2 + 2e^-$

$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2\,Cl^-$$

The calomel electrode is reversible with respect Cl^- and its potential can be calculated by using the equation

$$E_{cell} = E^\circ - \frac{0.0591\log[Cl^-]^2}{n}$$

The potential of calomel electrode depends on the concentration of KCl used. The potential decreases with increasing the concentration of KCl

For saturated KCl » 0.241 V

1M KCl » 0.280V

0.1M KCl » 0.334V

Advantages:

1. Easy to construct.
2. Easy to maintain
3. Electrode potential is stable over long period and reproducible.
4. They can use even in oxidizing solution.
5. The cell potential does not vary with temperature.

Applications;

Use as secondary reference electrode

1. for the measurement of single electrode potential given electrodes,
2. During the measurement of pH of a given solution

Ion Selective electrodes: are the indicators electrodes, which are selectively respond

to specific ion in the mixture.

Example: Glass electrode

In ion, selective electrode there is a thin membrane which are selectively responds to specific ion in the mixture, hence ion selective electrode also called as membrane electrodes.

Depends on the nature of the membrane ion selective electrode are of different types

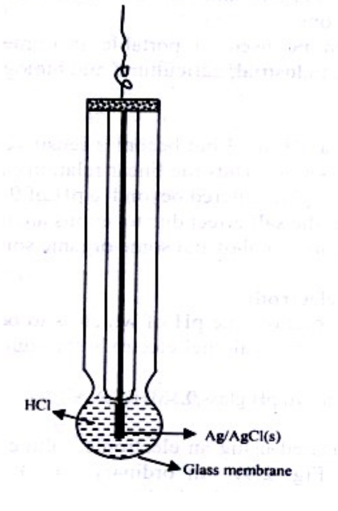
1. Crystalline Membrane ion selective electrodes
   a) Single crystal membrane ion selective electrode, Ex LaF_3 for F^- ions
   b) Poly Crystalline membrane ion selective electrodes, Ag_2S for S^{2-} & Ag^+
2. Non crystalline membrane ion selective electrodes
   a) Glass membrane electrode, for Na^+ and H^+
   b) Liquid membrane electrodes, for K^+
   c) Immobilized liquid in rigid polymer matrix, for Ca^{2+} and NO_3^-

Construction and working of glass electrode:

Principle; "When a thin glass membrane separates two solutions of different pH values, a potential difference is setup across the membrane which is directly Proportional to difference in pH."

The glass membrane function like an ion exchange resin which exchanges with the solution as follows.

$$Na^+Gl^- + H^+solu.^- \rightleftharpoons H^+Gl^- + Na^+ solu.^-$$



For a particular type of glass potential varies with H^+ ions concentration

Construction; A glass electrode consists a thin walled glass bulb, (special type of glass of Low melting point and high electric conductivity) contain 0.1N HCl. A Pt or AgCl/Ag wire dipped in the solution provides electric connection.

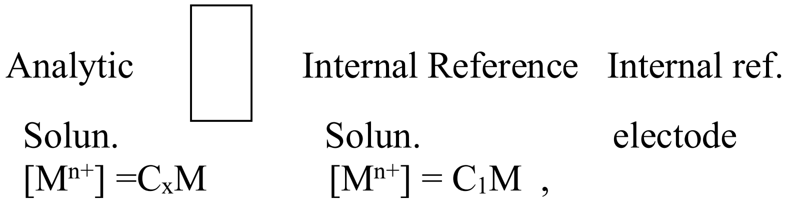
Cell representation; Pt or AgCl/ Ag / HCl (0.1N) / glass//

Applications; Glass electrode is used to determine pH of a given solution by using the equation

$$\boxed{E_G = E^o_G - 0.0591pH}$$

Working of glass electrode/ Derivation of the equation $E_G = E^o_G - 0.0591pH$

Ion selective electrode generally consists of an ion selective membrane in contact with analytic solution on one side and internal reference solution on the other side. An internal reference electrode is in contact with reference solution as shown in fig.



Let us consider the glass electrode dipped in a solution of concentration ‘C_x’ with respect to H^+ ion, If C_1 is the concentration of solution inside the bulb then the observed potential is kind of boundary potential(E_b) that developed across the membrane is given by

$$E_b = E_x - E_1$$

$$Eb = 0.0591 \log Cx/C1$$

$$E_b = L-.0591P^H$$

$$E_G = E_b + E\ int.ref. + Eassy.$$

$$E_G = L-0.0591P^H + E_{int.ref.} + E_{ass}$$

$$E_G = E^0_G - 0.0591pH$$

Where $E^0{}_{G} = L + E_{int.ref.} + E_{assy} =$ contant

Advantages of glass electrode;

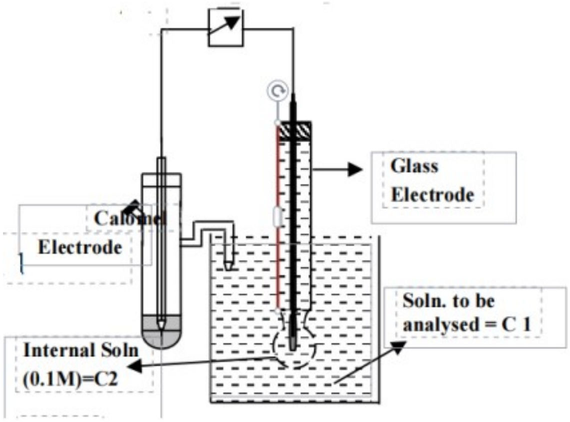
1) It is simple and easy to construct
2) It can be used in oxidizing and reducing solution
3) It does not get poisoned
4) Results are accurate
5) Can be used in colour and turbid solution

Limitations;

1) Due to high resistance of the glass, ordinary potentiometer and voltmeter cannot be worked out. Hence, electronic devices ate required, which are costly.
2) It does not function properly in pure alcohol and some organic solvents.
3) Accuracy can achieve between th pH 1-9. If pH > 9 alkaline error occur due to Na^+ and pH < 1 , the salt effect due to anions are observed.

Determination of pH of a given solution using glass electrode:

In order to determine the pH of a given solution, the glass electrode is immersed in it and this half-cell is coupled with another half-cell such as calomel electrode through salt bridge as shown in fig.



<u>Cell representation</u>;

Calomel electrode// Solu. of unknown pH / glass/ HCl (0.1N)/ AgCl/Ag

Calculation:

$$Ecell = E_R - E_L$$

$$Ecell = E_G - E_{Cal}$$

Where $E_G = E^o_G - 0.0591pH$

$$E_{cell} = [E^o_G - 0.0591pH] - E_{cal}$$

$$E_{cell} = E^o_G - 0.0591pH - E_{cal}$$

$$\boxed{pH = \frac{E^o_G - E_{cell} - E_{cal}}{0.0591}}$$

Determination of e.m.f of the cell: The e.m.f of the cell is determined using VTVM (vacuum tube volt meter).

Determination of E^o_G of the cell: For the determination of E^o_G, the e.m. f of the cell is determine by taking a buffer solution in place of analytic solution as follows.

$$E^o_G = E_G + 0.0591p$$

Where E_G = Ecell+Ecal

Concentration Cells:

Definition: *Concentration cells are electrochemical cells in which the emf is arises due to the difference in the concentration of electrolyte around the electrodes.*

Concentration cells may consist of same electrodes and same electrolytes but the concentration electrolytes around the electrodes or concentration of electrodes are different.

Depends on the concentration difference between electrodes and electrolyte, concentration cells are classified as

1. Electrode concentration cells
2. Electrolyte concentration cells

Electrolyte concentration cells

These cells consist of two same electrodes dipping in the same electrolyte solution but the concentration of electrolyte around the electrode are different.

Examples; $Ag/ AgNO_3 \overrightarrow{(C_1M)} // AgNO_3 (C_2) M / Ag \quad C_2 > C_1$

2. Describe the construction and working of concentration cells with suitable examples.

example $Cu/CuSO_4\ (C_1M) \overrightarrow{//\ CuSO_4}\ (C_2\ M) / Cu$

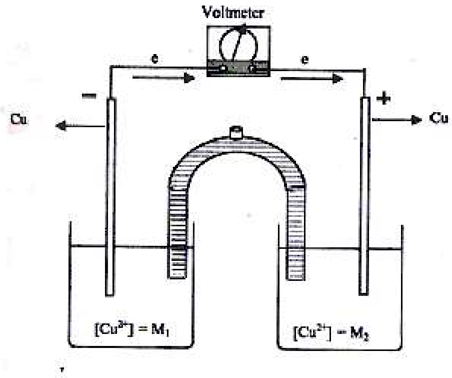


Fig.2.3.Concentration cell

The cell consisting of two electrodes of same metal (Cu) dipped in same electrolyte ($CuSO_4$) but the concentrations of electrolyte around the electrodes are different.

The solution –solution contact is given by dipping a salt bridge as shown in figure.

