FRONTIERS IN CHEMISTRY

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April – May, 2007

This is the third in the series of ebooks from the National Centre for Catalysis Research and the first upload of the chapters of this book was on 7th April 2007.

PREFACE

The Children's Club science programme has always been a challenge to us. In the past we have been conducting this programme for a number of years without any break. Every time, by a conscious effort, a theme has been chosen and all the presentations have been revolving around the theme chosen. This year "**Frontiers in Chemistry**" has been chosen as the theme, since it is felt that Chemistry is changing its face to a great extent due to its overlap on side with mathematics and physics and on the other side with biology. This overlap on both extremes has resulted chemistry to loose its original colour and it now exhibits a variety of colours like a rainbow.

The chemical processes have to change its inventory to bio sources and the chemical industry may turn out to be a biochemical based in the coming decade. We have already started hearing about bio refinery, bio-diesel and probably it will also lead to biochemical based chemical industry soon. There can be so many reasons for this change over.

On the scientific side, the introduction of new techniques which can virtually **see** at molecular level has revolutionized the way chemistry is practiced today. One has started looking at nano scale and started designing and fabricating tools at nano scale. This can have far reaching consequences and the expected surprises can be in almost all sectors of human endeavour.

It is therefore natural that the teaching and learning of Chemistry have also to change. This is evident from the methodology that one has to adopt since lecture based courses are not longer appealing and one has to use a variety of soft ware tools to demonstrate and make the molecules **perform** so that the teacher and the taught is enjoying the knowledge transfer process in a totally different platform.

Keeping all these factors into account, this years chemistry programme has been designed around the **Frontiers of Chemistry**. The lectures will be delivered by the research fellows of the National Centre for Catalysis Research, IIT Madras. We express our sincere thanks to each one of them for their effort.

The Science programme of the Children's club has been originally conceived by Mr.Narayanaswamy, the Secretary of the club. His support and enthusiasm have been the sole driving force for conducting this programme year after year. If there is any good arising out of this programme, the credit should naturally go to him.

We do hope you will enjoy the presentations and also find them enough challenging for your scientific curiosity.

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Chapter 1
INTRODUCTION TO FRONTIERS IN CHEMISTRY

B. Viswanathan

1. Introduction

The study of chemistry is changing its face. In 20th century, the study of chemistry required some foundations in mathematics. But as the 21st century is unfolding, the emphasis in chemistry is shifted to biology. In fact, the demarcation line that existed between chemistry and biology is slowly vanishing and now one either talks of chemical biology or biological chemistry. This change over is going to have many ramifications in the study of chemistry. This shift in emphasis will have many other consequences. Some of the changes that one can expect in the study of chemistry would be that the study of atoms and molecules and clusters will become routine and mapping of the wave functions will become possible and hence the chemical reactivity will become a predictable parameter.

The consequence of the overlap of chemistry will biology will manifest remarkably in our study of the energy conversion processes. Hitherto the energy conversion processes are governed by the Carnot limitation since the known and practiced energy conversion processes always involved thermal conversion in one step or other. As all of us know that thermal route for energy conversion is the least efficient one. Living systems as well as the individual components of living systems function with internal generation of energy. Internal generation of energy probably accounts for high efficiency. Chemists have to formulate energy conversion devices as efficient as the living systems and probably this will be one way of understanding life.

The chemical industry has been toying with the idea of achieving 100% selectivity and the possibility of by-product formation has been one of the stumbling blocks for this goal. This has resulted in desire for 100% atom economy and hence led to the concept of green chemistry. We will revert back to this concept at a later stage. Chemical industries have to change their raw material inventory and hence the process principles also have to be changed considerably.

Synthetic chemistry is the corner stone of chemical industry. Synthetic methodologies have to be changed alternate media, (ionic liquids) reaction conditions (high T and P) have to be room temperature and atm pressure. This means that the basic governing principles have be modulated and reformulated.

2. The sub-disciplines where remarkable changes are expected:

Let us consider some of the changes that can be expected. This aspect has been considered in the following paragraphs some selected title-wise the challenges one will face in the changing scene.

2.1. Synthesis and Manufacturing: This will involve creating and exploiting New Substances and New Transformations. Some Challenges for Chemists and Chemical Technologists can be listed as follows:

(i) Develop methods that will enable synthesis of all important molecules in reasonable yields using compact synthetic schemes, so that no useful compound is inaccessible to practical synthesis.

(ii) Develop novel transformations that perform with the selectivities typical of enzymatic reactions, so that geometric factors are more important than the intrinsic reactivity of a molecule.

(iii) Use computer methods to design important target molecules and design efficient ways to make them.

(iv) Exploit combinatorial methods to discover important properties in synthetic materials.

(v) Design synthetic procedures that can be varied systematically for the purpose of optimizing specific properties of the reaction products.

(vi) Understand fully the basic chemical and physical properties of surfaces, especially those of solid catalysts.

(vii) Develop versatile and reliable synthetic methodologies for hard matter (micro-structured materials such as nanoparticles and porous solids) that are as effective as those for synthesis of soft matter (complex organic and bio-molecules).

2.2. Chemical and Physical Transformations of Matter:

This practice of chemistry will give rise to some challenges to the chemists. They can be listed as follows:

(i) They have to perfect the tools to study reaction mechanisms of chemical and biochemical reactions, so the processes can be observed directly and more efficient syntheses can be designed rationally.

(ii) They have to develop reliable computer methods to predict the detailed pathways and rates of unknown chemical reactions, avoiding the need for creating and measuring them to determine their practicality.

(iii) They need to understand the chemistry and properties of large molecules, including biopolymers, to the level that small-molecule chemistry is understood.

(iv) They have to understand the behavior of molecules and substances in unusual environments: at extreme temperatures or pressures, absorbed on solid surfaces, or under shear flow.

(v) They have to learn the chemistry of molecules and substances in their excited states, or at or near their critical points, and at the nanoscale level in which surface characteristics can dominate bulk properties.

2.3. Isolating, Identifying, Imaging, and Measuring Substances and Structures

The tools have to be improved for imaging and determining structure so that detailed chemical structures can be determined with tiny amounts of non-crystalline material.

(i) The ability of instruments to detect and quantify very low concentrations of important substances, even in very small volumes has to be achieved.

(ii) Effective methods for detecting dangerous materials, even when they are hidden have to be formulated.

(iii) Understand the chemistry that occurs in interplanetary and interstellar space, for which spectroscopy is the primary tool available.

(iv) Develop instruments for on-line process control that bring the power of modern analytical and structure-determination methods to chemical manufacturing technology

2.4. Chemical Theory and Computer Modeling: From Computational Chemistry to Process Systems Engineering

(i) Develop computer methods that will accurately predict the properties of unknown compounds.

(ii) Develop reliable computer methods to calculate the detailed pathways by which reactions occur in both ground states and excited states, taking full account of molecular dynamics as well as quantum and statistical mechanics.

(iii) Develop reliable force fields for molecular mechanics calculations on complex systems, including those with metallic elements.

(iv) Invent computer methods to predict the three-dimensional folded structure of a protein - and the pathway by which folding occurs - from its amino acid sequence, so information from the human genome can be translated into the encoded protein structures.

(v) Devise experimental tests to establish the reliability of new theoretical treatments.

2.5. The Interface with Biology and Medicine

(i) Understand fully the chemistry of life, including the chemistry of the brain and memory.

(ii) Invent and learn to manufacture effective antiviral agents and antibiotics to fight all serious diseases, including those caused by drug-resistant pathogens.

(iii) Invent medicines that go beyond treatment to provide cure or prevention of life-limiting conditions and diseases such as cancer, Alzheimer's disease, mental illness, and diabetes.

(iv) Invent better ways to deliver drugs to their targets, including devices that can function as artificial organs.

(v) Learn how genetic variation among individuals will affect their responses to particular medicines.

(vi) Invent biocompatible materials for organ replacements and for artificial bones and teeth.

2.6. Materials by Design

(i) Invent improved structural materials that are stable at high temperatures and easily machined.

(ii) Invent materials with useful electrical and optical properties, including high-temperature superconductivity.

(iii) Invent materials that are lighter, stronger, and more easily recycled.

(iv) Invent materials for surface protection (paints and coatings) that are truly long-lasting and rugged.

(v) Understand and utilize the properties of nanoscale materials and materials that are not homogeneous.

(vi) Build materials with the kind of actuating response found in physiological systems such as muscle.

(vii) Develop and process materials in which complex structural assembly occurs spontaneously or with minimal guidance and in useful timescales to produce durable systems with diverse utility.

(viii) Create nanomaterials technology from nanoscale chemical science.

2.7. Atmospheric and Environmental Chemistry:

(i) Elucidate the entire complex interactive chemistry of our biosphere - the atmosphere, the earth, and its lakes, rivers, and oceans - and provide the scientific basis for policies that preserve our environment

(ii) (ii) Ensure that chemical manufacturing and chemical products are environmentally and biologically benign, never harmful.

(iii) (iii)Learn how to make products that are stable over their necessary life but then undergo degradation so they do not persist in the environment or in living creatures

(iv) Invent agricultural chemicals that do not harm unintended targets in any way and are not overly persistent.

(v) Develop selective catalysts that enable the manufacture of useful products without producing unwanted waste products and without using excessive energy

(vi) Invent processes for the generation and distribution of energy that do not release greenhouse gases or toxic contaminants into the atmosphere.

(vii) Help humans control their population growth by inventing birth control methods that are safe and effective, inexpensive, and widely available and accepted.

2.8. Energy: Providing for the Future:

(i) Develop more stable and less expensive materials and methods for the capture of solar energy and its conversion to energy or to useful products.

(ii) Design inexpensive, high-energy-density, and quickly rechargeable storage batteries that make electric vehicles truly practical.

(iii) Develop practical, less expensive, more stable fuel cells with improved membranes, catalysts, electrodes, and electrolytes.

(iv) Develop materials, processes, and infrastructure for hydrogen generation, distribution, storage, and delivery of energy for vehicles.

(v) Develop photo-catalytic systems with efficiencies great enough to use for chemical processing on a significant scale.

(vi) Learn how to concentrate and securely deal with the radioactive waste products from nuclear energy plants.

(vii) Develop practical superconducting materials for energy distribution over long distances.

The eight subdivisions are in no way exhaustive but they have been chosen because of familiarity and directions in these topics can be formulated with certain degree of certainty.

3. Green Chemistry:

Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products."   The generally accepted principles of Green Chemistry are:

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process to the final product
3. Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Chemical methods should be designed to preserve efficacy of function while reducing toxicity.

5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, innocuous when used.

6. 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.

7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.

8. Unnecessary derivatization (blocking group, protection/deprotection, and temporary modification of physical/chemical processes) should be avoided whenever possible.

9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11. Analytical methods needed to be further developed to allow for real time, in process monitoring and control prior to the formation of hazardous substances.

12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

3.1. Is Green Chemistry an Ethical Imperative for Research in Chemistry?

To answer this question we must consider the following points:

Do we live in a sustainable civilization?

Is the pursuit of sustainability an ethical imperative for humanity?

What role can chemistry play in allowing a high technology civilization to become sustainable?

Is moving technology towards sustainable processes an ethical imperative for chemists?

This leads us to the question of sustainability

3.2. Sustainability: An Ethical Imperative?

In a brilliant book, which should be read by anyone concerned about sustainability, "The Imperative of Responsibility: In Search of Ethics for the Technological Age" (The University of Chicago Press, Chicago, 1984) Hans Jonas argues that there is a need for a new ethics that will better enable our civilization to deal with the power over the ecosphere that it has acquired through science and technology.

The book opens as follows:

"All previous ethics — whether in the form of issuing direct enjoinders to do and not to do certain things, or in the form of defining principles for such enjoinders, or in the form of establishing the ground of obligation for obeying such principles — had these interconnected tacit premises in common: that the human condition, determined by the nature of man and the nature of things, was given once for all; that the human good on that basis was readily determinable; and that the range of human action and therefore responsibility was narrowly circumscribed. It will be the burden of the present argument to show that these premises no longer hold, and to reflect on the meaning of this fact for our moral condition. More specifically, it will be my contention that with certain developments of our powers the *nature of human action* has changed, and, since ethics is concerned with action, it should follow that the changed nature of human action calls for a change in ethics as well: this not merely in the sense that new objects of action have added to the case material on which received rules of conduct are to be applied, but in the more radical sense that the qualitatively novel nature of certain of our actions has opened up a whole new dimension of ethical relevance for which there is no precedent in the standards and canons of traditional ethics."

The greatly increasing pressure of technology-based human activity on the ecosphere has given rise to the uncertainty and the insecurity captured in the concept of sustainability.

Can we continue to operate our civilization as we have been doing without spoiling or even ruining the future possibly for ourselves and almost certainly for our descendants?

Since much of the technological power underlying the sustainability dilemma has been devised by chemists, it is reasonable for chemists to ask how chemistry might be advanced to contribute to the sustainability of our civilization.

Green chemistry is arising as a field representing the practical expression of the willingness of chemists to turn technology towards sustainability.

4. The imperatives of Nano-technology:

Nanotechnology is an enabling technology that will impact electronics and computing, materials and manufacturing, energy, transportation and so on.

