COURSE TITLE-CHEMISTRY FOR ELECTRONICS AND ELECTRICAL ENGINEERING STREAM
COURSE CODE-BCHEE102/202

MODULE 1
CHEMISTRY OF ELECTRONIC MATERIALS

SYLLABUS

Conductors and Insulators: Introduction, principle with examples. Semiconductors: Introduction, production of electronic grade silicon-Czochralski process (CZ) and Float Zone(FZ)methods. **Polymers:** Introduction, Molecular weight Number average, Weight average and numerical problems. Conducting polymers– synthesis and conducting mechanism of polyacetylene. Preparation, properties and commercial applications of graphene oxide. PCB: Electroless plating – Introduction, Electroless plating of copper in the manufacture of double-sided PCB.

Self-learning: Technological importance of metal finishing and distinction between electroplating and electroless plating.

CONDUCTORS AND INSULATORS

Principle of Conductors Insulators and semiconductors (Valence band theory):

Conductors – The materials which allow electricity to pass through them are called conductors. Examples – copper, iron, zinc etc.

Semiconductors – The materials which show conductivity in between that of conductors and insulators are called semiconductors. Examples – Si, Ge, As etc.

Insulators – The materials which do not allow electricity to pass through them are called insulators. Examples – wood, glass, stones etc.

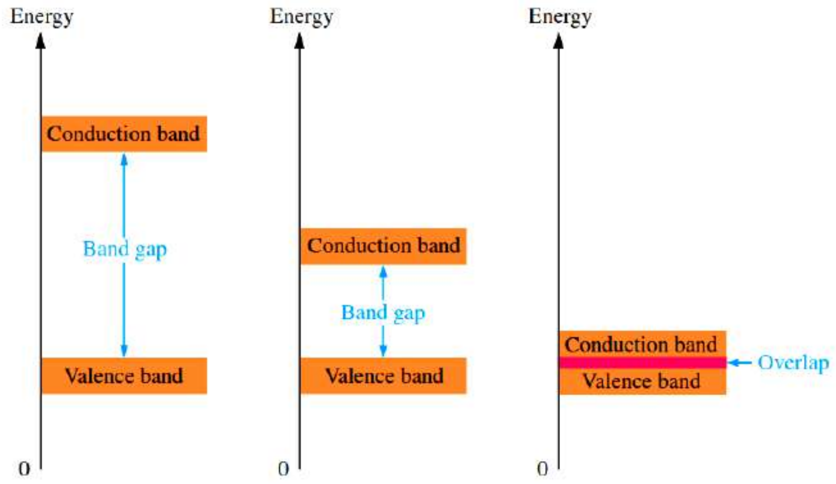
Valence Band- It is made up of those valence shell (outermost) orbitals which have electrons in them or highest energy band that is filled is known as the valence band For example, a sodium valence band is made up of $3s^1$ orbital.

Conduction Band- It is made up of those orbitals which are unoccupied by electrons either in valence shell or next to valence shell is called the conduction band. Thus, the orbitals of the conduction band are empty. Eg: In sodium after orbital 3s the next orbital is 3p which is empty so it forms a conduction band.

Forbidden Gap – The gap or energy difference between the valence band and conduction band is called the forbidden gap.

Band Theory:

According to the band theory of solids electrons jump from valence band to conduction band even at ordinary temperature and if this happens then the solid conducts electricity. Conductivity depends on the gap between the valence band and conduction band. If the gap or energy difference between the valence band and conduction band is more than or equal to 5eV then the material will behave as an insulator. If the energy difference between the valence band and conduction band is equal to or less than 3eV then the material or solid is called a semiconductor. If the valence band and conduction band overlap each other then the solid is called conductor.



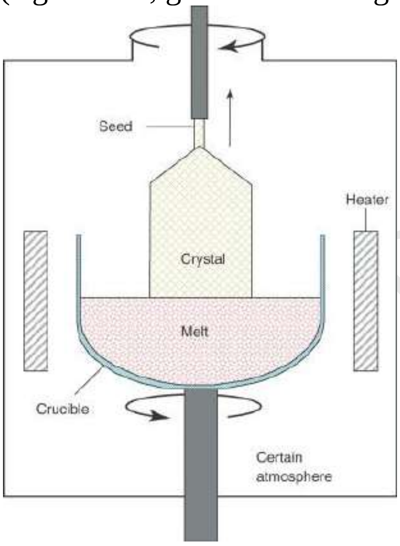
(a) Insulator (b) Semiconductor (c) Conductor

The reasoning behind it is that electrons can jump from valence band to conduction band and thus conduct electricity. While if the gap is too much between the valence band and conduction band (more than or equal to 5eV) then electrons can't jump from the valence band to the conduction band, hence these materials or solids can't conduct electricity. If the valence band and conduction band are neither overlapping nor at too much distance then a few electrons may jump from the valence band to the conduction band and these materials are called semiconductors.

Production of electronic grade silicon from quartz:

i) Czochralski Process (CZ)

The Czochralski method is a method of crystal growth used to obtain single crystals of semiconductors (e.g. silicon, germanium and gallium arsenide) metals. It is also known as crystal Pulling Technique.



Steps involved are

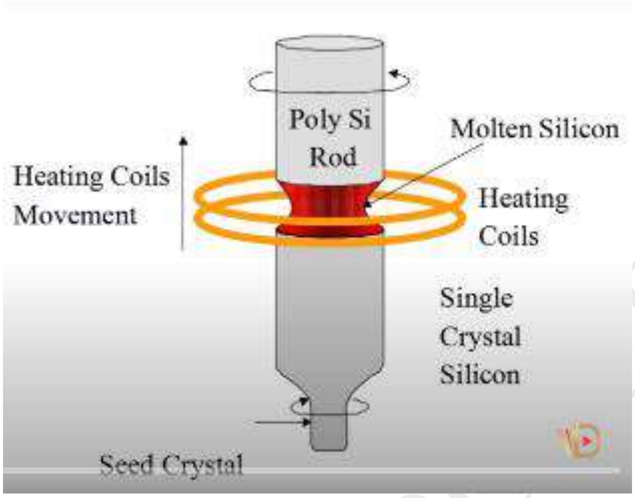
1. Electronic grade polycrystalline silicon crystal is taken in a quartz vessel placed in a graphite crucible.
2. Graphite container is heated from the surrounding heater. Heat from graphite crucible is transferred to quartz crucible. Polycrystalline silicon in the crucible melts in an inert atmosphere of argon.
3. When the material melts, the temperature is lowered so that it is kept at the melting point of the material (1400°C).
4. A single crystal of silicon (seed crystal) is attached to the tip of a puller rod and is immersed into the molten material. It acts as a starting point for the crystal formation.
5. The seed crystal is pulled out at a rate of 1.5-5cm per hour. During this process the seed crystal and crucible are counter rotated. The temperature of the melt is reduced when it comes in contact with crystal seed and hence it solidifies.

6. The crystallographic orientation of pulled crystal is same as that of seed crystal.
Advantages:

1. This method is cheaper
2. This method gives larger wafer size.

ii) Float Zone Method

Basic of this technique is that “impurities are more soluble in the molten Silicon than in the solid Silicon”. Zone refining consisting of a impure poly silicon rod or cylindrical tube, vertically clamped and heated with help of RF coil (radio frequency coil) to about 1000°C in an inert atmosphere.
Seed single crystal is placed at the bottom. When impure rod is heated at the bottom Silicon in that region gets melted and as moved upward the Silicon in that region gets melted and impurities also move towards molten zone. The lower molten region gets solidifies having orientation of seed single crystal. Thus by moving the heating coil over entire rod impurities also move and gets collected at the other end which can be cut off to get pure single crystal of Silicon.
This method is expensive but contains very less impurities than CZ method. This method gives smaller wafer size than CZ method.



POLYMERS

A polymer is a giant or macro molecule formed by the repeated union of several simple molecules called monomers. The repeating units (monomers) are linked through strong covalent bonds. Monomers are the building blocks of polymer.

$$H_2C{=}CH_2 \longrightarrow \left[-H_2C-CH_2-\right]_n$$

Classification

Based on the origin polymers are classified as natural polymers and synthetic polymers.

Natural polymers

These are obtained from natural sources such as plants and animals.

Example: Silk, starch, cellulose, proteins, wool etc.

Synthetic polymers

These are synthesized from simple molecules (i.e man made polymers)

Example: Polyethylene, PVC, polystyrene, nylon, plexiglass, polyesters, Teflon etc.

Polymerization

The chemical process by which the monomers are converted into polymers is called the polymerization reaction.

Molecular weight of Polymers:

The length of a polymer chain can be expressed in terms of molecular mass of the polymer. The molecular mass (M) of a homopolymer is related to the degree of polymerization (DP) by the relation M = DP x M, where, M is the molecular mass of the repeating unit.

The molecular mass of a hetero polymer is the sum of the products DP x M for each type of repeating unit. Polymers have varying chain lengths; hence two types of average molecular masses have been recognized namely, number average and weight average molecular mass.

Number average molecular mass:

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

Let the polymer chain consist of ‘n’ polymer chains of which n_1 of M_1 mol.wt., n_2 of M_2 mol.wt…… till n_i of M_i mol.wt.

Then, total no. of molecules = $n_1 + n_2 + n_3 + \ldots + n_i = \Sigma n_i$

Molecular weight contribution from all the species = $n_1M_1 + n_2M_2 + n_3M_3 + \ldots + n_iM_i = \Sigma n_iM_i$

Then, the number average molecular mass (M_n) of a polymer is given by the equation,

$$M_n = \frac{n_1M_1 + n_2M_2 + \ldots\ldots\ldots\ldots\ldots n_iM_i}{n_1 + n_2 + \ldots\ldots\ldots\ldots\ldots n_i}$$

$$\boxed{M_n = \frac{\Sigma\, n_iM_i}{\Sigma\, n_i}}$$

Where, n and M represent the number and molecular mass of each species present in the polymer.

Weight average molecular mass:

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

Weight of n_1 species = $W_1 = n_1M_1$

Then weight average molecular mass of a polymer is given by the equation,

$$M_w = \frac{W_1M_1 + W_2M_2 + \ldots\ldots\ldots\ldots\ldots\ldots W_iM_i}{W_1 + W_2 + \ldots\ldots\ldots\ldots\ldots\ldots W_i}$$

Where, W and M represent the weight and molecular mass of each species present in the polymer. Since W = nM, the above equation can be represented as,

$$M_w = \frac{n_1M_1^2 + n_2M_2^2 + \ldots\ldots\ldots\ldots\ldots\ldots n_iM_i^2}{n_1M_1 + n_2M_2 + \ldots\ldots\ldots\ldots\ldots\ldots n_iM_i}$$

$$\boxed{M_w = \frac{\Sigma\ n_iM_i^2}{\Sigma\ n_iM_i}}$$

Problems:

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

Number average molecular weight of the polymer,

$$M_n = \frac{\Sigma\ n_iM_i}{\Sigma\ n_i}$$

$$= \frac{1\,(1 \times 10^5) + 2(2 \times 10^5) + 3(3 \times 10^5) + 4(4 \times 10^5)}{1 + 2 + 3 + 4}$$

$$= 3.0 \times 10^5$$

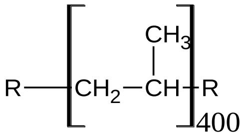
Weight average molecular weight of the polymer,

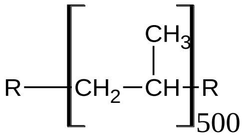
$$M_w = \frac{\Sigma\ n_iM_i^2}{\Sigma\ n_iM_i}$$

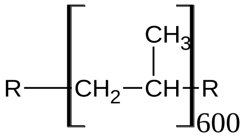
$$= \frac{1(1 \times 10^5)^2 + 2\,(2 \times 10^5)^2 + 3(3 \times 10^5)^2 + 4(4 \times 10^5)^2}{1(1 \times 10^5) + 2(2 \times 10^5) + 3(3 \times 10^5) + 4(4 \times 10^5)}$$

$$= 3.3 \times 10^5$$

2. A polymer of polypropylene is found to have the following composition.

a. 
$R-\left[CH_2-\overset{CH_3}{\overset{|}{CH}}\right]_{400}-R$ 20 %

b. 
$R-\left[CH_2-\overset{CH_3}{\overset{|}{CH}}\right]_{500}-R$ 30 %

c. 
$R-\left[CH_2-\overset{CH_3}{\overset{|}{CH}}\right]_{600}-R$ 50 %

Calculate the number average and weight average molecular mass of the polymer. [Atomic mass of C = 12, H = 1, Neglect the molecular mass of R.]

Molecular mass of (a) = [(12 x 3) + (6 x 1)] x 400 = 16 800

Molecular mass of (b) = [(12 x 3) + (6 x 1)] x 500 = 21 000

Molecular mass of (c) = [(12 x 3) + (6 x 1)] x 600 = 25 200

$$M_n = \frac{n_1M_1 + n_2M_2 + \ldots\ldots\ldots\ldots\ldots n_iM_i}{n_1 + n_2 + \ldots\ldots\ldots\ldots\ldots n_i}$$

$n_1 = 20$, $n_2 = 30$, $n_3 = 50$, $M_1 = 16800$, $M_2 = 21000$, $M_3 = 25200$

$$M_n = \frac{20x16800 + 30x21000 + 50x25200}{20 + 30 + 50}$$

$$= 22\ 260$$

$$M_w = \frac{n_1M_1^2 + n_2M_2^2 + \ldots\ldots\ldots\ldots\ldots n_iM_i^2}{n_1M_1 + n_2M_2 + \ldots\ldots\ldots\ldots\ldots n_iM_i}$$

$$= \frac{20x(16800)^2 + 30x(21000)^2 + 50x(25200)^2}{20x16800 + 30x21000 + 50x25200}$$

$$= 22\ 715$$

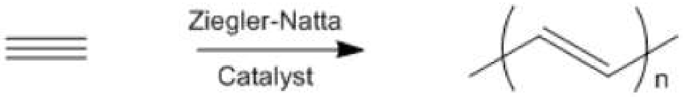
<u>Conducting polymers:</u>

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

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

<u>Synthesis</u>:

Polyacetylene are synthesized using Zeigler-Natta catalyst. The catalyst is suspended in silicone oil through which acetylene gas is passed, is stirred for two hours at 120 ^{o}C. Later it is cooled slowly to room temperature resulting in thin sheets of Polyacetylene.



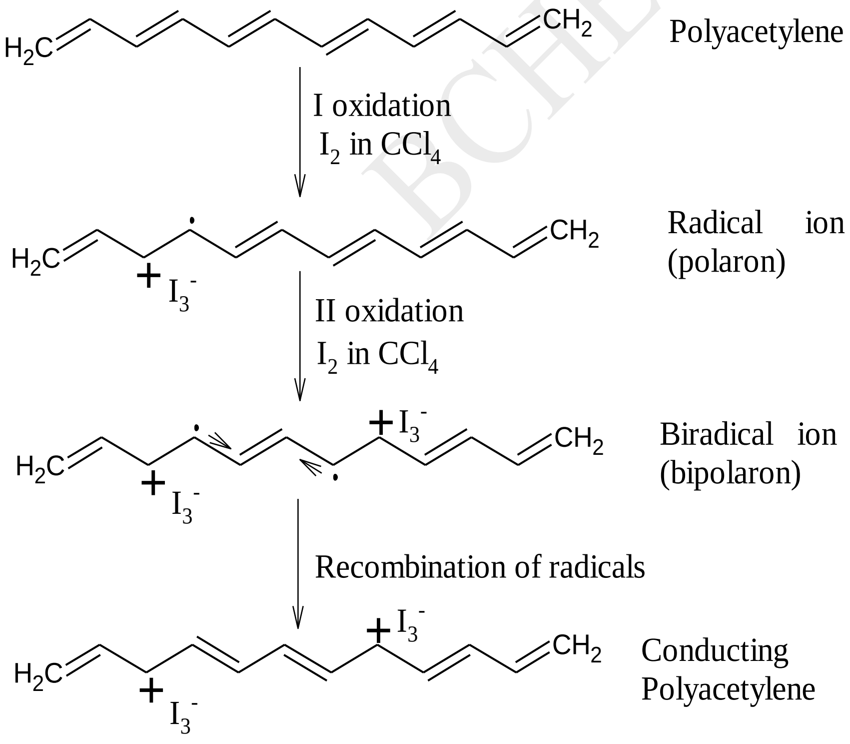
The conducting polymers are synthesized by doping in which charged species are introduced in organic polymers having pi- back bone. The important doping reactions are

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

3. Protonic acid doping (p- doping)

<u>Oxidative doping</u> (p- doping): In this process pi- back bone of a polymer is partially oxidized using a suitable oxidizing agent. Oxidizing agent takes away electron from pi-backbone of the polymer chain creating a hole. This creates positively charged site on polymer backbone, which are current carriers for conduction. The oxidizing agents used in p-doping are iodine in CCl_4 etc.

