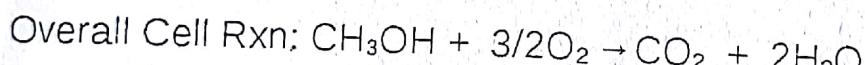
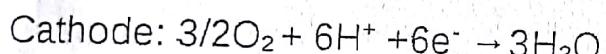
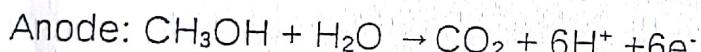


Methanol-Oxygen Fuel cell

Methanol and water are adsorbed on a catalyst usually made of platinum and ruthenium particles, and lose protons until carbon dioxide is formed. As water is consumed at the anode in the reaction, pure methanol cannot be used without provision of water via either passive transport such as back diffusion (osmosis), or active transport such as pumping.

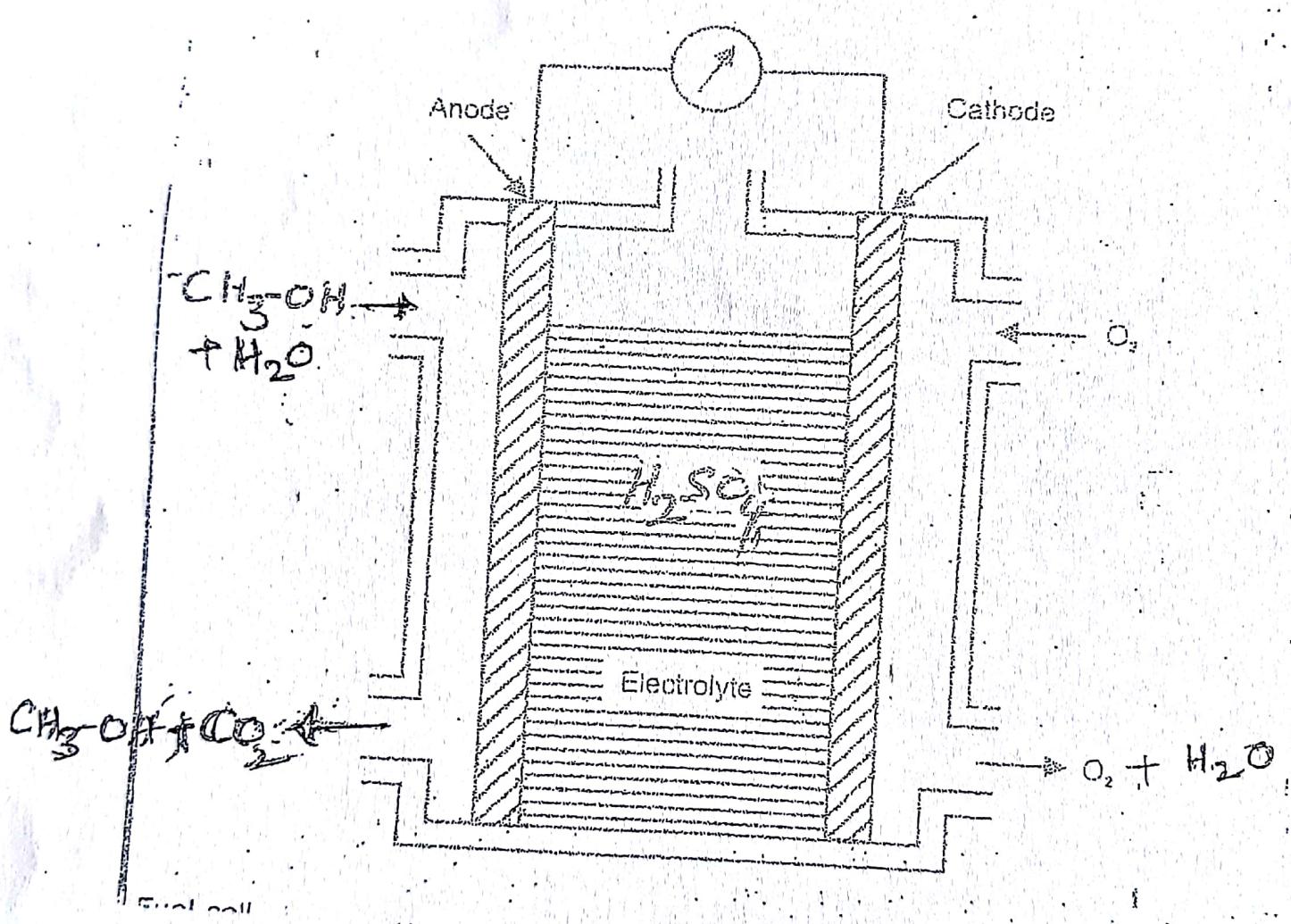
Platinum is used as a catalyst for both half-reactions. This contributes to the loss of cell voltage potential, as any methanol that is present in the cathode chamber will oxidize. If another catalyst could be found for the reduction of oxygen, the problem of methanol crossover would likely be significantly lessened. Furthermore, platinum is very expensive and contributes to the high cost per kilowatt of these cells.