The following cell reaction takes place.

$$Cu \longrightarrow Cu^{2+}(C1M) + 2e^-$$

$$\underline{Cu^{2+}(C2M) + 2e^- \longrightarrow} \quad Cu$$

$$Cu^{2+}(C2M) \longrightarrow Cu^{2+}(C1M)$$

The e.m.f of such cell can be calculated as follows;

$E\ cell = E_R - E_L$

$$[E^o + \frac{0.0591}{n} \log C_2] - [E^o + \frac{0.0591}{n} \log C_1]$$

$$E^o + \frac{0.0591}{n}\log C_2 \;-\; E^o - \frac{0.0591}{n}\log C_2$$

$$\boxed{E_{cell} = \frac{0.0591}{n}\log [C_2/C_1]}$$

Examples; 2 Zn/ $ZnSO_4$ (C_1M) $\overset{\longrightarrow}{//}$ $ZnSO_4$ (C_2 M) / Zn

Examples; 3 Ag / $AgNO_3$ (C_1M) $\overset{\longrightarrow}{//}$ $AgNO_3$ (C_2 M) / Ag

Numerical problems based on concentration cell

The following equations

1. For concentration cell

$$E_{cell} = \frac{2.303RT}{nF}\log [C_2/C_1]$$ if T is >< 25°C or 298°K

$$E_{cell} = \frac{0.0591}{n}\log [C_2/C_1]$$ if T is = 25°C or 298°K

1. A concentration cell was constructed by immersing two silver electrodes in 0.01M & 10M AgNO3 solution. Calculate e.m.f of the cell.

Solution:

Concentration of AgNO3 at anode [M1] = 0.01M

Concentration of AgNO3 at Cathode [M2] = 10 M

Number of moles of electrons (n) =1

$$E_{cell} = \frac{0.0591}{n}\log\frac{[M2]}{[M1]}$$

$$E_{cell} = \frac{0.0591}{1}\log\frac{[10M]}{[0.01]}$$

Ecell = **0.1773V**

2. Calculate e.m.f. of the cell at 298K,

$Cd(s)/Cd^{2+}(aqs)(0.01M)\overset{\longrightarrow}{//}Cd^{2+}(aqs)(0.1M)/Cd(s)$

$$E_{cell} = \frac{0.0591}{n}\log\frac{[M2]}{[M1]}$$

$$E_{cell} = \frac{0.0591}{1}\log\frac{[0.1M]}{[0.01]}$$

Ecell = **0.02955V**

3. **C**alculate the e.m.f of the cell, $Cu(s) / Cu^{2+}(aqs)$ (0.072M) // $Cu^{2+}(aqs)$ (0.32M) /Cu

Ans.Ecell= 0.01914V

The e.m.f. of the cell is positive i.e. +0.1914 Volts hence the cell reactions are spontaneous.

4. Calculate the e.m.f of the following concentration cell at 298K.

$Ag(s)/Ag^{+}(aqs)(0.01M)//Ag^{+}(aqs)(0.5M)/Ag(s)$

Ecell =0.1004V

5.0 $Zn(s)/Zn^{2+}(aqs)(0.024M)//Zn^{2+}(aqs)(0.048M)/Zn(s)$

Calculate the emf at 27^0C

$$E_{cell} = \frac{2.303xRT}{nF}\log\frac{[0.048]}{[0.024]}$$

$$E_{cell} = \frac{2.303x8.314x300}{2x96500}\log[2]$$

$E_{cell} =$ 0.008958V

6.0 The following concentration cell at 25^0 C consisting of Zinc electrode immersed in a Solution of zinc ions of1.5 molar and 0.01molar concentrations.Write the cell scheme, cell reactions & calculate e.m.f of the cell.
Solution:

Concentration of Zn^{2+} ions at anode [M1] = 0.01M

Concentration of Zn^{2+} ions at Cathode [M2] = 1.5 M

Number of moles of electrons (n) =2

Cell scheme: →
$Zn(s) / Zn^{2+} (aqs) (0.01M) // Zn^{2+} (aqs) (1.5M) /Zn(s)$

Cell Reactions:

At Anode, $Zn \rightarrow Zn^{2+}(0.01M)+2e^-$

At Cathode, $Zn^{2+}{}_{(1.5M)}+2e^- \rightarrow +\ Zn (s)$ -Reduction

$Zn^{2+}{}_{(1.5M)} \rightarrow Zn^{2+}(0.01)$

$$E_{cell}= \frac{0.0591}{n} \log\frac{[M2]}{[M1]}$$

$$E_{cell}= \frac{0.0591}{2} \log\frac{[1.5M]}{[0.01]}$$

Ecell = 0.0643V

7.0 The cell potential of concentration cell
$Ag(s)/AgNO3(aqs)(0.002)//AgNO3(aqs)(XM)/Ag(s)$
is 0.0751 V at 25 °C. Write the cell reactions and calculate the value of X.
Solution:

Concentration of Ag^+ ions at anode [M1] = 0.002

Concentration of Ag^+ ions at Cathode [M2] = X M

Cell potential of Ag concentration cell, Ecell = 0.0751 V

At Anode, $Ag \rightarrow Ag^+{}_{(0.002)}+e^-$

At cathode, $Ag+_{(XM)}+e^- \rightarrow Ag$

$Ag^+(XM) \rightarrow Ag^+(0.002)$

$$E_{cell}= \frac{0.0591}{n} \log\frac{[M2]}{[M1]}$$

$$E_{cell}= \frac{0.0591}{1} \log\frac{[XM]}{[0.002]}$$

$$\boldsymbol{0.0751 = 0.0591}\log\frac{[XM]}{[0.002]}$$

$$\frac{[X]}{[0.002]} = \text{Antilog} \frac{[0.0751]}{[0.0591]} = 18.652$$

Module 3, Analytical Techniques

1.Briefly explain the principle,instrumentation and working of potentiometry.

POTENTIOMETRY: The measurement of e.m.f. (electromotive force) to determine the concentration of ionic species in solution is referred to as potentiometry.

THEORY: According to nerst equation

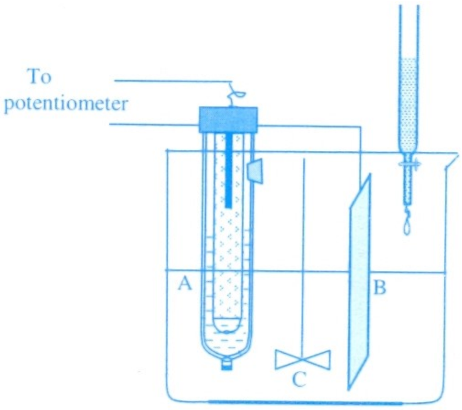
$$E = E^o + \frac{0.0591}{n} \log[M^{n+}]$$

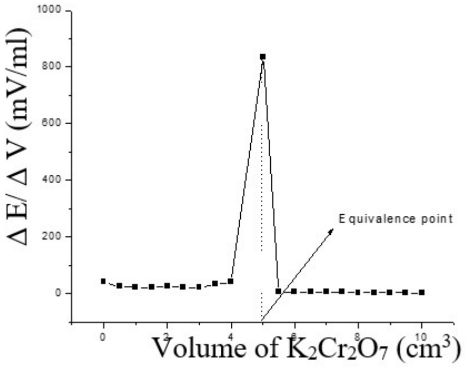
$$E=E^o + \frac{0.0591}{n} \log \frac{[\text{oxidise species}]}{[\text{reduced species}]}$$

$$E = E^o + \frac{0.0591}{n} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

Beyond the equivalence point the ratio shifted to $Cr_2O_7^{2-}$ /Cr^{3+} Thus, an abrupt increase in the potential of the solution in the vicinity of the equivalence point is observed.

INSTRUMENTATION: A simple arrangement of potentiomertic titration is as shown in fig.





A Potentiometer consists of a reference electrode, an indicator electrode and a device for measuring the Potential.

Experiment: A known volume of the analyte (FAS) is taken in a beaker and its potential is determined by using the above setup. The titrant $K_2Cr_2O_7$ is added about 0.5cc in each time and corresponding potential is recorded.Near the equivalence point there is sharp rise in potential. The end point is determined by plotting $V_{K2Cr2O7}$ >< $\frac{\Delta E}{\Delta V}$

Volume of $K_2Cr_2O_7$ in Cm^3	E in Volts	ΔE	ΔV	$\frac{\Delta E}{\Delta V}$
0.0				
0.5				
1.0				

$(N_1V_1)_{Fe\ solu.} = (N_2V_2)_{K2Cr2O7}$

$N1 = \frac{N_2V_2}{V_1}$

Amount of FAS = $N1 \times$ Eq. Wt. of Fe--------g/dm^3

2.Briefly explain the principle,instrumentation and working of Coductometry.

