

*Go, change the world*

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**UNIT-I:****Sustainable chemistry and E-waste management:**

Biomaterials: Introduction, Bio-degradable and bio-compatible polymeric materials: synthesis and applications (Polymers and hydrogels in drug delivery).

Green Chemistry: Introduction, 12 principles with real life examples, Validation of greenness using software.

E-waste: Hazards and toxicity, segregation and recycling (Hydrometallurgy, pyrometallurgy and direct recycling). Extraction of valuable metals from E-waste.

Battery waste management and recycling, circular economy - case studies.

**1.1 BIODEGRADABLE POLYMERS:**

It is observed that plastic bucket kept in sunlight and rain for long time loses its lustre and strength. This deterioration in properties is due to a phenomenon called ‘polymer degradation’, which is characterised by an uncontrolled change in the molecular weight or constitution of the polymer. Conventionally, the degradation is a reduction in the molecular weight of the polymer.

In developing countries, environmental pollution by synthetic polymers has assumed dangerous proportions. Petroleum-derived plastics are not readily biodegradable and because of their resistance to microbial degradation, they accumulate in the environment. In addition, in recent times oil prices have

increased markedly. These facts have helped to stimulate interest in biodegradable polymers. Biodegradable plastics and polymers were first introduced in 1980s. Polymers from renewable resources have attracted an increasing amount of attention over the last two decades, predominantly due to two major reasons: firstly environmental concerns, and secondly the realization that our petroleum resources are finite. There are many sources of biodegradable plastics, from synthetic to natural polymers. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources. Biodegradation of polymeric biomaterials involves cleavage of hydrolytically or enzymatically sensitive bonds in the polymer leading to polymer erosion. A vast number of biodegradable polymers have been synthesized recently and some microorganisms and enzymes capable of degrading them have been identified.

“Thus, the biodegradable polymers are the polymers which will degrade by the action of naturally occurring microorganisms like bacteria, fungi or sunlight”.

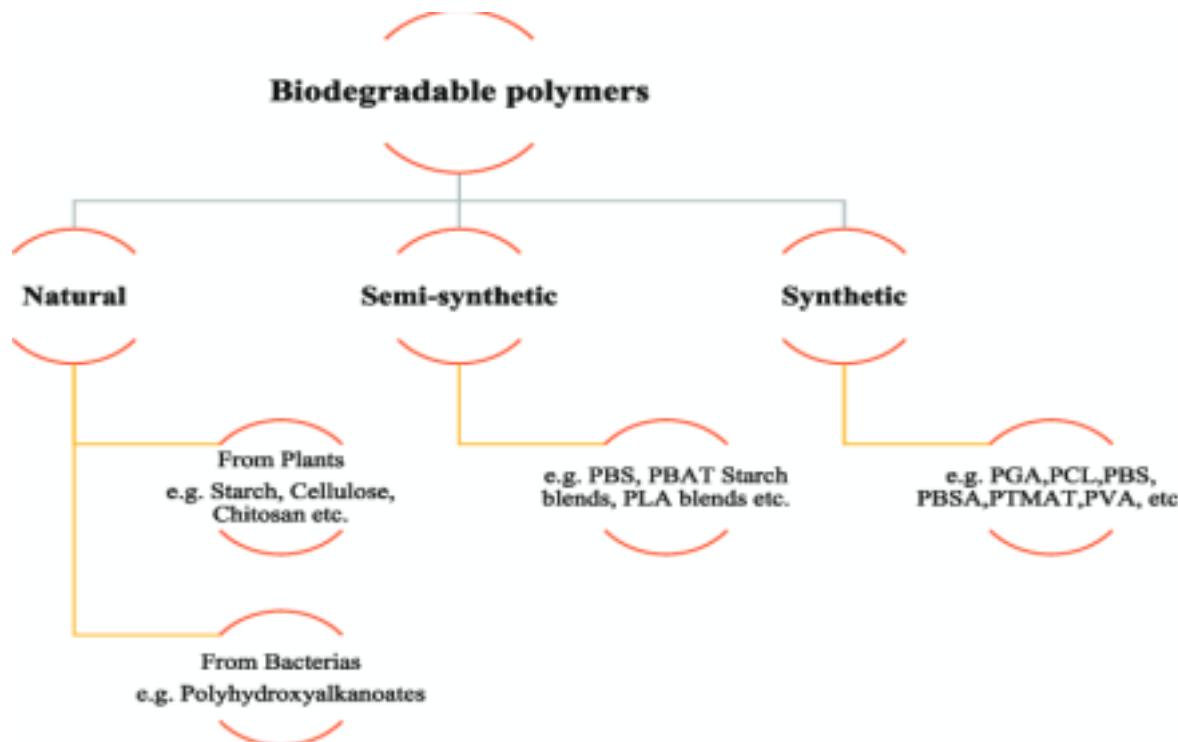
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### **Requirements of Biodegradable polymers:**

1. Biodegradable polymers should have hydrolysable linkages like esters, amides or ether.
2. They should be hygroscopic in nature.
3. The product formed after degradation should act as compost.

### **Classification of biodegradable polymers:**

The biodegradable polymers can be classified according to their chemical composition, origin and synthesis method, processing method, economic importance, application, etc.



**Figure 1. 1.** Classification of Biodegradable polymers

### POLY LACTIC ACID (PLA):

The basic building block of PLA is the lactic acid (LA). It is a simple chiral molecule which exists as two enantiomers, L- and D-lactic acid, optically active. It can be produced by fermentative or chemical synthesis. Today the most popular route is fermentation, in which sugars and starches are converted into lactic acid by bacterial fermentation using an optimized strain of *Lactobacillus*.

### Properties:

- (i) The PLA is a semi-crystalline polymer with glass transition temperature around 55 to 59 °C and melting point 174-184 °C.
- (ii) It shows a good mechanical strength, high Young's modulus, thermal plasticity and has good processability.

(iii) It is unstable in wet conditions, which can undergo chain disruption in the human body and degrades into nontoxic by products, lactic acid, carbon dioxide and water which are subsequently eliminated through the Krebs cycle and in the urine.

### **Synthesis of Poly Lactic Acid:**

There are two important methods for PLA synthesis:

- (i) Direct polycondensation of lactic acid and
- (ii) Ring opening polymerization of lactic acid cyclic dimer,

known as lactide. Following reactions show the reaction

mechanism for both of them.

**Figure 1.2: Synthetic route for the synthesis of Poly lactic acid**

**In direct condensation**, solvent is used and higher reaction times are required. The resulting polymer is a material of low to intermediate molecular weight.

**Ring-opening polymerization (ROP)** of the lactide needs catalyst (Stannous octoate ( $\text{Sn}(\text{Oct})_2$ )) but results in PLA with controlled molecular weight.

Depending on monomer used and controlling reaction conditions, it is possible to control the ratio and sequence of D and L-lactic acid units in the final polymer.

### Applications of biodegradable polymers in medical field:

<b>Wound management</b>	• Pins • Rods • Screws • Tacks • Ligaments
• Sutures • Staples • Clips • Adhesives • Surgical meshes	• PLA are used in Fracture fixation and Ligament augmentation
<b>Orthopedic devices</b>	

Table 1.1: Applications of biodegradable polymers

### 1.2 Bio-compatible polymeric materials:

Biocompatible polymers are both synthetic (man-made) and natural and aid in the close vicinity of a living system or work in intimacy with living cells. These are used to gauge, treat, boost, or substitute any tissue, organ or function of the body.

#### Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) OR PHBV

It is a thermoplastic linear aliphatic polyester. It is obtained by the copolymerization of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.

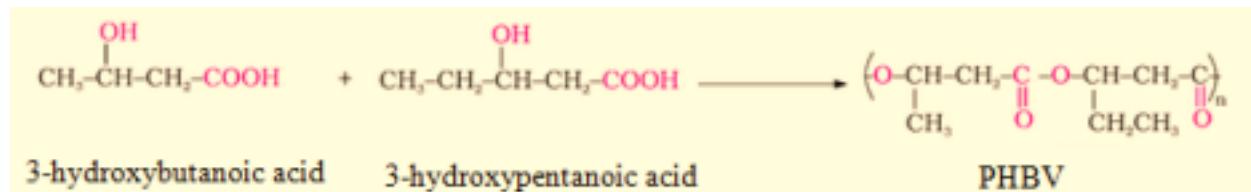


Figure 1.3: Synthetic route for PHBB

**Properties:** It is biodegradable, nontoxic, biocompatible plastic produced naturally by bacteria and a good alternative for many non-biodegradable synthetic polymers. PHBV undergoes bacterial degradation in the environment.

#### Degradation

When disposed, PHBV degrades into carbon dioxide and water. PHBV undergo bacterial

degradation. PHBV, just like fats to human, is an energy source to microorganisms. Enzymes produced by them degrade it and are consumed.

### **Applications:**

- (1) It is used in controlled release of drugs, medical implants and repairs, specialty packaging, orthopedic devices and manufacturing bottles for consumer goods.
  - (2) It is also biodegradable which can be used as an alternative to non-biodegradable plastics
- ### **1.3 Hydrogels**

Is a water-swollen, and cross-linked polymeric network produced by the simple reaction of one or more monomers.

### **OR**

A polymeric material that exhibits the ability to swell and retain a significant fraction of water within its structure, but will not dissolve in water is known as **Hydrogel**.

### **Important features of hydrogels:**

- The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains.
- Hydrogels have similarities with human soft tissues in composition, structure, and properties.
- Due to their superior biocompatibility and low toxicity, hydrogels play a significant role in the biomedical fields
- Hydrogels are considered to be the most prospective alternative materials for soft tissue due to their exceptional mechanical properties.

Therefore, they are widely used in drug delivery, cell culture, tissue engineering, and other biomedical and biomimetic applications.

Hydrogels can be divided in two categories by the forming molecule types, natural polymer and synthetic polymer.

**Natural hydrogels** include collagen, silk fibroin, hyaluronic acid, chitosan, alginate and hydrogels derived from decellularized tissues.

Their unique properties include: biocompatibility, biodegradability, low cytotoxicity, the possibility to tailor the hydrogel into an injectable gel and their similarity to physiological environment.

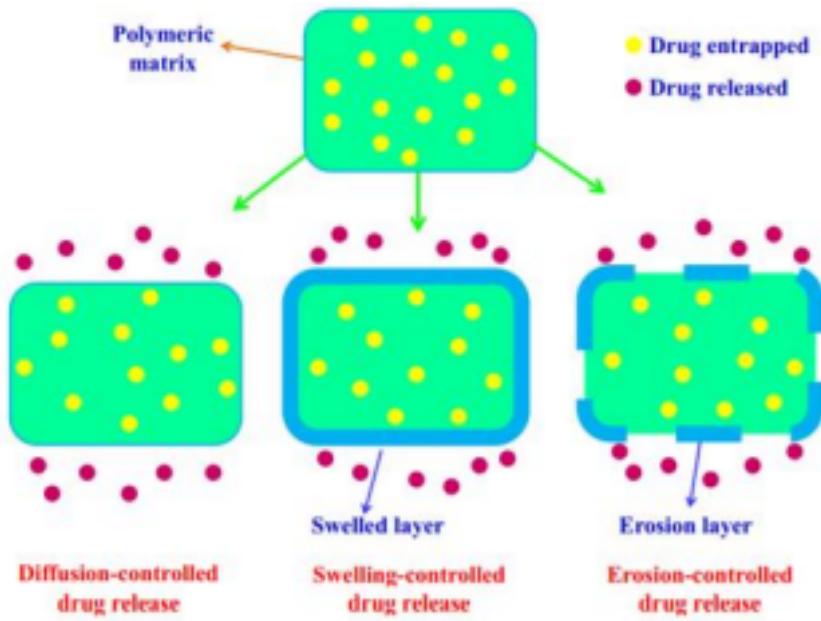
**Synthetic hydrogel includes** Polyhydroxyethyl methacrylate (PMMA), Polyvinyl alcohol (PVA), Polyethylene glycol (PEG), etc

### **Application of Hydrogel in Drug delivery**

Due to their compatibility with living tissues and ability to preserve embedded proteins in their natural state, hydrogels are good vehicles for delivering drugs into the body. Hydrogels as drug delivery agents are appealing for a number of reasons. They are mainly composed of water so they can shrink in their dry state to become small enough to swallow, and then can expand and swell in the stomach to avoid passing into the small intestine. They can also be loaded with medicine and release it in a controlled manner.

Such controlled drug delivery systems are used to deliver drugs at certain rates for predefined periods of time. These systems have been used to overcome the limitations of regular drug formulations.

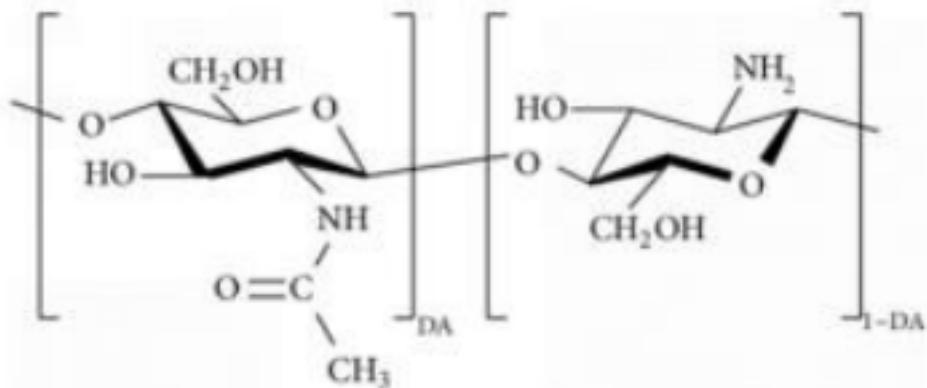
Polymers are generally used as **drug delivery systems** (DDSs) because the drug release from these systems is predominantly controlled by the polymeric matrix. The drug release takes place from the polymeric DDSs with different mechanisms which are known as diffusion, swelling, erosion and stimulus-based methods that are presented schematically in Figure 1.4



**Figure 1.4:** Mechanism of drug release from a polymeric matrix including diffusion, swelling, and erosion controlled methods

**Chitosan:** It is a polysaccharide industrially obtained by N-deacetylation of chitin, the second most common natural polysaccharide in biomass after cellulose.

It is a linear copolymer composed of two sub-units, D-glucosamine and N-acetyl-D-glucosamine units linked by a  $\beta$  (1 $\rightarrow$ 4) glycosidic bond (**Figure 1.5**).



**Figure 1.5:** Chitosan chemical structure

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal. Green chemistry is also known as **sustainable chemistry**. Green Chemistry helps us solve many future problems, including sustainable energy and food production, protecting our environment by proper management, providing safe drinking water, and promoting better human and environmental health. Everything around us, all commodities that we use day and night is the inventions of chemistry. We cannot exist without chemistry as what we breathe is itself a result of chemical reactions.

### **Importance of Green Chemistry:**

- Prevents pollution at the molecular level.
- Applies innovative scientific solutions to real-world environmental problems.
- Results in source reduction because it prevents the generation of pollution.
- Reduces the negative impacts of chemical products and processes on human health and the environment.
- Lessens and sometimes eliminates hazard from existing products and processes.
- Designs chemical products and processes to reduce their intrinsic hazards.

**Chemical disasters:**

(i) **1956: Minamata disease** was first discovered in Minamata city in Japan. It was caused by the release of methyl mercury in the industrial wastewater from a chemical factory.

(ii) **1961: Itai-itai disease** was caused by cadmium poisoning due to mining in Toyama Prefecture in Japan.

(iii) **1976: The Seveso disaster** was an industrial accident that occurred in a small chemical manufacturing plant near Milan in Italy. It resulted in the highest known exposure to 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin in residential population.

(iv) **1984: The Bhopal disaster** was an industrial catastrophe that took place at a pesticide plant owned and operated by Union Carbide (UCIL) in Bhopal India resulting in the exposure of over 500,000 people. It was caused by methyl Iso cyanate (MIC) gas.

(v) **1986: The Chernobyl disaster** was a nuclear accident at the Chernobyl nuclear plant in Ukraine. It resulted in a severe release of radioactive materials. Most fatalities from

the accident were caused by radiation poisoning.

(vi) **1989: Exxon Valdez**, an oil tanker hit a reef and spilled an estimated minimum 10.8 million US gallons (40.9 million litres) of crude oil. This has been recorded as one of the largest spills in United States history and one of the largest ecological disasters. **History of Green chemistry:**

1. In 1990 the Pollution Prevention Act was passed in the United States. This act helped create a modus operandi for dealing with pollution in an original and innovative way. This paved the way to the green chemistry concept.
2. **Paul Anastas and John Warner** coined the two letter word “**green chemistry**” and developed the twelve principles of green chemistry.
3. In 2005, Ryoji Noyori identified three key developments in green chemistry: use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations and the use of hydrogen in asymmetric synthesis.

**Green chemistry focuses on to**



**Nobel Prize in Green chemistry:**

1. The Nobel Prize Committee recognized the importance of green chemistry in 2005 by awarding Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock the Nobel Prize for

Chemistry for "the development of the metathesis method in organic synthesis".

2. Frances Arnold won in 2018, it for the directed evolution of enzymes, a technique she has pioneered over the past 25 years and has used to pursue new avenues within green chemistry and to engineer reactions completely new to nature.

### Principles of Green chemistry

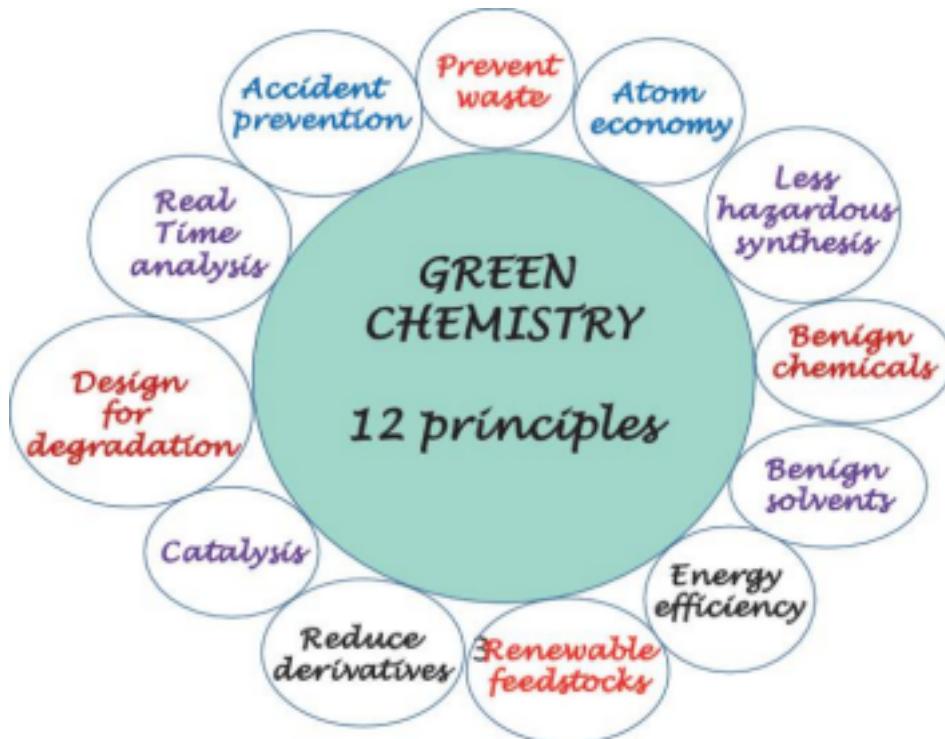


Figure 1.6: Green principles of Chemistry

The twelve principles of green chemistry are:

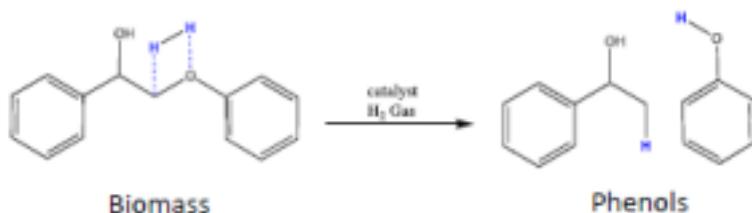
(1) **Prevention:** It is better to prevent waste than to treat or clean up waste after it has been created. • Carry out a synthesis in such a way so that formation of waste (by-products) is minimum or absent.

- Cost involved in the treatment and disposal of waste adds to the overall production cost.
- The unreacted starting materials also form part of the waste.
- If discharged causes pollution and requires expenditure for cleaning-up

### Case study: Phenols

Phenols are widely used in household products and as intermediates for industrial synthesis. Conventional method of obtaining phenols from petroleum products/derivatives of phenols (benzene, toluene, xylenes). As this method is not sustainable it is dependent on depleting resources.

**Alternative method suggested:** Production of phenols from biomass waste using depolymerisation. This method uses abundant product (waste) as a starting material.



### (2) Atom economy: Synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product.

In 1990, Barry Trost introduced the concept of synthetic efficiency: Atom Economy. It refers to the concept of maximizing the use of raw materials so that the final product contains the maximum number of atoms from the reactants.

- The ideal reaction would incorporate all of the atoms of the reactants.
- The atomic economy is measured as the ratio of the molecular weight of the desired product over the molecular weights of all reactants used in the reaction.

Chemists globally consider that if the yield of a reaction is above 90%, the reaction is good.

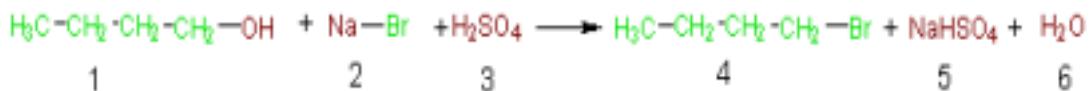
$$\% \text{ yield} = \frac{\text{Actual yield of the product}}{\text{Theoretical yield of the product}} \times 100$$

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$$\% \text{ atom economy} = \frac{\text{Formula weight of atoms utilized}}{\text{Formula weight of the reactants used in reaction}} \times 100$$

The following equation illustrated the atom economy of this reaction by showing all of the

reactant atoms that are incorporated into the desired product in green,



While those that are wasted are shown in brown. Likewise the atoms of the desired product are in green and the atoms composing the unwanted products are in brown. **Table 2** provides another view of the atom economy of this reaction. In columns 1 and 2 of this table, the formulas and formula weights (FW) of the reactants are listed. Shown in green (columns 3 and 4) are the atoms and weights of the atoms of the reactants that are incorporated into the desired product (4), and shown in brown (columns 5 and 6) are the atoms and weights of atoms of the reactants that end up in unwanted side products. Focusing on the last row of this table it can be seen that of all the atoms of the reactants (4C, 12H, 5O, 1Br, 1Na and 1S) only **4C, 9H**, and **1Br** are utilized in the desired product and the bulk (**3H, 5O, 1Na, 1S**) are wasted as components of unwanted products. This is an example of poor atom economy!

A logical extension of Trost's concept of atom economy is to calculate

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
1 C <sub>4</sub> H <sub>9</sub> OH	74	4C,9H	57	HO	17
2 NaBr	103	Br	80	Na	23
3 H <sub>2</sub> SO <sub>4</sub>	98	—	0	2H,4O,S	98
<b>Total</b> 4C,12H,5O,BrNaS	275	4C,9H,Br	137	3H,5O,Na,S	138

**Table 1.2:** Calculation of Atom economy

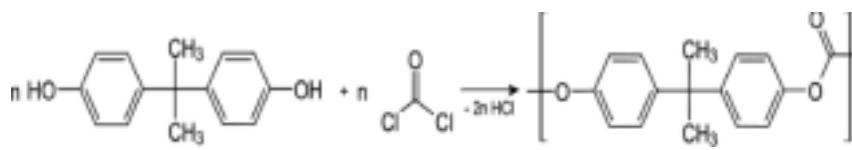
The percentage atom economy can be done by taking the ratio of the mass of the utilized atoms (137) to the total mass of the atoms of all the reactants (275) and multiplying by 100. As shown below this reaction has only 50% atom economy.

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$$\begin{aligned} \% \text{ Atom Economy} &= (\text{FW of atoms utilized}/\text{FW of all reactants}) \times 100 \\ &= (137/275) \times 100 = 50\% \end{aligned}$$

(3) **Less hazardous chemical syntheses:** Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

### Case study: Synthesis of Polycarbonate: Phosgene process



Monomers: Bisphenol-A and Phosgene

### Disadvantages:

- (i) Phosgene is highly toxic and corrosive
- (ii) It requires large amount of CH<sub>2</sub>Cl<sub>2</sub> (Phosgene)
- (iii) Polycarbonate is contaminated with Cl impurities

**Alternative method (Greener approach)** for above synthesis of Polycarbonate suggested using Bisphenol-A & Diphenyl carbonate.

Its advantages are (i) eliminates the use of phosgene (ii) It produces higher-quality Polycarbonates.

**(4) Designing safer chemicals:** Chemical products should be designed to preserve efficacy of function while reducing toxicity.

Safer chemicals can be designed by

(a) Manipulation of chemical bonds, chemical functional groups:

- Reactive functional groups have a greater potential to be toxic. Removing these groups is likely to reduce toxicity.

(b) Elimination of the molecular initiating event that activates pathway

- While difficult to achieve, if the chemical is modified not to interact with the biological pathway, no biological effect is triggered and the toxicity can be avoided.

(c) Reducing or eliminating bioavailability.

- If a chemical does not absorb into a body, it cannot cause harm.

**Before synthesizing any chemicals we can make use of**

- (i) Related literature report if already available.
- (ii) **Toxicology study** -that involves the study of the adverse effects of chemical substances on living organisms.
- (iii) **Software** related to above viz., Toxicity estimation software tool (TEST), OLED test

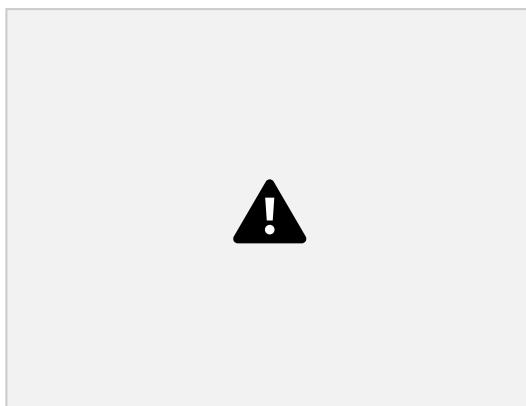
guidelines for toxicity software testing, Tox Navigation, etc.

**(5) Safer solvents, and auxiliaries:** The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used. Solvents account for the vast majority of mass wasted in syntheses and processes. Moreover, many conventional solvents are toxic, flammable, and/or corrosive.

Solvents volatility and solubility have contributed to air, water and land pollution, have increased the risk of workers' exposure, and have led to serious accidents.

**Green solvents: Water, Acetone, Ethanol, 2-Propanol, 1-Propanol, Ethyl acetate, Isopropyl acetate**

**Case study: Chicken feathers used in computer chips**



To manufacture computer chips- many chemicals, large amount of water and energy are required. Washing chemicals requires lot of water. In 2003, Industrial estimate of chemicals and fossil fuels require to make computer chip was **630: 1**

**That means it takes 630 times the weight of the chip in source material just to make one chip.** Researchers in the University of Delaware's ACRES program -Affordable Composites from renewable sources have developed a **computer processor made from chicken feathers**. Chicken feathers because they have shafts that are hollow but strong, and made mostly of air, **a great conductor of electricity**.

**(6) Design for energy efficiency:** Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

Most energy is used for heating, cooling, separations and pumping. Ideally, all reactions are

performed at ‘ambient’ conditions room temperature and atmospheric pressure in order to minimize energy usage. Sonochemistry, microwave, and photo assisted chemistry are known to save energy, improve reaction time, and catalytic activity.

Sonochemistry	Microwave	Photo assisted
<p>Uses of high frequency (20-100 kHz) sound waves to promote chemical reaction.</p> <p>Used in the production of triglycerides from methyl transesterification.</p>	<ul style="list-style-type: none"> <li>• Uses a high-frequency electric field to heat or cool the local environment with electrical charges.</li> <li>• Avoids unnecessarily prolonged residence time at a given temperature.</li> </ul>	Naturally occurring, such as using the sun as a catalyst.

**(7) Use of renewable feedstock:** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

Biomass production in nature nearly around 180 billion metric tons/year. But only about 4% utilized by humans (food, ethanol, sweeteners).



**Case study: Producing polymers from renewable resources (PHAs)** Polyhydroxyalkanoates (PHAs) are a broadly useful family of natural, environmentally friendly, and high performing, bio based plastics.

The development of microorganisms that produce polyhydroxyalkanoates (PHAs) are from renewable feedstocks such as cornstarch and cellulose hydrolysate. •The microorganisms have proven to be applicable to conventional commercial equipment and can even be recycled using this same equipment.

**•They can be used in biodegradable products, such as credit cards.**

•They are comparable with polyolefin which are made from petroleum feedstocks in terms of strength, melting point, and can be manufactured with the existing equipment.



(8) **Reduce derivatives:** Unnecessary derivatization (use of blocking groups, protection/deprotection and temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

#### **What is derivatization?**

Increasing the number of steps which can be done by protection/deprotection, temporary modification of physical/chemical processes is known as derivatization.

**Conventional approach****Green approach**

- Time saved
- Additional reagent/s saved
- Cost of the process reduced

**Case study:** Synthesis of **Ibuprofen** developed by the Boots Company of England has 6 step process, with **atom economy 40%** and lot of waste (by-products).

**Greener approach:** Contains only 3 steps for the synthesis of Ibuprofen with **atom economy 77 %** with less number by-products.

(9) **Catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric

reagents. Catalysts can facilitate complex reactions by:

- Lowering the activation energy of the reaction.
- Reducing temperature necessary to achieve a reaction.
- Controlling the site of the reaction (selectivity enhancement).

### Case study: Hydroquinone synthesis



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(10) **Design for degradation:** Chemical products should be designed so that at the end of their function they break down into harmless degradation products and do not persist in the environment.

Example: Insecticides and polymers are **non-biodegradable**.

DDT-Bioaccumulate in many plant and animal species and. Incorporate into the **food chain**.

Some of the insecticides are also responsible for population decline of beneficial insects

#### Greenery approach:

- Insecticides must be biodegradable during degradation the products themselves should not possess any toxic effects or be harmful to human health.
- It is possible to have a molecule which may possess functional groups that facilitate it for biodegradation.

### Case study: Synthesis of Polylactic acid



The

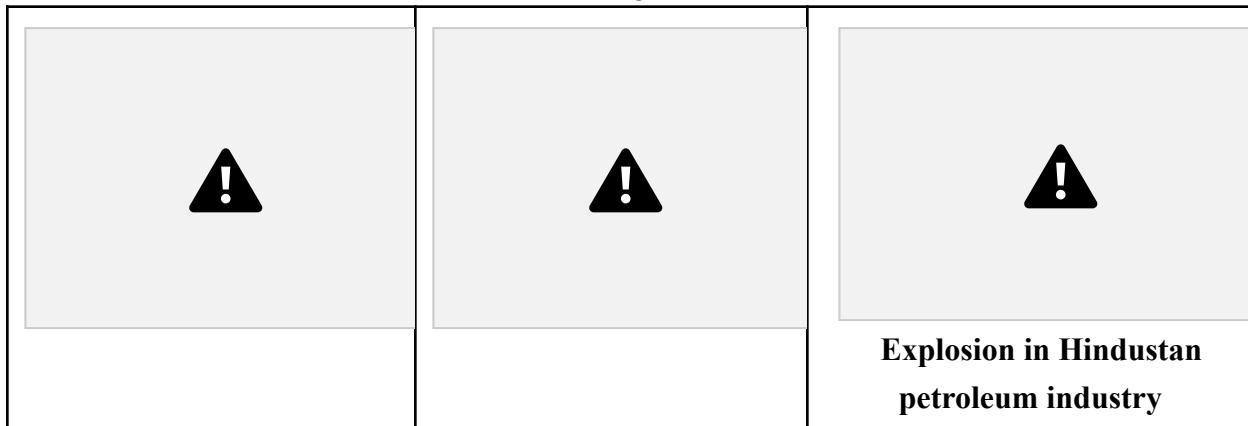
development of a bio based, compostable, and recyclable polylactic acid (PLA) polymer that uses 20–50 percent less fossil fuel resources than comparable petroleum-based polymers. (11)

**Real-time analysis for pollution prevention:** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

**Knowing when your product is “done” can save a lot of waste, time, and energy!** Analytical and modern methods help in real time analysis for pollution prevention. • Analytical methodologies should be so designed so that they require minimum usage of chemical, like recycling of some unreacted chemicals, for the completion of the reaction. • Placement of sensors to monitor the generation of hazardous products during chemical reaction is also advantageous.

(12) **Inherently safer chemistry for accident prevention:** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

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#### **Case study; Tragedy in Bhopal, India 1984**

In arguably the worst industrial accident in history, 40 tons of methyl isocyanate were accidentally released when a holding tank overheated at a Union Carbide pesticide plant, located in the heart of the city of Bhopal. 15,000 people died and hundreds of thousands more were injured. The hazards posed by toxicity, explosion, fire etc might be looked into and manufacturing plants should be so designed to eliminate the possibility of accidents.

**In the end we can say that Green chemistry is not a solution to all environmental problems but the most fundamental approach to preventing pollution.**

## 1.5 E-Waste

**E-Waste** is short for Electronic-Waste and the term is used to describe old, end-of-life or **discarded electronic appliances**.

**OR**

**E-waste** refers to any electronic devices that have reached the end of life.

It includes their components, consumables, parts and spares. Electronic products have become an integral part of the common man's life. The rapid growth in the electronic industry with technological advancements has resulted in significant changes in consumer patterns. This has accelerated the rate at which this equipment reach their end of 'useful' life leading to an increased rate of obsolescence in the electronics industry. This has resulted in an increase in e-waste generated, rendering it the fastest-growing segment of municipal waste.

**The most common types of E-waste are**

<b>Small Equipment's</b>	<b>Large Equipment</b>	<b>Temperature Exchange</b>
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		<b>Equipment</b>
<ul style="list-style-type: none"> <li>• Vacuum cleaners</li> <li>• Microwaves</li> <li>• Ventilation equipment</li> <li>• Toasters</li> <li>• Electric kettles, shavers</li> <li>• Video cameras, Calculators</li> <li>• Electrical and electronic toys</li> <li>• Small medical devices</li> </ul>	<ul style="list-style-type: none"> <li>• Washing machines</li> <li>• Clothes dryers</li> <li>• Dish-washing machines</li> <li>• Electric stoves</li> <li>• Large printing machines</li> <li>• Solar panels</li> </ul>	<ul style="list-style-type: none"> <li>• Refrigerators</li> <li>• Freezers</li> <li>• Air conditioners</li> <li>• Heat pumps</li> </ul>

### **Health and environmental impact of E-waste**

The quantum of E-waste generated is increasing at a rate of 5–10% per year and is a growing concern globally because of its toxicity. RoHS (Restriction of Hazardous Substance) directive restricts the use of certain hazardous substances like Pb, Hg, Cd, Cr, and polybrominated biphenyls in electrical and electronic equipment. These pose a risk to health or environment when treated

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inappropriate RoHS requires minimizing or substitution of these toxic substances with safer materials. This will reduce the load on a recycling plant and the negative impact on the environment.

### **Environment and health hazards**

**Lead:** Exerts toxic effects on various systems in the body such as the central (organic affective syndrome) and peripheral nervous systems (motor neuropathy), the hemopoietic system (anaemia), the genitourinary system (capable of causing damage to all parts of nephron) and the reproductive systems (male and female). **Mercury:** causes damage to the genitourinary system (tubular dysfunction), the central and peripheral nervous systems as well as the foetus. When inorganic mercury spreads out in the water, it is transformed into methylated mercury, which bio-accumulates in living organisms and concentrates through the food

chain, particularly by fish.

**Cadmium:** is a potentially long-term cumulative poison. Toxic cadmium compounds accumulate in the

human body, especially in the kidneys. There is evidence of the role of cadmium and beryllium in carcinogenicity.

**Polycyclic aromatic hydrocarbons (PAH):** Affects lung, skin and bladder. Epidemiological studies in the past on occupational exposure to PAH provide sufficient evidence of the role of PAH in the induction of skin and lung cancers.

### **Benefits of E-waste Recycling**

The benefits of the E-waste recycling process are obvious. Almost everyone owns an electronic device in today's environment. Recycling electronic garbage has become a need to preserve energy, resources, and landfill space. Consider the following benefits to better comprehend the positive impact of E-waste recycling.

- **Conserve natural resources**
- **Protects the environment**
- **Create Jobs**
- **Reduces global warming and saves landfills**
- **Makes things more affordable**
- **Reduces business costs**
- **Supports non-renewable recycling**
- **Conserve both land and energy**



**Figure 1.7:** General steps for recycling of E-waste

**General steps:**

**(1) Collection:** Gathering E-waste from various sources, enterprises, organizations and individuals.

**(2) Storage:** While safe storage may not appear critical, it can prove very important. For example, the glass screens of Cathode Ray Tubes (CRT), TVs and monitors are highly contaminated by lead. In the past, they were recycled into new computer monitors, but the growth of new technology and subsequent decline in demand for CRT products means much of this glass is now simply being stored indefinitely.

**(3) Manual Sorting, Dismantling and Shredding:** Disintegration of all the components and materials of the E-waste to analyse which can be reused and which can go as scrap. E-waste is then shredded into small pieces allowing for accurate sorting of materials, a key part of the process. **(4) Mechanical Separation:** The mechanical separation of the different materials actually consists of several processes one after the other. The two key steps are magnetic separation and water separation.

pull ferrous metals such as iron and steel from the mix of waste. In addition to this, an eddy current may also be used, separating the nonferrous metals. These materials can then be diverted to dedicated recycling plants for smelting. Other materials such as metal-embedded plastic and circuit boards are also separated at this stage.

b) **Water separation:** With a solid waste stream that now consists mainly of plastic and glass, water is used to separate the materials, further purifying for the separation of different plastics as well as hand-sorting obvious contaminants.