A methanol molecule reacts with a water molecule at the anode liberating carbon dioxide, 6 protons and 6 electrons—a very high electron yield. The carbon dioxide produced in the reaction is rejected by the acid electrolyte. Oxygen is reduced at the cathode, producing water, which is removed by the air flowing through the cathode compartment. The maximum voltage attainable from the overall reaction in the methanol-air cell is in theory 1.186 V, but in practice this is not achieved.

Applications :

1. Used as a power source for space vehicles
2. Used in emergency and portable power generation
3. Used as potable water



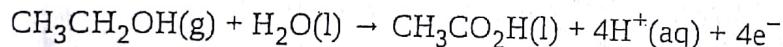
METHANOL-OXYGEN FUEL CELL

Breath analyser

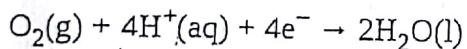
A breathalyzer or breathanalyser (a portmanteau of *breath* and *analyzer/analyser*) is a device for estimating blood alcohol content (BAC) from a breath sample.

Breath analyzers do not directly measure blood alcohol content or concentration, which requires the analysis of a blood sample. Instead, they estimate BAC indirectly by measuring the amount of alcohol in one's breath. Two breathalyzer technologies are most prevalent. Desktop analyzers generally use infrared spectrophotometer technology, electrochemical fuel cell technology, or a combination of the two. Hand-held field testing devices are generally based on electrochemical platinum fuel cell analysis and, depending upon jurisdiction, may be used by officers in the field as a form of "field sobriety test" commonly called PBT (preliminary breath test) or PAS (preliminary alcohol screening) or as evidential devices in POA (point of arrest) testing.

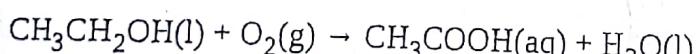
When the user exhales into a breath analyzer, any ethanol present in their breath is oxidized to acetic acid at the anode:



At the cathode, atmospheric oxygen is reduced:



The overall reaction is the oxidation of ethanol to acetic acid and water.



The electric current produced by this reaction is measured by a microcontroller, and displayed as an approximation of overall blood alcohol content (BAC) by the Alcosensor. In order to demand a person produce a breathalyzer sample an officer must have "reasonable suspicion" that the person drove with more than 80 mg alcohol per 100 mL of blood. The demand must be within three hours of driving.

HYDROGEN STORAGE METHODS

Our current global energy consumption is rapidly increasing while our primarily energy sources (fossil fuels) are rapidly depleting. Furthermore, the pollution and climate change represent undesirable side effects of global concern. To meet these major challenges, it is needed to shift from carbon-based non-renewable resources to carbon-neutral renewable sources of energy. Hydrogen has been considered as the fuel of the future and an alternative to depleting fossil fuels.

Hydrogen exhibits the highest heating value per mass of all chemical fuels. Furthermore, hydrogen is regenerative and environmentally friendly.

There are some reasons why hydrogen is not the major fuel of today's energy consumption.

