Solution for BCHEE102-Feb2025 VTU exam

CBCS SCHEME

USN ☐☐☐☐☐☐☐☐☐☐

BCHEE102/202

First/Second Semester B.E./B.Tech. Degree Examination,
Dec.2024/Jan.2025

Chemistry for EEE Stream

Time: 3 hrs. Max. Marks: 100

Note: 1. Answer any FIVE full questions, choosing ONE full question from each module.
2. VTU Formula Hand Book is permitted.
3. M : Marks , L: Bloom's level , C: Course outcomes.

		Module – 1	**M**	**L**	**C**
Q.1	**a.**	Explain the conductors, semiconductors and insulators based on band theory.	7	L2	CO1
	b.	Describe the purification of electronic grade Silicon by Float zone method.	6	L2	CO1
	c.	What are conducting polymers? Explain the mechanism of conduction in polyacetylene.	7	L2	CO1
		OR			
Q.2	**a.**	What is electrolessplating? Describe electroless plating of copper in the manufacture of double sided PCB.	6	L2	CO1
	b.	Explain the preparation, properties and commercial applications of graphene oxide.	7	L2	CO1
	c.	Define number average and weight average molecular weights. In a sample of a polymer, 20% molecules have molecular mass 15000 g/mol, 35% molecules have molecular 25000 g/mol and remaining molecules have molecular mass 20000 g/mol. Calculate the number average and weight average molecular weights of the polymer. Calculate PDI and comment on it.	7	L3	CO1
		Module – 2			
Q.3	**a.**	What are PV cells? Explain the construction and working of a typical PV cell. Mention its advantages.	6	L2	CO2
	b.	What are fuel cells? Describe the construction and working of methanol-oxygen fuel cell.	7	L2	CO2
	c.	Explain the construction and working of Lithium polymer battery. Mention its applications.	7	L2	CO2
		OR			
Q.4	**a.**	What are batteries? Describe the classification of battery with suitable examples.	6	L2	CO2
	b.	Explain the construction and working of Vanadium flow battery. Mention its applications.	7	L2	CO2

	c.	Explain the construction and working of sodium ion battery. Mention its applications.	7	L2	CO2
		Module – 3			
Q.5	a.	Define Corrosion. Describe electrochemical theory of corrosion taking iron as an example.	7	L2	CO3
	b.	What is anodisation? Explain anodisation of aluminium and mention its applications.	7	L2	CO3
	c.	Define corrosion penetration rate. A thick brass sheet of area 400 $inch^2$ is exposed to moist air. After 2 years of period, it was found to experience a weight loss of 375 g due to corrosion. If the density of brass is 8.73 $gram/cm^3$. Calculate CPR in mpy and mmpy units.	6	L3	CO3
		OR			
Q.6	a.	What is differential aeration corrosion? Describe differential aeration corrosion with suitable examples.	7	L2	CO3
	b.	Describe sacrificial anodic method of corrosion control with example.	6	L2	CO3
	c.	What is e-waste? Describe the ill effects of e-waste on environment and human health.	7	L2	CO3
		Module – 4			
Q.7	a.	Mention the properties and application of nano sensors and nano fibers.	6	L2	CO4
	b.	Describe the synthesis of nanomaterial by Sol-gel method. Mention its advantages and disadvantages.	7	L2	CO4
	c.	What are QLED's? Mention their properties and applications.	7	L2	CO4
		OR			
Q.8	a.	What are nano materials? Explain the following size dependent properties of nano materials: (i) Surface area (ii) Conducting property (iii) Catalytic property	7	L2	CO4
	b.	What are OLED's? Mention their properties and applications.	6	L2	CO4
	c.	What are perovskites materials? Give the properties and applications of perovskites materials in optoelectronic devices.	7	L2	CO4
		Module – 5			
Q.9	a.	What are concentration cells? The emf of a cell $Ag_{(s)}/AgNO_3(0.02M)//AgNO_3(xM)/Ag_{(s)}$ found to be 0.084 V at 298 K. Write the cell reactions and calculate the value of x.	6	L3	CO5
	b.	Describe the principle, instrumentation and application of potentiometric sensors for the estimation of Iron.	7	L3	CO5

	c.	What are reference electrodes? Explain the construction and working of Calomel electrode.	7	L2	CO5
		OR			
Q.10	a.	Describe the principle, instrumentation and application of conductometric sensors for the estimation of weak acid.	7	L3	CO5
	b.	What are ion selective electrodes? Explain the construction and working of glass electrode.	7	L2	CO5
	c.	Explain the principle and working of colorimetric sensors for the estimation of copper.	6	L3	CO5

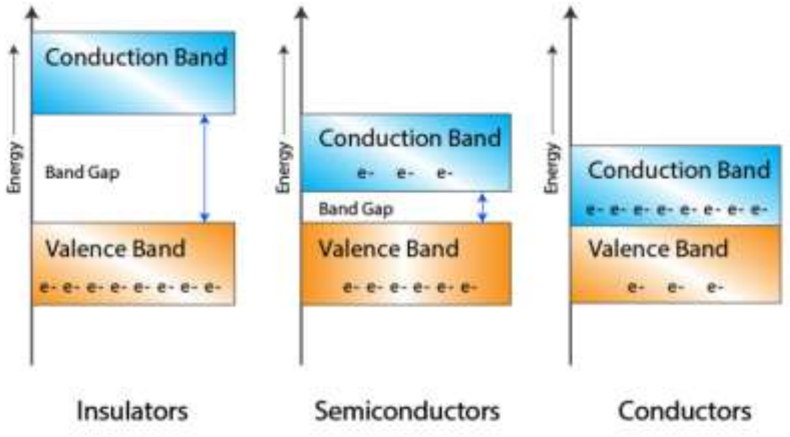
* * * * *

Answer 1a

Conductors are the materials or substances which allow electricity to flow through them. They conduct electricity because they allow electrons to flow easily inside them from atom to atom. Also, conductors allow the transmission of heat or light from one source to another. Example: metals (Fe, Cu etc)

A **semiconductor** is a material which has an electrical conductivity value falling between that of a conductor, such as copper, and an insulator, such as glass. Its resistivity falls as its temperature rises; metals behave in the opposite way. Its conducting properties may be altered in useful ways by introducing impurities ("doping") into the crystal structure. Example Silicon, Germanium

Insulators are the materials or substances which resist or don't allow the current to flow through them. In general, they are solid in nature. Also, insulators are finding use in a variety of systems. As they do not allow the flow of heat. The property which makes insulators different from conductors is its resistivity. Example: Dry wood, glass, rubber, ceramic, dry cotton, etc



Band Theory of conduction:

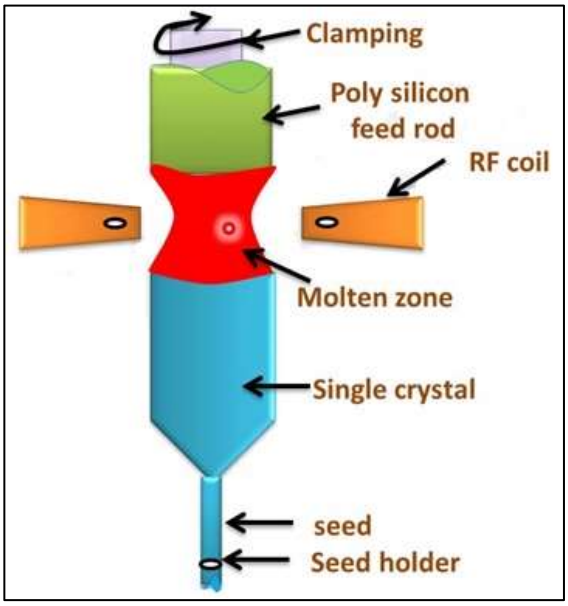
Conductors: According to band theory, a conductor is essentially a substance with its conduction bands and valence bands overlapping, permitting electrons to move freely between the valence band and the conduction band. In conductors, conduction band is only partially filled. This means there are spaces for electrons to move into conduction band and hence thee materials acts as conductors.

Semiconductors: In a semiconductor, the gap between the valence band and conduction band is smaller. The completely occupied valence band and the unoccupied conduction band classify semiconductors. As per band theory semiconductors will operate as insulators at absolute zero. Above this temperature there is sufficient energy available to move some electrons from the valence band into the conduction band and hence material acts as semiconductor. An increase in temperature increases the conductivity of a semiconductor because more electrons will have enough energy to move into the conduction band.

Insulators: An insulator has a large gap between the valence band and the conduction band. The valence band is full and no electrons can move up to the conduction band, hence these material can't conduct.

Anser 1b

Float-Zone method :



(i) A ***monocrystalline silicon seed crystal*** is brought into ***contact*** with one end of a ***polycrystalline silicon ingot***. Starting from here, an *RF* ***coil melts a small region of the polysilicon which, after cooling down, forms monocrystalline silicon*** with the crystallographic orientation of the seed crystal (e. g. <100>, <110> or <111>).

(ii) The ***RF coil and the melted zone move along the entire ingot***. Since most ***impurities are less soluble in the crystal than in the melted silicon***, the molten zone carries the impurities away with it.

(ii) The ***impurities concentrate near the end of the crystal*** where finally they can simply be ***cut away***.

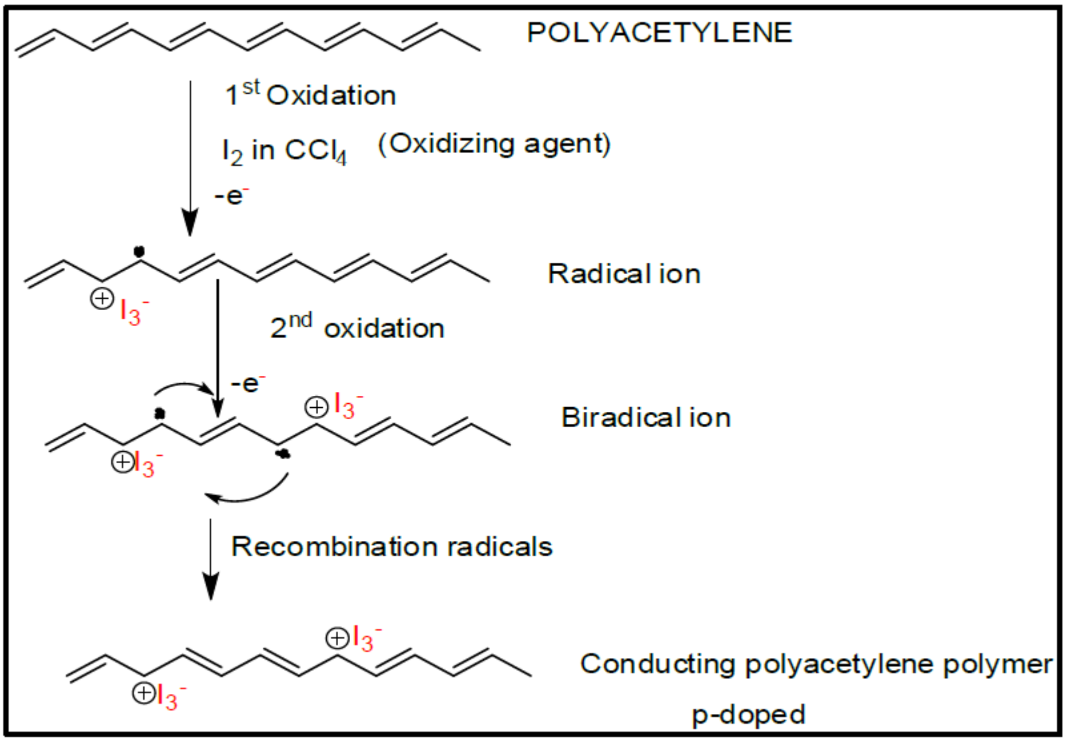
(iii) This procedure can be repeated one or more times in order to further reduce the remaining impurity concentration. **Doping is done during crystal growth by adding dopant gases such as phosphine (PH_3), arsine (AsH_3) or diborane (B_2H_6) to the inert gas atmosphere.**