- The field is interdisciplinary but everything starts with material science. Challenges include:
    - Novel synthesis techniques
    - Characterization of nanoscale properties
    - Large scale production of materials
    - Application development
- Opportunities and rewards are great and hence, tremendous worldwide interest
- Integration of this emerging field into engineering and science curriculum is important to prepare the future generation of scientists and engineers

5. Dreaming in chemistry

Chemists are familiar with dreaming. This dreaming exercise is going to continue and list us list one of the sets of dream reactions for which heterogeneous catalysts have to be formulated. A few of the reactions are given below

$CH_4 + ½ O_2 \rightarrow CH_3OH$

$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$

$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$

$nCH_4 \rightarrow C_nH_{2n+2} + (2n-2)H_2$

$DME \rightarrow C_2H_5OH$

$H_2 + O_2 \rightarrow H_2O_2$

$2NO \rightarrow N_2 + O_2$

$2N_2 + 2H_2O + 5O_2 \rightarrow 4HNO_3$

Other processes which will dominate the scene include the following:

- Heterogeneous catalysts for assymmetric synthesis
- Photolytic water splitting (hydrogen economy)

- Biomimetics, synthetic enzymes
- Non-thermal processes in general

In addition to this heterogeneous catalysis, it is possible that the sensors field also will face considerable changes. This is because that we have learnt how to functionalize the surfaces and hook bio-molecules on the surfaces which will remarkably change our capability for detection and quantification. It is clear that chemists are in for a tremendous change in the next few years. In Table 1 what are new in chemistry are listed. It must be stated that this is only an indicative list and no way an exhaustive list.

Table 1. What is new in Chemistry?

- **Atmospheric chemistry**
- **Biotechnology**
- **Cell biology**
- **Cell and molecular biology**
- **ceramics**
  Composites
- **Computational Chemistry**
- **Crystallography**
- **Electrochemistry**
- **Harmonic analysis**
- **Liquid crystals**
- **Magnetic technology**
- **Marine geology and geo- physics**
- **Materials science**
- **Microbiology**
- **Microscopy**
- **Molecular biology**
- **Nanotechnology**
- **Oceanic sciences**
- **Optics and photonics**
- **Organic chemistry**
- **Particle technology**
- **Petroleum and geo-systems**
  Photonic band gap materials
- **Photonics**
- **Polymers and plastics**
- **Process industries**
- **quantum computation**
- **Quantum optics and atom optics**
- **Radiocarbon**
- **Soil science**
- **Surface science**
- **Thermodynamics**
- **Tri-biology**
- **The ultra-fast phenomena**

Chapter - 2
PERFORMANCE MATERIALS

M. Helen

Introduction

Performance or *active* or *smart*, material is a material, such as an alloy, ceramic, gel or polymer, that is able to modify their functional characteristics if stimulated with electrical or magnetic fields, temperature, light, pH and moisture. To date the most well established application of performance materials are in the field of piezoelectric, shape memory alloys, magneto/electro-strictive ceramics, magneto/electro-rheological fluids, optics and structural monitoring. They can substitute dozens of actuators and sensors. They are adaptive with the environmental conditions, permits to simplify components, permits to reduce size, weight and cost and new functions can be developed.

Piezoelectric Materials

Many ceramics, polymers and molecules are permanently *polarized*: a part of the molecule is positively charged, while other part of the molecule is negatively charged. When an electric field is applied to these materials, these polarized molecules will align themselves with the electric field, resulting in induced dipoles within the molecular or crystal structure of the material Fig 1. Furthermore, a permanently-polarized material such as quartz (SiO_2) will produce an electric field when the material changes dimensions as a result of an imposed mechanical force. These materials are *piezoelectric*, and this phenomenon is known as the *piezoelectric effect*.

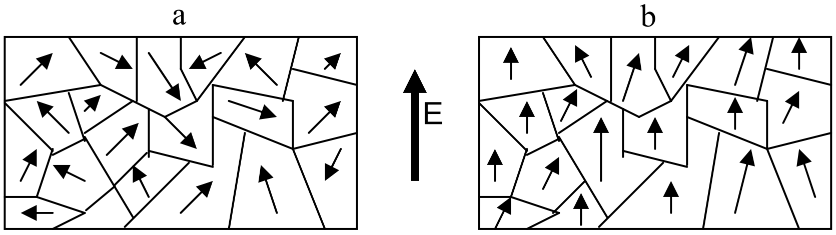

Fig. 1. (a) In the absence of electric field the domains have random orientation of polarization; (b) the polarization within the domains aligns in the direction of the applied electric field

The piezoelectric effect in various crystalline substances is a useful property that leads to the detection of analytes (antibodies, ions, volatile gases and vapors). The piezoelectric sensors (Chemical or biosensor) is thought to be one of the most sensitive analytical instruments developed to date, being capable of detecting antigens in the picogram range. Piezoelectric materials are also used in acoustic (sound) transducers, which convert acoustic waves into electric fields, and electric fields into acoustic waves. Transducers are found in telephones and musical instruments such as guitars and drums. Quartz, a piezoelectric material, is often found in clocks and watches.

Ferroelectric Materials

Ferroelectric materials are crystals which are polar without an electric field being applied. This state is also termed spontaneous polarization. Ferroelectric crystals similar to a ferromagnetic material possess regions with uniform polarization called ferroelectric domains. Within a domain, all the electric dipoles are aligned in the same direction.

Thin films of ferroelectric devices are being considered for application in numerous electronic and electro-optic devices such as nonvolatile semiconductor memories [1], optical waveguide devices, switching capacitors for integrated circuitry, and imaging sensors. Non-volatile ferroelectric memories (NVMs) have several advantages over other memory devices, mainly related to the unique features of write operation (fast, with high endurance, without need for high voltage). Another competitive advantage is the possibility of replicate functionality of several memory types in the same device. In spite of this, they cannot be considered as the universal memory because of the limited read endurance and the destructive read-out.

Shape Memory Alloys

Shape memory alloys are materials that remember their original shape and return to it when heated, even if apparent residual deformation was introduced below a certain temperature. The most effective and widely used alloys include NiTi, CuZnAl, and CuAlNi.

In general, NiTi can exist in a two different temperature-dependent crystal structures (phases) called *martensite* (at low temperature) and *austenite* (at higher temperature). When martensite NiTi is heated, it begins to change into austenite. When austenite NiTi is cooled, it begins to change onto martensite (Fig.2). The temperature at which these phenomenon starts is called austenite start temperature and martensite start temperature respectively. NiTi can have three different forms: martensite, stress-induced martensite (superelastic), and austenite. When the material is in its martensite form, it is soft and ductile and can be easily deformed. *Superelastic* NiTi is highly elastic (rubber-like), while austenitic NiTi is quite strong and hard (similar to titanium)

A variety of forms and the properties of shape memory alloys make them extremely useful for a range of medical applications like aids for disabled, arterial clips, key-hole surgery instruments. These alloys are also used in air conditioners and other home appliances and in automobiles.

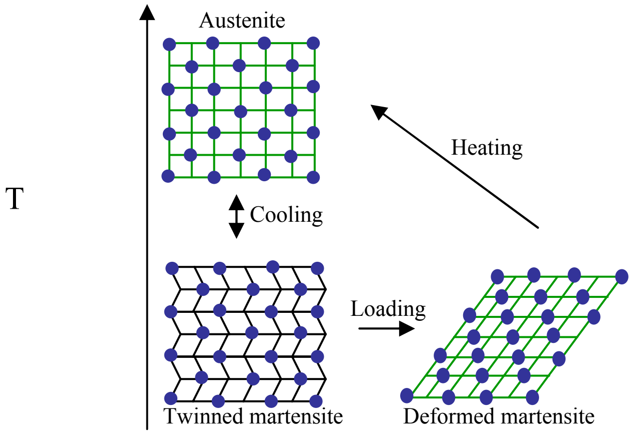

Fig. 2. Transformation from the austenite to the martensite phase and shape memory effect of NiTi alloy

Smart Hydrogels

Hydrogels are a type of polymer that can absorb large amounts of water (99%), and can swell up to 1000% times its original volume. It can be triggered via a number of mechanism such as a change in temperature or pH. The swelling behaviour of responsive hydrogels makes them attractive for microactuator applications. Both temperature and pH-responsive hydrogels have been applied for flow control in microfluidic devices requiring no external power supply.

Earliest biomedical application of hydrogels is as alternative to glasses - contact lenses. Silicone hydorgels and polyacrylamides are used for this purpose due to its good mechanical stability, favorable refractive index and high oxygen permeability.

Degradable poly(2-hydroxyethyl methacrylate) hydrogel with well-defined architectures are used as scaffolds in tissue engineering.

Magneto/Electro-strictive Materials

Magnetostriction is the material property that causes a material to change its length when subjected to an electromagnetic field. Magnetostriction properties also cause materials to generate electromagnetic fields when they are deformed by an external force. Magnetostrictive materials can thus be used as sensors and actuators.

The electrostrictive material undergoes dimensional change under the influence of applied field. Electrostrictive materials strain proportionally to the square of the applied voltage. They are unlike piezoelectric materials in that they are not poled. They are also highly non-linear since they respond to the square of the applied voltage. A typical electrostrictive material is lead magnesium niobate (PMN) used to construct an ultrasonic transducer for non-destructive evaluation.

Magneto/Electro-rheological Materials

Magnetorheological materials experience a dramatic change in their viscosity by application of a magnetic field. These materials typically consist of tiny iron particles dispersed in a fluid. Magnetorheological fluids are used in car shocks, damping washing machine vibration, prosthetic limbs, exercise equipment, and surface polishing of machine parts.

Electrorheological materials exhibits rheological property in presence of an applied electric field. Scientists at the Hong Kong University of Science and Technology have developed a new class of electro-rheological fluids exhibiting 10 times high yield stress (the strength of the materials in solid state) than the previously achievable electro-rheological solid thus opening the vast potential of active mechanical devices such as vibration dampers, shock absorbers, brakes, clutches and valves. This electro-rheological fluid consists of dielectric microparticles dispersed in an insulating liquid- silicone oil.

Electrochromic materials

An electrochromic material is one where a reversible color change takes place upon reduction (gain of electrons) or oxidation (loss of electrons), on passage of electrical current after the application of an appropriate electrode potential. Commercial applications of electrochromic materials in devices include anti-glare car rear-view mirrors, electrochromic strips as battery state-of-charge indicators and electrochromic sunglasses. Proposed applications include ‘smart windows’ (based on modulation of either the transmitted or reflected solar radiation) for use in cars and in buildings, re-usable price labels, protective eyewear, controllable aircraft canopies, spacecraft thermal control, and controllable light-reflective or light-transmissive display devices for optical information and storage.

Transition metal coordination complexes are potentially useful as electrochromic materials because of their intense coloration and redox reactivity. Chromophoric properties arise from low-energy metal-to-ligand charge transfer (MLCT), intervalence charge transfer, intraligand excitation, and related visible region electronic transitions. Because these transitions involve valence electrons, chromophoric characteristics are altered or eliminated upon oxidation or reduction of the complex. Polymeric systems based on coordination complex monomer units, which have potential use in all-solid-state systems, are frequently investigated.

A typical and most widely studied example is the tungsten trioxide (WO_3) system, since its electrochromism was first reported in 1969. Tungsten oxide has a nearly cubic structure which may be simply described as an “empty-perovskite” type formed by WO_6 octahedra that share corners. The empty space inside the cubes is considerable and this provides the availability of a large number of interstitial sites where the guest ions can be inserted. Tungsten trioxide, with all tungsten sites as oxidation state W^{6+}, is a transparent thin film. On electrochemical reduction, W^{5+} sites are generated to give the electrochromic (blue coloration to the film) effect. Although, there is still controversy on the detailed coloration mechanism, it is generally accepted that the injection and extraction of electrons and metal cations (Li^+, H^+, etc.) play an important role. WO_3 is a cathodically ion insertion material. The blue coloration in the thin film of WO_3 can be erased by the electrochemical oxidation. The generalized equation can be written as,

$$\underset{\text{Transparent}}{WO_3 + xM^+ + e^-} \longrightarrow \underset{\text{Blue}}{M_xW^{6+}{}_{(1-x)}W^{5+}{}_xO_3}$$

The fractional number of sites which are filled in the WO_3 lattice is indicated by the subscript x. At low x the films have an intense blue color caused by photoeffected intervalence charge transfer (CT) between adjacent W^{5+} and W^{6+} sites. At higher x, insertion irreversibly forms a metallic “bronze” which is red or golden in color. The process is promoted by cathodic polarization which induces ion insertion and electron injection: the inserted ions expand the lattice of the guest oxide while the compensating electrons modify its electronic structure and in turn its optical properties. It can be stated simply that the injected electrons are trapped by a W^{6+} forming a W^{5+} while M^+ remains ionized in the interstitial sites of the WO_3 lattice. This gives rise to the formation of tungsten bronze having electrical and optical properties different from those of the pristine oxide. In fact, the pristine state WO_3 is a pale-yellow and a poor electrical conductor, while in the intercalated M_xWO_3 state it becomes highly conducting and blue in color.

Conclusion

The significant increase of the level of living and production is connected more often with the launching of new materials with better properties. The concept of engineering materials and structures which respond to their environment is a significant concept. The technological benefits of performance or smart or active materials have begun to be identified and exploited in a wide range of applications from aerospace, to civil engineering and domestic products. It is therefore important that the technological and financial implications of these materials and structures are addressed.