1. First of all, hydrogen is just an energy carrier. And, although it is the most abundant element in the universe, it has to be produced, since on earth it only occurs in the form of water and hydrocarbons. This implies that we have to pay for the energy, which results in a difficult economic dilemma.
2. The second difficulty with hydrogen as an energy carrier is its low critical temperature of 33 K (i.e. hydrogen is a gas at ambient temperature). For mobile and in many cases also for stationary applications the volumetric and gravimetric density of hydrogen in a storage material is crucial.
3. The technical obstacles in hydrogen economy is hydrogen storage and transportation issue
4. Lastly, the purity requirement of hydrogen used in fuel cells – with current technology, an operating fuel cell requires the purity of hydrogen to be as high as 99.999%.

Currently, global hydrogen production is 48% from natural gas, 30% from oil, and 18% from coal; water electrolysis accounts for only 4%.

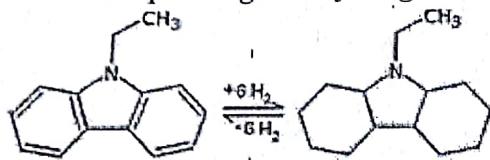
Storage of Hydrogen

The storage and transportation of hydrogen remains a major challenge in realizing hydrogen economy. Different strategies for hydrogen storage have been developed.

- (1) high-pressure gas cylinders (up to 800 bar),
- (2) liquid hydrogen in dewars or cryogenic tanks (at 21K),
- (3) adsorbed hydrogen on materials with a large specific surface area adsorbents (Zeolites, Carbon materials and porous coordination polymers or Metal-Organic Frameworks) (at T<100 K),
- (4) absorbed on interstitial sites in a host metal (at ambient pressure and temperature),
- (5) chemically bonded in covalent and ionic compounds (at ambient pressure), and
- (6) through oxidation of reactive metals, e.g. Li, Na, Mg, Al, Zn with water.

1. Hydrogen is generally stored as gas in compressed form because it is very light with low density of 0.084 kg/m^3 . The energy content of hydrogen gas at ambient pressure and temperature is 10 MJ/m^3 , which demands extremely large volume for hydrogen storage. The conventional hydrogen storage tank is significantly heavier than hydrocarbon storage tank for storing the equal amount of energy. Hydrogen storage needs special attention due to embrittlement (caused by hydrogen diffusion being smallest molecule in size) of materials of construction of pressure vessels. Therefore, it becomes necessary to use special alloys or composite fiber reinforced containers. Compressed gas storage also poses issues of high potential energy and safety hazards due to possibility of explosion of pressure vessels. However, it is possible to have necessary safety practices with suitable blast walls and monitors/sensors and ensure compatible and safe high pressure storage bottles.
2. Storage and transportation of hydrogen as a liquid is another possibility. Liquid hydrogen or slush hydrogen may be used, as in the Space Shuttle. However liquid hydrogen requires cryogenic storage and boils around 20.268 K (-252.882°C or -423.188°F). The energy required to liquefy hydrogen (gas at 300oK and 1 bar pressure) is about 47 MJ / kg of hydrogen. Hence, its liquefaction imposes a large energy loss (as energy is needed to cool it down to that temperature). The tanks must also be well insulated to prevent boil off.
3. Solid state storage of hydrogen is a much safer and efficient method than pressurized or cryogenic storage of hydrogen:
 - a. Metal hydrides, such as MgH_2 , NaAlH_4 , LiAlH_4 , LiH , LaNi_5H_6 , TiFeH_2 and palladium hydride, with varying degrees of efficiency, can be used as a storage medium for hydrogen, often reversibly. Some are easy-to-fuel liquids at ambient temperature and pressure, others are solids which could be turned into pellets. These materials have good energy density by volume, although their energy density by weight is often worse than the leading hydrocarbon fuels.
Most metal hydrides bind with hydrogen very strongly. As a result, high temperatures around 120°C (248°F) – 200°C (392°F) are required to release their hydrogen content. This energy cost can be reduced by using alloys which consists of a strong hydride former and a weak one such as in LiNH_2 , LiBH_4 and NaBH_4 . These are able to form weaker bonds, thereby requiring less input to release stored hydrogen. However, if the interaction is too weak, the pressure needed for rehydriding is high, thereby eliminating any energy savings.