Theory: The principle involve the measurement of change in specific conductance during the course of chemical reactions

$$K = \frac{1}{R} x \frac{l}{a}$$

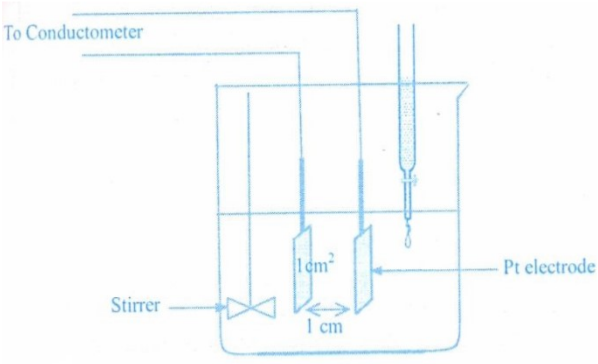
Where l/a is constant known as cell constant and R is resistance of conductor. Specific conductance of solution is based on

1. Concentration/ number ions in solution

2. Mobility of the ions in solution

3. During a chemical reaction there will be change in specific conductance of solution due to replacement of one type of ions with other type. Measurement of this change is the basis of conductometry

INSTUMENTATION: The conductometr consisting of conductivity cell and a device to measurespecific conductance of solution

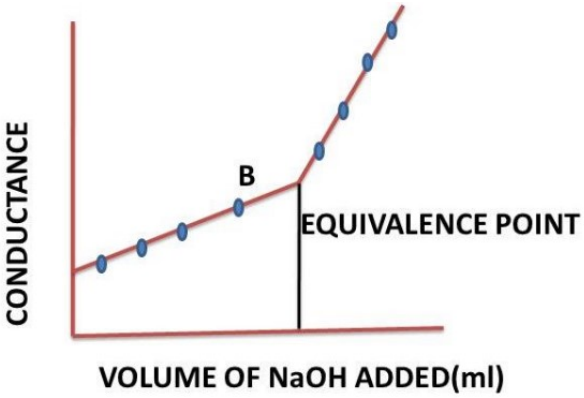


Conductometric titration unit

Experimental: A known volume of analyte solution (HA) is taken in beaker in a beaker and measure the specific conductance by using above setup.Add 0.5 cc of NaOH for each time and record the specific conductance.Initially specific conductance is decreases and suddenly increases at the equivalence point is recorded.End point is determine by plotting the graph V_{NaOH} ><K

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Vol. NaOH added in cc	Conductance Ohm^{-1}Cm^{-1}
0.0	
0.5	
1.0	
1.5	



$(N_1V_1)_{NaOH} = (N_2V_2)_{CH3COOH}$

$N_2 = \frac{N_1V_1}{V_2}$

Amount of CH_3COOH = N_2 x Eq. Wt. of CH_3COOH

N_2 x 60---------g

Mdule-4, Polymers and Green Fuel

Polymers: Introduction, Molecular weight - Number average,weight average and numerical problems.

Conducting polymers – Synthesis and conducting mechanism of poly-acetylene and commercial applications

Preparation, properties, and commercial applications of Kevlar

Green Fuels:

Green Fuels: Introduction to different types of fuels, past and future perspective of green fuels. construction and working of solar photovoltaic cell, advantages, and disadvantages, Green hydrogen: Introduction to properties of hydrogen pertaining to fuel. Introduction to electrolysis of water.green hydrogen: Introduction to properties of hydrogen pertaining to fuel. Introduction to electrolysis of water.

Generation of hydrogen by electrolysis of water: Alkaline water electrolysis (Explain the electrolysis of water with diagram and electrode reactions) and mention any 4 advantages.

Electrolysis of water – Proton Exchange Membrane Electrolysis (Explain the electrolysis of water with diagram and electrode reactions) and mention any 4 advantages

1

POLYMERS

A polymer is a material of high molecular weight obtained by the covalent linkage of several small repeating chemical units called monomers.

e.g.: $n\,CH_2 = CH_2 \longrightarrow -(CH_2 - CH_2 - CH_2 - CH_2)-_n$

Ethylene (Monomer) Polyethylene (Polymer)

Monomers: they are the simplest molecules, combine with each other to form a long chain compounds with high molecular weight known as polymers.

The number of monomers in a polymeric chain indicates its **degree of Polymerization**

The properties of polymer are totally different to that of monomer, although the basic composition is same. Polymers have very high molecular weight ranging from 10^3 to 10^7.

Polymerisation: -

"Polymerisation is a process of converting monomer of low molecular weight into polymer of high molecular weight."

$n\,CH_2 = CH_2 \longrightarrow (-CH_2 - CH_2 - CH_2 - CH_2 -)_n$

Ethylene (Monomer) Polyethylene (Polymer)

Molecular Mass of Polymers

Molecular mass of polymer is very important parameter, directly related to its physical properties such as softening temperature, tensile strength, impact strength and glass transition temperature. In a polymer block the polymer chains will have different chain length due to varying degree of polymerization. It is very difficult to express molecular mass of a polymer due to varying chain length and each polymer will have different molecular mass. Therefore, molecular mass of polymers is expressed in two different ways i.e.

1. **Number average molecular mass.**
2. **Weight average molecular mass.**

1. Number average molecular mass($\overline{Mn}$):

Number average molecular mass is sum of total mass of all the molecules (NM) divided by the total number of molecules (N).

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \dots\dots\dots\dots\dots\dots\dots.}{N_1 + N_2 + N_3 \dots\dots\dots\dots\dots\dots\dots..}$$

Where, N_1, N_2, N_2……are number of molecules having molecular mass M1, M_2, M_3………

N_1M_1, N_2M_2, N_3M_3……are Total mass of N_1, N_2, N_3---------- molecules.

$$\overline{M}_n = \sum \frac{N_iM_i}{N_i}$$

2.Weight average molecular mass ($\overline{M}_W$)

Weight average molecular mass is sum of product of total weight (W) and molecular mass (M) all the molecules divided by the total weightof all the molecules (NM).

$$\overline{M}_w = \frac{W_1M_1 + W_2M_2 + W_3M_3 + \dots\dots\dots\dots\dots\dots\dots.}{W_1 + W_2 + W_3 \dots\dots\dots\dots\dots\dots\dots..}$$

Where,

$$\overline{M}_w = \frac{N_1M_1 \times M_1 + N_2M_2 \times M_2 + N_3M_3 \times M_3 + \dots\dots\dots\dots\dots\dots\dots.}{N_1M_1 + N_2M_2 + N_3M_3 + \dots\dots\dots\dots\dots\dots\dots.}$$

W1, W2, W2……are weight of molecular and W = N1 M1, N2M2, N3 M3……are Molecular mass of molecules.

$$\overline{M}_W = \sum \frac{N_iM_i^2}{N_iM_i}$$

Numerical problems on polymers

1. In sample of a polymer, 100 molecules have molecular mass 1000 g/mol, 200 molecules have molecular mass 10,000 g/mol and 300 molecules have molecular mass 20,000 g/mol. Calculate number average ($\overline{M}_n$) and weight averagemolecular mass ($\overline{M}_W$) of polymer sample.

Solution:

N1=100,

M1=1000g/mol.
N2=200,

M2=10,000g/mol.
N3=300,

M3 =20,000g/mol.

Number average molecular mass

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

$$\overline{M}_n = \frac{100 \times 1000 + 200 \times 10,000 + 300 \times 20,000}{100 + 200 + 300}$$

$\overline{M}_n$**= 13,500 g/mol.**

Weight average molecular mass

$$\overline{M}_W = \sum \frac{N_i M_i^2}{N_i M_i}$$

$$\overline{M}_W = \frac{100 \times (1000)^2 + 200 \times (10,000)^2 + 300 \times (20,000)^2}{100 \times 1000 + 200 \times 10,000 + 300 \times 20,000}$$

$\overline{M}_W$**= 14,839.5g/mol.**

2.In sample of a polymer, 25% molecules have molecular mass 12000 g/mol, 30% molecules have molecular mass 25,000 g/mol and 45% molecules have molecular mass 35,000 g/mol. Calculate number average ($\overline{M}_n$) and weight average molecular mass ($\overline{M}_W$) of polymer sample.

N1=25, M1 =12000 g/mol.

$N2=30$, $M2 = 25,000$ g/mol.

$N3=45$, $M3 = 35,000$ g/mol.

Number average molecular mass

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

$$\overline{M}_n = \frac{25 \times 12000 + 30 \times 25,000 + 45 \times 35,000}{25 + 30 + 45}$$

$\overline{M}_n$ **= 26,250 g/mol.**

Weight average molecular mass

$$\overline{M}_W = \sum \frac{N_i M_i^2}{N_i M_i}$$

$$\overline{M}_W = \frac{25 \times (12000)^2 + 30 \times (25,000)^2 + 45 \times (35,000)^2}{25 \times 12000 + 30 \times 25,000 + 45 \times 35,000}$$

$\overline{M}_W$ **= 29512.38g/mol**

3.A polymer polyethylene is having the following composition. Calculate number average ($\overline{M}_n$) and weight average molecularmass ($\overline{M}_W$) of poly ethylene sample. Given atomic mass of C=12 and H=1.

$-(CH_2 - CH_2)-_{200}$ -- 15%

$-(CH_2 - CH_2)-_{400}$ -- 35%

$-(CH_2 - CH_2)-_{600}$ -- 50%

Solution:

N1=15, N2=35, and N3=50.

M1=[(atomic mass of Carbon x Number of carbon atoms) +(atomic mass of Hydrogen x Number of Hydrogen atoms)] x 200]

M1 =[(12X2)+(1X4)] X 200 = 5,600 g/mol.

M2 =[(12X2)+(1X4)] X 400 = 11,200 g/mol.