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Chapter - 3

COMPOSITE MATERIALS

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There is an immense need of materials and systems that must in future aim at higher levels of sophistication and miniaturization, be recyclable and respect the environment, be reliable and consume less energy. Composite materials are the perfect option to achieve the above goals. Composite materials already made their impact in much scientific advancement. For example composite materials usage has increased in number of products, starting from simple consumer goods to advanced aerospace space structures. The composite materials are nothing but hybrid materials formed by integration of two or more materials. They have different properties from their constituents. The engineering of these materials associates with the meeting the desired properties. The remarkable enhancement in the physical and chemical properties of the composite materials with slight modification of constituents drew the attention of the world towards these composite materials. The ability of these materials has extended their applications in many research fields for specific applications because of the above mentioned tunable properties.

Composite materials can be classified based on the presence of polymer as the one constituent in the composite i.e, polymer based composites and non-polymer based composites. The majority of composite materials are polymer based composites. The interesting materials among the polymer based composites are organic – inorganic composite materials, as these composite materials can solve the challenges in the field of future technology such as energy supply, storage and production(fuel cells, batteries, super capacitors, solar cells) and information technology. Ideally, the portioning of the inorganic and organic species on the nanometer scale is expected to creat a homogeneous composite showing the advantageous physico-chemical properties of both moieties. To date for the organic moiety, the main focus of research has been on polymers(e.g. proton exchange membranes in fuel cells). Attractive candidates for the inorganic parts are semi conductors, (such as TiO_2, CdS) and magnetic oxides. One of the most prominent recent examples of such nanocomposites are novel solidstate solar cells. They are based on films containing semiconductive, nanocrystalline TiO_2, an electrolyte and a sensitizing dye. Further important examples of inorganic components are magnetic nanoparticles, such as Fe_2O_3, which could be used for any kind of fluidic magnetic material. Considering these potential applications, composites should fulfill the following requirements (among others): high conductivity of the electrolyte, low vapor pressure and reasonable thermal stability of the organic part (with respect to the conductivity, etc.), optimized viscosity, homogenous distribution of the inorganic and organic phases on the nanometer scale (no macroscopic phase separation), solvent- free processing, a reasonable chemical stability (electrochemical, redox, and hydrolytic stability) and improved processing properties with regard to fluidity requirements (films). The properties of the inorganic and organic species should be maintained in the composite, but eventually also new desired properties could be obtained. These composites can also used to decrease other properties like electrical conductivity or permeability for gases like oxygen or water vapor. Organic-inorganic hybrid materials allowed the development of new materials for industrial applications in many areas: optics, electronics, ionics, mechanics, energy, environment, biology, medicine for example as membranes and separation devices, functional smart coatings, fuel and solar cells, catalysis, sensors and intelligent therapeutic vectors that combine targeting, imaging, therapy and controlled release properties.

Several organic–inorganic composite materials are existing in nature. Nature has remarkable ability of combining the organic and inorganic components at the nanoscale. This allows the construction of several natural materials that found a compromise between different properties of functions (mechanics, density, permeability, colour, hydrophobia, etc.). This high level integration associates several aspects: miniaturization whose object is to accommodate a maximum of elementary functions in a small volume, hybridization between organic and inorganic components optimizing complementary possibilities, functions and hierarchy. As far as man made composite materials are concerned, the possibility to combine properties of organic-inorganic components for materials design and processing is a very old challenge that likely started since ages (Egyptian inks, green bodies of china ceramics etc.).

The organic – inorganic composites are not simply physical mixtures. The constituents of organic and inorganic parts form miscible homogeneously composite systems or heterogeneous systems where at least one of the components domains has a dimention ranging some Å to several nanomaterials.

The properties of these composite materials are not only the sum of the individual contributions of both phases, but the role of the interfaces could be predominant. Based on the nature of the interface these materials can be divided into two classes.

class I, organic and inorganic components are embedded and only weak bonds (hydrogen, vander Waals or ionic bonds) give the cohesion to the whole structure. In class II materials, the two phases are linked together through strong chemical bonds (covalent or iono-covalent bonds).

Maya blue is an excellent example for the class I composites. Maya blue is a hybrid organic–inorganic material with molecules of the natural blue indigo encapsulated within the channels of a clay mineral known as palygorskite. It is a manmade composite material that combines the color of the organic pigment and the resistance of the inorganic host, a synergic material, with properties and performance well beyond those of a simple mixture of its components. The pictures made by using Maya blue pigment had withstood more than twelve centuries under different severe atmospheric conditions and showed extreme stability and resistance towards biodegradation.s

Synthetic strategies for the synthesis of composite materials:

Conventional sol-gel or hydrothermal routs are used to synthesize amorphous composite materials. Organically modified metal alkoxides or metal halides when condensed with or without simple metallic alkoxides amorphous organic inorganic composites will be formed. The solvent may or may not contain a specific organic molecule, a biocomponent or polyfunctional polymers that can be crosslinkable ot that can interact or be trapped within the inorganic components through a large set of interactions (H-bonds, π- π interactions, van der Waals). These stratergies are simple, low cost and yield amorphous nanocomposite materials.

These materials, exhibiting infinite microstructures, can be transparent and easily shaped as films or bulks. They are generally polydisperse in size and locally heterogeneous in chemical composition. However, they are cheap, very versatile, present many interesting properties and consequently they give rise to many commercial products shaped as films, powders or monoliths.

The use of bridged precursors such as silsesquioxanes $X_3Si–R_9–SiX_3$ (R_9 is an organic spacer, X = Cl, Br, OR) allow the formation of homogeneous molecular hybrid organic–inorganic materials which have a better degree of local organisation. In recent work, the organic spacer has been complemented by using two terminal functional groups (urea type). The combination within the organic bridging component of aromatic or alkyl groups and urea groups allows better self-assembly through the capability of the organic moieties to establish both strong hydrogen bond networks and efficient packing via p–p or hydrophobic interactions.

Hydrothermal synthesis in polar solvents (water, formamide, etc.) in the presence of organic templates had given rise to numerous zeolites with an extensive number of applications in the domain of adsorbents or catalysts. More recently new generations of crystalline microporous hybrid solids have been discovered. These hybrid materials exhibit very high surface areas (from 1000 to 4500 $m^2 g^{-1}$) and present hydrogen uptakes of about 3.8 wt% at 77 K. Moreover, some of these new hybrids can also present magnetic or electronic properties. These hybrid MOF (Metal Organic Frameworks) are very promising candidates for catalytic and gas adsorption based applications.

Dispersion of nanobuliding blocks (NBBs): The NBBs can be clusters, organically pre- or post- functionalized nanoparticles (metallic oxides, metals, chalcogenides, etc.), nano-core–shells or layered compounds (clays, layered double hydroxides, lamellar phosphates, oxides or chalcogenides) able to intercalate organic components. These NBB can be capped with polymerizable ligands or connected through organic spacers, like telechelic molecules or polymers, or functional dendrimers.

Templated growth of inorganic components on organic surgactants: in this approach the selfassembly of organic surfactants into preorganized shapes have been used as templates for the inorganic components, where they undergo condensation and forms continuous ordered network. This approach yields a new class of periodically organised mesoporous hybrid silicas with organic functionality within the walls. These nanoporous materials present a high degree of order and their mesoporosity is available for further organic functionalisation through surface grafting reactions. After removal of the organic template a highly ordered porous silica network will be formed this can be further used like a template for the formation of mesoporous carbons.

Composites preparation by using electrospinng**:** Electrospinning provides a simple and versatile method for generating ultrathin fibers from a rich variety of materials that include polymers, composites and ceramics. Electrospinning (a drawing process based on electrostatic interactions) provides a simplest approach to nanofibers with both solid and hollow interiors that are exceptionally long in length, uniform in diameter and diversified in composition. Unlike other methods for generating 1D nanostructures, the formation of a thin fiber via electrospining is based on the uniaxial stretching (or elongation) of a viscoelastic jet derived from a polymer solution or melt.

Fibers and non-woven porous mats of SWNT reinforced polymer nanocomposite films produced by using electrospinning are found to be potential material for spacecraft applications. Next generation spacecraft will require ultra-lightweight materials that possess specific and unique combinations of properties such as radiation and atomic oxygen resistance, low solar absorptivity, high thermal emissivity, electrical conductivity, tear resistance, ability to be folded and seamed, and good mechanical properties. The objective of this work is to incorporate sufficient electrical conductivity into space durable polyimides to mitigate static charge build-up. The challenge is to obtain this level of conductivity (10^{-8} S/cm) without degrading other properties of importance, particularly optical transparency. Several different approaches were attempted to fully disperse the SWNTs into the polymer matrix. These included high shear mixing, sonication, and synthesizing the polymers in the presence of pre-dispersed SWNTs. Acceptable levels of conductivity were obtained at loading levels less than one tenth weight percent SWNT in the polymer – SWNT composites (prepared by using electrospinning) without significantly sacrificing optical properties

Applications of organic-inorganic composite materials:

The choice of the polymers is usually guided mainly by their mechanical and thermal behavior. But, other properties such as hydrophobic/hydrophilic balance, chemical stability, bio-compatibility, optical and/or electronic properties and chemical functionalities (i.e. solvation, wettability, templating effect, etc.) have to be considered in the choice of the organic component. The organic in many cases allows also easy shaping and better processing of the materials. The inorganic components provide mechanical and thermal stability, but also new functionalities that depend on the chemical nature, the structure, the size, and crystallinity of the inorganic phase (silica, transition metal oxides, metallic phosphates, nanoclays, nanometals, metal chalcogenides). Indeed, the inorganic component can implement or improve electronic, magnetic and redox properties, density, refraction index etc.

Organic molecules (dyes and active species) in amorphous sol-gel matrices: In the development of optical systems such as luminescent solar concentrators, dye lasers, sensors, photochromic and photovoltaic devices, the organic molecules play an important role. However, the thermal instability of these compounds has precluded their incorporation into inorganic oxide matrices. By using sol–gel derived glasses this limitation has been minimized. Since then, many organic dyes such as rhodamines, pyranines, spyrooxazines, chromemenes, diarylethenes, coumarins have been incorporated into silica or aluminosilicate based matrices, giving transparent films or monoliths with good mechanical intigriity and excellent optical quality.

‘‘Silica–organic chromophore–surfactant’’ pH sensitive hybrid composites in a wide acido-basic range. Indeed, the co-entrapment in silica based monoliths of the surfactants with an extensive series of pH indicators greatly modifies the indicating performance of the pH probe; Photochromic materials designed from spyrooxazines embedded in hybrid matrices that give very fast optical responses depending on the tuning of dye–matrix interaction. This implies a perfect adjustment of the hydrophobic – hydrophilic balance. Such novel materials can be synthesized either from cocondensation between $MeHSi(OR)_2$ and $HSi(OR)_3$ reactive precursors or from telechelic $[(COO)PEG]^{2-}$ chains connected by $[(BuSn)1_2O_{14}(HO)_6]^{2+}$ tin-oxo clusters. Both hybrid matrices are flexible and can incorporate large amounts of photochromic dyes in soft aprotic domains allowing intense and fast optical responses.

Several drastic conditions are required to elaborate efficient solid-state organic dye lasers. Indeed the laser material must exhibit excellent transparency without scattering, well-polished surface, good slope efficiency, high output energy pumping, sufficient thermal conductivity, long lifetime, and stability to aging. These exigencies can be achieved in

composite materials by optimizing the dye/matrix system.

Composite materials also found applications in the field of cosmetics and controlled release of ‘‘active ingredients’’ and, in particular, for applications concerning skin care and protection. They are based on the encapsulation of active organic components within more or less porous silica micro-capsules. Undesirable skin alterations and melanomas created by sun induced premature skin aging need the use of efficient but biocompatible sunscreens. Nowadays, commercial sunscreens are directly applied to the skin and usually contain an extremely high amount of active ingredients. This can be detrimental to health when they are adsorbed by skin and they are not photostable, thus generating free radicals that may cause damage to the DNA. The hybrid materials developed by Sol–Gel technologies answered to these points. Indeed, by encapsulating the active organic UV filters (80% w/w of the final product) in silica micro-capsules the contact of these potent chemicals with the skin is reduced, and damage from free radicals that may get trapped within the porous host is prevented. These ‘‘UV-pearls’’ incorporated into a suitable cosmetic vehicle to achieve high Sun Protection Factors (SPF), while affording an improved safety profile as the penetration of the UV absorbers is markedly reduced, have already been adopted by companies for sunscreens and daily wear cosmetics. Silica rainbow pearls containing organic dyes have also been developed for cosmetics applications and silica active-pearls containing an effective acne medication such as benzoyl peroxide, which are as effective as antibiotics but do not causes bacterial resistance or stomach upset. Benzoyl peroxide in direct contact with skin provokes skin irritation, dryness and hyper-pigmentation in many patients. Sol–gel active-pearls have undergone successful commercial development because embedding the benzoyl peroxide active ingredient in a silica shell prevents it from coming into contact with the epidermis while gradually delivering it into the follicular region where acne bacteria are found.

Composites for biomedical applications:

Natural materials offer remarkable hydrodynamic, aerodynamic, wetting and adhesive properties. Evident interesting applications concern surface coatings with anti-fouling, hydrophobic, protective or adhesive characteristics and also cosmetic products. One way to take advantage of the emerging field of biomimetics is to select ideas and inventive principles from nature and apply them in engineering products.1 Materials reproducing structures described in animals and plants already exist: ‘‘Riblets’’ are plastic films covered by microscopic grooves inspired by shark or dolphin skin that are placed on airplane wings in order to reduce the hydrodynamic trail and economize fuel.