b. Liquid organic hydrogen carriers (LOHC)



Unsaturated organic compounds can store huge amounts of hydrogen. These *Liquid Organic Hydrogen Carriers* (LOHC) are hydrogenated for storage and dehydrogenated again when the energy/hydrogen is needed. Research on LOHC was concentrated on cycloalkanes at an early stage, with its relatively high hydrogen capacity (6-8 wt %) and production of CO_x-free hydrogen. Heterocyclic aromatic compounds (or N-Heterocycles) are also appropriate for this task. A compound that stands in the focus of the current LOHC research is N-ethylcarbazole (NEC) but many others do exist. More recently dibenzyltoluene, which is already industrially used as a heat transfer fluid in industry, was identified as potential LOHC. With a wide liquid range between -39 °C (melting point) and 390 °C (boiling point) and a hydrogen storage density of 6.2 wt% dibenzyltoluene is ideally suited as LOHC material. More recently, formic acid (FA) has been suggested as a promising hydrogen storage material with a 4.4wt% hydrogen capacity.

- c. While literally hundreds of intermetallic alloys have been prepared and their hydrogenation potentials assessed, relatively few have the right combination of properties that permit their use for hydrogen storage or other applications. The most viable candidates include alloys with the following compositions: A₂B (e.g., Mg₂Ni), AB (e.g., TiFe), AB₂ (e.g., ZrMn₂) and AB₅ (e.g., LaNi₅). The advantage of many intermetallic alloys is the ability to alter their hydrogen sorption behavior by substitution for either or both the A and B metals that often improve their performance in various applications.
- d. Ammonia (NH₃) releases H₂ in an appropriate catalytic reformer. Ammonia provides high hydrogen storage densities as a liquid with mild pressurization and cryogenic constraints. It can also be stored as a liquid at room temperature and pressure when mixed with water. Ammonia is the second most commonly produced chemical in the world and a large infrastructure for making, transporting, and distributing ammonia exists. Ammonia can be reformed to produce hydrogen with no harmful waste, or can mix with existing fuels and under the right conditions burn efficiently.
- e. Encapsulation : Cell Energy technology is based around the encapsulation of hydrogen gas and nano-structuring of chemical hydrides in small plastic balls, at room temperature and pressure

f. **Amine borane complexes:** Prior to 1980, several compounds were investigated for hydrogen storage including complex borohydrides, or aluminohydrides, and ammonium salts. These hydrides have an upper theoretical hydrogen yield limited to about 8.5% by weight. Amongst the compounds that contain only B, N, and H (both positive and negative ions), representative examples include: amine boranes, boron hydride ammoniates, hydrazine-borane complexes, and ammonium octahydrotriborates or tetrahydroborates. Of these, amine boranes (and especially ammonia borane) have been extensively investigated as hydrogen carriers. During the 1970s and 1980s, the U.S. Army and Navy funded efforts aimed at developing hydrogen/deuterium gas-generating compounds for use in the HF/DF and HCl chemical lasers, and gas dynamic lasers. Earlier hydrogen gas-generating formulations used amine boranes and their derivatives. Ignition of the amine borane(s) forms boron nitride (BN) and hydrogen gas. In addition to ammonia borane (H_3BNH_3), other gas-generators include diborane diammoniate, $H_2B(NH_3)_2BH_4$.

Applications other than transportation

Hydrogen has the potential to replace LPG and CNG for cooking because it has superior characteristics to LPG and PNG fuel in terms of ignitability, low ignition delay and higher flame stability.

(i) Thermalysis Process

The natural synthesis of nanoparticles by "thermolysis" is characterized by subjecting the metal precursors (usually organometallic compounds in oxidation state zero) at high temperatures together with a stabilizing compound to thermal decomposition. Thermal decomposition provides remarkable control over size and is well suited for scale up to larger quantities.