**(5) Recovery:** The materials, now separated, are prepared for sale and reuse. For some materials, such as plastic or steel, this means joining another recycling stream. Others may be processed onsite and sold directly alongside usable components separated in the early stages **Extraction of valuable metals from E-waste**

E-waste is classified as hazardous material therefore should be managed properly. However, the presence of precious metals (PMs) in E-waste such as gold (Au), silver (Ag), platinum (Pt), Gallium (Ga), palladium (Pd), tantalum (Ta), tellurium (Te), germanium (Ge) and selenium (Se) makes it attractive for recycling.

Electronic products have become an integral part of the common man's life. The rapid growth in the electronic industry with technological advancements has resulted in significant changes in consumer patterns. This has accelerated the rate at which these equipment reach their end of 'useful' life leading to an increased rate of obsolescence in the electronics industry. This has resulted in an increase in e-waste generated, rendering it the fastest-growing segment of municipal waste. The Basel Convention requires waste substances or objects to be disposed. The quantum of E-waste generated is increasing at a rate of 5–10% per year and is a growing concern globally because of its toxicity. RoHS (Restriction of Hazardous Substance) directive restricts the use of certain hazardous substances like Pb, Hg, Cd, Cr, and polybrominated biphenyls in electrical and electronic equipment. These pose a risk to health or environment when treated inappropriately. ROHS requires minimizing or substitution of these toxic substances with safer materials. This will reduce the load on a recycling plant and the negative impact on the environment.

During pre-processing metal fraction separated from E-waste. Once this operation is carried out there are various routes for E-waste processing. The following section will explain in more detail about various routes.

1) Hydrometallurgical processes 2) Pyro metallurgical processes 3) Bio-metallurgical processes

**Pyrometallurgy**, as traditional method to recover precious and non-ferrous metals from E-waste, includes different treatments on high temperatures: incineration, melting etc. Pyrometallurgy is a heat-based extraction and purification process. As with the water-based process, pyrometallurgy generally involves three steps:

**Roasting:** This refers to the heating of compounds in air and transforming sulphide ores into oxides, creating gas.

**Smelting:** Smelting is used in furnaces to reduce metals and usually involves the formation of carbon dioxide, for example, reducing iron ore in a blast furnace. In addition, tin, copper, and lead ores are smelted.

**Refining:** In refining processes, metals are sorted by exploiting their chemical and metallurgical properties. The separation of metals is achieved by smelting in furnaces at high temperatures. Refining covers a wide range of processes involving different kinds of furnaces and electrolytic processes.

Pyrometallurgical processes could not be considered as best available recycling techniques anymore because some of the PCB components, especially plastics and flame retardants, produce toxic and carcinogenic compounds.

**Hydrometallurgy** is the process used to extract metals from ore, which is achieved by recovering and dissolving the metals as salt in successive water-based steps, including leaching, purification, and recovery of the targeted metal by selective precipitation or electrowinning. This method plays an essential role in extracting strategic and rare metals.

Hydrometallurgy process is divided into three stages;

a) Leaching, b) Solution concentration and purification c) Metal recovery

**Leaching** is an important and first stage of Hydrometallurgical process.

It is the extraction process in which soluble substances are extracted from a solid by means of a solvent. After that the extract obtain from leaching is often subjected to concentration and

purification before the metal recovery. The final step may involve precipitation or cementation process.

### **Hydrometallurgical process extraction of copper from PCB's**

**Composition of PCB's:** Printed circuit board is an essential part of the all electrical and electronic equipment's. It is composed of polymers, ceramics and metals which all are come under Hazardous and non-hazardous categories. About 40% heavy metals present in it which are turned into hazardous residue if the discarded PCB's are not disposing properly.

PCBs are varies according to the manufacturer and the year of its manufacturing and technology

**Table 3** shows the composition of PCB

Metals	Availability (wt%)
Copper	30.57
Aluminium	11.69
Zinc	1.86
Tin	7.3
Nickel	1.58
Iron	15.21
Lead	6.71

**Table 1.3:** Composition of PCB

## **METHODOLOGY**

The waste PCB of a discarded computer used in study. It is commonly used PCB that can be easily available at the E-waste disposal area or an electronic shops. For the recovery of metals, waste PCB was cut into small pieces and finally into powdered form.

- (1) The grinded E-Waste powder contains plastic, ferrous and nonferrous metals. (2)
- Density separation method is used to separate the Metallic and non-metallic parts. (3)
- For separation of ferrous and nonferrous metals, Electromagnetic separator is used.
- (4) For experimental purpose 8 gm of nonferrous metal was taken.
- (5) The metal powder was dissolved into H<sub>2</sub>SO<sub>4</sub> and stirred at 80° C, temperature for about 4 hr.
- (6) The solution was transferred and 40 ml of **Aquaregia** (30 ml HCl and 10 ml HNO<sub>3</sub>) was

added to the filtered solution. The resulting solution was stirred for 60 mins at a temperature  $80^{\circ}\text{C}$ ,

The following reactions took place:



(7) Electrolysis: From the above solution, copper is extracted by electrolysis



process.

**Figure 1.8:** Electrolytic process

The sample was taken for electrolysis. To extract Cu from the solution, electrolysis process was carried out in a cubic reactor of size 12 cm X 8 cm X 7 cm as shown in **Figure 1.8**. Iron Anode and Copper cathode were used for electrolysis. The anode and cathode chambers were separated by an anti-acid filter cloth. The required potential was maintained to carry to electrolysis process. Finally copper metal is deposited.

### Advantages

1. Economically viable for low-grade E-waste materials.

2. Feasible for small scale applications with high metal recoveries.

### **Advantages of Battery recycling**

**Reduces landfills:** as the wasted batteries are taken to the recycling units, the amount dumped in the landfills are reduced considerably. This in turn reduces land, air and water pollution.

**Saving of resources:** battery recycling saves resources. In short, fewer resources are utilized in the creation of new batteries because most of the contents used are recycled. The existing resources are reused for the making of new products.

**Pollution is minimized:** this is one of the major attractions of recycling of batteries. Since it is abundantly found, it is very important to recycle as it is non-biodegradable. This reduces pollution to a great extent.

**Job opportunities:** a lot of job opportunities are created in the recycling industry. Right from collection of batteries from waste dumping areas and collection centres till the delivery of the final product to the market, a lot of opportunities are created.

**Environment becomes clean:** the cleanliness of the surrounding increases as very little waste is dumped. This has a positive impact on the environment. This in turn protects the biodiversity.

**Reduces global warming:** the dumping of waste and its burning causes emission of various toxin gases like sulphur, carbon, nitrogen and so on. This gets absorbed into the atmosphere which in turn triggers global warming and climate change.

### **Disadvantages of battery recycling**

• The value of the recycled products is comparatively low as compared to newer products. •

Recycling is not a cost effective method as huge investment is required in setting up of industries.

• Recycling does not guarantee good quality products.

• The breakdown of batteries in the recycling process causes emission of toxins that are harmful and thus polluting the environment.

### **Recycling of Lead-Acid Batteries**

The major source of raw material for lead recycling are starter batteries from motor vehicles.

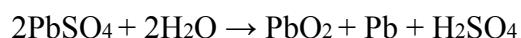
Modern car batteries consist of a PP (Polypropylene)-casing, plates (grids and paste), connectors/poles and bridges and PP-separators as insulators between the plates. Paste consists of Pb, PbO<sub>2</sub> and PbSO<sub>4</sub>.



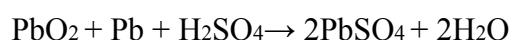
**Figure 1.9:** (a) Composition of Lead acid battery (b) Diagram of Lead –acid battery

The electro-chemical reactions which take place during charge and discharge of a lead acid battery are:

#### **Charging:**



#### **Discharging:**



### **Metallurgical aspects of lead recycling from battery scrap**

Lead acid batteries are recycled pyrometallurgically with initial physical separation and subsequent hydrometallurgical steps

1. Spent batteries are broken/crushed into small pieces.
2. After breaking, the material is passed to a sink/float operation. This hydrodynamic process separates the metal from separators and casing material.
3. The casing material is usually polypropylene (PP), although acrylonitrile butadiene styrene is becoming more widespread because of its higher strength. Separation is accomplished by virtue of the density difference between materials using a fluid of intermediate density

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between the solid phases. Since the density of PP is less than that of water, while the density of lead metal/compound is much higher, sink/float operation is extremely effective, achieving almost complete quantitative segregation.

4. Plastics are subsequently cleaned and sent for recycling into new battery cases or for other uses. Lead, grid straps and battery paste (a combination of the PbO<sub>2</sub>, PbO and PbSO<sub>4</sub>) are removed from the bottom of the sink/float operation and sent to storage for water removal prior to smelting.

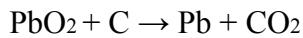
A typical flowchart for secondary lead recycling is shown in **Figure 1.10**.



**Figure 1.10:** Flow chart for Recycling of Lead-Acid Batteries

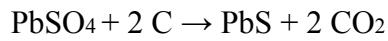
**Lead recovery:** Either the components of an accumulators like lead, plastics, acids, etc. are at first separated and then processed individually.

The first type of chemical reaction converts  $\text{PbO}_2$  into  $\text{Pb}$  through a reduction process:

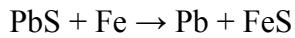


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**Sulphur removal:** The second type converts  $\text{PbSO}_4$  into  $\text{PbS}$ , again through a reduction process:



Finally  $\text{PbS}$  is converted into  $\text{Pb}$  through the following reaction

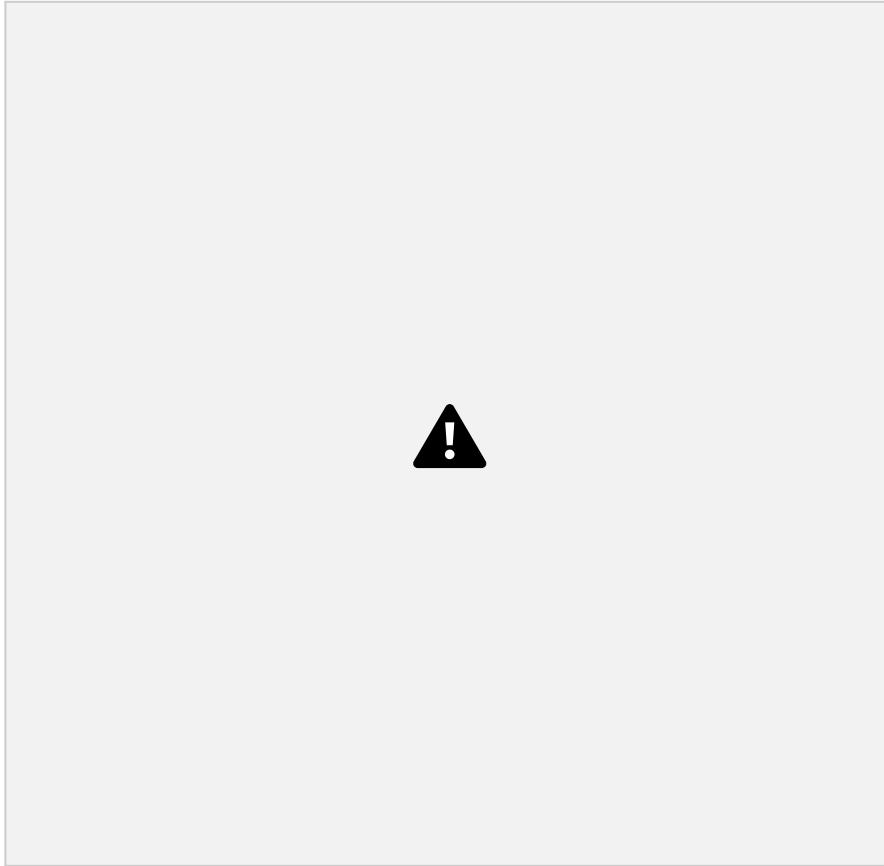


Removal of Sulphuric acid can be done by neutralizing with soda ash or caustic



### **Pyrometallurgical extraction of cobalt form spent mobile phone**

This process is widely used for the commercial recovery of Co from spent mobile phones. The commonly used treatment of spent Lithium ion batteries (LIBs) is similar to the ore smelting.



**Figure 1.11:** Flow chat for extraction of metal

1. Before the smelting process, the modular LIBs are first disassembled into separate cells and then fed into a heating furnace. These materials further are reduced by preheating, pyrolysis and smelting, successively.
2. In the preheating zone, the heating temperature should be lower than 300 °C to ensure complete evaporation of the electrolyte without explosion. And in the pyrolysis zone, the furnace temperature is controlled above 700 °C. The purpose of this is to remove the plastic from the battery.
3. In the smelting reduction zone, the material is smelted into alloys of Cu, Co, Ni, and Fe, with the aid of carbon reductant, along with Li, Al, Si, Ca, and some Fe slag.

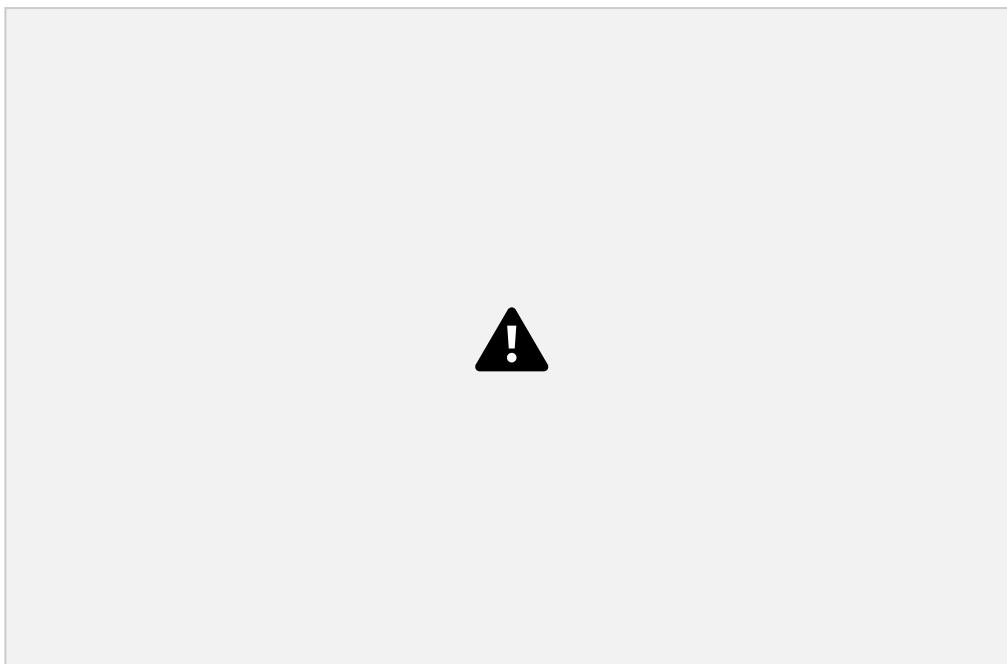
market value of cobalt.

4. In order to recover Li from the spent LIBs, the **selective pyrolysis** method of an arc furnace can be used to convert some electrode materials into Co alloys and Li concentrate. After that, the Li is extracted by hydrometallurgy, and then it is transshipped and stored through the form of  $\text{Li}_2\text{CO}_3$ . And other components can be extracted further.  
The specific steps are shown in the flow sheet (Figure 1.11). This method can be used not only to recycle electrode materials, but also to recycle Li and Fe, etc. in the electrolyte, which greatly improve the recovery efficiency.

## 1.6 A Circular Economy approach to E-Waste Management

The origin of the concept of circular economy (CE) dates back to 1989, when environmental Economists David W. Pears and R. Kerry Turner introduced the circular economic system.

A circular economy not only minimizes wastes by closing the products and/or material loops in the industrial ecosystem; but it also changes the economic logic by replacing ‘production’ with ‘sufficiency’ by the means of **reuse, refurbishment, remanufacturing and recycling**. The Conventional Economic System was based on linear models where natural resources were exploited and converted into some products which were to become waste eventually. There was no flexibility in crafting and design of products so that they could be reused or recycled. On the other hand, the Circular Economy Approach works on an innovative economic model to tackle the global crises of pollution, loss of biodiversity, climate change and e-waste management. A circular economy approach favours closed loop systems where resources are employed carefully to create innovative products which can be used for longer periods of time by reusing, sharing, refurbishing and recycling. Longer periods and smart design also imply greater productivity. Therefore, the circular economy approach is going to be the backbone of sustainable economies of the future.



**Figure 1.13:** Illustration of the circular economy concept

## **COMPUTATIONAL CHEMISTRY – UNIT II**

### **Scope of Computational Modelling**

Due to the advancement of technologies the speed of research work is supplemented by the usage of various tools and software. In many cases the computational research is done at the initial stage followed by the experimental work. In order to do interdisciplinary research, the expertise from different categories is essential. A background of computing with domain knowledge is always beneficial. The challenge is always how do we incorporate the existing knowledge/skill and build up new knowledge/skills to contribute effectively.

At one time, computational chemistry techniques were used only by experts extremely experienced in using tools that were for the most part difficult to understand and apply. Today, advances in software have produced programs that are easily used by any chemist. Along with new software comes new literature on the subject. There are now books that describe the fundamental principles of computational chemistry at almost any level of detail. A number of books also exist that explain how to apply computational chemistry techniques to simple calculations appropriate for student assignments. There are, in addition, many detailed research papers on advanced topics that are intended to be read only by professional theorists.

The group that has the most difficulty finding appropriate literature are working chemists, not theorists. These are experienced researchers who know chemistry and now have computational tools available. These are people who want to use computational chemistry to address real-world research problems and are bound to run into significant difficulties. This unit is chosen to cover a large number of topics, with an emphasis on when and how to apply computational techniques rather than focusing on theory. It gives a clear description with just the amount of technical depth typically necessary to be able to apply the techniques to computational problems. There are many good books describing the fundamental theory on which computational chemistry is built. The description of that theory as given here is very minimal. We have chosen to include just enough theory to explain the terminology used in computing.

Many computational chemistry techniques are extremely computer-intensive. Depending on the type of calculation desired, it could take anywhere from seconds to weeks to do a single calculation. There are many calculations, such as ab initio analysis of biomolecules, that cannot be done on the largest computers in existence. Likewise, calculations can take very large amounts of computer memory and hard disk space. In order to complete work in a reasonable amount of time, it is necessary to understand what factors contribute to the computer resource requirements. Ideally, the user should be able to predict in advance how much computing power will be needed.

There are often trade-offs between equivalent ways of doing the same calculation. For example, many ab initio programs use hard disk space to store numbers that are computed once and used several times during the course of the calculation. These are the integrals that describe the overlap between various basis functions. Instead of the above method, called conventional integral evaluation, it is possible to use direct integral evaluation in which the numbers are recomputed as needed. Direct integral evaluation algorithms use less disk space at the expense of requiring more CPU time to do the calculation. An in-core algorithm is one that stores all the integrals in RAM memory, thus saving on disk space at the expense of requiring a computer with a very large amount of memory. Many programs use a semidirect

algorithm, which uses some disk space and a bit more CPU time to obtain the optimal balance of both.

## Cost and Efficiency

Chemistry's impact on modern society is most readily perceived in the creation of materials, be they foods, textiles, circuit boards, fuels, drugs, packaging, etc. Thus, even the most ardent theoretician would be unlikely to suggest that theory could ever supplant experiment. Rather, most would opine that opportunities exist for combining theory with experiment so as to take advantage of synergies between them.

With that in mind, one can categorize efficient combinations of theory and experiment into three classes. In the first category, theory is applied *post facto* to a situation where some ambiguity exists in the interpretation of existing experimental results. For example, photolysis of a compound in an inert matrix may lead to a single product species analyzed by spectroscopy. However, the identity of this unique product may not be obvious given a number of plausible alternatives. A calculation of the energies and spectra for *all* of the postulated products provides an opportunity for comparison and may prove to be definitive. In the second category, theory may be employed in a simultaneous fashion to optimize the design and progress of an experimental program. Continuing the above analogy, *a priori* calculation of spectra for plausible products may assist in choosing experimental parameters to permit the observation of minor components which might otherwise be missed in a complicated mixture (e.g., theory may allow the experimental instrument to be tuned properly to observe a signal whose location would not otherwise be predictable).

Finally, theory may be used to predict properties which might be especially difficult or dangerous (i.e., costly) to measure experimentally. In the difficult category are such data as rate constants for the reactions of trace, upper-atmospheric constituents that might play an important role in the ozone cycle. For sufficiently small systems, levels of quantum mechanical theory can now be brought to bear that have accuracies comparable to the best modern experimental techniques, and computationally derived rate constants may find use in complex kinetic models until such time as experimental data are available. As for dangerous experiments, theoretical pre-screening of a series of toxic or explosive compounds for desirable (or undesirable) properties may assist in prioritizing the order in which they are prepared, thereby increasing the probability that an acceptable product will be arrived at in a maximally efficient manner.

## Molecular Interactions:

Molecular interactions are attractive or repulsive forces *between* molecules and between non-bonded atoms. Molecular interactions are important in all aspects of chemistry, biochemistry and biophysics, including protein folding, drug design, pathogen detection, material science, sensors, gecko feet, nanotechnology, separations, and origins of life. Molecular interactions are also known as noncovalent interactions, intermolecular interactions, non-bonding interactions, noncovalent forces and intermolecular forces. All of five of these phrases mean the same thing.

*Non-Bonding Interactions.* Molecular Interactions are *between* molecules, or between atoms that are not linked by bonds. Molecular interactions include cohesive (attraction between like), adhesive (attraction between unlike) and repulsive forces between molecules. Molecular interactions change (and bonds remain intact) when (a) ice melts, (b) water boils, (c) carbon dioxide sublimes, (d) proteins unfold, (e) RNA unfolds, (f) DNA strands separate

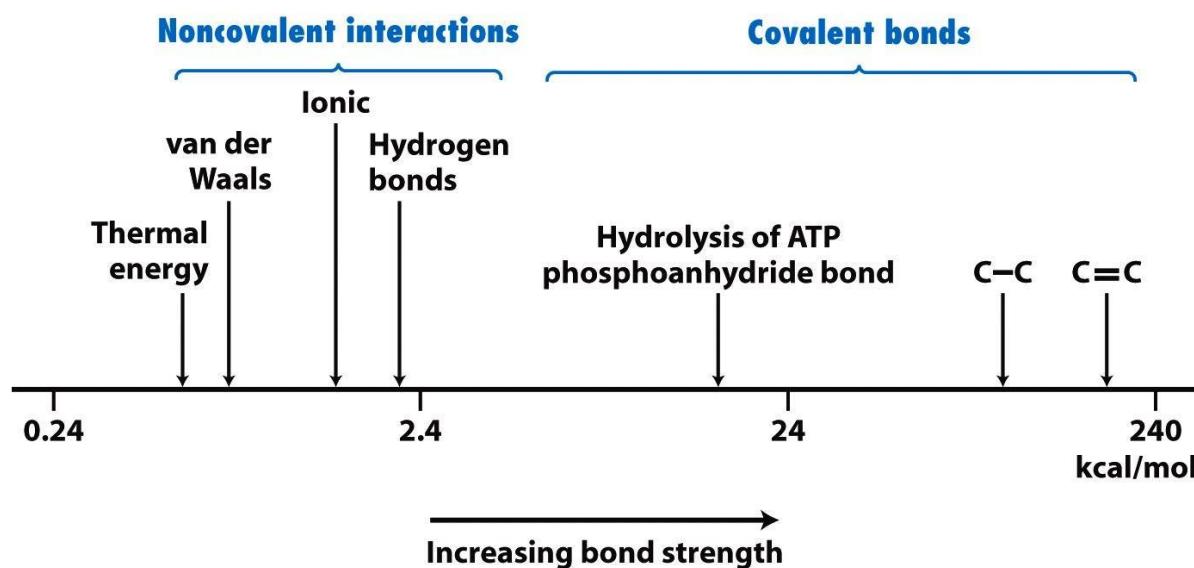
and (g) membranes disassemble. The enthalpy of a given molecular interaction, between two non-bonded atoms, is 1 - 10 kcal/mole (4 - 42 kJ/mole), which in the lower limit is on the order of RT and in the upper limit is significantly less than a covalent bond.

**Bonding Interactions.** Bonds hold atoms together *within* molecules. A molecule is a group of atoms that associates strongly enough that it does not dissociate or lose structure when it interacts with its environment. At room temperature two nitrogen atoms can be bonded ( $N_2$ ). Bonds break and form during chemical reactions. In the chemical reaction called fire, bonds of cellulose break while bonds of carbon dioxide and water form. Bond enthalpies are on the order of 100 kcal/mole (400 kJ/mole), which is much greater than RT at room temperature; bonds do not break at room temperature.

**Boiling Points.** When a molecule transitions from the liquid to the gas phase (as during boiling), ideally all molecular interactions are disrupted. Ideal gases are the ONLY systems where there are no molecular interactions. Differences in boiling temperatures give good qualitative indications of strengths of molecular interactions in the liquid phase. High boiling liquids have strong molecular interactions. The boiling point of  $H_2O$  is hundreds of degrees greater than the boiling point of  $N_2$  because of stronger molecular interactions in  $H_2O$  (liq) than in  $N_2$ (liq). The forces between molecules in  $H_2O$  (liq) are greater than those in  $N_2$ (liq).

## Bond Strength

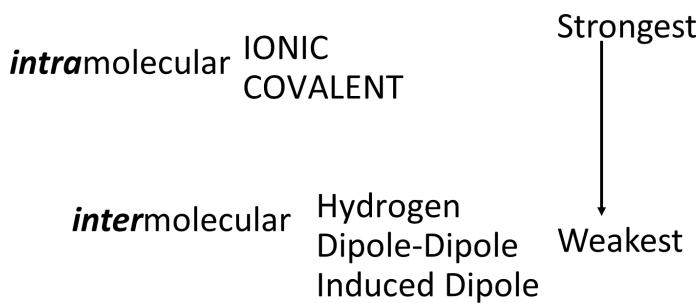
Noncovalent interactions are weak electrical bonds between molecules. Noncovalent interactions (1-5 kcal/mol) are typically ~100-fold weaker than covalent bonds.



## Intermolecular Forces

- Intermolecular forces are interactions that exist between molecules. Functional groups determine the type and strength of these interactions.
- There are several types of intermolecular interactions.
- Ionic compounds contain oppositely charged particles held together by extremely strong electrostatic interactions. These ionic interactions are much stronger than the intermolecular forces present between covalent molecules.

- Covalent compounds are composed of discrete molecules.
- The nature of the forces between molecules depends on the functional group present. There are three different types of interactions, shown below in order of increasing strength:
  - van der Waals forces
  - dipole-dipole interactions
  - hydrogen bonding

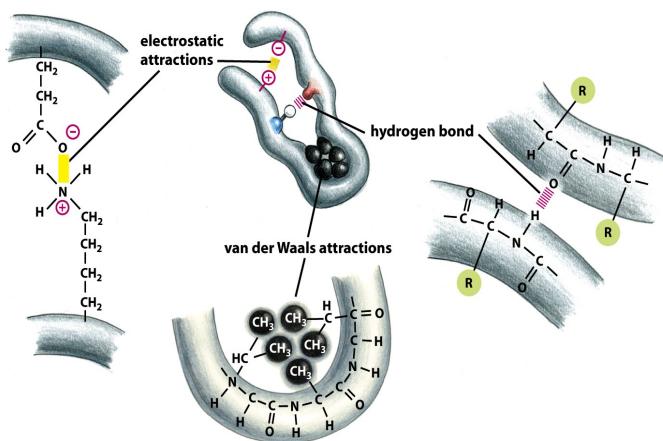


## Noncovalent interactions determine protein structure

- Amino acids are connected by *covalent* bonds called peptide bonds.
- Four types of *noncovalent* interactions between amino acids affect protein structure:

### van der Waals interactions

- Electrostatic interactions (salt bridges)
- Hydrogen bonds
- Hydrophobic forces



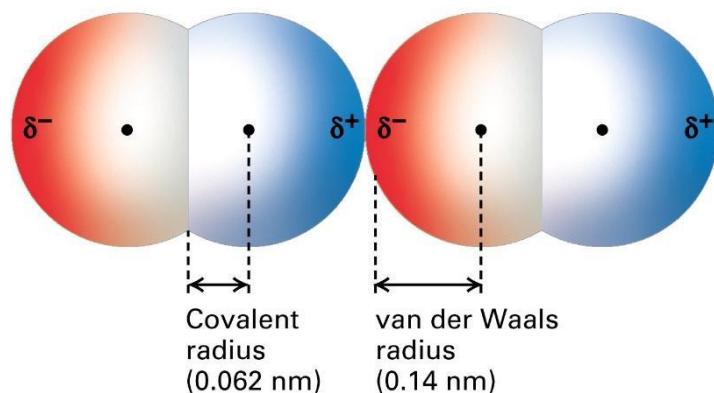
### Short range repulsion

Atoms take space. Force two atoms together and they will push back. When two atoms are close together, the occupied orbitals on the atom surfaces overlap, causing electrostatic repulsion between surface electrons. This repulsive force between atoms acts over a very short range, but is very large when distances are short.

The repulsive energy goes up as  $(d_i / R)^{12}$ , where  $R$  is the distance between the atoms and  $d_i$  is the distance threshold below which the energy becomes repulsive.  $d_i$  depends on the types of atoms. The large exponent means that when  $R < d_i$  then small decreases in  $R$  cause large increases in repulsion. Short range repulsion only matters when atoms are in very close proximity ( $R < d_i$ ), but at close range it dominates other interactions. Because this repulsion rises so sharply as distance decreases it is often useful to pretend that atoms are hard spheres, like very small pool balls, with hard surfaces (called van der Waals surfaces) and well-defined radii (called van der Waals radii).

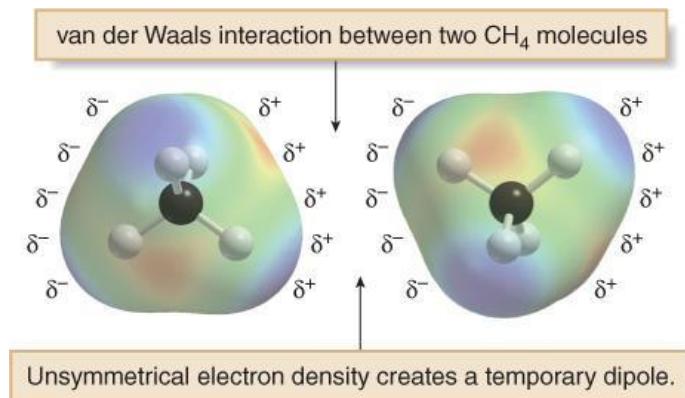
### Van der Waals Forces

Van der Waals interactions are bonds between fluctuating, induced dipoles within the electron clouds of interacting molecules. These bonds can occur between nonpolar or polar molecules. van der Waals bonds are extremely dependent on the distance of separation between molecules, and are significant only when the electron clouds of the molecules are just touching. van der Waals interactions are demonstrated for two O<sub>2</sub> molecules and the covalent and van der Waals radii are shown.



- Van der Waals forces are also known as London forces.
- They are weak interactions caused by momentary changes in electron density in a molecule.
- They are the only attractive forces present in nonpolar compounds.
- All compounds exhibit van der Waals forces.

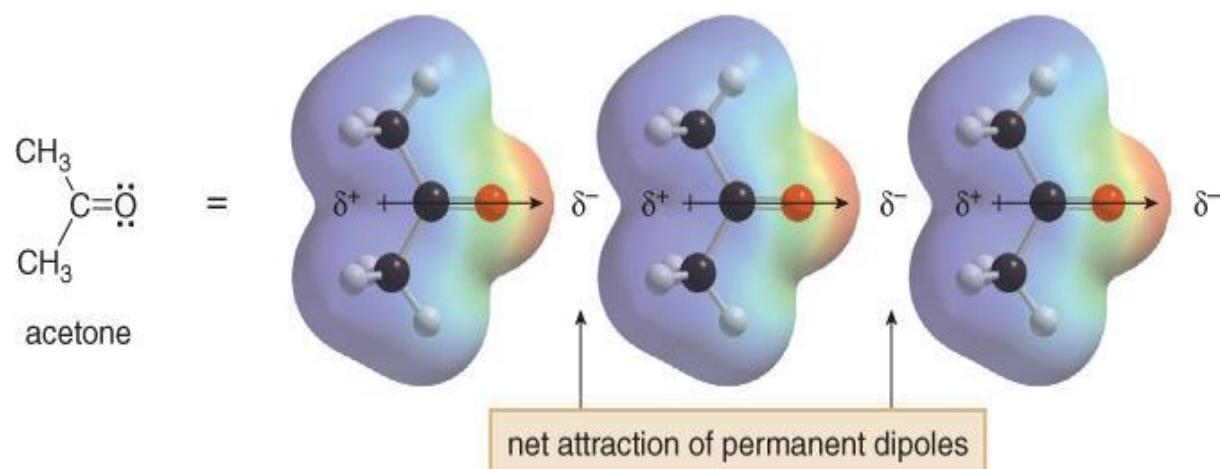
The surface area of a molecule determines the strength of the van der Waals interactions between molecules. The larger the surface area, the larger the attractive force between two molecules, and the stronger the intermolecular forces



Even though  $\text{CH}_4$  has no net dipole, at any one instant its electron density may not be completely symmetrical, resulting in a temporary dipole. This can induce a temporary dipole in another molecule. The weak interaction of these temporary dipoles constitutes van der Waals forces.

### Dipole-Dipole Interactions

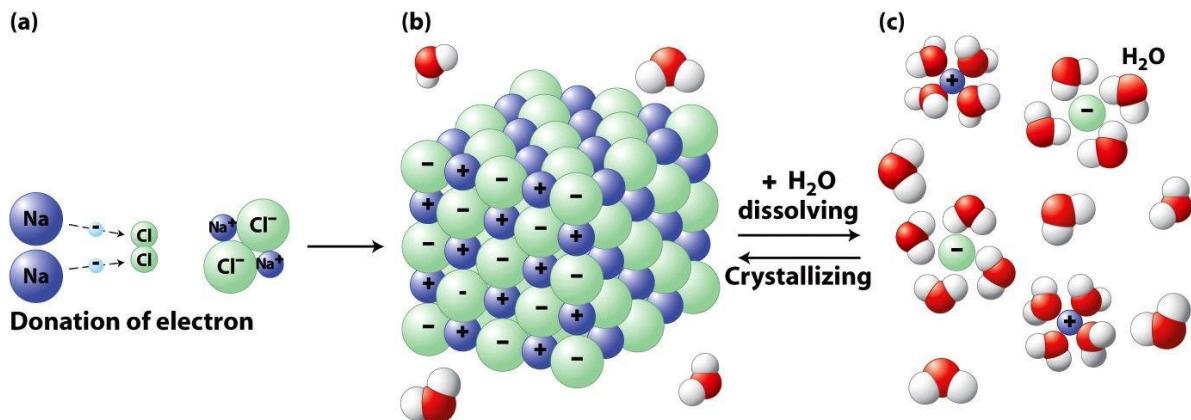
Dipole—dipole interactions are the attractive forces between the permanent dipoles of two polar molecules.



Consider acetone. The dipoles in adjacent molecules align so that the partial positive and partial negative charges are in close proximity. These attractive forces caused by permanent dipoles are much stronger than weak van der Waals forces.

### Electrostatic Interactions

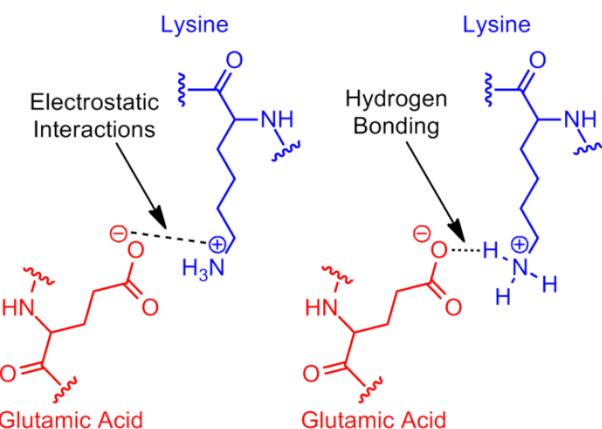
Ionic compounds such as  $\text{NaCl}$  are readily dissolved in water. Solvation spheres of water molecules surround ions in solutions. Water molecules orient so that the negative ends of their dipoles contact cations and the positive ends contact anions in solution.



Favorable electrostatic interactions cause the vapor pressure of sodium chloride and other salts to be very low. If you leave crystals of table salt ( $\text{NaCl}$ ;  $\text{Na}^+$ =cation,  $\text{Cl}^-$ =anion) on a hot pan, how long does it take before they vaporize and sublime away? A very very long time; electrostatic interactions are very very strong. The electrostatic interactions within a sodium chloride crystal are called ionic bonds. But when a single cation and a single anion are close together, within a protein, or within a folded RNA, those interactions are considered to be non-covalent electrostatic interactions.