<u>Mechanism of conduction in polyacetylene by Oxidative doping</u>



<u>Step 1:</u> The Polyacetylene is treated with suitable oxidizing agent such as Iodine in CCl_4 leads to the

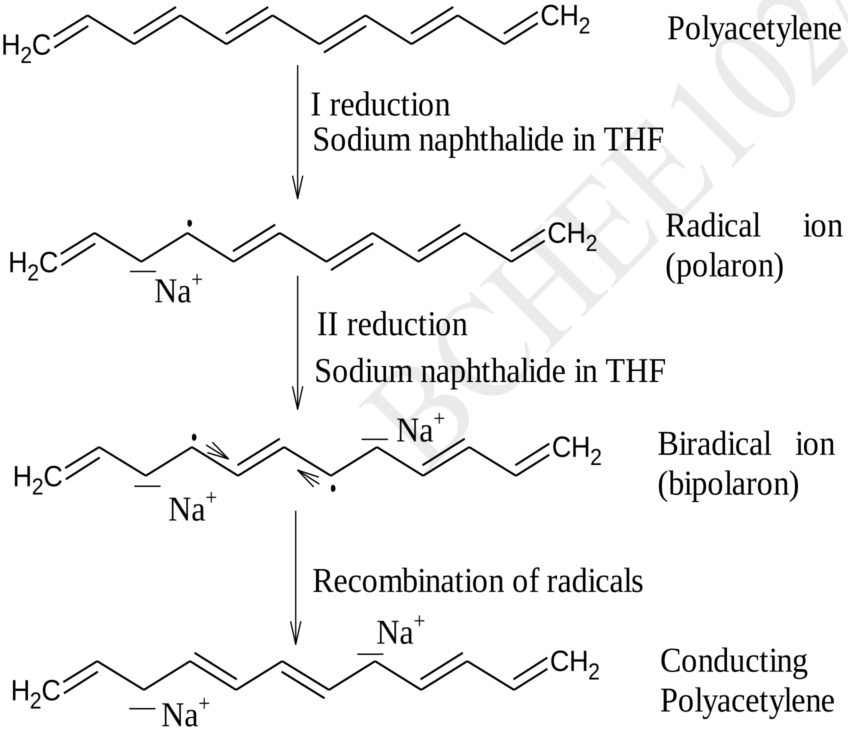
formation of delocalized free radical ion called polaron.one electron is removed from pi-backbone of the polymer chain leaving behind positive charge on one carbon atom.

Step 2: The second oxidation with the same oxidizing agent of the chain containing polaron produces two positive charges. The positively charged sites on the polymer chains are compensated by anions I^-_3.and thus polymer is electrically neutral.

Step 3: Next the radical recombination takes place to form a double bond. The delocalized positive charges on the polymer chain are mobile, not the dopant anions. Thus, by applying potential the delocalized positive charges move and thus making a conductive polymer.

Reductive doping (n- doping): In n- doping, pi back bone of a polymer is partially reduced by a suitable reducing agent. This creates negatively charged sites on polymer backbone. These negatively charged sites are responsible for the conduction. Reducing agent is solution of sodium naphthalide in tetrahydrofuran.

Mechanism of conduction in polyacetylene by Reductive doping



Step 1: The Polyacetylene is treated with suitable reducing agent such as sodium naphthalide in tetrahydrofuran leads to the formation of delocalized free radical ion called polaron. One electron is added to the polymer chain.

Step 2: The second reduction with the same reducing agent of the chain containing polaron produces two negative charges. The negative charged sites on the polymer chains are compensated by cations Na^+ and polymer as a whole is electrically neutral.

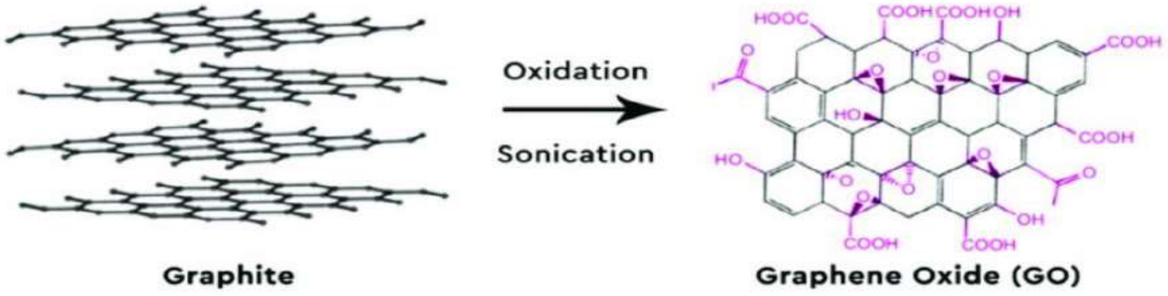
Step 3: Next the radical recombination takes place to form a double bond. The delocalized negative charges on the polymer chain are mobile, not the dopant cations. Thus, these delocalized negative charges are current carriers for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction.

Applications

- As electrode material for commercial rechargeable batteries (coin type batteries).
- As sensors-humidity sensor, gas sensor and radiation sensor etc.
- In electrochromic display windows.
- In light emitting diodes
- Corrosion inhibitors
- In fuel cells as the electro catalytic materials.
- As film membranes for gas separations.

Graphene Oxide

Graphene oxide (GO) is the oxidized derivative of graphite. A single sheet of carbon atom taken out of graphite is graphene. Graphene oxide is a compound of carbon, oxygen, and hydrogen arranged in variable ratio.When functional groups such as epoxide, hydroxyl, carboxyl, and carbonyl group are added to graphene layer resulting material is graphene oxide.



Preparation

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

Properties

- Because of the presence of oxygen functional groups such as hydroxyl, alkoxy, carbonyl, carboxylic acid, etc. GO is hydrophilic in nature, so it can easily dissolve in water and organic solvent.
- It can also mix with a matrix such as a polymer and ceramic to improve their mechanical and electrical properties.
- GO is hygroscopic that depends on humidity. The increase of humidity content causes swelling of GO films and decreases the tensile modulus.

- GO has more surface area, so it is more reactive.
- Thin films of GO exhibit a high optical transparency.
- Poor conductor of heat and electricity.

Applications

- Graphene oxide sheets have been used to prepare strong paper-like materials, membranes, thin films, and composite materials.
- GO shows the best antimicrobial activity, so used in the purification of water.
- Graphene oxide is used as electrode material in super capacitors, lithium-ion and sodium-ion batteries
- Graphene oxide sheets used as a catalyst in photocatalytic water splitting.
- Graphene oxide is used to store hydrogen.
- Graphene oxide finds uses in a wide variety of nanomedical applications including tissue engineering, cancer treatment, medical imaging, and drug delivery.
- GO forms transparent protective and conductive coatings.
- It finds applications in future electron such as transistors (FETs) and organic light emitting devices.
- GO is good sensor for hydrogen, nitrogen dioxide and humidity.
- Chemically modified GO and GO based composites are effective adsorbents for removal various pollutions from wastewater and separation of radiochemical wastes.

Electroless plating:

Electroless plating is a method of depositing a metal or alloy over a substrate (conductor or nonconductor) by controlled chemical reduction of the metal ions by a suitable reducing agent without using electrical energy.

. The surface to be plated should be catalytically active so that in the beginning of the plating reaction, the surface of the substrate catalyses the reduction. Once the substrate is covered by the metal or alloy Scoating, the coating catalyses the reduction. The process continues with building of successive layers of the metal or alloy.

The electroless plating process can be represented as

$$\text{Metal ions} + \text{Reducing agent} \xrightarrow{\text{catalyst surface}} \text{Metal} + \text{Oxidized product}$$

The catalytic metals such as Ni, Co, steel, Fe, Al, Cu, brass etc. do not require surface preparation before electroless plating on them. Non catalytic metals need activation. This is done by dipping in palladium chloride – hydrochloric acid solution. Non conductors like glass, plastics, ceramics etc. are first activated in a solution of $SnCl_2$ and HCl. After rinsing it is immersed in a solution of $PdCl_2$ and HCl.

Advantages of electroless plating

- Use of electrical power and electrical contacts are eliminated.

- Semiconductors and insulators like plastics can also be plated.
- Electroless baths have better throwing power.
- Hydrogen gas liberated is not trapped in blind holes.
- Electroless coating are harder than that produced by conventional electroplating.
- No levelers are required.
- Resulting deposits have unique chemical, mechanical and magnetic properties.

Electroless plating of copper

1. Pretreatment and activation of the surface:

i) If object is active metal like Ni, Co , Fe activation is not required. It is washed using organic solvents followed by washing with dil.acid.

ii) If object is inactive metal like Cu, Ag , brass activation is done by dipping in PdCl2 in Conc. HCl

iii)Non-metallic objects are activated by dipping in SnCl2 solution containing HCl , followed by dipping in palladium chloride to get a thin layer of Pd.

2. Plating bath solution:-

A solution of copper sulphate (12g per litre)

Reducing agent– formaldehyde(8g per litre)

Buffer - sodium hydroxide(15g per litre) and Rochelle salt(14g per litre)

EDTA – complexing agent (20g per lt)

pH-11 and temperature 25°C.agent and exaltant(20g per lt), pH-11 and temperature 25°C.

Reactions

Cathode:- $Cu^{+2} + 2e^- \longrightarrow Cu$

Anode:- $2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$

Over all reaction:- $Cu^{+2} + 2HCHO + 4OH^- \longrightarrow Cu + 2HCOO^- + 2H_2O + H_2$

Formaldehyde and Cu^{+2} ions consumed during the reaction are replenished periodically.

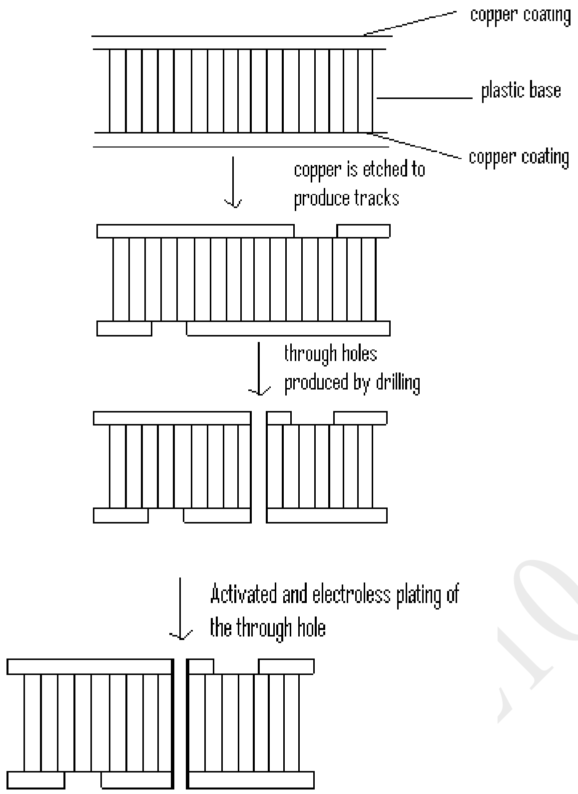
Applications:-

1) For plating on non conductors.
2) For decorative plating on plastics.
3) For producing through - hole connections.
4) For metalising printed circuit boards.

Through hole connections are necessary when double sided printed circuit boards are fabricated. The electrical connections between two sides of the board are made by drilling hole and then plating through holes by electroless plating.

For the manufacture of double sided printed circuit boards, the plastic board is initially covered with copper layers by coating thin layers of electroformed copper foils. The copper coated board is printed with an etch – resistant pattern of the circuit or the tracking required on both the sides. On etching with suitable etchent the copper except below the printed pattern is etched away, leaving the circuit pattern. The connection between two sides is made by drilling hole followed by activation and plating through holes by electroless plating.

The steps involved in the process is shown as follows



Important questions

1. Draw and explain the band diagram of conductors, semiconductors and insulators.
2. Describe the purification of electronic grade silicon from quartz by Czochralski process.
3. Explain the preparation, properties and commercial applications of graphene oxide.
4. Define the following (i) conducting polymers (ii) Number average molecular weight (iii) Weight average molecular weight.
5. What is electroless plating? Describe electroless plating of copper in the manufacture of double-sided PCB.
6. A polydisperse sample of polystyrene is prepared by mixing three monodisperse samples in the following proportions. 1g of 10000 molecular weight, 2g of 50000 molecular weight and 2g of 100000 molecular weight. Determine number average and weight average molecular weight. Find the index of polydispersity.

MODULE 2

ENERGY CONVERSION AND STORAGE

SYLLABUS

Batteries: Introduction, classification of batteries. Components, construction, working and applications of modern batteries; Na-ion battery, solid state battery (Li-polymer battery) and flow battery (Vanadium redox flow battery).

Fuel Cells: Introduction, construction, working and applications of methanol–oxygen and polymer electrolyte membrane (PEM) fuel cell.

Solar Energy: Introduction, importance of solar PV cell, construction and working of solar PV cell, advantages and disadvantages.

BATTERIES

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

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

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

Batteries are classified as Primary, Secondary and Reserve batteries:

Primary batteries:

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

Secondary batteries:

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

Reserve batteries:

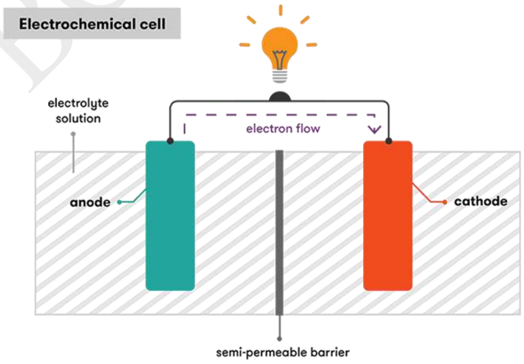
- Reserve batteries are a battery in which a key component is separated from rest of the components prior to activation.

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

COMPONENTS OF BATTERY

Cells are comprised of 4 essential components.

1. **Anode:** is the negative that releases electrons to the external circuit$M \rightarrow M^{n+} + ne^-$
2. **Cathode:** is the positive that acquires electrons from the external circuit$M^{n+} + ne^- \rightarrow M$
3. **Electrolyte:** is the medium that provides the ion transport mechanism between the cathode and anode of a cell. Electrolytes are often thought of as liquids with dissolved salts, acids, or alkalis that are required for ionic conduction.
4. **Separator:** Separates anode and cathode made up of cellulose, polymer etc. This prevents short circuiting.

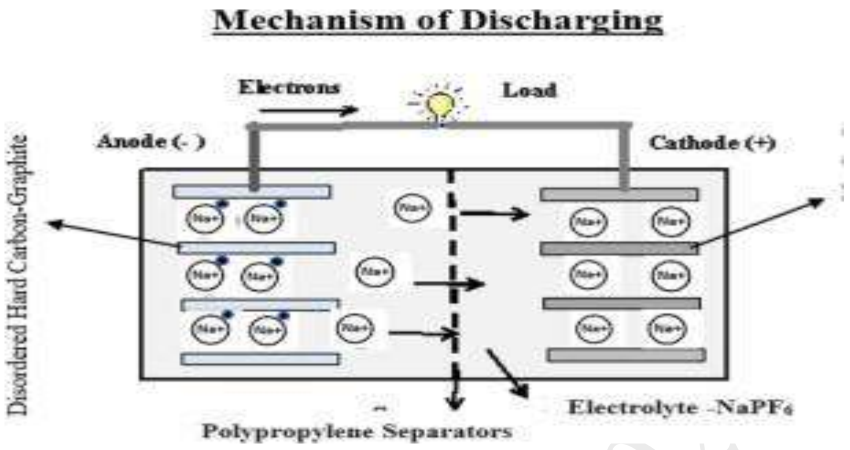


SODIUM ION BATTERY

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

Construction

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



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

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

Separator: Porous polymer film.

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

Working principle:

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

Discharge reactions:

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

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

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

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

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

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

Applications:

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

Advantages of SIBs

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

Dis advantages of sodium ion battery.

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

SOLID STATE BATTERY (LITHIUM POLYMER BATTERY)

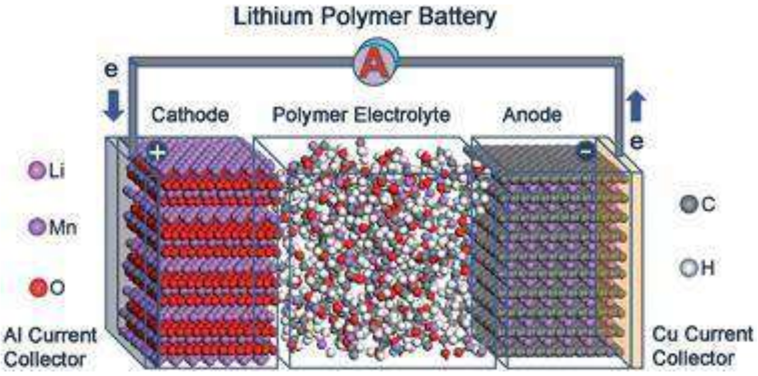
Solid-state battery is a battery that uses solid electrodes and a solid electrolyte likepolymer gel electrolyte, ceramic etc.