Advantage of the float-zone technique: (i) **Very low impurity concentration (oxygen and carbon) in the silicon crystal as compared to CZ silicon**, (since the melt does not come into contact with a quartz crucible, and no hot graphite container is used). (ii) **dopant concentration in the final crystal is rather homogeneous**

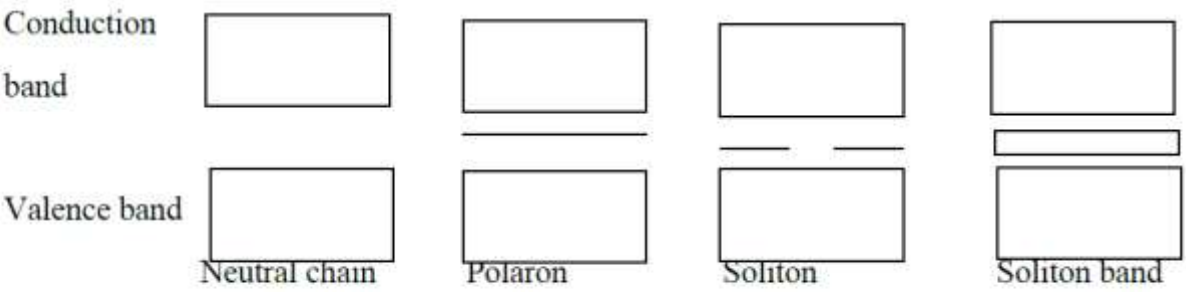
Disadvantage: FZ silicon is more expensive than CZ silicon, and the crystal diameter is limited.

Answer 1c: Polymers which can conduct electricity are called conducting polymers.

Mechanism of conduction in polyacetylene:
(i) By Oxidative doping (p-doping): In this process, π-back bone of polymer is partially oxidized using a suitable oxidizing agent such as I2 in CCl4. The removal of an electron from the polymer π-back bone leads to the formation of delocalized radical ion called polaron. A second oxidation of chain containing polaron produces bipolaron which on radical recombination yields two charge carries on each chain. The positive charge sites on the polymer chain are compensated by anion I3- formed by the oxidizing agent during doping. The delocalized positive charges on the polymer chain are mobile, not the dopant anions. Thus these delocalized positive charges are current carriers for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction.

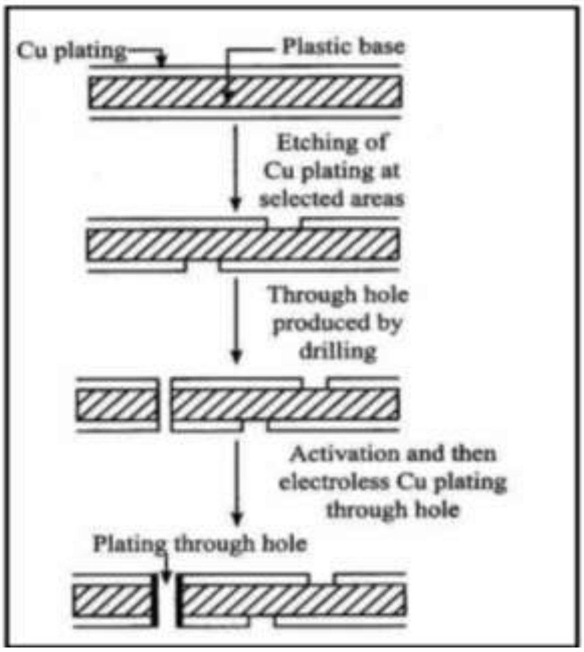


If polyacetylene is heavily doped, polarons form pairs called solitons. In polyacetylenes the solitons are delocalized over 12 carbon atoms. Due to the formation of soliton, a new localized electronic state appears in the middle of the energy gap. When the doping is high, several charged solitons form soliton band. This band can later merge with edges of valence and conduction bands thus exhibiting conductivity.



Answer 2a: Electroless plating is the controlled deposition of a continuous film of a metal from its salt solution on a catalytically active surface of the substrate by a suitable reducing agent, without the use of electrical energy.

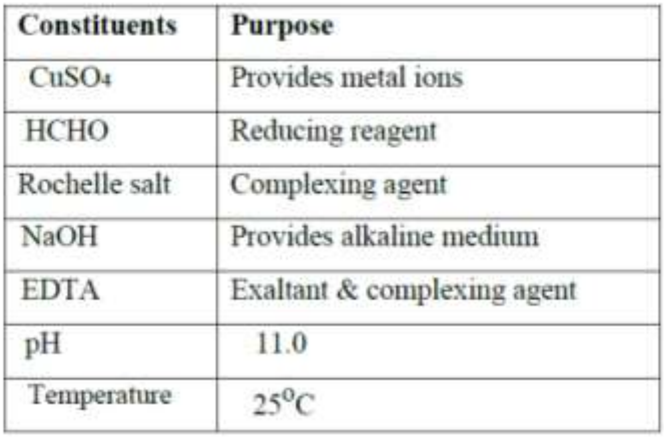
Electroless-plating of Copper on PCB



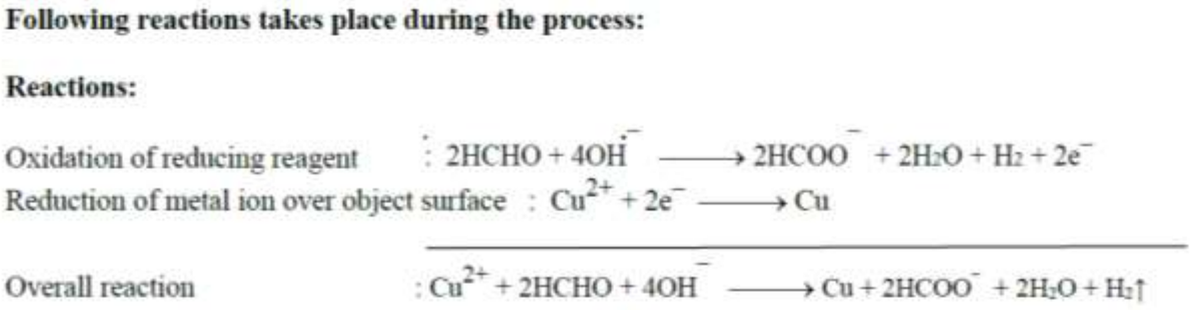
Activation of surface: The base of a printed circuit board is a plastic material such as epoxy or phenolic polymer or a glass fiber reinforced polymer composite. It is activated by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$ leads to deposition of Pd.

$SnCl_2 + PdCl_2 \rightarrow Pd + SnCl_4$

In the manufacture of double sided PCB, the board is clad on either side with thin electroformed copper foils. Then both sides of the copper clad board are printed with etch-resistant circuit patterns. Rest of the unprotected copper foil is etched (formation of tracks) away by using an acid. This leaves only the circuit patterns on both sides of the board. Electrical connection between the two sides of PCB is made by drilling a hole through the board. The hole is then activated & electroless plated with copper, as it can't be electroplated. The composition of the electroless plating bath & the procedure given below.



Constituents	**Purpose**
$CuSO_4$	Provides metal ions
HCHO	Reducing reagent
Rochelle salt	Complexing agent
NaOH	Provides alkaline medium
EDTA	Exaltant & complexing agent
pH	11.0
Temperature	25°C



Following reactions takes place during the process:

Reactions:

Oxidation of reducing reagent : $2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$

Reduction of metal ion over object surface : $Cu^{2+} + 2e^- \longrightarrow Cu$

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

Answer 2b

Graphene Oxide

- Graphene oxide (GO) is a layered carbon structure with oxygen-containing functional groups (=O, -OH, -O-, -COOH) attached to both sides of the layer as well as the edges of the plane.

Properties of Graphene Oxide:

- As with any 2D carbon material, GO can also have either single layer or multilayer structure.
- A structure with one layer is graphene oxide; two layers of graphene oxide are referred to as a two-layered GO, GO with five to ten layers is called multi layered GO, and material with eleven or more layers is called graphite oxide.
- In contrary to graphene, GO is hydrophilic, and it is hence relatively simple to prepare a water- or organic solvent-based suspensions.
- Highly oxidized forms of GO are electric insulators with a bandgap of approximately 2.2 eV.
- Simplistically, GO is a monolayer sheet of graphite containing hydroxyl, carboxyl, and epoxy oxygen groups on its basal plane and edges, resulting in a mixture of sp2 and sp3 hybridized carbon atoms.
- The properties of graphene can be changed by the functionalization of graphene oxide. The chemically-altered graphene’s could possibly be used in several applications.
- Graphene Oxide has a high surface area, and so it can be fit for use as electrode material for batteries, capacitors and solar cells.
- Graphene Oxide is cheaper and easier to manufacture than graphene, and so may enter mass production and use sooner.
- GO can easily be mixed with different polymers and other materials, and enhance properties of composite materials like tensile strength, elasticity, conductivity and more.

Synthesis of Graphene Oxide:

- There are several ways to prepare graphite oxide/graphene oxide. The most common way is to use an oxidizing agent in an acidic environment.
- In this procedure, phosphoric acid is mixed with sulphuric acid in the ratio 1:9 and potassium permanganate and graphite added in the ratio 6:1 in an ice bath.
- The mixture is then heated at $50_{o}C$ and stirred for 12 h
- After cooling down, the mixture is poured onto ice
- Finally, 30% H2O2 is added in order to remove the excess of potassium permanganate.
- Phosphoric acid works as a dispersive and etching agent, as well as a stabilizer of the oxidation process, which makes the synthesis of GO safe.
- This route produces a higher yield of GO with a higher level of oxidation and a more regular structure.

Applications of Graphene Oxide:

- Air pollution caused by the industrial release of harmful gases such as CO_2, CO, NO_2, and NH3.
- GO can be employed in catalysis for converting polluting gases during industrial processing.

- The approach of GO application in this area can be divided into two paths: pollutant adsorption and conversion.
- The functional groups of few-layered GO composites exhibit unique adsorption behaviour towards different gases like acetone, formaldehyde, H_2S, SO_2 , and NOx can be adsorbed by GO-based composites.
- Small-molecule drug delivery seems to be another promising medical application of GO. Small molecules of drugs can be attached to a GO surface using pH-sensitive linkers.