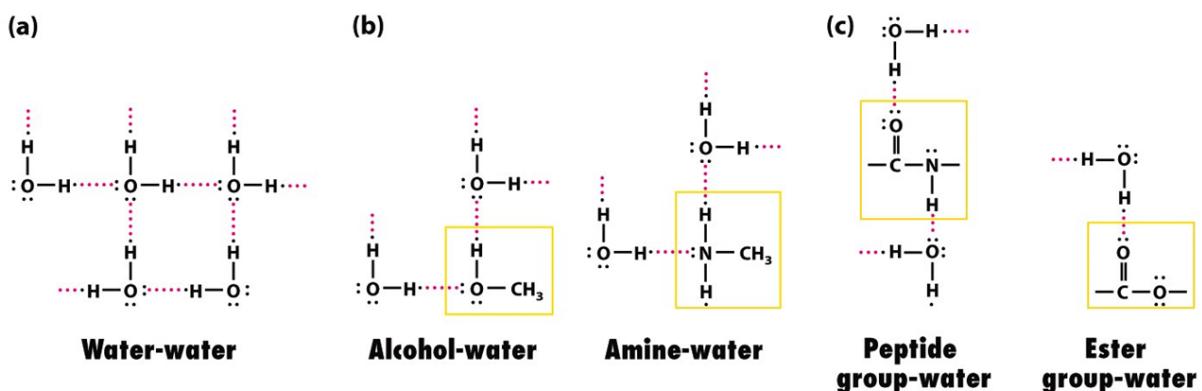
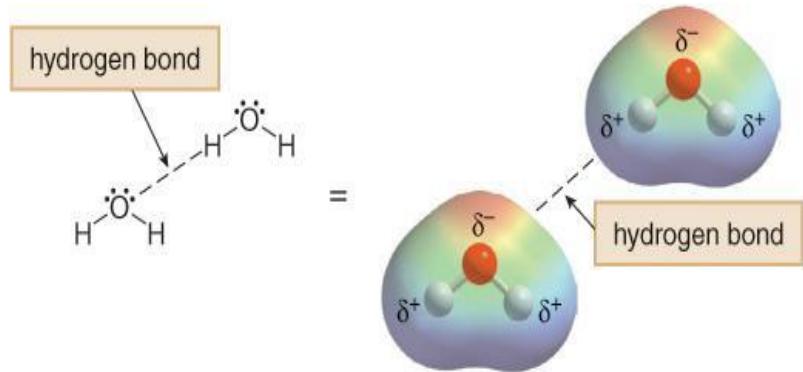
### Electrostatic Interactions (Salt Bridge)

A salt bridge is *a non-covalent interaction between two ionized sites*. It has two components: a hydrogen bond and an electrostatic interaction. Salt bridges in proteins are bonds between oppositely charged residues that are sufficiently close to each other to experience electrostatic attraction.



### Hydrogen Bonding

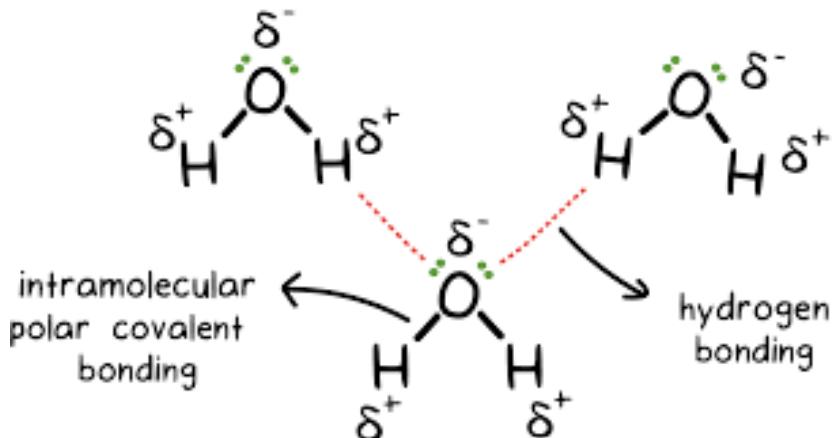
Hydrogen bonding typically occurs when a hydrogen atom bonded to O, N, or F, is electrostatically attracted to a lone pair of electrons on an O, N, or F atom in another molecule.



*Why hydrogen?* Hydrogen is special because it is the *only* atom that (i) forms covalent sigma bonds with electronegative atoms like N, O and S, and (ii) uses the inner shell (1S) electron(s) in that covalent bond. When its electronegative bonding partner pulls the bonding electrons away from hydrogen, the hydrogen nucleus (a proton) is exposed on the back side (distal from the bonding partner). The unshielded face of the proton is exposed, attracting the partial negative charge of an electron lone pair. Hydrogen is the only atom that exposes its nucleus this way. Other atoms have inner shell non-bonding electrons that shield the nucleus.

Water is a **POLAR** molecule, there are unshared pairs of electrons on the central atom.

More on **intermolecular** forces Hydrogen “Bonding”. STRONG **intermolecular** force Like magnets. Occurs *ONLY* between H of one molecule and N, O, F of another molecule



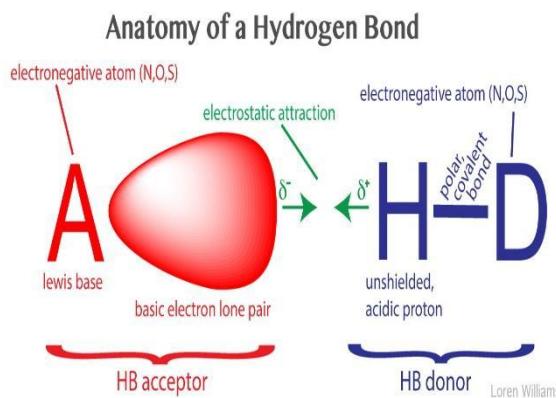


Figure 5 illustrates the hydrogen bond, elements of a including the HB acceptor and HB donor, the lone pair and the exposed proton. N, O, S are the predominant hydrogen bonding atoms (A & D) in biological systems.

A hydrogen bond is *not* an acid-base reaction, where the proton ( $\text{H}^+$ ) is fully transferred from H-D to A to form D<sup>-</sup> and HA<sup>+</sup>. However, the strength of a hydrogen bond correlates well with the acidity of donor H-D and the basicity of acceptor A. In a hydrogen bond, the H<sup>+</sup> is partially transferred from H-D to A, but H<sup>+</sup> remains covalently attached to D. The H-D bond remains intact.

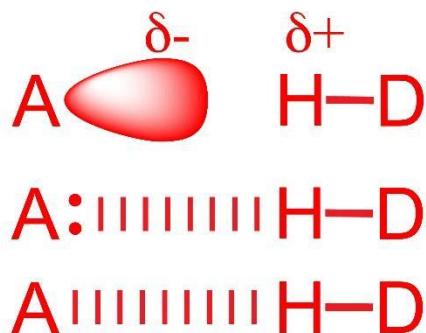


Figure 6 illustrates representing a hydrogen base (for example the N in NH<sub>3</sub> or the O in H<sub>2</sub>O) and the atom D is electronegative (for example O, N or S). The conventional nomenclature is confusing: a hydrogen bond is not a covalent bond.

three different styles for bond. Atom A is the Lewis

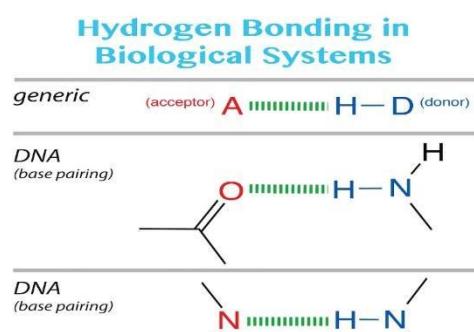


Figure 7 shows the most common hydrogen bond acceptors and donors in biological macromolecules.

The most common hydrogen bonds in biological systems involve oxygen and nitrogen atoms as A and D. Keto groups ( $=O$ ), amines ( $R_3N$ ), imines ( $R=N-R$ ) and hydroxyl groups (-OH) are the most common hydrogen bond acceptors in DNA, RNA, proteins and complex carbohydrates. Hydroxyl groups and amines/imines are the most common hydrogen bond donors. Hydroxyls and amines/imines can both donate and accept hydrogen bonds.

In traversing the Period Table, increasing the electronegativity of atom D strips electron density from the proton (in H-D), increasing its partial positive charge, and increasing the strength of any hydrogen bond. Thiols (-SH) can both donate and accept hydrogen bonds but these are generally weak, because sulfur is not sufficiently electronegative. Hydrogen bonds involving carbon, where H-D equals H-C, are observed, although these are weak and infrequent. C is insufficiently electronegative to form good hydrogen bonds. Hydrogen bonds are essentially electrostatic in nature, although the energy can be decomposed into additional contributions from polarization, exchange repulsion, charge transfer, and mixing.

Hydrogen bond strengths form a continuum. Strong hydrogen bonds of 20-40 kcal/mole (82 to 164 kJoule/mole), generally formed between charged donors and acceptors, are nearly as strong as covalent bonds. Weak hydrogen bonds of 1-5 kcal/mole (4 - 21 kJoule/mole), sometimes formed with carbon as the proton donor, are no stronger than conventional dipole-dipole interactions. Moderate hydrogen bonds, which are the most common, are formed between neutral donors and acceptors are from 3 - 12 kcal/mole (12 - 50 kJoule/mole)).

A hydrogen bond is not a bond. It is a molecular interaction (a non-bonding interaction).

### Molecular Topology:

One property of molecules appears to be very close to a binary relation: that is two atoms in a given molecule are either bonded or not bonded. Therefore, molecules can be represented by graphs when the only property considered is the existence or not of a chemical bond. This property is called molecular topology.

- In chemistry, topology provides a way of *describing and predicting the molecular structure within the constraints of three-dimensional (3-D) space.*

These graphs represent different chemical objects: molecules, reactions, crystals, polymers, clusters, etc. The common feature of chemical systems is the presence of *sites* and *connections* between them. Sites may be atoms, electrons, molecules, molecular fragments, groups of atoms, intermediates, orbitals, etc. The connections between sites may represent bonds of any kind, bonded and nonbonded interactions, elementary reaction steps,

rearrangements, van der Waals forces, etc. Chemical systems may be depicted by *chemical graphs* using a simple conversion rule:

$$\begin{array}{l} \text{Site} \leftrightarrow \text{vertex} \\ \text{connection} \leftrightarrow \text{edge} \end{array}$$

A special class of chemical graphs are *molecular graphs*. Molecular graphs are chemical graphs which represent the *constitution* of molecules. They are also called *constitutional graphs*.

- In these graphs vertices correspond to individual atoms and edges to chemical bonds between them.

Molecular graphs are necessarily connected graphs. As examples the molecular graphs corresponding to propane and cyclopropane are shown in Figure 10.

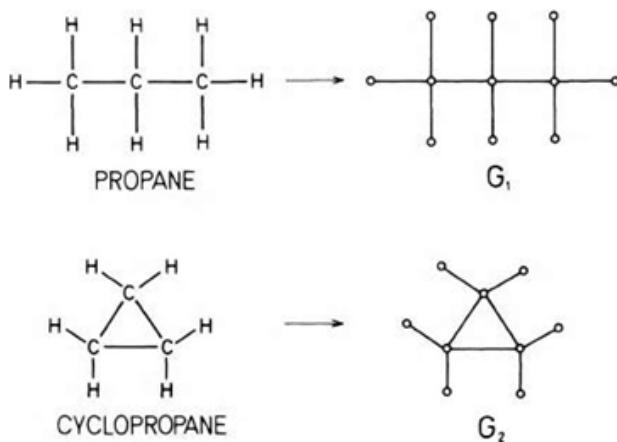


Figure 10 The molecular graphs corresponding to propane and cyclopropane

- In order to simplify the handling of molecular graphs, *hydrogen-suppressed graphs*, i.e., graphs depicting only molecular skeletons without hydrogen atoms and their bonds, are often used. They are also called *skeleton graphs*.

The hydrogen-suppressed graphs are almost universally used in chemical graph theory, because the neglect of the hydrogen atoms and their bonds in most cases cannot be the cause of any ambiguity. The hydrogen-suppressed graphs corresponding to butane and cyclobutane are given in Figure 11.

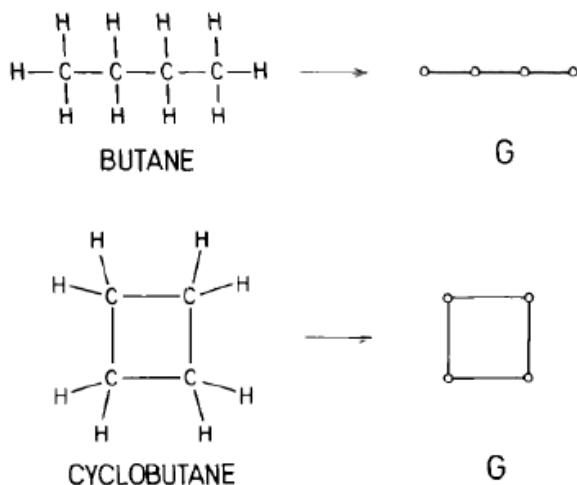


Figure 11 The hydrogen suppressed molecular graphs depicting butane and cyclobutene

The molecular graph grossly simplifies the complex picture of a molecule by depicting only its constitution (i.e., the chemical bonds between the various pairs of atoms in the molecule) and neglecting other structural features (e.g., geometry, stereochemistry, chirality). Even so, a simple picture of a molecule as the molecular graph can enable one to make useful predictions about physical and chemical properties of molecules. Since the predictions of properties and reactivities of molecules are of prime interest to chemists, the development of chemical graph theory is, thus, justified.

Molecular graphs depicting constitutional formulae of molecules represent their *topology*. This is a chemist's view of molecular topology. However, a more precise definition of molecular topology may also be given using the concept of the molecular graph. A *topological space* is formed by a set and the topological structure defined upon the set. A simple connected (molecular) graph can be associated with a topological space if it can be shown that a topological structure is defined upon its vertex-set.

### Graph theoretical matrices

The chemical graphs can be handled in many different representations for calculations to draw meaningful information. In mathematics matrix algebra is very easy to do such calculations. One of the ways to represent chemical graphs for computational purpose is graph theoretical matrix. Graphs, adequately labeled, may be associated with several matrices.

- A graph  $G$  is *labeled* if a certain numbering of vertices of  $G$  is introduced. Here two graph-theoretical matrices, i.e., the adjacency matrix and the distance matrix will be discussed. They are also sometimes referred to as topological matrices. These matrices may be used for identifying certain properties of graphs, which would not otherwise easily emerge.

### The Adjacency Matrix

The most important matrix representation of a graph  $G$  is the *vertex-adjacency matrix*  $A = A(G)$ . This matrix is also of importance in chemistry and physics. The vertex-adjacency matrix  $A(G)$  of a labeled connected graph  $G$  with  $N$  vertices is the square  $N \times N$  symmetric matrix which contains information about the internal connectivity of vertices in  $G$ .

- Vertex-adjacency matrix is defined as,

$$A_{ij} = \begin{cases} 1 & \text{if, and only if } (i, j) \in E(G) \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

$$A_{ii} = 0 \quad (2)$$

Therefore, a nonzero entry appears in  $A(G)$  only if an edge connects vertices  $i$  and  $j$ . For example, the following vertex-adjacency matrix can be constructed for a labeled graph  $G$  (Figure 12).

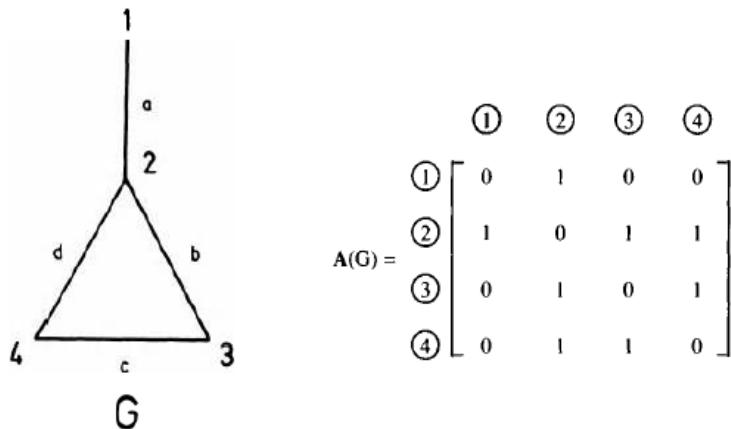


Figure 12 A vertex and edge labelled graph  $G$

The adjacency matrix is symmetrical about the principal diagonal. Therefore, the transpose of the adjacency matrix  $A$  leaves the adjacency matrix unchanged,

$$A^T(G) = A(G) \quad (3)$$

This transpose  $A^T$  is formed by interchanging rows and columns of the matrix  $A$ .

The *edge-adjacency matrix* of a graph  $G$ ,  $EA = EA(G)$ , is determined by the adjacencies of edges in  $G$ . It is very rarely used.

- The edge-adjacency matrix is defined as

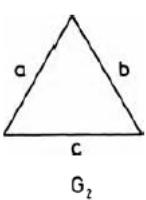
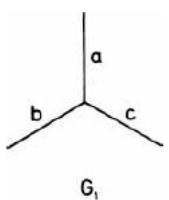
$$(EA)_{ij} = \begin{cases} 1 & \text{if edges } e_i \text{ and } e_j \text{ are adjacent} \\ 0 & \text{otherwise} \end{cases} \quad (4)$$

$$(EA)_{ii} = 0 \quad (5)$$

For example, the following edge-adjacency matrix can be constructed for a labeled graph  $G$  in Figure 12:

$${}^E\mathbf{A}(G) = \begin{bmatrix} \textcircled{a} & \textcircled{b} & \textcircled{c} & \textcircled{d} \\ \textcircled{a} & 0 & 1 & 0 & 1 \\ \textcircled{b} & 1 & 0 & 1 & 1 \\ \textcircled{c} & 0 & 1 & 0 & 1 \\ \textcircled{d} & 1 & 1 & 1 & 0 \end{bmatrix}$$

Although both the vertex-adjacency matrix and the edge-adjacency matrix reflect the topology of a molecule, they differ in their structure. However, it should be noted while the vertex-adjacency matrix uniquely determines the graph, the edge-adjacency matrix does not. In other words, there are known non-isomorphic graphs with identical edge-adjacency matrices. A pair of such non-isomorphic graphs is shown in Figure 13. The corresponding edge-adjacency matrix is given by



$${}^E\mathbf{A}(G_1) = \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} = {}^E\mathbf{A}(G_2)$$

Figure 14 A pair of nonisomorphic graphs ( $G_1$  and  $G_2$ ) which possess the identical edge-adjacency matrix.

Graphs  $G_1$  and  $G_2$  have obviously different vertex-adjacency matrices.

### The Distance Matrix

The *distance matrix* (which is also sometimes called the metrics matrix) is, in a sense, a more complicated and also a richer structure than the adjacency matrix. It is a graph-theoretical (topological) matrix less common than the adjacency matrix, but it has been increasingly used in the last two decades. in many different areas of chemistry and physics. It has been pointed out an interesting fact that the distance matrix has also found considerable use in the areas of research which are relatively remote from chemistry and physics and to a great extent non mathematical, such as anthropology, geography, geology, ornithology, philology, and psychology.

- The distance matrix  $D = D(G)$  of a labeled connected graph  $G$  is a real symmetric  $N \times N$  matrix whose elements  $(D)_{ij}$  are defined as follows:

$$(D)_{ij} = \{e_{ij}, \text{ if } i \neq j; 0, \text{ if } i = j\} \quad (6)$$

where  $e_{ij}$  is the length of the shortest path (i.e., the minimum number of edges) between the vertices  $v_i$ , and  $v_j$ . The length is also called the *distance* between the vertices  $v_i$ , and  $v_j$  thence the term distance matrix. For example, the following distance matrix can be constructed for a labeled graph  $G$  (Figure 15):

$$D(G) = \begin{bmatrix} \textcircled{1} & \textcircled{2} & \textcircled{3} & \textcircled{4} & \textcircled{5} & \textcircled{6} \\ \textcircled{1} & 0 & 1 & 1 & 2 & 3 & 3 \\ \textcircled{2} & 1 & 0 & 1 & 1 & 2 & 2 \\ \textcircled{3} & 1 & 1 & 0 & 2 & 3 & 3 \\ \textcircled{4} & 2 & 1 & 2 & 0 & 1 & 1 \end{bmatrix}$$

Figure 15 A label graph G

The distance matrix has found a widespread application in chemistry in both explicit and implicit forms. The first explicit use of the distance matrix was employed for studying the permutational isomers of stereo chemically nonrigid molecules. The distance matrix in explicit form is also used to generate the ***distance polynomial*** and the ***distance spectrum***.

### Topological indices

- A single number that can be used to characterize the graph of a molecule is called a *topological index*. (The term *graph-theoretical index* would be more accurate than topological index, but the latter is more common in the chemical literature.)

A topological index, thus, appears to be a convenient device for converting chemical constitution into a number. Evidently, this number must have the same value for a given molecule regardless of ways in which the corresponding graph is drawn or labeled. Such a number is referred to by graph theorists as a *graph invariant*. For example, one of the simplest graph invariants (topological indices) is the number of vertices in the graph (the number of atoms in the molecule). Hence, it could be simply said that topological indices are graph invariants. It should also be pointed out that topological indices do not generally allow the reconstruction of the molecular graph, implying that a certain loss of information has occurred during their creation.

Topological indices were introduced 150 years ago, and the very fact that they are still in use today is demonstration of their durability and versatility. There are more than 120 topological indices (including information-theoretic indices) available to date in the literature, with no sign that their proliferation will stop in the near future. This large (and every increasing) number of topological indices indicates that perhaps a clear and unambiguous criterion for their selection and verification is still missing, although some attempts along these lines have been reported. Moreover, a large number of topological indices also lead to a question to what extent are they orthogonal? In other words, is it possible that some topological indices express predominantly the same type of constitutional information: the difference residing in the scaling factor? Several analyses on the example of alkane trees with up to 12 vertices indicate that a number of topological indices are strongly intercorrelated i.e., that many of them contain to a great extent the same type of structural information.

One of the ultimate targets of theoretical chemists is to build schemes that would allow accurate predictions of the bulk properties of matter from the knowledge of molecular

structure. We are still far away from this ideal., but one way of trying to achieve this goal is by means of topological indexes since they serve as convenient descriptors of molecular structure.

Most of the proposed topological indices are related to either a vertex adjacency relationship (connectivity) in the molecular graph G or to graph- theoretical (topological) distances in G. Therefore, the origin of topological indices can be traced either to the adjacency matrix of a molecular graph or to the distance matrix of a molecular graph. Furthermore, since the distance matrix can be generated from the adjacency matrix, most of the topological indices are really related to the latter matrix.

The interest in topological indices is mainly related to their use in *nonempirical* quantitative structure-property relationships (QSPR) and quantitative structure-activity relationships (QSAR). The latter use in such areas as pharmacology, toxicology, environmental chemistry, and drug design is intensively studied by many researchers.

## Examples of topological indices

### Zagreb Indices

The first and second Zagreb indices ( $M_1$  and  $M_2$ ) are another set of classic vertex-based descriptors developed in 1972 and 1975, respectively. They were called the Zagreb group indices as their authors were members of the “Rudjer Bošković” Institute in Zagreb, Croatia. In these indices one counts the connections from each vertex (node, carbon).

- The first Zagreb index  $M_1(G)$  is equal to the sum of squares of the degrees of the vertices, and the second Zagreb index  $M_2(G)$  is equal to the sum of the products of the degrees of pairs of adjacent vertices of the underlying molecular graph G.

$$M_1 = \sum_{i=1}^n \delta_i^2$$

$$M_2 = \sum \delta_i \delta_j$$

For pentane, each would be calculated as:



Figure 16 A label graph of pentane

$$M_1 = 1^2 + 2^2 + 2^2 + 2^2 + 1^2 = 1 + 4 + 4 + 4 + 1 = 14$$

$$M_2 = 1 \times 2 + 2 \times 2 + 2 \times 2 + 2 \times 1 = 2 + 4 + 4 + 2 = 12$$

For 2-methylpentane, each would be calculated as:

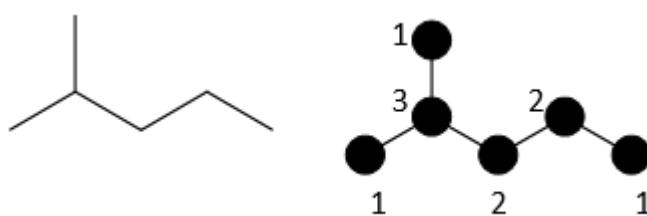


Figure 17 A label graph of 2-methylpentane

$$M_1 = 1^2 + 1^2 + 3^2 + 2^2 + 2^2 + 1^2 = 1 + 1 + 9 + 4 + 4 + 1 = 20$$

$$M_2 = 1 \times 3 + 1 \times 3 + 3 \times 2 + 2 \times 2 + 2 \times 1 = 3 + 3 + 6 + 4 + 2 = 18$$

There are thousands of 2D descriptors that are frequently applied in modeling or predicting properties or biological functions. What is interesting is that these graphs are often descriptors that are reduced to a single value that can be used to make meaning of the physical world. Zagreb group indices were introduced to *characterize branching*.

### Wiener Index

One of the first mathematical representations of chemical structure used for prediction of properties was developed in 1947 by Harold Weiner. It is defined as the sum of distances between any two carbon atoms (pairs of nodes) in the molecule.

- Mathematically it is represented as:

$$W(G) = \frac{1}{2} \sum_{u,v \in G} d(u,v)$$

Where G represents the total atoms in the molecule, u and v are individual carbon atoms and  $d(u,v)$  is the distance in bonds between any two carbon atoms in the shortest path between any two atoms. In using this index, Weiner showed that the index value is closely correlated with the *boiling point of a series of alkanes*. Further work also showed that it correlated with other physical properties such as *density, surface tension and viscosity*.

To calculate the Wiener index for a molecule, for each pair of atoms in the structure, count the distance between atoms. Take the sum of all distances and divide by two. For example in the case of ethane, which only has two nodes:

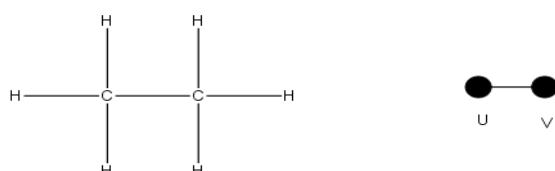


Figure 18 A label graph of ethane

	<b>u</b>	<b>v</b>
<b>u</b>	0	1

$$W(G) = \frac{1}{2}(1 + 1) = \frac{1}{2}(2) = 1$$

v	1	0
---	---	---

Pentane has 5 nodes, and distances between each node are calculated and summed.

	A	B	C	D	E	total
A	0	1	2	3	4	10
B	1	0	1	2	3	7
C	2	1	0	1	2	6
D	3	2	1	0	1	7
E	4	3	2	1	0	10

$$W(G) = \frac{1}{2}(10 + 7 + 6 + 7 + 10) = \frac{1}{2}(40) = 20$$

### The Platt Number

Platt was also interested in devising a scheme for predicting physical parameters (*molar volumes, boiling points, heats of formation, heats of vaporization*) of alkanes. He introduced an index  $F = F(G)$ , which is equal to the total sum of edge-degrees in a graph  $G$ . The *edge-degree* of an edge  $e$ ,  $D(e)$ , is the number of its adjacent edges. This index was named the *Platt number*.

- The Platt number of a graph  $G$  is defined by

$$F(G) = \sum_{i=1}^M D(e_i), \text{ The Platt number, thus represents the first neighbor's sum.}$$

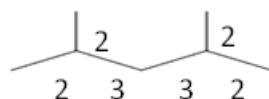


Figure 19 A label

graph of 2, 4 di-methyl pentane

### The Largest Eigenvalue

- The characteristic (spectral) polynomial  $P(G;x)$  of a graph  $G$  is the characteristic polynomial of its adjacency matrix,

$$P(G;x) = \det |xI - A|$$

where  $A$  and  $I$  are, respectively, the adjacency matrix of a graph  $G$  with  $N$  vertices and the  $N \times N$  unit matrix. A graph eigenvalue  $x_i$  is a zero of the characteristic polynomials.  $P(G;x_i) = 0$

for  $i = 1, 2, \dots, N$ . The complete set of graph eigenvalues  $\{x_1, x_2, \dots, x_N\}$  forms the spectrum of the graph. The eigenvalues are all real and the interval in which they lie is bounded.

- According to the Frobenius theorem, the limits of the graph spectrum are determined

by the maximum valency of a vertex  $D_{\max}$  in a graph:  $-D_{\max} \leq x_i \leq D_{\max}$

The largest eigenvalue,  $x_i$ , in the graph spectrum may be used as a topological index. For example, it has been found that  $x_i$  can be employed as a *measure of branching* and that (alkane) trees can be well ordered according to  $x_i$ . In Figure 20 as an example, the ordering of alkane trees with seven vertices is shown. The smallest value of  $x_i$  belongs to C7 chain and the largest value of  $x_i$  to the most branched C7 alkane tree. The largest eigenvalue is not a very discriminative index, because in many cases the same  $x_i$  value belongs to two (or more) non-isomorphic molecular graphs. One such degenerate pair appears also in the alkane trees shown in Figure 20.

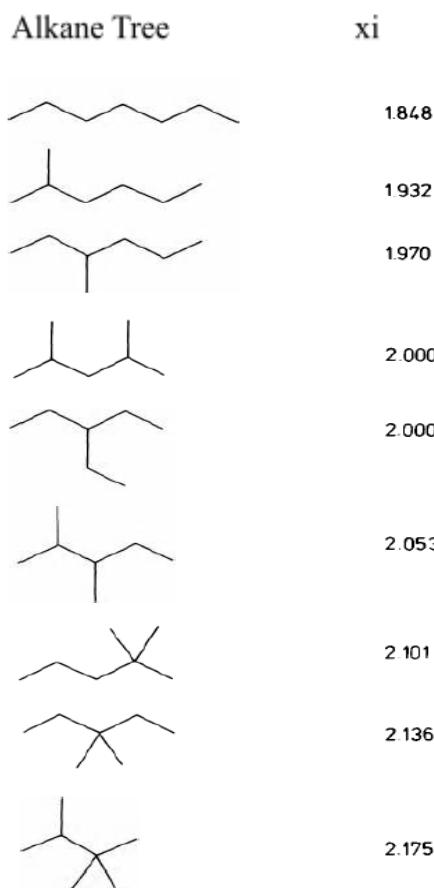


Figure 20 The ordering of alkane trees with seven vertices according to the increasing value of  $x_i$ . This order follows the intuitive notion of branching

## QSAR/QSPC concept for Insilco prediction of properties

- Quantitative structure property relationships (QSPR) and, when applied to biological activity, quantitative structure activity relationships (QSAR) are methods for determining properties due to very sophisticated mechanisms purely by a curve fit of that property to aspects of the molecular structure.

This allows a property to be predicted independent of having a complete knowledge of its origin. For example, drug activity can be predicted without knowing the nature of the binding site for that drug. Structure–property relationships are qualitative or quantitative empirically defined relationships between molecular structure and observed properties. In some cases, this may seem to duplicate statistical mechanical or quantum mechanical results. However,

structure–property relationships need not be based on any rigorous theoretical principles. The simplest case of structure–property relationships a qualitative rule of thumb. For example, the statement that branched polymers are generally more biodegradable than straight-chain polymers is a qualitative structure–property relationship. When structure–property relationships are mentioned in the current literature, it usually implies a quantitative mathematical relationship. Such relationships are most often derived by using curve-fitting software to find the linear combination of molecular properties that best predicts the property for a set of known compounds. This prediction equation can be used for either the interpolation or extrapolation of test set results. Interpolation is usually more accurate than extrapolation. When the property being described is a physical property, such as the boiling point, this is referred to as a quantitative structure–property relationship (QSPR). When the property being described is a type of biological activity, such as drug activity, this is referred to as a quantitative structure–activity relationship (QSAR). Our discussion will first address QSPR. All the points covered in the QSPR section are also applicable to QSAR, which is discussed next.

## **QSPR/QSAR**

A stepwise procedure of QSPR is given below.

- Step 1- Compilation of list of compounds and their experimental property value

Compilation of list of compounds for which the experimentally determined property is known. Ideally, this list should be very large. Often, thousands of compounds are used in a QSPR study. If there are fewer compounds on the list than parameters to be fitted in the equation, then the curve fit will fail. If the same number exists for both, then an exact fit will be obtained. This exact fit is misleading because it fits the equation to all the anomalies in the data, it does not necessarily reflect all the correct trends necessary for a predictive method. In order to ensure that the method will be predictive, there should ideally be 10 times as many test compounds as fitted parameters. The choice of compounds is also important. For example, if the equation is only fitted with hydrocarbon data, it will only be reliable for predicting hydrocarbon properties.

- Step 2- Geometry of molecule

To obtain geometries for the molecules. Crystal structure geometries can be used; however, it is better to use theoretically optimized geometries. By using the theoretical geometries, any systematic errors in the computation will cancel out. Furthermore, the method will predict as yet un-synthesized compounds using theoretical geometries. Some of the simpler methods require connectivity only.

- Step 3- Molecular Descriptor

Molecular descriptors must then be computed. Any numerical value that describes the molecule could be used. Many descriptors are obtained from molecular mechanics or semiempirical calculations. Energies, population analysis, and vibrational frequency analysis with its associated thermodynamic quantities are often obtained this way. Ab initio results can be used reliably, but are often avoided due to the large amount of computation necessary. The largest percentage of descriptors are easily determined values, such as molecular weights, topological indexes, moments of inertia, and so on.

- Step 4- Correlation

Once the descriptors have been computed, it is necessary to decide which ones will be used. This is usually done by computing correlation coefficients. Correlation coefficients are a measure of how closely two values (descriptor and property) are related to one another by a linear relationship. If a descriptor has a correlation coefficient of 1, it describes the property exactly. A correlation coefficient of zero means the descriptor has no relevance. The descriptors with the largest correlation coefficients are used in the curve fit to create a property prediction equation. There is no rigorous way to determine how large a correlation coefficient is acceptable.

Intercorrelation coefficients are then computed. These tell when one descriptor is redundant with another. Using redundant descriptors increases the amount of fitting work to be done, does not improve the results, and results in unstable fitting calculations that can fail completely (due to dividing by zero or some other mathematical error). Usually, the descriptor with the lowest correlation coefficient is discarded from a pair of redundant descriptors.

A curve fit is then done to create a linear equation, such as  $\text{Property} = c_0 + c_1d_1 + c_2d_2 + \dots$  where  $c_i$  are the fitted parameters and  $d_i$  the descriptors. Most often, the equation being fitted is a linear equation like the one above. This is because the use of correlation coefficients and linear equations together is an easily automated process. Introductory descriptions cite linear regression as the algorithm for determining coefficients of best fit, but the mathematically equivalent matrix least-squares method is actually more efficient and easier to implement. Occasionally, a nonlinear parameter, such as the square root or log of a quantity, is used. This is done when a researcher is aware of such nonlinear relationships in advance.

- QSAR is also called traditional QSAR or Hansch QSAR to distinguish it from the 3D QSAR method. This is the application of the technique described above to biological activities, such as environmental toxicology or drug activity.

In order to parameterize a QSAR equation, a quantified activity for a set of compounds must be known. These are called lead compounds, at least in the pharmaceutical industry. Typically, test results are available for only a small number of compounds. Because of this, it can be difficult to choose a number of descriptors that will give useful results without fitting to anomalies in the test set. Three to five lead compounds per descriptor in the QSAR equation are normally considered an adequate number. If two descriptors are nearly collinear with one another, then one should be omitted even though it may have a large correlation coefficient.

In the case of drug design, it may be desirable to use parabolic functions in place of linear functions. The descriptor for an ideal drug candidate often has an optimum value. Drug activity will decrease when the value is either larger or smaller than optimum. This functional form is described by a parabola, not a linear relationship.

The advantage of using QSAR over other modelling techniques is that it takes into account the full complexity of the biological system without requiring any information about the binding site. The disadvantage is that the method will not distinguish between the contribution of binding and transport properties in determining drug activity. QSAR is very useful for determining general criteria for activity, but it does not readily yield detailed structural predictions.

## Predicting Molecular Geometry

Computing the geometry of a molecule is one of the most basic functions of a computational chemistry program. However, it is not trivial process. The user of the program will be able to

get their work done more quickly if they have some understanding of the various algorithms within the software. The user must first describe the geometry of the molecule. Then the program computes the energies and gradients of the energy to find the molecular geometry corresponding to the lowest energy.

- **Specifying Molecular Geometry**

One way to define the geometry of a molecule is as a set of Cartesian coordinates for each atom. Graphic interface programs often generate Cartesian coordinates since this is the most convenient way to write those programs. It is becoming more common to use programs that have a graphical builder in which the user can essentially draw the molecule. There are several ways in which such programs work. Some programs allow the molecule to be built as a two-dimensional stick structure and then convert it into a three-dimensional structure. Some programs have the user draw the three-dimensional backbone and then automatically add the hydrogens. This works well for organic molecules. Some programs build up the molecule in three dimensions starting from a list of elements and hybridizations, which can be most convenient for inorganic molecules. Many programs include a library of commonly used functional groups, which is convenient if it has the functional groups needed for a particular project. A number of programs have specialized building modes for certain classes of molecules, such as proteins, nucleotides, or carbohydrates.

- **Geometry optimization**

Many computational chemistry programs will do the geometry optimization in Cartesian coordinates. This is often the only way to optimize geometry in molecular mechanics programs and an optional method in orbital-based programs. A Cartesian coordinate optimization may be more efficient. Cartesian coordinates are often preferable when simulating more than one molecule since they allow complete freedom of motion between separate molecules. Geometry optimizations that run poorly either take a large number of iterations or fail to find an optimized geometry. There are many different algorithms for finding the set of coordinates corresponding to the minimum energy. These are called *optimization algorithms* because they can be used equally well for finding the minimum or maximum of a function.

Example of softwares for coordinate generation and geometry optimization are Discovery studio, Avogadro, CORINA etc

The materials in Unit-II are compiled from different reference sources.

1. COMPUTATIONAL CHEMISTRY, A Practical Guide for Applying Techniques to Real-World Problems, Darid C. Young
2. Essentials of Computational Chemistry by Christopher J. Cramer
3. Molecular Interactions and the Behaviors of Biological Macromolecules, by Loren Dean Williams  
[https://williams.chemistry.gatech.edu/structure/molecular\\_interactions/mol\\_int.html](https://williams.chemistry.gatech.edu/structure/molecular_interactions/mol_int.html)
4. Chemical graph theory, Nenad Trinajstic, Ph.D., Professor of Chemistry, The Rugjer Boskovic Institute Zagreb, The Republic of Croatia
5. Topological Index calculator:  
<https://www.cs.gordon.edu/courses/organic/topo/manual-v3/manual.html>

## Syllabus

Computational chemistry: Scope, cost and efficiency of computational modeling. Stabilizing interactions: Bonded and non-bonded interactions. Molecular topology, topological matrix representation, topological indices, QSAR/QSPC concept for insilico prediction of properties. 3D co-ordinate generation for small molecules, geometry optimization.