Various metal nanoparticles have been prepared by the thermal decomposition of low-valent complexes involving olefinic or carbonyl ligands. For example cobalt nanoparticles are prepared by the thermal decomposition of cobalt carbonyls. Ag, Pt, Ru, Rh, Cu, Ir, Zn, Co and Ni nanoparticles are prepared by the decomposition of their olefinic complexes.

9.6 NANOSCALE MATERIALS

(a) Nanocrystals or Nanoclusters

Nanoclusters or nanocrystals are fragments of solid comprising somewhere between a few atoms and a few tens of thousands of atoms. They are material particles having at least one dimension smaller than 100 nanometers and composed of atoms in either a single- or poly-crystalline arrangement. They are made up of equal subunits, such as, atoms of a single element, molecules or even combinations of atoms of several elements in subunits with equal stoichiometries (alloys, etc.).

Examples: $(Na)_n$, $(SF_6)_n$, $(H_2O)_n$, $(Cu_3Au)_n$, $(ClCH_3C_6H_5CO_2H)_n$, $(TiO_2)_n$, etc.

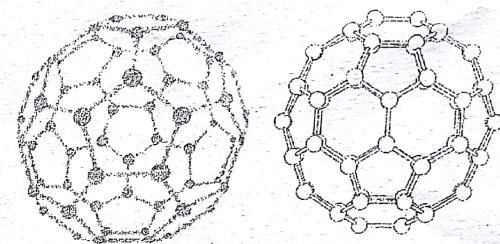
These can include, e.g., fullerenes, metal clusters (agglomerates of metal atoms), large molecules, such as proteins, and even hydrogen-bonded assemblies of water molecules, which exist in water at ambient temperatures.

(b) Fullerenes

Fullerenes are made by heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by the condensation of carbon vapor consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes consisting of even number of carbon atoms up to 350 or above. Fullerenes are cage-like molecules. C_{60} molecule has a shape like soccer ball and called Buckminsterfullerene (Fig. 9.8).

It contains twenty-six-membered rings and twelve five-membered rings. A six-membered ring is fused with six- or five-membered rings but a five-membered ring can only fuse with six-membered rings. All the carbon atoms are equal and they are sp^2 hybridized. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalized in molecular orbitals, which, in turn, give aromatic character to molecule. This ball shaped molecule has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C-C distances of 143.5 pm and 138.3 pm respectively. Spherical fullerenes are also called Bucky balls in short.

The fullerenes are soluble in common solvents such as benzene, toluene or chloroform.

Fig. 9.8 Structure of C_{60}

Uses

- In optics the fullerenes were proposed to use for the electrophotographical imaging, opt filters, photopolymer sensibilizers, nonlinear optical materials.
- In electronics they are used as the molecular switchers, diodes, transistors, resistors lithography, collar cell elements, magneto-optical recorders, photoelectronic devices.
- In military sphere the fullerenes are used as the optical and microwave absorption coating to prevent aircraft and missiles from radar detection.
- Fullerenes are chemically reactive and can be added to polymers and elastomers to create new copolymers with specific physical and mechanical properties.

(c) Carbon nanotubes

Nanotubes are the 1D quantum cylinders nanoscopic in diameter while micro/macrosopic in length so they are quantum macrocrystals possessing potential unique properties. Carbon nanotubes are members of the fullerene structural family. Their name is derived from their long, hollow structures with the walls formed by one-atom-thick sheets of carbon, called graphene. Carbon nanotubes are single sheets of graphene rolled into cylinders. The diameter of the tubes are typically of nanometer dimensions, while the lengths are typically micrometers. Carbon nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). Individual nanotubes naturally align themselves into "ropes" held together by van der Waals forces. Multi-walled nanotubes (MWNTs) consist of multiple rolled layers (concentric tubes) of graphene.

Carbon nanotubes are generally produced by three main techniques, arc discharge, laser ablation and chemical vapor deposition. In arc discharge, a vapor is created by an arc discharge between two carbon electrodes with or without catalyst. Nanotubes self-assemble from the resulting carbon vapor. In the laser ablation technique, a high-power laser beam impinges on a volume of carbon containing feedstock gas (methane or carbon monoxide).

