Unit 5
Nanomaterials

- **Introduction:-**

1) Nanomaterials are the materials of which a single unit is sized (in at least one dimension) between 1 and 1000 nanometers (10^{-9} meter) but is usually 1 to 100 nm (the usual definition of nanoscale).
2) Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties.
3) Naturally occurring nanomaterials may be organic & inorganic.

   Organic- wax crystals covering a lotus leaf, spider and spider-mite silk, natural colloids (milk, blood), horny materials (skin, hair), our bone matrix etc.

   Inorganic- Natural inorganic nanomaterials occur through crystal growth in the chemical conditions of the earth crust like fires represent particularly complex reactions and can produce pigments, cement, fumed silica etc
4) Nanomaterials are also prepared artificial or synthesized in laboratories. The organic nanomaterials are carbon-based fullerenes while inorganic nanomaterials such as silicon.

- **Synthesis:-**

1) Synthesis of nanomaterials (material having size 1 to 100 nm) can be done by various ways these methods are divided as Bottom up & Top down.
2) Bottom Up Methods:-
   a) In bottom methods arrangement of atoms or molecules is in nanostructured arrays. Bottom methods use raw materials that may be solid, liquid or gas. These methods are of two types Chaotic And controlled.
   b) Chaotic processes involve the elevating the constituent atoms or molecules to a chaotic state and then suddenly changing the conditions so as to make that state unstable. Control of nanoparticle formation is controlled through manipulation of the end state of the products.
   e.g. of chaotic processes are Laser ablation, Exploding wire, Arc, Flame pyrolysis, precipitation synthesis etc.
   c) Controlled Processes involve the controlled delivery of the constituent atoms or molecules to the site(s) of nanoparticle formation such that the nanoparticle can grow to a prescribed size in a controlled manner.
   e.g. of controlled processes are Self-limiting growth solution, Self-limiting chemical vapor precipitation and Shaped pulse fem to second laser techniques,

3) Top Down Methods:-

   Knowledge of processes for bottom-up assembly of structures remains in their infancy in comparison to traditional manufacturing techniques. As a result, the most mature products of nanotechnology (such as modern CPUs) rely heavily on top-down processes to define structures. The traditional example of a top-down technique for fabrication is lithography in which instruments (such as a modern stepper) are used to scale a macroscopic plan to the nanoscale.

- **Applications:-**

1) Most applications are limited to the bulk use of passive nanomaterials. Examples include titanium dioxide and zinc oxide nanoparticles in sunscreen, cosmetics and some food products.
2) Silver nanoparticles in food packaging, clothing, disinfectants and household appliances such as Silver Nano; carbon nanotubes for stain-resistant textiles; and cerium oxide as a fuel catalyst.
3) Medicinal use of nanomaterials-To help treat disease and prevent health issues. Nanotechnology has provided the possibility of delivering drugs to specific cells using nanoparticles. The overall drug consumption and side-effects may be lowered significantly by depositing the active agent in the morbid region only and in no higher dose than needed.
4) Industrial applications of nanotechnology- also applied to or developed for application to a variety of industrial and purification processes.
5) Green Nanotechnology- Purification and environmental cleanup applications include the desalination of water, water filtration, wastewater treatment, ground water treatment etc.
6) Applications of nanomaterials can be extended for construction materials, military goods, and nano-machining of nano-wires, nano-rods, few layers of grapheme.
7) Energy- Nanomaterials can be used as insulators which help saving energy. Reduction of energy consumption or increasing the efficiency of energy production is achieved. E.g. solar cells, panels, or surfaces sprayed with nanoparticles turning to a solar energy collector etc.
8) Information and communication is improved with the use of nanoparticles e.g. in CPUs or DRAM devices.

- <u>**Types of Nanomaterials**</u>

The unique properties of these various types of intentionally produced nanomaterials give them novel electrical, catalytic, magnetic, mechanical, thermal, or imaging features that are highly desirable for applications in commercial, medical, military, and environmental sectors. These materials may also find their way into more complex nanostructures and systems. As new uses for materials with these special properties are identified, the number of products containing such nanomaterials and their possible applications continues to grow.

Most current nanomaterials could be organized into four types:

I. Carbon Based Materials
II. Metal Based Materials
III. Dendrimers
IV. Composites

I. Carbon Based Materials

These nanomaterials are composed mostly of carbon, most commonly taking the form of a hollow spheres, ellipsoids, or tubes. Spherical and ellipsoidal carbon nanomaterials are referred to as fullerenes, while cylindrical ones are called nanotubes. These particles have many potential applications, including improved films and coatings, stronger and lighter materials, and applications in electronics.

II. Metal Based Materials

These nanomaterials include quantum dots, nanogold, nanosilver and metal oxides, such as titanium dioxide. A quantum dot is a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, and whose size is on the order of a few nanometers to a few hundred nanometers. Changing the size of quantum dots changes their optical properties.

III. Dendrimers

These nanomaterials are nanosized polymers built from branched units. The surface of a dendrimer has numerous chain ends, which can be tailored to perform specific chemical functions. This property could also be useful for catalysis. Also, because three-dimensional dendrimers contain interior cavities into which other molecules could be placed, they may be useful for drug delivery.

IV. Composites

Composites combine nanoparticles with other nanoparticles or with larger, bulk-type materials. Nanoparticles, such as nanosized clays, are already being added to products ranging from auto parts to packaging materials, to enhance mechanical, thermal, barrier, and flame-retardant properties.