## **Unit III: Materials for memory and display technology**

**3.1 Memory device:** A memory device is a piece of hardware used to store data. Most electronic devices such as computers, mobile phones, tablets, etc all have a storage device that stores data or programs.

### **3.2 Basic concepts of electronic memory:**

- An electronic memory device is a form of semiconductor storage which is fast in response and compact in size and can be read and written when coupled with a central processing unit (CPU, a processor).
- In conventional silicon-based electronic memory, data are stored based on the amount of charge stored in the memory cells. Organic/polymer electronic memory stores data in an entirely different way, for instance, based on different electrical conductivity states (ON and OFF states) in response to an applied electric field.
- Organic/polymer electronic memory is likely to be an alternative or at least a supplementary technology to conventional semiconductor electronic memory.

### **3.3 Classification of electronic memory devices**

According to the device structure, electronic memory devices can be divided into four primary categories: transistor-type, capacitor-type, and resistor-type and charge transfer-type.

#### **(1) Transistor-type electronic memory device**

A transistor is a miniature electronic component that can work either as an amplifier or a switch.

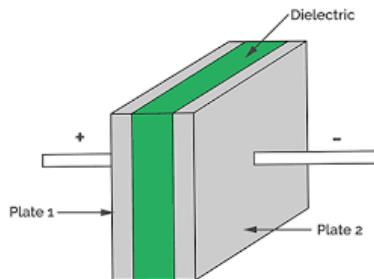
- It is converted to p-type and n-type semiconductor by doping trivalent and pentavalent impurities.
- A computer memory chip consists of billions of transistors, each transistor is working as a switch, which can be switched ON or OFF. Each transistor can be in two different states and store two different numbers, ZERO and ONE.
- Since chip is made of billions of such transistors and can store billions of Zeros and Ones, and almost every number and letter can be stored.

#### **(2) Capacitor- type electronic memory device**

Capacitors have two parallel plate electrodes and charges are stored in these electrodes under an applied electric field.

- Data can be stored in these devices based on different charge stored in the cell. Charges stored in the cell maintain electric polarization that can be switched between two stable states by an external electric field.

- Organic and polymeric ferroelectric materials can be used in capacitor-type electronic memory device.



**Fig 4.1: Capacitor**

**One common example of a transistor-type and capacitor type electronic memory device** is Dynamic Random Access Memory (DRAM). DRAM is widely used as the main memory (RAM) in computers and electronic devices.

**Basic structure of DRAM:** DRAM consists of a grid of memory cells, where each cell is made up of a capacitor and a transistor. The **capacitor** stores a charge, representing the binary state (0 or 1), and the **transistor** acts as a switch that controls the flow of charge in and out of the capacitor.

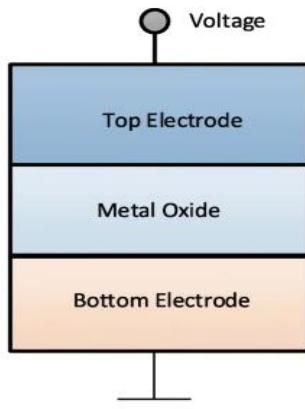
**Storage Mechanism of DRAM:** The information in DRAM is stored in the form of electrical charges in the capacitors. When a charge is present in the capacitor, it represents a binary '1,' and when there is no charge, it represents a binary '0.' The transistor is used to read and write data by controlling the flow of charge.

### (3) Resistor-type electronic memory device

Resistor-type memory devices are a type of electronic memory that uses resistors to store information.

- The memory cell consists of a resistor-type material that can change its resistance when an electric field is applied. The resistance can be set to high or low states, representing binary values (0 or 1).
- The resistors are arranged in a particular pattern to store the information.
- Unlike transistor and capacitor memory devices, resistor-type memory does not require a specific cell structure (e.g. Field Effecting Transistor) or to be integrated with the CMOS (complementary metal-oxide-semiconductor) technology.

The structure comprises of an insulating layer (I) sandwiched between the two metal(M) electrodes and supported on a substrate (glass, silicon wafer, plastic, or metal foil). Initially, the device is under high resistance state or “OFF” and logically “0” state, when resistance changed or under external applied field changes to low resistance state or “ON” logical value “1”



**Fig 4.2: Resistor**

#### (4) Charge transfer type electronic memory device

Charge-transfer type electronic memory devices typically involve the movement of charge carriers (usually electrons) within the device to store and retrieve data.

- This type of electronic device is based on the Charge Transfer Effects of a charge transfer complex. A charge transfer (CT) complex consists of two parts, one electron donor and other an electron acceptor.
- It is also called as a donor–acceptor (D– A) complex. The conductivity of a CT complex is dependent on the ionic binding between the D–A components. In CT complex, a partial transfer of charges occurs from donor part to the acceptor part.
- This results in difference in conductivity. CT complexes exhibit bistable states due to difference in conductivity. This behavior is used to design molecular electronic devices.

### 3.4 Types of organic memory materials

There are three classes of materials which can exhibit bistable states and are used inorganic memory devices. They are:

**i) Organic molecules, ii) Polymeric materials and iii) Organic- inorganic hybrid materials.**

Under each category, lots of different types of molecules exhibiting memory effect are available.

Few of them are described here:

#### 3.4.1 Organic molecules used for memory device

Small organic molecules containing both an electron donor and an electron acceptor are an important type of material for organic electronic memory devices.

Examples: Pentacene, Perfluoropentacene, etc

#### 3.4.2 Criteria for organic molecules/polymers used as semiconductor materials

The selection of organic molecules/polymers as semiconductor materials for electronic devices

is based on various criteria, taking into account the specific requirements of the application. Here are some key criteria for choosing organic molecules/polymers as semiconductor materials:

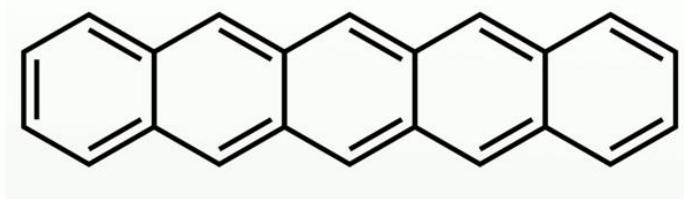
- a) Conjugation and  $\pi$ -Electron System:** Molecules with extended conjugation and a well-defined  $\pi$ -electron system tend to exhibit semiconducting properties. This allows for efficient charge carrier transport within the material.
- b) Bandgap Energy:** The bandgap of the material is crucial. The bandgap determines the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The bandgap influences the type and efficiency of charge carriers (holes or electrons) in the semiconductor.
- c) Substituent Effects:** The introduction of specific functional groups or substituents can influence the electronic properties, molecular packing, and stability of organic semiconductors. This allows for the tailoring of properties to meet specific device requirements.
- d) Environmental Stability:** Some organic semiconductors may be sensitive to environmental factors such as moisture and oxygen. It's important to consider the environmental stability of the material, especially for applications where devices may be exposed to varying conditions.
- e) Cost and Scalability:** The cost of production and the scalability of manufacturing processes are critical considerations. Organic semiconductors are often favored for their potential for low-cost and large-area fabrication.

### 3.4.3 The p -type organic semiconductor material “Pentacene”

Pentacene is a polycyclic aromatic hydrocarbon consisting of five linearly fused benzene rings.

- It is an organic semiconductor that generates excitons upon absorption of ultra-violet or visible light, making it very sensitive to oxidation.
- The extended  $\pi$ -system allows the continuous delocalization of  $\pi$ - electrons and there is a lateral overlapping of pi-electrons between the molecules.

In the context of organic electronics, pentacene is often used as a semiconductor in organic thin-film transistors (OTFTs) and other electronic devices.



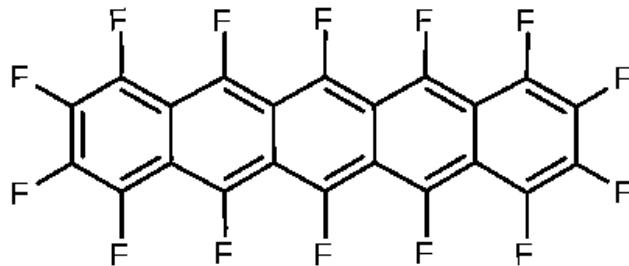
**Fig 4.3: Pentacene structure**

### 3.4.4 The n -type organic semiconductor material “Perfluoropentacene”

Perfluoropentacene is a derivative of pentacene where all hydrogen atoms in the pentacene structure

are replaced by fluorine atoms. It is used in molecular thin-film devices such as OLEDs.

- The introduction of fluorine atoms can affect the electronic structure and improve certain performance aspects.
- Fluorine substitution is known to enhance stability and alter the molecular packing in films, potentially leading to improved charge transport properties.



**Fig 4.4: Perfluoropentacene**

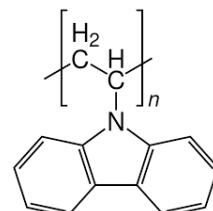
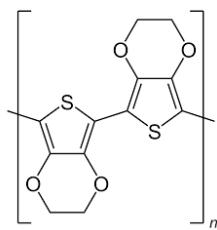
### 3.5 Polymeric material for Organic memory device

Polymeric materials are commonly used in organic memory devices due to their unique properties, such as flexibility, processability, and the ability to tailor their electronic properties.

#### **Example (1) Poly(3,4-ethylenedioxythiophene): Polystyrene Sulfonate (PEDOT:PSS)**

Is a conductive polymer blend commonly used in organic electronic devices. It has been investigated for use in organic memory devices due to its good electrical conductivity and stability. Modifications and optimizations of PEDOT:PSS have been explored to enhance its memory performance.

**Example (2) Poly(N-vinylcarbazole) (PVK):** PVK is a widely studied polymer in organic electronics. It has been employed as a host material in organic light-emitting diodes (OLEDs) and as a charge transport layer in organic solar cells. PVK and its derivatives have also been investigated for their potential in organic memory devices.



**Fig 4.5: (PEDOT:PSS):**

**PVK**

Some more examples as polymers used organic semiconductors

**(3) Polythiophenes:** Poly(3-hexylthiophene) (P3HT)

**(4) Polyfluorenes:** Poly(9,9-dioctylfluorene) (PFO)

### **3.6 Organic-inorganic hybrid materials**

Organic-inorganic hybrid materials combine the unique properties of both organic and inorganic components, offering a versatile platform for various applications, including memory devices. These hybrid materials often leverage the organic component for flexibility and processability, while the inorganic component provides enhanced electronic or optical properties.

Generally, organic-inorganic hybrid materials are composed of organic layers containing inorganic materials. Inorganic materials used are allotropes of carbon like fullerenes, carbon nanotubes, graphene and metal nanoparticles, semiconductor nanoparticles and inorganic quantum dots (QDs).

Here are some examples of organic-inorganic hybrid materials used in memory devices:

#### **a) Metal-Organic Frameworks (MOFs):**

Example: MOFs incorporating organic ligands and metal ions or clusters.

#### **b) Hybrid Organic Ferroelectric Materials:**

Example: Organic ferroelectric polymers combined with inorganic ferroelectric materials.

#### **c) Organic-Inorganic Nanocomposites**

These are the hybrid electronic memory devices in which organic polymer with appropriate functional group is clubbed with metal nanoparticles, quantum dots and metal oxide nanoparticles.

An example is a composite of 8-hydroxyquinoline- containing polymer with gold nanoparticle sandwiched between two metal electrodes. Bistable electronic transition states are observed when an electric field is applied due to charge transfer between the Au nanoparticles and 8-hydroxy-quinoline.

### **3.7 Bio-composite based memory devices**

Bio-composite-based memory devices represent a fascinating and emerging area of research at the intersection of materials science, biology, and electronics. These devices leverage bio-inspired or bio-compatible materials to create memory storage components.

#### **a) DNA-Based Memory Devices:**

Material: DNA (deoxyribonucleic acid)

Application: DNA has been investigated for use in non-volatile memory devices. DNA strands can be used to store information through sequence variations or by exploiting the inherent charge and structural characteristics of DNA.

Properties: DNA is known for its information-carrying capacity and ability to self-assemble.

Researchers are exploring its potential for data storage.

**b) Protein-Based Memory Devices:**

Material: Proteins, such as bacteriorhodopsin

Application: Bacteriorhodopsin, found in the membranes of certain bacteria, has been explored for use in optical memory devices. It can undergo reversible photochemical reactions, making it suitable for information storage.

Properties: Bacteriorhodopsin exhibits light-sensitive properties, allowing for the creation of bio-composite-based memory devices with potential applications in optical storage.

**c) Peptide-Based Memory Devices:**

Material: Peptides

Application: Peptide-based materials are being investigated for their potential in resistive switching memory devices. These devices use changes in resistance to store information.

Properties: Peptides offer a wide range of structural and functional diversity, making them attractive for designing novel memory devices.

**d) Cellulose-Based Memory Devices:**

Material: Cellulose and cellulose derivatives

Application: Cellulose, a natural polymer found in plant cell walls, has been explored for use in flexible and biodegradable memory devices.

Properties: Cellulose-based materials are abundant, renewable, and environmentally friendly. They have potential applications in sustainable and biocompatible memory devices.

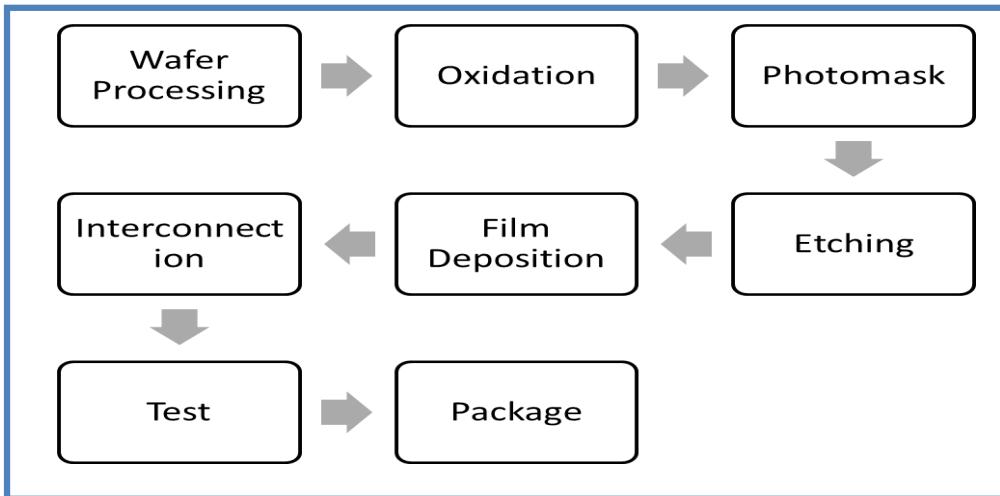
### 3.8 Manufacturing of semiconductor chips

A semiconductor chip is an electric circuit with many components such as transistors and wiring formed on a semiconductor wafer. An electronic device comprising numerous these components is called “integrated circuit”. The layout of the components is patterned on a photomask (reticle) by computer and projected onto a semiconductor wafer in the manufacturing processes described below. Entire manufacturing process takes time, from start to packaged chips ready for shipment, at least six to eight weeks.

**Fabrication Steps:** It is a multiple-step sequence of photolithographic and chemical processing steps (such as surface passivation, thermal oxidation, planar diffusion and junction isolation) during which electronic circuits are gradually created on a wafer made of pure semiconducting

material.

Entire manufacturing process can be divided into 8 steps.



**Fig 4.6: Overview of fabrication steps of semiconductor chip**

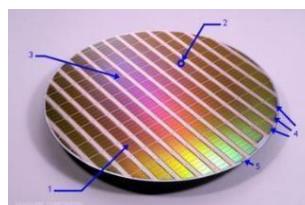
**(i) Wafer Processing:** A wafer, also called a disc, is a thin round glossy slice of a silicon rod (or Germanium) that is cut using specific diameters for the fabrication of integrated circuits. Most wafers are made of silicon extracted from sand.

Once silicon is extracted from sand, it needs to be purified before it can be put to use. First, it is heated until it melts into a high-purity liquid then solidified into a silicon rod, or ingot, using common growing methods like the Czochralski (chokh-RAL-skee) process or the Floating Zone process. In these processes, a cylindrical ingot of high purity monocrystalline semiconductor, such as silicon or germanium, called a boule, is formed by pulling a seed crystal from a melt. These ingots are then sliced into wafers about 0.75 mm thick. The thin slice obtained through cutting process is called “die” that is an unprocessed “raw wafer”. The die surface is uneven and polished to remove surface defects through grinding and chemical etching processes then to smooth surface through polishing to obtain mirror-smooth finish. The flawless surface allows the circuit patterns to print better on the wafer surface during the lithography process.

Once the wafers are prepared, many process steps are necessary to produce the desired semiconductor integrated circuit. Donor impurity atoms, such as boron, phosphorus, arsenic, or antimony in the case of silicon, can be added to the molten intrinsic material in precise amounts in order to dope the crystal, thus changing it into an extrinsic semiconductor of n-type or p-type.



**Fig 4.7 a) Si wafer**



**b) finished wafer**

**(ii) Oxidation:** The role of oxidation process is to form a protective film on the surface of wafer. It

can protect the wafer from chemical impurities; prevent leakage current from entering circuit, diffusion during ion implantation and the wafer from slipping off during etching.

**(iii) Photomask:** A photomask is basically a “master template” of an IC design. Photomask is the use of light to print circuit patterns onto wafer. A photomask is an opaque plate with holes or transparencies that allow light to shine through in a defined pattern. (Previously, photomasks used to be produced manually by using rubylith and mylar).

The wafer is then covered with a light-sensitive coating called 'photoresist'. There are two types of resist: positive and negative. The main difference between positive and negative resist is the chemical structure of the material and the way that the resist reacts with light. With positive resist, the areas exposed to ultraviolet light change their structure and are made more soluble – ready for etching and deposition. The opposite is true for negative resist, where areas hit by light polymerize, meaning they become stronger and more difficult to dissolve. Positive resist is most used in semiconductor manufacturing because its higher resolution capability makes it the better choice for the lithography stage.

**(iv) Etching:** The next step is to remove the degraded resist to reveal the intended pattern. During 'etch', the wafer is baked and developed, and some of the resist is washed away to reveal a 3D pattern of open channels. Etch processes must precisely and consistently form increasingly conductive features without impacting the overall integrity and stability of the chip structure.

Removal is any process that removes material from the wafer; examples include etch processes (either wet or dry) and chemical-mechanical planarization (CMP).

Wet etching uses chemicals solutions to remove oxide films. In wet etching, the exposed thin film on the surface layer is dissolved using chemicals, such as hydrofluoric acid or phosphoric acid, and removed. This forms the pattern. Advantages are low cost, fast etching speed and high productivity. Wet etching is not suitable for fine circuit diagrams. There is also a dry etching method in which the wafer surface is bombarded with ionized atoms to remove the film layer.

Now dry etching **has been widely used for fine circuit diagrams.**

**Dry etching has three different types:**

**Chemical etching -which uses gas (Hydrogen fluoride), physical sputtering**-ions in the plasma are used to strike and remove the excess oxide layer **and** Reactive ion etching

**(v) Film deposition:** To create the micro devices inside the chip, deposit layers of thin films and remove excess parts by etching and add some materials to separate the different devices. Thin film layers of silicon oxide, aluminum and other metals that will become the circuit materials are formed on the wafer. Thin films of conducting, isolating or semiconducting materials – depending on the type of the structure being made are deposited on the wafer to enable the first layer to be printed on it. This important step is commonly known as 'deposition'.

**Implantation of Impurities:** Once patterns are etched in the wafer, the wafer may be bombarded with positive or negative ions to tune the electrical conducting properties of part of the pattern.

Raw silicon – the material the wafer is made of is not a perfect insulator or a perfect conductor. Silicon electrical properties are somewhere in between. In order to give the silicon substrate semiconducting properties, impurities, such as phosphor or boron ions, are implanted in the wafers.

**(vii) Test:** The main goal of the test is to check whether the quality of the semiconductor chip meets a certain standard, thereby eliminating the defective products and improving the reliability of the chip. Electronic Die sorting (EDS) is a testing method for wafers.

Once the front-end process has been completed, the semiconductor devices or chips are subjected to a variety of electrical tests to determine if they function properly. The percent of devices on the wafer found to perform properly is referred to as the yield.

**(viii) Package:** Single wafers are cut into individual chips by cutting. The entire packaging system is divided into five steps. Namely wafer sawing, single wafer attachment, interconnection, molding and packaging.

The entire process of creating a silicon wafer with working chips consists of thousands of steps and can take more than three months from design to production. To get the chips out of the wafer, it is sliced and diced with a diamond saw into individual chips. Cut from a 300- mm wafer, the size most often used in semiconductor manufacturing, these so-called 'dies' differ in size for various chips. Some wafers can contain thousands of chips, while others contain just a few dozen.

The chip die is then placed onto a 'substrate'. This is a type of baseboard for the microchip die that uses metal foils to direct the input and output signals of a chip to other parts of a system. And to close the lid, a 'heat spreader' is placed on top. This heat spreader is a small, flat metal protective container holding a cooling solution that ensures the microchip stays cool during operation.

### **3.9 Display Systems: Photoactive and electro active materials**

**Photoactive materials**, also known as photosensitive or photosensitive materials, are substances that exhibit a change in their properties when exposed to light.

Photoactive materials belong to the huge field of photonics, where materials that actively interact with light are tuned and optimized to achieve effects such as;

- light emission (LEDs and lasers, just to name the most common ones)
- light detection, with related signal amplification (e.g., in photomultipliers) and processing operations.
- Alternatively, they can be used to develop light-sensitive circuits and switches (such as

with photoresistors)

**Electroactive materials are substances** that can undergo reversible changes in their electrical properties when subjected to an external electrical stimulus, such as an electric field or voltage. These materials find applications in various technologies, including sensors, actuators, batteries, and capacitor.

### 3.10 Materials for display technology

#### 3.10.1 Liquid crystals

##### Introduction:

Liquid crystals are state of matter which has properties between those of conventional liquids and those of solid crystals. There are many different types of liquid –crystal phases, which can be distinguished by their different optical properties (such as textures).

Liquid crystal (LC) phases represent a unique state of matter characterized by both mobility and order on a molecular and at the supramolecular levels. This behaviour appears under given conditions, when phases with a characteristic order intermediate to that of a three dimensionally ordered solid and a completely disordered liquid are formed. Molecules in the crystalline state possess orientational and three dimensional positional orders. That is the constituent molecules of highly structured solids occupy specific sites in a three dimensional lattice and points their axes in fixed directions as illustrated in Fig.



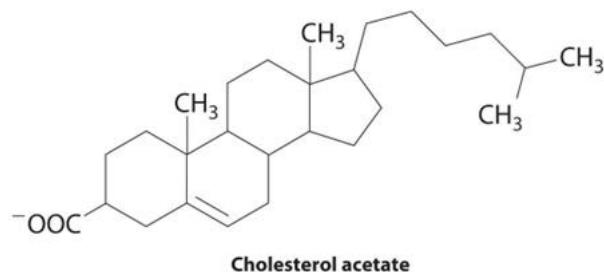
**Fig 4.8:** Schematic representation of molecular packing in the a) Crystals, b) & c) liquid crystals and d) liquid state

**Liquid crystals are another class of matter in which the extent of molecular ordering is in between highly ordered solid and completely disordered liquid state.**

**Hence liquid crystals show anisotropy.**

Liquid crystal refers to the intermediate status of a substance between solid (crystal) and liquid. When crystals with a high level of order in molecular sequence are melted, they generally turn liquid, which has fluidity but no such order at all. However, thin bar-shaped organic molecules,

when they are melted, keep their order in a molecular direction although they lose it in molecular positions. In the state in which molecules are in a uniform direction, they also have refractive indices, dielectric constants and other physical characteristics similar to those of crystals, depending on their direction, even though they are liquid. This is why they are called liquid crystal.



**Fig 4.9:** An example of liquid crystal molecule

### Basic requirements of a liquid crystal

$\text{C}_6\text{H}_{13}-\text{C}_6=\text{N}-\text{C}_6-\text{C}_6-\text{C}_6-\text{C}_5\text{H}_{11}$ $\text{C}_8\text{H}_{17}-\text{C}_6=\text{N}-\text{C}_6-\text{C}_6-\text{C}_6-\text{C}_7\text{H}_{15}$ $\text{C}_6\text{H}_{13}-\text{O}-\text{C}(=\text{O})-\text{CH}_2-\text{C}_6-\text{C}_6-\text{C}_6-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_{13}$	<ul style="list-style-type: none"> <li>• Each molecule be elongated in shape and has rigid central part in it.</li> <li>• Each molecule has flexible end</li> </ul>
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### 3.10.2 Types of Liquid crystals:

Liquid crystals can be divided into

- 1) Thermotropic, 2) Lyotropic and 3) Metallotropic.

**Thermotropic and lyotropic liquid crystals** consist mostly of organic molecules, although a few minerals are also known. Thermotropic LCs exhibit a phase transition into the LC phase as

temperature changes.

**Lyotropic liquid crystals** exhibit phase transitions as a function of both temperature and concentration of molecules in a solvent (typically water).

**Metallotropic liquid crystals** are composed of both organic and inorganic molecules; their LC transition additionally depends on the inorganic-organic composition ratio.

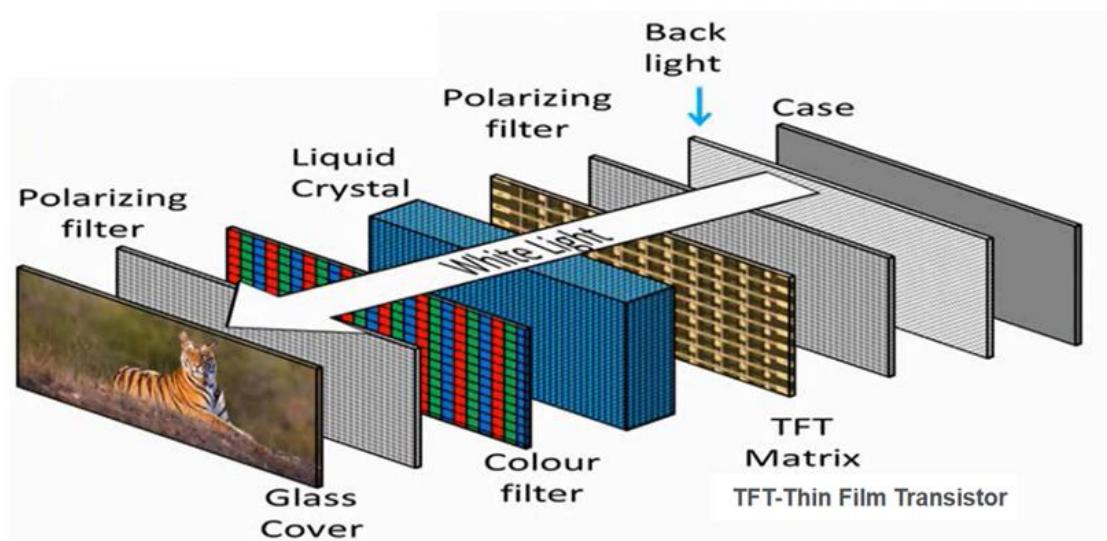
### 3.10.3 Application of Liquid crystals in display: Liquid Crystal Display (LCD)

Liquid crystals find wide use in liquid crystal displays, which rely on the optical properties of certain liquid crystalline substances in the presence or absence of an electric field. This field has grown into a multi-billion dollar industry, and many significant scientific and engineering discoveries have been made.

#### Principle of liquid crystal display

A liquid crystal display (LCD) has liquid crystal material sandwiched between two sheets of glass. Without any voltage applied between transparent electrodes, liquid crystal molecules are aligned in parallel with the glass surface. When voltage is applied, they change their direction and they turn vertical to the glass surface. They vary in optical characteristics, depending on their orientation. Therefore, the quantity of light transmission can be controlled by combining the motion of liquid crystal molecules and the direction of polarization of two polarizing plates attached to the both outer sides of the glass sheets. LCDs utilize these characteristics to display images.

#### Working principle of an LCD



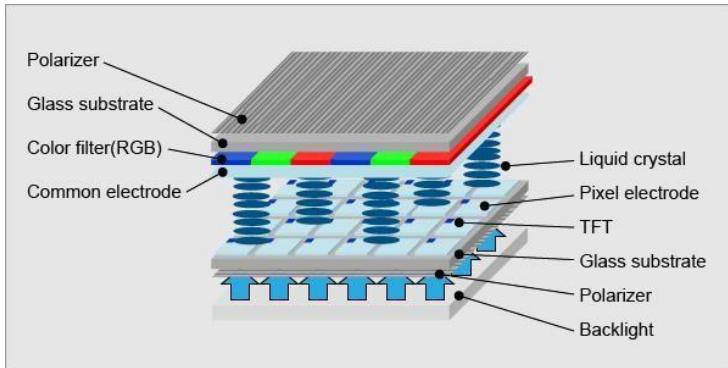
**Fig.4.10:** Schematic representation of LCD

The working principle of an LCD is based on the optical properties of liquid crystals.

- a) LCD consists of a layer of liquid crystal material sandwiched between two transparent electrodes.
- b) When an electric field is applied to the liquid crystal, it twists the orientation of the liquid crystal molecules, which changes the polarization of the light passing through the liquid crystal.
- c) Polarizing filter is placed in front of and behind the liquid crystal layer to control the orientation of the light passing through it.
- d) The LCD also has a backlight, which shines light through the liquid crystal layer to produce an image. The LCD can display images in color by using filters that absorb different colors of light.
- e) Each pixel of an LCD contains three sub-pixels that can **produce red, green, and blue colors**. By adjusting the voltage applied to each sub-pixel, the LCD can create millions of different colors.
- f) Overall, the working principle of an LCD is based on the manipulation of light using liquid crystals and polarizing filters to create images.
- g) The LCD can display images in color by using filters that absorb different colors of light.
- h) Each pixel of an LCD contains three sub-pixels that can **produce red, green, and blue colors**. By adjusting the voltage applied to each sub-pixel, the LCD can create millions of different colors.
- i) Overall, the working principle of an LCD is based on the manipulation of light using liquid crystals and polarizing filters to create images.

## TFT LCD

An LCD consists of many pixels. A pixel consists of three sub-pixels (Red/Green/Blue, RGB). In the case of Full-HD resolution, which is widely used for smartphones, there are more than six million ( $1,080 \times 1,920 \times 3 = 6,220,800$ ) sub-pixels. To activate these millions of sub-pixels a TFT is required in each sub-pixel. TFT is an abbreviation for "Thin Film Transistor". A TFT is a kind of semiconductor device. It serves as a control valve to provide an appropriate voltage onto liquid crystals for individual sub-pixels. A TFT LCD has a liquid crystal layer between a glass substrate formed with TFTs and transparent pixel electrodes and another glass substrate with a color filter (RGB) and transparent counter electrodes. In addition, polarizers are placed on the outer side of each glass substrate and a backlight source on the back side. A change in voltage applied to liquid crystals changes the transmittance of the panel including the two polarizing plates, and thus changes the quantity of light that passes from the backlight to the front surface of the display. This principle allows the TFT LCD to produce full-color images.



**Fig.4.11:** Structure of a TFT LCD

### 3.10.3 Light-emitting diodes (LEDs)

Light-emitting diodes (LEDs) are solid-state devices that use semiconductors and electroluminescence to create light. Essentially, LEDs convert electric energy directly into light, which differs from traditional incandescent lighting, which uses heat energy to generate light, which typically result in a significant waste of energy through heat loss. In comparison, LED technology is often referred to as “cold light technology”, due to the lower heat output from LEDs, and the fact they don’t waste energy in the form of non-light producing heat.

LED technology should not be confused with LCD (liquid crystal display) technology. LED screens are a completely different technology to LCD screens.

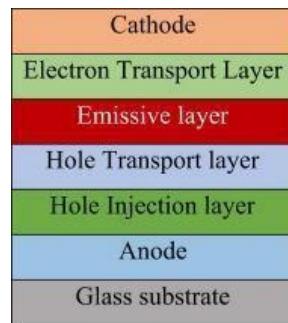
**Advantages of LEDs:**

1. Very low voltage and current are enough to drive the LED.  
Voltage range – 1 to 2 volts. Current – 5 to 20 milliamperes.
2. Total power output will be less than 150 milliwatts.
3. The response time is very less – only about 10 nanoseconds.
4. The device does not need any heating and warm up time.
5. Miniature in size and hence lightweight.
6. Have a rugged construction and hence can withstand shock and vibrations.
7. An LED has a lifespan of more than 20 years.

### **3.10.4 Organic light emitting diode (OLED)**

**Organic light emitting diode:** Organic Light Emitting Diode popularly known as OLED is a solid-state device that consists of thin films of organic molecules that generate a bright light on the application of electric current. They are made by a series of organic thin films placed between two conductors.

**Construction:** The multilayer stack consists of a hole injection layer (HIL), a HTL, an electron-blocking layer (EBL), an emission layer (EML), a hole-blocking layer (HBL) and an electron transport layer (ETL). The various blocking and transport layers ensure effective injection of electrons and holes, as well as their subsequent transport to the EML, where they recombine radiatively. The iridium complex is a phosphorescence emitter that allows for highly efficient emissions by harvesting the energy of both singlet and triplet excitons.



**Fig.4.12:** The general structure of a multilayer OLED

### Working of OLED

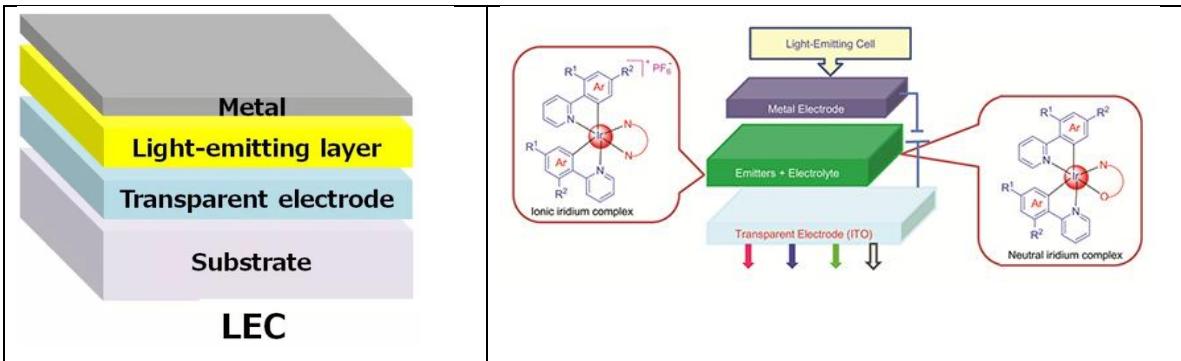
- (i) When a voltage is applied across the OLED, a current flow through the device and into the emissive layer.
- (ii) As the current passes through the emissive layer, the organic molecules become excited and move to a higher energy state.
- (iii) When they return to their original energy state, they release energy in the form of photons, which create the visible light that we see.

### OLED technology advantages:

- **Flexible:** It is possible to make OLED displays flexible by using the right materials and processes.
- **Very thin:** OLED displays can be made very thin, making them very attractive for televisions and computer monitor applications.
- **Colour capability:** It is possible to fabricate OLED displays that can generate all colours.
- **Power consumption:** The power consumed by an OLED display is generally less than that of an LCD when including the backlight required. This is only true for backgrounds that are dark, or partially dark.
- **Bright images:** OLED displays can provide a higher contrast ratio than that obtainable with an LCD.

### 3.10.5 Light-emitting electrochemical cell (LEC)

The light emitting electrochemical cell (LEC) is a newly invented illumination technology. The LEC was invented by Pei and co-workers in 1995. The LEC is a solid-state thin-film device, which comprises an active material sandwiched between a cathode and an anode (p-n junction doping structure) as its key constituent parts. Those large-area devices emit light when powered by a battery. LEC can be thin, flexible, and light-weight and be driven to essentially any emission color by the low voltage of a battery. It can also be extremely low cost, since it can be fabricated with low-cost printing and coating methods similar to how newspapers are fabricated.



**Fig.4.13:** Structure of Light-emitting electrochemical cell

An active-material film sandwiched between two charge-injecting electrodes, one of which must be transparent in order to let the light generated in the active material escape the device structure, as schematically shown in Figure. The active material contains a mixture of a semiconducting and luminescent conjugated compound and mobile ions, and when a sufficiently large voltage is applied between the two electrodes, an electrochemical doping process is initiated in the active material. Eventually, light-emission is generated within a thinlayer, the p-n junction zone, in the active material.

LECs contain ionic compounds in the light-emitting layer, have attracted considerable interest for their solid-state lighting and next generation display applications. Compared with conventional organic light-emitting diodes (OLEDs), LECs contain simple device architecture (generally only one light-emitting layer), and can use air-stable metals (e.g. Al, Ag and Au) as the cathodes directly. In particular, LECs based on ionic transition metal complexes (iTMCs) have received more attention because of their several advantages over conventional polymer-based LECs.

Solid-state light-emitting electrochemical cells (LECs) show the advantages of a simple fabrication process, low-voltage operation, and compatibility with inert electrodes. Employment of air-stable materials for both electrodes and the use of a thick and uneven active material and hence cost-effective all-ambient solution-based fabrication of LEC devices.

### The operation of a light-emitting electrochemical cell

The LEC differs from the OLED by the presence and action of mobile ions. These ions are

intermixed with a luminescent organic semiconductor in the active material, which is sandwiched between an anode and a cathode. The organic semiconductor is characterized by a highest occupied molecular orbital (HOMO), a lowest unoccupied molecular orbital (LUMO), and an energy gap between the LUMO and HOMO. The energy gap defines the emission colour of the luminescent organic semiconductor.