Construction

Anode : Porous carbon intercalated with lithium ions. Copper foil is used as currentcollector.

Cathode: Partially lithiated cobalt oxide compound. Aluminium foil is used as currentcollector.

Electrolyte :Solid polymer films/gel like polymer electrolyte.



Working principle:

- The principle of operation and construction of Li-polymer batteries are identical to those of Li-ion batteries.
- These batteries operate on the principle of de-intercalation and intercalation of lithium ions from positive electrode materials to negative electrode materials during charging and vice versa during discharging.
- Li-polymer batteries use lithiated carbon intercalation material as anode and transition metal oxide as active material for cathode.

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

At anode: $Li_xC_6 \rightarrow C_6 + xLi^+ + xe^-$

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

Overall reaction: $Li_xC_6 + Li_{(1-x)}CoO_2 \rightarrow LiCoO_2 + C_6$

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

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

Applications : They are used in cardiac pacemakers, laptops, cell phones, portable LCD, TV and aerospace applications.

Advantages of solid state battery

- Greater energy density,
- A longer life
- The greater safety,
- All in a smaller size.

Disadvantages of Solid-State Battery

- The mass production and manufacturing of solid-state batteries are quite complex.
- Perfect material for the electrolyte with an ideal ionic conductivity is yet to befound.

FLOW BATTERY (VANADIUM REDOX FLOW BATTERY-VRFB)

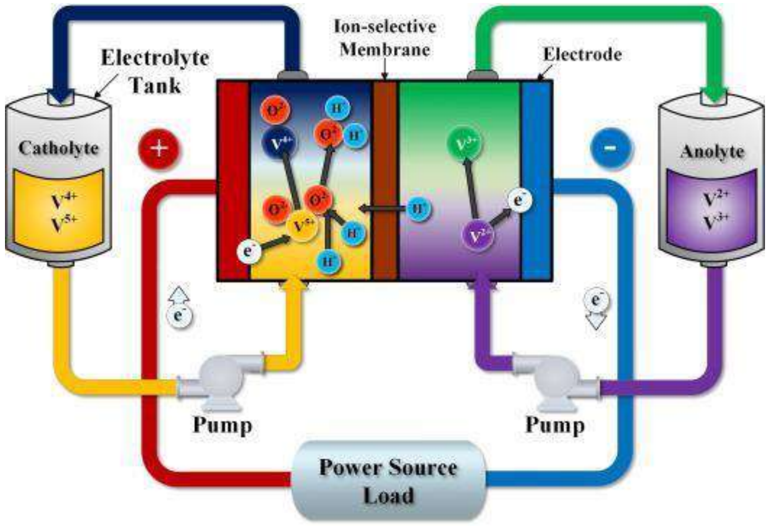
Flow battery is a type of electrochemical cell where **chemical energy** is provided when two liquids, separated by a membrane and circulated in order to enable ion exchange between them accompanied by flow of **electric current** through an external circuit occurs through the membrane while both liquids circulate in their own respective space.

The fundamentals of Vanadium RFB

The **vanadium redox battery** (VRB),is a type of flow battery. It employs vanadium ionsas charge carriers.

- The battery uses vanadium's ability to exist in a solution in four different oxidationstates to make a battery with a single electroactive element instead of two.
- In an all-vanadium RFB (VRFB) system, vanadyl sulphate in sulphuric acidsolution is employed as initial electrolyte at both sides.
- The same element at different oxidation states can be converted to one another atthe electrodes.

Figure shows a basic schematic of VRFBs



CONSTRUCTION

- A vanadium redox battery consists of an assembly of power cells in which two electrolytes are separated by a proton exchange membrane.
- The electrodes in a VRB cell are carbon based. The most common types are carbon felt, carbon paper, carbon cloth, and graphite felt
- Both electrolytes are vanadium-based. The electrolyte in the positive half-cells contains VO^{+} and VO^{2+} ions, while the electrolyte in the negative half-cells consists of V^{3+} and V^{2+} ions.

Working Principle

At the positive electrode, V(IV)/V(V) redox couple are generally VO^{2+} and VO_2^{+}

At the negative electrode, V(II)/V(III) redox couples are either the vanadium(II) ion or thevanadium(III) ion

Discharge

Negative electrode(oxdn) : $V^{2+} \rightarrow V^{3+} + e^{-}$

Positive electrode(redn) : $VO_2^{+} + 2H^{+} + e^{-} \rightarrow VO^{2+} + H_2O$

Recharge

Positive electrode(oxdn) : $VO^{2+} + H_2O \rightarrow VO_2^{+} + 2H^{+} + e^{-}$

Negative electrode(redn) : $V^{3+} + e^{-} \rightarrow V^{2+}$

Applications

- Commercial & Industrial, Electric Vehicle charging
- Telecommunications
- Solar, Wind and Residential.

FUEL CELLS

INTRODUCTION TO FUEL CELL

Definition: Fuel cells are defined as galvanic cells in which chemical energy of a fuel isdirectly converted into electrical energy by means of redox reactions involving fuels andoxidants. Fuel cells give direct current as long as fuel and oxidant are supplied.

A general fuel cell is represented as: **Fuel│electrode│electrolyte│electrode│oxidant**

Working principle:

At anode: fuel undergoes oxidation as **Fuel → Oxidized product + ne^-**

At cathode: the oxidant gets reduced as **Oxidant + ne^- → Reduced product**

The electrical output is a result of flow of electrons from anode to cathode through theexternal circuit.

Advantages of fuel cells:

- High efficiency of energy conversion process (75%).
- They are eco-friendly as the products of the overall reactions are not toxic andhence pose no pollution problems.
- They can produce direct currents for long periods at a low cost.
- Recharging of fuel cells is not needed
- No moving parts and so elimination of wear and tear

Limitations of fuel cells:

- The electrode used is Pt, Ag or alloys of noble metals, which are costly.
- The power generated is moderate.

METHANOL-OXYGEN FUEL CELL

Methanol is preferred as a fuel because it is one of the most electro active organic fuels inlow temperature range due to the following reasons.

- It has low carbon content
- It possesses a readily oxidizable – OH group.
- It has high solubility in aqueous solution.

Construction:

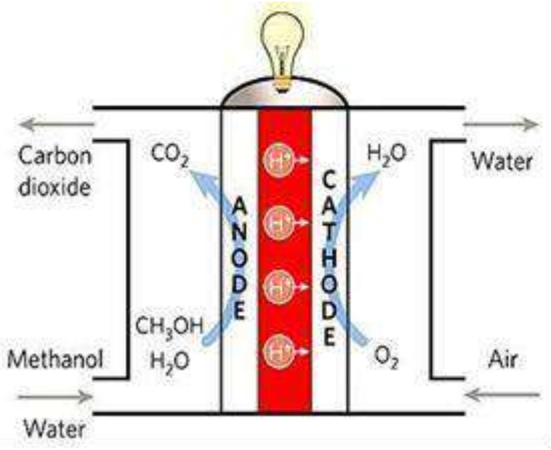
Anode : Porous Ni electrode impregnated with Pt/Pd catalyst

Cathode : Porous Ni electrode coated with Ag catalyst

Fuel : Methanol

Oxidant : O_2/Air

Electrolyte : H_2SO_4



Working principle:

- Methanol mixed with sulphuric acid (3.7M) is circulated through the anode chamber.
- Pure oxygen is passed through the cathode chamber and sulphuric acid (electrolyte) is placed in the central compartment.
- A membrane is inserted adjacent to the cathode on the inner side to minimize diffusion of methanol into the cathode thereby reducing the concentration of methanol near the cathode. In the absence of a membrane, methanol diffuses through the electrolyte into the cathode and undergoes oxidation.

The EMF the cell is 1.20V at 250CThe electrode reactions are:

At anode: $CH_3OH\ (l) + H_2O\ (l) \rightarrow CO_2\ (g) + 6H^+(aq) + 6e^-$

At cathode: $3/2\ O_2\ (g) + 6H^+\ (aq) + 6e^- \rightarrow 3H_2O\ (l)$.

Overall reaction: $CH_3OH\ (l) + 3/2\ O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)$.

Note: An advantage of the use of an acid electrolyte is that the CO2, a product of thereaction can be removed easily. In case of alkaline electrolyte (KOH), it combines with CO2 and gets converted into carbonate. This decreases the efficiency because of the increasing concentration polarization at the electrode surface and decreasing the conductivity if the electrolyte.

Applications:

- Military applications
- Large scale power production

POLYMER ELECTROLYTE MEMBRANE (PEM) FUEL CELL

Polymer electrolyte membrane (PEM) is also known as Proton-exchange membrane fuel cells (PEMFC), are a type of fuel cell being developed mainly for transport applications.

This fuel cell uses polymer as an ion exchange membrane such as Teflon as electrolyte. These membranes are superior conductors of protons and are used when operating temperatures are below 120^0C.

Construction:

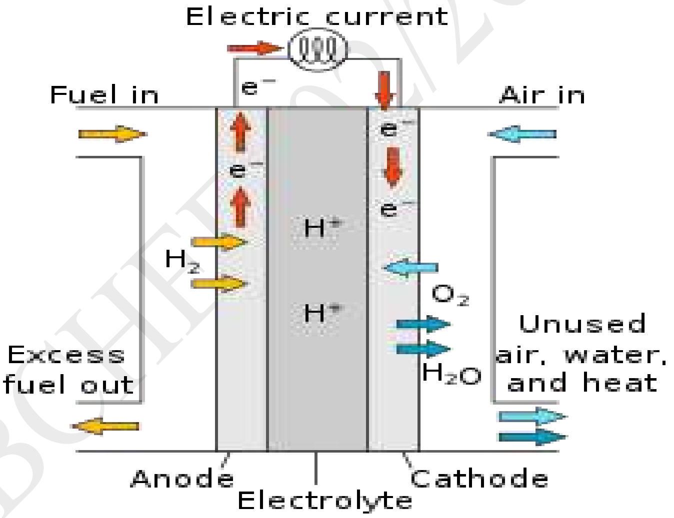
Anode : Porous carbon electrodes impregnated with Pt. are used as electrode.

Cathode: Porous carbon electrodes impregnated with Pt. are used as electrode.

Fuel : H_2

Oxidant : O_2/Air

Electrolyte : Polymer as an ion exchange membrane



Working Principle and reactions

- A proton exchange membrane fuel cell transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy
- A stream of hydrogen is delivered to the anode side. At the anode side itis catalytically split into protons and electrons.

  At the anode (oxidation): $H_2 \rightarrow 2H^+ + 2e^-$
- Protons permeate through the polymer electrolyte membrane to the cathode side.
- Meanwhile, a stream of oxygen is delivered to the cathode side
- Oxygen molecules react with the protons permeating through the polymer electrolyte membrane and the electrons arriving through the external circuit toform water molecules.

At the cathode (reduction): $1/2O_2+2H^++2e^-\rightarrow H_2O$

The overall cell reaction: $H_2+1/2O_2\rightarrow H_2O$

Applications: Transport applications, as well as for stationary fuel-cell applications andportable fuel-cell applications

Differentiate between fuel cell and a conventional battery.

	Fuel cell	**Battery (conventional cell)**
1	In Fuel cells reactants are fed from outside and the products are removed Constantly.	Batteries are not being supplied with reactants constantly. Reactants are the integral part of the battery
2	They do not store chemical energy. Fuel cells are energy conversion Devices	They store chemical energy. Batteries are energy storage devices
3	They offer high energy conversions i.e, are more efficient	Efficiency of a battery is low.
4	They operate as long as the reactants are supplied to the electrodes from outside and do not need recharging	They operate until reactants stored in it are completely used up and secondary batteries need recharging
5	No toxic species are formed in a fuel cell and are more eco-friendly	Less eco-friendly

SOLAR ENERGY

INTRODUCTION TO SOLAR ENERGY

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

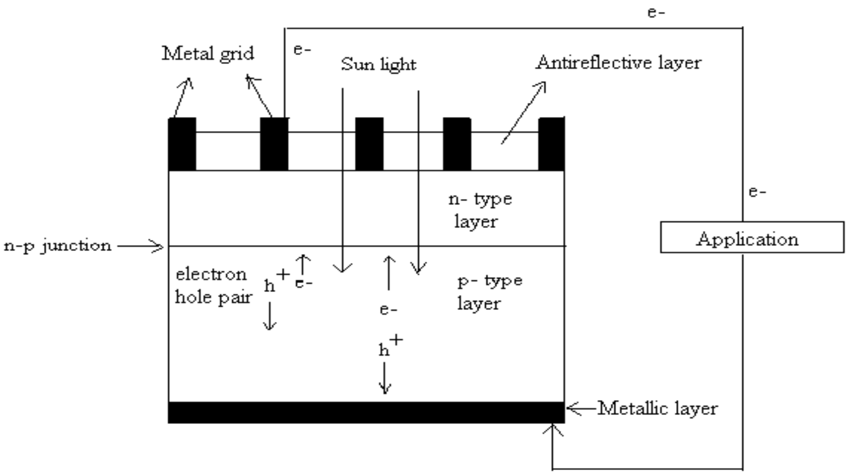
Applications of solar energy: Solar energy is most commonly used in calculators, watches and other portable electronic devices as power supply source. In remote village places solar energy is the only way to meet energy requirements for lighting, domestic water supply and irrigation by using solar pumps. Solar energy is directly used for cookingin solar cooker, for heating rooms to maintain warmth and for heating water.

PHOTOVOLTAIC CELLS OR SOLAR CELLS

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

Construction & working of a photovoltaic cell: The solar cell is a semiconductor diode. A typical photovoltaic cell is composed of a thin wafer consisting of a ultra thin layer of phosphorous doped (n-type) silicon on top of boron doped (p-type) silicon. Hence a p-n junction is formed between the two. A metallic grid forms one of the electrical contacts of the diode and allows light to fall on the semiconductor between the grid lines. An anti reflective layer between the grid lines increases the amount of light transmitted to the semiconductor. The cell's other electrical contact is formed by the metallic layer on the back of the solar cell. A conventional solar cell is shown in Fig.

When light radiation falls on the p-n junction diode, electron-hole pairs are generated by the absorption of the radiation. The electrons are drifted to and collected at the n-type end and the holes are drifted to and collected at the p-type end. When these two ends are electrically connected through a conductor, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced and available for use such as lighting spinning of fans, working of motors.



Solar cell structure

Applications

1. Toys, watches, calculators
2. Remote lighting systems
3. Solar water pumps
4. Satellites
5. Emergency power

Advantages of PV cells::

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

Disadvantages of PV cells:

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

Important Questions

1. Explain classification battery (a) Primary batteries (b) Secondary batteries (c) Reservebatteries.

2. Explain the construction, working and applications of Na-ion battery.

3. What is solid state battery? Explain the construction, working and applications of Li-polymer battery..

4. What are flow batteries? Explain the construction and working of Vanadium redox flowbattery. Mention its applications.

5. Define fuel cells?Explain the construction, working and applications of methanol-oxygen fuel cell.

6. Describe the construction, working and applications of polymer electrolyte membranefuel cell.

7. What are photovoltaic cells? Explain the construction and working of solar photovoltaiccell. Mention their advantages and disadvantages?

8. Define PV cells. List out advantages and disadvantages of PV cells.

MODULE 3
CORROSION AND ELECTRODE SYSTEM

SYLLABUS

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

E-waste Management: Introduction, sources, types, effects of e-waste on environment and human health, methods of disposal, advantages of recycling. Extraction of copper and gold from e-waste.

Self-learning:Recycling of PCB and battery components

CORROSION

INTRODUCTION

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

CORROSION

Corrosion is defined as "the process of deterioration or destruction of metals or alloys from its surface by the surrounding environment through chemical or electrochemical changes."

The process of corrosion is the transformation of pure metal into its undesired metallic compounds. The life of a metal object gets shortened by the corrosion process.

Example:

i. Rusting of iron – a reddish brown scale formation on iron and steel objects. It is due to the formation of hydrated ferric oxide.

ii. Green scales formed on copper vessels. It is due to the formation of basic cupric carbonate [$CuCO_3$ + $Cu(OH)_2$]

Cause of corrosion:

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

Effects of Corrosion/global loss

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

Chemical corrosion (Dry corrosion)

Chemical corrosion occurs due to the direct chemical reaction between the metal and the gases present in the corrosive environment. This type of corrosion is generally observed in the absence of moisture or conducting electrolyte medium. Therefore, it is also known as dry corrosion.

Eg: Oxidation of metals or alloys on exposure to oxygen in air. Reaction of corrosive gases such as HCl, H_2S, SO_2, Cl_2, F_2, NH_3 etc. with metal and alloy surfaces.

Electrochemical corrosion (Wet corrosion)

Electrochemical corrosion involves reactions in aqueous medium. The conducting surface of the metal undergoes an electrochemical reaction with the moisture and oxygen present in the atmosphere. This process can be explained on the basis of electrochemical theory of corrosion.