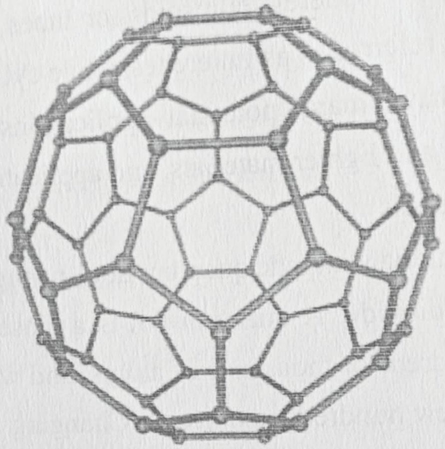
- **Characteristics and Applications**

A. Fullerenes

i) Fullerene is one of the allotropic forms of the carbon. The other name of fullerene is buckminsterfullerene. In this allotropic form of carbon, the carbon molecules are arranged in a series and form a cage like structure. This structure of fullerene is hollow in nature.In this allotropic form when the carbon molecules are arranged in a cylindrical form, they form a tube like structure. These tube-like structures are known as carbon nanotubes.

ii) In nature, fullerenes, especially the C_{60} sphere, are highly symmetrical. Fullerenes have a similar structure to graphite, which is made up of a sheet of connected hexagonal rings, but they have pentagonal (or sometimes heptagonal) rings that prevent the sheet from being planar. Buckyballs and buckytubes are terms used to describe them depending on their shape. Cylindrical fullerenes are referred to as nanotubes. C_{60} is the most common fullerene, with no two pentagons sharing an edge. A C_{60} molecule's average carbon-carbon bond length is 1.44 angstrom.

iii) Types of fullerene- Buckminsterfullerene, Endohedral Fullerene, Herbal fullerenes, Buckyball Clusters, Nanotubes, Megatubes, Linked bucky ball and chain Dimers, Herbal fullerenes



iv) Properties of Fullerene

Physical Properties of Fullerene

- Fullerene shows variation in behaviour and structure on changing the temperature. At a higher temperature the fullerene is converted into the C_{70} form.
- Fullerene shows change in structure under different pressures.
- The ionization enthalpy of fullerene is 7.61 electron volts.
- The electron affinity of fullerene is 2.6 to 2.8 electrons volts.

Chemical Properties of Fullerene

- Fullerene (C_{60}) resembles an electrophile in the chemical reactions.
- Fullerene can act as an electron acceptor group. It can easily accept three electrons or more. Therefore, it can behave as an oxidizing agent.
- Fullerenes are doped with the alkali or alkaline earth metals, so that it can exhibit superconductivity properties.
- Ferromagnetism is a property of fullerene.
- Carbon molecules abound in fullerene. As a result, it's very soluble in organic solvents.

v) The use of buckminsterfullerene is based on its chemical properties and its physical properties.

- Fullerene is used as conductors.
- It can be used as an absorbent for gases.
- Fullerene is used as lubricants.
- Some forms of the fullerenes are used in making cosmetics related materials.
- Carbon nanotubes are made up of graphene sheets.
- Some forms of fullerenes are used in biomedical applications.
- Fullerenes are used in making carbon nanotubes based fabrics and fibres.

B. Carbon Nanotubes

A carbon nanotube (CNT) is one of the most important nanomaterials. Before 1991, only two main allotropes of carbon were known. In 1991, a Japanese physicist, SumioLizima invented CNT (another allotrope of carbon).

Nanotubes are formed by folding or rolling two-dimensional graphite into a cylindrical shape structure. Nanotubes are hollow from inside. The diameter of the nanotube is around 1-3 nanometers. The length of the carbon nanotube is much higher than its diameter. Nano tube length generally goes to a few micrometers. In short, carbon nano (CNT) is a folded form of the two-dimensional graphene sheet. CNT (carbon nanotubes) exhibit extraordinary mechanical properties.

➢ Properties of Carbon Nanotube

i) Carbon nanotubes are stiff. They are as stiff as a diamond (the hardest natural material in nature).

ii) The gravitational weight of the nanotube is very low.&density of the carbon nanotubes is one-fourth of that of steel.

iii) Carbon nanotubes are stronger than steel. They exhibit extraordinary mechanical properties. Carbon nanotubes are ten times stronger than steel.

iv) Carbon nanotubes have a high thermal capacity. Therefore, it does not expand on heating like that of steel. Therefore carbon nanotubes uses in making bridges and aircrafts material

v) In carbon nanotubes, each carbon atom is surrounded by three other carbon atoms through covalent bonds. These carbon-carbon covalent bonds forms lattice in the shape of hexagons.The crystalline structure of carbon nanotubes exists in the form of regular hexagons.

vi) Carbon nanotubes are elastic, good conductors of heat&electricticity.

vii) Carbon nanotubes are chemically neutral. So, they are chemically stable. Therefore, carbon nanotubes resist corrosion.