When a voltage is applied between the cathode and anode, the mobile ions (being positive cations and/or negative anions) redistribute within the active material toward the electrode/active material interfaces. The cations and anions form electric double-layers (EDLs) at the cathodic and the anodic interfaces, respectively. These EDLs will screen the bulk of the active material from (most of) the external voltage and confine a large electric field within the EDLs. If the applied voltage is equal to, or larger than, the energy gap of the organic semiconductor, the high electric fields in the EDLs will facilitate balanced electron and hole injection into the LUMO and HOMO levels, respectively, of the organic semiconductor.

The initially injected electrons and holes are electrostatically compensated by a further redistribution of the mobile ions in order to preserve electroneutrality in the bulk of the active material. At the cathode, the electrons injected on the organic semiconductor will be compensated by cations and at the anode; the injected holes will be compensated by anions. This process is termed electrochemical doping, specifically n-type doping at the cathode and p-type doping at the anode, and the organic semiconductor increases its conductivity significantly during the doping process. With time, the highly conducting p- and n-type doping regions grow in size and eventually make contact under the formation of a p-n junction. Subsequently injected electrons and holes can recombine at the p-n junction under the formation of electron-hole pairs (excitons), which can either decay radiatively (as light) or nonradiatively (as heat).



## Department of Chemistry

<b>Semester: I</b>						
<b>CHEMISTRY OF SMART MATERIALS AND DEVICES</b>						
<b>(Category: Professional Core Course) Stream: CS (Theory and Practice)</b>						
<b>Course Code</b>	:	CHY211AI		<b>CIE</b>	:	100 Marks
<b>Credits: L:T:P</b>	:	3:0:1		<b>SEE</b>	:	100 Marks
<b>Total Hours</b>	:	42L+ 30P		<b>SEE Duration</b>	:	3 Hours

### **Unit 4. Smart materials for sensors**

*“The students should be able to understand the importance of chemistry and nanomaterials for designing the smart devices and sensors for engineering and biomedical applications. For the design of smart devices (RFID) and sensors (electrochemical/piezo), the significance of electromagnetic property of materials, redox chemistry, and understanding the electrocatalytic nature of materials is discussed. Students can also realize the Radio Frequency (RF) IDs made of graphene, CNT based wireless applications. The importance of synthesizing and functionalizing the novel nanomaterials such as carbon nanotubes, graphene and polyaniline can be understood for developing smart devices”.*

### **Lecture plan: Smart sensors and devices**

**Lecture-1:** Introduction to smart materials and technology, Internet of things, Internet of nanothings.

**Lecture-2:** RFID device, meaning, working principle of RFID, classification of RFID tags, (Based on the availability and frequency), Materials for RFID tag (CNT, Graphene, polyaniline)

**Lecture-3:** Carbon nanotubes (CNTs)-meaning, types, structures; Synthesis by CVD method, functionalization-physical, chemical; properties

**Lecture-4:** Graphene-meaning, structure of graphene; Synthesis by Modified hummer's method, functionalization-physical, chemical; properties

**Lecture-5:** Polyaniline-Synthesis via chemical oxidative polymerization of aniline, different structures of Polyaniline, electronic properties, Applications of CNT, Graphene in logistic information, intelligent packaging systems

**Lecture-6:** Sensors: Introduction, types of sensors (Piezoelectric and electrochemical)

**Lecture-7:** Strain sensors- working principle, nanomaterials used, applications

**Lecture-8:** Electrochemical Sensors- working principle, types of electrodes, significance of each electrode, sensing mechanism.

**Lecture-9:** Applications of Electrochemical sensor for biomolecules-Glucose-Diabetic management, Vitamin-C (Ascorbic acid) Electrochemical-VOCs, and Gas sensor

## **Internet of Things (IoT) and Radio Frequency Identification Technology (RFID)**

**Internet of Things (IoT) technology:** It is a new technology being developed in 1999. The purpose of this technology is that to connect, communicate, control and operate the activities of all the things through internet. This technology is an integration of hardware (sensors, telecommunication) devices and software programs. This technology is an integration of internet and sensor network, via (Radio Frequency Identification) RFIDs devices. If this technology involve the smart devices made-up of nanomaterials, it is called Internet of nanothings (IONTs). It interconnects the nanoscale devices with the Internet and the present communication technology.

**RFID:** It is a wireless, an electronic device/tag, which uses electromagnetic field to identify, track and connect with the objects attached with tags. The required data/information of the object is collected and recorded by means of radio frequency signal. It is expected that this tag should be able to function autonomously without the involvement of human in any harsh environmental conditions.

### **Working principle of RFID system:**

- The RFID consists of READER, ANTENNA, TAG, TRANSPONDER, COMPUTER
- The RFID reader emits radio waves with a specific frequency using its ANTENNA.
- RFID tags within the reader's range receive these radio waves and are activated.
- In case of passive system, when 'RFID TAG' enters the 'READER' area, the ANTENNA will transmit induced current, which activates the 'RFID TAG' to transmit the information to the 'READER'. In case of active system, when the RFID TAG enters the READER area, the embedded battery powers the RFID TAG in order to complete the communications with each other.
- The activated RFID tags send information stored in their memory, such as a unique identifier or other data, back to the reader via radio waves.

- The RFID reader processes the received data and may transmit it to a computer system or database for further processing and analysis.

The schematic representation of RFID working principle is shown below:

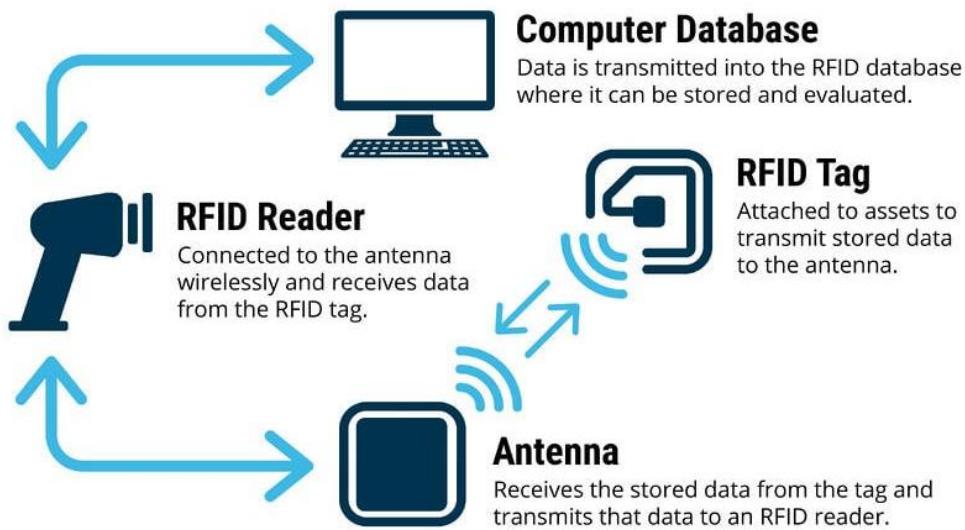


Figure 4.1. RFID working components

## Classification of RFID tags

Based on the power requirements, the RFID is classified as follows:

- Passive RFID Tag:** It is a RFID tag with no inbuilt power source (Battery) designed to use in small range (up to 10 m) tracking systems, operates on low, high or ultra-high frequency. However, it receives power from the reading antenna, whose electromagnetic wave induces a current in the RFID tag's antenna. It is very thin and has a long service life.
- Active RFID Tag:** It has its own power source, such as battery, inbuilt. It is used for long scanning and reading range (up to 100 m), operates only at high frequency. The price is relatively high, volume is larger than the Passive tag because of the built-in battery.

	Passive RFID Tag	Active RFID Tag
1. Power Source	They do not have an internal power source	They have an internal power source, typically a battery
2. Range (Read Distance)	They have a shorter read range, typically up to a few meters	They have a longer read range, often extending to tens or even hundreds of meters.

<b>3. Cost</b>	generally less expensive	more expensive due to the inclusion of a battery and additional electronics.
<b>4. Size</b>	smaller and more compact	larger and bulkier due to the battery
<b>5. Data Storage and Complexity</b>	have limited data storage capacity and are primarily used for storing a unique identifier (EPC - Electronic Product Code)	more extensive data storage capabilities and can store additional information beyond just an identifier.
<b>6. Lifespan</b>	have a longer lifespan	have a limited lifespan based on the battery's capacity,
<b>7. Real-Time Tracking</b>	generally not well-suited for real-time tracking because they only transmit data when activated by an RFID reader's signal.	can provide real-time tracking capabilities due to their continuous transmission of data

Further, the RFID is classified based on the working frequency range.

Types	Low-Frequency	High-Frequency	Ultra High-Frequency
Frequency Range	100~500 KHz	10~15 MHz	850~950 MHz~2.45 GHz
inductive distance	shorter	longer	longest
reading speed	slower	relatively high	fastest
penetration ability	good	Average	bad

### Materials for RFID tag:

The RFID tags are fabricated by low cost inkjet-printed technique. Various types of conductive inks with different fillers such as metal nanoparticles, carbon nanotubes (CNT), graphene and polymer (polyaniline) have been developed for printed electronics. For the fabrication of RFID Tags, carbon nanotubes, graphene and polyanilines are generally used, as they can be used as inks for ink jet printing of RFID tags.

(For more understanding read: <https://doi.org/10.1039/C7RA07191D>)

## **Applications of RFID Technology:**

- **Retail:** RFID helps retailers improve inventory accuracy, reduce out-of-stock items, and enhance the overall shopping experience.
- **Healthcare:** RFID is used for patient tracking, medication management, and tracking medical equipment to improve patient care and safety.
- **Manufacturing:** RFID is employed to monitor the production process, track work-in-progress, and manage inventory in manufacturing plants.
- **Transportation and Logistics:** RFID is crucial for tracking packages, containers, and vehicles in transportation and logistics operations, leading to improved efficiency and security.
- **Smart Cards:** RFID technology is used in contactless smart cards for payment systems, public transportation, and identification.
- **Waste Management:** RFID tags on waste bins enable efficient collection and management of waste, optimizing routes for garbage trucks.
- **Livestock and Agriculture:** RFID tags are used to identify and track livestock and monitor crops for better agricultural management.

## **Carbon Nanomaterials:**

**Carbon nanotubes** are a new form of a hexagonal network of carbon atoms rolled up in the form of cylindrical shape.

### **Types of CNTs:**

1. **Single-Wall Nanotube (SWNT) (Arm Chair, Zig-Zag and Chiral)**
2. **Multi-Walled Nanotubes (MWNT)**
  - Multiple rolled layers of graphene sheets

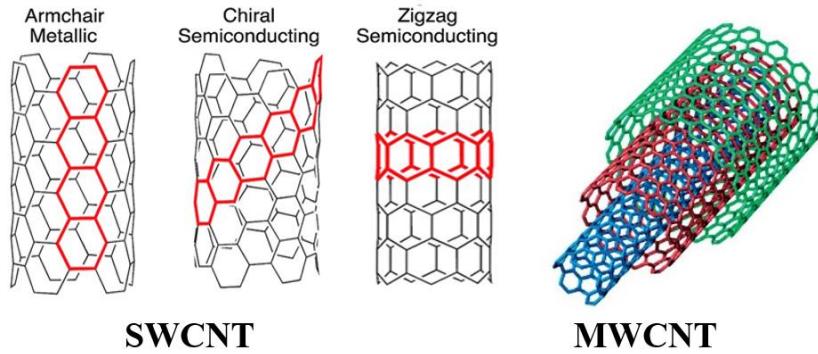


Figure 4.2. Types of carbon nanotubes

### **Synthesis of CNTs by modified CVD method:**

Chemical Vapor Deposition: Requirements:

- High Temperature Tubular furnace (500 to 1500 °C)
- Source of Carbon: Methane, ethylene, hydrocarbon gas, xylene, natural gas
- Substrate: carbon, quartz, silicon

- Inert gas: Argon, Hydrogen, Nitrogen
- Catalyst: Ferrocene, Nickelloocene, Cobaltocene

**Principle:** In this technique, carbon nano tubes grow from the decomposition of hydrocarbons at temperature range of 500 to 1200 °C in the inert atmosphere on the catalyst activated substrate.

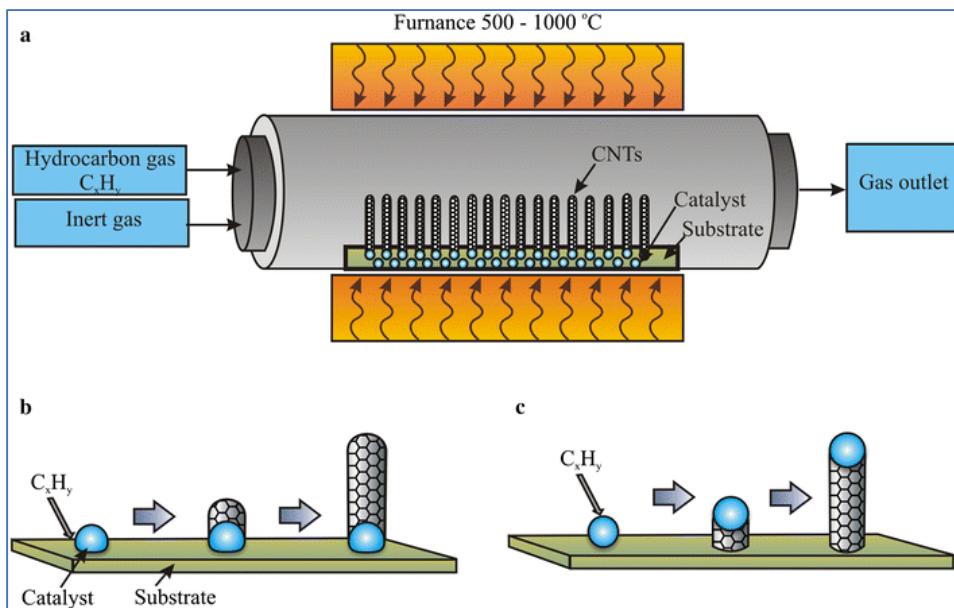


Figure 4.3. CVD experimental set up used for synthesizing carbon nanotubes

Ref: Zaytseva et al. Chem. Biol. Technol. Agric. 3, 17 (2016).

<https://doi.org/10.1186/s40538-016-0070-8>

**Furnace:** The instrumental setup consists of a tubular furnace equipped with an inert atmosphere setup, temperature and reactant precursors flow controller.

**Steps:** Procedure involves as follows

- ❖ The cleaned quartz/carbon/silica substrate is placed in the middle of the tubular furnace.
- ❖ In order to maintain the inert atmosphere inside the furnace, initially the air/oxygen present inside the tubular furnace has to be removed by passing the argon or nitrogen gas for about 30 min.
- ❖ After maintaining the inert gas atmosphere, the required temperature is set with slow heating rate.
- ❖ The hydrocarbon precursors in gaseous forms along with ferrocene and Benzene/toluene vapors are pumped into the reaction chamber.
- ❖ The furnace is heated up to 850–1000 °C and 550–700 °C for SWCNT and MWCNT production respectively.
- ❖ Initially, at high temperature, due to the thermal decomposition of hydrocarbon, carbon atoms are formed and dissolved in the metal nanoparticle catalyst.

- ❖ Once the threshold concentration of carbon in the catalyst reached, a semi fullerene cap type of structure is formed due to precipitation of carbon atoms. This acts as a seed for further crystal growth, which further continues to grow in tubular form results in to CNT.
- ❖ After the formation of CNT on catalyst is completed as shown in the above figure, the supply of the reactant/catalyst vapors are stopped.
- ❖ Then the furnace temperature is reduced slowly to room temperature and supply of the inert gas also stopped.
- ❖ The CNT formed on catalyst is taken out along with the substrate, subjected to purification.

### **Mechanism of CNTs growth:**

1. **Diffusion** of Hydrocarbon gas
2. **Adsorption** of Hydrocarbon gas on the surface active site of catalyst particles.
3. **Dissociation** (Homolytic fission) of Hydrocarbon in to highly reactive free radicals of 'C' and 'H'.
4. Repetition of steps 1, 2 and 3 leading to increase in concentration (saturation) of free radicals.
5. **Precipitation** (aggregation) of carbon free radicals results into crystal growth in the form tube on the surface. 'H' free radicals escape as  $H_2$  gas.

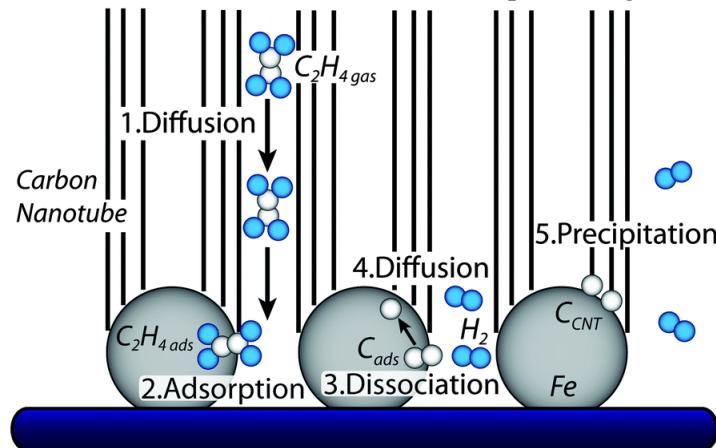


Figure 4.4. Steps involved in CNTs growth.

### **Functionalization of CNT:**

CNTs are non-polar in nature and hence may not have chemical affinity/solubility in water or organic compounds. Therefore, the application of pure CNTs is limited. The modification/ functionalization of CNTs with functional groups like -OH, -COOH, -NH<sub>2</sub>, -NHCONH<sub>2</sub> etc , makes it the most attractive and ultimate candidate for many biomedical and engineering applications. The modification/ functionalization of CNTs can be simply divided into

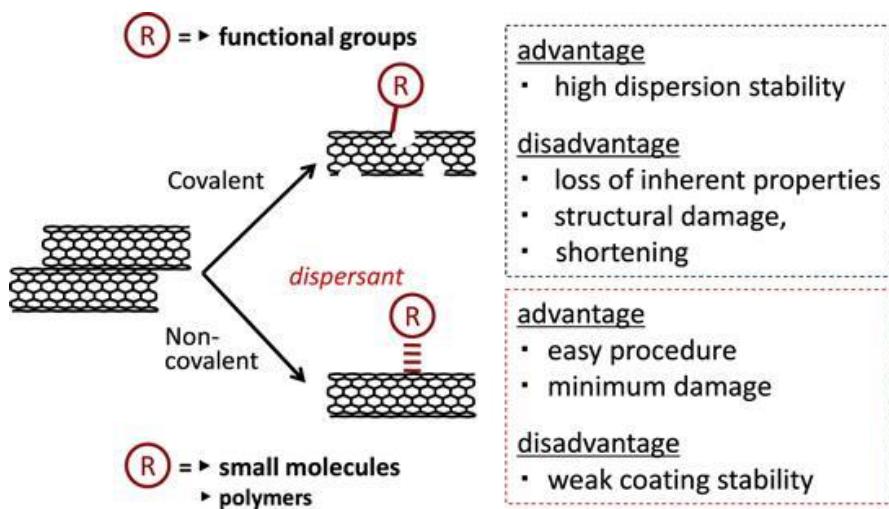
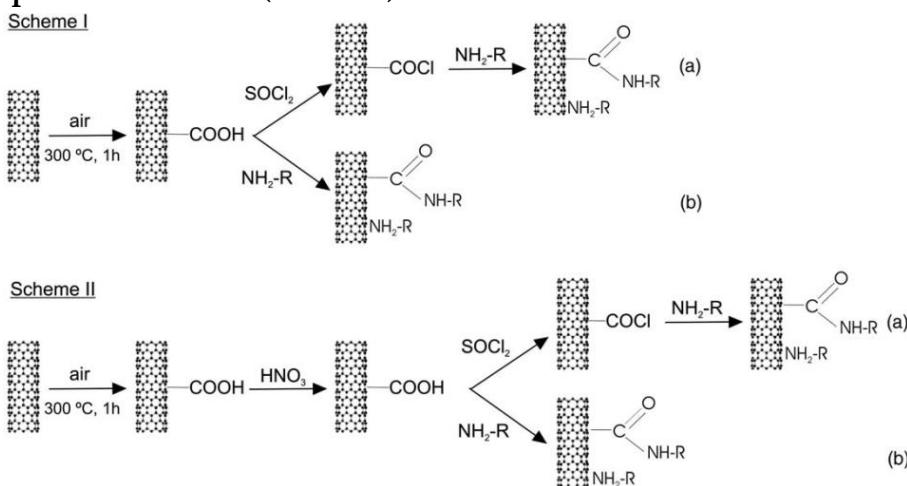


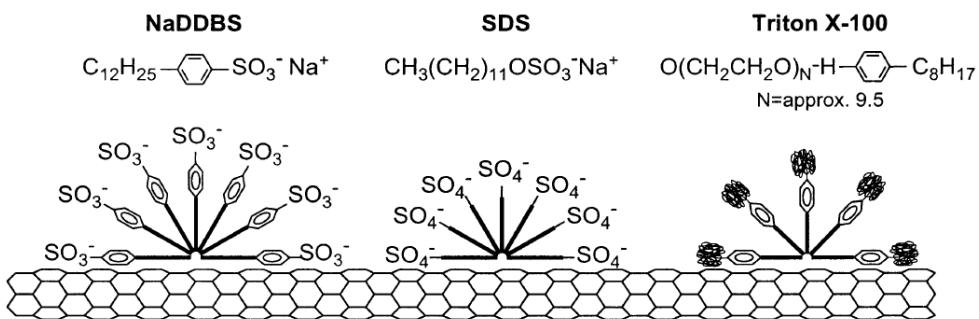
Figure 4.5. Types of CNTs functionalization.

- Chemical (covalent) functionalization:** It involves the formation of true chemical bond between CNT and functional groups. The functional groups can be attached to the edge or side wall carbon atoms, which results into different properties. Direct covalent sidewall functionalization is associated with a change of hybridization from  $sp^2$  to  $sp^3$  and a simultaneous loss of  $p$ -conjugation system.
- Physical (Non-covalent) functionalization:** It involves the physical binding of molecules, metallic atoms, polymers with CNT by vander wall's forces. Like in case of covalent functionalization, it does not destroy the conjugated system of the CNTs sidewalls. Therefore the most of the structural properties of the CNT is still retained. The CNTs are functionalized non-covalently by **aromatic compounds, surfactants, and polymers**, employing  $\pi$ - $\pi$  stacking or hydrophobic interactions.

#### Examples for Chemical (covalent) functionalization:



## Physical (Non-covalent) functionalization:



## Applications of CNTs:

- RFIDs, Sensors, IoNTs sensors
- Optoelectronic devices (Field Emission Display ( FED))
- As *electrodes in batteries, capacitors and super capacitor electrodes.*
- As *electrode catalyst supports in Polymer Electrolyte Membrane (PEM) fuel cells*
- *Hydrogen Storage material in hydrogen fuel car.*
- As *electrically powered artificial muscles.*
- Electro catalyst for water splitting, H<sub>2</sub> production.
- Adsorbent and photocatalyst for organic pollutants degradation.
- Sensor for heavy metal ion, gases, volatile organic compounds and biomolecules.
- Drug carriers

**Graphene:** Graphene is a newly found allotrope of carbon, consisting of single layer atoms in hexagon pattern. It is a purely carbon-based, honeycomb-structured, one-atom thick layer of carbon atoms (two dimensional sheet), bonded to one another by sp<sup>2</sup> hybridization.

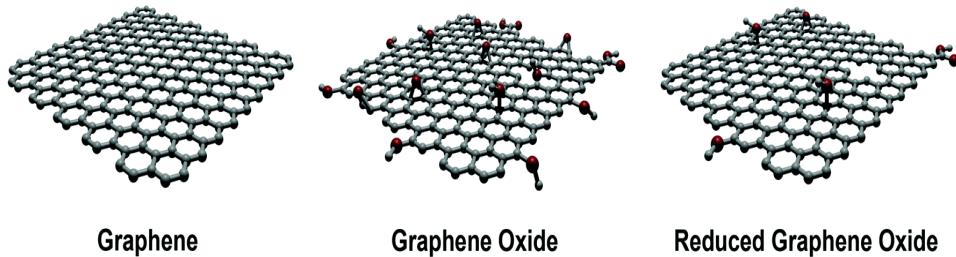


Figure 4.6. Structures of Graphene, Graphene Oxide and Reduced Graphene Oxide.

## Synthesis of Graphene Oxide and Reduced Graphene Oxide-Modified Hummer's Method:

In a typical procedure, graphite (2 g) and NaNO<sub>3</sub> (2 g) were combined with H<sub>2</sub>SO<sub>4</sub> (90 ml) in a 500 ml glass beaker and stirred for 30 min in an ice bath. Then KMnO<sub>4</sub> (10 g) is slowly added to the above solution under ultra sonication at 50°C for 2 h. About 200 ml of distilled water and 12 ml of H<sub>2</sub>O<sub>2</sub> (35%) are then slowly added to the above solution, and the resulting solution is washed with dil HCl (10%) followed by concentrated HCl (37%). The washed product is dried in hot air oven at 80 °C for 24h. The final product obtained is called graphene oxide (GO) powder. The GO powder is further subjected to reduction by reacting with sodium borohydride. In addition to this, thermal, or photo-thermal reduction methods are also used to obtain reduced graphene oxide (rGO) structure.

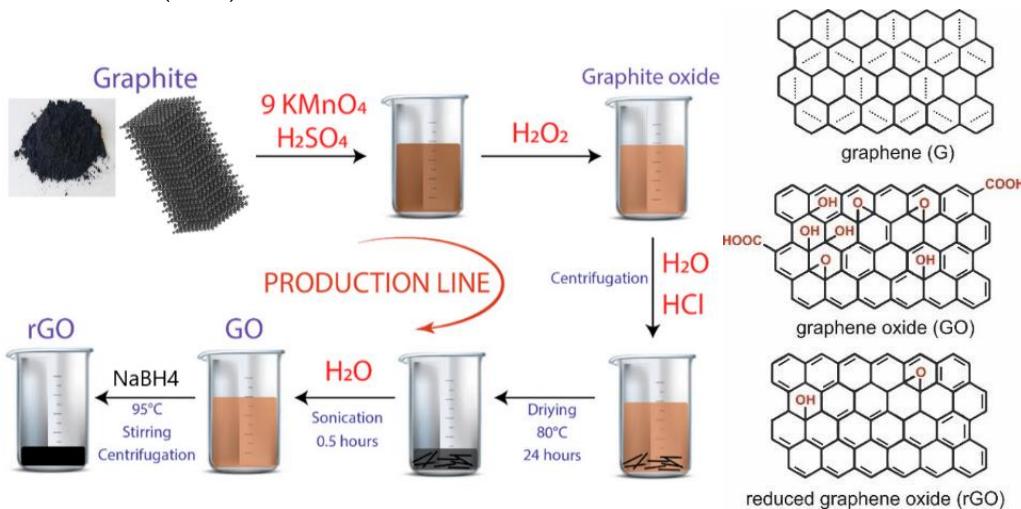
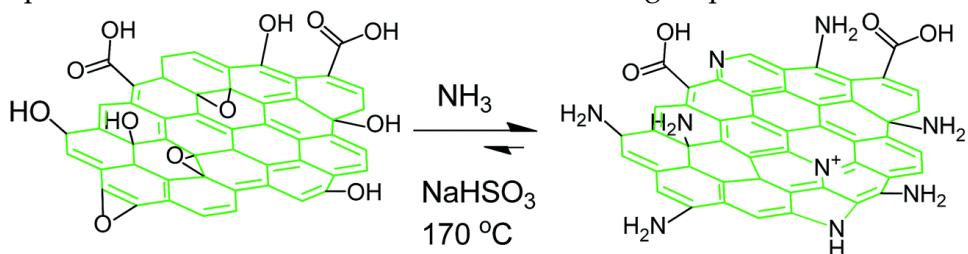


Figure 4.7. Modified hummers method steps for making graphene oxide

## Functionalization of Graphene

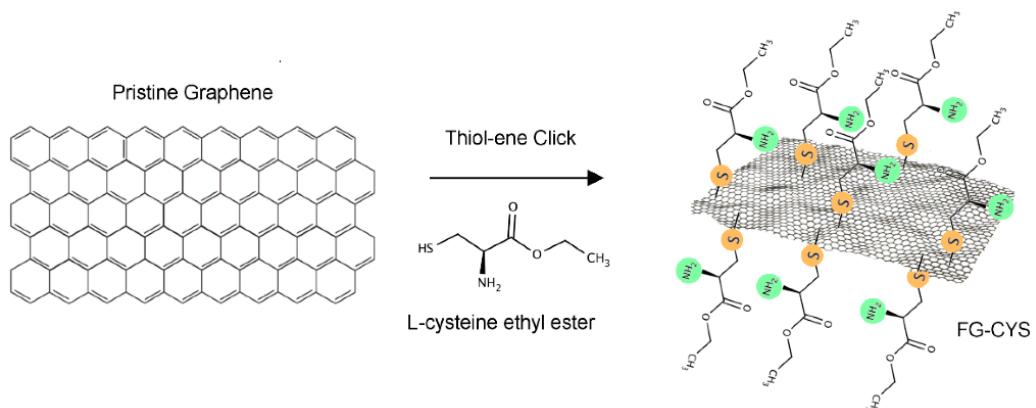
The functionalization is similar to CNT. It has two types (1) Covalent (chemical) and (2) Non-covalent (Physical) functionalization. The functionalization reduces the cohesive force between the graphene sheets and also to manipulate the physical and chemical properties.

The graphene oxide can be functionalized with amine group as follows.



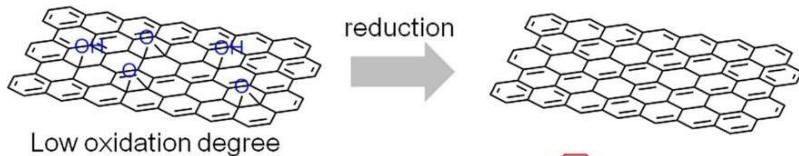
Ref: <https://doi.org/10.1039/C5CC08252H>

The graphene oxide can be functionalized with cysteine and thiolene group as follows.

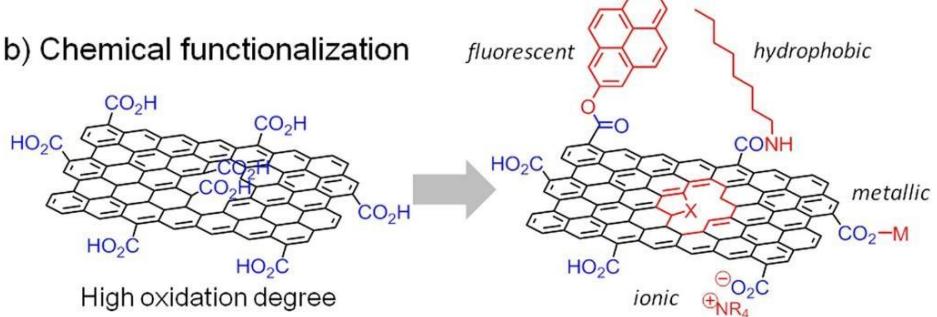


Ref: <https://doi.org/10.3390/ma14112830>

#### a) Recovery of graphene structure



#### b) Chemical functionalization



Ref: <https://doi.org/10.1038/srep21715>

## Graphene Applications

RFID, IoNTs, Solar Cells, Batteries, Fuel cells, Medicine (Drug Delivery, Cancer Treatment, Gene Delivery, Photothermal Therapy, Diabetes Monitoring, Dialysis, Bone and Teeth Implantation, Tissue Engineering and Cell Therapy), UV Sensors, Biosensors, Transistors, Wearable Electronics, Flexible Screens, Optoelectronics, Optical Sensors, Water Purification, Desalination, Lubricants.

## Polyaniline

- ❖ Polyaniline (PANI) that has been extensively used as conducting polymer.
- ❖ Band gaps in the reduced and oxidized form of polyaniline are 4.3 and 2.7 eV respectively.
- ❖ Intrinsically conductive polymer used in various applications, including drug delivery, photovoltaic cells, plastic batteries, display devices, microelectronics, chemically modified electrodes, corrosion protection, and polymer light-emitting diode (PLED) displays



## Preparation of Polyaniline

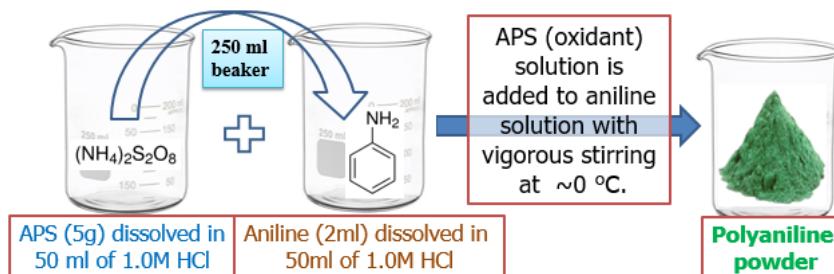
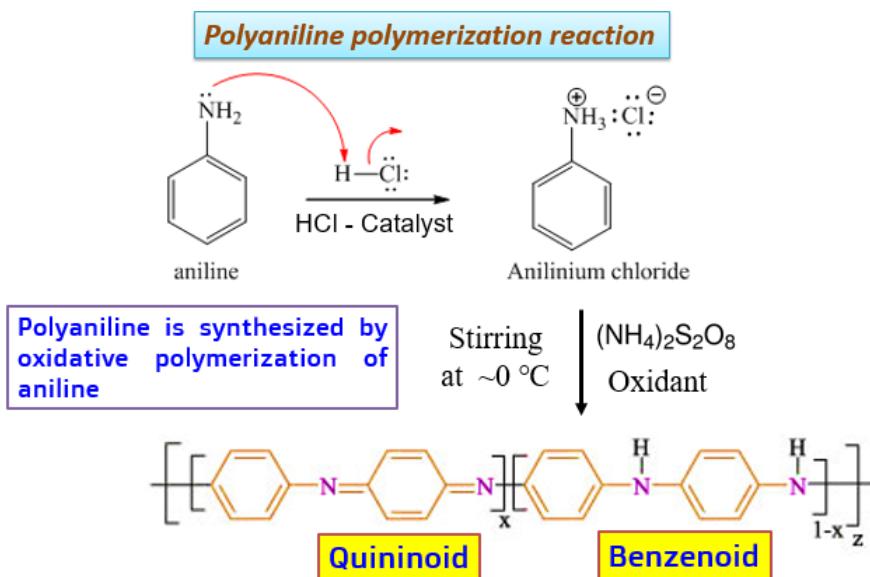


Figure 4.8. Reaction of polyaniline synthesis

- ❖ After the polymerization reaction, the resultant mixture is filtered and washed successively using 1.0M HCl followed by double distilled water, several times until the washings become colorless.
- ❖ Finally the residue was washed with acetone and dried at  $60\text{ }^{\circ}\text{C}$ .

The reaction mechanism of conversion of aniline to conducting polyaniline is as shown below.



## Different forms of POLYANILINE

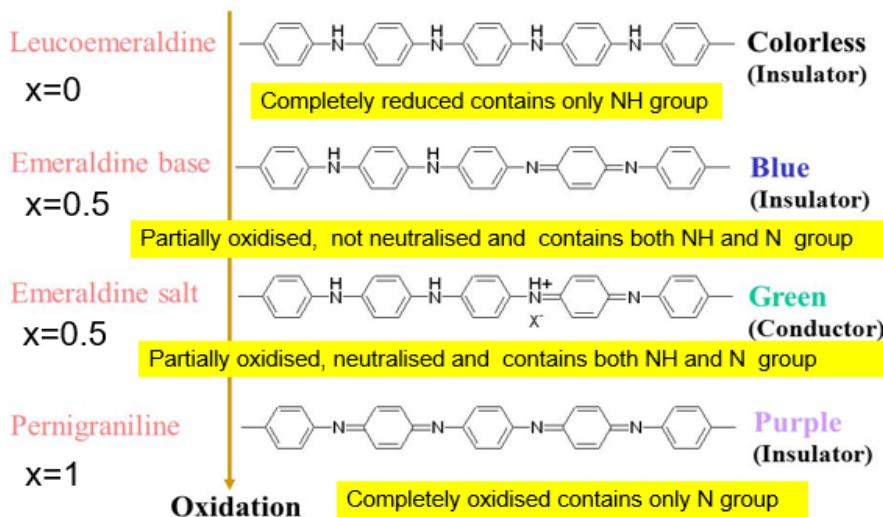


Figure 4.9. Structural differences of various forms of polyaniline –conducting and insulating forms

### Sensor

It is device that measures change in a physical (heat, light, sound, pressure etc) and/or chemical (pH, smell, taste, concentration, humidity etc) parameters of interest in an environment and transforms it into an electronic signal.