M3 =[(12X2)+(1X4)] X 600 = 16,800 g/mol

Number average molecular mass

$$\overline{\mathbf{M}}_{\mathbf{n}} = \sum \frac{\mathbf{N}_i \mathbf{M}_i}{\mathbf{N}_i}$$

$$\overline{\mathbf{M}}_{\mathbf{n}} = \frac{15 \times 5{,}600 + 35 \times 11{,}200 + 50 \times 16{,}800}{15 + 35 + 50}$$

$\mathbf{M}_{\mathbf{n}}$ **= 13,160 g/mol.**

Weight average molecular mass

$$\overline{\mathbf{M}}_{\mathbf{W}} = \sum \frac{\mathbf{N}_i \mathbf{M}_i^2}{\mathbf{N}_i \mathbf{M}_i}$$

$$\overline{\mathbf{M}}_{\mathbf{W}} = \frac{15 \times (5{,}600)^2 + 35 \times (11{,}200)^2 + 50 \times (16{,}800)^2}{15 \times 5{,}600 + 35 \times 11{,}200 + 50 \times 16{,}800}$$

$\overline{\mathbf{M}}_{\mathbf{W}}$**= 14,417.02g/mol.**

5.Calculate the number average ($\overline{\mathbf{M}}_{\mathbf{n}}$) and weight average molecular mass ($\mathbf{M}_{\mathbf{W}}$)of a polymer with the following composition. Given atomic weight ofC=12, Atomic weight of H=1 and Atomic weight of Cl =35.5.

--[--CH2-CH Cl --]200 is 40 %;
--[--CH2-CH Cl --]400 is 30 % ;
--[--CH2-CH Cl --]500 is 30% .

Solution

N1=40, N2=30, and N3=30.

M1=[(atomic mass of Carbon x Number of carbon atoms) +(atomicmass of Hydrogen x Number of Hydrogen atoms)+ (atomic mass of Chloride x Number of Chloride atoms]x 200

M1 = [(12x2)+(1x3)+(35.5x 1)] x 200 = 12,500 g/mol.
M2 = [(12x2)+(1x3)+(35.5x 1)] X 400 = 25,000 g/mol.
M3 = [(12x2)+(1x3)+(35.5x 1)] X 500 = 31,250 g/mol.

Number average molecular mass

$$\overline{\mathbf{M}}_{\mathbf{n}} = \sum \frac{\mathbf{N}_i \mathbf{M}_i}{\mathbf{N}_i}$$

$$\overline{\mathbf{M}}_{\mathbf{n}} = \frac{40 \times 12{,}500 + 30 \times 25{,}000 + 30 \times 31{,}250}{40 + 30 + 30}$$

M_n= 21,875 g/mol

Weight average molecular mass

$$\overline{\mathbf{M}}_{\mathbf{W}} = \sum \frac{\mathbf{N}_i \mathbf{M}_i^2}{\mathbf{N}_i \mathbf{M}_i}$$

$$\overline{\mathbf{M}}_{\mathbf{W}} = \frac{40 \times (12{,}500)^2 + 30 \times (25{,}000)^2 + 30 \times (31{,}250)^2}{40 \times 12{,}500 + 30 \times 25{,}000 + 30 \times 31{,}250}$$

$\overline{M}_W$= 24685.7.45g/mol.

6.A polymer sample contain 5 molecules having a molecular weight of 2000, 4 molecules having a molecular weight of 3000 and 3 molecules having a molecular weight of 4000. Calculate number average ($\overline{M}_n$) andweight average molecular mass (M_W).

Solution:

N1=5,	**M1 =2000g/mol.**
N2=4,	**M2 =3,000g/mol.**
N3=3,	**M3 =4,000g/mol.**

Number average molecular mass

$$\overline{\mathbf{M}}_{\mathbf{n}} = \sum \frac{\mathbf{N}_i \mathbf{M}_i}{\mathbf{N}_i}$$

$$\overline{\mathbf{M}}_{\mathbf{n}} = \frac{5 \times 2000 + 4 \times 3{,}000 + 3 \times 4{,}000}{5 + 4 + 3}$$

$\mathbf{M}_{\mathbf{n}}$**= 2,833.3 g/mol.**

Weight average molecular mass

$$\overline{\mathbf{M}}_{\mathbf{W}} = \sum \frac{\mathbf{N}_i \mathbf{M}_i^2}{\mathbf{N}_i \mathbf{M}_i}$$

$$\overline{\mathbf{M}}_{\mathbf{W}} = \frac{5 \times (2000)^2 + 4 \times (3{,}000)^2 + 3 \times (4{,}000)^2}{5 \times 2000 + 4 \times 3{,}000 + 3 \times 4{,}000}$$

$\overline{\mathbf{M}}_{\mathbf{W}}$**= 3058.82g/mol.**

7.A polymer sample contains 2, 3 and 4 molecules having molecular weight $2\text{x}10^3$, $3\text{x}10^3$ and $4\text{x}10^3$ respectively. Calculate the number average ($\mathbf{M}_{\mathbf{n}}$) and weight average molecular mass ($\overline{\mathbf{M}}_{\mathbf{W}}$) of polymer.

Solution:

N1=2, M1 =$2\text{x}10^3$ =2000 g/mol.

N2=3, M2 =$3\text{x}10^3$=3000 g/mol.

N3=4, M3 =$4\text{x}10^3$ =4000g/mol.

Number average molecular mass

$$\overline{\mathbf{M}}_{\mathbf{n}} = \sum \frac{\mathbf{N}_i \mathbf{M}_i}{\mathbf{N}_i}$$

$$\overline{\mathbf{M}}_{\mathbf{n}} = \frac{2 \times 2000 + 3 \times 3{,}000 + 4 \times 4{,}000}{2 + 3 + 4}$$

$\overline{\mathbf{M}}_{\mathbf{n}}$**= 3,222.22 g/mol.**

Weight average molecular mass

$$\overline{M}_W = \sum \frac{N_i M_i^2}{N_i M_i}$$

$$\overline{M}_W = \frac{2 \times (2000)^2 + 3 \times (3{,}000)^2 + 4 \times (4{,}000)^2}{2 \times 2000 + 3 \times 3{,}000 + 4 \times 4{,}000}$$

$\overline{M}_W$ **= 3,413.79g/mol.**

8.A polymer sample contains 1,2,3 and 4 molecules having molecular weights 1x 10^5, 2x10^5 , 3x10^5 and 4x10^5 respectively. Calculate the number average ($\overline{M}_n$) and weight average molecular mass (M_W) of the polymer.

Solution:

N_1=1, M_1 =2x10^5 =2,00,000 g/mol.
N_2=2, M_2 =3x10^5=3,00,000g/mol.
N_3=3, M_3=1x10^5 =1,00,000g/mol.
N_4=4, M_3 =4x10^5 =4,00,000g/mol.

Number average molecular mass.

$$\overline{M}_n = \frac{1 \text{ x } 1{,}00{,}000 + 2 \times 2{,}00{,}000 + 3 \times 3{,}00{,}000 + 4 \times 4{,}00{,}000}{1 + 2 + 3 + 4}$$

$\overline{M}_n$ **= 3,00,000 g/mol.**

Weight average molecular mass

$$\overline{M}_W = \sum \frac{N_i M_i^2}{N_i M_i}$$

$$\overline{M}_W = \frac{1 \times (1{,}00{,}000)^2 + 2 \times (2{,}00{,}000)^2 + 3 \times (3{,}00{,}000)^2 + 4 \times (4{,}00{,}000)^2}{1 \text{ x } 1{,}00{,}000 + 2 \times 2{,}00{,}000 + 3 \times 3{,}00{,}000 + 4 \times 4{,}00{,}000}$$

$\overline{M}_W$ **= 3,33,333.3 g/mol.**

Conducting Polymers

An organic polymer with highly delocalized pi-electron system having electric conductivity in the order of a conductor is called as conducting polymers.

Examples: **Polyacetylene, Polypyrrole, Polyaniline, etc.**

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

(i) Linear structure with rigid chain

(ii) Alternative single and double bond with highly delocalized Pi electrons throughout the polymer chain.

Conducting polymers have been classified into two types

1. Extrinsically Conducting Polymers

2. Intrinsically Conducting Polymers

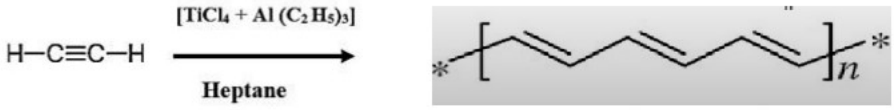
1. Extrinsically Conducting Polymers: They are prepared by mixing conducting fillers like metal fibres, metal oxides or carbon black with insulating polymers.

2. Intrinsically Conducting Polymers: In these types of polymers, conductivity is due to the organic polymers themselves. They conduct electricity when doped with oxidizing or reducing agents.

Synthesis of Polyacetylene (1977 Shirakowa)

The first conducting polymer synthesized was polyacetylene. The polyacetylene is synthesized by passing Acetylene gas through heptane solution in presence of Ziegler-Natta Catalyst [$TiCl_4$+ Al ($C_2H_5)_3$].

Mechanism of Conduction of polyacetylene



Polyacetylene can be converted into a conducting polymer by doping it with electron donor or electron acceptor dopants.

CONDUCTING MECHANISM OF POLYACETYLENE

REDUCTIVE DOPING (n- type doping).