➢ Types of Carbon Nanotubes

a. Single-walled Carbon nanotubes

Single-walled Carbon Nanotubes- it is represented as SWCNT. The Single-walled Carbon nanotubes exist in a 1-d structure. Some examples of Single-walled CNT are armchair and zig-zag Single-walled Carbon nanotubes

Properties of Single-walled Carbon Nanotubes are:

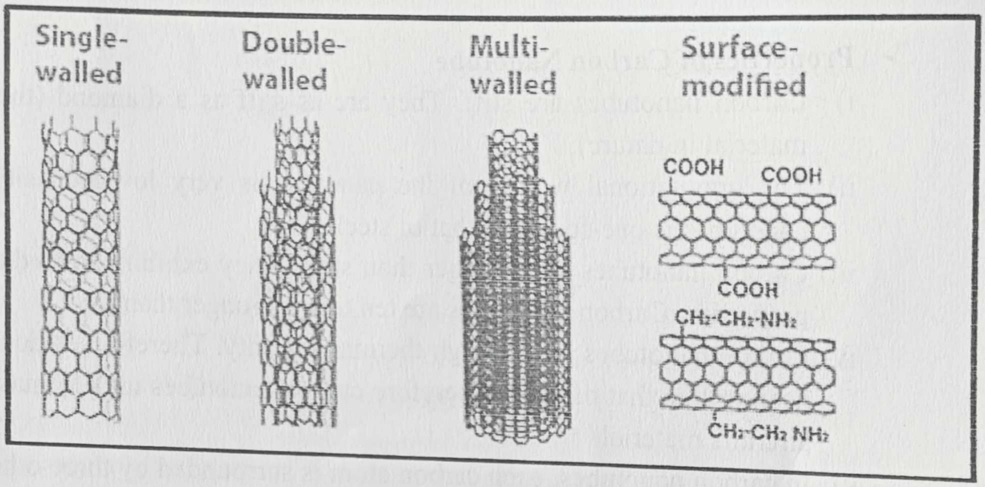
- The diameter of Single-walled Carbon nanotubes is 2nm.
- The length of Single-walled Carbon nanotubes is around 2 micrometres.
- They exist in a one-dimensional structure. Therefore, it is also known as a nanowire.
- Electronics can be miniaturized by using a Single-walled Carbon nanotube.
- Their band gap varies from 0-2 electron volts (eV).
- They show conductivity like a semiconductor. Therefore, they exhibit both metallic and semiconductivitybehaviour.

b. Multi-walled Carbon nanotubes

Multi-walled Carbon Nanotubes- It is represented as MWCNT. It is composed of several nested carbon nanotubes. This type of nanotubes has two diameters, one is known as outer diameter and another one is known as inner diameter. An example of Multi-walled Carbon nanotubes is chiral Multi-walled Carbon nanotubes.

Properties of Multi-walled Carbon Nanotubes are given below:

- The outer diameter of Multi-walled Carbon nanotubes is around 2-20 nanometres.
- The inner diameter of Multi-walled Carbon nanotubes is 1-3 nm.
- The length of Multi-walled Carbon nanotubes is around 5-6 micrometres.



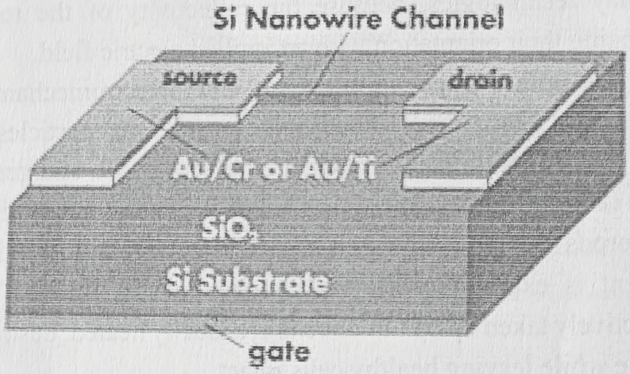
➢ **Uses**

- Composite materials containing carbon nanotubes are being used in sporting goods.
- Carbon nanotubes are used to make bullets proof jackets.
- Carbon nanotubes can be used to make aircraft and space craft's body.
- Carbon nanotubes can be used to build high-performance nanoscaled thin-film transistors to replace silicon-based transistors because of the semiconducting properties of carbon nanotubes.
- Carbon nanotubes can be used to make biosensors and electrochemical sensors.
- Carbon nanotubes are used in making electrodes to study electrochemical reactions because of their excellent electrical properties.

C. Nanowires

1) Nanowires are based up on a flat substrate of semiconductor materials, such as silicon and germanium. Nanowires are simply very tiny wires. They are composed of metals such as silver, gold or iron. The small nanowire is created by nanoparticles with a diameter as small as nanometer.
2) Basically the diameter of nanowires is one nanometer, engineer's works with 30 and 60 nanometers. A nanowire plays a significant role in field of quantum computers and nanorobots are very tiny machines which are planned for a specific function or tasks repeatedly with some accuracy at nonascale dimension.

3) There are two basic approaches to synthesizing nanowires: top-down and bottom-up. A top-down come within reach of reduce a large piece of substance to small pieces. Nanowire transistors made with conventional lithographic fabrication methods can improve performance in nonascale electronics.
4) A bottom-up approach synthesizes the nanowire by combining component and atoms. Most synthesis techniques use a bottom-up approach. A wide variety of elemental, binary and compound semiconductor nanowires has been synthesized via the VLS method, and comparatively good control over the nanowires diameter and diameter distribution has been achieved.
5) There are different types of nanowires in technology, they are: Metallic nanowires, semiconducting nanowires, insulating nanowires. The structure of nanowires is very simple, made of variety of materials.
6) A simple Silicon Nanowire Transistors is shown in figure. Silicon nanowire transistor simplifies both processing and allows the devices to be switched on and off more easily.