**Transducer:** A transducer is a device that transforms a signal from one energy form to another energy form.

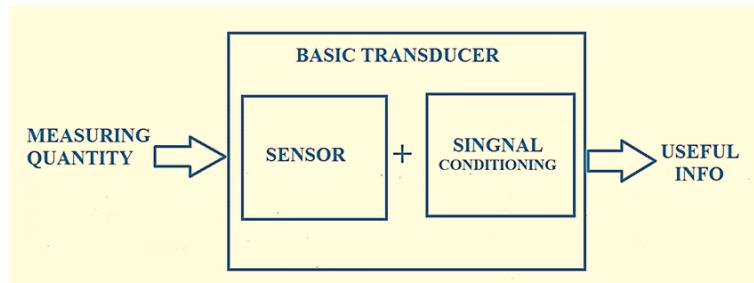
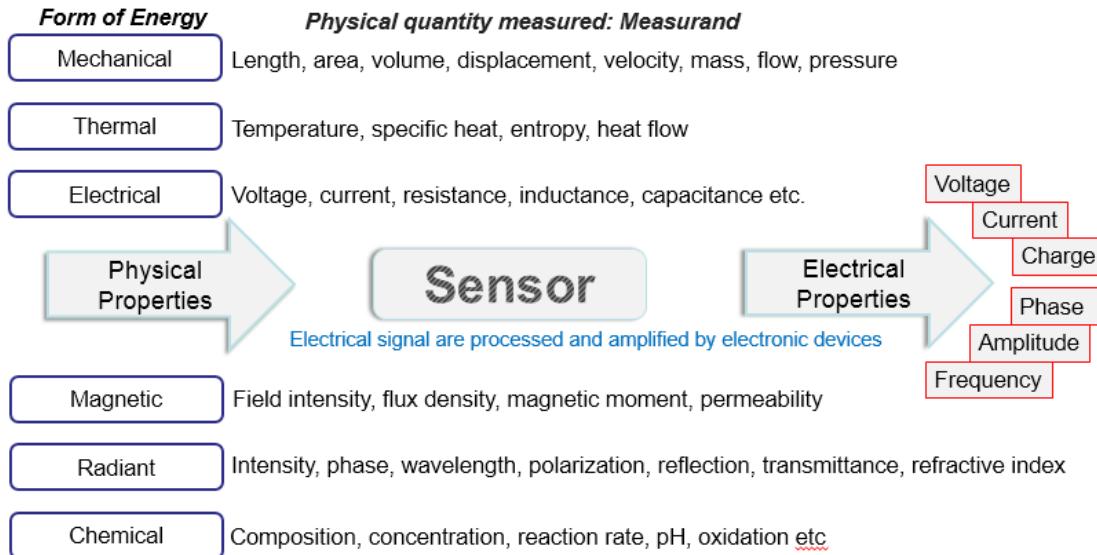


Figure 4.10. Schematic representation of sensor device



## Piezoelectric (PE) Sensors

“Piezo” is word derived from Greek, it means for “press” or “squeeze”. A piezoelectric sensor is a device, which converts physical parameters like acceleration, strain, pressure, vibration, temperature, or force into an electrical charge which can then be measured. The schematic representation of PE sensor is shown below.

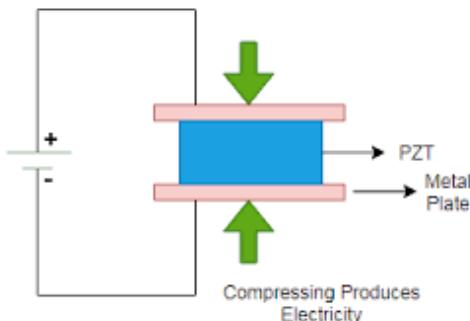


Figure 4.11. Schematic representation of Piezoelectric sensor

The PE sensor is widely used in biomedical, wearable electronics, and self-power energy harvesting devices. The piezoelectric sensors are mostly fabricated by using the perovskite ceramic material (lead zirconate titanate (PZT)) and also other lead-free ceramic piezoelectric sensors using bismuth sodium titanate (BST), barium titanate ( $\text{BaTiO}_3$ ), boride and silicide ceramics ( $\text{TiB}_2$ ,  $\text{TaSi}_2$ ,  $\text{WSi}_2$ , etc.).

### Characteristics of PE sensors:

The good PE sensor should exhibit:

High strength, High stability, High voltage output, Highly flexible, Wide frequency range, Impact resistance, High mechanical strength, Elastic compliance etc

**Strain Sensor:** Upon applying the external force on an object, the strain (permanent/temporary) is induced in the object due to its structural (internal) deformation, this results in change in internal resistance of the object, which can be measured by using the device called strain sensor. Various nanomaterials like graphene, CNT, PVDF, and their hybrids are used in these sensors.

Strain sensors widely used in flexible and wearable electronic devices for medical applications, civil engineering structures, mechanical engineering, aircrafts structures, etc

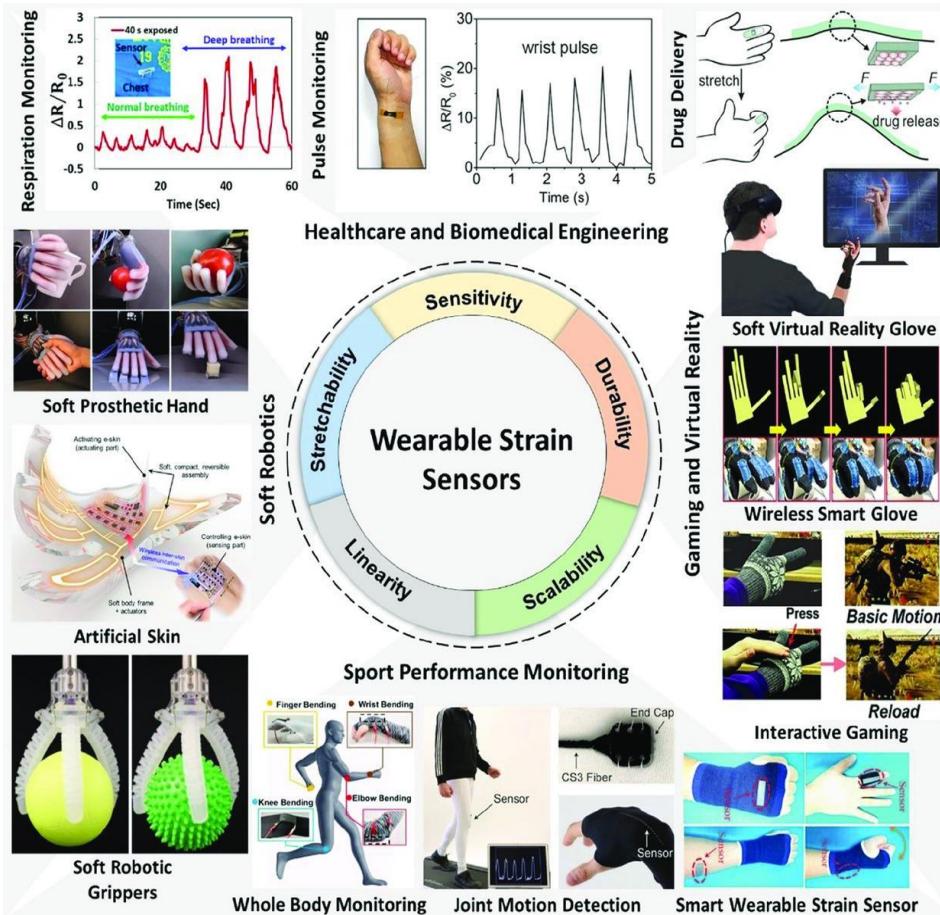


Figure 4.12. Wearable and stretchable strain sensors and their potential applications [for more understanding read: <https://doi.org/10.1002/aisy.202000039>]

**Strain sensors** are widely used in medical industry applications, are as follows:

- ❖ **Pulse measurement** – PE sensors are very sensitive to record pulse measurements and effective in monitoring the patients' health.
- ❖ **Stethoscopes** – Due to high sensitivity and robustness PE sensors, they are often used within stethoscopes.

- ❖ **Anaesthesia Effectiveness** - PE sensors are capable of accurately measuring the muscles stimulations, and hence can be helpful in understanding the effectiveness of anaesthesia.
- ❖ **Sleep Studies** - PE sensors can be attached to various parts of the patient body and can be used to measure the smallest movements of patients during the sleep also.

PE sensors are very popularly finds their application in wearable and stretchable electronics used in healthcare and biomedical engineering, sport performance monitoring, soft robotics, and gaming and virtual reality.

**Electrochemical (EC) Sensors:** a device that converts chemical composition data of the analyte into an analytically usable signal.

**Working principle:** The basic principle of EC sensor is that it measures the current produced by chemical reactions in the electrochemical system. The main components of the sensor are (a) electrodes system, (b) transducer (c) amplifier and (d) recorder. In electrochemical sensor, the electrode system consist of three electrodes such as working electrode, counter/auxiliary electrode and reference electrode. It has a potentiostat, which is an electronic instrument that controls the voltage between two electrodes. Working electrode (WE) is very sensitive to any change in analyte solution, provides the surface for the analyte to undergo reaction, when the potential is applied between WE and RE. The CE helps in completing the circuit by allowing the reaction, which is opposite to WE reaction, to happen. If an oxidation reaction happens at WE, reduction reaction will take place at CE, and vice versa. The RE is independent of the analyte and other ions concentration. Its potential is constant while measuring the potential of WE. By measuring the current of redox reaction, the analyte can be identified. The figure 4.13 represents the electrode system of the EC sensor. For the EC sensor system as shown in figure 4.13(a), the RE can be Standard Hydrogen Electrode (SHE), calomel electrode, silver-silver chloride, CE can be Gold, platinum and carbon electrodes, and WE can be Carbon, glassy carbon electrode (GCE).

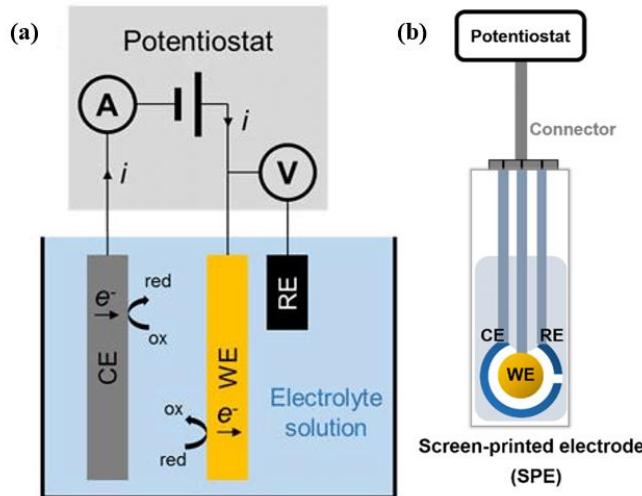


Figure 4.13. Three electrode systems used in electrochemical sensor (a) Combination of three distinct electrodes (b) Screen printed carbon electrode (all three combined)

The electrode shown in figure 4.13(b), is named as screen printed electrode, which is low cost, disposable, which are fabricated by printing the ink of carbon, silver, gold, and platinum on plastic (Flexible Polyester Film) or ceramic substrate. WE are generally printed by graphite or carbon (graphene, CNT) based ink, RE are printed by silver/silver chloride ink and CE is by carbon ink.

The EC sensor used to for various analytes such as hydrogen peroxide, glucose, urea, alcohol etc, which are adsorbed on receptors (nanomaterials, Graphene, CNTs metal oxides). They undergo redox reaction upon applying voltage, the resultant current (electrons released) is measured by transducer, which is characteristic property of a biomolecule under study. Then the current is quantified by using amplifier and recorder as shown below.

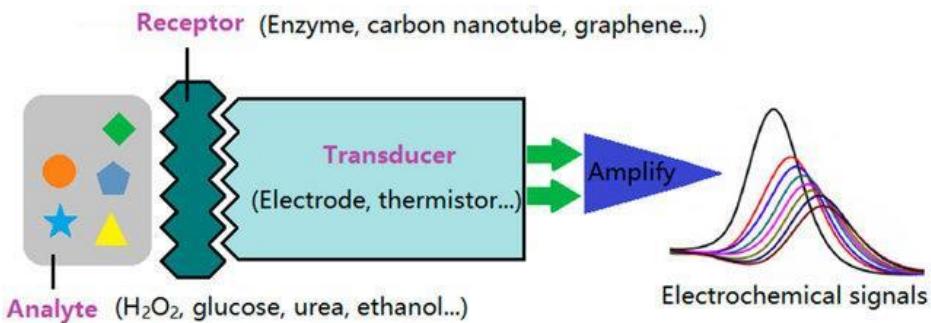
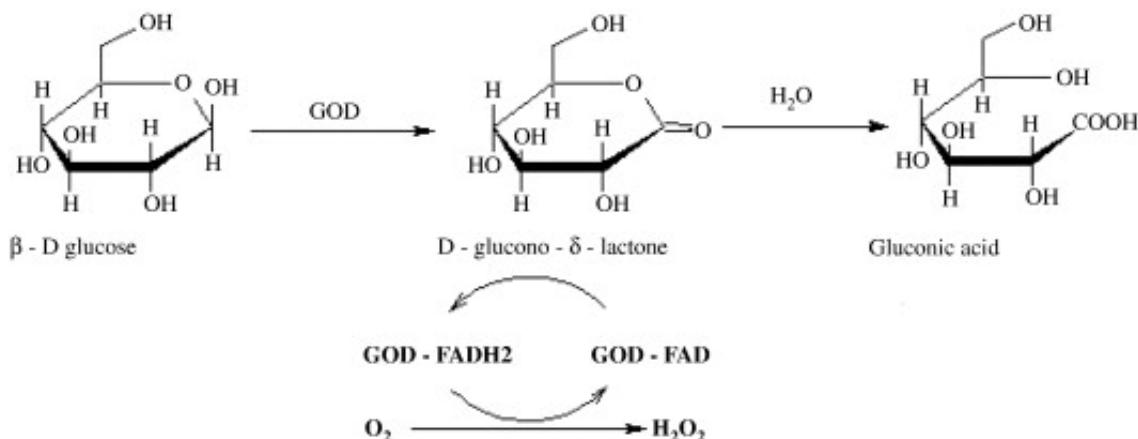
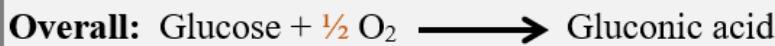
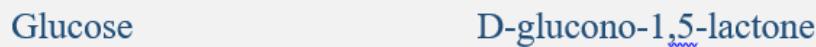


Figure 4.14. Electrochemical sensor components; Analyte, Receptor, Transducer and recorder

## Applications of Electrochemical sensor for biomolecules

### Glucose sensor in diabetes management

In EC sensor, glucose and oxygen react in the presence of nanomaterials or glucose oxidase (GOx) functionalized WE, and thus oxygen is consumed and hydrogen peroxide is produced (as shown in equation below). Further, the glucose concentration can be detected indirectly by electron transfer of oxygen at CE as shown in reaction.



### Ascorbic acid sensor

Ascorbic acid (AA) is also called as Vitamin C, an essential nutrient and antioxidant required for the human body. Unfortunately, the human body cannot produce/synthesize this biomolecule, and hence it should be consumed by food and drugs. The deficiency of AA lead to scurvy, mental disorder, cancer, etc. Similar to glucose, the AA can also be analyzed in EC sensor and the following schematic representation depicts the sensor mechanism of AA.

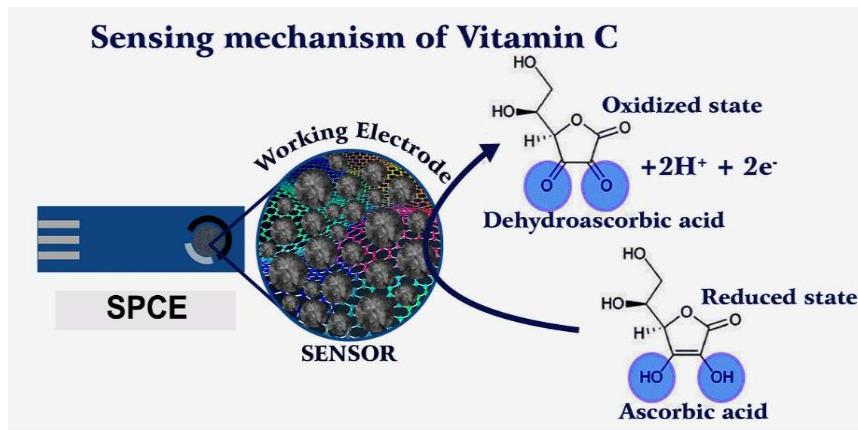


Figure 4.14. The SPCE is functionalized with nanomaterials and possible redox reaction of AA at WE.

### VOCs sensor

Volatile organic compounds are the organic molecules having very low solubility in water and exhibit a high vapor pressure. They are liberated in industries such as pharma, biotech, paints, vanishes.

Some examples of VOCs are Phosgene, benzene, ethylene glycol, formaldehyde, methylene chloride, tetrachloroethylene, toluene, xylene, acetone, alcohol, and 1,3-butadiene etc. These VOCs are very dangerous to health upon inhaling, which effects to the liver, kidneys, or central nervous system, even some VOCs are suspected or proven carcinogens.

Further, the healthy individual's exhaled breath has major VOCs such as isoprene (12-580 ppb), acetone (1.2-1,880 ppb), ethanol (13-1,000 ppb), methanol (160-2,000 ppb) and other alcohols. Today, human exhaled breath analysis using gas sensors and e-noses (as shown below), is helping the diagnosing a wide range of diseases.

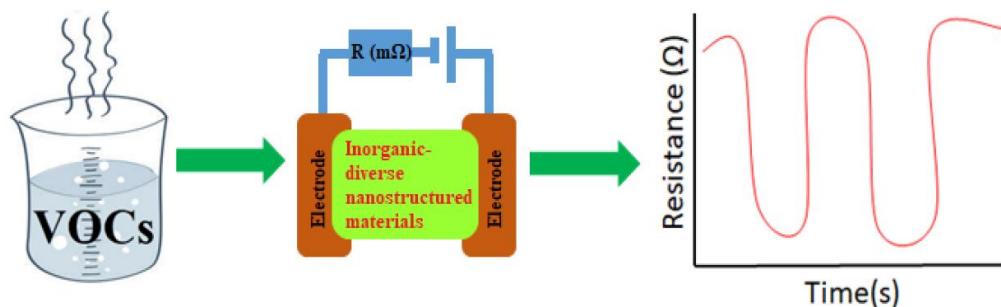
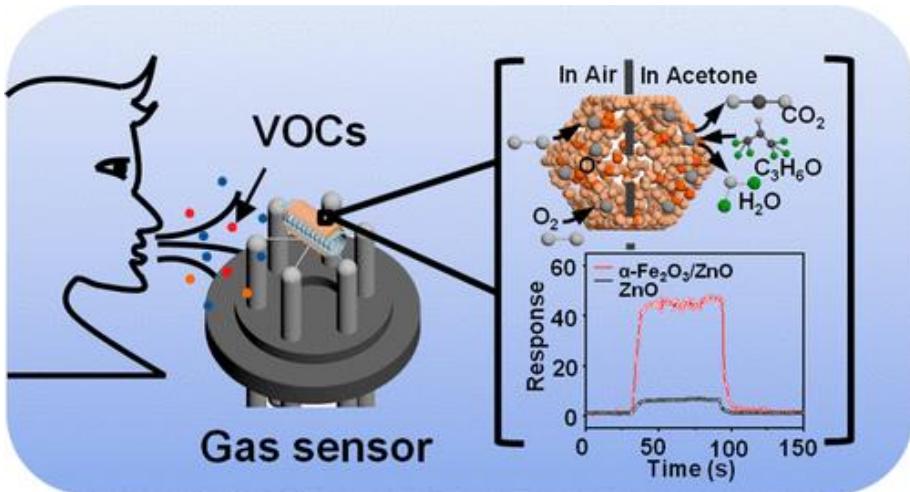


Figure 4.15. Schematic illustration of device based sensing of diverse nanostructures to volatile organic compounds (VOCs). [<https://doi.org/10.3390/s21020633>]



For more information (<https://doi.org/10.1021/acsanm.2c00769>)

### Electrochemical Gas sensors

Electrochemical sensors operate by reacting with the analyte and producing an electrical signal. Most electrochemical gas sensors are amperometric sensors, generating a current that is linearly proportional to the gas concentration. The principle behind amperometric sensors is the measurement of the current-potential relationship in an electrochemical cell where equilibrium is not established. The current is quantitatively related to the rate of the electrolytic process at the sensing electrode (also known as working electrode) whose potential commonly is kept constant using another electrode (the so-called reference electrode).

Electrochemical gas sensors also called as electrochemical gas detectors, which are designed to identify and measure the quantity of the concentration of gasses like oxygen, carbon dioxide, carbon monoxide, hydrogen, NOx, SOx, POx, LPG, H<sub>2</sub>S etc . These gases are produced from industrial emissions, vehicle exhaust and open burning of garbage waste, which needs to be monitored. Therefore the electrochemical gas sensors can be effective tool for analyzing them, as it consumes less power than other conventional gas sensors.

The schematic representation of working electrochemical gas sensor is as follows:

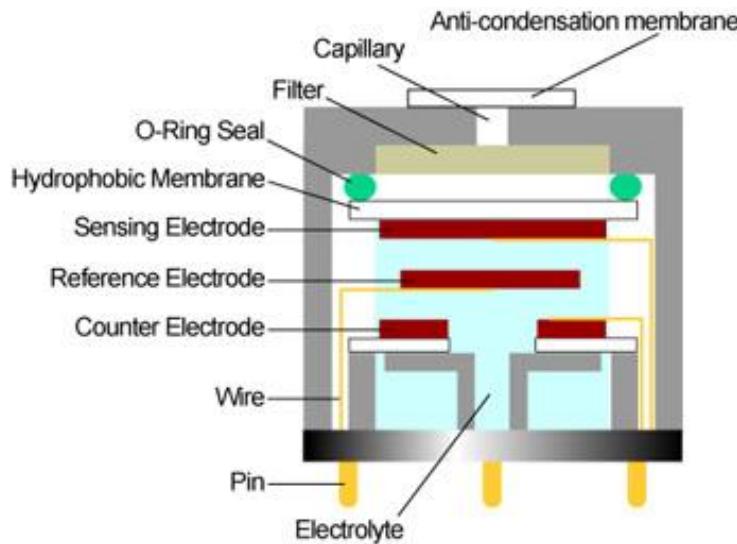


Figure 4.17. Schematic illustration of EC sensor

<https://www.membrapor.ch/electrochemical-gas-sensors/>

### The electrochemical gas sensor works as follows:

- Target gas molecules that come in contact with the sensor first pass an anti-condensation membrane which serves also as a protection against dust.
- Then the gas molecules diffuse through a capillary, potentially through a subsequent filter, and then through a hydrophobic membrane to reach the surface structure of the sensing electrode.
- There the molecules are immediately oxidized or reduced on active catalytic sites, consequently producing or consuming electrons, and thus generating an electric current.
- The design of the sensing electrode is crucial in order to both achieve a high reactivity towards the target gas and to inhibit undesired responses to interfering gases.
- The electrochemical cell is completed by the so-called counter electrode which balances the reaction at the sensing electrode. The ionic current between the counter and sensing electrode is transported by the electrolyte inside the sensor body, whereas the current path is provided through wires terminated with pin connectors.
- Commonly, a third electrode is included in an electrochemical sensor (3-electrode sensor). The so-called reference electrode serves to maintain the potential of the sensing electrode at a fixed value. For this purpose and generally for the operation of an electrochemical sensor a potentiostatic circuit is needed. [<https://doi.org/10.1016/j.jece.2021.105650>]

The EC gas sensor system consists of combination of two or three electrodes which are called reference, working, auxiliary/counter electrodes and ionic conductor between them as shown in figure 4.18. In this setup, the ionic conduction of the electrolyte, which in contact with WE and CE, complete the circuit. When gas molecules (CO) reacted with WE as shown in reaction below, @WE,  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ : The electrons released at WE are made to pass through externally and the  $\text{H}^+$  ion internally towards CE. By measuring the current flow, the type and quantity of gas sensor can be measured.

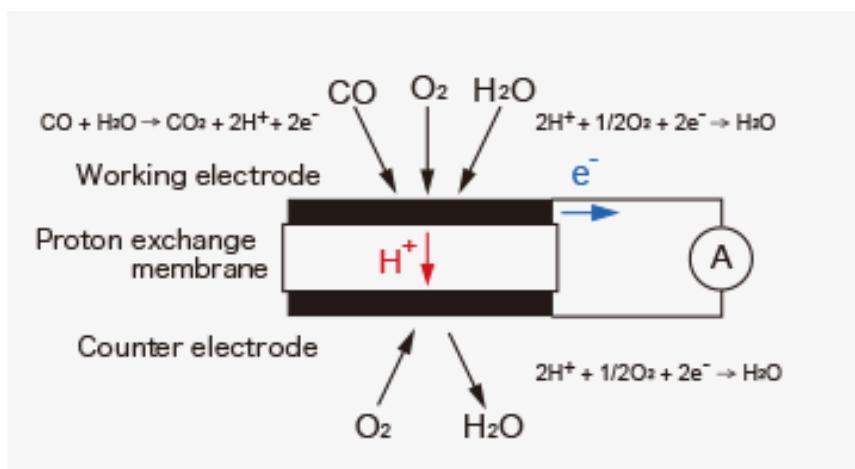


Figure 4.18. Schematic illustration of EC CO gas sensor

### Model Questions:

Q. No	Questions	Marks	COs	BTL
1	Name the smart device that works with the help of radio frequency waves.	2	1	1
2	Express the significance of RFID in smart devices.	4	3	1
3	Describe the role of important components of RFID.	4	3	1
4	Distinguish the types of RFID.	4	2	2
5	Explain the role of IoNTs technology in advancing the engineering and medical field.	4	3	2
6	List the nanomaterials used in RFID for IoNTs technology.	2	1	1
7	Draw the structures of CNT and graphene.	4	2	3
8	Analyze the structural differences between CNT and Graphene.	4	2	3

9	Construct the CVD setup for the fabrication of CNT and elaborate the synthesis protocol with mechanism of crystal growth.	6	4	4
10	Categorize the two types of functionalized CNTs and summarize them with suitable examples.	6	1	4
11	List the properties of CNTs	2	1	1
12	Propose the synthesis protocol for making GO from graphite.	5	2	3
13	Describe the modified Hummer's method for the synthesis of rGO.	5	3	2
14	Recommend the protocol for converting graphene to graphene-NH <sub>2</sub> .	2	4	4
15	Illustrate the physical/chemical functionalization of graphene with suitable example	4	1	2
16	Predict the product when graphene oxide is subjected to reduction in hydrogen environment.	2	2	3
17	Elaborate the chemical oxidative polymerization of aniline	4	2	2
18	Draw the various structures of PANI and identify the conducting polymer among them.	4	2	3
19	Explain the working principle of sensor with schematic diagram.	4	1	1
20	List the type of sensors	2	1	1
21	Explain the working principle of Piezoelectric sensor with schematic diagram.	4	2	3
22	List the important characteristics of Piezoelectric sensor.	2	1	1
23	List the applications of Piezoelectric sensor.	4	1	1
24	Demonstrate the working principle of electrochemical sensor	4	3	2
25	Highlight the role of three electrodes used in EC sensor	3	3	2
26	Elaborate the application of EC sensor sensor in diabetes management	4	4	4
27	Propose the possible structural change of ascorbic acid responsible for EC sensor signal.	2	3	3
28	Describe the working principle of Electrochemical Gas sensors	4	3	2

Semester: I/II				
<b>CHEMISTRY OF SMART MATERIALS AND DEVICES</b>				
(Category: Professional Core Course) Stream:CS (Theory and Practice)				
<b>Course Code</b>	<b>:</b>	22CHY12A	<b>CIE</b>	<b>:</b> 100+50 Marks
<b>Credits: L:T:P</b>	<b>:</b>	3:0:1	<b>SEE</b>	<b>:</b> 100 Marks
<b>Total Hours</b>	<b>:</b>	42L+ 30P	<b>SEE Duration</b>	<b>:</b> 3 Hours

## Unit-V

### Advanced energy systems

#### *Syllabus*

**Battery technology:** Introduction to Electrochemistry, characteristics of battery, Lithium-Ion battery, Sodium ion battery. Battery technology for e-mobility: Super capacitors: Storage principle, types (EDLC, pseudo and asymmetric capacitor) with examples and applications. Photovoltaics: organic/inorganic solar cells, quantum dot sensitized (QDSSC's). Photo catalytic water splitting.

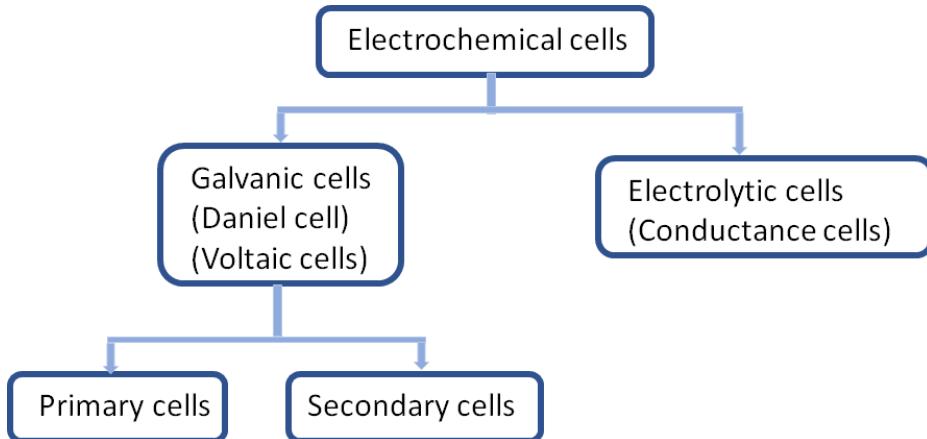
#### **5.1. Battery technology**

##### **Introduction to electrochemistry**

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

##### **Electrochemical Devices**

Electrochemical cell is a device in which chemical energy is converted into electrical energy or electrical energy into chemical energy by oxidation-reduction reaction. The electrode where oxidation occurs is called anode and the electrode where reduction occurs is called cathode.



**Figure 5.1:** Classification of electrochemical cells

#### Types of electrodes:

- **Metal-metal ion electrode:** This type of electrode consists of a metal in contact with a solution of its own ions. Eg: 1. Zinc in a solution of zinc sulphate, copper in a solution of copper sulphate.
- **Metal-metal ion salt electrode:** This type of electrode consists of a metal in contact with one of its sparingly soluble salts and a solution of a soluble salt having a common anion with the sparingly soluble salt. Eg: 1. Calomel electrode  $\text{Hg(l)} | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{KCl}$  Or  $\text{Pt, Hg(l)} | \text{Hg}_2\text{Cl}_2(\text{s}) | \text{KCl} (\dots\text{M})$ , Silver-Silver chloride electrode  $\text{Ag, AgCl(s)} | \text{KCl} (\dots\text{M})$
- **Metal gas electrode:** A gas electrode consists of a particular gas flushed around an inert electrode (Pt), which is dipped in a solution containing ions to which the gas is reversible. The metal provides electrical contact and facilitates the establishment of equilibrium between the gas and its ions. Eg: SHE:  $\text{Pt} | \text{H}_2 (1\text{atm}) | \text{H}^+ (1\text{M})$ , Chloride electrode  $[\text{Pt}/\text{Cl}_2/\text{Cl}]$ .
- **Redox electrode:** This type of electrode consists of an inert electrode (Pt or Au) immersed in a mixed solution containing both the oxidized and reduced forms of a molecule or ion. Eg:  $\text{Pt} / \text{Fe}^{2+}: \text{Fe}^{3+}$ ,  $\text{Pt} / \text{Sn}^{2+}: \text{Sn}^{4+}$
- **Ion selective electrode:** In ion selective electrode, a membrane is in contact with a solution, with which it can exchange ions. These are the electrodes which certainly respond to specific ions and determine the potential. Example-Glass electrode.
- **Reference electrode:** Reference electrodes are those whose potentials are known.

#### Introduction to battery:

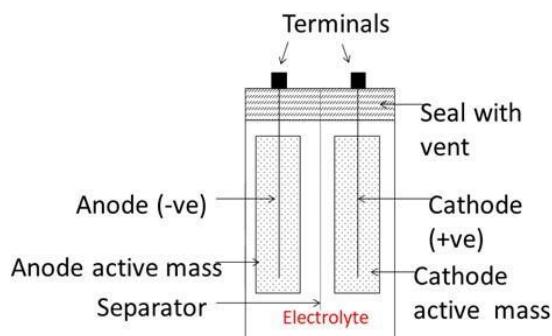
**CELL:** A cell designates a single unit. The conversion of chemical energy into electrical energy is a function of cells or batteries.

**BATTERY:** A Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage.

**Uses:** Batteries are used in calculators, watches and pacemakers for heart hearing aids, computers, car engines, standby power supplies, emergency lightning in hospitals, electroplating industrial tractions and military and space applications. Batteries have revolutionized the telecommunication system and are ushering a new era of transportation with the possible replacement of petrol driven automobiles by the electrically powered ones. In modern days portability of electronic equipment's in the form of handsets has been made possible by batteries.

**Components of Battery:** The cell consists of three major components.

- Anode: The anode selected with the following properties in mind; efficiency as a reducing agent, high coulombic output (Ah/g) good conductivity, stability, ease of fabrication and low cost.
- (Cathode: The cathode must be an efficient oxidizing agent, be stable when in contact with the electrolyte, and have a useful working voltage.
- Electrolyte: The electrolyte must have good ionic conductivity but not be electrically conductive. This would cause internal short circuiting. Electrolyte should be non-reactive with the electrode materials.



**Figure 5.2:** Structure of typical battery

**Mechanism of working of battery:** During discharging, the Battery acts as voltaic cell i.e. oxidation takes place at the negative electrode (anode) and reduction takes place at the positive electrode (cathode). During charging, The Battery acts as an electrolytic cell. The current flow is reversed and oxidation takes place at the positive electrode (anode) and reduction takes place at the negative electrode (cathode).

#### Criteria for commercial batteries

An efficient commercial cell should have following basic characteristics

- Portability: cells should be easily transportable without any environmental issues
- Compact: Battery should be more compact and lightweight
- Economy: batteries should have less price with continuous electric supply.
- Power and energy density: batteries should have high power and energy density
- Recharging; It should be able to charge as well as discharge battery in faster rate with recyclability
- Cycle and shelf life: Batteries should be having high cycle life and shelf life without self-discharge.

### **Characteristics of battery**

The suitability of any battery for particular application is based on certain characteristic properties. Some of the important characteristics of battery are

The suitability of any battery for particular application is based on certain characteristic properties. Some of the important characteristics of battery are

➤ **Voltage (V):** In general, high voltage is desired from any battery. The voltage of any battery depends on the emf of the cells which constitute the battery system. The emf of the cell depends on the free energy in the overall cell reactions as given by Nernst equation.  $E_{cell} = E^{\circ}_{cell} - \frac{2.303 RT}{nF} \log Q$  Where  $E_{cell}$  = Ecathode – Eanode and  $Q$  is the ratio of the molar concentrations of product and reactants. From the above equation, emf of the cell and the voltage available from the battery is dependent on the standard electrode potential difference between the cathode and anode, temperature and the extent of the cell reaction. To get required high voltage, the difference in the standard electrode potential should be more; temperature of the reaction and  $Q$  value should be low. The conductivity of the electrolyte should be high.

$$E_{cell} = E^{\circ}_{cell} + \frac{2.303RT}{nF} \log \frac{\text{Product}}{\text{Reactant}}$$

➤ **Current (A):** Current is a measure of the rate at which the battery is discharging. Higher the rate of spontaneous reaction, higher is the current. Higher the surface area of the electrodes, higher is the rate of reaction. Current is measured in Ampere (A).

$$I = \frac{V}{R}$$

Where  $I$  is the current,  $V$  is voltage and  $R$  is resistance of the battery.

- **Capacity (Ah):** Capacity is a measure of the amount of electricity that may be obtained from the battery. It is expressed in Ah (ampere hours). It is proportional to the amount of charge in Coulombs that may be transported from anode to cathode through the external circuit. The charge (C) in Coulombs is given by the Faraday's relation:

$$C = \frac{w \times n \times F}{M}$$

Where, C is Capacity of battery (in Ah), W is Weight of the active material (Kg), n is number of electrons involved in discharge reaction, F is Faraday's constant, 96500 C/mol, M is Molar mass of electro active materials.

- **Electricity density (Wh/Kg):** It is the amount of electricity stored in the battery per unit weight of the battery. i.e., it is the capacity per unit weight. It can be expressed in Coulombs/kg or in A/kg. The weight includes the weight of all components of the battery (i.e. total weight of active material, electrolyte, terminals etc.). A high storage density depends on a good battery design and also the appropriate selection of electrode reaction.

$$\text{Energy density} = \frac{I(\text{current}) \times t(\text{time}) \times V(\text{Voltage of a battery})}{\text{Capacity of a battery}}$$

- **Power density (W / Kg):** The ratio of the power available from a battery to its weight or its volume (W / V) is called power density. The power density will decrease during discharge and while recharge it will increase.

$$\text{Power density} = \frac{I(\text{current}) \times V(\text{EMF of battery})}{\text{Mass of electroactive material}}$$

- **Energy efficiency:** it is the ratio of energy released during discharge to energy consumed during charging. The energy efficiency of a rechargeable battery is given by

$$\text{Energy Efficiency} = \frac{\text{Energy released during charging}}{\text{Energy supplied during charging}} \times 100$$

- **Cycle life:** The number of recharges per discharge cycle that are possible before the failure of a secondary battery is called cycle life. In a secondary battery it is essential for the discharge per recharge cycle to perform the active material in a suitable state for further discharge reaction. The discharge per recharge cycle depends on the correct chemical composition, morphology and proper distribution of active material in the battery.

- **Shelf life:** The duration of storage under specific conditions at the end of which battery still retains the ability to give specific performance is called shelf life. Shelf life for most of the storage must be good. Good shelf life for a battery is possible when there is no self-discharge or corrosion in current collectors.

### **Classification of batteries:**

Majorly batteries are classified into three categories

- **Primary battery:** non-rechargeable (cell reactions are irreversible) - Self-discharges whether used or not, lechlanche cells (Zn/C) - Popular low-cost system, Applications: Torch light, portable radios, toys, novelties, etc. Mg/MnO<sub>2</sub> CELLS - High-capacity system: Applications: Military communication equipment, voting machines, etc.
- **Secondary battery:** Rechargeable (cell reactions are reversible), Lead-Acid Battery (Pb/H<sup>+</sup>), Nickel-Cadmium Battery (Ni-Cd), Nickel-Iron Battery (Ni-Fe), Nickel-Metal hydride Battery (Ni-MH), Lithium battery (Li-LiMxOy), lithium-Ion battery (C-LiMxOy), Lithium-Ion Polymer Battery (C-LiMxOy)
- **Reserve battery:** one of the key cell components, usually the electrolyte, is kept isolated from the rest and is added at the time of need Examples: Mg/Cu<sub>2</sub>Cl<sub>2</sub>, Mg/AgCl (sea water activated battery), Applications: Torpedoes, Sea beacons (Mainly in Meteorology and Defense fields), Li/FeS<sub>2</sub> (Thermally activated battery). Applications: In Missiles and rockets.