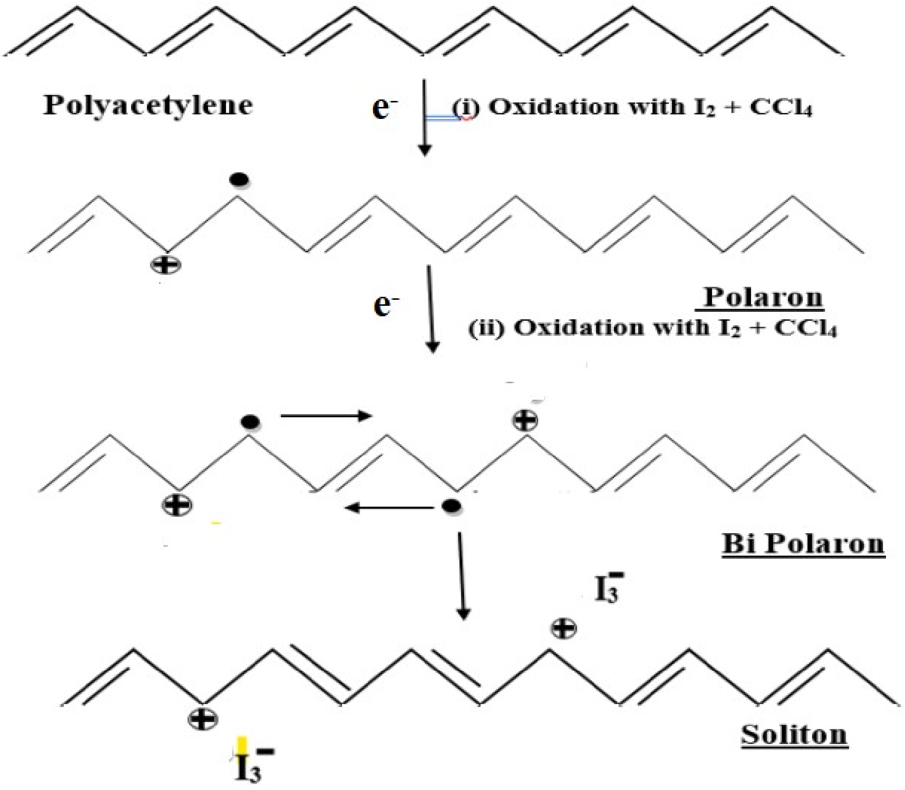
Poly acetylene chain is doped with reducing agent such assodium or Lithium naphthalides. Reducing agent supplies electrons to pi back bone of the chain Thus polymer becomes n type conductor.

OXIDATIVE DOPING (P -type of doping).

In this process pi-back bone of poly acetylene polymer is partially oxidized using suitable oxidizing agent such as I_2, CCl_4, $AlCl_4$, HBF_4 etc. The oxidizing agent take away electrons from polymer back bone of the chain creating hole. hence the polymer becomes P-type semiconductor.

Removal of electron from Pi backbone system creates positively charged radical ion or Polaron.

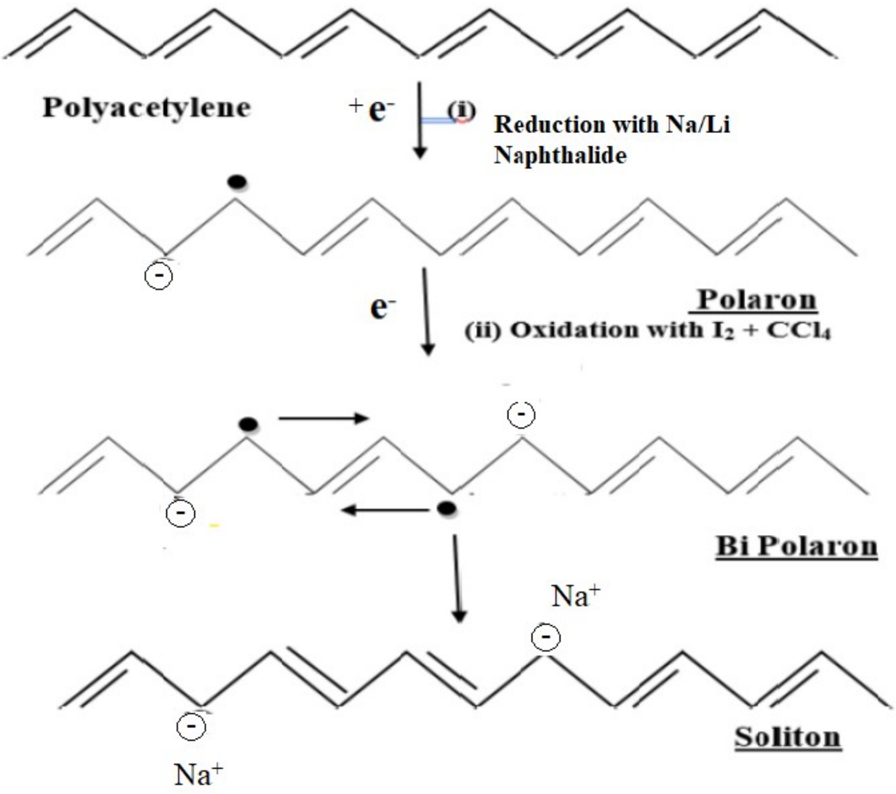
The polaron further oxidised and holes are induced on polymer chain generating positively charged Bi-polaron. The recombination of free radicals will occur to from a conducting polyacetylene (Soliton).



OR

REDUTIVE DOPING (n -type of doping).

Poly acetylene chain is doped with reducing agent such assodium or Lithium naphthalides. Reducing agent supplies electrons to pi back bone of the chain Thus polymer becomes n type conductor.



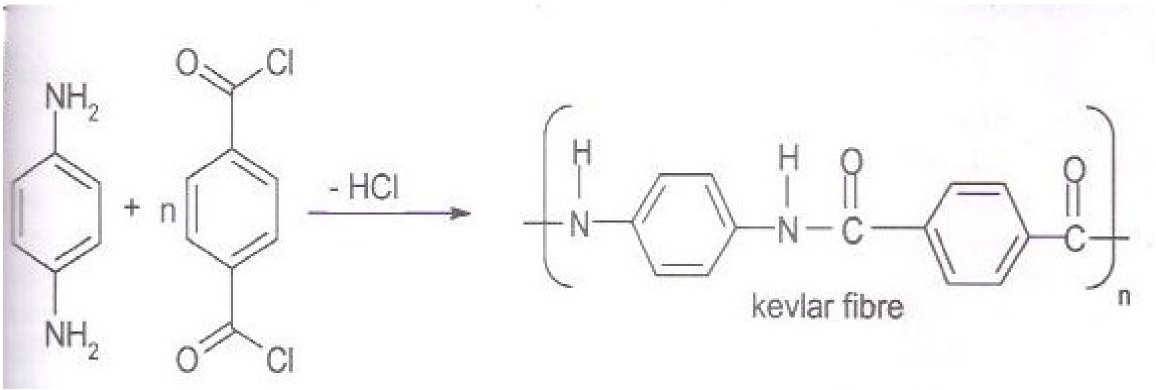
Properties & Applications of Conducting Polymers:

Properties.	**Applications.**
1. Conducting polymers have high melting and softening temperature. 2. Due to low hydrogen contents shows excellent chemical, thermal and oxidative stability 3. They are insoluble in many organic solvents 4.	1. Used in manufacture of chemical sensors,corrosion inhibitors,electromagnetic shielding etc . 2. Also used in compact electronic devices such as transistors, LED, lasers 3. They als used as radar absorptive coating on air craft, in the manufacture of PCB etc.

Kevlar

It is an aromatic poly amide with the name poly para-phenylene terepthamide. It is prepared by condensation of para-phenylene diamine and terepthaloyl chloride.“

Synthesis of Kevlar: It is synthesized by condensation Polymerisation of Terphthaloyl chloride and1, 4 phenylene-diamine with elimination of hydrochloric acid.



Properties.	**Applications.**
1. Kevlar has high tensile strength, high abrasion resistance.	1. Used in manufacture of lightweight boats.
2. It is light weight.	2. Manufacture of Bullet-proof vests, body armors, Aircraft panels.
3. It is very strong.	3. Puncture resistant tyres.
4. It is chemical and heat resistant.	4. Manufacture of helmets.

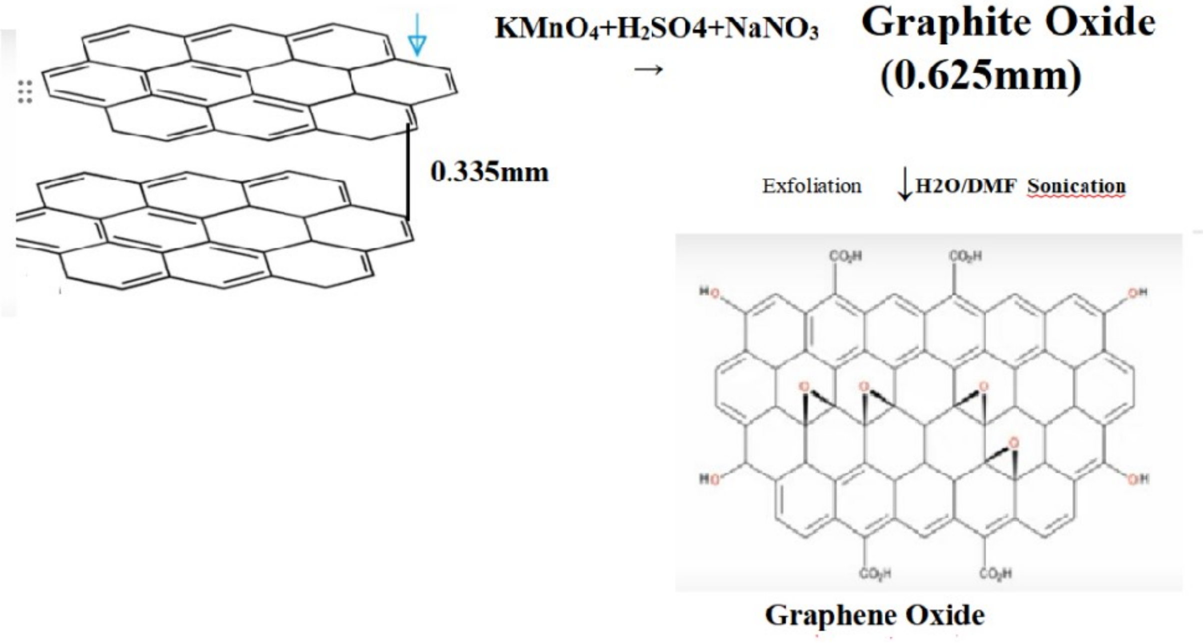
Preparation properties and commercial applications of Graphene Oxide

A single sheet of carbon atom separated from the graphite is called Graphene. It is two dimensional nanosheet with thickness equal to single carbon atom, When oxygen containing functional groups like epoxide, -COOH, -OH etc is added to to the Graphene layer the resultant material is Graphene oxide.