Inorganic–organic composite materials can be used as filling composites in dental applications. These composites feature tooth-like properties (appropriate hardness, elasticity and thermal expansion behaviour) and are easy to use by the dentist as they easily penetrate into the cavity and harden quickly under the effect of blue light. Moreover, these materials feature minimum shrinkage, are non-toxic and sufficiently non-transparent to X-rays. However, the composition of the hybrid material and the chemistry behind it depends strongly on its later application: as filler/particles, as matrix materials, as composites, as glass ionomer cements or as bonding. Traditional plastic filling composites had long-term adhesion problems and a high degree of polymerisation shrinkage resulting in marginal fissures. The dual character of the ORMOCERs as inorganic–organic copolymers is the key for improving the properties of filling composites. The organic, reactive monomers are bound in the sol–gel process by the formation of an inorganic network. Thus, in the subsequent curing process, polymerisation takes place with less shrinkage. Furthermore, abrasion resistance, in particular, is significantly enhanced by the existing inorganic Si–O–Si network.

Composite materials for microelectronics:

Organically modified resins retain important roles in electrical component coatings such as resistors and molding compounds, as well as spin-on dielectrics in microelectronic interlayer and multilayer dielectric and planarization applications. Simply methyl or hydride substitution of alkoxysilanes allowed the development of commercial products such as: Glass-Rock1 by Owens–Illinois, for sealing cathode-ray tubes; Techneglas1 by NEC, for dielectric applications, Accu-Spin1 by Honeywell, for spin-on glass applications, etc.

Composite materials for membrane applications:

Protonic conducting memrane can be used in many energy technological applications such as fuel cells, water electrolysis, hydrogen separation, sensors and other electrochemical devices. However, polymer electrolyte membrane usually lacks thermal stability, resulting in narrow operational temperature windows. So, a new class of polymer membrane with high temperature stability and protonic conductivity is desired for many industrial applications. This has been achieved by preparing organi-inorganic composite membranes. In these membranes the inorganic components gives the stability and required protonic conductivity and the organic polymers enhances the flexibility to process it into thin films.

In the fuel cell core, the main important part for cell efficiency and durability is the proton exchange membrane. Its role is to allow proton transport from the anode to the cathode, to be an electron nonconductive material and to act as a gas separating barrier (H_2, O_2). Typical membranes are made of organic polymers containing acidic functions such as carboxylic, sulfonic or phosphonic groups which dissociate when solvated with water, allowing H_3O^+ hydrated proton transport. Therefore, the membrane performance is related to the ionic group amount and to the hydration rate. Moreover, the membrane needs to be chemically (highly acidic medium) and thermally (from 80 to 140 °C) stable. Nafion®, is dominating the market of ionomeric membranes for fuel cell, shows high proton conductivity below 100 °C and high chemical stability. While it has the disadvantage of very high methanol permeability, which not only reduces fuel efficiency but also decreases the cathode performance. Proton exchange membranes with lowmethanol permeation may allow the use of methanol fuels with higher concentration that increases the energy density. The drawback of perfluorinated membranes has prompted research into alternative composite membranes based on hydrocarbon polymer.
In this sense, proton conducting polymers such as poly- (benzylsulfonic acid) siloxane (PBSS) with very high proton conductivity has been prepared by a sol–gel process. The synthesis occurs in 2 steps: (i) triethoxybenzylsilane is first hydrolyzed and self condensed into a polybenzylsiloxane polymer (PBS), reaching an average molecular weight Mw = 20000, in the presence of trifluoromethanesulfonic acid as a catalyst, and then (ii) the sulfonation of PBS into PBSS is carried out in anhydrous dichloromethane. The PBSS obtained is thermally stable up to 300 °C. Moreover, the high coductivity (σ ranges from 2×10^{-3} to 10^{-2} S cm^{-1}) of PBSS, as well as its tensile strength, allow its use in several electrochemical devices at room temperature.

Conducting polymer composites in energy storage applications:

The electrochemical activity of the inorganic metal oxide cluster can be harness by integrating them with conducting organic polymer matrix to form a composite material.

Molecular hybrid materials formed from polyoxometalates dispersed in conducting polymers represent an innovative concept in energy storage. Energy storage devices such as fuel cells and renewable energy devices, such as photovoltaic or dye sensitized solar cells, will need the support of efficient energy storage technologies. Rechargeable lithium batteries and electrochemical supercapacitors are two of the most prominent alternatives in this respect. The development of new and efficient electrode materials is the challenge in the field of electrochemical supercapacitors. In this line of work we can find three kinds of electrode materials, namely, high surface area carbons, metal oxides and conducting polymers. But in addition to these conventional types, alternative materials such as hybrid organic –inorganic composite materials have found to be potential materials as supercapacitor electrodes. Conducting polymer and polyoxometalate composites are such emerging class of composite materials. Polyoxometalates resembles metal oxides, from both structural and electronic points of view; they are formed by a small number of metal centers (typically 6-18 tungsten or molybdenum moieties) coordinated by bridging oxygen atoms; they present well-known structures. And they undergo reversible mulielectron reduction process both electrochemically and photochemically, similarly to quantum sized oxide particles. The electrochemically deposited composite of the polyaniline and phsphomolybdic acid on graphite showed specific capacitance values upto 120 F/g. Another interesting class of composite electrode materials for supercapacitors are carbon nanotube (CNT) –RuO_2 composite. Carbon nanotubes are having high surface area, electronic conductivity and exhibits double layer capacitance. Whereas RuO_2 exhibits pseudocapacitnce. CNT-RuO_2 compoiste electrodes showed better specific capacitance because of the combination of double layer capacitance from CNT and pseudcapacitance from RuO_2.

Carbon nanotube (CNT) - metal nanoparticle(NP) composites:

CNT-NP composites have already proved as excellent electrocatalytic materilas with superior activities. Carbon nanotubes with high electronic conductivity and surface area along with ultimate dispersion of metal nanoparticles, enhances the activity of metal nanoparticles by anchoring them on CNTs through surface carboxylic groups. PtRu/CNT have shown better performance as an anode electrocatalyst for methanol oxidation in direct methanol fuel cells. In the same way Au/MWCNT showed remarkable elecrocatalytic activity towards oxygen reduction in acid medium.

Stealth technology:

This technology has been used with aircrafts, ships and missiles in order to make them less visible (ideally invisible) to radar, infrared and other detection methods.

Radar (Radio detection and ranging) is a system that uses electromagnetic waves to identify the range, altitude, direction, or speed of both moving and fixed objects such as aircrafts, ships, motor vehicles, etc. A transmitter emits radio waves, which are then reflected by the target and detected by a receiver, typically in the same location as the transmitter. The radar antenna measures the time it takes for the reflection to arrive and with that information can tell how far away the object is. In order to make the objects such as aircrafts not be detected by radars, we have to make the body of the aircraft in such a way that it will not reflect the radio waves send by the radar.

The metal body of an airplane is very good at reflecting radar signals and this makes it easy to find and track airplanes with radar equipment. The aim of stealth technology is to make an airplane invisible to radar. The ability to be undetected by radar, or perhaps less detectable, clearly gives a major advantage over enemy.

There are two different ways to create invisibility.There are two different ways to create invisibility:

- The airplane can be shaped so that any radar signals it reflects are reflected away from the radar equipment.
- The airplane can be covered in materials that absorb radar signals.

The use of radar absorbing materials (RAM) for the suppression of radar signature and the removal of false echoes from radar screens has been used for many years. The majority of the materials used have been of a parasitic nature, usually in the form of flat flexible sheets, heavily loaded with iron or ferrite powders that are bonded to the structure requiring treatment. Because of the heavy coatings the weight if the aircraft increases, it’s a hurdle. By reducing in weight of the aircraft the air friction during the motion can be reduced and thereby the speed can be increased. We can achieve this by incorporating the radar absorbing property within the structure rather than applying it parasitically would reduce the prohibitive weight penalties.

Hybrid coatings based on organically modified silicate (Ormosil)/$Ni_{0.5}Zn_{0.5}Fe_2O_4$ (10–30 wt.%) were synthesized through a sol–gel technique. Tetraethylenepentamine, 3-glycidoxypropyltrimethoxysilane, tetraethoxysilane and $Ni_{0.5}Zn_{0.5}Fe_2O_4$ were used as precursors for the hybrid coatings. These hybrid films were deposited via spin coating onto an aluminum alloy in order to improve the corrosion protection and to act as infrared stealth coatings.

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Chapter - 4
NANOMATERIALS

S. Navaladian

Introduction

The word "nano" originates from the Greek word for dwarf, and used to mean something tiny. As a prefix for a unit of time or length, it means one billionth of that unit. One nanometer (nm) is 10^{-9} meter. Nanomateials represents those materials that are in the size in the nano range. Bulk materials can be defined as the material made out large number atoms or ions that give rise to dimension of micro range or more. Many water molecules can easily occupy a sphere 1 nm in diameter. The DNA double helix is approximately 2 nm wide. The next question that arises in one's mind is as to how those small particles can be seen. Even the small aunt cannot be seen through our eye clearly in spite of the fact that its size is of millimeter range. When some microscopist could answere this question, the acceleration in the field of nanochemistry was tremendous. Today, one can see the word nano everywhere even in the commercial advertisement. It is because of versatile applications of nanomaterials. In general, as per the human nature, one believes some information only if he could see or notice it. That is the reason nanochemistry has developed only after the invention of electron microscopes. Today the researches in various fields are working in and around this nanochemistry. Apart from the interest, all our researches look some thing useful for our mankind. The proverb 'necessity is the mother of invention' has some meaning. In that way if one looks at the nanochemistry the applications are countless. It is because that entirely different properties and characters are exhibited by the materials in the nanorange.

Before going into the details of the nanomaterials, the basics of the nanochemistry is important. The morphology of the particles also affects the properties. In general, apart from the spherical shape, the material adopts so many other morphologies. The formation of non spherical morphology is due to some restriction during their growth. These materials are known as nanostructure materials. They are categorized into the three as to 1, 2 and 3-dimensional materials as shown in the Figure. 1.

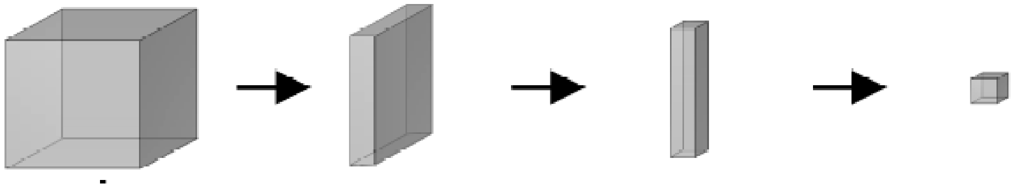

Fig. 1. The materials in various dimensions

Nanostructured materials:

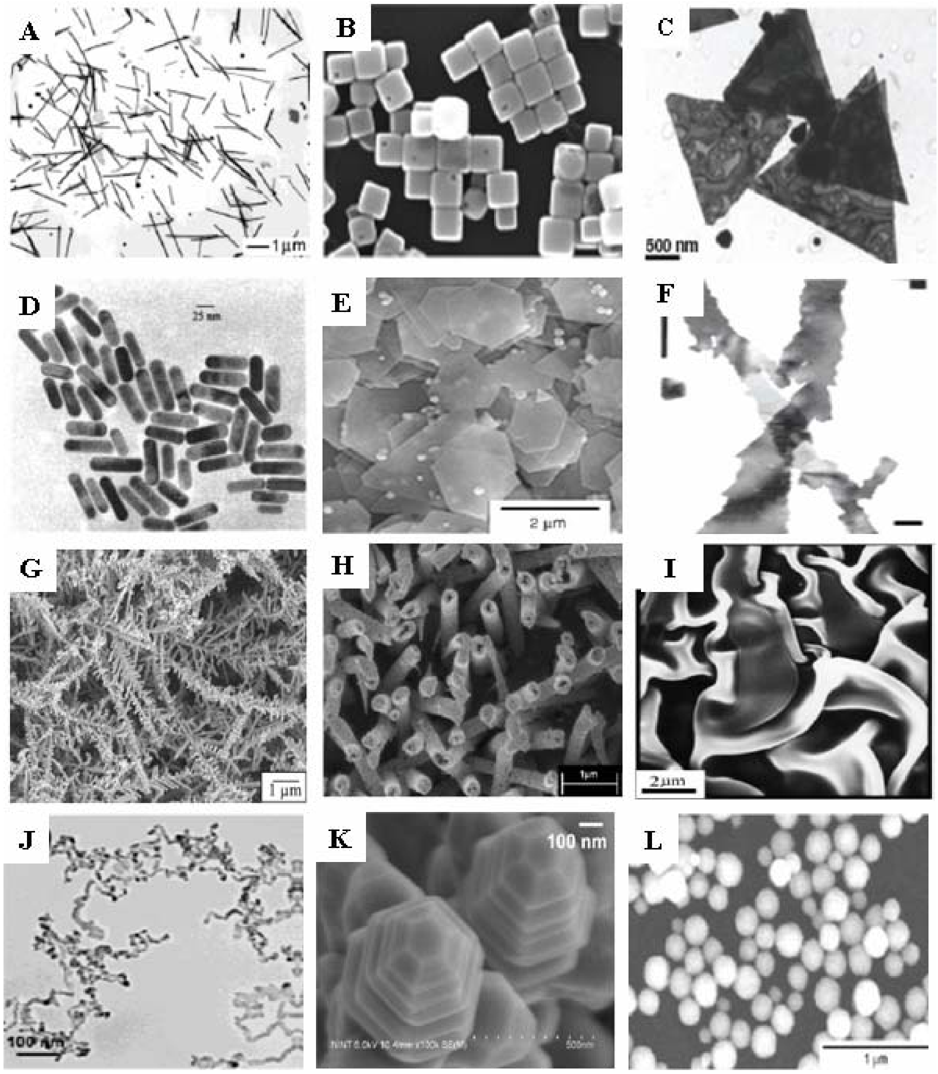

Fig. 2. TEM pictures of naoparticles of different morphological structures (A) rods (Ag) (high aspect ratio), (B) cubes (Au) , (C) triangular (Au) , (D) rods (Au) (low aspect ratio), (E) plates (Au), (F) strips (Au), (G) dendrites (Ag), (H) tubes (Au), (I) cloths (Ag), (J) wires (Au), (K) inukshuks (Au), (L) spheres (Au)

All the materials are found to be forming the nanostructured materials. Because of the restricted growth of the materials the formation of various morphologies such as nanorods, nanowires, nanotubes, nanoplates, triangles, nanocubes, hierarchical structures take pace. Examples of these materials are shown in Figure 2. Because of different dimension in different directions of these materials, the band structure varies from the spherical to other morphologies as shown in Figure. 4.