Electrochemical theory of corrosion

When a metal, such as iron/steel bar in concrete, is exposed to the environment, according to electrochemical theory corrosion of metal takes place due to the formation of anodic and cathodic regions on the same metal surface or when the two metals are in contact with each other. The electrons released at the anodic area are taken up by the cathodic area.

Following are the electrochemical changes occur gradually.

- Anodic and cathodic areas are formed resulting in the formation of minute galvanic cells.

- Oxidation (corrosion) takes place at the anodic area metal is converted into metal ions with the liberation of electrons and move towards cathode.
- The electrons released at the anodic area migrate to the cathodic area and reduction takes place.

Electrons flow from the anodic to cathodic area and cause reduction depending on the nature of the corrosive environment. Since the metal cannot be reduced further, metal atoms in the cathodic region are unaffected by the cathodic reaction.

Electrochemical theory of corrosion can be explained by taking iron as an example.

Step I: Reaction at anodic area

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

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

Step II: Reaction at cathodic area

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

1. ***In the presence of oxygen***: oxygen in the environment dissolves in the moisture
   a. In acidic medium, H^+ ions reduced to H_2O

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

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

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

      Both the reactions involve absorption oxygen.
2. ***In the absence of oxygen:***
   a. In acidic medium, H^+ ions reduced to hydrogen gas

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

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

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

      Both the reactions involve evolution of hydrogen gas.

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

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

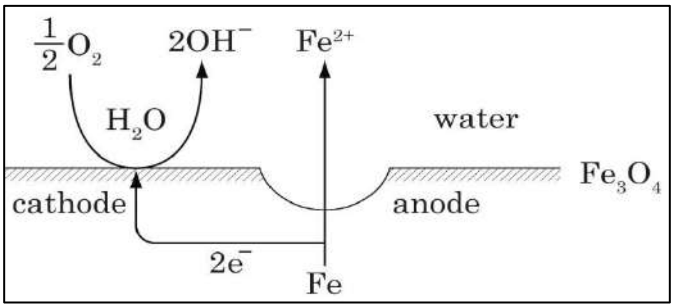
$Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2$

Step IV: Formation of Rust

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

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

b. In the limited amount of DO, $Fe(OH)_2$ is converted into black rust (ferrouos ferric oxide), $Fe_3O_4.3H_2O$.
$3Fe(OH)_2 + \frac{1}{2} O_2 \rightarrow Fe_3O_4.3H_2O$ (black rust)



TYPES OF CORROSION

1. Differential metal corrosion/Galvanic corrosion/bimetallic corrosion

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

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

The following reactions occur during differential metal corrosion.

At the anode : $M \longrightarrow M^{+n} + ne^-$

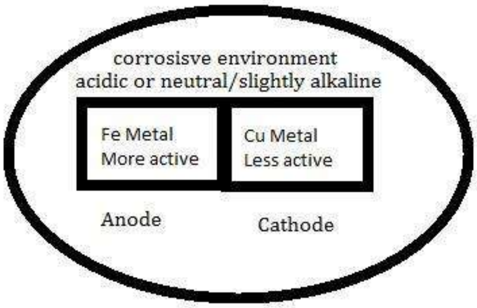
At the cathode : Depending on the nature of the corrosion environment the cathode reaction is either hydrogen evolution or oxygen absorption.

(i) $2H^{+\,+} 2e^- \longrightarrow H_{2\,(g)}$

(ii) $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

For example, if a piece of iron combined with copper is exposed to corrosive atmosphere. Iron acts as anode in the presence of copper (iron is placed above copper in the electrochemical series). In such case, iron undergoes corrosion and copper is unaffected.

Example: Let us consider a bimetallic sample of iron and copper



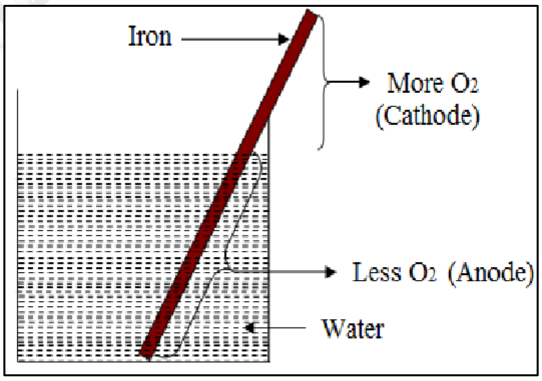
- The standard electrode potential of Fe is – 0.44 V which is less than that of Cu whose standard electrode potential is 0.34 V
- Hence in this case iron acts as anode and undergoes corrosion whereas copper acts as cathode and remains un attacked.

Differential aeration Corrosion

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

- Part of the metal exposed to lower concentration of oxygen will have lower potential and therefore acts as anode. This part undergoes corrosion.
- The other part of the metal exposed to higher concentration of oxygen acts as cathode and remains unaffected.
- ***At the anode*** (less O_2 concentration): $M \rightarrow M^{n+} + n e^-$
- ***At the cathode*** (more O_2 concentration): $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

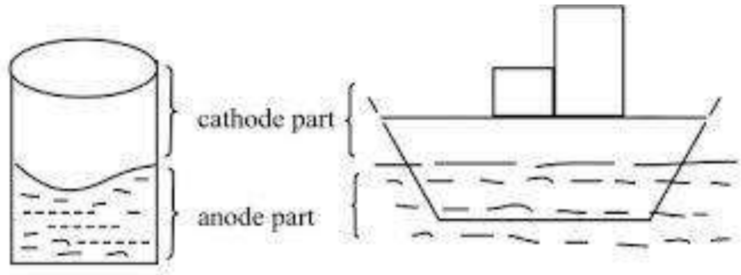
Examples



- Part of the nail inside the wall which is exposed to lower oxygen concentration than the exposed part, undergoes corrosion.
- Window rods inside the frame suffer corrosion but not the exposed parts.
- Metal under dirt, dust, scale, or water undergoes corrosion.
- Paper pins inside the paper get corroded, and the exposed part is free from corrosion.

Water line corrosion and pitting corrosion are the two cases of differential aeration corrosion.

Water line corrosion:



Water storage steel Tank

Ship in sea

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

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

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

$2Fe(OH)_2 + \frac{1}{2} O_2 + H_2O \rightarrow Fe_2O_3.3H_2O$ (Rust)

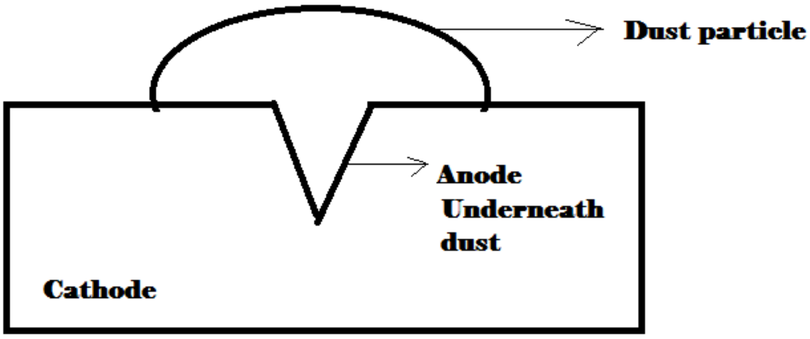
Pitting corrosion:

- Pitting corrosion is a localized corrosion on the small area of the metal surface resulting in the formation of pits or holes.
- The pitting corrosion is generally initiated by the deposition of sand, water drop, dust etc. or due to the breakdown of the protective film.
- The metal below the deposit is exposed to lower oxygen concentration acts as anode and the metal surrounding the deposit acts as cathode since it is exposed to higher concentration of oxygen.
- Corrosion starts under the dust resulting in a pit. The pit grows and ultimately may cause failure of the metal.

Corrosion reactions:

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

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



CORROSION CONTROL

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

The following methods are used to protect metals against corrosion:

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

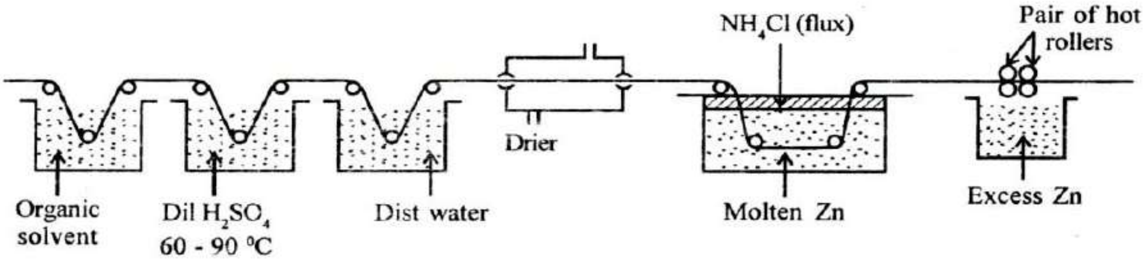
Galvanization:

Is an example of metal coating which involves the deposition of a protective metal over the surface of a base metal.

Definition: Galvanizing (Galvanization) is a process of coating a base metal surface with zinc metal. Galvanization is carried out by hot dipping method.

The galvanization process involves the following steps.

- The metal surface is first washed with organic solvents to remove oil and grease deposits.
- Rust and other deposits are removed by washing with dilute sulphuric acid (pickling).
- Finally the article is washed with water and air dried.
- The article is then dipped in a bath of molten zinc, maintained at $425\text{-}430^0$C and covered with a flux of ammonium chloride to prevent the oxidation of molten zinc.
- The superfluous (excess) zinc on the surface is removed by passing through a pair of hot rollers, which wipes out excess of zinc coating and produces a thin coating.



Galvanization of metal sheet

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

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

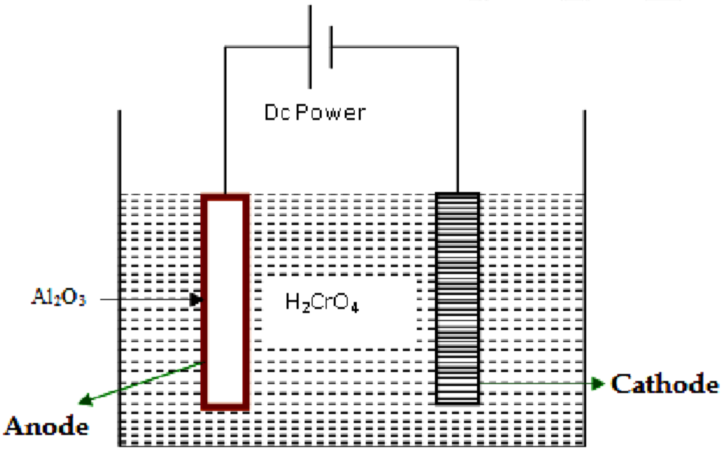
Anodization :

Anodizing: It involves the electrolytic oxidation of metal surface to produce a tightly adherent & durable oxide layer by passing electric current through an electrolyte to impart more protection against corrosion. Base metal is made as anode in an electrolytic bath of suitable composition, and by-passing direct electric current.

Anodized coating is generally produced on non-ferrous metals like Al, Zn, Mg and their alloys. The most used baths are chromic acid and sulphuric acid or their mixtures. After anodizing, the oxide coating is sealed by immersing in boiling water.

Anodizing of Aluminium involves the following steps.

Electrolytic cell:
Anode: Aluminum or required metal
Cathode: Cu / Steel/Lead
Electrolyte: 5-10 % chromic acid
or 10 % H_2SO_4
Temperature: 35°C
Voltage: 40 V
Current density: 10-100 A /m2



- The article to be anodized is degreased, thoroughly polished, connected to the anode and steel or copper or lead is made as the cathode.
- The electrolyte consists of 5-10 % chromic acid. The temperature of the bath is maintained at 35°C. A current density of 10-100 A/m^2 is applied which oxidizes the outer layer of Al to Al_2O_3. An oxide layers of Al_2O_3 with a thickness 2-8 µm is formed.
- The outer part of the oxide film formed may be slightly porous and it is sealed by dipping in boiling water. This treatment converts porous alumina at the surface of coating into its monohydrate ($Al_2O_3.H_2O$) which occupies more volume, thereby the pores are sealed.
- For higher thickness 10% H_2SO_4 can be used as the electrolyte.
- The article can be colored by immersing for about 20 minutes in an aqueous solution of the dye stuff at 50-60°C. Finally, the object is treated with nickel or cobalt acetate followed by boiling water treatment to improve corrosion resistance.

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

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

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

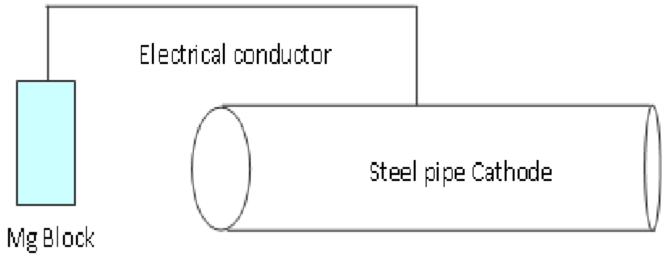
Applications: It is used to provide attractive, highly durable exteriors, roofs, ceilings, floor, lobbies, escalators and staircases, soap boxes, tiffin carriers, window frames etc.

Cathodic Protection:

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

Sacrificial anode method:

- In this method the metal to be protected from corrosion is converted into cathode by connecting into a metal which is anodic to it.
- The base metal is usually iron, copper or brass.
- Metals like Mg, Al and Zn are more active and hence are commonly used as sacrificial anodes.
- These metals being more active acts as anode undergo corrosion and supply electrons to the specimen.
- In this way the protected metals acts as cathode.
- Since anodic metals are scarified to protect the metal structure this technique is called sacrificial anode method.



Example: Mg or Zn block connected to steel pipelines

A magnesium block connected to a buried oil storage tank. Fig(a)

Mg bars are fixed to the sides of ocean-going ships to act as sacrificial anodes. Fig(b)

CORROSION PENETRATION RATE (CPR)

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

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

The Corrosion penetration rate also referred as corrosion rate.

Corrosion penetration rate depends on following factors;

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

Following formula is used to determine CPR

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

Where ,

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

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

Note-to remember

	mmpy	**mpy**
K	**87.6**	**534**
W	**mg**	**mg**
D	**g/cm^3**	**g/cm^3**
A	**cm^2**	**Inch^2**

Conversion factor
1m^2=100*100cm^2
1m^2=1550inch^2
1inch^2=6.45cm^2
1cm^2=0.155inch^2

PROBLEMS

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

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

Solution

To find mmpy

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

= 87.6x35x1000/8.4x100x6.45x365x24

= 0.064mmpy

To find mpy

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

= 534x35x1000/8.4x100x365x24

= 2.54mpy

E-WASTE MANAGEMENT

Electronic waste or e-waste is a term for electronic products that have become unwanted, non-working or obsolete and have essentially reached the end of their useful life. Because technology advances at such a high rate, many electronic devices become trash after a few short years of use.

Sources

E–waste refers to the generation of waste from the engineering world which is dominated by the use of electronic / electrical devices and equipment.

(a) Waste generated from the products used for data processing such as computers, computer devices like monitor, speakers, keyboards, printers, calculators, phones, digital / video cameras, radios.

(b) Calculators, electronic devices used for entertainment like TV, DVDs, CD players, VCRs and MP3 players.

(c) Equipment or devices used for communication like phones, landline phones, fax etc.

(d) Laboratory with equipment's such as calorimeters, hot plates, microscopes.

(e) Household equipment's such as vacuum cleaner, microwave ovens, washing machines, air conditioners etc.

Characteristics:

(a) Hazardous components in e-waste: Electronic waste consists of a large number of components of various sizes and shapes some of which contain hazardous component that need to be removed for separate treatment.

(b) Material composition of e-waste: E-waste contains a mixture of various metals, particularly copper, aluminium and steel attached to, covered with or mixed with various types of plastics and ceramics. Precious metals have a wide application in the manufacture of electronic appliances serving as contact material due to their high chemical stability and their good conducting properties. Platinum group metals are used among other things in switching contacts.

It is obvious that the copper and precious metals make-up more than 80 % of the value for most of the e-waste samples. Recovery of precious metals and copper remain as the major economic driver for a long time.

Types of e-waste

Any appliance that runs on electricity has the potential to cause damage to the environment if it is not disposed of in a responsible way. Common items electronic waste are:

- Large household appliances (refrigerators/freezers, washing machines, dishwashers)

- Small household appliances (toasters, coffee makers, irons, hairdryers)
- Information technology (IT) and telecommunications equipment (personal computers, telephones, mobile phones, laptops, printers, scanners, photocopiers)
- Consumer equipment (televisions, stereo equipment, electric toothbrushes)
- Lighting equipment (fluorescent lamps)
- Electrical and electronic tools (handheld drills, saws, screwdrivers)
- Toys, leisure and sports equipment
- Medical equipment systems (with the exception of all implanted and infected products)
- Monitoring and control instruments
- Automatic dispensers.