Graphene oxide is obtained from cheap and most abundant material known as graphite by controlled oxidation by Hummers Method .

Graphite is subjected to reaction with anhydrous mixture of con. H_2SO_4 +$KMnO_4$+$NaNO_3$. Oxidation reaction is completed within 2hrs. at less than 20°C. Hydrolysis of graphite oxide in the presence of polar solvent dimethylformamide (DMF) and sonication results in complete exfoliation in water, yielding individual graphene oxide sheets.

Graphite → Graphitic Oxide → Graphene Oxide (GO)



Properties.	**Applications.**
1. Good Charge mobility 2. High thermal and electric conductivity 3. High surface area 4. Bio-compatibility and lower cytotoxicity 5. High young's modulus and tensile strength	1. It is used in manufacture of Energy storage devices, LED. Optical switching and communication, Transparent electrodes, photo-detector etc 2. In the manufacture of cost effective water purifier 3. In sensors and biosensors 4. Due to compatibility can be used in transplant and implant medical devices

Green Fuels

Green fuels are carbon-neutral or carbon-free fuels obtained from renewable sources such as sun light. Wind, water, Biomass, Biogas etc.

Green fuel provides real benefits for the environment and best alternate if the fissile fuels get exhaust.

Advantages of green fuel:

- using green fuels, the emission green house gasses can be successfully to 30% of the combustion rate.
- Green fuels are most economical renewable energy sources and best alternate to fossil fuel.
- The use of Green energy sources is a long term option to reduce CO_2 emissions worldwide.
- Green fuels are environment friendly because the power comes from natural resources and renewable
- Green fuels responsible for producing more energy hence it is referred to as “energy bounce”

Different types Green Fuels,

1. Solar Power
2. Wind Power
3. Hydropower
4. Biomass
5. Biofuels

SOLAR ENERGY

Radiation from the sun constitute solar energy .It is freely available and inexhaustible energy source. The sun radiating the energy in the order of $20x10^{20}$KJ/year. This energy almost 10000 times more than actual requirements.

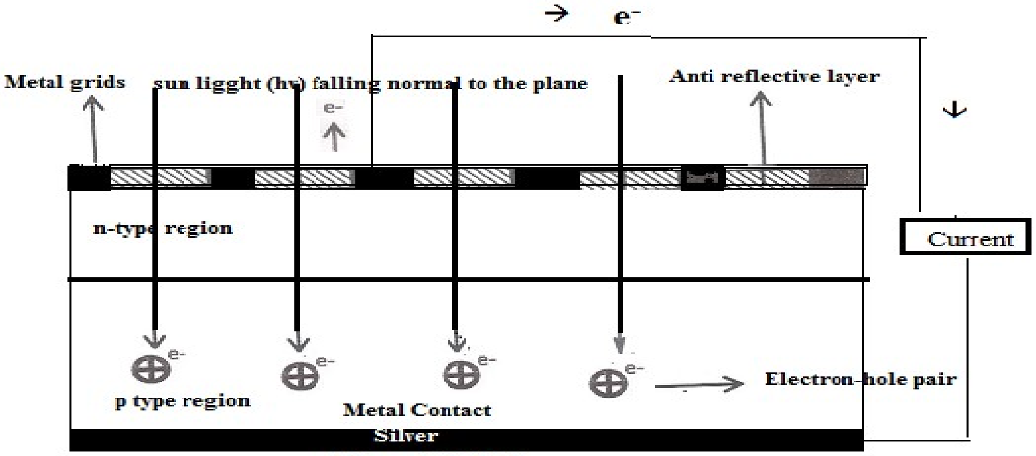
Solar energy is used for many solar appliances such as solar water heater, solar cooker, solar vegetable drier, solar power generator, distillation plants, and solar cells.

Photovoltaic cells are the semiconductor devices that convert solar energy directly into electric current current. A photo cell works on the following functions

1] Photo generation of charge carries [+ve and -ve] in a light absorbing material.

2] Separation of charges by a potential gradient (p-n junction) within the mate

Construction and working of photovoltaic cell:



Photovoltaic Cell

A typical silicon PV cell mainly consists of a p-n junction diode made from Si semiconductor. It has two electric contacts; one is metallic grid over n-type and second is a layer of silver metal at the back of p-type semiconductor. An antireflective layer is coated in between the metal grids to prevent reflection of solar light.

When light radiation falls on the p-n junction diode, electron-hole pairs are generated by the absorption of the radiation. The electrons are drifted to n-type end and the holes are drifted to p-type side. When these two ends are electrically connected through a conductor, there is flow of current between the two ends through the external circuit. Thus photoelectric current is produced.

Advantages of photo voltaic cell

1. Photo voltaic cells generate solar power relatively with low pollution and are environmental friendly.
2. Photo voltaic cell generates solar power at low cost and is more economical.
3. Photo voltaic cells require less maintenance.
4. Since conventional energy resources are fast depleting; photo voltaic cells are considered to be the future sustainable energy source.
5. The photovoltaic solar power contributes in controlling the man made global warming due to CO2.

Disadvantages of photo voltaic cell

1. Photovoltaic cells are expensive to install.
2. Photovoltaic cells work only in presence of sunlight.
3. The photovoltaic cells produce only DC voltage.
4. They occupy larger space and often dust accumulates over panels reducing the efficiency

Applications

PV can meet the need for electricity for parking meters, temporary traffic signs, emergency phones, radio transmitters, water irrigation pumps, lighting for

Roadways and many more applications

Green Hydrogen

The hydrogen is found to be promising green fuel that can be produced from green routes with zero or low contribution to the environmental pollution.

Properties and Advatages of Hydrogen Pertaining to Fuel:

1. The Hydrogen is a lightest element, tasteless, odourless, colourless gas with low density and solubility.

2. Hydrogen is highly flammable hence it takes a small amount of energy to ignite.

4. On burning hydrogen, it emits only water vapour and does not produce carbon dioxide, and is considered zero pollutant / zero emissions.

5. It has the ability to run a fuel-cell engine when compared to an internal combustion engine.

6. The amount of energy liberated during the combustion of hydrogen, is about 2.5 times greater than hydrocarbon fuels.

7. Since hydrogen produces extraordinary amounts of energy, it is used as fuel to run automobile vehicles, rockets and generation of electricity in fuel with zero emissions.

Disadvantages of Hydrogen as Fuels

- Production Hydrogen is a costly affair
- Hydrogen is less soluble and less dense, hence compressing hydrogen gas into liquids is very difficult
- It is a odourless and highly inflammable gas,hence it is very dangerous is accident occurs.

Generation of energy (green hydrogen) by electrolysis of water

The process of decomposing water (H_2O) into hydrogen (H^+) and hydroxide (OH^-) ions by passing an electric current is known aselectrolysis.

The electrolysis can be carried by passing current through two platinum electrodes dipped in water, which acts as anode (+) and cathode (–). The hydrogen (H^+) and hydroxide (OH^-) ions move to the opposite electrodes to liberate pure hydrogen (H_2) and oxygen (O_2) gases.

At anode oxidation of water molecules occur liberates oxygen gas and H^+ ions. The

Half cell reaction as shown in fig.

At anode

$$H_2O\ (l) \rightarrow \tfrac{1}{2}O_2(g) + 2H^+\ (aq.) + 2e^-$$

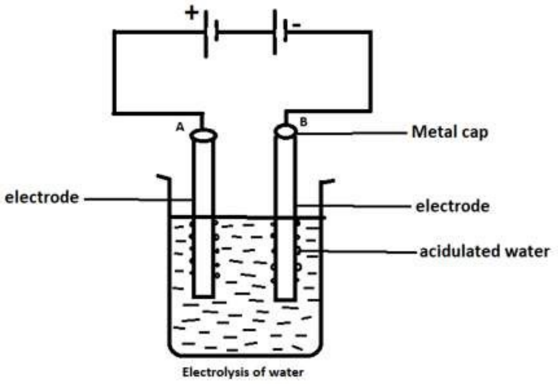
At cathode H^+ ions acquire electrons reduce to hydrogen gas.