7) **Properties of nanowire**
   a) **Mechanical property-** The enormous amount of grain boundaries in a bulk material are made of nanoparticles which allow extending the grain boundaries sliding leads to high flexibility.
   b) **Magnetic property-** In the magnetic property of nanoparticles the energy of magnetic anisotropy might be that miniature that the vector of magnetization fluctuates thermally, this is called super magnetism. Combining the particles with high energy of anisotropy with a super magnetic may over leads to a new class of permanent magnetic materials.
   c) **Optical property-** In optical property the allotment of non-agglomerated nano particles in a polymer are used to the directory of refraction. In addition, such a procedure may manufacture material with non-linear optical properties or visual property.

8) **Applications**
   i) An inorganic nanotube is a cylindrical molecule often composed of metal oxides, or group III-Nitrides and morphologically similar to a carbon nanotube. Inorganic nanotubes have been observed to occur naturally in some mineral deposits.

ii) Bacterial nanowires (also known as microbial nanowires) are electrically conductive appendages produced by a number of bacteria most notably from (but not exclusive to) the *Geobacter* and *Shewanella* genera.

iii) Molecular wires (or sometimes called molecular nanowires) are molecular chains that conduct electric current. They are the proposed building blocks for molecular electronic devices. Their typical diameters are less than three nanometers, while their lengths may be macroscopic, extending to centimeters or more.

iv) An optical rectenna is a rectenna (rectifying antenna) that works with visible or infrared light. A rectenna is a circuit containing an antenna and a diode, which turns electromagnetic waves into direct current electricity. The term **nantenna** (nano-antenna) is sometimes used to refer to either an optical rectenna, or an optical antenna by itself.

v) In nanotechnology, **nanorods** are one morphology of nanoscale objects. Each of their dimensions range from 1–100 nm. One potential application of nanorods is in display technologies, because the reflectivity of the rods can be changed by changing their orientation with an applied electric field.

Another application is for microelectromechanical systems (MEMS). Nanorods, along with other noble metal nanoparticles, also function as the diagnostic agents. Nanorods absorb in the near IR, and generate heat when excited with IR light. This property has led to the use of nanorods as cancer therapeutics. Nanorods can be conjugated with tumor targeting motifs and ingested. When a patient is exposed to IR light (which passes through body tissue), nanorods selectively taken up by tumor cells are locally heated, destroying only the cancerous tissue while leaving healthy cells intact.

vi) A nanowire battery uses nanowires to increase the surface area of one or both of its electrodes. All of the concepts replace the traditional graphite anode and could improve battery performance.

vii) Silicon nanowires, also referred to as SiNWs, are a type of semiconductor nanowire. Such nanowires have promising applications in lithium ion batteries, thermoelectrics and sensors.

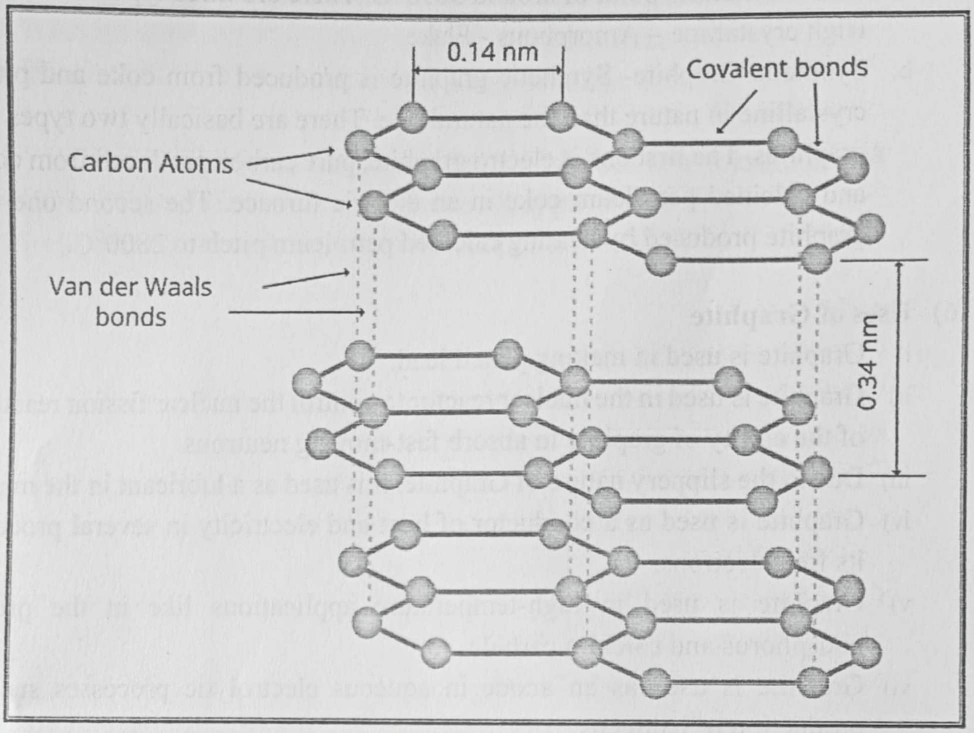
D. Graphite

1) Graphite is one of the very common allotropes of carbon. It is also the most stable allotrope of carbon and thus used in electrochemistry as the standard state for defining the heat of formation of carbon compounds.