Pollutants in e-waste

Pollutants or toxins in e-waste are typically concentrated in circuit boards, batteries, plastics, and LCDs (liquid crystal displays). Pollutants and their occurrence in waste electrical and electronic equipment are:

Pollutants	Occurrence
Arsenic	Semiconductors, diodes, microwaves, LEDs (Light-emitting diodes), solar cells
Barium	Electron tubes, filler for plastic and rubber, lubricant additives
Brominated flame- proofing agent	Casing, circuit boards (plastic), cables and PVC cables
Cadmium	Batteries, pigments, solder, alloys, circuit boards, computer batteries, monitor cathode ray tubes (CRTs)
Chrome	Dyes/pigments, switches, solar
Cobalt	Insulators
Copper	Conducted in cables, copper ribbons, coils, circuitry, pigments
Lead	Lead rechargeable batteries, solar, transistors, lithium batteries, PVC (polyvinyl chloride) stabilizers, lasers, LEDs, thermoelectric elements, circuit boards
Liquid crystal	Displays
Lithium	Mobile telephones, photographic equipment, video equipment (batteries)
Mercury	Components in copper machines and steam irons; batteries in clocks and pocket calculators, switches, LCDs
Nickel	Alloys, batteries, relays, semiconductors, pigments
PCBs (polychlorinated biphenyls)	Transformers, capacitors, softening agents for paint, glue, plastic

Effect of e-waste on environment and human health:

The consequences of improper e-waste disposal in landfills or other non-dumping sites pose serious threats to current public health and can pollute ecosystems for generations to come. When electronics are improperly disposed and end up in landfills, toxic chemicals are released, impacting the earth's air, soil, water and ultimately, human health.

The Negative Effects on Air:

Contamination in the air occurs when e-waste is informally disposed by dismantling, shredding or melting the materials, releasing dust particles or toxins, such as dioxins, into the environment that cause air pollution and damage respiratory health. E-waste of little value is often burned, but burning also serves a way to get valuable metal from electronics, like copper. Chronic diseases and cancers are at a higher risk to occur when burning e-waste because it also releases fine particles, which can travel thousands of miles, creating numerous negative health risks to humans and animals. Higher value materials, such as gold and silver, are often removed from highly integrated electronics by using acids, desoldering, and other chemicals, which also release fumes in areas where recycling is not regulated properly.

The air pollution caused by e-waste impacts environment. Over time, air pollution can hurt water quality, soil and plant species, creating irreversible damage in ecosystems.

The Negative Effects on Soil and water:

When improper disposal of e-waste in regular landfills or in places where it is dumped illegally, heavy metals such as mercury, lithium, lead, and barium and flame retardants can seep directly from the e-waste into the soil, causing contamination of soil and underlying groundwater or contamination of crops that may be planted nearby or in the area in the future. When the soil is contaminated by heavy metals, the crops become vulnerable to absorbing these toxins, which can cause many illnesses and doesn't allow the farmland to be as productive as possible.

When large particles are released from burning, shredding or dismantling e-waste, they quickly re-deposit to the ground and contaminate the soil and water as well. The amount of soil contaminated depends on a range of factors including temperature, soil type, pH levels and soil composition.

Through these pathways, acidification and toxification are created in the soil and water, which is unsafe for animals, plants and human beings.

Brominated flame retardants:

Brominated flame retardants (BFRs) have routinely been added to consumer products for several decades in a successful effort to reduce fire-related injury and property damage. The widespread production and use of BFRs strong evidence of increasing contamination of the environment, wildlife, and people; and limited knowledge of potential effects heighten the importance of identifying emerging issues associated with the use of BFRs.

These do not decompose easily in the environment, and long term exposure can cause impaired memory function and learning. Pregnant women exposed to brominated flame retardants have been shown to give birth to babies with behavioural problems as it interferes with oestrogen and thyroid functioning.

As mentioned, electronic waste contains toxic components that are dangerous to human health, such as mercury, lead, cadmium, polybrominated flame retardants, barium and lithium. The negative health effects of these toxins on humans include brain, heart, liver, kidney and skeletal system damage.

Lead: Lead is a naturally-occurring element that can be harmful to humans when ingested or inhaled, particularly to children under the age of six. Lead found in most computer monitors and televisions, lead exposure leads to intellectual impairment in children and serious damages to human reproductive systems, the nervous system and blood. Lead poisoning can cause a number of adverse human health effects, but is particularly detrimental to the neurological development of children.

Cadmium: The kidney is the critical target organ for the general population as well as for occupationally exposed populations. Cadmium is known to accumulate in the human kidney for a relatively long time, from 20 to 30 years, and, at high doses, is also known to produce health effects on the respiratory system and has been associated with bone disease. Found in rechargeable batteries for laptop computer and other electronic devices, can cause damage to kidneys and bones.
Mercury: Elemental and methyl mercury are toxic to the central and peripheral nervous systems. The inhalation of mercury vapour can produce harmful effects on the nervous, digestive and immune systems, lungs and kidneys, and may be fatal. The inorganic salts of mercury are corrosive to the skin, eyes and gastrointestinal tract, and may induce kidney toxicity if ingested.

Neurological and behavioural disorders may be observed after inhalation, ingestion or dermal exposure of different mercury compounds. Symptoms include tremors, insomnia, memory loss, neuromuscular effects, headaches and cognitive and motor dysfunction. Kidney effects have been reported, ranging from increased protein in the urine to kidney failure. Mercury (Hg), which is used in lightening devices in flat screen monitors and televisions can cause damage to the breast milk.

Plastic compounds: Poly vinyl chloride (PVC) cabling is used for printed circuit boards, connectors, plastic covers and cables. When burnt or land-filled, these PVCs release dioxins that have harmful effects on human reproductive and immune systems.

Disposal methods

Land filling: This is the most common methodology of e-waste disposal. Soil is excavated and trenchers are making for burying the e-waste in it. However, landfill is not an environmentally sound process for disposing off the e-waste as toxic substances like Cd, Pb and Hg are released inside the soil and ground water.

Incineration: This is a controlled way of disposing off the e-waste and it involves combustion of electronic waste at high temperature in specially designed incinerators. This e-waste disposal method is quite advantageous as the waste volume is reduced extremely and energy obtained is also utilized separately. However it is also not free from disadvantages with the emission of the harmful gases, mercury and cadmium in the environment.

Reuse: Reuse of electronic equipment has first priority on the management of e-waste because the usable lifespan of equipment is extended to secondary market, resulting in a reduced volume of waste stream encompassing treatment.

Re-manufacturing: It is a process in which used products are dissembled, cleaned, repair or refurbished, reassembled and qualified for new or like - new equipment.

Recycle: Recycling of e-waste can be broadly divided into three major steps.

- Dis-assembly • Upgrading
- Refining

Advantages of Recycling E-Waste

The top 5 benefits of recycling e-waste include the following:

- Reduces Landfill Sites
- Preserves Natural Resources
- Prevents Toxic Chemicals from Polluting the Ecosystem
- Creates New Business & Employment Opportunities
- Promotes Mindful Consumerism.

Extraction of Gold and Copper from PCB's (e-waste)

E-waste contains 10mtimes more excessive concentration of gold compared to ores. Concentration of copper in PCB is 20-40 times more than that is present in the ore. Hence, e-waste can act as a vital source of precious metal and can satisfy their demand in various industries.
There are three stages in metal recovery by hydrothermal method

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

Pretreatment stage

In the pretreatment stage, e-waste is manually dismantled to separate various fractions like metals, ceramics, plastics, wood and paper. Technics such as gravity separation, electrostatic separation, Magnetic separation and eddy current separations are used to separate metals from other fractions.

Chemical treatment stage

In the chemical treatment step, targeted metals are leached into solution by treating with appropriate chemical reagents.
Acid leaching is the most common method used to extract copper. H_2SO_4 / HNO_3 in the presence of oxidizing agent H2O2 is used in the process.

$$Cu + \frac{1}{2} O_2 + 2H^+ \longrightarrow Cu^{2+} + H_2O$$

Cyanide leaching is the most common method used for to extract gold metal. Sodium salt of 3-nitrobenzene sulfonic acid with Potassium cyanide (KCN) in the presence of oxygen is used as leaching agent. A water-soluble dicyanoaurate gold complex is obtained in this process.

$$4Au + 8CN + O_2 + 2H_2 \longrightarrow 4\ Au(CN)_2^- + 4(OH)^-$$

Metal recovery stage

In this step, metal is recovered from leach solutions. Copper metal can be recovered by electrodeposition. Pure copper metal taken as cathode and inert anode are dipped in leaching solution. When current is applied, copper is electrodeposited on cathode.

Gold can also be extracted from leaching solution by electrodeposition of gold from dicyanoaurate gold complex. Pure gold metal is taken as cathode and inert metal like stainless taken as anode. Both are dipped in leaching solution containing gold cyanide complex. Under approximate electroplating conditions, gold from the leached solution is electrodeposited on cathode.

Question bank

1. Explain the electrochemical theory of rusting of iron. (Imp)
2. Define cathodic protection. Explain the sacrificial anode technique for prevention of corrosion.
3. Explain Differential metal corrosion.
4. Explain differential aeration corrosion with suitable examples. (Imp)
5. Explain waterline corrosion with examples.
6. Explain the process of galvanization with neat diagram. (Imp)
7. What is anodizing? Explain anodizing of aluminium.
8. Mention the sources of e-waste and explain the need for e-waste management.
9. Explain the extraction of gold and copper from e-waste. (Imp)
10. Explain the methods of disposal of e waste. (Imp)
11. What is the effect of e waste on environment and human health. (Imp

MODULE 4
NANOMATERIALS AND DISPLAY SYSTEM

SYLLABUS

Nanomaterials: Introduction, size dependent properties of nanomaterials (Surface area, Catalytic, Conducting), preparation of nanomaterials by sol-gel and co-precipitation method with example. Introduction, properties and applications. Nanofibers, Nanophotonics, Nanosensors.

Display Systems: Liquid crystals (LC's)-Introduction, classification, properties and application in Liquid Crystal Displays (LCD's). Properties and application of Organic Light Emitting Diodes (OLED's)and Quantum Light emitting diodes(QLED's).

Perovskite Materials: Introduction, properties and applications in optoelectronic devices.

Self-learning: Properties &electrochemical applications of carbon nanotubes and graphene.

Nano materials

Introduction: Nanomaterial's have one of its dimensions in the range of 1- 100 nm are known to use forcenturies.

Nano materials are promising because at Nano scale, its physical and chemical properties differ significantly from its bulk structured materials.

For instance, bulk silver is non-toxic whereas silver nanoparticles can kill viruses upon contact.

- Properties like electrical conductivity, colour and strength change when the Nano scale is reached.
- It is already having a significant commercial impact, which will assuredly increase in the future.Applications of Nanomaterial's in Real life

1. The range of commercial products available today is very broad, including stain-resistant andwrinkle free textiles, cosmetics, sunscreens, electronics, paints and varnishes etc.
2. Nano coatings and Nano composites are finding uses in consumer products, such as windows, sportsequipment, bicycles and automobiles.
3. There are UV- blocking coatings on glass bottles which protect beverages from damage by sunlight,and longer lasting tennis balls using butyl rubber/nano-clay composites.
4. Nano scale titanium dioxide for instance is finding application in cosmetics, sunblock cleans, and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings

General properties and applications of nanomaterial's

- Nano structured semiconductors are known to show various non-linear optical properties.
- Nano sized metallic powders have been used to produce gas tight materials dense parts and porous coatings
- Force transfer, for high density information storage and magnetic refrigeration.
- Nanostructured metal clusters and colloids have a special impact in catalytic applications.
- Nanostructured metal-oxide (MnO_2) finds application for rechargeable batteries for cars orconsumer goods.

Size dependent properties of nanomaterial's

Materials in the nanometre scale exhibit physical properties distinctively different from that of the bulk material

1. Surface area
2. Electrical properties
3. Optical properties
4. Catalytic properties
5. Thermal properties

Surface Area

1. When a bulk material is subdivided into individual nanomaterials, the total volume remains thesame, but the collective surface area is enormously increased.
2. Nanomaterial's have a large proportion of atoms existing at the surface.
3. Properties like catalytic activity gas adsorption and chemical reactivity depend on the surface area.
4. Therefore nanomaterial's can show specific surface related properties thatare not observed in bulk materials.

Example:

Bulk gold is catalytically inactive, but gold nanoparticles are catalytically very active for selective redox reaction.

Electrical properties

1. Some metals which are good conductor in bulk become semiconductor or insulator as their size isdecreased to nano level.
2. The reason is that the electronic bands in bulk material are continuous due to overlapping oforbitals of billions of atoms.
3. Nanomaterial's very few atoms or molecules are present and so the electronic bonds become separate and separation between different electronic states varies with the size of nanomaterial

Optical properties

1. The nanomaterial's of different size can scatter radiation of differentwavelengths.

   Example:

   Colour of few colloidal solutions is due to this scattering effect.
2. Nano particles of metals exhibit unique optical property called as surface'Plasmon resonance'.
3. When lights hit the surface of metals particle, electron present on the surface (Surface Plasmon) starts oscillating back and forth in a synchronized way in a small space and the effect is known as surface Plasmon resonance.
4. Depending on the frequency of oscillation resonating electrons capture radiation of differentwavelength.

Catalytic properties

1. The catalytic property of materials depends on particle size.
2. If the size of the particles reduces from bulk to Nano scale, surface to volume increases drastically,that leads to very high catalytic activity of same material.

Example:

Catalytic properties of gold nanoparticles. Although bulk gold samples are practically inert, nanometre sized gold particles have been proven to be highly active for several reactions, including

- Low- temperature oxidation of CO
- Partial oxidation of hydrocarbons.
- The water-gas shift reaction.
- Reduction of nitrogen oxides when dispersed over certain oxides and carbides.

Thermal properties (Melting point)

1. Melting point is defined as the temperature at which the atoms, ions or molecules in a substance have enough energy to overcome the intermolecular forces that hold them in a fixed position in a solid.
2. As the size of the material decreases to Nano scale, their melting point decreases. Because surface atoms are in contact with only fewer atoms in nanomaterial's and require lesser energy to overcome inter-molecular forces.

Synthesis of nanomaterial

There are two approaches to the synthesis of nanomaterials

1. Bottom up synthesis
2. Top-down synthesis

In the bottom-up approach, molecular components arrange themselves into more complex assemblies'atom-by-atom, molecule-by-molecule, cluster-by- cluster from the bottom.

Example:

Growth of a crystal

In the **top-down approach**, Nano scale devices are created by using larger externally controlled devices to direct their assembly. The top-down approach often uses the traditional workshop or micro-fabrication methods in which externally controlled tools are used to cut, mill, shape and order. Attrition and millingfor making nanoparticles are typical top-down processes.

Bottom-up approaches, in contrast arrange molecular components themselves into some useful conformation using concept of molecular self -assembly. The bottom -up approach has been well knownto the chemists for a long time.

This approach plays a very important role in preparing nanomaterials having very small size where the top-down process cannot deal with the very tiny objects.

The **bottom-up approach** generally produces nanostructure with fewer defects as compared to the nanostructures produced by the top-down approach.

The main driving force behind the bottom-up approach is the reduction in Gibbs free energy. Therefore,the materials produced are close to their equilibrium state.

In top-down techniques, significant crystallographic defects can be introduced to the processed patterns. Example Nanowires made by lithography are not smooth and can contain a lot of impurities and structuraldefects on its surface.

In spite of the defects, the top down approach plays an important role in the synthesis and fabrication of nanomaterials. The present state of nanoscience can be viewed as an amalgamation of bottom up chemistry and top-down engineering techniques.

Synthesis by Sol-Gel method

Sol-gel method of synthesizing nanomaterial's is very popular amongst chemists andis widely employed to prepare oxide nanomaterial.

The sol-gel process can be characterized by a series of distinct steps.

1. Preparation of sol

A stable colloidal solution called sol is prepared. (The sol is a liquid suspension of solid particles ranging in size from 1nm to 1 micron). It is prepared by hydrolysis and partial condensation of precursors such as metal alkoxide.

$\text{M-O-R} + H_2O \rightarrow \text{M-OH} + \text{ROH}$ (hydrolysis)

$\text{M-O-R} + \text{M-OH} \rightarrow \text{MOM} + \text{ROH}$

2. Conversion of Sol to Gel

Further condensation of sol into a three-dimensional network produces a gel material (The gel is a diphasic material in which the solids encapsulate the solvent)

3. Aging of the Gel

Polycondensation reaction continues until the gel transforms into a solid mass accompanied by contraction of the gel networks and expulsion of solvent from gel pores. The aging process of gels can exceed 7 days.

4. Drying of Gel

Water and other volatile liquid are removed from the gel network.
If isolated by thermal evaporation, the resulting monolith is termed a Xerogel. If the solvent (such aswater) is extracted under-critical or near super critical conditions, the product is an aerogel.