The half-reaction is as follows:

$$2H^+\ (aq.) + 2e^- \longrightarrow H_2\ (g)$$

The overall chemical reaction is

$$H_2O\ (l) \rightarrow H_2\ (g) + \tfrac{1}{2}O_2\ (g)$$



Electrolysis of water

Generation of Hydrogen by Alkaline Water Electrolysis:

Alkaline water electrolysis is a technology for large-scale hydrogen production by using renewable energy.

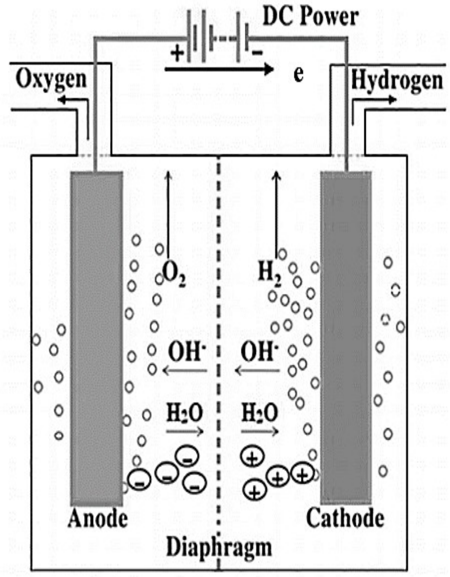
Alkaline water Electrolysis is carried out by using aqueous solution of KOH or NaOH as an alkaline electrolyte. The cell consisting the following components.

Anode: Porus carbon electrode in which Ni particles are dispersed as electrocatalyst

Cathode: Porus carbon electrode on which Ni is coated as electrocatalyst

Electrolyte: Aqueous Solution of KOH or NaOH

Separator: Polymer membrane anion exhager



$$\textbf{Anode:}\quad 2OH^{-}(aq) \longrightarrow \tfrac{1}{2}O_2(g) + H_2O(l) + 2e^-$$

$$\textbf{Cathode:}\quad 2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^{-}(aq)$$

$$\textbf{Overall Reaction:}\quad H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g))$$

Advantages of Alkaline Water Electrolysis:

1. Alkaline water electrolysis is an easier, cheaper, and simple method for the production of Hydrogen.
2. Ni is used as an electrocatalyst at the electrodes which are cheaper
3. Pure Carbon free hydrogen gas is obtained from this method
4. By make using the excess solar energy, we can produce H_2 gas and stored as chemical energy.

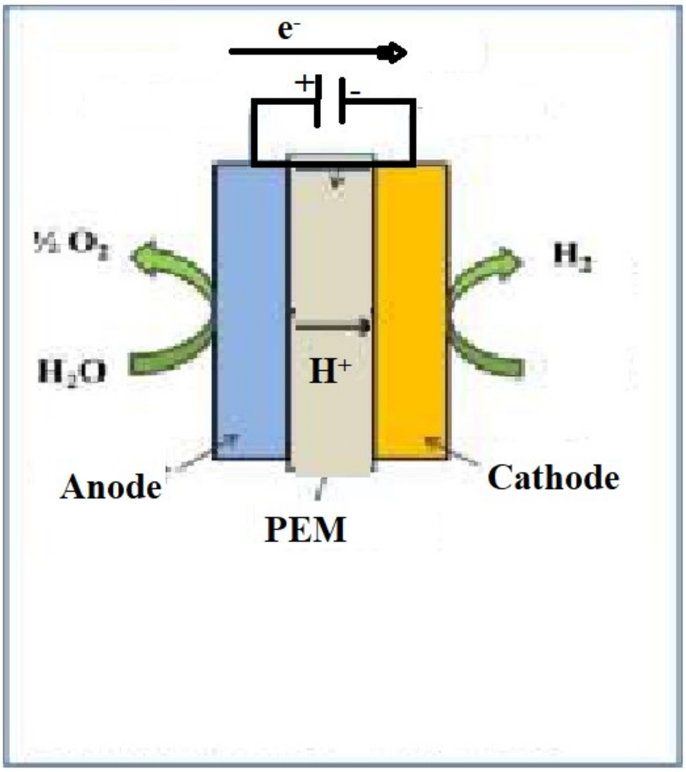
Generation of Hydrogen by PEM Water Electrolysis:

Polymer electrolyte membrane water electrolysis can be carried out by using cation exchange polymer membrane such as Nafion (sulphonated tetera fluoro poly ethylene based fluoro polymer).The cell consisting of following components

Anode: Porus carbon electrode in which Iridium particles are dispersed as electrocatalyst

Cathode: Porus carbon electrode on which Pt is coated as electrocatalyst

Electrolyte:PEM (Nafion)



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

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

Overall Reaction: $H_2O \rightarrow O_2 + H_2$

Advantages of PEM Water Electrolysis:

1. In PEM water electrolysis, electrolyte used is is a solid polymer membrane, hence there will be no chance of leakage of electrolyte.
2. Polymer membrane is chemically stable and non corrosive.
3. pure carbon free hydrogen is obtain from the from this method
4. PEM cell can powered by cheap current obtained from solar energy
5. Lower operation costs.

MODULE 5: E-Waste Management (8hr)

Sl/No.	Topics	Duration
1	E-Waste: Introduction, sources of e-waste, Composition and Characteristics,	1hr.
2	Need for e-waste management concerning global perspective	1hr.
3	Toxic materials used in manufacturing electronic and electrical products; health hazards due to exposure to e-waste.	1hr.
4	Recycling and Recovery: Different approaches of recycling (separation,thermal treatments)	1hr.
5	hydrometallurgical extraction, pyrometallurgical methods and direct recycling.	1hr.
6	Extraction of gold from e-waste (Explain the Principle and experimental procedure)	1hr.
7	Role of stakeholders in the environmental management of e-waste: Who are called stakeholders – a local and global perspective	1hr.
8	Role of stakeholders - producers, consumers, recyclers, and statutory bodies.	1hr.

E-Waste Management (Electronic waste)

1. What is an e-waste ? give the sources and composition of e-waste

“ All electronics and electrical item which are discarded on completion of their useful life is known as e-waste”.

SOURCES	• Computer Peripherals:Monitor, key board, mouse, mother board, lap tops,CDs, etc. • Telecommunication devices: Phones,cellphones, routers, pagers, fax machine etc. • House hold appliances:TV, fridges, washing machine, video players, ovens etc • Industrial Devices: Sensors, medical devices, automobile devices etc. • Electrical devices: Switches, wires, bulbs etc.
COMPOSITIN	**65%** of iron, steel, and other metallic materials including costly metals like Pt, Au, Ag, and toxic metals like lead, Hg, Cd, Cr, etc. e-waste contains **21%** of polymeric non biodegradable materials including PVCs, poly chlorinated biphenyls and Brominated flame retardant plastics. **11.85%** of CRT (cathode ray tube) and LCD screens and other materials like glass, wood,plywood and ceramics etc.

2.What is the composition of e-waste?Mention the hazardous chemicals present in e-waste.

Hazardous and non hazardous substances. Hazardous substances are toxic, and can effect the quality of ecosystem as well as effect on human health. These include

a) Heavy metals like Cd,Cr.Pd and Hg

b) Organic compounds like CFC's, polyclic aromatic hydrocarbons (PAH's), poly chlorinated biphenyls (PCB's), polybrominated diphenyl ether (PBDES) etc.

Characteristics of e-Waste:

3.What are the characteristics of e-waste?

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

1. **Complexity:** E-waste often contains a complex mixture of materials, making it challenging to recycle and dispose properly. E.g., Uranium and plutonium from various sources.

2. **Hazardousness:** E-waste can contain hazardous materials such as heavy metals, flame retardants, radioactive isotopes, dioxins, and batteries, which can cause significant environmental and health risks.

3. **Volatility:** E-waste is a rapidly growing waste stream due to the increasing use of electronic devices and the limited lifespan of many electronic products.

4. **Global issue:** E-waste is a global issue, as electronic devices are manufactured, used, and discarded worldwide.

5. **Resource depletion:** The extraction of raw materials for electronic devices contributes to resource depletion, and the improper disposal of e-waste can lead to environmental contamination and waste of valuable resources.

6. **Environmental and health impacts:** Improper disposal of e-waste can lead to significant environmental and health impacts, including soil and water contamination, air pollution,and harmful to human health.

Need of e-waste management concerning Global perspective:

4. Explain the need for e-waste management

E-waste management refers to process of handling, recycling and disposing of electronic waste. E-waste management is necessary because it help to address several environmental, health and resource related concerns

1. **Environmental impact:** improper disposal of e-waste in result in release of toxic substances into the environment causing, soil, air, and water pollution

2. Resource depletion: e-waste contains valuable material such as Pt, Au, Ag, Cu etc that can be recovered and recycled. This you can help to conserve natural resources and reduces extraction of new resources.

3. Reducing the greenhouse gases and hence preventing global warming

4. Recycling of e-waste reduce the land field area

5. E-Waste is a complex mixture of metals, organic compounds, and ceramics. Due to these facts,proper, & efficient e-waste management is required.

5.Briefly discuss health hazard due to exposure to e-waste

Major problems with the e-waste is passing of toxic metals and organic compounds present in e-waste in to ecosystem that is air,water and soil and ultimately to living being.

1.E-waste negatively impacts the ground water. The toxin which is available in e-waste can enter ground water which is often used as drinking water. So it can impact on human health, as these toxins are carcinogenic.