2) Graphite is not an element or a compound, it's an allotrope of carbon. It doesn't have any chemical formula of its own. Graphite is a good conductor of heat and electricity with a density of 2.09–2.23 g/cm^3. Graphite was accidentally synthesized by Edward G. Acheson for the first time when he was working on a high-temperature experiment on carborundum. He found that at around 4150^{0}C, the silicon in the carborundum gets vaporized, whereas leaving behind the carbon in the graphitic form.

3) Graphite is a big covalent structure with each carbon atom joined with three other carbon atoms with covalent bonds. Each carbon atom is sp^2 hybridized. These carbon

atoms form a layer like structure with a hexagonal arrangement of carbon atoms. These layers have weak forces between them. Due to these weak forces, the layers can slip over each very easily. Each carbon atom has one non bonded electron, which becomes delocalized.



4) **Properties of Graphite**

Physical Properties of Graphite

- Graphite is a good conductor of electricity due to its free delocalized electron which is free to move throughout the sheets.
- Graphite is insoluble in organic solvents and water, this is because the attraction between solvent molecules and carbon atoms is not strong enough to overcome the covalent bonds between the carbon atoms in the graphite.
- Graphite has a high melting point of 3650 ^{0}C near the melting point of Diamond.
- Due to its layer-like structure, it is soft and slippery in nature.
- Graphite has the ability to absorb high-speed neutrons.

Important **Chemical** Reactions

- Reaction with air - Carbon in the form of Graphite, burns in the air to form Carbon Monoxide and carbon Dioxide depending upon the availability of air or oxygen.

$$C(s)+O_2 \rightarrow CO_2(g)C(s)+O_2 \rightarrow CO_2(g)$$

$$2C(s)+O_2(g) \rightarrow 2CO(g)$$

$$2C(s)+O_2(g) \rightarrow 2CO(g)$$

- Reaction with Water - Carbon in the form of Graphite doesn't react with water in normal conditions. Under certain circumstances, the given reaction becomes possible and forms water gas which is a mixture of carbon monoxide and hydrogen gas.

$$C+H_2O \rightarrow CO+H_2$$

5) **Types of Graphite**

a. Natural Graphite- Natural Graphite, an excellent conductor of heat and electricity, is a mineral composed of graphitic carbon. It is stable over a range of temperatures, with the melting point of around 3650°C. There are three types of natural graphite. High crystalline – Amorphous - Flake

b. Synthetic Graphite- Synthetic graphite is produced from coke and pith. It is less crystalline in nature than the natural one. There are basically two types of synthetic graphites. The first one is electro graphite, pure carbon produced from coal tar pitch, and calcined petroleum coke in an electric furnace. The second one is synthetic graphite produced by heating calcined petroleum pitch to 2800^0C.

6) **Uses of Graphite**

i) Graphite is used in making pencil lead.
ii) Graphite is used in the nuclear reactor to control the nuclear fission reaction because of the ability of graphite to absorb fast-moving neutrons.
iii) Due to the slippery nature of Graphite, it is used as a lubricant in the machine parts.
iv) Graphite is used as a conductor of heat and electricity in several processes due to its free electrons.
v) Graphite is used in high-temperature applications like in the production of phosphorus and calcium carbide.
vi) Graphite is used as an anode in aqueous electrolytic processes such as in the production of halogens.
vii) Graphite is used as an electrical material in the electric motor as a carbon brush.
viii) Due to its resistant nature towards chemicals and high melting temperatures, it is used to make crucibles.
ix) Graphite materials are used as the anode material for lithium-ion batteries.
x) **Chemical Industry** - In the chemical field, graphite is used in many hot climates, such as in the production of phosphorus and calcium carbide in arc furnaces. Graphite is used as an anode in certain electrolytic processes in liquids such as halogen production (chlorine and fluorine).
xi) **Nuclear Industry** - Large quantities of high-purity electro graphite are used to produce presidential sticks and display components in nuclear reactors. The lowest absorption of neutrons leads to the building of suitability of electro graphite and high thermal conductivity, with high strength and high temperatures.
xii) **Electricity applications** - The manufacture of carbon brushes in electric motors have incorporated a huge amount of graphite which is used as an electric material. Here, the service life of a component and performance depends largely on the distance and structure.
xiii) **Mechanical Applications** - Graphite is widely used as an engineering material in all applications such as piston rings, thrust bearings, journal bearings, and vanes. Carbon-based seals are used in petrol pumps and on the engine walls of several aircraft engines.

- **Questions**

Q.1 What are Nanomaterials? Explain different applications of it. **4M**

Or

Write the applications of nanomaterials in chemistry. **5M**

Q. 2 What is fullerene? Write its properties & applications.**5M**

Q. 3 What is CNT? Write its properties & applications. **5M**

OR

Explain carbon nanotubes with its properties & applications. **5M**

Q. 4 Describe nanowires with its properties & applications. **6M**

Q. 5 Explain graphite with its properties & applications. **6M**

Department of First Year Engineering (F. Y. B. Tech.)

ACADEMIC YEAR 2022- 2023 (SEM: I)

Course: Applied Chemistry

Course code: 221FYL111

Unit: 6 Battery Technology & Fuel Cells

5.8 NEED FOR ENERGY STORAGE-BATTERIES

There is increasing demand for electrical energy and heat energy constantly and there is going to be energy crisis. The power supply has become intermittent now.