Apart from these, hierarchical structures are also known (Figure.2 (K)), where primary building blocks associate into more complex secondary structures that are integrated into the next size level in the hierarchy. This organizational scheme continues until the highest level in the hierarchy is reached. These hierarchical constructions may exhibit unique properties that are not found in the individual components. Hierarchy is a characteristic of many self-assembling biological structures and is beginning to emerge as a hallmark of materials self-assembly that encompasses multiple length scales. Superlattices, the type of nanoparticle array, are known in the nanochemistry. A periodic multilayer which is synthetic and where a unit cell, consisting of successive layers that are chemically different from their adjacent neighbors, is repeated. The example is shown in Figure 3 where Au cubic particles superlattice with oleic acid is shown. Oleic acid can be seen in between the cubic Au particles.

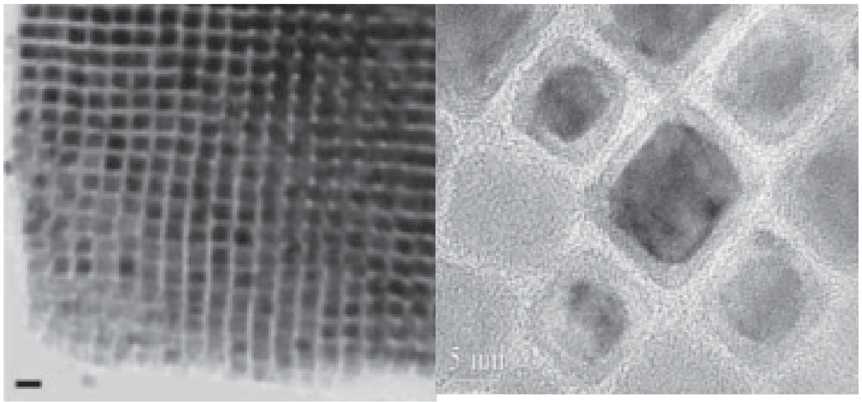

Fig. 3. TEM pictures of superlattice of the gold nanoparticles and oleic acid

Properties:

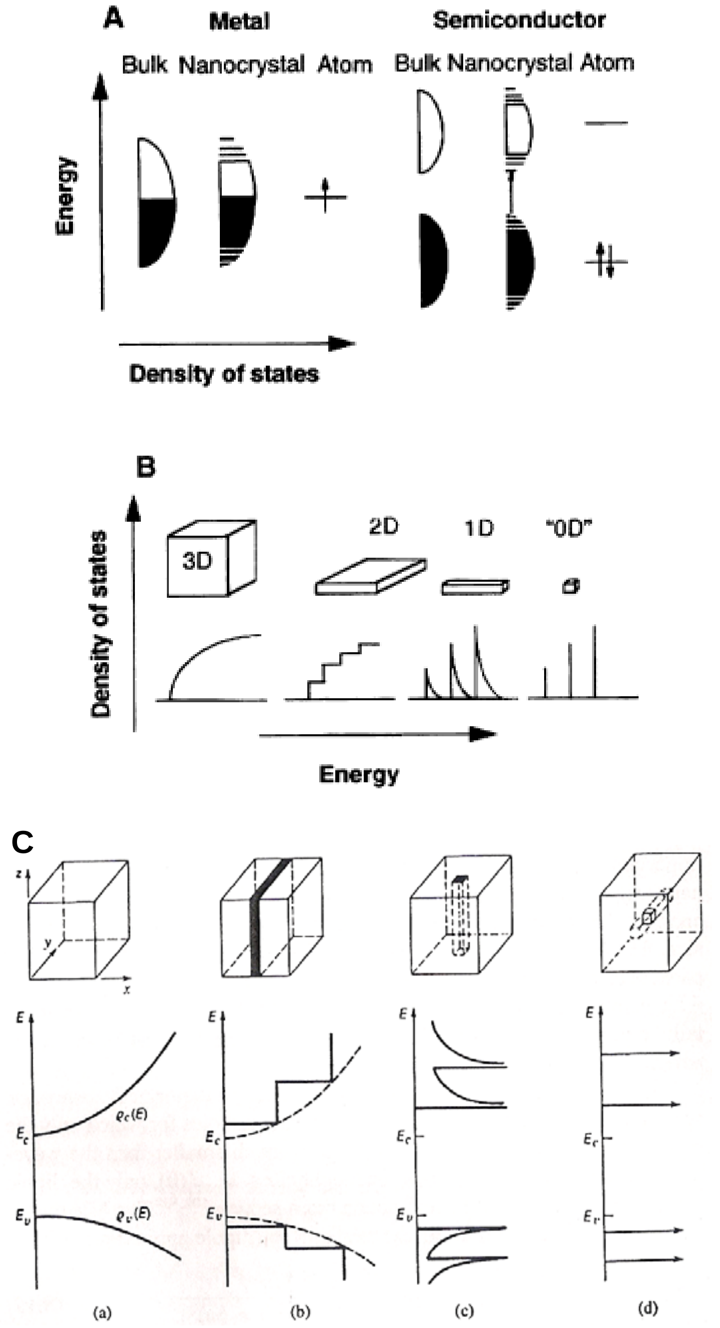

Fig. 4. The variation of the band gap (A) and the density of states (B), and band structure(C) variation with respect to the change in the morphogy of the Nanosemicondctor

The change in the properties of the nanomatreials as compared to the bulk materials is tremendous. This change in the size makes these materials to have different electronic changes in terms of energy and number of levels. This makes these materials behave electronically different. These in turn alter the redox behavior of the materials. Physical properties such as surface area also vary due to the availability of more interfaces in the small range. The surface to volume ratio is more in the nanostate than in the bulk. Band gap and density state diagram are shown in Figure 4.

Properties of nanomaterial that are different from bulk are variation of the redox properties, band gap variation, anomalous melting points, enhance toughness and strength, unusual crystal structures (in metals). As for the band gap, it increases as the particle size decreases due to the loss of in-between energy levels during the size reduction. This variation of band gap can be realized from the UV-Vis spectrum of the corresponding materials. The blue shifts indicate the formation of the nano semiconductors, namely, TiO_2. This property is well exploited in the photocatalysis, that is light harvesting.

In catalysis, these nanomaterials are efficient in terms of surface area and redox properties. Au has been known as inactive material up to the last decade. However, it was understood that Au is catalytically active when it is below 5 nm. This indicates that redox properties are different when it is below 5 nm. Now the gold is known active for many reactions. The problem of the size effect remains unclear. The making of these nanomaterials need some specific methodology.

Synthesis of nano materials:

The major classification of synthesis of these nanomaterials is of two types,

1. Top down approach
2. Bottom up approach

Top-down approach:

The nanosized materials are prepared at the expense of the bulk material in this technique. Examples are ball- milling and laser ablation techniques. These methods enable one to synthesize the particles of polydispersity. Poly dispersity means the particles of different size range. This is the disadvantage of this method.

Bottom –up approach:

The nanosized materials are be prepared from dissolved species to nano particles through the chemical reactions such as precipitation or reduction. Examples are chemical reduction, thermal decomposition methods, and controlled precipitation. Nevertheless, this method can be used to synthesize the particles of almost in the similar size range (monodispersity). The synthesis of Au nanoparticles using the sodium borohydride as reducing agent and citric acid as the capping agents is an opt example for this method. This method yields the Au particles of 2-4 nm. It is not easy to achieve because it needs the some strategy using the chemistry of the reaction. In other words, the colloidal chemistry takes the main role in the synthesis based chemical methods in solution. The nucleation and growth rate should be controlled. In general, the growth of the nuclei occurs at once the saturation occurs in the growth solution. The kinetics of the growth of the particle is fast to attain the stable particle size. The initially formed tiny particles are called as nuclei over which the other atoms or molecules stacks and thus the growth occurs. The driving force for this growth is to reduce the surface energy of the small growth species. This growth extends as long as the atoms are available in the solution. In this case, if all nuclei are formed at once, this is known as homogeneous nucleation. All the nuclei may be formed at different times. Then it is called as heterogeneous nucleation. Homogeneous nucleation results in the monodispersed particle whereas the heterogeneous nucleation gives rise to the formation of poly-dispersed particles. Thus, by controlling the growth, one can achieve the needs in synthesis of the nanonmaterial.

Capping agents:

Capping agents are the chemical compounds that have the functional groups, through which they can have chemically interact with the surface of the nanomaterials. Because of this interaction of the metal and capping agents, the agglomeration of the small particles to the big articles is prevented. This chemical affinity of the particular compound towards particular material varies. For examples, thiols cap the Au surface better than the other metals and amine based capping agents bind Ag than the Au surface. Examples of these capping agents are thiols, citric acid or citrates and polymers like polyvinyl pyrollidone (PVP), poly vinyl alcohol (PVA). These capping agents not only act as stabilizing agents, but also act as morphology-directing agents. The preferential adsorption of capping agents on the particular plane of the nuclei leads to the formation of anisotropic structures. It is worthwhile to mention that the growth rate of the different plane varies due to there stability. However, this preferential growth of the capping agents changes the fate of the growth by arresting the particular planes. This cetyltrimethyammonium bromide (CTAB), a capping agent, preferentially adsorb at {100} plane of the Au nuclei, so that formation of Au nanorods along the {111} direction occur. In general, the preparations of any nanomaterial can be achieved by using the suitable methodology. In literature, various methods are known for the synthesis of nanomaterials. Some of the methods are template synthesis, solvotheremal and sol-gel technique. Once the materials are synthesized, they have to be characterized by using the electron microscopes like transmission electron microscopes (TEM) to confirm whether the nanoparticle are formed.

Characterization:

The characterization techniques such as TEM are necessary to prove the nanoparticle formation in the nanochemistry. In the case of metal nanoparticles like Au and Ag, the UV-visible spectrum is also important to confirm their formation. The metals like Au, Ag, Al, Cu, and Na are able to produce the color when they are in the nanostate.

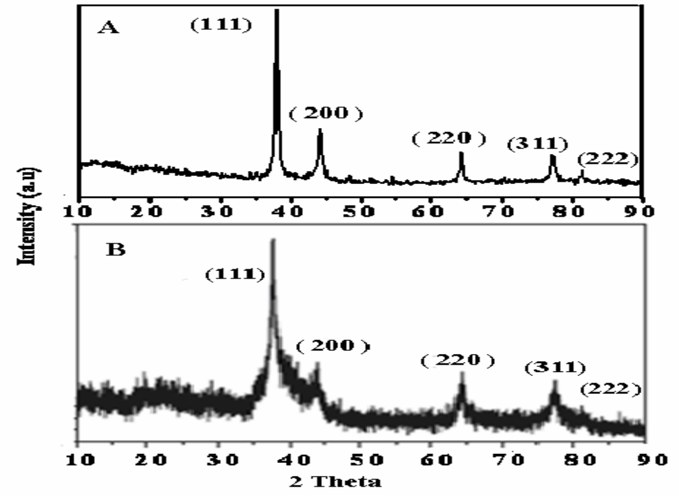

Fig. 5. XRD powder pattern of the bulk silver (A) and silver nanoparticles (B)

In other words, this phenomenon is absent in the case of their bulk counter parts. These surface electrons of the metals are called as plasmon. This color exhibiting properties are known as surface-plasmon resonance for Au and Ag nanoparticles. These surfaceelectrons interacting with the particular wavelength of the light. Why it is only confined to the nanometal is that wavelength should be greater than the size of the particles. The semiconductor nanomaterials can be also confirmed by the blue shift in the absorption attributed to the increase in the band gap. XRD powder pattern is also important characterization technique for the nanomaterials. In general, XRD pattern of nanomaterials will show the broadening of the peaks (Figure 6).