2.Combustion of e-waste in the open field releases hydrocarbons in to the atmosphere. Hydrocarbons can contribute to green house gases and global warming.

3.Most of the heavy metals are carcinogenic in particular, the matter released on burning of e-waste in the open field discharge metal particles which enters the human body and causes skin damages, head ache, chronic gastric, gastric ulcers etc.

4.Heavy metal like Cd metal can damages kidneys and Pb metal can damage central nervous system, decrease IQ among the children, Hg greatly affect neurons.

5.Placenta collected from mother who live near e-waste dumping sites have shown very high concentrations of toxic chemicals.

6. Different hazardous chemicals can accumulate in blood, serum and urinary tract and finely shown synergistic effect with a cumulative impact.

7.Even contamination like heavy metals and organic compound such as furans, dioxine PCBs, PAHs and polybrominated diphynyl can adversely affects birth rate, damaging DNA, chromosome, etc.

6.What are the Toxic material used in electronics and electrical products?Mention their ill effect

Toxic Materials	**Sources**	**ill Effects**
Pb	Circuit boards, cathode ray tubes, solder, and Lead – acid batteries.	Pb damages the nervous system, blood system, kidney and also affect the development of brain in children
Hg	Fluorescent lamps, batteries, flat screen monitors and other electronic products.	Hg greatly affect neurons
Cd	Ni – Cd batteries, circuit boards, and other electronic products.	Cd metal can damages kidneys and reproductive system.
B (BFRs)	As a flame retardant to reduce the risk of fire in electronics and electrical appliance	Long rage exposure can lead to impaired memory function and learning. Pregnant women give birth to babies with behavioral problems
PVC	cables, wires.	Damages the central nervous system (CNS), which causes dizziness, drowsiness, and headaches
Ba	cathode ray tubes.	brain swelling, damage to heart, liver and spleen.
CFCs	As coolant in AC's, refrigerator etc	Depletion of ozone layer, global warming

e-waste Recycling and Recovery Different Approaches

7.Briefly discuss the various steps involved in recycling of e-waste.

Process of Recycling and Recovery: Different approaches are employed in recycling of e-waste to recover metals are

1.Pre treatment process

2.Pyrometallurgical method

3. hydrometallugical method

4.Direct recycling

5. Thermal treatment

1. Prereatment process:

i) **Collection and transport:** It is a process of collecting e-waste from various sources and transport to e-waste recycling centre for further processing

ii) **Dismantling:** After collecting the e-waste from various sources, it is subjected to manual dismantling into various components using mechanical tools. This has been done to upgrade the items and also to segregate the fraction like metals, ceramics,plastics, woods glass etc

iii) Shredding: Those materials which are not suitable for reuse is subjected to Crushing and grinding in order to reduce the size of the e-waste materials known as shredding. The shredded pieces are then sorted into different fraction category wise based on their composition.

iii) **Separation:** This involves the shredded fraction physically separated in to different metallic and non metallic substance's by using various techniques such as **Magnetic separation Gravity separation and electrostatic separation .**

2. Pyrometallurgical Method

Pyrometallurgical method refers to the process of extracting valuable metals and other materials from e-waste using high temperatures.

This methods include: Smelting, Refining,Incineration and pyrolysis.

Heavy metals are separated by this technique

3. Hydrometallurgical Method

Hydrometallurgical Method is the extraction of valuable metals and other materials from electronic waste through chemical reactions in aqueous solutions. The process typically involves the following steps:

i) Pte-treatment ii) Chemical treatment iii) recovery of metals.

Direct recycling: This method involve the recovery of valuable materials from the e-waste without carrying out the intermediate process or any chemical reaction

The separated materials are the processed to extract the valuable components and prepare them for reuse.

5. **Thermal treatments:** Incineration (Thermal treatment): Non-recyclable material can be used for energy generation through incineration. Incineration have two benefits such as the volume of e-waste can be reduced significantly and generating energy for other applications.

8. What are the advantages of recycling of e-waste

1.Reduces Landfill Sites: The more we recycle, the less waste we generate and reduced landfill sites.

2.Preserves Natural Resources: Recycling e-waste enables valuable materials to be recovered and reused to manufacture new products, which saves energy and preserves natural resources.

3.Prevents Toxic Chemicals from Polluting the Ecosystem: Electronic components contain a number of toxic chemical substances which posses health and environmental hazards. Hence recycling is preventing environmental pollution caused by e-waste.

4.Creates New Business & Employment Opportunities: Recycle and reuse create an an immense opportunity for innovative research & development and creative business models for sustainable solutions.

8.Discuss the following:

(i) Pyrometallurgy (ii) Hydrometallurgy

i) Pyrometallurgical method

Pyrometallurgical method refers to the process of extracting valuable metals and other materials from e-waste using high temperatures.

This method include:

1.Pretreatment: This step involves the fragmentation and size reduction of electronic waste to prepare it for further process.

2. Smelting: The e-waste is melted in a furnace and then separated into individual metals and other materials.

3. Refining: The metals from the smelted e-waste are further processed to remove impurities to improve their quality.

4. Incineration: It is a controlled combustion of e- waste with suitable emission units. The incinerator has two connected furnace in which e-waste is burn at 800^{o}C in first furnace and in the second stage, the gaseous products of the first incinerator are further oxidize at 1100^{o}C. Heavy metals are collected in the bottom of fly ash.

5. **Pyrolysis of e-waste :** Pyrolysis is a thermal decomposition of e-waste in an oxygen free environment. During pyrolysis the metallic components can be recover easily by separation.

Hydrometallurgical extraction of e-waste

Hydrometallurgical extraction is a process used to extract valuable metals and other materials from electronic waste through chemical reaction in aqueous solution.

This process typically involves the following steps:

1. Pretreatment
2. Chemical treatment
3. Metal recovery stage

1. Pte-treatment: This step involves the fragmentation and size reduction of electronic waste to prepare it for further process.

2. **Chemical treatment Stage:** In this stage metal are made to leach with acid, alkali, sodium metabisulphate solution, cyanide solution etc.During this process, metals are dissolved in leaching solution and separated from solid waste.

3. Metal recovery stage: The Leachate is then processed to separate the metals and other materials.Purification of metals can e done through precipitation or ion exchange or solvent extraction or electrodeposition techniques.

Extraction of gold from e-waste (Hydrometallurgy):

9.Explain the principle and various steps involved in extraction of gold (hydrometallurgy)

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

Experimental procedure:

1. Pretreatment: The e-waste containing the gold fraction such as CPU's, Mother board cell phone etc is subjected to shredding in order to reduce the size.

Chemical Treatment

i). Leaching: The metals, including gold, are leached from the e-waste using a suitable reagent, such as aqua regia (a mixture of hydrochloride acid and nitric acid), to dissolve the gold.

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

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

$2H[AuCl_4] + 3Na_2S_2O_5 + 3H_2O \rightarrow 2Au + 3SO_2 + 3Na_2SO_4 + 8HCl$

3. Metal recovery stage:

I) Purification: The precipitated gold is then purified through processes such as ion exchange or electrodeposition, or distillation, to remove impurities and improve its quality.

Ii) Recovery: The purified gold is then recovered for reuse.

Advantages:

High yield expected.

Faster extraction of gold is possible.

Disadvantages:

Chemicals are used.

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

10.Write a note on direct recycling of e-waste

Direct recycling of e-waste:

Direct recycling of e-waste refers to the process of recovering valuable materials from electronic waste without the need of intermediate processing steps or without any chemical reaction. This process includes shredding (cutting into pieces), granulating (converting into small particles) and sorting (separating) which are used to separate the different components of e-waste like metals plastic and glass.

The separated materials are then processed to extract the valuable components and prepare them for reuse.

Advantages of direct recycling process:

1. Lower energy inputs,
2. Low cost input,
3. Low environment impact,
4. Higher quality end products recovery,
5. Bulk volume Recycling

Role of stakeholders (local and global perspective) in the environmental management of e-waste.

11.Write a note on various stake holder in e-waste management

Stake holders are referred to government, private organizations, companies or individuals who are either directly or indirectly involved in management of e-waste.

stakeholders in the environmental management of e- waste may include:

Statutory body (Governments): Responsible for creating and enforcing regulations and policies to manage e-waste, as well as promoting public awareness and education about e-waste management.

Producers (Manufacturers): Responsible for the design, production, and disposal of electronic products, and may be involved in the collection and recycling of e-waste.

Consumers: Consumers play a significant role in e-waste management. They are responsible for proper disposal of their electronic devices after use. They can also help reduce e-waste by buying products that are designed to be eco-friendly and by using their devices for as long as possible.

E-**waste recyclers and processors:** Responsible for the safe and responsible management of e- waste, including the collection, dismantling, and recycling of electronic waste.

Global perspectives: Stakeholders from global prospective in the environmental management of e-waste may include:

International community: Including consumers, NGOs, and civil society organizations, that can raise awareness about e-waste issues, demand responsible e-waste management practices, and push for change at the international level.

International organizations: Such as the United Nations, World Trade Organization, and the International Telecommunication Union that are responsible for setting global standards for e-waste management and promoting cooperation and collaboration among countries.

Transnational corporations: Responsible for the design, production, and distribution of electronic products on a global scale, and have a significant impact on e-waste management practices.

Global e-waste trade networks: Responsible for the transportation and processing of e-waste between countries and may impact the environmental and health outcomes of e-waste management.

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