It is most convenient to have stored electrical energy (or solar energy) for guaranteed use whenever required. Batteries are the most viable alternatives for the purpose.

Batteries can be regarded as **storehouses** for electrical energy on demand. Electrical energy from batteries can be considered as **the portable power**. Can be easily carry from hand.

Dry cells have been invented in early 20^{th} century and various rechargeable batteries have come up then after to dominate. Various batteries like lead-acid battery, nickel-cadmium battery, Zn-HgO battery, fuel batteries, lithium batteries, Li^+ – ion batteries, etc. have been developed now as rechargeable batteries.

Batteries are required for electronic consumer devices like walkman, radio, mobiles, remote controller, watches, calculators, computers etc. and also for household and military use of batteries for light, search light purposes, for laboratory experiments, for use in satellite, interplanetary explorations with rockets. Batteries are also required for starting, lighting and ignition purposes in motor vehicles. Although in very small proportion, presently two-wheelers, cars are run on batteries which do not cause any pollution.

The basis of the battery technology is that the chemical energy derived from chemical reactions in battery, is converted into the electrical energy and this energy can be used as and when required. The efficiency of conversion of chemical energy of a reaction in battery into electrical energy is very high 60-80% as against 20-35% efficiency of heat engines. Further the efficiency of conversion of electrical energy into other forms of energy (mechanical sound light) is also very high. This is the reason why batteries are most preferable for applications.

5.9 BASIC TERMS REGARDING BATTERIES

1. **Battery :**

It is the parallel or series combination of two or more cells. A single cell has low voltage but such combination can give higher voltage.

2. **Charging :**

When a secondary battery gets discharged, the reaction in battery is reversed by providing electrical energy from external D.C. source. On complete charging, the products formed during discharge, are converted into reactants.

3. **Number of charge-discharge cycles :**

The number of times, the discharged secondary battery can be charged, is known as charge-discharge cycles e.g. a nickel-cadmium battery can be charged for about 3000 times. The lead-acid battery in its life can be charged about 250 times (provided reactants not leaked and battery is not kept discharged for long period). After that the battery capacity fades. Sometimes internal short-circuit spoils the secondary battery.

4. **Energy density :**

The performance of a battery in terms of electrical energy (watt-hours) obtained from unit volume, is called as energy density. Its unit is Wh/L.

5. **Specific energy :**

The battery performance expressed as electrical energy (watt-hours) obtained from unit weight, is known as specific energy and its unit is Wh/kg.

6. **Power density :**

The number of watts obtained from unit volume is called as power density and its unit is W/L.

A graph of energy density of a battery with power density, gives idea about the power at which energy begins to fall off rapidly.

5.10 TYPES OF BATTERIES

Types of batteries are as follows :

1. Primary battery
2. Secondary battery
3. Flow battery or fuel cells
4. Reserve battery

1. **Primary battery :** The battery once discharged has to be discarded, is the primary battery. Such battery cannot be recharged e.g. dry cell (Zn | MnO_2, H_2O, NH_4Cl | graphite).
2. **Secondary battery :** The battery which gets discharged on use but can be charged again and again, is known as secondary cell. e.g. Ni-Cd battery, lead-acid battery, etc.
3. **Flow battery or Fuel cells :** A device in which gaseous reactants flow through the battery and undergo combustion reaction, to produce electricity, is known as flow battery.
4. **Reserve battery :** In this battery, active materials are kept separated by special arrangement and when the battery is to be used, an activation device makes it work. Such a battery is designed for long storage before use.

The secondary batteries should satisfy the following :

(i) Have longer cycle life, high power density.
(ii) It should not leak or vent matter from it.
(iii) It should have low cost per unit energy.
(iv) It should be suitable for the application.
(v) The active materials in a battery should be stable.
(vi) It should be usable over a wide temperature range.
(vii) It should maintain its capacity from cycle to cycle, overcharge ability.
(viii) It should be safe and easily disposable.

5.11 NICKEL-CADMIUM BATTERY

Ni-Cd batteries are the commonly used rechargeable batteries today, for various consumer applications. This is an alkaline storage battery. It is prepared in discharged state by taking anode as cadmium spongy electrode and the cathode is highly porous nickel impregnated with NiO(OH) nickel oxyhydroxide. The electrolyte is the KOH in a gel medium. The battery can be represented as :

$$\mathrm{Cd} \mid \underset{(\mathrm{gel})}{\mathrm{KOH}} \mid \underset{(\mathrm{gel})}{\mathrm{NiO\ OH}} \mid \mathrm{Ni}$$

The discharging reactions are :

Anode : $Cd + 2\bar{O}H \rightarrow Cd(OH)_2 + 2e^-$

Cathode : $2\,NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2\bar{O}H$

Net reaction : $Cd + 2NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$

The charging reactions are exactly reverse of discharging reactions.