5. Dehydration

To stabilize the gel against any rehydration the surface-bound M-OH groups are removed by calcining(heating) the monolith at temperature up to 800oC.
The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

Advantages Sol-gel method

- Low temperature route (below 2000C)
- Uniform particle size distribution
- Can easily shape materials into complex geometries in gel state
- Simple, effective method to produce high quality coatings

Co-precipitation method

Introduction:

- Simultaneous occurrence of nucleation growth, coarsening’s and /or agglomeration.
- Co-precipitation reaction exhibits the following characteristics.
- Insoluble species-high super-saturation
- Nucleation is a key step
- Ostwald ripening and aggregation size, morphology, and properties of the products.
- Chemical reaction

Typical Co-precipitation method

Metals-reduction from aqueous solution, electrochemical reduction, and decomposition of metal organic precursors.

1. Oxides-aqueous and non-aqueous solution.
2. Metal chalcogenides-reaction precursors.
3. Micro-wave/Sonicated assisted Co-Precipitation.

Advantages

- Easy control of particle size and composition
- Various possibilities to modify the particle surface state and all homogeneity.
- Low- temperature
- Energy efficient
- Do not involve use of organic solvent.

Disadvantages

- Not applicable to unchanged species.
- Trace impurities may also get precipitated with product.
- Time consuming.
- Batch to batch reproducibility problem.
- This method does not work well if the reactants have very different precipitation rates**.**

Synthesis of the magnetite nanoparticles (Coprecipitation method)

Material required

- Materials Ferrous chloride tetrahydrate (AR grade,) and ferric chloride anhydrous (AR grade,) wereused as the precursors.
- Ammonium hydroxide 25 wt. % NH3 in water (AR grade,) was used as the precipitating agent.
- Oleic acid (AR grade,) and hexanoic acid (AR grade,) were used as the coating agents.
- Ethanol (AR grade) was used to remove the excessive coating agent. All of the materials were usedwithout further purification.
- Water was deionized prior to use.

Synthesis of the magnetite nanoparticles

(a) The magnetite nanoparticles were prepared via the chemical coprecipitation method by the following 1.5 g of $FeCl_2·4H_2O$ and 3.0 g of $FeCl_3$, with the molar ratio of ferric ion to ferrous ion in the solution of 2.45, were dissolved in 100 ml of deionized water under a nitrogen gas flow with vigorous stirring at various temperatures (0–90 ◦C).

(b) A 10 ml of 25 wt% NH_4OH (excess base concentration) and various concentrations of the coating agents (oleic acid or hexanoic acid at concentrations between 0.2 and 1.0%, v/v) were added to the solution, then the solution color changed from orange to black rapidly.

(c) The coated magnetite nanoparticles were filtered and thoroughly washed with deionized water to remove chloride ions and then washed with ethanol several times to remove excess coating agent, and finally dried in a vacuum at 80 ◦C for 24 h.

The bare magnetite nanoparticles were prepared by the same procedure except without the coating agent and ethanol.

Nano fibres

Nanofibers are defined as fibers with diameters less than 100 nm. In the fabric industry, this classification is often extended to include fibers as large as 1,000 nm diameter, which referred to microfibers.

Nanofibers properties

a. Nanofibers have excellent mechanical properties.
b. They have satisfactory biodegradability along with nontoxic biodegradability.
c. Nanofibers provide higher surface area, when used as Nano fillers reduce the chain mobility. These can carry load, increase toughness, and abrasion resistance.
d. Carbon nanofibers, polymer nanofibers, graphite nanofibers, collagen nanofibers, cellulose nanofibers, etc.,
e. Nanofibers are used in making different textile materials with desired characteristics. Nanofibers have attracted a great deal of attention due to their remarkable properties.
f. Compared to conventional fibrous structures, Nano fibers are lightweight with small diameters, controllable pore structures and high surface-to volume ratio, making them ideal for use in

applications as varied as filtration, sensors, protective clothing, tissue engineering, functional materials and energy storage

Applications of nanofibers

- CNFs are very suitable for electrical and thermal conductivity applications due to their high degreeof crystalline orientation.
- The various CNF-based composites as gas sensors to detect H_2S, NH_3, NO_2, and explosive gases (CO, CH_4, H_2, and ethanol) at low ppm concentrations.
- They proved that this fiber mat has better drug delivery properties with excellent clearance of undelivered fibers with hemo compatibility and low toxicity post intravenous administration.
- CNFs have unique characteristics such as high electronic conductivity, high surface area, easy functionalization, and insignificant toxicity among all CNM, including CNTs, and are extensively used in various end applications including agriculture
- The important application examples reviewed include carbon and polymer nanofibers in structural carbon fiber reinforced polymer (CFRP) matrix composites, polymer nano fiber-reinforced nano composites for medical use and modification of thermosetting polymer by polymer/CNF composite nanofibers.

Definition Nanophotonics or nano-optics Definition:

Nanophotonics or nano-optics is a part of nanotechnology that investigates the behavior of light on nanometer scales as well as interactions of nanometer- sized objects with light. Nanophotonics is also considered a branch of electrical engineering, optics, and optical engineering—as well as being a branchof nanotechnology

Nanophotonics properties

- In Nanophotonics, material is structured at the nanoscale in order to create new optical properties for a large variety of applications. Prominent examples of commercial nanophotonic devices are diffractive optical elements (DOEs) (including Fresnel lenses and blazed gratings) or distributed feedback lasers (DFB).
- photonic crystals,
- photonic metamaterials, and
- Plasmonic elements.
- In photonic crystals, periodic optical nanostructures result in photonic bandgaps equivalent to electronic bandgaps in crystalline material. The resulting optical properties, where certain optical waves are not propagating, are used in applications including optoelectronic devices.
- Some vertical-cavity surface-emitting lasers (VCSELs), for example, use metasurfaces in the formof sub-wavelength gratings on the laser emission window.
- The top surface gratings develop birefringence effects, which, as a consequence, lead to laser modeselection in VCSELs for certain modes with specific light polarizations.
- The active zone design, the distributed Bragg reflector, and the top grating structure in modern VCSELs together form a complex nanoscale laser system, which needs to be built with the highest precision.
- It has a wide range of applications in areas such as biosensors, optical data transfer, or even innovative photovoltaic cells.

- Non-classical plasmonic light propagation in combination with advanced nm–scale device structuring capabilities provided, for example, by electron beam lithography (EBL) offers great opportunities to design innovative devices for various applications.

Application of Nanophotonics

1. Researchers have investigated a variety of nanophotonic techniques to intensify light in the optimallocations within a solar cell.
2. Nanophotonics has also been implicated in aiding the controlled and ondemand release of anti- cancer therapeutics like adriamycin from nanoporous optical antennas to target triple-negative breast cancer and mitigate exocytosis anti-cancer drug resistance mechanisms and therefore circumvent toxicity to normal systemic tissues and cells.
3. It also allows sensitive spectroscopy measurements of even single molecules located in the hot-spot, unlike traditional spectroscopy methods which take an average over millions or billions of molecules.
4. Nanophotonics in the form of subwavelength near-field optical structures, either separate from the recording media, or integrated into the recording media, were used to achieve optical recording densities much higher than the diffraction limit allows
5. The band-gap engineered titanium dioxide is used as a photoanode in efficient photolytic and photo- electro-chemical production of hydrogen fuel from sunlight and water.
6. Silicon photonics is a silicon-based subfield of nanophotonics in which nano-scale structures of the optoelectronic devices realized on silicon substrates and that are capable to control both light and electrons

Nano sensors Definition

"Nanosensors are chemical or mechanical sensors that can be used to detect the presence of chemical species and nanoparticles, or monitor physical parameters such as temperature, on the nanoscale"

Nano sensors being nanometre in scale have the ability to detect the minute particles.

Some of the uses of Nano sensors are:

- In medical diagnostics and understanding neurophysiology;
- In pollution monitoring to detect various chemicals;
- To monitor temperature, humidity, displacement, etc.;
- To monitor plant signalling and metabolism to understand plant biology.

Working principle of Nano sensors

- Nano sensors possess the capability to measure to the point of single molecule level.
- The components of Nano sensors include an analyte, sensor, transducer (a device which converts one form of energy to another) and detector.
- Normally Nano sensors work by tracking the electrical changes in the sensor materials.
- The analyte diffuses from the solution to the surface of the sensor and reacts specifically and efficiently, this changes the physicochemical properties of the transducer surface, which leads to a change in the optical or electronic properties of the surface of transducer, this change is converted into electrical signal which is detected. This is shown below

Properties of Nano-sensor

- Optical Nano sensors measures change in light intensity;
- Electrochemical Nano sensors measures change in electric distribution; Piezoelectric Nano sensorsmeasures change in mass;
- Calorimetric Nano sensors measures change in heat.

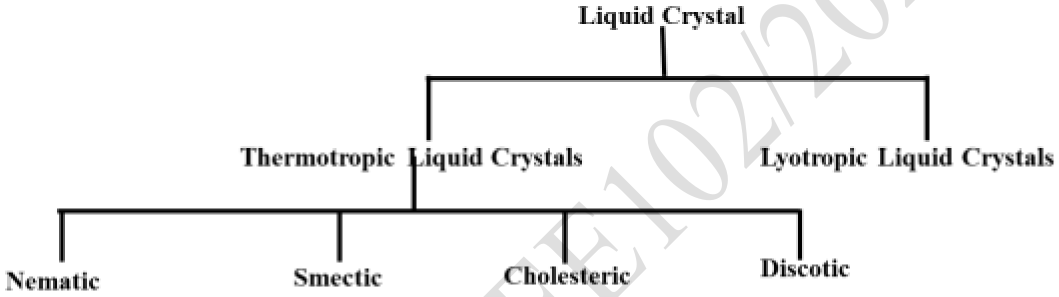
Application Nano sensors

- To detect various chemicals in gases for pollution monitoring
- For medical diagnostic purposes either as blood borne sensors or in labon-a-chip type devices
- To monitor physical parameters such as temperature, displacement and flow
- To monitor plant signaling and metabolism to understand plant biology
- To study neurotransmitters in brain for understanding neurophysiology.

LIQUID CRYSTALS

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

Classification:



Liquid crystals are classified into two types

Thermotropic liquid crystals

Lyotropic liquid crystals

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

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

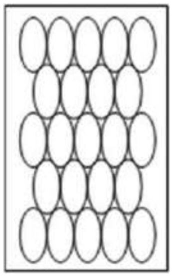
p-cholesteryl benzoate (Solid) $\xrightarrow{145°C}$ *p*-cholesteryl benzoate (liquid crystal)

Types of Thermotropic liquid crystals:

There are four types

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

a) Nematic Liquid Crystals (NLC)

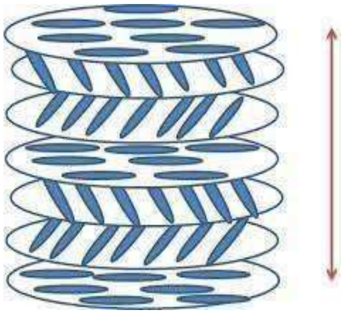


1. These are formed by the compounds that are optically inactive.
2. The molecules have elongated shape and are oriented parallel to thedirector.
3. These molecules possess intermolecular force of the attraction such that they stay parallel to one another to form nematic liquid crystals.

Ex: a) P-Azoxy Anisole (PAA)

b) P-Azoxy Phenetole

b. Chiral Liquid Crystals or Cholesteric Liquid Crystals



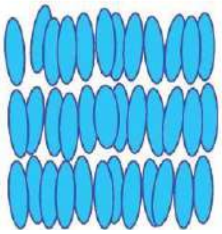
1. These are formed by optically active compounds having chiralcenter.
2. Hence molecules acquire spontaneous twist about an axis normal to molecular direction.
3. The twist may be right or left depending on molecular conformation.
4. Molecules in successive layers are slightly twisted and form helical pattern.

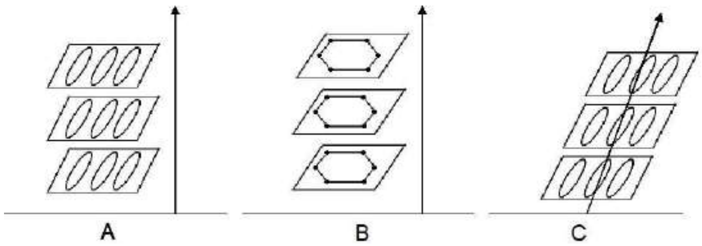
Ex: a) Cholesteryl benzoate

b) Cholesteryl formate etc.

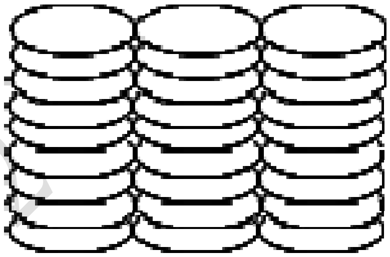
c. Smectic Liquid Crystals (SLC):

1. These liquid crystals have small amount of positional order and orientational order.
2. If the director is perpendicular to the plane, it is called smectic A. These are least ordered of the Orthogonal smectic phases
3. If the director is perpendicular to the plane and molecules are arranged in hexagonal order, it is called smectic B.
4. If the director makes an angle other than 90°, it is called smectic C.





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



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

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

Ex: 1) Soap water mixture

2) Phospholipid water mixture

Properties

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

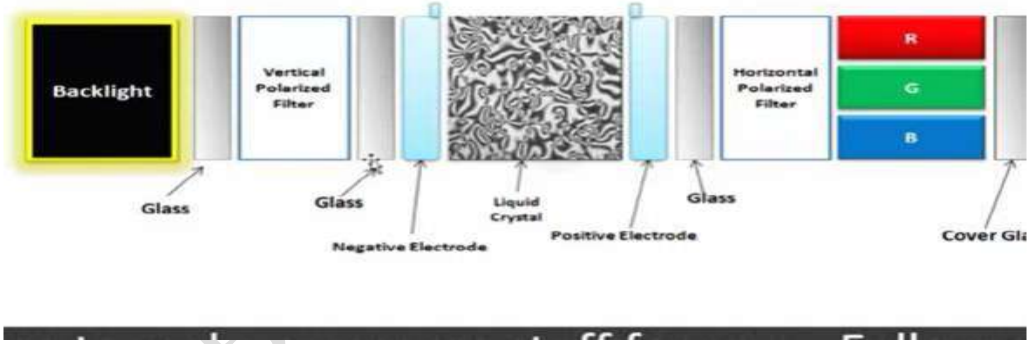
Applications of liquid crystals:

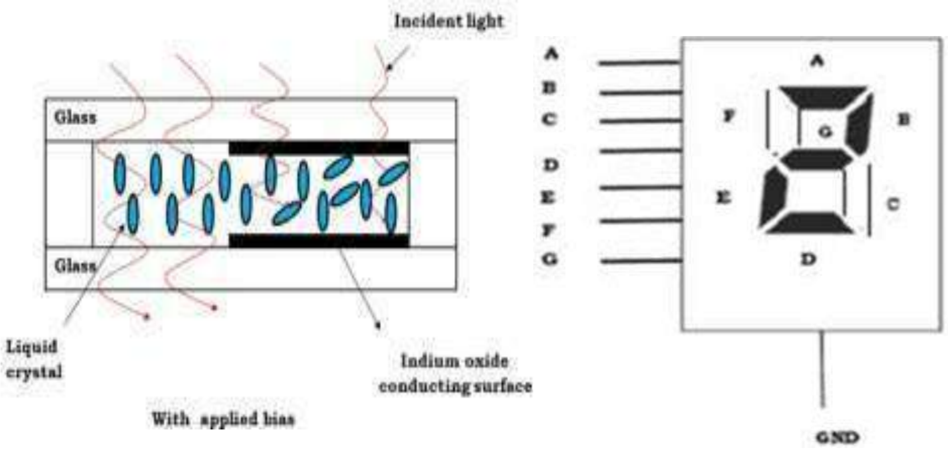
1. The liquid crystal layer in LCDs allows for the display of images and text through the use of electrical currents that control the orientation of the crystals.
2. Liquid crystals are used in watches, calculators, mobile telephones, laptops, computers etc.
3. These are used in blood pressure instrument,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

Application of Liquid Crystal in Display System (LCD):

Working principle:

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





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

For Example,

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

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

Organic Light Emitting Diodes (OLED's)

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

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

Properties:

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

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

Applications

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

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

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

4. OLEDs can also be architectural lighting.

Quantum Light Emitting Diodes (QLED's)

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

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

Properties:

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

Applications

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

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

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

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

PEROVSKITE MATERIALS –

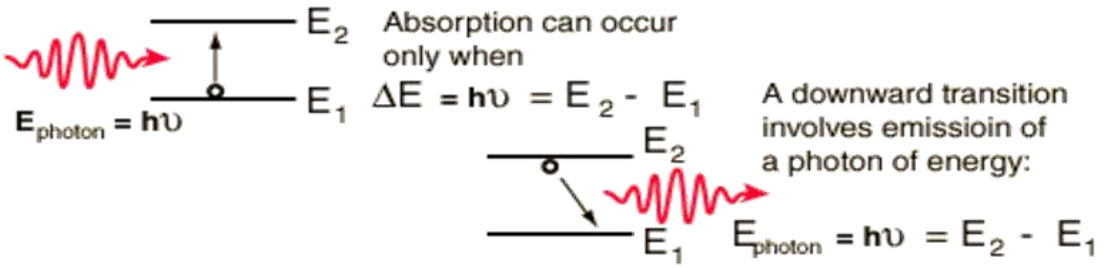
- Perovskite materials are 3 dimensional ABX_3 type materials where A is an organic cation commonly methylammonium cation, B is the metal cation either Pb^{+2} or Sn^{+2} and X is a halide ion like chloride, bromide or iodide.
- This material has cubic structure. The hybrid of organic and inorganic perovskites have strong intermolecular hydrogen bonds between amino and halide group ions.
- The metals of group 14 including exibit Pb^{+2} or Sn^{+2} good optoelectronic properties and potential for low temperature device fabrication.
- Use of least electronegative halide anions improves the Perovskite structure for strong absorption over wide band gaps.
- Because of all the above properties perovskite materials are used in making Optoelectronic devices

Optoelectronic Devices

- Optoelectronic devices are electronic devices that can strongly interact with light. They can absorb light and converting light into electrical signals or generate light from electrical energy.
- These are the devices which operate on both light and electrical currents.
- The light used which may be in the visible, infrared or ultraviolet spectral region.