Answer 2c

Solution:

Number average molecular weight = $\dfrac{N_1M_1 + N_2M_2 + N_3M_3}{N_1 + N_2 + N_3}$

$$= \frac{(20 \times 15000) + (35 \times 25000) + (45 \times 20000)}{20+45+35}$$

= 20750 g/mol

Weight average molecular weight = $\dfrac{N_1M_1^2+N_2M_2^2+ N_3M_3^2}{N_1M_1 + N_2M_2 + N_3M_3}$

$$= \frac{(20 \times 15000 \times 15000) + (35 \times 25000 \times 25000) + (45 \times 20000 \times 20000)}{(20 \times 15000) + (35 \times 25000) + (45 \times 20000)}$$

= 21385.5 g/mol

PDI= Mw/Mn = 21385.5/20750 = 1.03

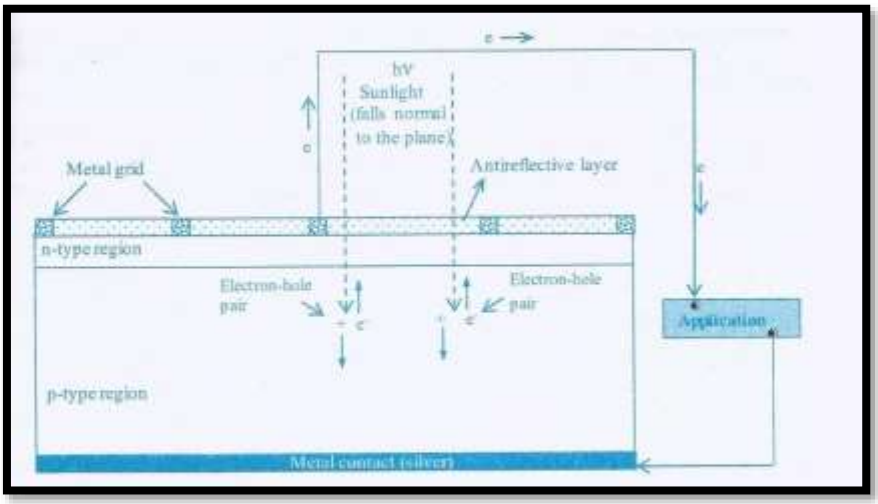
Answer 3a

Photovoltaic Cells:

Photovoltaic cells or solar cells are semiconductor device that converts sunlight into direct current (DC) electricity. As long as light is shining on the solar cell, it generates electrical power. When light stops, electricity stops.

Construction & Working of PhotoVoltaic Cells

Construction:



- PhotoVoltaic Cells consist of a semiconductor diode (p-n junction) made of a silicon.
- Silicon wafer or very thin silicon slices are made by silicon blocks and they are doped by p-type and n-type dopents to make p-n junction.
- It has two electrical contact, on one of its sides, a mettalic grid is used and on the other side a layer of noble metal (such as Ag) is used.
- The metal grid permits the light to fall on the diode between the grid lines.
- The part between the metallic grid is coated with antireflective compound. eg TiO_2

Working:

- Electromagnetic radiation consists of particle called photon (hν). They carry a certain amount of energy given by the Plank quantum equation.

$$\mathbf{E = hc/\lambda}$$

Where, h = Planck's constant, c = velocity of light, λ = wavelength of the radiation

- The electromagnetic radiation (sunlight) falls normal to the plane of the solar cell, the photons which possess energy sufficient to overcome the barrier potential are absorbed, electrons are ejected and electron-hole pairs are formed.
- The electrons move towards the n-region (as it is positively charged). The electrons are driven into the external circuit and used for various applications or appliances.

Advantage of Photovoltaic cells -

1. It is unlimited, inexhaustible and renewable source of energy.
2. The solar cell operates reliably for a long period of time with no maintenance.
3. A photovoltaic system can be constructed to any size based on energy requirement.
4. Easy to operate
5. Quick installation.
6. Can be integrated into new or existing building structure.
7. Completely pollution free during its use.

Answer 3b

Definition: A fuel cell is a device that converts the chemical energy of a fuel (hydrogen, natural gas, methanol, gasoline, etc.) and an oxidant (air or oxygen) into electricity.

Construction, working and applications of methanol–oxygen fuel cell.

It is good example for liquid fuel cell. They use either acidic or alkaline medium. The preferred electrolyte is the acidic. Methanol is an efficient active organic fuel at low temperature.

Construction: Methanol – oxygen fuel cell consist of

1. Anode – It is a porous Nickel (Ni) electrode impregnated with Pt/Pd catalyst.
2. Cathode - It is a porous Nickel (Ni) electrode coated with silver (Ag) catalyst.

3. Electrolyte – Aqueous sulphuric acid (H_2SO_4), 3.7 M.
4. Active components: (a) Fuel – Methanol mixed with sulphuric acid supplied at anode. (b) Oxidant – Pure oxygen is supplied at cathode.

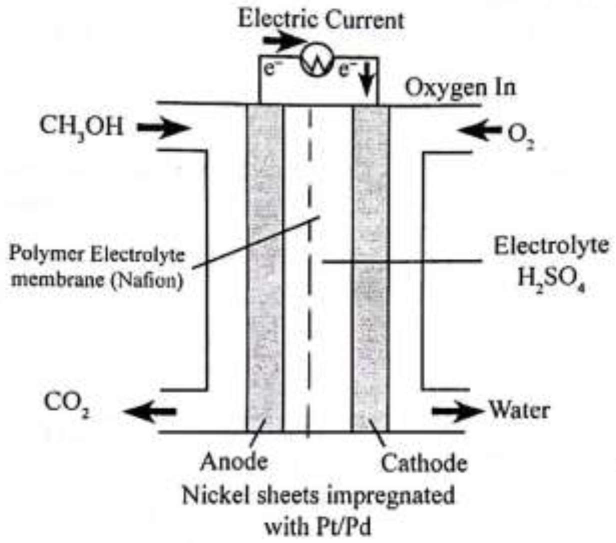


Figure: Methanol – oxygen fuel cell

Working:

Cell reaction;

Anode Reaction: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Cathode Reaction**:** $3/2\ O_2 + 6\ H^+ + 6e^- \longrightarrow 3\ H_2O$

Overall Cell Reaction: $CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2\ H_2O$

H_2O and CO_2 are formed as by-products but they do not harm the cell functioning because they are removed as and when they are formed.
Cell Potential : 1.2 V
Applications:
1. used in automobiles, military applications.
2. Power backup and portable instruments.
3. In large scale power production.

Answer 3c. Lithium polymer (LiPo) Batteries The science behind LiPo batteries is the same as in other Li-ion batteries: chemical energy is converted to electrical energy when electrons travel from the battery's anode to its cathode, creating an electrical current. The cathode contains a lithium metal oxide (such as lithium-cobalt oxide ($LiCoO_2$)), which provides lithium ions, whereas the anode contains a lithium carbon (such as graphite).

The anode and cathode are separated by an electrolyte that interacts with the anode to generate electrons, which creates a charge gradient in the cell. As the anode becomes negatively charged, the electrons travel along a conducting wire to the cathode. The whole system thus undergoes an electrochemical redox reaction (reduction/oxidation): the anode loses electrons and becomes oxidized while the cathode gains electrons and is reduced.

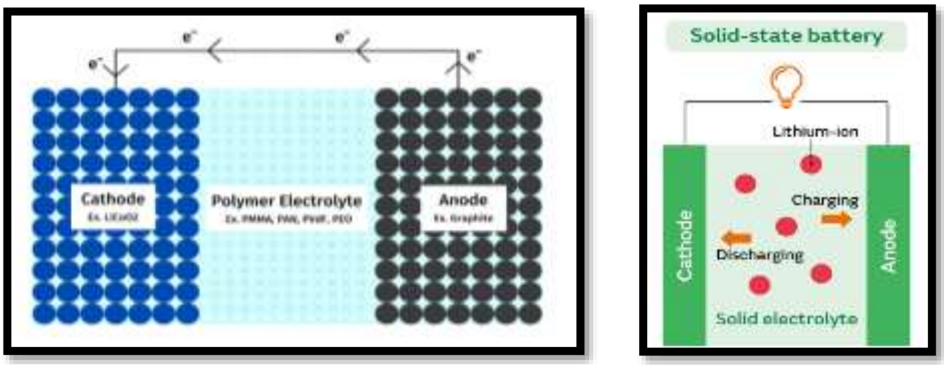


Figure: LiPo Battery

Anode: Lithium intercalated Carbon or graphite

Cathode: lithium transition metal oxides (such as lithium-cobalt oxide ($LiCoO_2$)),

Electrolyte & Separator: High conductivity semisolid (gel) polymers electrolyte polymer electrolytes and include poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN)

Working:

At anode: $$Li_xC_6 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} xLi^+ + xe^- + C_6$$

At cathode: $$LiCoO_2 + xLi^+ + xe^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} Li_{1+x}CoO_2$$

Overall cell reaction: $$xLiC_6 + LiCoO_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} Li_{1+x}CoO_2 + xC_6$$

Applications: These batteries provide higher specific energy than other lithium battery types and are used in applications where weight is a critical feature, such as mobile devices, radio-controlled aircraft and some electric vehicles.

Answer 4a

Battery is a device consisting of two or more galvanic cells arranged in series or parallel or both, that can generate electrical energy.

Batteries are classified under the following categories:

- **Primary battery:** In primary batteries, chemical energy stored in the battery is converted to electrical energy spontaneously as long as active materials are present. This battery cannot be recharged, because cell reaction is irreversible. *Example:* Zn-MnO_2 battery, Li-MnO_2 battery.

- **Secondary battery:** This battery can be recharged by passing electric current, because cell reactions are reversible. The redox reaction is reversed during recharing. Electrical energy is stored in the form of chemical energy in these batteries and used when needed. *Example:* Lead acid battery, Ni-MH battery, Li-ion battery. Primary cells act only as galvanic cell, whereas, a secondary cell can act both as galvanic cell and electrolytic cell. During discharging it acts as galvanic cell converting chemical energy to electrical energy and during charging process it acts as electrolytic cell converting electrical energy to chemical energy

- **Reserve battery:** In this battery, one of the key component is stored separately, and is incorporated into battery when required. When long storage is required, reserve batteries are often used, since the active component of the cell is separated until needed, thus reducing self-discharge.

Example: Mg-AgCl battery. They are activated by adding sea water. These batteries have high reliability and long shelf life, hence they find applications in missiles and submarines. Another example is zinc-air batteries where the cell is sealed until use, the seal is removed to admit air and activate the cell when needed.

Answer 4b. Flow battery: A flow battery, or redox flow battery, is a type of electrochemical cell where chemical energy is provided by two chemical components dissolved in liquids that are pumped through the system on separate sides of a membrane. Example: **Vanadium redox flow battery**

Vanadium redox flow battery: The vanadium redox battery (VRB), also known as the vanadium flow battery (VFB) or vanadium redox flow battery (VRFB), is a type of rechargeable flow battery. It employs vanadium ions as charge carriers.

Construction: A vanadium redox battery consists of an assembly of power cells in which two electrolytes are separated by a proton exchange membrane.

Electrodes: The electrodes in a VRB cell are carbon based. The most common types are carbon felt, carbon paper, carbon cloth, and graphite felt. Recently, carbon nanotube-based electrodes have attracted interest from the scientific community.