**Lithium-ion batteries:** A Lithium-ion battery is a rechargeable battery which stores the energy by reversible reduction of lithium ions. This battery is widely used in the portable electronic gadgets, e vehicles and all medical equipment because of their energy density and compactness. This type of battery is more advanced when compared to other types of battery such as lead acid and nickel cadmium battery. Further these types of batteries are majorly classified as primary and secondary batteries.

### **Criteria of selection of anode materials for lithium-ion battery**

Desired characteristics of anode materials

- Large capability of Lithium adsorption: porous anodes
- High efficiency of charge/discharge
- Excellent cyclability: high cycle life
- Low reactivity against electrolyte: Chemical stability
- Fast reaction rate
- Low cost
- Environmental -friendly, non-toxic

- Commercial anode materials used in lithium batteries: Hard Carbon, Graphite

### **Criteria of selection of Cathode materials for lithium-ion battery**

Desired characteristics of Cathode materials

- High discharge voltage
- High energy capacity
- Long cycle life
- High power density
- Light weight
- Low self-discharge
- Absence of environmentally hazardous elements

Commercial cathode materials for lithium ion battery: LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiNiO<sub>2</sub>, LiFePO<sub>4</sub>

### **Electrolytes used in the lithium-ion battery**

Electrolyte is one of the important components of the battery ecosystem. In general ether-based electrolytes along with lithium salts are used as electrolytes.

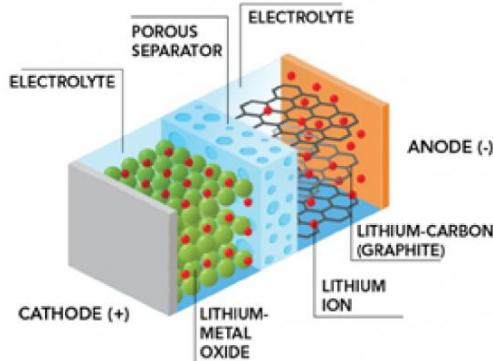
The electrolyte should have following Characteristics in order to employ them in battery technology

- Inert: solvent stability
  - High ionic conductivity, low viscosity
  - low melting point & high dielectric constant ( $\epsilon$ )
  - Appropriate concentration of Lithium salt
  - Chemical/thermal stability, High flash point (T<sub>f</sub>), nontoxic,
  - Low cost
  - Environmental -friendly, non-toxic
- Commercial electrolytes: LiPF<sub>6</sub> in Carbonate solvent, propylene carbonate, 1,2 dimethoxyethane

### **Role of electrolyte in battery technology**

- Ion conductor between cathode and anode
- Generally, Lithium salt dissolved in organic solvent
- Solid electrolyte is also possible if the ion conductivity is high at operating temperature.

**Separators:** Separator is a membrane placed between a battery electrode. The main function of a separator is to keep the two electrodes apart to prevent electrical short circuits while also allowing the transport of ionic charge carriers that are needed to close the circuit during the passage of current in an electrochemical cell.



**Figure 5.3:** separator in battery technology

**Primary lithium batteries:** These are batteries in which redox reactions proceed only in the one direction. The reactants in these batteries are consumed after a certain period of time, rendering them dead. A primary battery cannot be used once the chemicals inside it are exhausted. An example of a primary battery is the dry cell – the household battery that commonly used to power TV remotes, clocks, and other devices. Best example for this battery is the lithium-ion battery.

#### **Lithium Primary battery (Li-MnO<sub>2</sub>-Battery)**

In primary lithium-ion batteries, lithium metal is used as anode and manganous dioxide used as cathode. During the discharge lithium gets converted into lithium ion and it reacts with MnO<sub>2</sub> to become an irreversible LiMnO<sub>2</sub> compound. Hence this type of battery is the primary battery.

**Anode:** Li

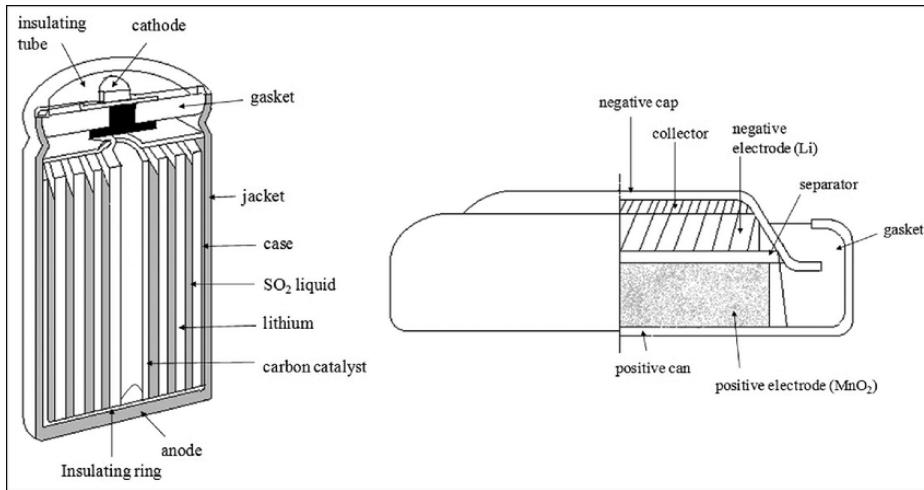
**Cathode-**MnO<sub>2</sub>(heat treated)

Electrolyte-Lithium salt like LiCl, LiBr, LiAlCl<sub>4</sub> in mixed organic solvent like 1, 2-dimethoxy ethane and Propylene carbonate Reactions:

Anode reaction: ..... Li → Li + + e-

Cathode reaction: ..... Li + + MnO<sub>2</sub> + e- → MnO<sub>2</sub>(Li<sup>+</sup>)

Overall reaction..... Li + MnO<sub>2</sub> → MnO<sub>2</sub>(Li<sup>+</sup>)



**Figure 5.4:** Structure of non-rechargeable lithium-ion battery (button cell)

### Secondary lithium-ion batteries:

These are the rechargeable lithium-ion batteries. Here electroactive materials are converted into electro inactive materials during discharge and during charging again this electro inactive material can be converted into electroactive materials with the help of external electricity. Examples: Lithium cobalt oxide battery, Lithium Nickel Cobalt Aluminium Oxide, Lithium iron phosphate etc...

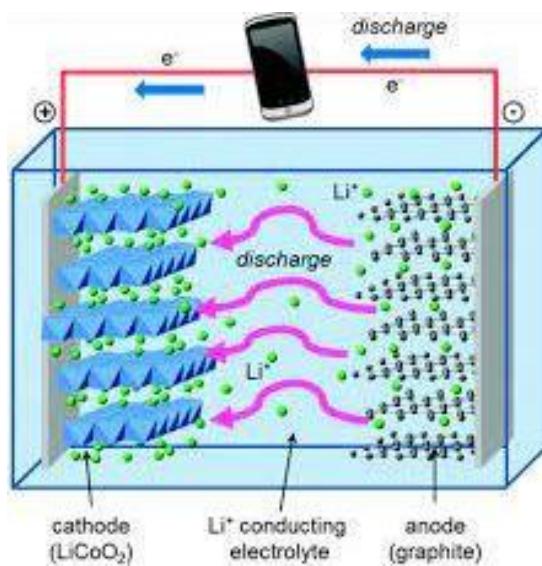
Li-ion batteries can use a number of different materials as battery electrodes. The most common combination is that of lithium cobalt oxide (cathode) and graphite (anode), which is most commonly found in portable electronic devices such as cellphones and laptops. Other cathode materials include lithium manganese oxide and lithium iron phosphate. Li-ion batteries typically use dimethoxy ether as electrolyte with lithium salts.

#### Lithium cobalt oxide battery

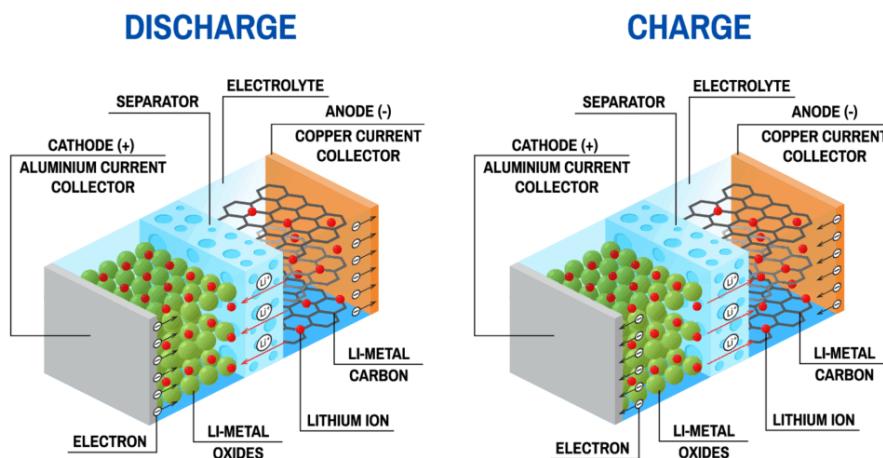
Lithium Cobalt is a mature, proven, industry-standard battery technology that provides long cycle life and very high energy density. The polymer design makes the cells inherently safer than "canned" construction cells that can leak acidic electrolyte fluid under abusive conditions. The cell voltage is typically 3.7 Volts.

#### Construction of LiCoO<sub>2</sub> battery

- Positive electrode: Lithiated form of a transition metal oxide (lithium cobalt oxide-LiCoO<sub>2</sub> or lithium manganese oxide LiMn<sub>2</sub>O<sub>4</sub>)
- Negative electrode: Carbon (C) usually graphite (C<sub>6</sub>)
- Electrolyte: solid lithium-salt electrolytes (LiPF<sub>6</sub>, LiBF<sub>4</sub>, or LiClO<sub>4</sub>) and organic solvents

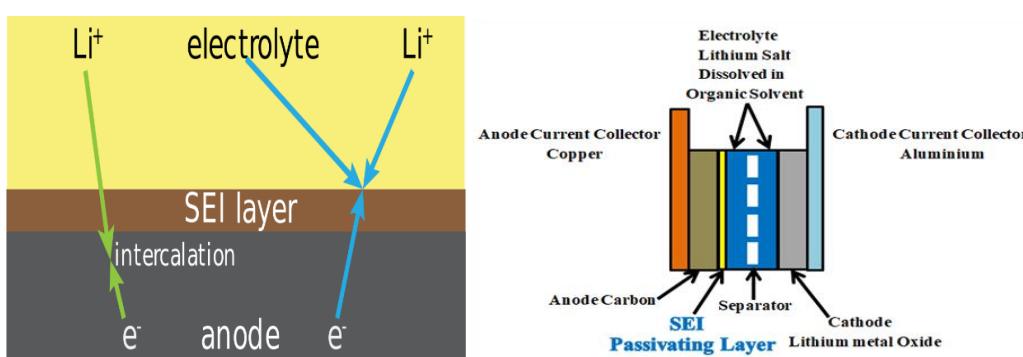


**Figure 5.5a:** Structure of lithium-ion battery



**Figure 5.5b:** Schematic representation of  $\text{LiCoO}_2$  battery working mechanism

**Solid electrolyte interphase (SEI) layer:** A passivation layer called the solid electrolyte interphase (SEI) is formed on electrode surfaces from decomposition products of electrolytes. The SEI allows  $\text{Li}^+$  transport and blocks electrons in order to prevent further electrolyte decomposition and ensure continued electrochemical reactions.

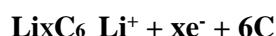


**Figure 5.6:** Role of solid electrolyte interphase

**Mechanism of working:** in lithium cobalt oxide batteries, generally lithium salts are used as electrolytes along with 1, 2 dimethoxy ethane and propylene carbonate. The main reason behind the selection of this solvent is its density and high boiling inert nature. During the discharging reaction the lithium metal in the anode compartment converts into lithium ion and it moves through SEI and separator towards cobalt cathode. In the cathode it reacts with Cobalt oxide and the electron to form  $\text{LiCoO}_2$ . And this process is reversible during charging. During discharging movement of lithium ions takes place from anode to cathode and it moves from cathode to anode when connected to an external power supply.

### Charging and discharging reaction

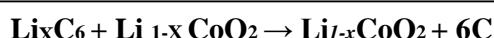
At anode



At cathode

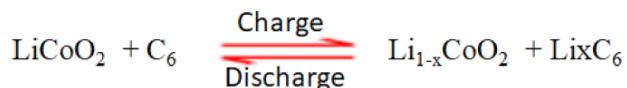


Overall reaction



In the above reaction x can be 1 or 0, With discharge the Co is oxidized from  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$ .

The reverse process occurs when the battery is being charged. The chemical reaction that takes place inside the battery is as follows, during charge and discharge operation:



### Advantages and limitations of lithium-ion batteries

When compared to other types of commercial batteries such as lead acid and nickel metal hydride batteries lithium batteries have several advantages. Few of them listed below

#### Advantages of lithium-ion batteries:

- Lightweight compared to other batteries
- Higher theoretical energy density than other types of batteries
- Rate of loss of charge is very less
- Operates at higher voltages than other batteries

- High adaptability to several applications
- As there is no memory effect, no need to completely drain the battery
- Low self-discharge compared to lead acid battery
- Easy maintenance

#### **Limitations of lithium-ion batteries:**

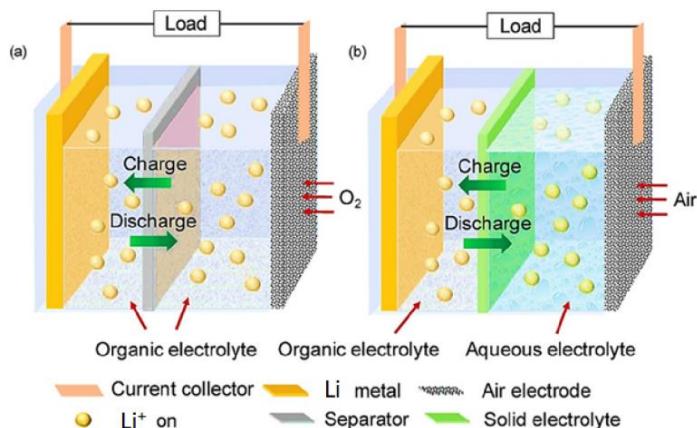
- Sourcing of lithium is difficult
- As lithium is not abundant, extraction of it doesn't meet global need
- Expensive than the other commercially available battery
- This battery is temperature sensitive; at higher temperature it may degrade with explosion
- Extra protection is required if want to employ them in large scale application
- Disposal may a problem because of heavy metal cathodes

#### **Metal air batteries**

Metal air battery is one of the most advanced batteries in which metal incorporated in a carbon matrix acts as anodes and air itself-acts as cathode. Amongst all the studied metal air battery lithium air battery is more attractive because of its high energy density along with light weight.

In general lithium ions move between the anode and the cathode across the electrolyte. Under discharge conditions, electrons follow from the external circuit to do electric work and the lithium ions migrate to the cathode. During charging the lithium metal in the anode, freeing O<sub>2</sub> at the cathode. In case of non-aqueous lithium air batteries Li<sub>2</sub>O<sub>2</sub> or LiO<sub>2</sub> are the byproducts. Similarly in aqueous lithium air battery LiOH is the byproduct. Further aqueous lithium air battery requires a protective layer to protect the lithium metal in the anode.

#### **Components and working of lithium air battery**



**Figure 5.7: lithium air battery**

Generally, lithium air batteries consist of lithium anode and porous cathode which will allow air from it. Then air itself-acts as cathode. Also, these lithium air batteries can have different electrolyte systems such as aqueous and non-aqueous. The chemical reaction in these types of batteries is given below.

### **Non aqueous lithium air battery**

Anode: lithium metal

Cathode: Oxygen (air)

Anodic reactions:  $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$

Cathodic reactions:  $\text{Li}^+ + \text{e}^- + \text{O}_2 \rightarrow \text{LiO}_2^*$



### **Aqueous lithium air battery**

Acidic electrolyte



Alkaline aqueous electrolyte



The electrical energy is provided by the chemical reaction between the lithium metal and O<sub>2</sub> from the air. The oxygen electrode has to be porous in order to allow the transport of gasses. The lithium electrode will be protected by a solid electrolyte interphase (SEI), which can be artificially prepared or spontaneously formed by the reaction of lithium with the electrolyte. Lithium-air batteries can also be built in the full solid state by using a solid electrolyte.

The main advantages of lithium air batteries are

- High theoretical specific energy of lithium
- Light weight of lithium
- Use of light weight oxygen
- High theoretical capacity of lithium metal

In the case of non-aqueous lithium air batteries, two main discharge products have been proposed: Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>O. In the case of aqueous lithium-oxygen batteries, the theoretical specific energies are lower, due to the presence of hydrating water molecules in some of the species involved in the reactions. The main byproduct in the aqueous lithium air battery is LiOH.

- Limitations of lithium air battery
- Poor reversibility
- Inferior long term cyclability

- Electrolyte evaporation

## 5.2. Supercapacitor

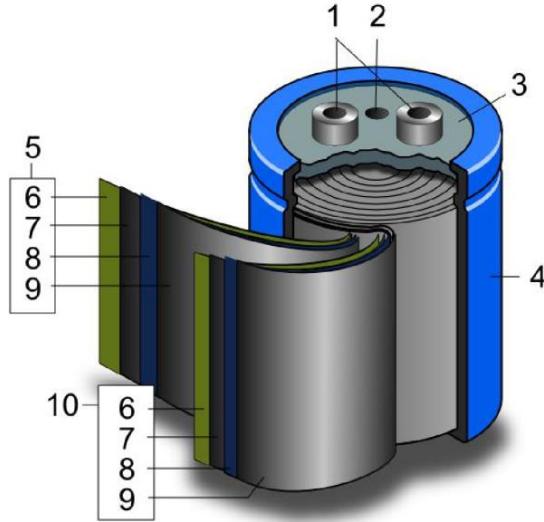
### Introduction to super capacitor

Supercapacitors, also known as electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors. In doing so, supercapacitors are able to attain greater energy densities while still maintaining the characteristic high-power density of conventional capacitors. A supercapacitor (SC), also called an ultracapacitor, is a high-capacity capacitor with a capacitance value much higher than other capacitors, but with lower voltage limits, that bridges the gap between electrolytic capacitors and rechargeable batteries. It typically stores 10 to 100 times more energy per unit volume or mass than electrolytic capacitors, can accept and deliver charge much faster than batteries, and tolerates many more charge and discharge cycles than rechargeable batteries.

**Definition:** A supercapacitor is a double-layer electrolytic capacitor that can store large amounts of energy nearly 10 to 100 times more energy when compared to the electrolytic capacitors. It is widely preferred over batteries because of its faster charging capacity and faster delivery of energy. It has more charging and discharging cycles than rechargeable batteries. The capacitance of this capacitor is also measured in Farad's (F). The main advantage of this capacitor is its efficiency and high-energy storage capacity.

### Construction of Supercapacitor

Electrochemical capacitors (supercapacitors) consist of two electrodes separated by an ion-permeable membrane (separator), and an electrolyte ionically connecting both electrodes. When the electrodes are polarized by an applied voltage, ions in the electrolyte form electric double layers of opposite polarity to the electrode's polarity. For example, positively polarized electrodes will have a layer of negative ions at the electrode/electrolyte interface along with a charge-balancing layer of positive ions adsorbing onto the negative layer. The opposite is true for the negatively polarized electrode. Additionally, depending on electrode material and surface shape, some ions may permeate the double layer becoming specifically adsorbed ions and contribute with pseudo capacitance to the total capacitance of the supercapacitor.



**Figure 5.8:** Schematic representation of super capacitor (1. terminals, 2. safety vent, 3. sealing disc, 4. aluminum can, 5. positive pole, 6. separator, 7. carbon electrode, 8. collector, 9. carbon electrode, 10. negative pole)

### Working of supercapacitor

Two electrodes form a series circuit of two individual capacitors C<sub>1</sub> and C<sub>2</sub>. The total capacitance C<sub>total</sub> is given by the formula

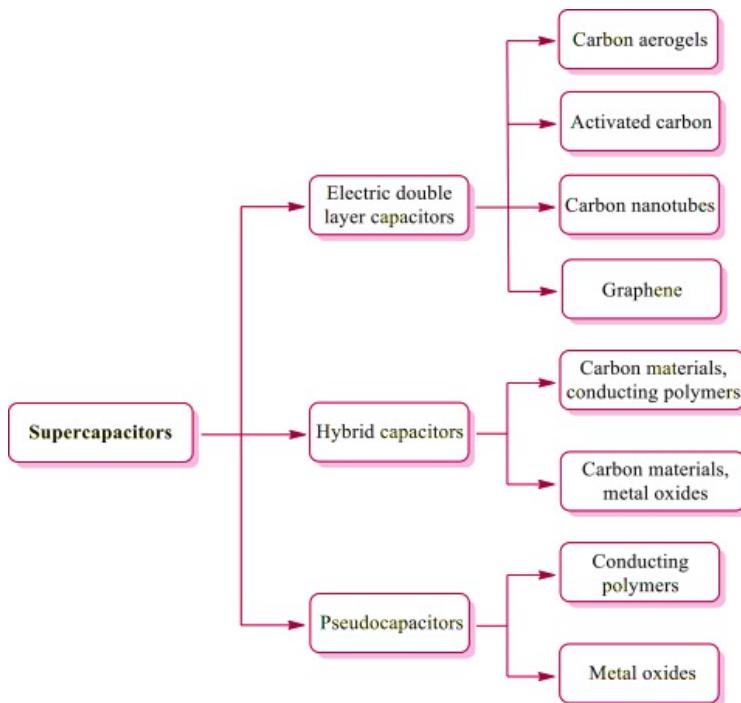
$$C_{\text{total}} = \frac{C_1 \cdot C_2}{C_1 + C_2}$$

Supercapacitors may have either symmetric or asymmetric electrodes. Symmetry implies that both electrodes are made of the same materials and have the same capacitance value, yielding a total capacitance of half the value of each single electrode (if C<sub>1</sub> = C<sub>2</sub>, the C<sub>total</sub> =  $\frac{1}{2} C_1$ ). For asymmetric capacitors, the total capacitance can be taken as that of the electrode with the smaller capacitance (if C<sub>1</sub> >> C<sub>2</sub>, the C<sub>total</sub>  $\approx C_2$ ).

### Principles of Energy storage

The supercapacitor has the self-discharging capacity and unlimited charging-discharging cycles. These types of capacitors can work with low voltages (2-3 volts) and can be connected in series to produce high voltage, which is used in powerful equipment. It can store more energy and releases instantly and more quickly when compared to batteries. When this capacitor is connected to the circuit or DC voltage source, the plates are charged and opposite charges are formed on both sides of the separator, which forms a double-layer electrolytic capacitor. To charge a supercapacitor, connect the positive side of the voltage source to the positive terminal of the supercapacitor and the negative side of the voltage source

is connected to the negative terminal of the supercapacitor. If the supercapacitor is connected to a 15 volts voltage source, then it charges up to 15 volts. As the voltage is increased beyond the applied voltage source, the supercapacitor may get damaged. So, the resistor is connected in series with the voltage source and capacitor to decrease the amount of current flowing through the capacitor and it doesn't get damaged. The constant current supply and limited voltage supply is suitable for the supercapacitor. When the voltage is increased gradually, the amount of current flowing through the capacitor changes. In the fully charged mode, the current drops by default.



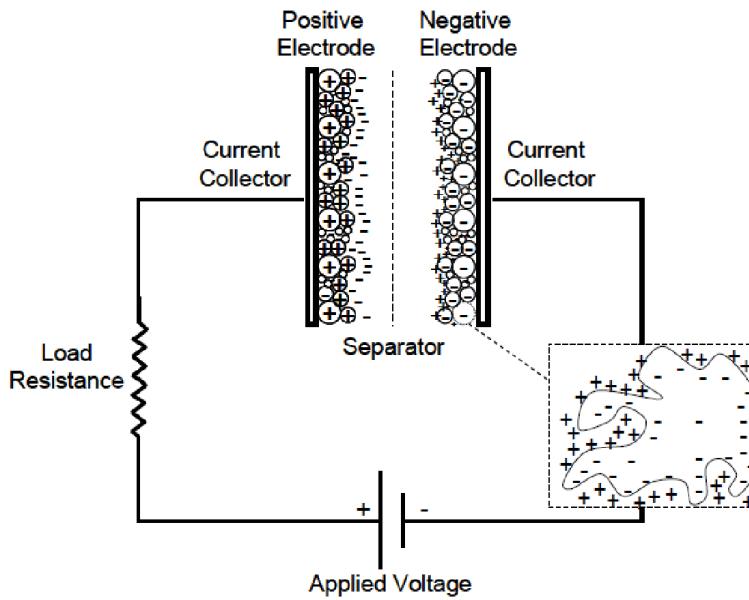
**Figure 5.9:** super capacitors classification

- **Electrostatic double-layer capacitors (EDLCs) :** EDLCs use carbon based materials as electrodes with higher electrostatic double-layer capacitance, achieving separation of charge in a Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte.
- **Electrochemical pseudo-capacitors:** Use metal oxide or conducting polymer electrodes with a high amount of electrochemical pseudocapacitance additional to the double-layer capacitance. Pseudocapacitance is achieved by Faradaic electron charge-transfer with redox reactions, intercalation or electrosorption.
- **Hybrid capacitors:** Hybrid capacitors are lithium-ion capacitors, use electrodes with differing characteristics.

## **Electrostatic double-layer capacitors (EDLCs)**

Electrochemical double-layer capacitors (EDLCs) are constructed from two similar carbon-based electrodes, an electrolyte, and a separator. These type of supercapacitors store the energy very similar to conventional capacitors. These EDLCs store charge electrostatically, or non-Faradaically, and there is no transfer of charge between electrode and electrolyte. These EDLCs store the charge using an electrochemical double-layer. As voltage is applied, charge accumulates on the surface of both the electrodes. This is followed by the natural attraction of unlike charges, ions in the electrolyte solution diffuse across the separator into the pores of the electrode of opposite charge. In this architecture, electrodes are designed to avoid recombination of ions. Due to this, a double-layer of charge is produced at each electrode. These double-layers, coupled with an increase in surface area and a decrease in the distance between electrodes, allow EDLCs to achieve higher energy densities than conventional capacitors. Due to the non-transferring of charges between electrolyte and electrode, there are no chemical or composition changes associated with non-Faradaic processes. For this reason, charge storage in EDLCs is highly reversible, which allows them to achieve very high cycling stabilities. The performance characteristics of an EDLC can be adjusted by changing the nature of its electrolyte.

An EDLC can utilize either an aqueous or organic electrolyte. Aqueous electrolytes, such as  $\text{H}_2\text{SO}_4$  and KOH, generally have lower minimum pore size requirements compared to organic electrolytes, such as acetonitrile. In these EDLCs, generally carbon-based materials are used because of their higher surface area, lower cost, and more established fabrication techniques than other materials, such as conducting polymers and metal oxides. Different forms of carbon materials that can be used to store charge in EDLC electrodes are activated carbons, carbon aerogels, and carbon nanotubes.



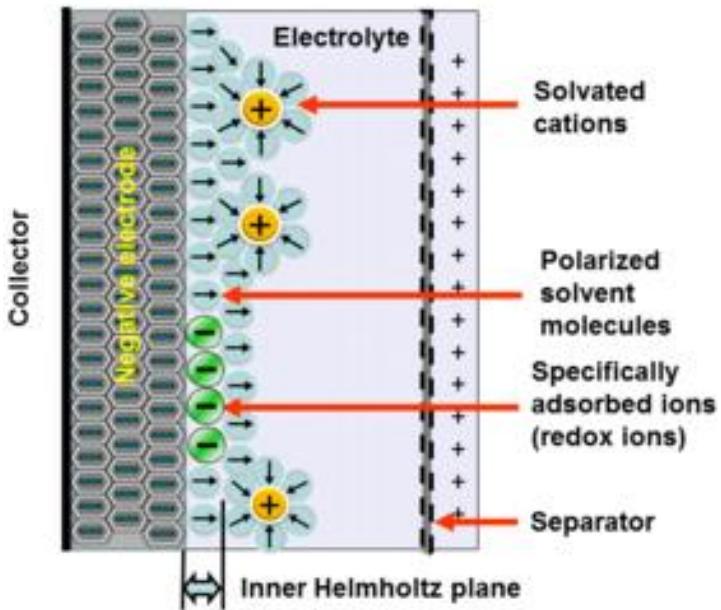
**Figure 5.10:** Electrolytic double layer capacitor

### Electrochemical Pseudo capacitance:

Applying a voltage at the electrochemical capacitor terminals moves electrolyte ions to the opposite polarized electrode and forms a double-layer in which a single layer of solvent molecules acts as a separator. Pseudo capacitance can originate when specifically adsorbed ions

out of the electrolyte pervades the double-layer. This pseudo capacitance stores electrical energy

by means of reversible redox reactions on the surface of suitable electrodes in an electrochemical capacitor with an electric double-layer. Pseudo capacitance is accompanied with an electron charge-transfer between electrolyte and electrode coming from a de-solvated and adsorbed ion whereby only one electron per charge unit is participating. This faradaic charge transfer originates by a very fast sequence of reversible redox, intercalation or electrosorption processes. The adsorbed ion has no chemical reaction with the atoms of the electrode since only a charge-transfer takes place. The electrons involved in the faradaic processes are transferred to or from valence electron states (orbitals) of the redox electrode reagent. They enter the negative electrode and flow through the external circuit to the positive electrode where a second double-layer with an equal number of anions has formed. The electrons reaching the positive electrode are not transferred to the anions forming the double-layer, instead they remain in the strongly ionized and "electron hungry" transition-metal ions of the electrode's surface. As such, the storage capacity of faradaic pseudo capacitance is limited by the finite quantity of reagent in the available surface.



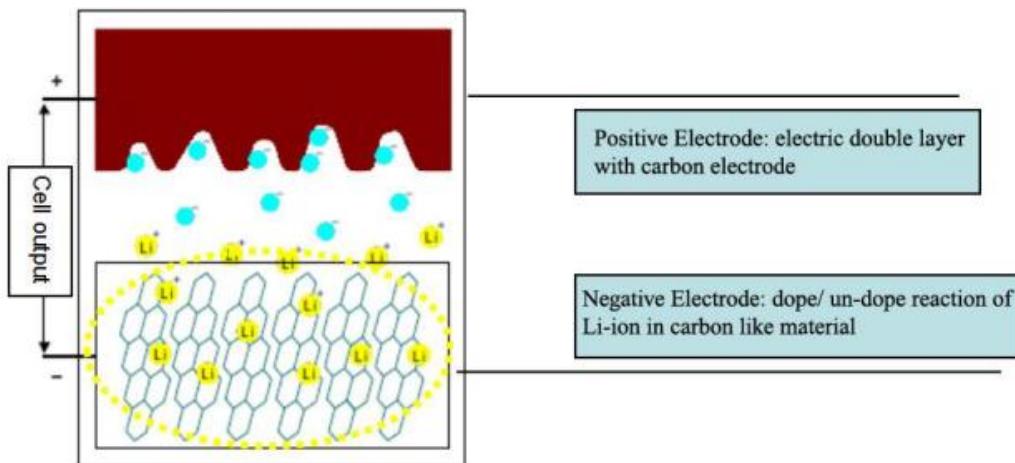
**Figure 5.11:** Electrochemical pseudo capacitance

The pseudo-capacitors store electrical energy by electron charge transfer between electrode and electrolyte. This can be done by Redox (reduction-oxidation reaction). Reduction-oxidation: Reduction-oxidation occurs when one atom gains (or losses) an electron and another atom loses (or gains) an electron. In pseudo capacitors oxidation-reduction reaction occurs in between electrode and electrolyte solution. In pseudo-capacitors, the charge storage (capacitance) results from the charge transfer between electrolyte and electrode. When voltage is applied to the pseudo-capacitor, the charged atoms or ions in the electrolyte move towards the oppositely charged electrode. In between the surface of the electrode and adjacent electrolyte, two electric layers or electric double layers are formed. These two electric layers are separated by electrolyte molecules. The charged atoms in the electrolyte within the double layer act as electron donors and transfer electrons to the atoms of the electrode. As a result, the atoms in electrons become charged. Thus, charge is stored at electric double layers. The pseudo-capacitors use conductive polymers or metal oxide as electrodes. The amount of electric charge stored in a pseudo-capacitor is directly proportional to the applied voltage.

### Hybrid Capacitors

Hybrid supercapacitors have higher operating voltage (3.8 V maximum) and much higher capacitance and energy density (up to 10 times) than symmetric supercapacitors. They also have much lower self-discharge and standby current. They can be discharged to zero volts for safety; hybrid supercapacitors cannot be discharged fully. From a construction standpoint, they are very similar, but a hybrid supercapacitor uses an anode made from graphite laced with

lithium and a different electrolyte. Utilizing both Faradaic and non-Faradaic processes to store charge, hybrid capacitors have achieved energy and power densities greater than EDLCs without the sacrifices in cycling stability and affordability that have limited the success of pseudo capacitors. The schematic representations of hybrid capacitors are given below.



**Figure 5.12:** schematics representation of hybrid capacitor

## Materials Used in supercapacitors

### Electrode materials

Supercapacitor electrodes are generally thin coatings applied and electrically connected to a conductive, metallic current collector. Electrodes must have good conductivity, high temperature stability, long-term chemical stability (inertness), high corrosion resistance and high surface areas per unit volume and mass. Other requirements include environmental friendliness and low cost. The amount of double-layer as well as pseudo capacitance stored per unit voltage in a supercapacitor is predominantly a function of the electrode surface area. Therefore, supercapacitor electrodes are typically made of porous, spongy material with an extraordinarily high specific surface area, such as activated carbon. Additionally, the ability of the electrode material to perform faradaic charge transfers enhances the total capacitance.

### Electrodes for EDLCs

The most commonly used electrode material for supercapacitors is carbon in various manifestations such as activated carbon (AC), carbon fibre-cloth (AFC), carbide-derived carbon (CDC), carbon aerogel, graphite (graphene), graphane and carbon nanotubes (CNTs).

Carbon-based electrodes exhibit predominantly static double-layer capacitance, even though a small amount of pseudo capacitance may also be present depending on the pore size distribution. Pore sizes in carbons typically range from micropores (less than 2 nm) to mesopores (2-50 nm), but only micropores (<2 nm) contribute to pseudo capacitance.

- 1) **Activated carbon:** Activated carbon was the first material chosen for EDLC electrodes. Activated carbon is an extremely porous form of carbon with a high specific surface area. The bulk form used in electrodes is low-density with many pores, giving high double-layer capacitance. Solid activated carbon, also termed consolidated amorphous carbon (CAC) is the most used electrode material for supercapacitors and may be cheaper than other carbon derivatives.
- 2) **Activated carbon fibres:** Activated carbon fibres (ACF) are produced from activated carbon and have a typical diameter of 10 µm. They can have micropores with a very narrow pore-size distribution that can be readily controlled. Advantages of ACF electrodes include low electrical resistance along the fibre axis and good contact to the collector.
- 3) **Carbide-derived carbon:** Carbide-derived carbon (CDC), also known as tunable nanoporous carbon, is a family of carbon materials derived from carbide precursors, such as binary silicon carbide and titanium carbide, that are transformed into pure carbon via physical processes. Carbide-derived carbons can exhibit high surface area and tunable pore diameters (from micropores to mesopores) to maximize ion confinement
- 4) **Graphene:** Graphene is an atomic-scale honeycomb lattice made of carbon atoms. Graphene has a theoretical specific surface area of 2630 m<sup>2</sup>/g which can theoretically lead to a capacitance of 550 F/g. In addition, an advantage of graphene over activated carbon is its higher electrical conductivity. The two-dimensional structure of graphene improves charging and discharging. Charge carriers in vertically oriented sheets can quickly migrate into or out of the deeper structures of the electrode, thus increasing currents. Such capacitors may be suitable for 100/120 Hz filter applications, which are unreachable for supercapacitors using other carbon materials.
- 5) **Carbon nanotubes:** Carbon nanotubes (CNTs), also called buckytubes, are carbon molecules with a cylindrical nanostructure. They have a hollow structure with walls formed by one-atom-thick sheets of graphite. These sheets are rolled at specific and discrete ("chiral") angles, and the combination of chiral angle and radius controls properties such as electrical conductivity, electrolyte wettability and ion access. Nanotubes are categorized as single-walled nanotubes (SWNTs) or multi-walled nanotubes (MWNTs). Carbon nanotubes can greatly improve capacitor performance, due to the highly wettable surface

area and high conductivity.

### **Electrode materials for Pseudo capacitors**

1. **Metal oxides:** The electrodes of transition metal oxides that exhibited high amounts of pseudo capacitance. Oxides of transition metals including ruthenium ( $\text{RuO}_2$ ), iridium ( $\text{IrO}_2$ ), iron ( $\text{Fe}_3\text{O}_4$ ), manganese ( $\text{MnO}_2$ ) or sulfides such as titanium sulfide ( $\text{TiS}_2$ ) alone or in combination generate strong faradaic electron-transferring reactions combined with low resistance. The transition metal electrodes offer excellent reversibility, with several hundred-thousand cycles.
2. **Conducting polymers:** Conducting polymers have a relatively high capacitance and conductivity with relatively low cost compared to carbon-based electrode materials. In particular, the n/p-type polymer configuration, with one negatively charged (n-doped) and one positively charged (p-doped) conducting polymer electrode, has the greatest potential energy and power densities. Additionally, it is believed that the mechanical stress on conducting polymers during reduction-oxidation reactions limits the stability of these pseudo capacitors through many charge-discharge cycles. This reduced cycling stability has hindered the development of conducting polymer pseudo capacitors in commercial scale.

### **Electrode materials for hybrid capacitors**

In recent years, researchers mainly focused on three different types of hybrid capacitors, distinguished by their electrode configuration: composite, asymmetric, and battery-type respectively.