TEM and SEM (scanning electron microscope) are operating with different principle that the transmitted electron and scanned electron respectively. Scematic of TEM and SEM are shown in Figure. 6. The TEM needs higher frequency of electron than the SEM. Typical TEM works at 100 KV of electron beam that penetrates the carbon-coated films where the sample is dispersed. Detector receives the transmitted electrons and it will be converted to optical black and white picture and saved in the computer or photographed using the in-built camera. Nanoparticle present in the grids can be seen in the shadow as can be from Figure 7. SEM operated with low energy of 30 KV where the sample is just scanned with the electron beam, the reflected electrons are detected, and the image is thus created. It is operating with the same principles of normal photograph where the reflected light is exploited. Recently, high-resolution TEM instruments are known and using these one can analyze the lattice of the nanomaterials. But the difference between with TEM and HR-TEM is the only change in the energy of the electron used. HR-TEM operates at 300 KV. The lattice fringes can be seen in the HR-TEM picture. Atomic force microscopy is also utilized in characterizing the nanomaterials though it is as good as TEM and SEM. Mainly AFM can be utilized for analyzing the surface morphology like up and downs. Scientists have long imagined the possibility of manipulating individual atoms and molecules using scanning probe microscopes, that indeed make it possible not just to "see" individual atoms and molecules on the surfaces of materials (i.e., create images) but to move atoms and molecules on the nanoscale as well. Competitive programs with this new perspective should, by definition be interdisciplinary, involving physics, chemistry, biology, medicine, and materials science, among other fields.

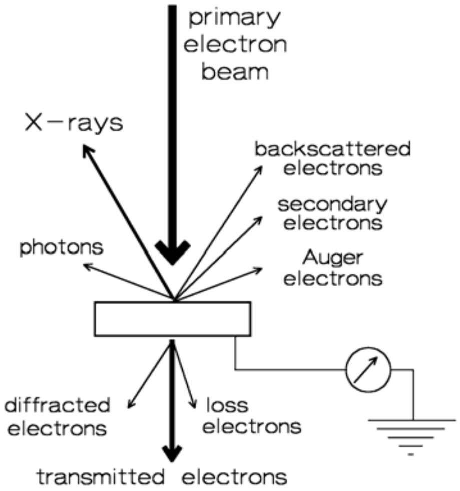

Fig. 6. Schematic representation of the electrom microscope

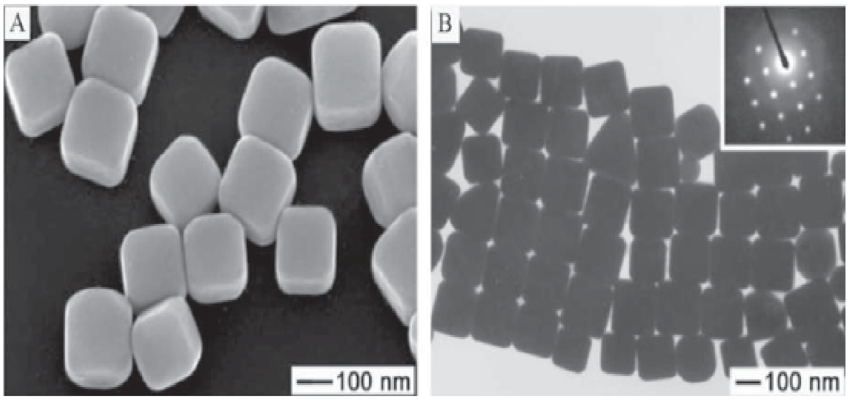

Fig. 7. Difference between the SEM (A) and TEM (B).Inset shows the selective area electron diffraction patterm (SAED)

Applications

Nanochemistry is one of the frontier areas of science due to its versatile application in various fields. Nanomaterials find applications in the fields such as miniaturization in electronics, catalysis, optics, biological and in the elegy sector. In addition, nanomaterials yield next-generation computer chips, better insulation materials, tougher and harder cutting tools, elimination of pollutants, high energy density batteries, high-power magnets, high-sensitivity sensors, automobiles with greater fuel efficiency, aerospace components with enhanced performance characteristics, longer-lasting satellites, longer-lasting medical implants, ductile, machinable ceramics, large electrochromic display devices.

Metal nanostructures find applications in biochemical and medical applications. Ag naoparticles act as a antibacterial agents. Au nanotrinaular particles or plates find applications in the identifying and treating the cancer cells using IR radiation. Since these Au nanotriangles and plates adsorb electromagnetic radiation from the IR region due to the SPR property. The naotubes can be used as thermometers by filling with gallium. Lot of applications of nanomaterials is explored on daily basis.

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Chapter - 5
SILICON SUBSTITUTES

M. Sankaran

1. Introduction

1.1. General introduction to Silicon and its application

Silicon is the second most common element in the upper layer of the earth's crust: about 25% of the crust consists of silicon (only oxygen exceeds it in abundance). However, silicon is usually not found free, but mainly in its oxides and silicates. Most silicon oxides appear as sand, quartz, rock crystal, amethyst, agate, flint, and opal. Most silicates appear as granite, hornblende, asbestos, feldspar, clay and mica.

Silicon (Si) belongs to the IVA family in the periodic table, which consists of carbon, silicon, germanium, tin and lead. Its atomic number is 14, the outer electron configuration of each of these atoms is s^2p^2. Carbon and silicon are nonmetals, while tin and lead are metals, and germanium and gray tin are typical semiconductors. Amorphous silicon is a brown, inflammable powder which can easily melt or vaporized. Its specific gravity is 2.35. It can be easily reduced. Whereas crystalline silicon is found, similar to carbon, very hard, melts at 1400 °C and vaporizes at high temperatures. Silicon combines with many elements including boron, carbon, titanium, and zirco zirconium in the electric furnace. It readily dissolves in molten magnesium, copper, iron, and nickel to form silicides. Most oxides are reduced by silicon at high temperatures. The physical and chemical properties of the silicon are tabulated in Table 1.

Table 1. The physical and chemical properties of silicon

Silicon Data

Atomic Radius (Å): 1.46 Å

Atomic Volume cm^3/mol : $12.1 cm^3/mol$

Covalent Radius: 1.11 Å

Crystal Structure: Cubic face centered

Ionic Radius: 0.4 Å

Chemical Properties	**Physical Properties**
Electrochemical Equivalents: 0.26197 g/amp-hr Electron Work Function: 4.52 eV Electronegativity: 1.9 (Pauling); 1.74 (Allrod Rochow) Heat of Fusion: 50.55 kJ/mol Incompatibilities: Chlorine, Fluorine, Oxidizers, Calcium, Cesium Carbide, Alkaline Carbonates First Ionization Potential: 8.151 Second Ionization Potential: 16.345 Third Ionization Potential: 33.492 Valence Electron Potential: 144 Ionization Energy (eV): 8.152 eV	Atomic Mass Average: 28.0855 Boiling Point: 2628 K, 2355 °C, 4271 °F Melting Point: 1683 K, 1410°C, 2570 °F Heat of Vaporization: 384.22 kJ/mol Coefficient of Lineal Thermal Expansion/K^{-1}: $4.2E^{-6}$ Electrical Conductivity: $2.52E^{-12}$ 10^{6}/cm Thermal Conductivity: 1.48 W/cmK Density: 2.33 g/cm^{3} @ 300 K Enthalpy of Atomization: 439.3 kJ/mole @ 25 °C Enthalpy of Fusion: 46.44 kJ/mole Enthalpy of Vaporization: 439 kJ/mole Flammability Class: Combustible Solid in powder Molar Volume: 12.05 cm^{3}/mole Optical Refractive Index: *unknown* Relative Gas Density (Air=1): *unknown* Specific Heat: 0.71 J/gK Vapor Pressure: 4.77 @ 1410 °C Estimated Crustal Abundance: 2.82×10^{5} mg per kg Estimated Oceanic Abundance: 2.2 mg per liter

2. Silicon and Electronics

2.1 Why Si is semiconductor? And its properties

The semiconductor property of silicon is due to its mechanical, optical and electrical property. The conductivity can be varied over several orders of magnitude by the addition of certain types of impurities. In semiconductors, both the mobile negative carriers (electrons) as well as mobile positive carriers (holes) are present. Contrary to metals, the conductivity of semiconductors can be varied over wide range, and is a function of the impurity content.

In semiconductors both mobile negative carriers (electrons) as well as mobile positive carriers (holes) are present. The impurity atoms which have been added to semiconductor (i.e. each donor or acceptor) will be ionized.

(a). N-type semiconductor (conduction by electrons):

$$\text{DONOR (fixed)} \longrightarrow \text{DONOR}^{+}\text{ (fixed)} + \text{electron}^{-}\text{ (mobile)}$$

If all donors are ionized, then the donor concentration is equal to the mobile electron concentration.

(b). P-type semiconductor (conduction by holes):

$$\text{ACCEPTOR (fixed)} \longrightarrow \text{ACCEPTOR}^{-}\text{ (fixed)} + \text{hole}^{+}\text{ (mobile)}$$

If all acceptors are ionized then the acceptor concentration is equal to the mobile hole concentration.

Illumination and temperature increases result in the simultaneous generation of mobile electrons and holes although in an n-type semiconductor the electron concentration is higher (majority carriers) than the hole concentration (minority carriers) and in a p- type semiconductor the opposite is the case. If the donor impurities are added to the semiconductor the majority carriers are electrons and the minority carriers are holes.

There has to be equilibrium between both types of carriers which is a function of temperature:

$$n\,p = f(T)$$

If there are many holes then only very few electrons can exist.

Minority carriers in a semiconductor can usually be disregarded if conductivity is of concern, for transistor action however, they are of prime importance.

For electronic applications, the main interest towards the elemental silicon is as a conductor of electricity. By adding controlled amounts of impurities one determines the sign of the charge carriers and their density. By doing this in well-defined limited areas, we can construct electronic devices that rectify, amplify, and sensitive to light, emit light, and store and move electric charge on command.

Silicon remained as the most widely used semiconductor because of its unique advantages. Among these are (1) In it's elemental form, so composition is not a problem; (2) it forms a tough, adhering insulating oxide, SiO_2, that can be used for isolation and protection; and (3) a large variety of impurity atoms are available for controlling its conduction properties.

Impurities are added to control the characteristics of the semiconductor are called dopants. The majority carriers, electrons in this case, will far out number the minority carriers, the holes in the valence band. Silicon with a pentavalent dopant is called n-type silicon (P or As). On the other hand, we may use a dopant that has only three valence electrons, such as B, Ga or Al. These dopants are called acceptors because they accept an electron to create a mobile hole. These levels are only just above the valence band in the Fig. 1. The holes are shown in the valence band. Silicon with a trivalent impurity is called p-type silicon.

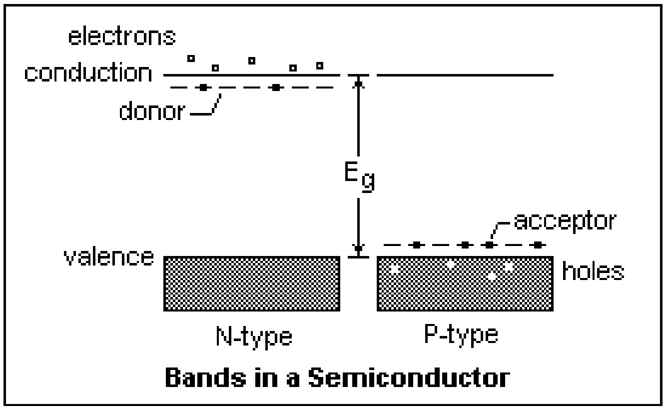

Fig 1. Bands in a semiconductor formed in N - type and P - type semiconductor

A p -type region can diffused into an n -type substrate as shown in Fig. 2. At a certain depth, there is a sudden change from P to N, called a PN junction, without any disruption to the crystal structure. If the P end is positive, and the N end is negative, an electric field points from P to N. It drives the holes toward the junction in the P region, and the electrons toward the junction in the N region, so the current flows in the same direction, P to N. When the holes meet the electrons at the junction of the P and N materials, they recombine, while new holes are created at the P terminal and new electrons at the N terminal. The PN junction is forward-biased and carries current easily. The arrow in the diode symbol points from P-type to N-type, in the direction of easy current flow. The P-type material is the anode, the N-type the cathode.

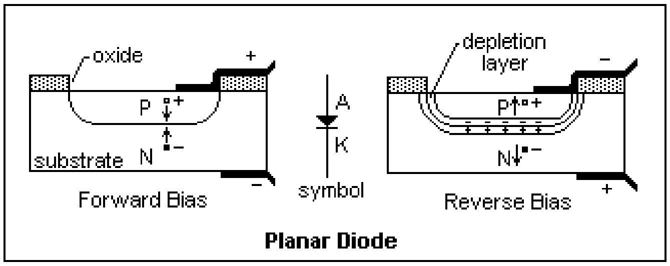

Fig 2. Pictorial representation of characteristics of planar diode

When polarity is reversed, making the P region negative and the N substrate positive, the electric field that results drives the holes and electrons away from the junction on each side. This creates a depletion layer with no charge carriers of either sign. Current cannot pass through this layer. As the carriers move away from the junction, they uncover the negative acceptors and the positive donors, so an electric field is created that cancel the applied field. The semiconductor now acts like an open circuit. The voltage across it is equal to the applied voltage. That is, the PN junction rectifies.

A simple device easily created with planar technology is the Field-Effect Transistor, or FET. This device controls a current by means of a voltage applied to it. Since no current is drawn by the control circuit, no power is required to operate it, and the power gain is effectively infinite. The main terminals of the device, called source and drain though they are actually alike and either can be chosen as the source. Whichever way we apply a voltage between them, no current will flow because there will be a reverse-biased junction at one electrode or the other. Conventionally, the drain has the reverse-biased junction.