Electrolytes: Both electrolytes are vanadium-based. The electrolyte in the positive half-cells contains VO_2^+ and VO^{2+} ions, while the electrolyte in the negative half-cells consists of V^{3+} and V^{2+} ions. The electrolytes can be prepared by several processes, including electrolytically dissolving vanadium pentoxide (V_2O_5) in sulfuric acid (H_2SO_4). The solution remains strongly acidic in use.

Membrane: The most common membrane material is perfluorinated sulfonic acid (PFSA) (Nafion). polytetrafluoroethylene (Teflon).

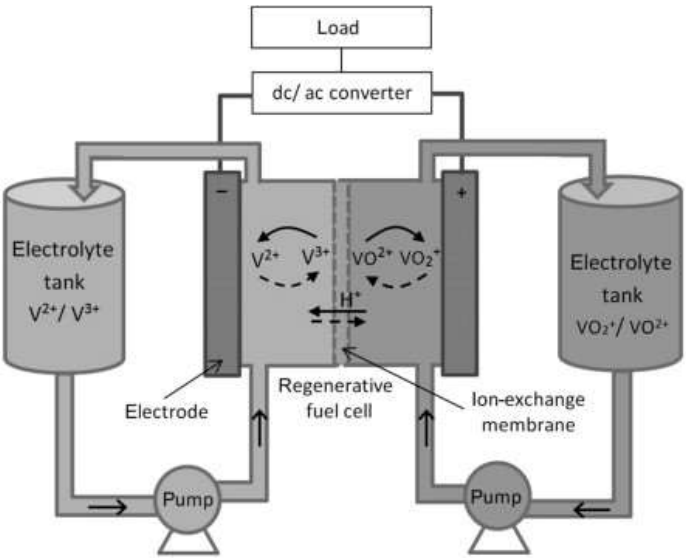
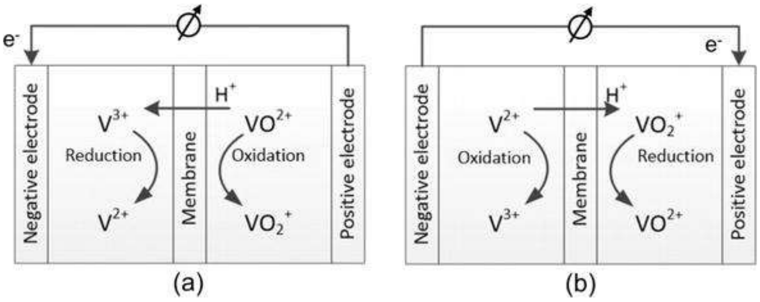


Figure. A diagram of a vanadium redox flow battery



(a) (b)

Figure. Vanadium redox flow battery: (a) charge reaction and (b) discharge reaction.

Working:

Negative electrode: $V^{2+} \underset{\text{Charge}}{\overset{\text{Discharge}}{\longleftrightarrow}} V^{3+} + e-$

Positive electrode: $VO_2^+ + e- + 2H^+ \underset{\text{Charge}}{\overset{\text{Discharge}}{\longleftrightarrow}} VO^{2+} + H_2O$

Overall reaction: $VO_2^+ + V^{2+} + 2H^+ \underset{\text{Charge}}{\overset{\text{Discharge}}{\longleftrightarrow}} VO^{2+} + V^{3+} + H_2O$ (E^0 =1.26 V)

Application: Vanadium batteries are typically used for grid energy storage, i.e., attached to power plants/electrical grids.

Answer 4c. Battery is a device which convert chemical energy into electrical energy on demand through redox titrations. OR

Battery is a device consisting of two or more galvanic cells arranged in series or parallel or both, that can generate electrical energy.

Construction:

Anode: Non-graphitic anodes, which consist largely of various carbonaceous materials (such as carbon black, pitch-based carbon-fibers, hard carbons etc)

Cathode: layer and tunnel type transition metal oxides, transition metal sulfides and fluorides etc

Electrolyte: The most common electrolyte formulations for SIBs are $NaClO_4$ or $NaPF_6$ salts in carbonate ester solvents (particularly propylene carbonate).

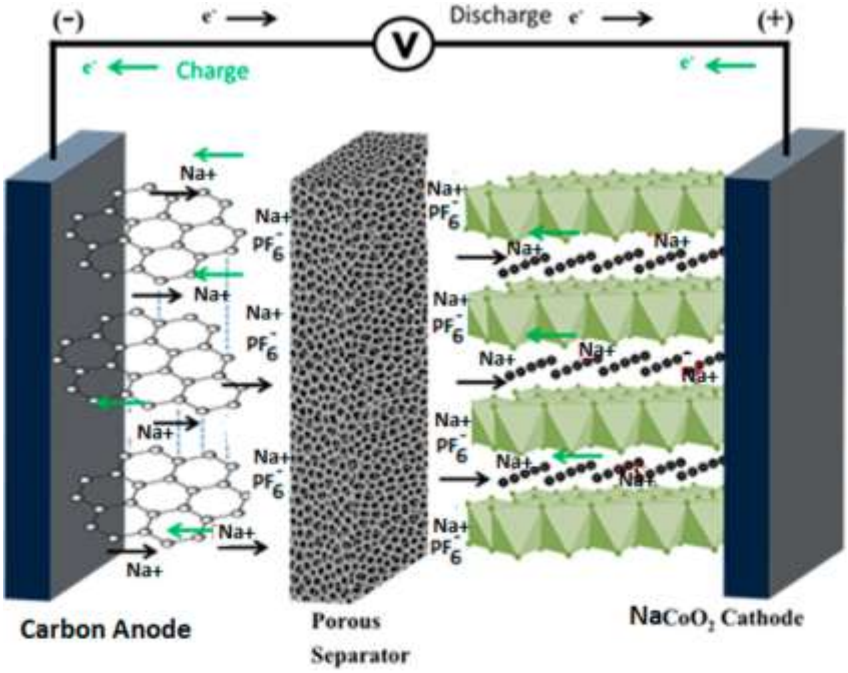


Figure. Na-ion Battery (SIB)

Working principles of SIBs

When the battery is being charged, Na atoms in the cathode release electrons to the external circuit and become ions which migrate through the electrolyte toward the anode, where they combine with electrons from the external circuit while reacting with the layered anode material. This process is reversed during discharge.

At anode: $$Na_xC_6 \overset{\text{Discharge}}{\rightleftharpoons} xNa^+ + xe^- + C_6$$

Charge

At cathode: $NaMO_2 + xNa^+ + xe^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Na_{1+x}MO_2 + C_6$

Overall cell reaction: $Na_xC_6 + Na\,MO_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Na_{1+x}MO_2 + C_6$

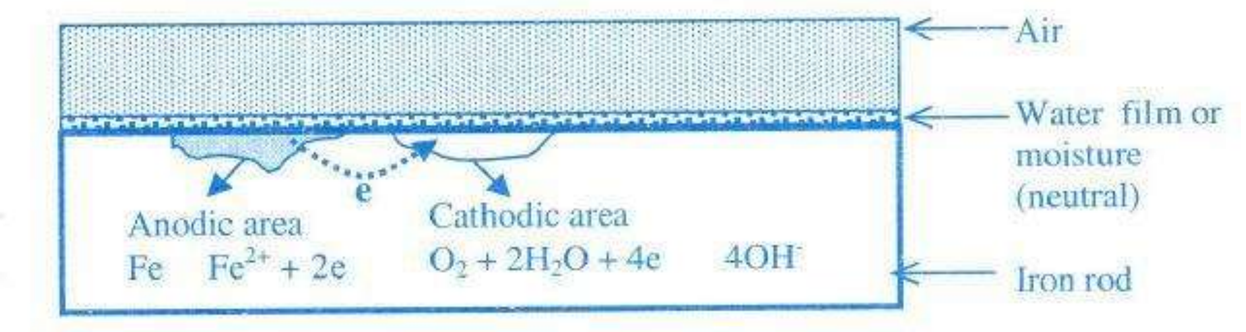
Applications: Sodium-ion batteries can be used for a broad range of battery applications, including renewable energy storage for homes and businesses, grid storage, and backup power for data and telecom companies.

Answer 5a

Definition: Corrosion is defined as the **destruction of metal or alloys from its surface by the surrounding environment through chemical or electrochemical changes**.

Eg. 1. Rusting of Fe

Electrochemical theory of corrosion: Most of the corrosion problems are best explained on the basis of electrochemical theory.



(i) According to electrochemical theory, corrosion of metals takes place due to the formation of minute galvanic cells over the surface of metal. Thus anodic and cathodic regions are formed on the same metal surface or when two metals are in contact with each other in the presence of a conducting medium.

(ii) At the anodic region oxidation reaction takes place and the **metal gets converted into its ions by liberating electrons**. Consequently, **metal undergoes corrosion at the anodic region**.

$M \longrightarrow M^+ + ne^-$

Ex: $Fe \longrightarrow Fe^{2+} + 2e^-$

(iii) The electrons flow from the anodic to cathodic area and at the cathodic region, reduction takes place. Since metal cannot be reduced further**, metal atoms at the cathodic region are unaffected by the cathodic reaction**. Some constitutions of the corrosion medium take part in the cathodic reaction. There are three possible ways in which the reduction can take place.

(i) If the solution is aerated and almost neutral, oxygen is reduced in presence of water to OH- ions according to the equation.

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

(ii) If the solution is deaerated and almost neutral the cathodic reaction involves formation of hydroxyl ions with evolution of hydrogen gas.

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

(iii) If the solution is deaerated and acidic, the H^+ ions are reduced to H_2

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

(iv) The electrons liberated at the anodic region migrates to the cathodic region constituting corrosion current, the metal ions liberated at the anode and some anions liberated at the cathode diffuse towards each other through the conducting medium-range and form a corrosion products.

Corrosion of iron produced Fe^{2+} ions and OH^- ions at the anode and cathode sites respectively. These ions diffuse towards each other and produce insoluble $Fe(OH)_2$.

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

In an oxidizing environment, it is oxidized to ferric oxide and the rust is hydrated ferric oxide.

$$2Fe(OH)_2 + \frac{1}{2}O_2 + (n-2)H_2O \longrightarrow [Fe_2O_3.nH_2O]\ [\text{Rust}]$$

Corrosion of metal continues as long as both anodic and cathodic reactions take place simultaneously

Answer 5b.

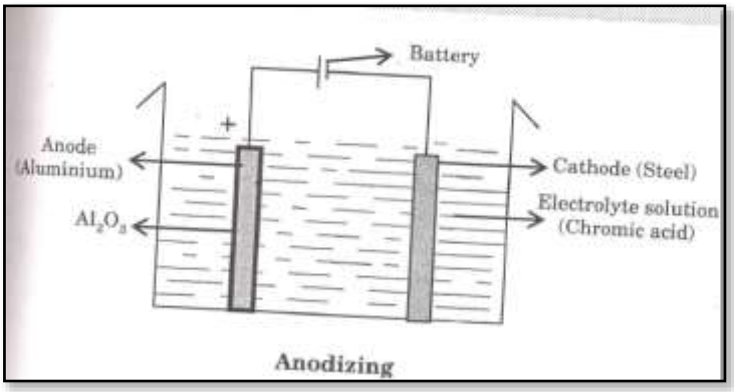
Anodizing : It is a process in which a protective passive oxide film is artificially (chemically or electrochemically) produced on certain metals. It is also called as anodic oxidation process.