Working Principle

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



Properties and applications in optoelectronic devices

The hybrid organic and inorganic perovskites have some excellent properties that made them best functional materials for optoelectronic devices. Few important properties are

1. Long electron hole diffusion lengths
2. Ultra-fast charge transportation
3. High dielectric constant
4. Swift charge recombination
5. Long carrier lifetimes
6. Direct bandgaps for stronger and broader absorption with larger absorption coefficient
7. Low-cost production and ease of processing and fabrication.

Application in Optoelectronics Devices

- Photodiode- which convert optical signal into electrical energy, used for telecommunication
- Solar Cells – which convert light energy into electrical energy
- Light Emitting Diodes – which convert electrical energy into light, used for display, lighting and remote control.
- Laser Diodes – Data storage

Important questions

1. Explain the properties and application of nanomaterials?
2. Explain the preparation of nanomaterial by sol gel method.
3. Explain the properties and applications of nanophotonics and nanosensors,
4. Explain the classification of liquid crystals. Mention any four properties and applications of liquid crystals.
5. Discuss the working of Liquid Crystal Display.
6. What is OLED? Mention any four properties and applications of OLED.
7. What is QLED? Mention any four properties and applications of QLED.
8. Explain the properties and applications of perovskite materials.

MODULE 5
SENSORS IN ANALYTICAL TECHNIQUES

SYLLABUS

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

Sensors: Introduction, working principle and applications of Conductometric sensors, Electrochemical sensors, Thermometric sensors, and Optical sensors.

Analytical Techniques: Introduction, principle and instrumentation of Colorimetric sensors; its application in the estimation of copper, principle and instrumentation of Potentiometric sensors; principle and instrumentation of its application in the estimation of iron, Conductometric sensors; its application in the estimation of weak acid.

Self-learning: IR and UV-Visiblespectroscopy.

ELECTRODE SYSTEM

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

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

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

CELL TERMINOLOGY

- **Current:** The flow of electrons through a wire or any conducting medium is called current.
- **Anode** The anode is the negative that releases electrons to the external circuit and oxidizes during the electrochemical reaction.
- **Cathode** The cathode is the positive electrode that acquires electrons from the external circuit and is reduced during the electrochemical reaction.

- **Singe Electrode/Half-cell** A device consisting of a single electrode immersed in an electrolytic solution and thus developing a definite potential difference.

- **Single electrode potential or electrode potential (E):** The tendency of an electrode to lose (oxidation potential) or gain (reduction potential) electrons when it is in contact with the solution of its own ions.

Or

The potential developed when an electrode is in equilibrium with a solution of its own ions. It is denoted by “E”.

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

Ex: $E^0_{Zn} = -0.76V$ & $E^0_{Cu} = +0.34V$

- **Electromotive force (EMF) of a cell:** The maximum potential difference between the electrodes of Galvanic cell. It is denoted by EMF or E_{cell}.

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

TYPES OF ELECTRODES

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

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

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

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

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

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

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

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

ION SELECTIVE ELECTRODE

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

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

External reference electrode — Ion selective electrode

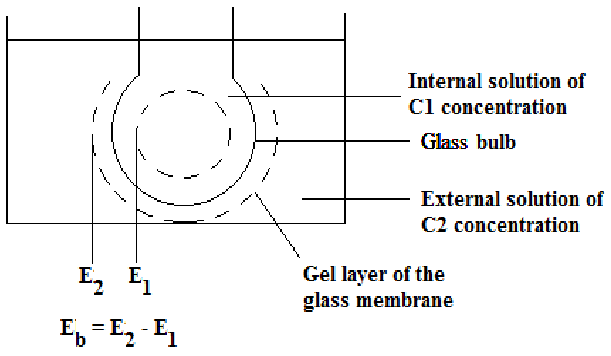
GLASS ELECTRODE

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

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

Working principle:

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



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

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

$$E_B = E_2 - E_1$$

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

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

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

Since concentration of C_1 is known,

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

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

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

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

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

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

The membrane undergoes an ion exchange reaction; Na^+ ions on the glass are exchanged for H^+ ions. The boundary potential established due to the above reaction is mainly responsible for the glass electrode potential E_G is given by

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

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

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

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

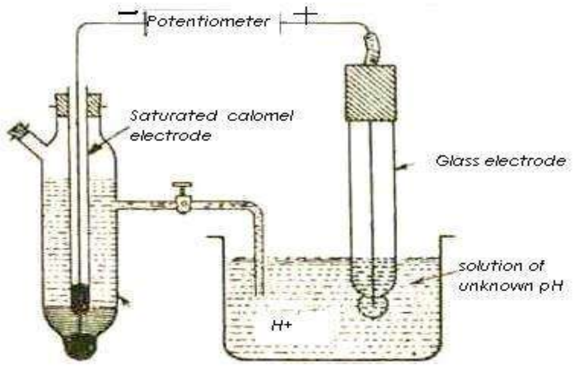
$$\mathbf{E_G = E_G^0 - 0.0591\ pH} \ldots\ldots\ldots\ldots (6)$$

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

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

Determination of pH of the solution by using glass electrode

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



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

or

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

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

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

$= E_G - E_{cal}$

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

$0.0591pH = E^o_G - E_{CAL} - E_{CE}$

Therefore, **pH =** $\dfrac{E^o_G - E_{CAL} - E_{CE}}{0.0591}$

Where, E^0_G and E_{cal} are constants. By substituting E_{cell} value, p^H of an unknown solution is calculated.
Note: E^0_G value is evaluated by dipping the glass electrode in a solution of known P^H and measuring EMF of the cell formed when combined with calomel electrode.

REFERENCE ELECTRODE

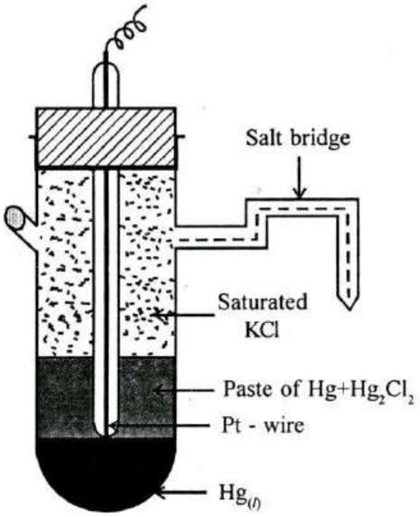
Any electrode of constant and reproducible potential, used to determine the potential of other electrode is called reference electrode.

Ex: Standard hydrogen electrode — primary reference electrode
Calomel electrode — secondary reference electrode
Ag-AgCl electrode — secondary reference electrode

Construction, working and applications of calomel electrode

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

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



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

As anode:	**As cathode:**
$2Hg \rightarrow Hg_2^{2+} + 2e^-$	$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2Cl^-$
$\underline{Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2}$	$\underline{Hg_2^{2+} + 2e^- \rightarrow 2Hg}$
$2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$

The net reversible electrode reaction is

$$½\ Hg_2Cl_2 + e^- \rightarrow Hg\ (l) + Cl^-\ (aq)$$

Electrode potential of calomel electrode is given by:

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

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

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

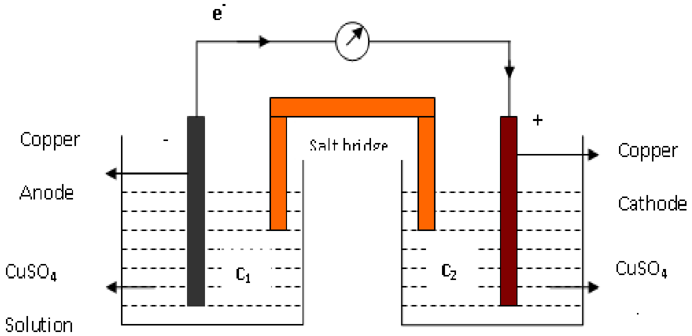
Advantages of calomel electrode (a secondary reference electrode):

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

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

CONCENTRATION CELLS

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



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

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

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

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

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

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

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

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

Applications: Used to determine the valence state of metal ions

SENSORS

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

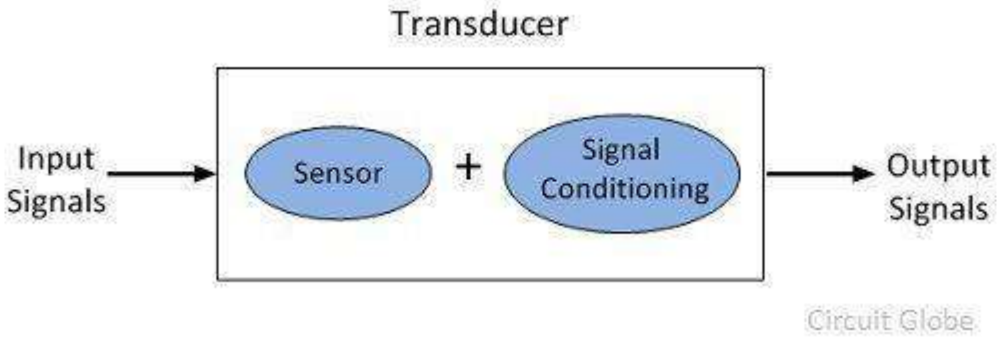
Sensors are found in a wide range of applications, from industrial automation and control to consumer electronics and healthcare. For example, sensors are used in automobiles to monitor engine performance, in smartphones to detect user input and orientation, and in medical devices to monitor vital signs.

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

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

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

Components of sensors



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

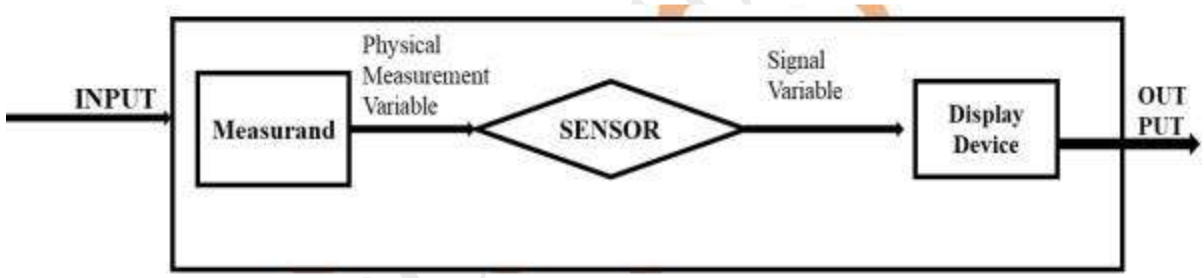
Measurement process for the instrumentation model

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

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

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

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



CONDUCTOMETRIC SENSORS:

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

Principle:

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

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

$$E = I\,R$$

Where; I → current, R→ Resistance

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

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

$$R = \text{Ᵽ}.\ l/a$$

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

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

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

Where l/a is known as the cell constant

'R' is the resistance of solution

Instrumentation and procedure

The instrument used for measurement of conductance is called conductometer.

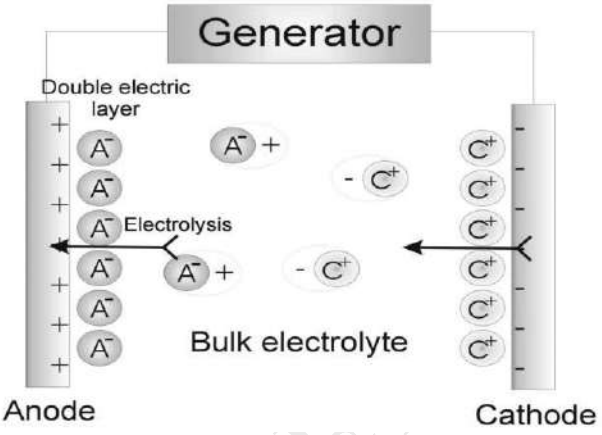
It consists of,

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

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

Working

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



Applications:

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

ELECTROCHEMICAL SENSORS

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

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

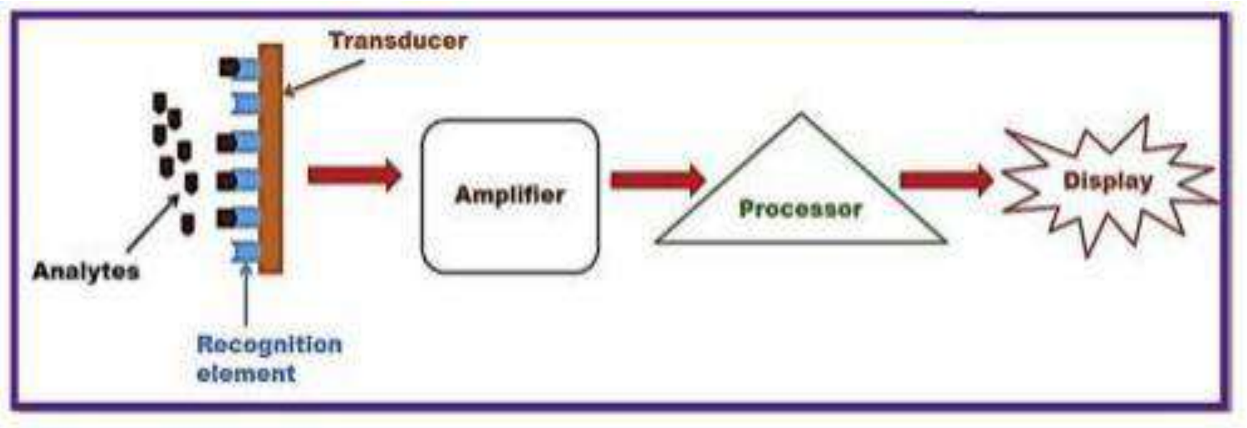
Electrochemical sensors divided into several types based on their mechanism of operation and the type of reaction involved.

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

Working principle

An electrochemical sensor mainly consists of two main components,

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



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

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

Applications

- Electrochemical sensors are considered attractive tools to determine important molecules or biomarkers (BP,temp.) that are used for the diagnosis of diseases and disorders.
- They are used for the monitoring of toxic levels of different substances in food quality and environmental control.
- The biosensor application areas of these sensors extend to medical and biomedical applications, process control, bioreactors, quality control, agriculture, bacterial and viral diagnosis, industrial wastewater control.
- The oxygen sensors are used to determine dissolved oxygen in boiler water and to monitor dissolved oxygen concentrations in hydrogen fuel cell..
- Used in water analysis and environmental monitoring.

- Used in soil parameter analysis and in agricultural applications

OPTICAL SENSORS

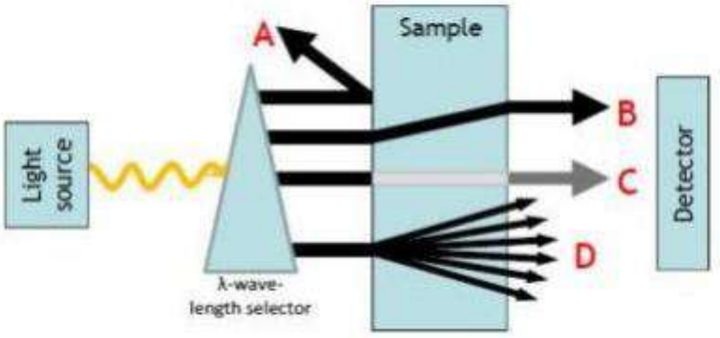
Optical sensors are devices that use light and converts in to electric signals for detecting and measuring physical or chemical properties of a sample.