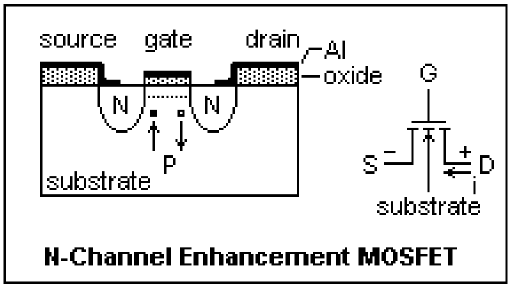

Fig. 3. Schematic diagram of N- Channel enhancement MOSFET

A thin layer of oxide, perhaps only 0.1 μm thick, is deposited between the two electrodes, and on top of it is evaporated an Al gate electrode. When a positive voltage applied with respect to the source to the gate, an electric field appears under it in the P-type substrate. This field drives away holes and attracts electrons to the thin layer just under the gate. At some voltage, electrons will predominate and the type of the region will be inverted from P to N. This means that the reverse-biased junction at the drain will disappear, and this will allow current to flow from drain to source (electrons from source to drain, as the names indicate). The transistor has now "turned on" and conducts. This control is exerted purely by the voltage at the gate electrode. The device is usually called a MOSFET (metal oxide – semiconductor – field effect transistor) (Fig. 3.), whether metal or polysilicon is used for the gate electrode. Microprocessors and memory chips are all MOSFET's.

The advanced MOS technology and very large scale integration (VLSI) – both based on the extraordinary properties of the Si-SiO_2 system – opened the way for the necessary mass market in silicon integrated circuits for use in information technology. Most, importantly, it is obvious that a uniform, high purity, perfect single crystal piece silicon material alone would be of extremely limited technological use. It is only when material is suitably altered and structured controlled, reproducible processes and then made into useful device that it becomes valuable.

3. Why to replace silicon and silicon based components?

- Silicon and silicon-based components require millions of gallons of water and temperatures of 300-500°C to manufacture. A wide range of solvents are used in silicon and in semiconductor manufacture, including highly toxic xylene and toluene. The semiconductor industry uses hundreds of thousands of gallons of such solvents.

- Silicon chips can malfunction at high temperatures, often from the heat generated in their own circuitry.
- Conventional computer chips are made from a thin slice of silicon. This is manufactured by cooling pure, molten silicon so that as it solidifies a crystal of the material forms in a certain direction.
- Silicon wafers are then chemically "doped" with impurities to improve their ability to carry an electrical charge.
- The types of impurities added affect the direction of the charge. However, the weakness of devices based on silicon is their sensitivity to heat. This factor requires fans or other gadgets to cool them down and limits their future miniaturisation.

According to Moore’s law, which predicts a decrease in feature sizes by a factor of 0.7 every 3 years, silicon transistors have become smaller and smaller in order to achieve higher intergration density, higher speed, lower power consumption and lower cost. Many challenges have to be addressed for the making devices like, lithography, metallization, power dissipation and circuit design. Focusing on the device, the manadatory improvement in performance will be the key issue for further downscaling. Therefore, novel architectures and new materials that would replace the silicon are needed, to improve the electrical parameters further and thus pave the way to much smaller transistors than those expected in the past.

4. Substitutes to silicon

Low-dimensional nanomaterials are of interest, since they exhibit highly anisotropic or dimension-tunable properties, which are important attributes in nanodevice applications. Recently, carbon nanotubes (CNTs) are promising low-dimensional nanomaterials because of their interesting properties, such as small diameter, high mechanical strength, high thermal and chemical stabilities, excellent heat conduction, interesting electrical and electronic properties. CNTs can be either metallic or semiconducting, with the semiconducting band gap depending upon the tube diameter, geometry, and chirality. CNTs, composite materials like ceramics and organic molecules are totally well-suited with the Si-based microelectronics. This type of one dimensional material behaves as substitutes for silicon and silicon based compounds.

Nanotubes belong to a promising group of nanostructured materials. Although other nanotubes based on boron nitride and molybdenum have been reported, currently carbon nanotubes are by far the most important group. The single-walled carbon nanotubes are used in macroelectronic applications as compared to silicon and silicon based materials. Carbon nanotubes offer extremely high field-effect mobilities, lower operating voltages and better electronic characteristics while retaining the ability to be placed onto a wide variety of substrates. The main technological issue is the development of a reliable device fabrication methodology. Carbon nanotubes exhibit favorable electronic properties compared to other materials that can be deposited on large substrates. As a comparison to other electronic materials, effective electron mobility is shown by Carbon nanotubes. This effective mobility is scaled by the overall length and width of the active region on the device.

The important use of elemental silicon is as a semiconductor. Silicon is often compared to carbon. Compared to similarities the difference between Si and C are more significant.

- "What is so special about Carbon?"
- Is it the four valency of carbon?
- Is the ability to bond with another carbon atom?
- Is it the chiral nature of the bond?
- Is it the number of compounds that can be formed?
- Is it the tetrahedral orientation of the bonds?
- Is it the electronic configuration of the atom of carbon?
- Is it that carbon exists in a variety of allotropic modifications?
- Is it the position in the periodic table that makes it special?
- Is it that its atomic orbitals can give rise to multiple hybridizations?
- Is it that the atomic energy values of the orbitals of carbon have specificity?
- Is it that carbon is main constituent of all our energy resources?

4.1 Si versus C: what are the differences?

Carbon and silicon are the two most important elements in the Periodic Table for obvious reasons. They occupy the central stage of the early rows of the Periodic Table by being the first and the second members of Group IV. Carbon, unique in nature is also the factor which differentiates these two elements. Despite the fact that silicon and carbon both have four valence orbitals and four electrons, the two elements have very different properties. Silicon differs from carbon, in terms of several properties listed in Table 2.

Table 2. Comparison of properties of silicon and carbon

S. No	**Properties**	**Carbon**	**Silicon**
1	Lattice constants (Å)	3.567	5.43
2	Bulk modulus (GPa)	442	98.8
3	Thermal coefficient of linear expansion (10^{-6}/K)	1.0	2.59
4	Thermal conductivity (W/cm.K)	~20	1.56
5	Dielectric constants	5.7	11.9
6	Band Gap Eg (eV)	(5.48) 7.3	(1.11)3.48
7	dEg/dT (meV/K)	(-0.05) -0.6	(5)
8	dEg/dT (meV/GPa)	(5)	(-14)

- The most important distinction between Si and C is the difference in electronegativity (χ). In contrast to carbon, silicon (χ=1.90) is less electronegative than hydrogen (χ=2.20), thereby polarizing the Si---H bonds in the opposite sense, i.e. as Siδ+---Hδ− This implies that nucleophilic attacks on silanes usually occur at the silicon centers.
- The larger atomic size of silicon gives rise to longer Si---Si bonds of 2.35 Å and weaker Si---Si bonds with bond energy of 222 kJ mol^{-1}, in comparison to C---C bonds of 1.54 Å with bond energy of 345.6 kJ mol^{-1}.
- The π–π overlaps for silicon (smaller than those of carbon by roughly an order of magnitude), Si=Si bonds of 2.16 Å, with bond energy of 327 kJ mol^{-1}, are weaker than C=C bonds of 1.34 Å with bond energy of 602 kJ mol^{-1}.
- The energy difference between the valence s- and p-orbitals for silicon is only half of the corresponding value for carbon (Si ($E_{3p}-E_{3s}$ = 5.66 eV) versus C ($E_{2p}-E_{2s}$ = 10.60 eV)). As a result, silicon tends to utilize all three of its valence p-orbitals, resulting in sp^3 hybridization, in contrast to carbon which can "activate" one valence p-orbital at a time to give sp, sp^2, and sp^3 hybridizations.

4.2 Structural characteristics, processing and applications

In 1991, Iijima described for the first time the new form of carbon called carbon nanotubes (CNT). CNTs are formed by rolled graphite sheets, with an inner diameter starting from 0.7 nm upto several nm and a length of 10–100 µm as shown in Fig. 4.

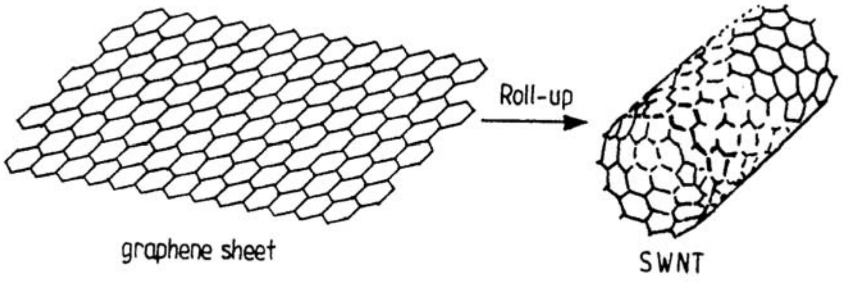

Fig. 4. The graphene sheet rolled to form cylindrical single walled nanotube (SWNT)

The helicity of the nanotubes is usually described by the Hamada vector, which indicates how the graphene sheet is rolled up along a lattice vector with components (n, m). The values of the integers n and m identify the general geometry of SWNT. The tubes with n = m are named 'armchair'; tubes with either n = 0 or m = 0 are named 'zigzag'; all others have chiral symmetry. The schematic representation is given in Fig. 5. One can view a single-walled carbon tube as a rolled up sheet or strip of sp^2-bonded graphene. The atoms are located using a pair of integers (n, m) and the lattice vector C = na1 + ma2 as shown in Fig. 5a. A tube can be classified using the pair of integers by viewing the rolling up of the sheet as the 'placement' of the atom at (0,0) on the atom at (n, m). Hence, different diameter tubes and helical arrangements of hexagons can arise by changing (n, m) as shown in Fig.5b. The electron energy levels are split into subbands owing to the restricted geometry perpendicular to the tube axis.

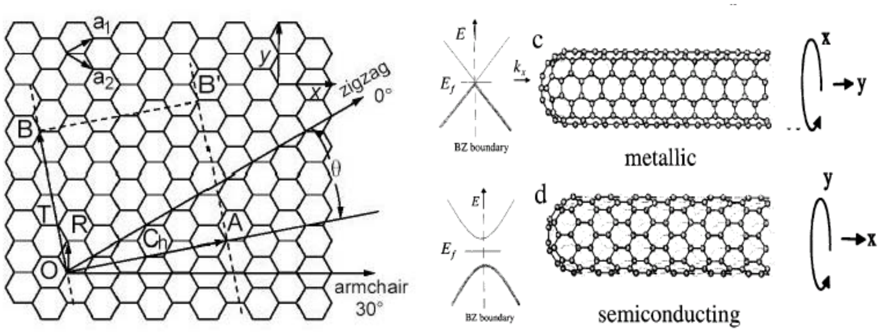

Fig. 5. (a) Basic structure of a sheet of graphene. Consider the carbon atoms to be placed on each point on the edge of the hexagon. (b). Three different classification of nanotubes.

5. Carbon nanotube growth and device fabrication

A number of growth methods for nanotubes have been utilized like, arc discharge method, laser ablation technique, chemical vapor deposition method. The nanotubes are collected from the cold part of the deposited system and dispersed in a solvent. Deposited of the nanotubes – containing liquids and subsequent drying of the solvent leaves the nanotubes in randomly distributed places, some of them on contacts, where they can be used for electrical characterization. Usually nanotubes were grown from a catalyst in a carbon –containing gas atmosphere at temperature of 600-900°C. at the lower end of the temperature range the nanotubes grow with a number of concentric layers and are called multiwalled nanotubes, whereas at the higher end of the temperature band the nanotubes grow preferentially as single walled species with small diameter. Microelectronic patterning methods can be used to structure the catalyst layer, thereby defining places for selective growth.

5.1 Carbon nanotubes transistors and circuits

The fact that nanotubes are very good conductors, and that they also appear as semiconductors or even insulators, make them useful for minuscule electronic devices like logic circuits composed of several transistors. The making of tiny circuits might be promising for the semiconductor industry. This industry is focused to make computer chips smaller every year, but also has to make them as cheaply as possible. Semiconducting single walled carbon nanotubes were first demonstrated in to show a technologically exploitable switching behavior.

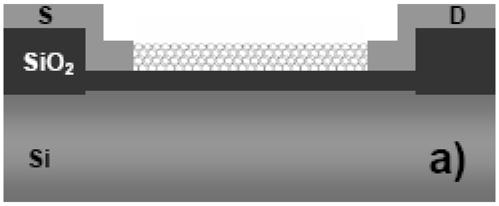

Fig. 6. Schematic side view of a back-gated SWNT-FET with 10 nm thick SiO_2 gate dielectric under the channel and 100 nm SiO_2 under the bonding pads

Essential devices like Field-Effect Transistors (FET) have been developed. They use a single semiconducting nanotube between two metal electrodes as the channel through which electrons flow. The current in this channel can be switched on or off by applying voltages to a nearby third "gate" electrode. It was found that this electrode can change the conductivity of the nanotube channel by a factor of 1 million or more, compared to silicon FETs (Fig.6). Because of its tiny size the carbon nanotube FET (CNT-FET) should switch reliably using less power than a silicon-based device. It is predicted that, such a nanoscale device could run at clock speeds of one terahertz or more. The first nanotube-based devices operated at very low temperatures, but in 1998 the first transistor was reported that worked at room temperature, with electrical characteristics remarkably similar to silicon devices.