Anodized coating is generally produced on non ferrous metals like Al, Zn, Mg and their alloys by anodic oxidation process.

In anodizing of aluminium, clean, polished aluminium is taken as anode and immersed in an electrolytic cell containing chromic acid or sulphuric acid. Inert electrodes like lead is generally used as cathode. The anodic oxide film formed on Al as aluminium oxide, which is porous. The pores are finally sealed by dipping in hot water to produce $Al_2O_3 .H_2O$, which acts as a non-porous protective layer preventing corrosion.

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

Cathode reaction: $6H^+ + 6e^- \rightarrow 3H_2$



Anodizing

Application:

I. **Metal such as Al, Mg etc are anodized to avoid corrosion.**
II. **Food preparation equipment.**
III. **Furniture & Sporting goods.**
IV. **Motor vehicle components.**

Answer 5c. Corrosion Penetration Rate (CPR) is defined in three ways: (1) the speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment, (2) the amount of corrosion lost per year in thickness, (3) the speed at which corrosion spreads to the inner portions of a material.

The CPR is calculated as follows:
CPR = (k x W) / (D x A x T)
where k = a constant depends on unit used.
when K = 534 the mpy will be used. when K = 87.6, mm/yr will be used.
W = total weight lost ($m_o - m$) m = weight after corroded m_o = weight before corroded
T = time taken for the loss of metal
A = the surface area of the exposed metal
D = the metal density in g/cm^3

Corrosion penetrating rate in mpy
CPR = KW/DAT
Weight loss, W= 375×10^3 mg
Density, D = 8.73 g/cm^3; Time, T = 2years= 2×365×24 hours
Area A = 400 in^2

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

CPR = 3.273mpy

Corrosion penetrating rate mm/y
CPR = KW/DAT
Weight loss, W= 375×10^3 mg
Density, D = 8.73 g/cm^3; Time, T = 2×365×24 hours
Area A = 400 in^2 = 400×6.45 cm^2

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

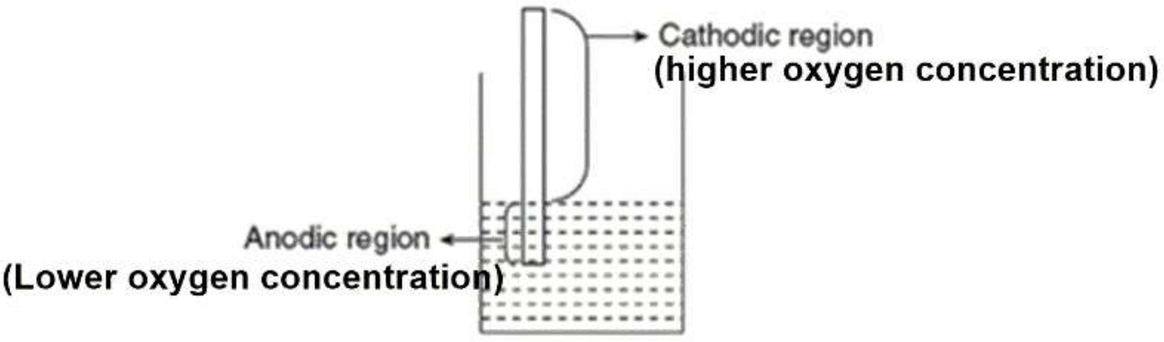
CPR = 0.0832 mm/y

Answer 6a.

Differential aeration corrosion (Concentration cell corrosion): Differential aeration corrosion occurs when the metal surface is exposed to two different concentration of air. The part of the metal exposed to lower oxygen concentration acts as anodic region and other acts as cathodic region. The difference in the oxygen concentration produces a potential difference which causes the corrosion. Example: Steel water tanks and ships floating in water for long time

At anode: $Fe \rightarrow Fe^{2+} + 2e^-$
(lower O_2 concentration)
At cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
(higher O_2 concentration)
Rust formation: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
(Ferrous hydroxide)
Further oxidation leads to rust formation.

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



Pure iron partially immersed in an aerated solution of NaCl.

Answer 6b. <u>Sacrificial anodic method:</u>

In this method, the base metal structure is converted into a cathode by connected it to a more active [higher up in galvanic series or less noble] metal. This active metal actually acts as an auxiliary anode. Mostly Zn, Mg, Al are the common auxiliary anodes used in this method. These metals being more active, acts as anode and undergo destruction and protect the metal structure. Since the anode material sacrifice to protect the metal structure, the method is known as sacrificial anode method. After continuous use exhausted sacrificial anodes are replaced by new ones as and when required. Eg: A Mg/ Zn block connected to buried oil storage tank, Mg/Zn base areas fixed to the side of ocean going ships, Mg/ Zn blocks area connected to the buried pipe lines.

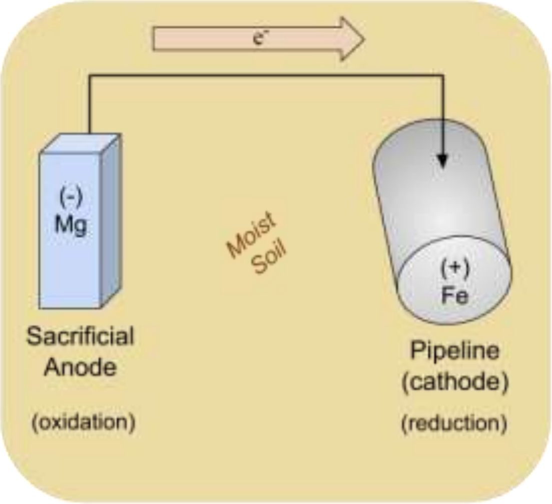


Fig: Cathodic Protection by sacrificial anode

Advantage:
(i)The method is simple.
(ii) low installation cost.
(iii) minimum maintenance cost.
(iv) Doesn't require power supply.
Disadvantages: Involves recurring expenditure for Replacement of consumed anodes.

Answer 6c. Definition: E-waste or electronic waste means discarded electrical or electronic devices or components.

Effects of e-waste on environment and human health: E-waste is a serious issue for our environment because it releases harmful toxic chemicals from the metals due to chemical reactions and these toxic chemicals harm our environment, therefore they must be handled with care when no longer wanted or needed.
Electronic scrap components, such as CPUs, contain potentially harmful materials such as lead, cadmium, beryllium, or brominated flame retardants. Improper disposal of e-waste is highly dangerous to the global environment involving significant risk to the health of workers and their communities
<u>Effects on Air quality:</u> Contamination in the air occurs when e-waste is informally disposed of 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. 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. The air pollution caused by e-waste impacts some animal species more than others, which may be endangering these species and the biodiversity of certain regions that are chronically polluted. Over time, air pollution can hurt water quality, soil, and plant species, creating irreversible damage to ecosystems.

Effects on Soil: When the improper disposal of e-waste in regular landfills or in places where it is dumped illegally, both heavy metals and flame retardants can seep directly from the e-waste into the soil, causing contamination of 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.

Effects on Water: After soil contamination, heavy metals from e-waste, such as mercury, lithium, lead, and barium, then leak through the earth even further to reach groundwater. When these heavy metals reach groundwater, they eventually make their way into ponds, streams, rivers, and lakes. Through these pathways, acidification and toxicity are created in the water, which is unsafe for animals, plants, and communities even if they are miles away from a recycling site. Clean drinking water becomes problematic to find.

Effects on Humans: 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. It can also considerably affect the nervous and reproductive systems of the human body, leading to disease and birth defects.

Answer 7a. Nanosensors are incredibly small sensors that utilize nanotechnology to detect and measure specific substances or physical conditions with high sensitivity due to their minuscule size and large surface area.

Properties of Nanosensors:

- Available in small sizes
- Requires less power to operate
- Less weight
- Works as data storage systems
- Great sensitivity, accuracy, scalability, efficiency, precision, and specificity
- Easy to execute.
- Provides a high-volume ratio.
- Response time is low.

Nanosensor Applications

They are used:

- To detect various chemicals in gases for pollution monitoring.
- Nanosensors have potential applications in the food sector, in food processing monitoring, food quality assessment, food packaging, food storage, shelf-life monitoring, and viability, as indicators of food safety and microbial contamination.
- For medical diagnostic purposes either as bloodborne sensors or in lab-on-a-chip type devices. The nanosensors provide an understanding of a person's health status through noninvasive detection of clinically relevant biomarkers in several biofluids such as tears, saliva, and sweat without sampling, complex manipulation, and treatment steps.
- To monitor physical parameters such as temperature, displacement and flow
- To monitor plant signaling and metabolism to understand plant biology
- To study neurotransmitters in the brain for understanding neurophysiology

Nano-fibers are slender, elongated, threadlike material with a diameter between 50 and 300 nanometers.

Properties of Nanofibers:

- Nanofibers have diameter 1000 times smaller than that of human hair
- high surface area with tunable porosity,
- 3D topography
- flexible surface functionalities
- and better mechanical properties (i.e., stiffness and tensile strength).
- Carbon nanofiber has a low density.
- The thermal conductivity ranges between 1950 – 6000 W/m K and electrical resistivity from 1×10^{-3} to 1×10^{-4}.
- Activated CNFs have a specific surface area with high adsorption capacity.

Applications of nanofibers:

- **Biosensors:** High sensitivity towards the target molecules, good electron transferability, a larger surface area for adsorption and being highly electrocatalytic towards the oxidation of small molecules like viruses, proteins and nucleic acids, glucose, hydrogen peroxide, dopamine, and cortisol they can be used efficiently in various clinical biosensing applications.
- **Wound dressing materials:** carbon-based nanofibers have been seeking more attention because of their excellent mechanical strength and biocompatibility. They are being used in the biomedical sector especially wound dressing, biomedicine and bioengineering.
- **Carbon nanofibers as supercapacitors:** PAN/polymethylmethacrylate (PMMA)/carbon composite nanofiber mats used as electrode material in a supercapacitor, characterized by a low loss after 10,000 charge-discharge cycles.
- **Carbon nanofibers for electrocatalytic applications**
- **Carbon nanofibers for CO_2 adsorption:**
- **Carbon nanofibers as cathode and anode material in advanced batteries:**

Answer 7b. The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

Step1: Formation of different stable solutions of the alkoxide or solvated metal precursor (the sol).

M-OR + H2O------------------► M-OH + HOR

Step 2: Gelation resulting from the formation of an oxide or alcohol bridged network (the gel) by polycondensation or poly esterification reaction. This results in a dramatic increase in the viscosity of the solution.