Properties: Carbon nanotubes, with one hundred times the tensile strength of steel, thermal conductivity better than all materials, and electrical conductivity similar to copper, but with the

ability to carry much higher currents, they seem to be a wonder material. Electronic, molecular and structural properties of carbon nanotubes are determined to a large extent by their nearly one dimensional structure. In general carbon nanotubes are associated with:

- High electric conductivity.
- High thermal conductivity.
- High mechanical strength, which results from the covalent sp^2 bonds formed between the individual carbon atoms.
- High thermal resistivity/stability.
- Enhanced chemical reactivity, compared with a graphene sheet, as a direct result of the curvature of the CNT surface which causes pi-orbital mismatch.

Uses

- Field Emitters/Emission: Conductive or reinforced plastics
- Molecular electronics: CNT based non-volatile RAM, CNT based transistors
- Energy storage
- CNT based fibers and fabrics
- CNT based ceramics
- Biomedical applications

(d) Nanowires

A nanowire is a nanostructure, with the diameter of the order of a nanometer with the ratio of the length to width being greater than 1000. Alternatively, nanowires can be defined as structures that have a thickness or diameter constrained to tens of nanometers or less and an unlimited length. They are also referred to as quantum wires. Nanowires can be metallic (Ni, Pt, Au, etc.), semiconducting (Si, GaN, etc.) or insulating (SiO_2 , TiO_2 , etc.). They belong to one-dimensional (1-D) nanomaterials.

Nanowires are prepared by using a number of techniques, including suspension, electrochemical deposition, vapor deposition, etc. But the most commonly used technique is vapor-liquid-solid (VLS) synthesis. The method uses either laser ablated particles or a feed gas as the source materials. Liquid metal (Au) nanoclusters in the form of a thin film on a substrate is used as the catalyst. The source enters the nanoclusters and begins to saturate them. On attaining super saturation, the source solidifies and grows outward from the nanocluster. By turning off the source, the final length of the nanowire can be adjusted.

The nanowires of a given material exhibit thermal, electrical, mechanical and optical properties different from the bulk material. For example, the conductivity of a nanowire will be much less than that of the corresponding bulk material.

Uses

- Data storage/transfer - transfer data up to 1,000 times faster, and store data for as long as 100,000 years without degradation.
- Batteries/generators - tiny, efficient solar panels, turning light into energy, able to hold 10 times the charge of existing batteries.

- Transistors.
- LED's.
- Optoelectronic devices.
- Biochemical sensors.
- Thermoelectric devices.

(e) Nanorods

Nanorods are solid nanostructures morphologically similar to nanowires but with aspect ratios (length divided by width) of approximately 3-to-5. They are formed from a variety of materials including metals, semiconducting oxides, diamonds (aggregated diamond nanorods produced from fullerenes are the hardest material so far discovered), and organic materials. Nanorods are produced by a number of techniques, including: a vapor-liquid-solid approach; mechanical alloying; direct chemical synthesis; plasma arc discharge; laser ablation; and catalytic decomposition.

Direct chemical synthesis method is one of the simple and most commonly used method for the synthesis of nanorods, with a combination of ligands acting as shape control agents. The ligands bond to different facets of the nanorod with different strengths. This allows different faces of the nanorod to grow at different rates, producing an elongated object.

Uses

- In display technologies, because the reflectivity of the rods can be changed by changing their orientation with an applied electric field.
- In microelectromechanical systems (MEMS).
- Nanorods, along with other noble metal nanoparticles, also function as theragnostic agents.
- As cancer therapeutics. Nanorods absorb in the near IR, and generate heat when excited with IR light. 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.
- Nanorods based on semiconducting materials as energy harvesting and light emitting devices.

(f) Dendrimers

Dendrimers are large and complex molecules with very well-defined chemical structures. The dendrimers are tree-like repetitively branched polymer molecules (Greek dendra = tree). They are also termed cascade molecules. They have particle size in the nanometer range. They are branching molecules with the branching beginning at the core. Depending on the core, the dendrimer can start with 3 to 8 (or more) branches, with 3 and 4 being the most common number. Figure 9.9 schematically represents a dendrimer.