1. **Composites:** Composite electrodes integrate carbon-based materials with either conducting polymer or metal oxide materials and incorporate both physical and chemical charge storage mechanisms together in a single electrode. The carbon-based materials facilitate a capacitive double-layer of charge and also provide a high-surface-area backbone that increases the contact between the deposited pseudocapacitive materials and electrolyte. The pseudocapacitive materials are able to further increase the capacitance of the composite electrode through Faradaic reactions. The examples of such hybrid capacitor electrodes are polypyrrole polymer-based electrodes.
2. **Asymmetric:** Asymmetric hybrids combine Faradaic and non-Faradaic processes by coupling an EDLC electrode with a pseudocapacitor electrode. In particular, the coupling of an activated carbon negative electrode with a conducting polymer positive electrode has

received a great deal of attention. The conducting polymer electrodes generally have higher capacitances and lower resistances than activated carbon electrodes, they also have lower maximum voltages and less cycling stability. Asymmetric hybrid capacitors that couple these two electrodes mitigate the extent of this tradeoff to achieve higher energy and power densities than comparable EDLCs. Also, they have better cycling stability than comparable pseudocapacitors.

3. **Battery-Type:** Like asymmetric hybrids, battery-type hybrids couple two different electrodes; however, battery-type hybrids are unique in coupling a supercapacitor electrode with a battery electrode. This specialized configuration reflects the demand for higher energy supercapacitors and higher power batteries, combining the energy characteristics of batteries with the power, cycle life, and recharging times of supercapacitors.

### **Importance of Electrolytes in supercapacitors**

Characteristics of electrolyte used in supercapacitors

- Wide potential window
- High ionic conductivity
- High chemical and electrochemical stability
- High chemical and electrochemical inertness to ES components
- Wide operating temperature range
- Well-matched with the electrolyte materials
- Low volatility and flammability
- Environmentally friendly
- Low cost

### **Advantages and limitations of super capacitor**

These super capacitors are having advantages as well as limitations, some of them highlighted below.

#### **Advantages of supercapacitor**

- High energy storage.
- Wide operating temperature (-40 °C to 60 °C).
- Eco-friendly.
- Quick charging time.
- Maximum life cycle.
- High cycle efficiency (95%).
- High specific power up to 17 kW/kg.
- Extremely low internal resistance.

- Safe

### **Limitations of super capacitors**

- Low energy density; usually holds 1/5 – 1/10 of a battery.
- Cannot use the full energy spectrum for some applications.
- The voltage varies with the energy stored.
- Have a high self-discharge rate.
- Individual cells have low voltages, and so serial connections are needed to obtain higher voltages.
- Requires expert electronic control.
- Cannot be used in AC and high frequency circuits.
- High cost.

### **Applications of supercapacitor**

- In the startup mechanism for Automobiles.
- Used in Diesel engine start up in submarines & tanks.
- In quickly recharged electric bus
- Backup power system in missiles.
- Power source for laptops, flash in cameras.
- Voltage stabilizer.
- To deliver high power and bridge power gaps
- Industrial and electronic applications
- Used in wind turbines, electric and hybrid vehicles
- Regenerative braking to release the power in acceleration
- To start power in start-stop systems
- Regulate voltage in the energy grid
- To capture and assist the power in lower loads and lifted loads
- Back-ups the power in a quick discharging state.

### **5.3. Photovoltaics**

#### **Introduction:**

Solar energy is a renewable energy and it is inexhaustible. The earth is receiving approximately  $1.8 \times 10^{11}$  MW of energy which is thousands of times larger than the requirement of energy for present consumption. Thus, solar energy is the only energy that fulfills all our present and future energy needs if we utilize it properly. Solar energy can be directly converted into heat energy or electricity. A solar cell, or photovoltaic cell, is an

electrical device that converts the energy of light directly into electricity by the photovoltaic effect.

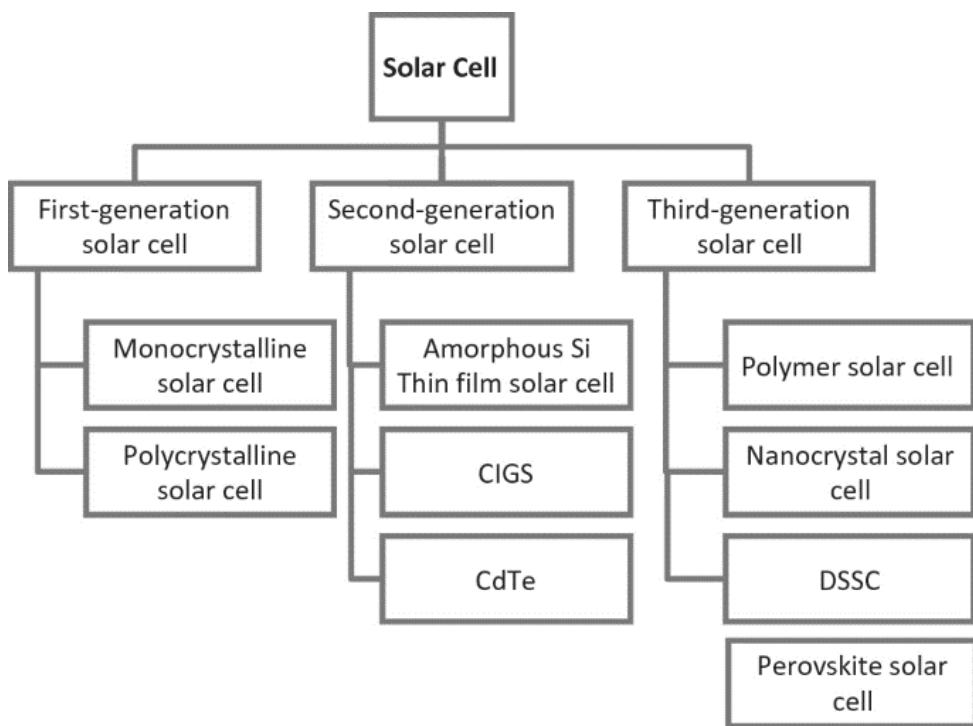
**Background:** After Edmund Bequerel discovered the photovoltaic effect, William Adams and Richard Day observed the photovoltaic effect in a sample of selenium placed between two metal electrodes. This was the first solid photovoltaic device. The photovoltaic effect in this device originates from the association of selenium and metal. Twenty years later, Charles Fritts developed the first large-area photovoltaic device. Each of these early cells consisted of a metal electrode/ semiconductor/ semi transparent thin metal electrode with a bottle neck to transmit incident light. Due to this limitation, the resulting power conversion efficiency was limited to less than 1%. In the 1950s, PV cells achieved significant improvement over PCE and found a first practical application. In 1954, Bell Labs revealed the first high-power silicon PV cell, which used a p-n junction and reported a PCE of 6%. Excited by this outstanding achievement, the New York Times forecasted that solar cells would eventually harness the “limitless energy of the sun.” In 1958, PV array-powered radios appeared on the US Vanguard I space satellite, and this was the first time PV technology was practically utilized. In this period, there also appeared PV cells made of cadmium sulphide, gallium arsenide, cadmium telluride, and indium phosphide. However, each technology had its own disadvantages. For example, cadmium, which is used in CdS and CdTe PV cells, is a toxic element, GaAs-based PV cells are very expensive to produce, and the indium used in InP PV cells is limited. Therefore, silicon-based PV cells were regarded as the most promising PV technology.

### **Advantages of Solar Cells**

- Solar cell is renewable energy which can be continuously drawn from the sun.
- It is economic friendly energy because once it is installed there will be minimum maintenance charges for small usage.
- Solar energy is environmentally friendly and green energy because it doesn't produce any greenhouse gasses and no pollutants.
- It doesn't involve any combustion reaction or radioactive residue hence no pollution
- Disadvantages of Solar Cells
- Space utilization: Solar cells required large area for installation
- It requires high investment cost for a big power plant
- During the rainy season power production is less hence grid maintenance will be difficult.
- Solar energy is produced only in the day time hence storage will be a big challenge

## Classification of solar cells

The solar cells are broadly classified as i) Inorganic solar cells and ii) Organic/polymer solar cells. Amongst them inorganic solar cells are currently in the global market. The amorphous silicon solar cells are classified under inorganic solar cells. There are three types of PV cell technologies that dominate the world market: monocrystalline silicon, polycrystalline silicon, and thin film. Higher efficiency PV technologies, including gallium arsenide and multi-junction cells, are less common due to their high cost, but are ideal for use in concentrated photovoltaic systems and space applications.[3] There is also an assortment of emerging PV cell technologies which include Perovskite cells, organic solar cells, dye-sensitized solar cells and quantum dots solar cells.

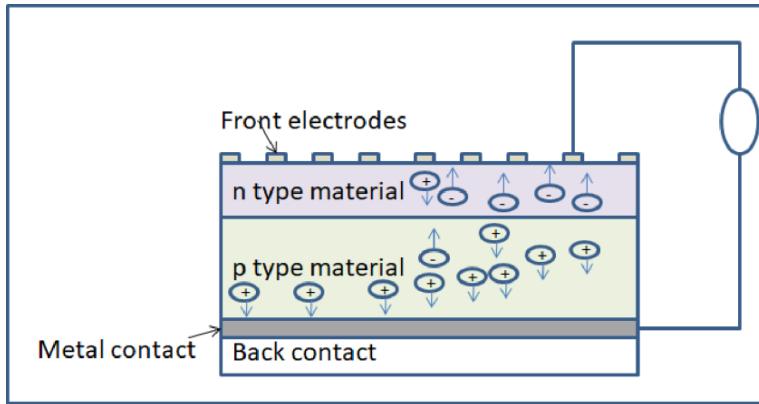


**Figure 5.13:** Classification of solar cells

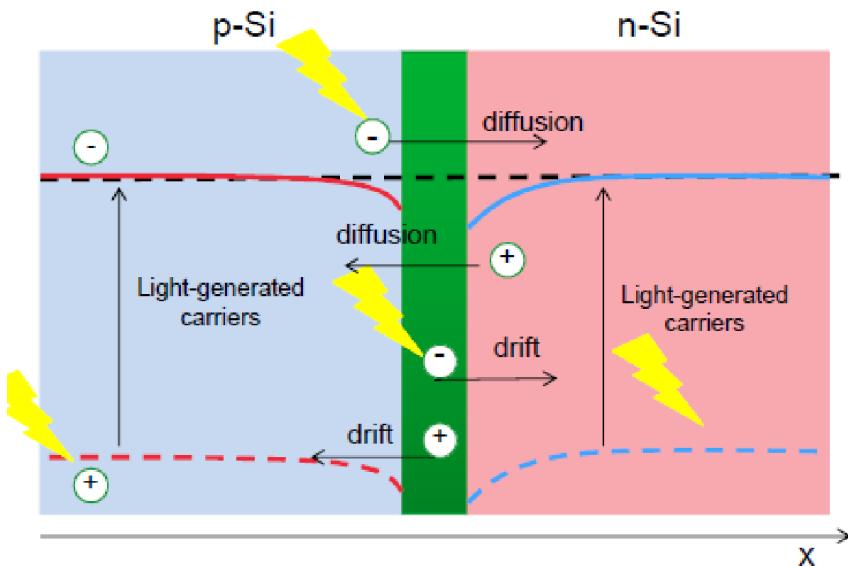
### Amorphous silicon solar cells

**Construction:** A typical silicon solar cell consists of n-type material (Phosphorus doped silicon) and a p-type (Boron doped silicon) material made of silicon. In the fabrication of devices these n-type and p-type materials are joined to form a p-n junction. On top of n type connecting front electrodes are placed. The metal back contact is attached to the p-type layer. An antireflective coating is filled in between the front electrodes to avoid the reflection of

sunlight. Finally p-type and n-type layers are joined externally to the circuit. The complete solar cells are sealed to avoid environmental contact.



**Figure 5.14:** Representation of amorphous silicon solar cells



**Figure 5.15:** Working mechanism of Silicon solar cells

**Working:** When sunlight is incident on solar cells, a photon strikes the p-n junction. Then an electron hole pair will be created at the junction by the absorption of photons. This electron hole pair diffuses towards the respective layer based on affinity. The electrons diffuse towards the n-type later and holes are diffused towards the p-type layer. These layers are connected externally through a circuit, hence current will be generated.

### Organic photovoltaics

**Brief history:** The first two-component OPV was proposed by Tang in 1986, but efficiencies remained very low for several years due to the reliance on bilayer cells. Excitons can only dissociate at the interface between donor and acceptor, and can generally only diffuse

approximately 10nm before decaying back to the ground state. In contrast, a total active layer thickness of above 100nm is usually required to absorb light efficiently – meaning bilayer cells are either too thin to properly absorb, or too thick for efficient exciton dissociation.

The solution to this was proposed in 1995, and is known as the bulk heterojunction (BHJ) cell.<sup>9,10</sup> Here instead of a strict two-layer system, the donor and acceptor materials are intimately mixed at the nanoscale level – allowing interfaces at an appropriate diffusion distance to be dispersed across the active layer whilst maintaining the necessary thickness for absorption.

**Introduction:** An OPV cell is a type of solar cell where the absorbing layer is based on organic semiconductors (OSC) – typically either polymers or small molecules. For organic materials to become conducting or semiconducting, a high level of conjugation (alternating single and double bonds) is required. Conjugation of the organic molecule results in the electrons associated with the double bonds becoming delocalized across the entire length of conjugation. These electrons have higher energies than other electrons in the molecule, and are equivalent to valence electrons in inorganic semiconductor materials. Laboratory OPV cells manufactured on glass. However, in organic materials, these electrons do not occupy a valence band but are part of what is called the ‘highest occupied molecular orbital’ (HOMO). Just like in inorganic semiconductors, there are unoccupied energy levels at higher energies. In organic materials, the first one is called the lowest unoccupied molecular orbital (LUMO). Between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the OSC is an energy gap - often referred to as the band gap of the material. With increased conjugation, the band gap will become small enough for visible light to excite an electron from HOMO to LUMO.

The bandgap in organic semiconductors is called HOMO-LUMO gap and it is determined by the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), it is usually in the range of 1-4 eV, similar as the bandgap of inorganic semiconductors.

**Exciton:** An exciton is a bound state of an excited electron and a hole which are attracted to each other and bounded by Coulomb forces.

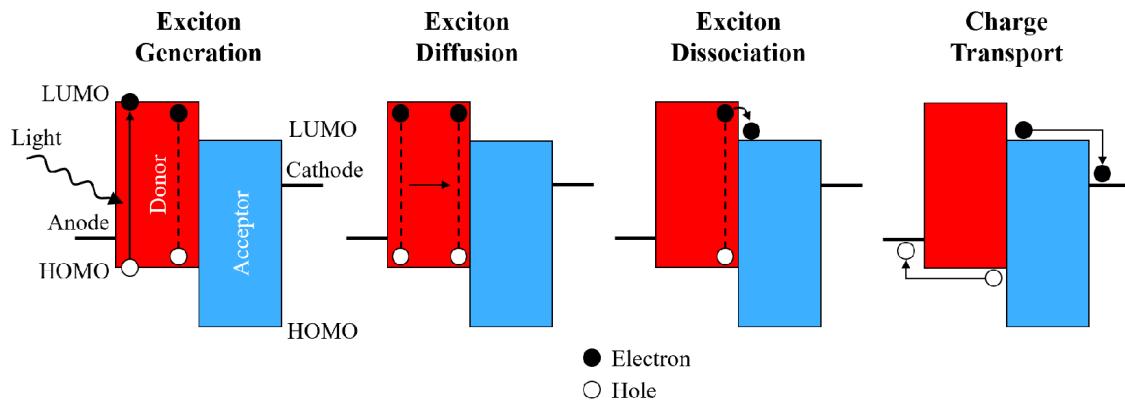
**Organic solar cells:** As with other PV technologies, the purpose of an OPV is to generate electricity from sunlight. This is achieved when the energy of light is equal to or greater than the band gap, leading to absorption and excitation of an electron – from the HOMO to the LUMO. The excited electron will leave behind a positively-charged space known as a ‘hole’.

Due to the opposite charges of the hole and electron, they become attracted and form an electron-hole pair, also known as an ‘exciton’. To remove the charged particles from the solar cell, the electron-hole pair must be separated, and this process is known as ‘exciton dissociation’. Typically in an inorganic semiconductor, the attraction between the electron and hole is small enough to be overcome by thermal energy at room temperature. This is due to a high dielectric constant – meaning there is significant screening between the electron and hole, reducing the attraction between them. The ease in separating the electron and hole allows easy exciton dissociation.

### **Working mechanism of organic solar cells:**

When sunlight falls on the cell some photons of the light are absorbed by the solar cell. Some of the absorbed photons will have energy greater than the energy gap between valence band and conduction band in the semiconductor crystal. Hence, one valence electron gets energy from one photon and becomes excited and jumps out from the bond and creates one electron-hole pair. These electrons and holes of e-h pairs are called light-generated electrons and holes. The light-generated electrons near the p-n junction are migrated to the n-type side of the junction due to electrostatic force of the field across the junction. Similarly, the light-generated holes created near the junction are migrated to the p-type side of the junction due to the same electrostatic force. In this way a potential difference is established between two sides of the cell and if these two sides are connected by an external circuit current will start flowing from positive to negative terminal of the solar cell.

The photoactive layer in modern organic solar cells usually consists of two materials, electron-donor and electron-acceptor, in order to successfully dissociate the tightly bound exciton that occurs in organic semiconductors. The exciton is dissociated by the electric field that arises at the donor-acceptor interface, which occurs because of the potential difference between the materials. The electron-donor is usually a polymer and the electron-acceptor a fullerene, small molecules or another polymer. The photovoltaic mechanisms in an organic solar cell can be described by four fundamental steps: Exciton generation, Exciton diffusion, Exciton dissociation and Charge carrier transport, which are illustrated in the following figure.



**Figure 5.16:** Steps involved in the current generation

**Step 1. Exciton generation:** Upon illumination of the active material, an electron is excited to the LUMO by absorption of a photon with energy larger than the HOMO-LUMO gap (band gap). The light absorption will generate electron-hole pairs, so-called excitons, where the electron and the hole are attracted to each other and bounded by Coulomb forces.

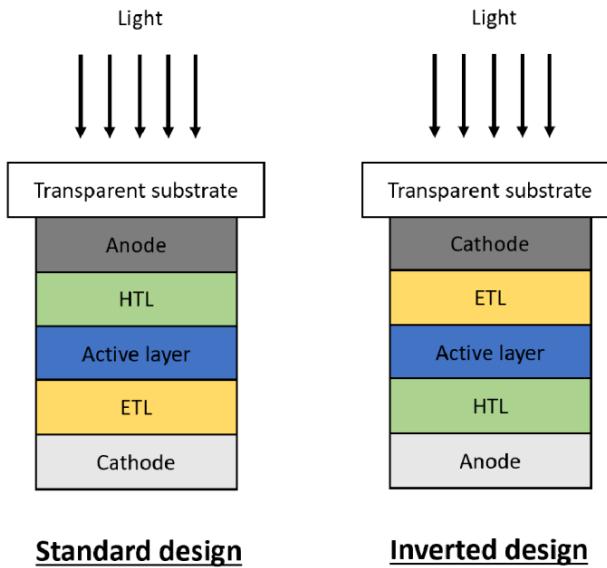
**Step 2. Exciton diffusion:** The generated exciton can diffuse through the material to the donor-acceptor interface. Due to the short lifetime of the exciton in organic materials, the exciton diffusion length is in the order of 10 nm.

**Step 3. Exciton dissociation:** If the exciton reaches the donor-acceptor interface within its lifetime, it dissociates into a free electron and hole due to the local electric fields caused by an energy level offset between the two materials.

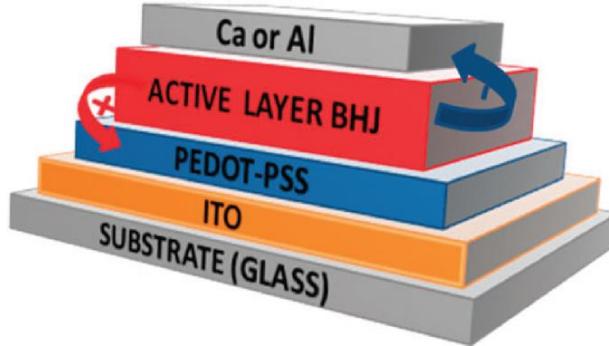
**Step 4. Charge carrier transport:** Free charge carriers are transported to the electrodes through the donor and acceptor material by an internal electric field caused by electrodes with different work functions. The electrons are collected at the cathode and the holes at the anode.

#### Device architecture

The device geometry of typical organic solar cells is illustrated in Figure. When designing the solar cells, it is preferable to choose materials for substrates, electrodes and electron transporting layer/hole transporting layer (ETL/HTL) with as large bandgap as possible, so all absorption happens in the active layer. Depending on if the solar cell is illuminated through the anode or the cathode the performance of the device can be different. That may depend on parasitic absorption from one of the materials before the active layer. Parasitic absorption refers to an optical absorption process that does not generate an electron/hole pair.

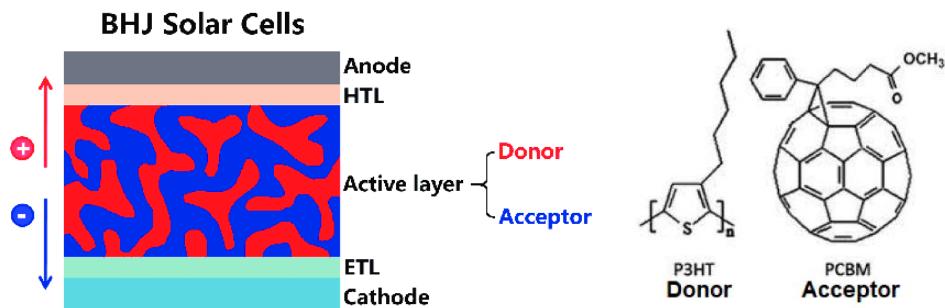


**Figure 5.17:** Device architecture of organic solar cells



**Figure 5.18:** Bulk heterojunction layer configuration

**Bulk hetero junction solar cells:** Bulk heterojunctions are made by creating interpenetrating networks of the donor and the acceptor components. With the two components interpenetrating one another, an exciton will never be far from the interface. The interfacial area will be large and the diffusion length of the excitons can be short. This puts many constraints on how to manage the morphology of the interpenetrating network. This is due to the fact that once the dissociation has taken place, the electron and the hole need to have a clear path to get to the cathode and the anode respectively. If the morphology is such that the path closes somewhere along the way, the electron and the hole will be lost. Bulk heterojunctions are described as systems of interpenetrating fingers of the donor component and the acceptor component sandwiched between the anode and cathode. This system has a large interfacial area, the interface is not far from where the exciton is generated, and once the exciton disassociates, the electron and the hole will have a clear path to their respective electrodes. Creating perfectly aligned interdigitating fingers.

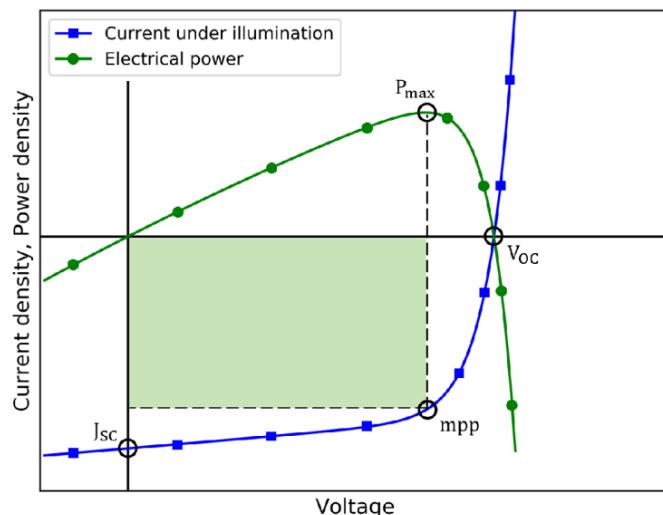


**Figure 5.19:** Representation of bulk heterojunction

### Recombination

At several stages, the electron and hole can recombine – at which point the absorbed energy used for initial excitation is wasted. This can happen in two ways i) The initially-produced electron-hole pair recombine before exciton dissociation. ii) Free electrons and holes can recombine, regardless of their source. These two steps lead to energy loss.

### Solar cells Characteristics



**Figure 5.20:** Current density and power density as a function of voltage

The electrical performance of a solar cell can be characterized by the short circuit current density ( $J_{SC}$ ), the open circuit voltage ( $V_{OC}$ ), the fill factor (FF) and the power conversion efficiency (PCE). These parameters can be found by current-voltage measurement of the solar cell. The current density and power density as a function of voltage for a solar cell is shown in Figure, together with the characterization parameters.

**Short circuit current density:**  $J_{SC}$  is the current density that flows through the solar cell when no voltage is applied.  $J_{SC}$  depends on several factors, such as the efficiency of the exciton

dissociation, charge transport, and charge extraction, but also the intensity and spectrum of the incoming light, and the absorption coefficients of the materials in the active layer.

$$J_{sc} = \frac{I_{sc}}{A}$$

Where, Isc is short circuit current, Jsc maximum current density and A is the area of a solar cell.

### **Open circuit voltage**

In organic solar cells, Voc is determined by the difference of the HOMO level of the donor and LUMO level of the acceptor. If the organic molecule employed has broad absorption, then more Open circuit voltage can be expected.

### **Fill factor**

FF characterizes how "square" the JV curve is and it represents how efficient the photo-generated carriers can be extracted out of a photovoltaic device. The fill factor is defined as

$$FF = \frac{V_{mpp} \times J_{mpp}}{V_{oc} \times J_{sc}}$$

**Power:** The generated output power of the solar cells is defined as

$$P_{max} = V_{mpp} J_{mpp} = FF \times V_{oc} \times J_{sc}$$

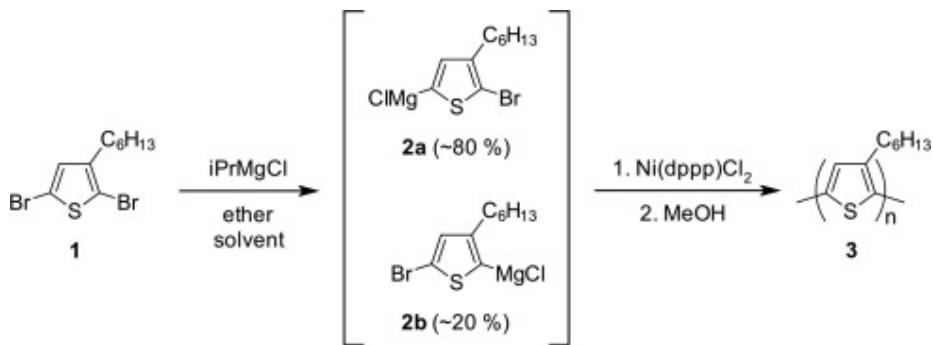
**Power conversion efficiency** of solar cells is defined as the ratio between the maximal generated power and the power of the incident light  $P_{in}$ .

$$PCE = \frac{P_{max}}{P_{in}} = FF \frac{V_{oc} \times J_{sc}}{P_{in}}$$

Where Pin is the radiation power on the earth is about 1000 watt/square meter hence if the exposed surface area of the cell is A then total radiation power on the cell will be 1000 A watts.

### **Materials used in organic photovoltaics**

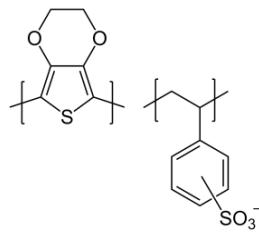
**Active materials:** in general, thiophene based conjugated molecules/polymeric structures are employed as active layers in organic photovoltaics. Because these materials have excellent thermal and electrical stability with adaptability. One of such materials is poly 3-hexylthiophene. This material has a very broad absorption spectrum which is matching to the solar spectrum hence it has been employed as an active layer. The synthesis of poly(3hexylthiophene) is represented in the figure below.



**Figure 5.20:** Synthesis of poly(3-hexylthiophene)

In the above synthesis 2,5 dibromo 3-hexylthiophene is treated with Grignard reagent to obtain the mono substituted product. Then this monosubstituted Grignard product is converted to polymer by the use of catalyst Dichloro(1,2-bis(diphenylphosphino)ethane) nickel. Then the obtained polymer is purified by reprecipitation using methanol.

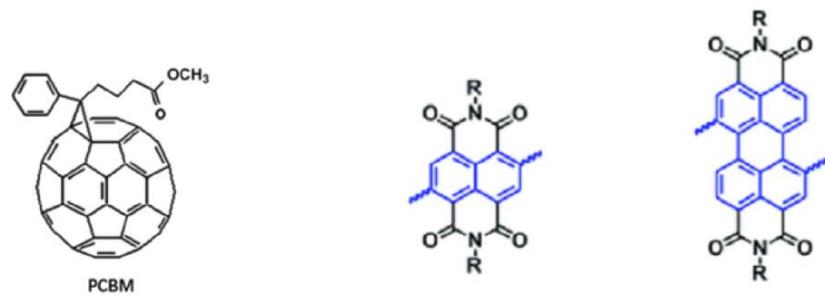
**Hole transport layer:** The HTL material is chosen based on many criteria. In order to create the driving force for holes to move towards the anode of the device, the HTL should have a high enough work function to match the HOMO of the donor. To prevent the drift of electrons towards the anode, the HTL should have its conduction band (CB) above the LUMO of the material. Another important criterion is, it should be transparent to light to pass through into the active layer. Further it should be cost effective. In general Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) is employed as HTL in organic photovoltaics because of its transparency and tunable work function. The structure of PEDOT: PSS is given below.



**Figure 5.21:** Structure of PEDOT: PSS

**Electron transport layer:** The main role of an electron transport layer (ETL) between the active layer and the cathode is to reduce the recombination of the free charge carriers (electrons and holes or exciton) with their counterparts. The LUMO level of the ETL material must be aligned to the LUMO level of the cathode material so as not to render the electron transport

towards the cathode. Examples of ETL material are PCBM-61, Napthalene and perylene dimides are represented below.



Phenyl-C<sub>61</sub>-butyric acid methyl ester    Naphthalene diimide,    Perylene diimide

**Figure 5.22:** Structures of electron transport materials

### Dye Sensitized Solar Cells

Photovoltaic effect is a process in which conversion of sunlight directly into electrical energy. The process of light dependent voltage between two electrodes in an electrode system was first discovered by Henry Becquerel in the year of 1839. In 1954 the first silicon solar cell was discovered and the initial efficiency was found to be 6%. The discovery of DSSC was started in 60s by German scientists Gerischer and Tributsch. Later Michel Gratzel, a Swiss scientist introduced a porous electrode consisting of Nano TiO<sub>2</sub> for construction of DSSC, which helped to increase the efficiency of solar cells up to 7%. This discovery of DSSC is a pioneer in the field of photovoltaics, thereafter vast research is going on in the field.

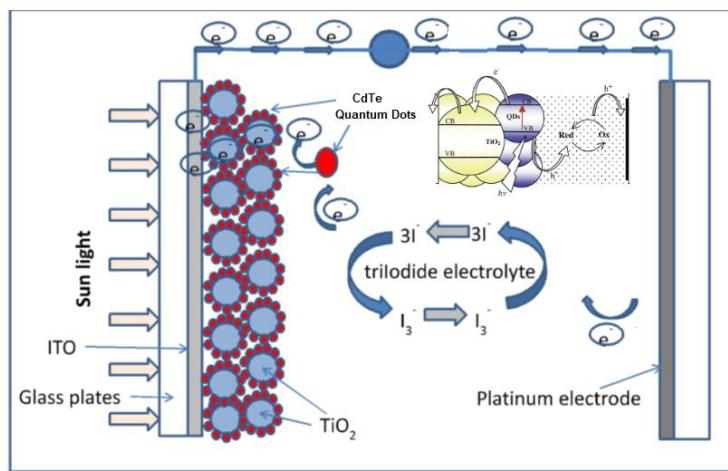
### Quantum dots (QDs)

Quantum dots are tiny particles or nanocrystals of a semiconducting material with diameters in the range of 2-10 nanometers. When they are illuminated by UV light, an electron in the quantum dot can be excited to a state of higher energy. In the case of a semiconducting quantum dot, this process corresponds to the transition of an electron from the valence band to the conductance band. The excited electron can drop back into the valence band releasing its energy as light. The color of that light depends on the energy difference between the conductance band and the valence band. Potential applications of these quantum dots include solar cells, LEDs, lasers, quantum computing, cell biology research and medical imaging. Examples for QD sensitizers such as CdS, CdSe, PbS, PbSe, CdTe etc.

### Quantum dot sensitized solar cells

It consists of two electrodes cathode and anode, generally cathode is made of graphite or platinum. Anode is made of transparent conducting oxide such as Indium tin oxide. Anode

is coated with a layer of nano porous materials ( $\text{TiO}_2$  or  $\text{ZnO}$ ). Further these nano porous materials are coated with  $\text{CdSe}$  quantum dots as light absorbing materials. Here the nano porous materials act as semiconductors and also it provides a way for electrons. The quantum dots with suitable energy levels help in the electron transfer process. A triiodide electrolyte system is employed in between the electrodes, which helps in the electron transfer process.



**Figure 5.23.** Construction and working of quantum dye sensitized solar cells.

### Mechanism of Working

When a light photon strikes the solar cell, it passes through the ITO layer and it reaches the quantum dots. Once the photon hits the quantum dots, it undergoes excitation with the liberation of an electron, which travels through the network  $\text{TiO}_2$  nanoparticles (because of matching in energy levels) and finally it reaches the cathode. The cell is completely filled with Triiodide electrolyte. The electron from the cathode directly reduces the triiodide molecule to three iodide molecules. Further this iodide molecule oxidizes to form triiodide again with the liberation of electrons, which can be easily absorbed by quantum dots. And a similar cycle continues whenever sunlight falls on the solar cells.

## 5.4. Green Fuel

Demand for green fuel technologies is rising given their potential to accelerate the transition to more sustainable forms of energy while still supporting current energy models with all their regional variations. Amongst all green fuels hydrogen is considered to be the best alternative. Hydrogen is a zero-emissions source of fuel for trains, buses and cars. It can be used as a feedstock gas for industries such as chemical, refining and steel. In addition, it is a source of heat and power for buildings, and can buffer energy generated from renewable sources.

### Hydrogen Production

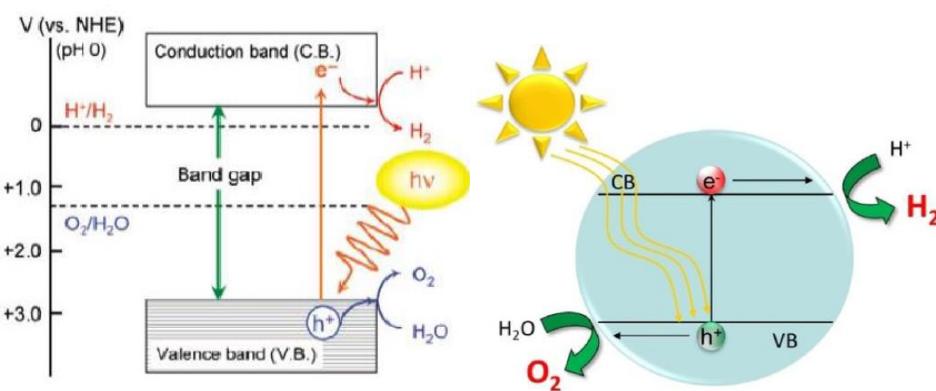
Over the last decades, an increasing interest has been devoted to the generation of hydrogen from solar-powered water splitting devices as a direct approach to generate a clean and sustainable energy vector. Among the different alternatives, a direct photocatalytic process is the most straightforward, where a light absorber is able to produce hydrogen and oxygen under light irradiation without an external bias.

### Photocatalytic water splitting:

The photocatalytic generation of solar fuels by suitable photocatalytic materials suspended in water is certainly one of the most attractive and challenging pathways for decarbonizing current energy systems. From the outside, it seems as a simple approach combining water, solar light, and a semiconductor. However, each of these components plays a key role in the overall efficiency of the reaction, and mostly, many factors including thermodynamic, kinetic, and other requirements hold back this technology from its maximum potential. Photocatalysts must be semiconductors. The minimum requirement is to generate electrons-hole pairs due to irradiation, normally by a UV-vis source. But it must also have a suitable crystalline phase, which ensures the formation of the electron-hole pairs and does not favor its recombination.

### Material requirement of photo catalysts

- Band gap: band gap of the materials used in catalysis should be more than 1.23 ev and sufficiently small to make efficient use of solar spectrum (<3eV). Ans it should be having band levels suitable for water splitting.
- High crystallinity: Defects can act as recombination sites
- Long term stability: Charge transfer used for water splitting and not for corrosion



**Figure 5.24:** Band diagram of catalyst

Water splitting electrode should be

- Efficient light absorber
- Charge separator

- Charge conductor

Photocatalytic water splitting is an artificial photosynthesis process with photocatalysis in a photoelectrochemical cell used for the dissociation of water into its constituent parts, hydrogen and oxygen, using light.

Water splitting electrodes work much like the leaves of the plants during photosynthesis. They absorb energy from the sunlight and use it to generate charge carriers. Negatively charged electrons and positively charged holes. These charges are delivered to water and water molecules swipe electrons away to form hydrogen gas and whereas holes strip the molecules of electrons to form oxygen gas.

### **Hydrogen Storage:**

Hydrogen energy storage is an area of growing interest due to the greater storage capacity offered by hydrogen over batteries, as well as the benefits offered by the renewable generation afforded by hydrogen as a fuel. Hydrogen can be stored either as a gas or as a liquid. Hydrogen gas storage typically requires the use of high-pressure tanks (350-700 bar or 5000-10,000 psi), while liquid hydrogen storage requires cryogenic temperatures to prevent it boiling back into a gas (which occurs at  $-252.8^{\circ}\text{C}$ ). Hydrogen can also be stored on the surface of (adsorption) or within solid materials (absorption).

### **General method of hydrogen storage**

In modern practice hydrogen can be stored in three different ways

1. As a gas under high pressures (in pressure cylinder)
2. In liquid form under cryogenic temperatures (at low temperature storage)
3. On the surface of or within solid and liquid materials (Metal hydrides as well as carbon nanotubes and metal organic frameworks)