M-OH + M-OR------------------ ► M-O-M + HOR
M-OH + M-OH ---------------- ► M-O-M + HOR

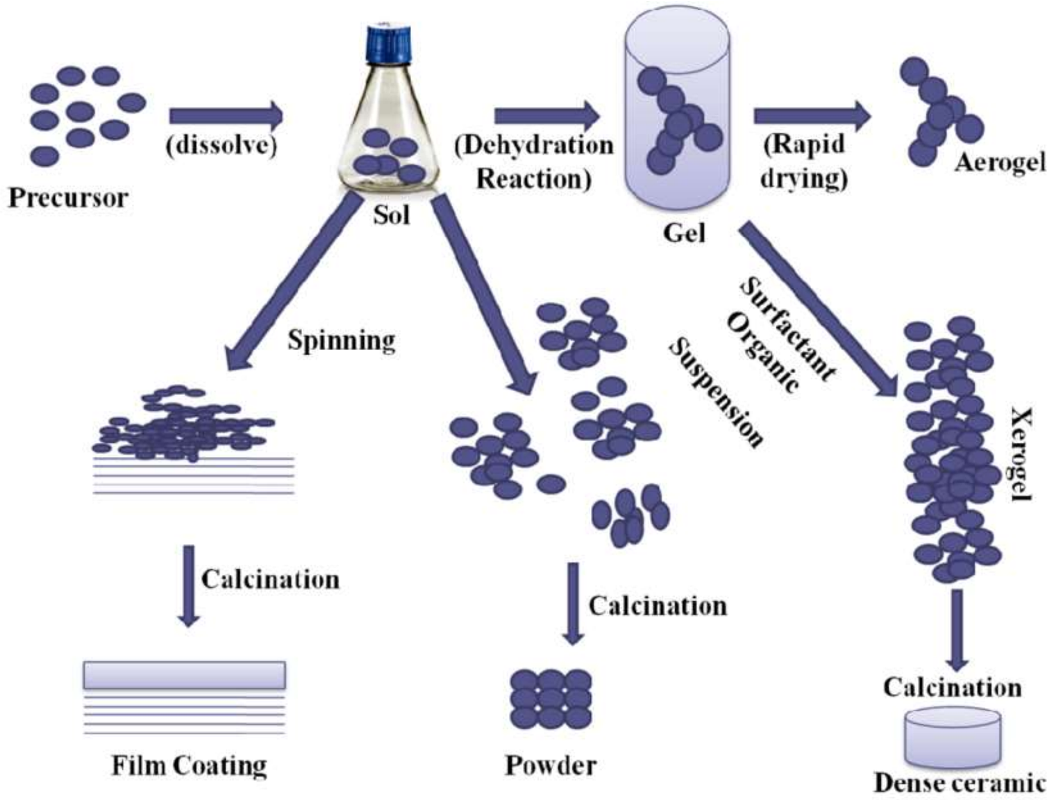
Step 3: Aging of the gel(synthesis), during which the polycondensation reactions continue until the gel transforms into a solid mass. This is accompanied by the contraction of the gel network and the expulsion of solvent from gel pores.

Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network. If isolated by thermal evaporation, the resulting is termed a xerosal. If the solvent (such as water) is extracted under supercritical or near supercritical conditions, the product is an aerogel.

Step 5: Dehydration, during which surface-bound M-OH groups are removed. This is normally achieved by calcination of the monolith at temperatures up to 800 0 C.

Step 6: Densification and decomposition of the gels at high temperature (T>800^0 C). The pores of the gel network collapse and the remaining organic species are volatilized.

The typical steps that are involved in sol gel processing are shown in fig. By different processes, one can get either nano film coating or nanopowder or dense ceramic with nanograins.



Example: Sol-Gel synthesis process ZnO NPs First of all, in a 100ml beaker 30 ml of water was added with 35 ml of triethanolamine(TEA) and drop wise ethanol was added with continuous stirring to get a homogeneous solution. After addition of 100 drops ethanol that was about 3 ml and continuous stirring results a homogeneous solution. Keeping the stoichiometry in mind a 2.0 gm batch of zinc oxide was prepared. Firstly, 30ml of water was mixed with 20 ml of TEA with constant stirring and drop wise addition of ethanol. The obtained homogeneous solution was kept at rest for 3.0 hours. For 2.0 gm batch of zinc oxide 5.49gm of zinc acetate dihydrate was mixed with 50ml water and 0.5M of solution was prepared which was subjected to continuous stirring to get a homogeneous solution. After that the two solutions were mixed together in 500ml beaker and drop wise ammonium hydroxide was added with continuous heating and stirring for 20minutesvia hot plate. Nearly 10ml of distil water was added during stirring. Then the solution was left for half an hour which results in the formation of white bulky solution. The obtained solution was then washed 10-12 times with distil water and filtered in a filter paper. The residue obtained waskept for drying in an oven at a temperature of about 95°C for 6 hours. The yellowish white powder obtained was then subjected to calcinations at a temperature of 600°C for 5 hours

Advantages

Uniformity: The raw materials are dispersed in a solvent, which results in uniform materials at the molecular level
Purity: The materials produced are highly pure
Low temperature: The method can be used to produce materials at low temperatures
Simplicity: The process is relatively simple

Disadvantages
Heat sensitivity: The materials produced can be sensitive to heat treatment, which can cause cracking
Residual porosity: It can be difficult to avoid residual porosity in the materials produced
OH groups: It can be difficult to avoid residual OH groups in the materials produced
Preferential precipitation: In multicomponent glasses, a particular oxide may precipitate preferentially during sol formation

Answer 7c Quantum dot light-emitting diode (QLED) use quantum dots for emission and attracted much attention for the next generation of display
Properties:

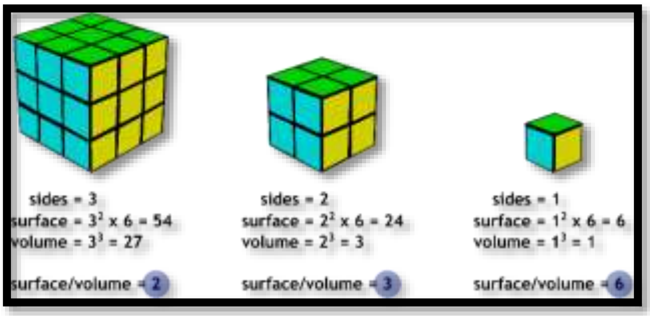
- high color saturation
- tunable color emission
- high stability.
- QLED display has advantages in flexible and robust application, which makes wearable and stretchable display possible in the future.
- energy efficient, thin-film display and solid-state lighting applications.
- facile scale-up capability
- Wide-viewing angle

Applications of QLED

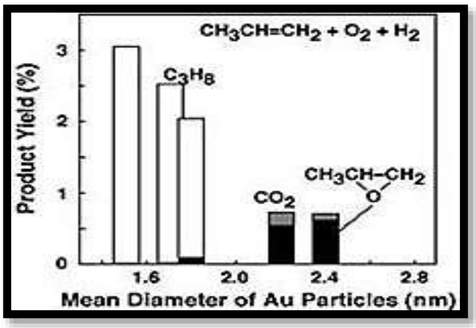
- quantum dot light-emitting diodes (QLED) are cost-effective electroluminescence devices ideal for large-area display and lighting applications.
- For photomedical applications: facilitate widespread clinical applications of photodynamic therapy (PDT) or photobiomodulation (PBM).
- Consumer electronics: Used in smart phones, tablets, laptops, and televisions.
- Lighting: Used in lighting applications
- Wearable devices:Used in smart watches and fitness trackers.
- Automotive displays:Used in automotive displays
- Medical devices: OLEDs are used in medical devices

Answer 8a. Nanotechnology can be defined as the manipulation of atoms and molecules (one billionth) scale (1-100 nm) to produce devices, structures, or systems with at least one novel or superior property. Materials having at least one dimension in the nanoscale are called **nanomaterials**.

Size-dependent properties 1). Surface area: In chemical reactions, this surface-to-volume ratio plays an important role. There is an enormous change in the properties of materials due to the increased surface area-to-volume ratio. The nanomaterials have a relatively larger surface area when compared to the same volume of the material produced in a larger form. So we know that material has high surface energy if it is small in size and vice versa. Therefore, nanoparticles have a large surface area to volume ratio and they possess large surface energy. Due to high surface energy materials are more reactive and also nanoparticles show enhanced stability and a broader scope of applications. In some cases, materials that are inert in their larger form are reactive when produced in their nanoscale form. This affects their strength or electrical properties. The ratio of surface area to volume of a material is given by $area/volume = 4\pi r2/\ 4/3\ \pi r3 = 3/r$



2) Catalytic properties: The factors such as very small size, very high surface-to-volume ratio, and the increasing number of atoms on the surface are the most important reasons for the emergence of catalytic properties in nanomaterials. Basically, when particles become very small (nanoscale), due to the very high curvature they find, they have many atoms on their surface, which are very weakly bonded to the lattice atoms of the lattice. Therefore, these particles have very high surface energy and are highly active, and it is said that surface atoms are in a state of physical instability and are chemically active, and are prone to perform many chemical reactions. It can be said that the main and determining reason for the emergence of catalytic properties in nanomaterials is their very high surface-to-volume ratio. The higher this ratio, the higher the catalytic properties in nanomaterials due to the increase in surface energy. In principle, the reason for these changes is due to changes in the electronic structure of materials, which can be justified by quantum mechanics.The effect of gold nanoparticle size on catalytic activity in the propene epoxidation reaction has been investigated, which shows that by reducing the size of gold nanoparticles, the yield of the product increases.



Answer 8b.

Organic Light Emitting Diodes (OLED's) operates on the principle of converting electrical energy into light, a phenomenon known as electroluminescence. OLED is a semiconductor device, in which the emissive electroluminescent layer is a film of organic compound which emit light in response to an electric current.

Properties of OLED's

- Very thin solid-state device.
- Lightweight: the substrates are shatter resistant unlike glass displays of LCD devices.
- High luminous power efficiency: an inactive OLED element does not generate light or consumes power, hence allowing true blacks.
- Fast response time making entertaining animations- LCDs reach as low as 1ms response time for their fastest colour transition.
- Wide-viewing angle: OLEDs enable wider viewing angle in comparison to LCDs because pixels in OLEDs emit light directly. The colours appear correct.

•Self-emitting hence, removing requirement of a backlight source.
•Colour tuning for full colour displays
•Flexibility- OLED displays are fabricated on flexible plastic substrates producing flexible organic LEDs.
•Cost advantages over inorganic devices- OLEDs are cheaper in comparison to LCD or plasma displays.
•Low power consumption

Applications of OLEDs

1. To build digital displays in TV screens, cell phones, PDAs, monitors, car radios, digital cameras.
2. OLEDs have wide applications in lightning
3. It is used in watches.
4. OLEDs have replaced CRTs (Cathode Ray Tubes) or LCDs (Liquid Crystal Display).

Answer 8c: Perovskite Materials is a material that has the same crystal structure as the mineral calcium titanium oxide (Perovskite).