Dendrimers consist of a core molecule and alternating layers of two monomers. Each pair of monomer layers completes a shell and a generation. The core generally consists of an amine core, although sugars and other molecules can be used. All core molecules have multiple reaction sites that are identical. Even the simplest core possible, ammonia (NH_3), has three amine reaction sites.

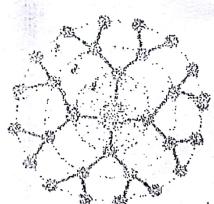


Fig. 9.9. Dendrimer

The core is mixed with an excess of the first monomer molecule which reacts with all of the core's reaction sites, giving rise to the first branches. This monomer molecule has two distinct reactive groups, one at each end. After one kind of end reacts, the other end will provide reaction sites for the next layer of the shell. An excess of the second monomer, again a molecule which has two distinct reactive groups, one at each end, is reacted with this first layer to give the second layer and complete the first shell and the first generation. Each unreacted outer end of the second monomer provides a reaction site which can react with multiple molecules. This provides the branching and the reaction sites for the next shell.

Uses

Applications of dendrimers typically involve conjugating other chemical species to the dendrimer surface that can function as detecting agents (such as a dye molecule), affinity ligands, targeting components, radioligands, imaging agents, or pharmaceutically active compounds. Such molecules could include tumor-targeting agents (including but not restricted to monoclonal antibodies), imaging contrast agents to pinpoint tumors, drug molecules for delivery to a tumor, and reporter molecules that might detect if an anticancer drug is working.

In general, the dendrimers can be used in variety of applications as:

- Medicinal and diagnosis applications,
- Gene therapy and chemical sensors,
- Drug delivery system,
- Adhesive and coatings,
- Light harvesting material,
- Catalyst, electronic applications,
- Separating agents, and many more.

(g) Nanocomposites

Nanocomposites are a class of materials in which one or more phases with nanoscale dimensions (0-D, 1-D, and 2-D) are embedded in a metal, ceramic, or polymer matrix. According to their matrix materials, nanocomposites can be classified as ceramic matrix nanocomposites (CMNC),

metal matrix nanocomposites (MMNCs), and polymer matrix nanocomposites (PMNCs). The reinforcing material can be made up of nanoparticles, nanosheets or nanofibres.

The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposites differ markedly from that of the component materials. For example, adding carbon nanotubes improves the electrical and thermal conductivity of the composite. Other kinds of nanoparticulates may result in enhanced optical properties, dielectric properties, heat resistance or mechanical properties such as stiffness, strength and resistance to wear and damage.

The nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement. The large amount of reinforcement surface area suffices a relatively small amount of nanoscale reinforcement for an observable effect on the macroscale properties of the composite. The percentage by weight (called mass fraction) of the nanoparticulates introduced can remain very low (on the order of 0.5% to 5%).

Uses

- In producing batteries with greater power output. In lithium ion batteries the anodes made of the silicon-carbon nanocomposite make closer contact with the lithium electrolyte, which allows faster charging or discharging of power.
- In speeding up the healing process for broken bones. The growth of replacement bone is speeded up when a nanotube-polymer nanocomposite is placed as a kind of scaffold which guides growth of replacement bone.
- In producing structural components with a high strength-to-weight ratio. For example, an epoxy containing carbon nanotube can be used to produce nanotube-polymer composite blades practical. These longer blades increase the amount of electricity generated by each windmill.
- In making lightweight sensors with nanocomposites.
- In making flexible batteries. A nanocomposite of cellulose materials and nanotubes could be used to make a conductive paper. When this conductive paper is soaked in an electrolyte, a flexible battery is formed.
- In making tumors easier to see and remove. Incorporation of magnetic nanoparticles and fluorescent nanoparticles in a nanocomposite makes it both magnetic and fluorescent. The magnetic property of the nanocomposite particle makes the tumor more visible during an MRI procedure done prior to surgery. The fluorescent property of the nanocomposite particle could help the surgeon to better see the tumor while operating.
- As light weight materials in vehicles; for fuel economy.
- As artificial joints, economically beneficial.
- In abrasion and wear resistant applications.