Example: (photometric) Colorimetric Sensors

Working Principle:

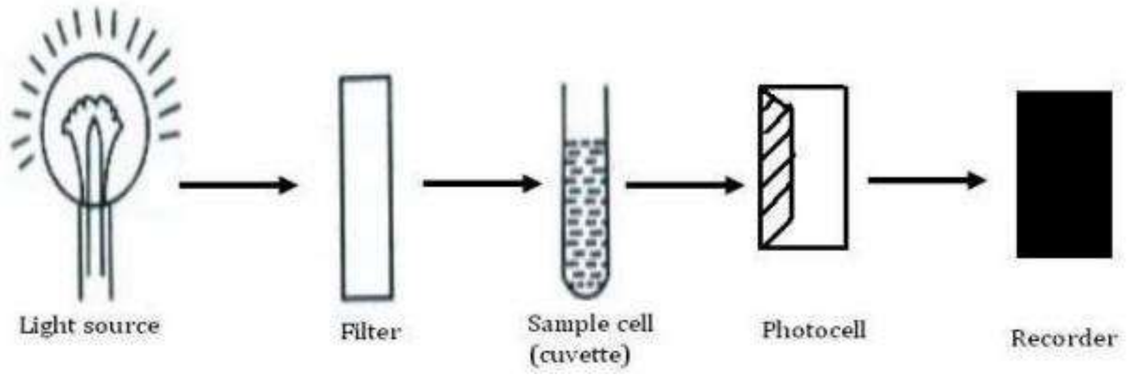
Optical sensors use visible ,IR and ultraviolet light to interrogate sensors for analysis.

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



Optical sensors working (Colorimetric Sensors)

- A monochromatic light is pass through analyte at particular wavelength.
- A part of light is absorbed by the analyte.
- The absorbance depends on the concentration of the solution and the path length of the light through the solution.
- The photocell converts emitted light into electrical signal
- These signals are recorded and displayed.



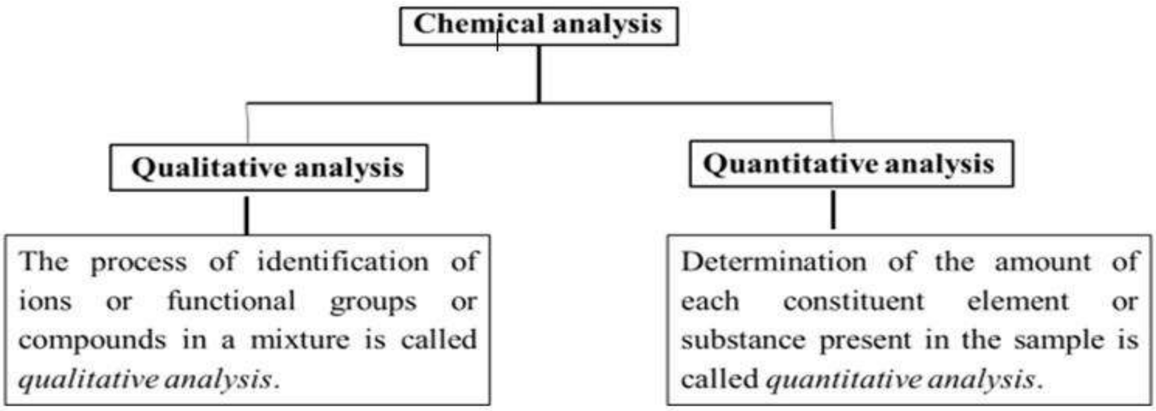
1. **Source**: tungsten bulb or lamp is used as a light source.
2. **Filter:** It is a device to provide desired wavelength range
3. **Sample cell:** sample is hold in glass cell.
4. **Photocell**: Converts the emitted light into electrical signal.
5. **Recorder:** to record the signal and display the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

ANALYTICAL TECHNIQUES

Introduction

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

Two types of chemical analysis,



The process of identification of ions or functional groups or compounds in a mixture is called *qualitative analysis*.

Determination of the amount of each constituent element or substance present in the sample is called *quantitative analysis*.

Potentiometric Titration

Aim: Determination of the weight of ferrous ammonium sulphate and ferrous iron in the given solution by potentiometric titration method.

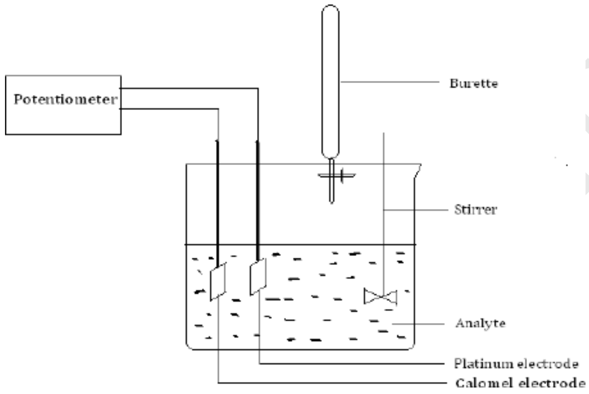
Theory: In this titration the amount of substance in the solution is determined by measuring the emf between two electrodes that are dipped into the solution. When the metal M is immersed in the solution containing its own ions M^{n+} ions, the electrode potential is given by Nernst equation,

$$E = E^0 + \frac{0.0591}{n} log[M^{n+}]$$

From this equation the potential of the electrode is directly proportional to the concentration of the ionic species present in the solution.

Instrumentation:

A potentiometer consists of a indicator electrode (e.g.: Platinum) and an saturated reference electrode (E.g.: Calomel electrode), stirrer & potentiometer to measure the potential values.
Emf of the solution can be measured by combining reference electrode with indicator electrode. The electrode which responds to the change in the concentration of the ion in the solution is called indicator electrode & reference electrode is one whose potential is constant. A known volume of the analyte is taken in beaker and its potential is measured. The titrant is added in increments of 0.5ml and potential is measured each time. Near the equivalence point there is a sharp increase in the potential. The end point is determined by plotting change in potential against volume of the titrant.

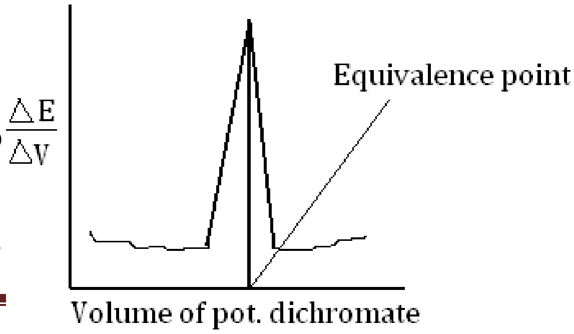


Applications

1. Estimation of concentration of the ionic species present in the given solution.
2. Coloured solution can also be titrated
3. Acid-base titration can also be done in this method.
4. In this method Oxidation-reduction titrations can also be carried out.
5. Precipitation reactions can also be carried out potentiometrically.

For example:

Procedure: Pipette out 25cm^3 of FAS solution into a 50 cm^3 beaker. Add one test tube full of dil H_2SO_4. Immerse Pt. & calomel electrodes into the solution, & connect the electrodes to a potentiometer. Fill the burette with $K_2Cr_2O_7$ solution. Add $K_2Cr_2O_7$ solution from the burette with increment of 0.5cm^3, stir well and measure the potential after each addition. Continue



the titration till the potential indicates a rapid jump with a drop of titrant. Plot the graph of ΔE/ ΔV v/s vol. of $K_2Cr_2O_7$.

Conductometric Titration

Conductance is ease with which current flows through the solution. It is reciprocal of resistance. $C=1/R = \Omega^{-1}$ or mho or Siemen

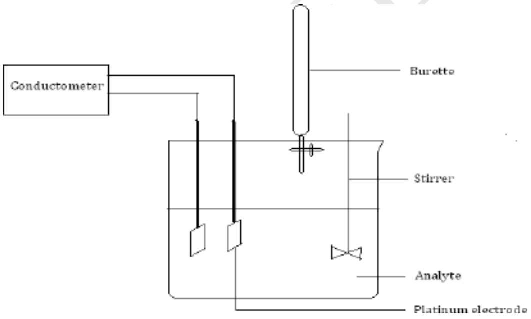
Theory:

The Conductance of the solution is explained by considering ohm's law.
According to ohm's law the current flowing through the conductor is directly proportional to voltage and inversely proportional to the resistance.

$$I=\frac{E}{R} \text{ or } \quad E = I R$$

The resistance of the any conductor is directly proportional to the length, inversely proportional to the area of cross section of the conductor Therefore R = S (l/a) where S is specific resistanceTherefore C = 1/R =1/S(a/l), K(a/l), K = specific conductance
It is defined as the conductance of the solution present between two parallel electrodes of $1cm^2$ area of cross section and 1cm apart.
The conductance of the solution is depending on mobility of the ion and number of the ion.

Instrumentation:
It consists of two platinum electrodes each of unit area of cross section placed at unit distance apart. The electrodes are dipped in the electrolytic solution taken in a beaker. It is connected to a conductometer to measure the conductance. The conductance is measured after the addition of the titrant at interval of 0.5 ml.



Types of conductance: There are three type's namely specific conductance, equivalence conductance, and molar conductance.
Specific conductance (K) is the conductance of the solution present between two parallel electrodes of $1cm^2$ area of cross section and 1cm apart.
$K = 1/R\ (l/a)$ $K = \text{Siemen } m^{-1}$
Equivalence conductance (λ) is the conductance of the solution when 1g equivalent weight of solution is placed between two electrodes of area $1cm^2$ at 1cm apart.
Molar conductance (μ) is the conductance of the solution when 1g molecular weight of solute is placed between two electrodes of area $1cm^2$ at 1cm apart

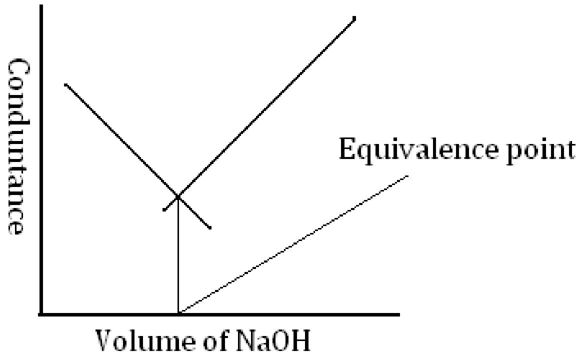
Application of Conductometric titration
It is used in the estimation of acids and bases present in the sample solutions. The possible combinations and conductance responses are explained below,

Strong acid v/s strong base (HCl v/s NaOH)
If the strong acid like HCl is titrated against a strong base such as NaOH, the conductance first

decreases due to replacement
of fast moving H^+ ions by slow moving Na^+ ions

$$HCl + NaOH \rightarrow NaCl + H_2O$$

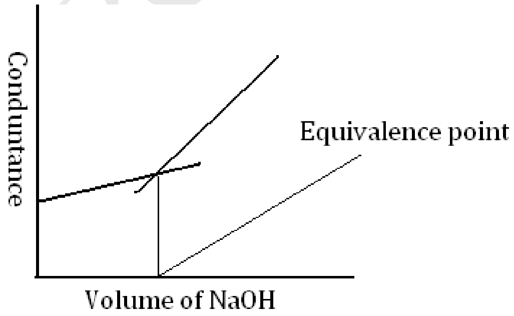
After the neutralization point, conductivity rapidly rises with further addition of NaOH because of continuous addition of fast moving OH^- ions. A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.



Weak acid v/s Strong base (CH_3COOH v/s NaOH)
Consider the titration of acetic acid against NaOH. The conductance of the acid will be initially low since acetic acid is a weak electrolyte. When NaOH is added to the acid, the salt formed is highly ionized and the conductance increases. On complete neutralization of the acid, further addition of base leads to an increase in the number of mobile OH^- ions. Hence the conductance increases sharply.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.



COLORIMETRIC SENSOR

Working principle –

- Colorimetric sensor is used to find out the concentration of substance present in its coloured solutions. This method is applicable only when there is change in intensity of color with change in concentration of species.
- It can be used to estimate the concentration of naturally colored substances and chemicals which give color on mixing with a suitable reagent.

- Higher the intensity of color, more will be the light radiation absorbed by it.

When a monochromatic light of intensity I_0 is incident on a transparent medium a part of light is absorbed

(I_a)and a part is reflected (I_r)and the remaining part is transmitted(I_t).

$I_0 = I_a + I_r + I_t$

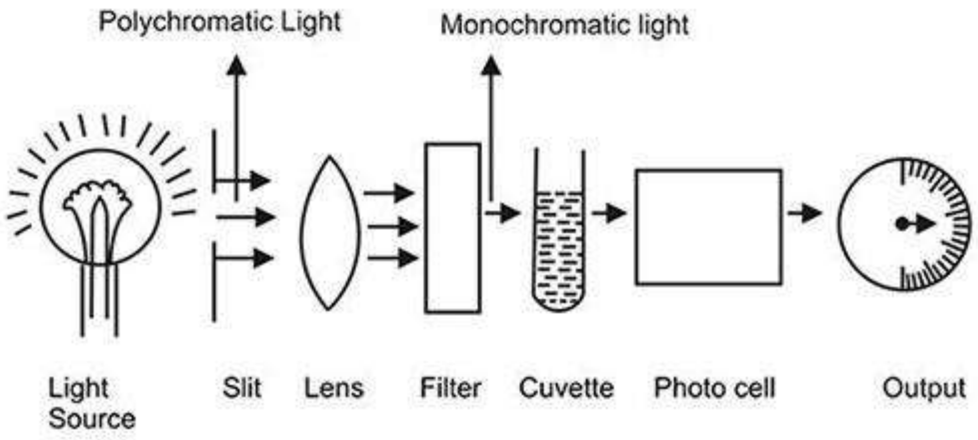
For a glass-air interface I_r is negligible. Therefore $I_0 = I_a + I_t$

$I_t / I_0 = T$ is called transmittance, $\log 1/T = \log I_0 / I_t$ is called the absorbance or optical density(A). The relation between absorbance(A) and concentration (c) and path length (t) is given by Beer lamberts law.

$$\mathbf{A = \log \frac{I_0}{I_t} = \varepsilon\, c\, t}$$

Where is the molar extinction coefficient, which is constant for a given substance at a given wavelength. If the path length is kept constant then A is proportional to c. Hence a plot of absorbance against concentration gives a straight line.
The absorbance is measured using a spectrophotometer at optimum wavelength.

INSTRUMENTATION



- Different parts of a colorimetric sensor are shown above.
- Polychromatic radiation from a lamp is passed through lens and monochromator(filter) to get monochromatic radiation of known wavelength.
- Then it is passed through sample taken in a cuvette which absorbs some part of the radiation and transmits remaining part.
- Light radiation absorbed is detected by photovoltaic →detector, amplified and finally displayed as numerical value.

Colorimetric estimation of copper –

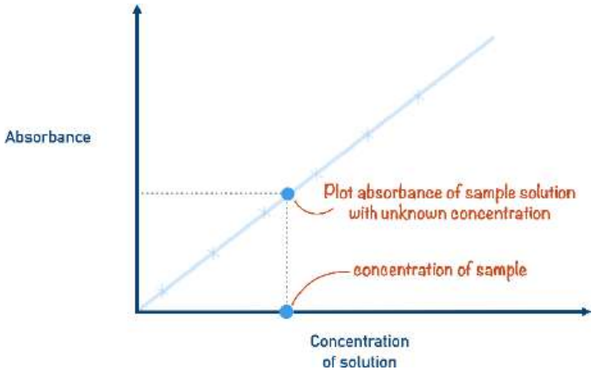
When a solution of cupric ions (example – copper sulphate) is treated with ammonia solution a characteristic deep blue color complex is formed. The intensity of blue color depends on the concentration of copper.

$Cu^{+2} + 4[NH_3] \rightarrow [Cu(NH_3)_4]^{2+}$ (DEEP BLUE)

The absorbance of light by this solution is measured at 620nm since this complex absorbs maximum light at this wavelength.

PROCEDURE

1. Prepare 100 ml of 0.1 M copper sulphate solution.
2. Draw out 2, 4 ,6, 8 ,10ml of copper sulphate stock solution into separate 25 ml standard flask and take the test solution in another standard flask.
3. Add 5ml of 1:1 ammonia solution to each flask and also to the flask containing test solution.
4. Dilute the solution with distilled water upto the mark and mix well.
5. Prepare the blank solution by taking only 5ml of ammonia and make the solution upto the mark with distilled water.
6. Measure the absorbance of all the solutions against blank at 620nm using a photoelectric colorimeter.
7. Draw a calibration curve by plotting optical density or absorbance against concentration of copper (in mg/ml).
8. From the graph determine the concentration of copper in the test solution and volume of test solution.



<u>Question bank –</u>

1. What are reference electrodes? Explain construction, working and application of calomel electrode.
2. What is ion selective electrodes? Discuss construction, working and application of glass electrode.
3. Write the derivation for potential of glass electrode.
4. Write a note on type of electrodes.
5. Explain the theory and instrumentation of Potentiometry
6. Explain the theory and instrumentation of Conductometry
7. What are colorimetric sensors. Explain its application in estimation of copper.
8. What are conductometric sensors. Write its application in estimation of weak acids.
9. Write a note on concentration cells.
10. Explain the determination of pH using glass electrode.
11. Explain the working principle of Conductometric sensors (conductometry), and Optical sensors (colorimetry).
12. What are Electrochemical Sensors? Explain its working and applications.
13. Explain the principle, working and applications of thermometric sensors.