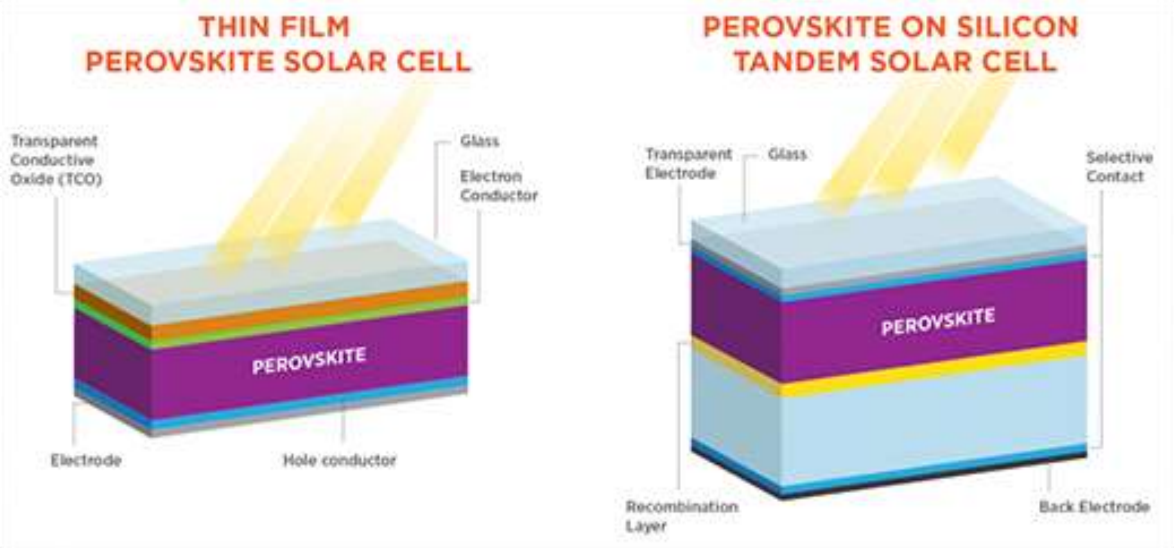
Properties of Perovskite Materials:

- ABX3 Type Crystal Structure; where A = cation (such as methyl ammonium ion), B = metal cation, and X = halide ion.
- Optical Properties: As one of the unique properties of metal-organic halide perovskites, the optical properties of photo-generated charge carriers have been researched. The specific excitonic absorption peaks of the metal-organic halide perovskite could be transited to various absorption spectra, and it changed significantly in visible light through the adjustment of metal atoms and halogens
- Electroneutrality; the perovskite formula must have a neutral balanced charge therefore the product of the addition of the charges of A and B ions should be equivalent to the whole charge of the oxygen ions.
- Dielectric properties: There are some properties inherent to dielectric materials like ferroelectricity, piezoelectricity, electrostriction, and pyroelectricity. One of the important characteristics of perovskites is ferroelectric behavior.
- Electrical conductivity: Some perovskites exhibited great electronic conductivity
- Superconductivity: One of the obvious properties of perovskites is superconductivity.
- Catalytic Activity: Perovskites exhibited high catalytic activity.
- Piezoelectric property: Piezoelectric Effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress. Various applications such as capacitors, piezoelectric devices, and ferroelectric devices have been designed by using traditional inorganic perovskite materials.

Applications in Optoelectronic devices

1. Solar cells: A perovskite solar cell is a type of solar cell, which includes a perovskite structured compound, most commonly a hybrid organic-inorganic lead or tin halide-based material, as the light-harvesting active layer.

Perovskite materials are usually cheap to produce and relatively simple to manufacture. They possess intrinsic properties like broad absorption spectrum, fast charge separation, long transport distance of electrons and holes, long carrier separation lifetime, which make them very promising materials for solid-state solar cells.



2. Photodetectors: Lead halide perovskites have also been used to fabricate high-performance photodetectors.
3. Apart from these perovskite materials can be used in Light-emitting devices, Lasers, Water splitting applications such as Oxygen reduction and oxygen evolution reactions, Hydrogen evolution reactions and solid oxide fuel cells.
4. Nanoperovskites are recently utilized in electrochemical sensing of alcohols, gases, amino acids, acetone, glucose, H_2O_2, and neurotransmitters exhibiting good selectivity, sensitivity, unique long-term stability, excellent reproducibility, and anti-interference ability.

Answer 9a.

Concentration Cells: In these cells, the two electrodes of same element is in contact with solution of same metal ion (electrolyte) but of different concentration.

Cell representation: Ag / Ag^+(C_1 = 0.02 M) // Ag^+(C_2 = x M) / Cu

The Electrode reactions are as follows:

At anode $\quad Ag \rightarrow Ag^+ (C_1 = 0.02\ M) + e^-$

At cathode $\quad Ag^+ (C_2 = x\ M) + e^- \rightarrow Ag$

EMF of cell is given by

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

$$\mathbf{0.084 = \frac{2.303 \times 8.314 \times 298}{1 \times 96500}\ \log \frac{X}{0.02}}$$

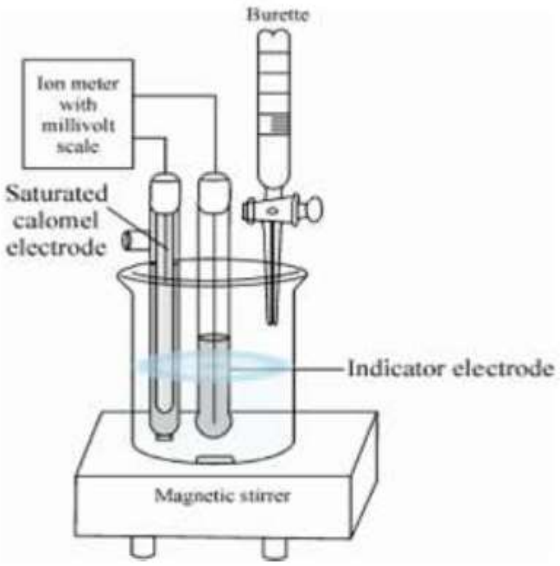
X = 0.526 M

Answer 9b

Principle: The procedure of using measurement of emf to determine the concentration of ionic species in solution is called as potentiometry also known as potentiometric titration. When a metal M is immersed in a solution containing its own ions M^{n+}, the electrode potential is given by Nernst equation.

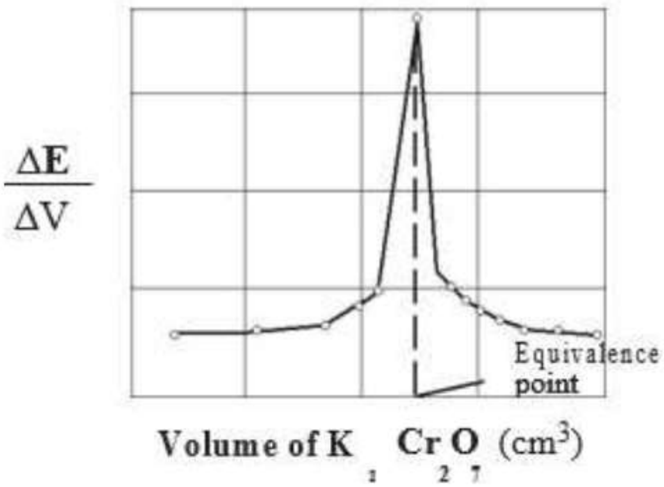
$$E = E^{o} + \frac{0.0591}{n} \log\left[M^{n+}\right]$$

Thus, the concentration can be calculated, provided E^{o} of the electrode is known. The principle involved in potentiometric titration is the measurement of emf between two electrodes, an indicator electrode, (the potential of which is function of the concentration of the ion to be determined) and a reference electrode of constant potential. In this method, the measurement of emf is made while the titration is in progress. The equivalence point of the reaction is revealed by a sudden change in potential in the plot of emf readings against the volume of titrant.



Instrumentation: It consists of: (i) Calomel electrode as a reference electrode, (ii) Platinum electrode as an indicator electrode, (iii) a device for measuring the potential and (iv) Magnetic stirrer.

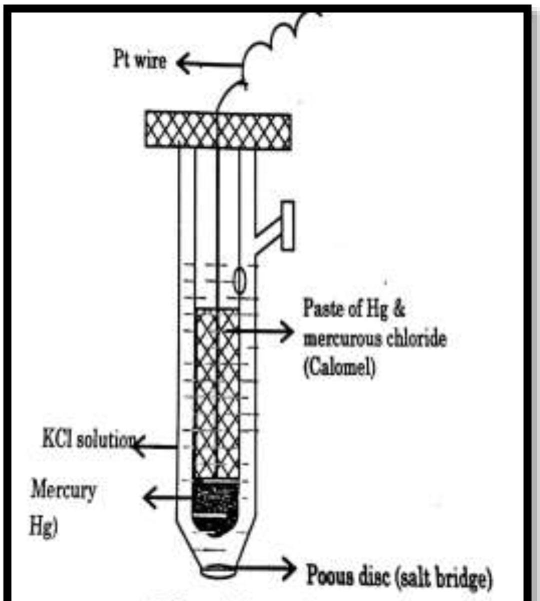
Application: Potentiometric estimation of FAS using standard $K_2Cr_2O_7$ solution: Pipette out 25ml of FAS into a beaker. Add 1 t.t dil H_2SO_4, immerse calomel electrode + platinum electrode into it. Connect the assembly to a potentiometer and measure the potential by adding $K_2Cr_2O_7$ in the increments of 0.5ml. Plot graph ΔE/ΔV against volume of $K_2Cr_2O_7$, and determine the equivalence point. From the normality and volume $K_2Cr_2O_7$, solutions calculate the normality and the weight of FAS in the given solution.



Answer 9c

Reference Electrodes : Reference electrodes are the electrodes whose potentials are known and they are used for the determination of potentials of other electrodes.

Calomel electrode: It is a metal – metal salt ion electrodes and also a secondary reference electrode.



Calomel electrode

Construction: It consists of mercury, mercurous chloride and a solution of KCl. It is made up of glass tube, Hg is placed at the bottom of the glass tube. It is covered with a paste of calomel ($HgCl_2$) and KCl solution. A solution of KCl is introduced above the paste through the side tube. Electrical contact is made through Pt wire (dipped in Hg). This glass tube is taken into another glass tube, which has a side tube and a porous plug at the bottom. This porous plug act as salt bridge. The conc of KCl solution used is either decinormal, normal or saturated. Correspondingly, the electrode is known as decinormal, normal or saturated calomel electrode. This constitutes one half cell. Calomel electrode can act as either anode or cathode. It is connected to the other half cell through salt bridge.
The calomel electrode is represented as, $Hg/Hg_2Cl_2(s)/Cl^-$ (anode) Or $Cl^-/Hg_2Cl_2(s)/Hg$ (Cathode)

Working: Depending on the potential of electrode with which the calomel electrode is connected, calomel electrode acts as anode or cathode.

(a). When it acts as anode, electrode reaction is

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

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

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

(b) When it acts as cathode, electrode reaction is

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

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

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

Thus, Net reversible electrode reaction is

$$\boxed{Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg + 2Cl^-}$$

Electrode potential is calculated using Nernst equation,

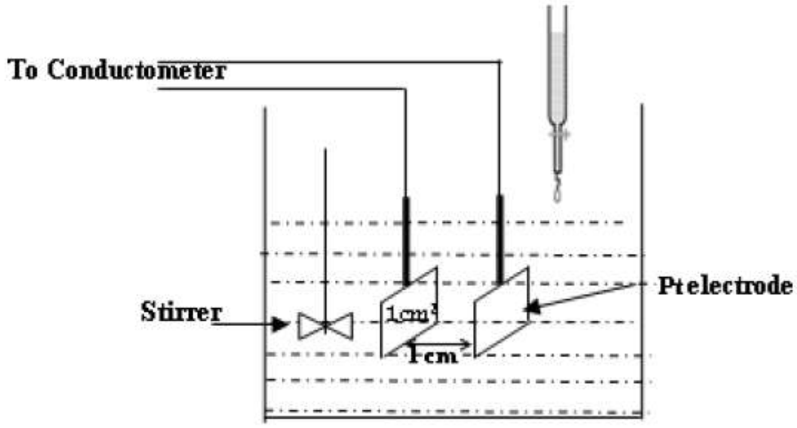
$$E_{cal} = E^\circ - \frac{2.303RT}{2F} \log [Cl^-]^2$$

Applications:1. It is used as secondary reference electrode in all potentiometric determinations.
2. Used in glass or combined electrode to determine the pH of the unknown solution.