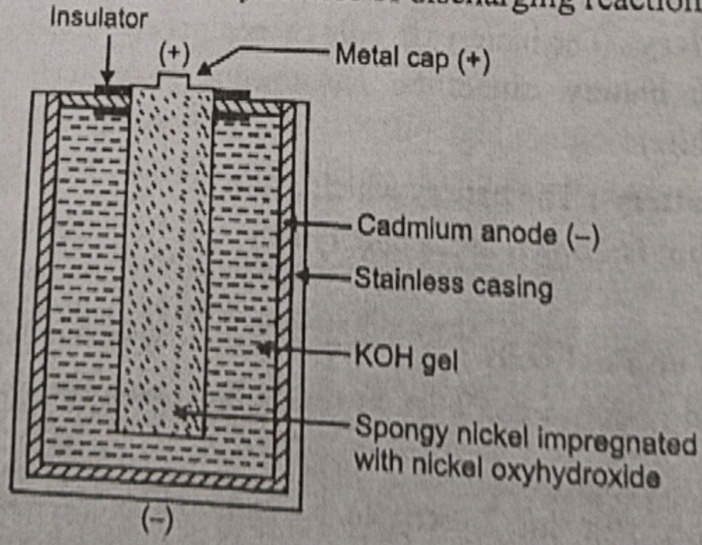


Fig. 5.15

Characteristics :

(i) The battery can be charged in short time about 15 minutes by special chargers.

(ii) It has long cycle life and it has over 300 charge-discharge cycles life.

(iii) One cell has working voltage of 1.3 volts.

(iv) It has high energy density = 325 Wh/L.
High specific energy = 230 Wh/kg
and High power density = 1.35 Amp.hours

(v) Cd in the cell is highly toxic.

(vi) It can be prepared in prismatic, buttonlike, cylindrical forms as per the requirements of applications.

Applications :

(i) Prismatic cells with pocket electrodes, are applicable for stationary and remote power requirements, load levelling.

(ii) Button cells are useful for small electronic devices.

(iii) Cylindrical cells are useful for common applications like torch, camera, audio uses, toys, calculator, mobiles etc.

(iv) Large sized cells are used in space applications in conjunction with solar cells. When a satellite is defacing sun, the solar cells charge the Ni-Cd cells and when it is at opposite side of sun, the Ni-Cd batteries provide power to satellite.

(v) Ni-Cd batteries are also used for air-craft, emergency lighting, diesel engines.

5.12 LITHIUM CELLS

A cell having lithium anode, is known as lithium cell. The cathode may be a solid like MnO_2, poly (2-vinyl pyridine) or a liquid like thionyl chloride or propylene carbonate, SO_2 etc.

The lithium cells have the property of forming high energy film with some solvents. When external circuit is completed, the lithium anode surface reacts with the solvent to form the thin film, which is conductive to only Li^+ and not electrons. The lithium ions are transferred to anode through this film. The organic compounds such as propylene carbonate, ether, tetrahydrofuran, dioxolane are the best used solvents for lithium cells. The electrolyte salts include lithium perchlorate, lithium tetrafluoroborate, lithium hexafluorophosphate, etc.

The lithium cells are in the designs of button cells, cylindrical cells, flat cells. Due to low conductivity of organic liquid, the cathode reactions happen slowly. Therefore, very thin separator and thin electrodes are used.

The lithium cells are of two types i.e. primary or non-rechargeable cells and secondary or rechargeable cells.

Primary Lithium Cells

1. Li-MnO_2 Cell :

Anode is the lithium in contact with organic solvent. The cathode is a metal coated with MnO_2 and it is in contact with electrolyte. The electrodes are separated by a very thin separator. Reactions taking place are :

Anode : $Li \rightarrow Li + e^-$

Cathode : $MnO_2 + Li + e^- \rightarrow LiMnO_2$

Cell voltage = 3 volts

Energy density = 400 Wh/litre

Applications : Cylindrical cells are used for camera. Button cells are used for watches, calculators and electronic devices.

2. Li - I_2 Cell :

Iodine forms a charge transfer complex with poly (2-vinyl pyridine), acting as cathode.

Anode : $Li \rightarrow Li^+ + e^-$

Cathode : $I_2 + 2e^- + 2\ Li^+ \rightarrow 2\ LiI$

Voltage : 2.5 volts

Energy density : 900 Wh/litre

Operating temp. : 37°C

Applications : It is a long-life cell, used for heart pacer. It is also used in medical electronics.

Some other lithium primary cells are Li-SO_2 cell, Li-$SOCl_2$ cell, etc.

Rechargeable Lithium cells :

1. Lithium ion cell :

Positive electrode is the lithiated transition metal oxide such as $LiCoO_2$ or $LiMnO_2$ mixed with a conductor and binder and then coated on a metal foil. The negative electrode consists of graphite and binder coated on another metal foil. The cell is charged in discharged state and then charged.

Anode : $LiCoO_2 \rightarrow Li_xCoO_2 + (1 - x)\ Li^+ + (1 - x)\ e^-$

Cathode : $C + yLi^+ + ye^- \rightarrow CLi_y$

Charge-discharge cycles : 1200

Voltage = 4.1 volt

Energy density = 250 Wh/L

Specific energy = 115 Wh/kg

Applications : Mobiles, laptops, camcorders, vehicles, other energy storage applications.

2. Polymer electrolyte lithium cell :

Anode is the lithium foil. Cathode is the metal coated with MoS_2 or V_2O_5. The lithium cell with liquid electrolyte can be designed but conducting polymer electrolyte is preferred. There is no need of separator if polymer electrolyte is used.

A lithium salt dissolved in polyethylene oxide can be used as polymer electrolyte. The polymer electrolyte cells however require about 50°C for operation.

These cells have poor charge retention. These have long shelf life and ability to bear overcharging. The lithium polymer electrolyte cells have high energy density, specific energy.

3. Lithium alloy cells :

Anode	:	Li, Al alloy
Cathode	:	Graphite / MnO_2 / V_2O_5
Electrolyte	:	Liquid organic electrolyte

The cell is safer, poor cycle life and it has low energy density. It is designed in coin cell form. It operates at higher temperature.

5.13 FUEL CELLS

Introduction

A fuel cell is a design in which a fuel is oxidized at anode by an oxidant (O_2 or air) at cathode, to convert the chemical energy of oxidation into electrical energy. The reactants are fed continuously and separately to the electrodes, separated by an ion conducting barrier. Catalytic oxidation of fuel occurs at anode and intermediate product formed diffuses to cathode through ion conducting medium to react with O_2 to form the product of reaction. The electrons liberated at anode travel through electrical load in external circuit. A large number of such cells are stacked and connected in series to get required output.

Types of fuel cells :

(I) On the basis of temperature of operation, fuel cells are classified as :

(a) **Low temperature fuel cells :** These cells operate below 100°C but need catalyst on the electrode to accelerate the reactions. H_2, N_2H_4, CH_3OH are usable as fuels for these cells. O_2 is the oxidant and pure feeds are required to avoid the poisoning of catalyst. Electrolyte is usually aq. KOH but dil. H_2SO_4 for $CH_3OH - O_2$ and polymer electrolyte for H_2-O_2 cell.

(b) **Moderate temperature fuel cells :** The cells operate at 100-250°C. Fuels like H_2, hydrocarbons are used in the cells and air (free from CO_2) is the oxidant. Electrolyte is KOH solution but phosphoric acid for hydrocarbon-O_2 cell and Pt as catalyst.

(c) **High temperature fuel cells :** These cells are operated at >500°C, the electrolyte is the mixture of fused alkali metal carbonates.

(II) On the basis of nature of electrolyte, fuel cells are classified as :

(A) Alkaline fuel cells (AFC) :

30 to 85% aq. KOH is the electrolyte. Porous carbon or plastic electrodes with catalyst like Pt, Au, Ag, metal oxides are used in these cells.

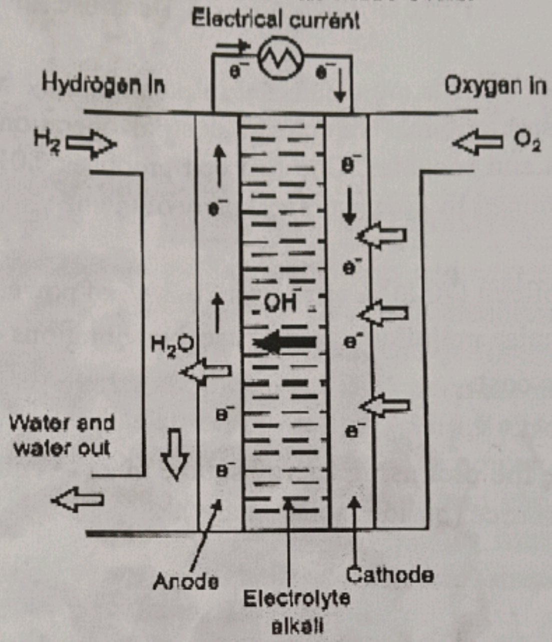


Fig. 5.16

Construction :

Anode is the porous graphite electrode impregnated with Pt powder catalyst. Cathode is also porous graphite electrode but impregnated with catalyst Ag. The anode and cathode are in the hollow cylindrical form having inlet for supply of H_2 gas, O_2 gas respectively. The two tubular electrodes are kept in an insulator pot filled with 30% to 50% KOH solution. There are water vapour venting small holes at the top of the pot. The H_2 and O_2 gases are at 4 to 5 atmospheric pressure during operation. Efforts are on to make more efficient and cheaper electrodes for fuel cells.

Reactions :

Cell Pt, Fuel | KOH | O_2, Ag

When the fuel cell is operated using H_2 gas supply to anode and O_2 gas supply for cathode, the reactions take place as below :

At Anode : $2H_2 + 4\bar{O}H \xrightarrow{Pt} 4H_2O + 4e^-$

At Cahode : $2H_2O + O_2 + 4e^- \xrightarrow{Ag} 4\bar{O}H$

Net reaction : $2H_2 + O_2 \rightarrow 2H_2O$

The product of the reaction is water in the beginning but when the cell warms up, it is in the form of water vapours which vent through hole on top of the container.

Applications :

1. Fuel cells are important for use in manned space shuttles.
2. Fuel cells are used for search lights for under sea use and in remote areas for lighting.
3. If enough number of cells are connected in parallel, they can provide sufficient voltage for transportation of vehicles, industrial operations, emergency power supply to houses and societies. One fuel cell produces 0.01 watt power. Higher power can be obtained by connection of many of them.

Advantages :

(i) High efficiency of cell (70-80% as against 20-30% of power plants and engines).

(ii) No thermal and noise pollution, clean to use. No vibrations during use.

(iii) Low maintenance cost.

(iv) Low operation cost.

(v) Fuel cells will be the promising energy source in 21^{st} century, where H_2 will be the main energy source (besides solar energy).

Limitations :

(i) High initial cost.

(ii) H_2 is not a primary fuel.

(iii) Life time of cell is long enough but not predictable accurately.

(iv) Large storage volume is required for H_2, O_2 cylinders and cell assembly.