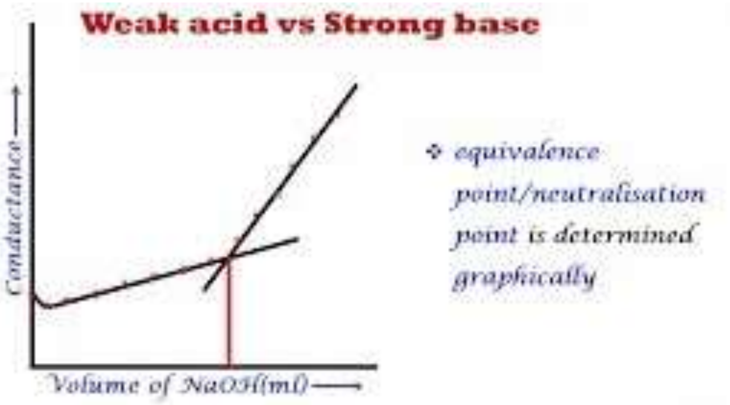
Answer 10a. Conductometric sensors are electrochemical devices that measure changes in electrical conductivity to detect analytes

Principle: Conductometric sensors are based on Ohm's law which states that the current i (amperes) flowing in a conductor is directly proportional to the applied electromotive force, E (volts), and inversely proportional to the resistance R (ohms) of the conductor. The reciprocal of the resistance is called the conductance (Ease with which electric current flows through a conductor). Specific conductance of a solution is defined as the conductance of a solution present between two parallel electrodes which have 1cm^2 area of cross section and which have kept 1 cm apart. The conductance of solution depends on the number and mobility of ions. The substitution of ions with different ionic mobility affects the electrolytic conductivity. Therefore, the equivalence point can be determined by means of conductivity measurement for a neutralization reaction between an acid and a base. Equivalence point is determined graphically by plotting conductance against titer values.

Instrumentation:
Conductometer consists of: (1) conductivity cell having two platinum electrodes; and a (ii) conductometer. A simple arrangement of conductometric titration is depicted in figure. The solution to be titrated is taken in the beaker.

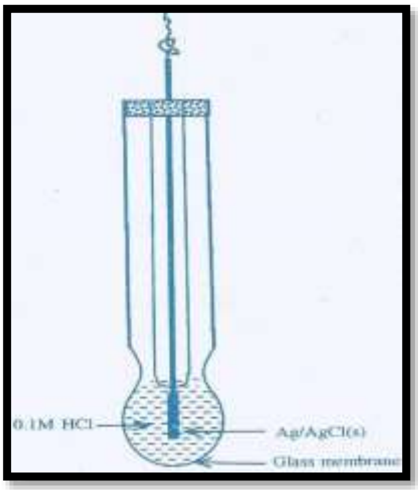


Application in the estimation of weak: Pipette out 50ml of sample into a beaker. Immerse the conductivity cell into it. Connect the conductivity cell to a conductivity meter and measure the
conductance by adding NaOH from the burette by increment of 1 ml. Plot a graph of conductance against volume of NaOH. Determine the neutralization point from the graph as shown below.



Weak acid with a strong base: (CH_3COOH Vs NaOH): In the conductometric titration of a weak acid with a strong base, the conductance of the acid will be initially low due to poor dissociation of acetic acid. On complete neutralization of the acid, further addition of base leads to an increase in the number of more mobile OH^- ions. Hence conductance increases sharply.

Answer 10b: **Ion Selective electrodes** These electrodes selectively respond to a specific ion in a mixture and potential developed is a function of concentration of that ion in the solution. These electrodes consist of a membrane which is capable of exchanging specific ions with solution with which it is in contact. These are also called as membrane electrodes. Eg. Glass electrode.

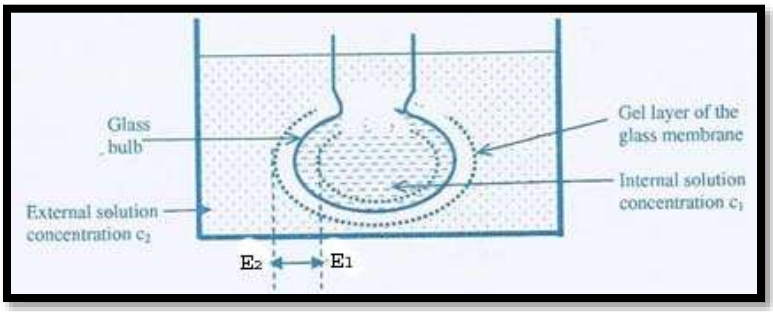


Glass Electrode Construction: The glass electrode consist of glass tube, the bottom of the glass tube is glass bulb made up of very thin glass membrane. The thickness of glass membrane varies from 0.03 mm to 0.1 mm. The membrane is made up of special glass of low melting point and high electrical conductivity. Its composition is SiO_2 – 72%, Na_2O- 22%, CaO- 6%. It can sense H^+ ions up to a pH of about 9. Glass bulb contains 0.1 N HCl (Assume concentration is C_2). An Ag/AgCl electrode (internal reference electrode) is placed in the solution and connected by a pt wire for electrical contact.

The electrode is represented as, Ag/AgCl (s)/ 0.1N HCl/ Glass

Working of glass electrode: When the glass electrode is dipped into any solution containing H^+ ions, the Na+ ions of the glass membrane are exchanged for H+ ions of the test solution.

$$H^+ + Na^+ Gl^- \longrightarrow Na^+ + H^+Gl^-$$



If a thin walled bulb containing an acid is immersed in another solution containing H^+ ions (fig), a potential is developed across the glass membrane. This is called the boundary potential E_b. It is a potential developed across the glass membrane when concentration of the solution inside and outside the glass membrane are different. The E_b is due to the difference in potential (E_2-E_1) developed across the gel layer of the glass membrane between the two liquid.

Mathematically it is represented as,

$E_b = E_2 - E_1$ Where, E_2= Potential due to H^+ present in outside solution (Unknown solution)
E_1 = Potential due to H^+ present in inside solution (known solution)

According to Nernst equation

$$E_b = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

$$E_b = \frac{0.0591}{n} \log C_2 - \frac{0.0591}{n} \log C_1 \text{.................}(1)$$

Where, C_2 is the concentration of H^+ ions of the solution into which glass membrane is dipped. The concentration of H^+ ion inside the bulb (C_1) is constant i.e. C_1 = 0.1 M.

Thus, $E_b = \frac{0.0591}{n} \log C_2 + K$ or

$= K + \frac{0.0591}{n} \log C_2$

Glass electrode selects only H^+ ions ignoring other ions.

Hence $C_2 = H^+$

$E_b = K + 0.0591 \log [H^+]$

Where, $\log [H^+] = -pH$

$$\boxed{\text{Thus, } E_b = K - 0.0591pH \text{ ---------------------}\mathbf{(2)}}$$

The combined glass electrode is dipped into acidic solution, then the potential of the glass electrode is given by….

$E_G = E_b + E_{Ag\text{-}AgCl}$ ……………………….(3)

From equation 1, theoretically if $C_1 = C_2$, E_b should be 0, however it has been observed practically that even when $C_1 = C_2$, a small potential is developed which is called as asymmetric potential (E_{asym}). Hence equation 3 can be rewritten as

$E_G = E_b + E_{Ag\text{-}AgCl} + E_{asym}$ ……………………….(4)

Substituting the value of E_b from equation (2) in equation (4)

$E_G = K - 0.0591pH + E_{Ag/AgCl} + E_{assy}$

$\boxed{E_G = E^o_G - 0.0591pH}$ **………………(5)** Where ($E^o_G = K + E_{Ag/AgCl} + E_{assy}$)

The above expression (eq 5) indicate that the potential of glass electrode, E_G varies with the pH of the acidic solution.

Answer 10c. Colorimetric sensors are optical sensors that detect analytes by the color change they cause

Principle: Colorimetry is a scientific technique that is used to determine the concentration of colored compounds in solutions.

When a beam of incident light of intensity $\mathbf{I_0}$ passes through a solution, a part of the incident lightis relected ($\mathbf{I_r}$), a part is absorbed ($\mathbf{I_a}$) and rest of the light is transmitted ($\mathbf{I_t}$)

Thus, $\mathbf{I_0 = I_r + I_a + I_t}$

In colorimeter, $\mathbf{I_r}$ is eliminated. For this purpose, the amount of light relected ($\mathbf{I_r}$) is kept constant by using cells that have identical properties. ($\mathbf{I_0}$) & ($\mathbf{I_t}$) is then measured. Colorimetry measurements are based on Beer-Lambert's law which states that when a monochromatic light passes through a transparent medium, the amount of light absorbed is directly proportional to the concentration and path length of the solution.

$\mathbf{A = \varepsilon ct}$ Where A is absorbance, ε is the molar extinction coefficient, c is the concentration, t is the path length. If t, the path length is kept constant, then, $A \propto c$. Hence a plot of absorbance against concentration gives a straight line.

Instrumentation: Photoelectric colorimeter consists of

(i) Tungsten lamp as the light source.
(ii) A filter which provides the desired wavelength range wherein the solution gives the maximum absorbance.
(iii) A sample cell
(iv) A photocell detector: Detector are photosensitive elements which converts light energy into electrical energy

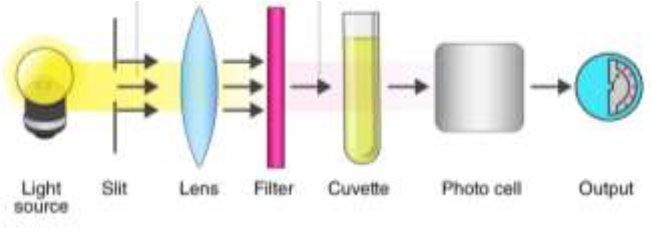


Fig: Schematic layout of colorimeter

Application: Colorimetric estimation of Cu in $CuSO_4$. Draw out 2, 4, 6, 8, and 10 ml cm_3 of the Copper sulphate solution into $50cm_3$ volumetric flask. Add $5cm_3$ of ammonia solution to each of them and dilute upto the mark with distilled water and mix well. Prepare a blank solution by diluting $5cm^3$ of ammonia solution in $50cm^3$ volumetric flasks. For test solution add 5ml of NH_3 and make up to the mark. Measure the absorbance of each of these against blank solution at 620 nm. Plot a graph of absorbance (OD) against volume of copper sulphate solution and determine the volume of copper sulphate solution in the test sample as shown in the figure and find the amount of copper present in it.