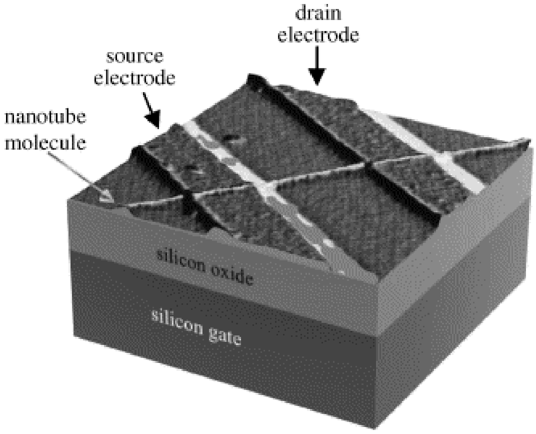

Fig 7. A single-molecule transistor that operates at room temperature, consisting of an individual semiconducting nanotube on two metal nanoelectrodes with the substrate as a gate electrode

The control of the chirality of the nanotubes constitutes a shortcoming of the process. Introducing a pentagon and a heptagon into the hexagonal carbon lattice of a nanotube creates a kink in the tube. In this way, two tube segments with different atomic and electronic structures can be fused together to create intramolecular metal–metal, metal–semiconductor, or semiconductor–semiconductor junctions that are only a few atoms in cross-section (Fig. 7). Note that a metal–semiconductor kink junction behaves like a molecular diode; electricity is permitted to flow only in one direction.

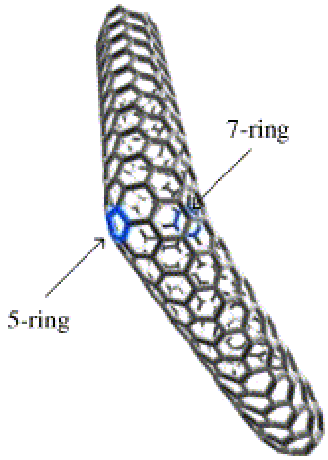

Fig 8. Model of a nanotube kink junction, with 5- and 7-rings; the tube segment at the top can be metallic whereas the bottom segment is semiconducting

Metal–metal junctions lead to an improved version of a single electron transistor (SET), which is another promising device. It has been proposed even as the future alternative to conventional silicon electronic components, but their practical use has been limited by the fact that they only operate at very low temperatures. The next step in assessing the suitability of these devices for computer electronics involves the integration of individual CNT-FETs to form logic gates (Fig.8). To build such logic circuits, nanotube devices, that use electrons (n-type FET) and holes (p-type) as the carriers of electricity, are needed. The problem was that all CNT-FETs showed p-type characteristics that mean that, they were ON for negative gate bias. Therefore, the first n-type CNT-FBT had a great impact; it was made by direct doping of the tube with an electropositive element such as potassium. Potassium atoms (K atoms evaporated from an alkaline metal dispenser) are adsorbed onto the surface of the nanotube, donating electrons to convert the nanotube from p- to n-type.

Using vacuum annealing or doping it is possible to make n-type CNT-FETs, p- and n-CNT-FETs on the same substrate can be fabricated. These complementary CNT-FETs are assembled to form the first intermolecular logic gates. At first, a

"NOT" gate or voltage inverter was demonstrated (Fig. 9). To use a logical gate as part of a more complicated computing system, a gain (output/input ratio) of 1 is required. The intramolecular inverter had a gain of 1.6 and, therefore, it can be used to drive another gate or a more complicated logic circuit.

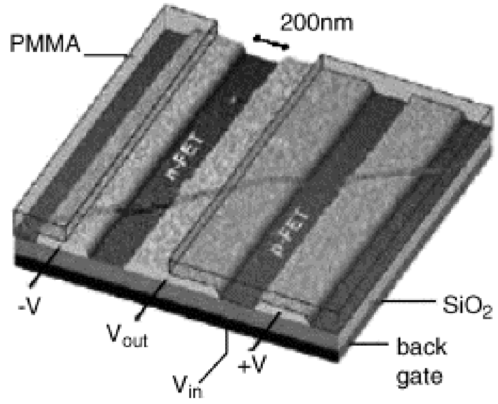

Fig 9. An AFM showing the design of an intramolecular logic gate consisting of a single nanotube bundle, positioned over the gold electrodes to produce two p-type CNT-FETs in series

The device is covered by PMMA, a window is opened by electron beam lithography to expose part of the nanotube, and subsequently, potassium is evaporated through this window to produce an n-CNT-FET, while the other CNT-FET remains p-type. Recently, other logic circuits were constructed from individual carbon nanotubes; a logic NOR, a static random-access memory cell (RAM), an ac ring oscillator, and another inverter constructed. In these circuits, one, two, or three transistors were used. They all operated at room temperature, had a high gain (>10), and a large on–off ratio (>10). To construct nanotube circuits, electron beam lithography was used to pattern local aluminium gate contacts and exposed them to air to form very thin insulating layers on the aluminium leads. The silicon dioxide insulator in former FETs was relatively thick, preventing sufficient capacitive coupling between the gate contact and the nanotube. Because of the reduced insulator thickness, the new nanotube transistors were able to operate with a highly increased gain ratio. Former nanotube devices placed on a chip switched simultaneously, because the controlling gate was the entire supporting silicon chip. But now each transistor can be controlled by its own local "gate" contact. These developments contributed to a better prospect for the use of nanotube logic circuits in chips.

Field emission has long been seen as a potential technology for replacing bulky, inefficient televisions and computer monitors with equally bright but thinner and more power-efficient flat-panel displays. It was shown that nanotubes emit electrons very efficiently when immersed in an electric field. Efficient field emission was also obtained from carefully aligned nanotubes, whereas randomly oriented nanotubes have been also used with similar results.

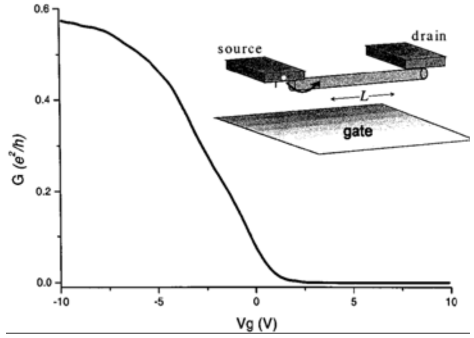

Fig.10. Conductance G versus gate voltage V of a p-type semiconducting SWNT field effect transistor. The device geometry is shown schematically in the inset

The tube conducts at negative and turns off with a positive. The resistance change between the on and off state is many orders of magnitude. This device behavior is analogous to a p-type metal–oxide–semiconductor field-effect transistor (MOSFET), with the nanotube replacing Si as the semiconductor. At large positive gate voltages, n-type conductance is sometimes observed, especially in larger-diameter tubes. The conductance in the n-type region is typically less than in the p-type region because of the work function of the Au electrodes (Fig.10). The Au Fermi level aligns with the valence band of the SWNT, making a p-type contact with a barrier for the injection of electrons. Semiconducting nanotubes are typically p-type at because of the contacts and also because chemical species, particularly oxygen, adsorb on the tube and act as weak p-type dopants. Experiments have shown that changing a tube’s chemical environment can change this doping level—shifting the voltage at which the device turns on by a significant amount.

Further improvement of this technology may lead to easy-to-make and low-cost flat panel displays. Considering the small sizes of carbon nanotubes, high performance may be expected for them due to sunlight trapping. Large surface area and high thermal conductivity enable a rapid heat transfer from carbon nanotubes to the surrounding environment. Furthermore, they are physically and chemically stable. Scientists have constructed a solar cell by synthesizing aligned carbon nanotubes on an Au film.

Table 4. Comparison of some important experimental transistor characteristics for CNTFETS and silicon MOSFETs

Properties	**p-CNTFET**	**MOSFET**
Drive current I_{ds} (mA/μm)	3.5	0.215 pFET
Transconductance (μS/μm)	6000	360 pFET
S (mV/dec)	70	71
On-resistance (Ω /μm)	342	4186 pFET
Gate length (nm)	2000	14
Normalized gate oxide (1/nm)	25/8 = 3.12	4/1.2 = 3.33
Mobility (cm^2/Vs)	3000	-
I_{off} (nA/μm)	1	100

A comparison has been made between on the performance of most advanced state of the art carbon nanotube transistor (CNTFETs) and silicon based transistor (Si-MOSFET). The results are tabulated in the Table 4. All the data for CNTFET were measured on single nanotube device and have been normalized to device width for comparison. From the results it showed that CNTFETs with semi conducting nanotubes are promising candidate for transistor devices with superior characteristics compared with silicon MOSFETs.

6. Challenges and future prospects

- Carbon nanotubes look very good promising candidates for electronic applications. Opportunities also exist for integrating nanotube electronics with other chemical, mechanical, or biological systems.
- The are also a host of other device geometries beyond the simple wire and FET structures described above that are under exploration. Examples include the p-n and p-n-p devices, nanotube/nanotube junctions, and electromechanical devices.

- More challenging is the issue of device manufacturability. Although a great deal of work has been done, the progress to date has been modest. For example, in tube synthesis, the diameter of the tubes can be controlled, but not the chirality. As a result, the tubes are a mixture of metal and semiconductors.
- In CVD, the general location for tube growth can be controlled by patterning the catalyst material, but the number of tubes and their orientation relative to the substrate are still not well defined. Furthermore, the high growth temperature (900 C) for CVD tubes is incompatible with many other standard Si processes.
- The alternative approach, depositing tubes on a substrate after growth, avoids this high temperature issue but suffers from the chirality and positioning limitations.
- To date, there are no reliable, rapid, and reproducible approaches to creating complex arrays of nanotube devices. This manufacturing issue is by far the most significant impediment to using nanotubes in electronics applications.
- While there has been significant fanfare around “circuits” made with nanotubes, in reality the accomplishments to date are a far cry from anything that would impress a device engineer or circuit designer. However, there appear to be no fundamental barriers to the development of a technology.

7. Other silicon substitutes materials

7.1 Organic electronics: a cleaner substitute for silicon

Until recently, plastics--ubiquitous in most areas of modern life--had yet to make inroads into the electronics industry; their molecular configuration made them non conducive to electrical flow, limiting their uses to shells for computers and insulation for wires. In recent year the plastic polymers can be manipulated so they may be fashioned into transistors, conductors, and other electrical components. Such uses for these carbon/hydrogen/oxygen-based polymers are the subject of the field of organic electronics. A wide variety of potential applications, transistors, electronic circuits, high-density energy storage devices, advanced emissive displays, and advanced photovoltaics. The benefits of plastics are substantial--in many cases, they offer a safer, cheaper, lighter alternative to silicon.

- Organic electronics involves a smaller set of hazardous compounds and materials than more traditional semiconductor based technologies.

- It may be possible to design organics that are soluble in less harmful solvents. Polymers also are lighter and can cost much less to manufacture than the silicon substrate.
- Organic fabrication is compatible with plastic substrates, which means you can use a very low-cost. Additionally, organics are good for large-area needs.
- For example, an organic photovoltaic cell could weigh 100 times less than a silicon-based cell and silicon wafer is more expensive than a sheet of plastic.
- The polymers won't be replacing silicon in certain applications, such as computer semiconductors, because silicon will always be significantly faster. However, plastics can serve as a substitute in applications where silicon is either impractical or too expensive to use, but this is a technology with great promise.

Organics would be ideal in the current technology of photovoltaic cells, most of which now use silicon. The lightness of organic photovoltaics would make them perfect for consumer applications such as recharging personal digital assistants, and their low cost would suit them for power generation in remote villages in developing countries.

7.2 Organic Photovoltaic Technology

Conventional solar cells convert light energy into electricity through the photovoltaic effect on semiconductor material like crystalline silicon. Though effective, this methodology of harnessing solar energy has its drawbacks in the form of high manufacturing costs and prices, decreasing availability of sufficient amounts of silicon, module assembly costs, rigidity of panels etc. To counter these factors, new technologies have emerged that make use of technologies that use cost-effective raw materials and processes. Research on developing organic-based solar cells started in the 1970s. Organic solar cells are a potentially cost-effective option for utilizing solar energy. The technology itself is in the process of development, and shows promise because of its ease of use, diversity of applications and manufacturing process.

Organic technology solar cells are essentially based on the photosynthesis process in plants. The absorption of light in organic cells is done by the ‘dye’ which substitutes for the silicon in conventional cells. This light causes the dye molecules to get excited and release electrons that are converted to electrical energy. The use of use of chemicals called dyes for the conversion process has led to organic cells also being known as “dye-sensitized solar cells.”

7.3 Can we replace silicon chips with biochips?

The present day computers store information on a thin wafer of silicon and the information is processed in the computer by reading zero’s and one’s produced as electrons passing through the switch represent one and the stoppage of electron flow as "zero". However silicon can not hold enough information or process information fast enough for such applications as artificial intelligence or robot vision.

In contrast a biochip can store more information and processes faster than the present silicon chip. The biomolecule that can be used is bactiorhodopsin that can work with the light at the speed of light faster than the flow of electrons through the silicon chip. The green light causes protein to fold and the folded protein is read as one. Where as the unfolded protein represents zero, Laser light are used to see the configuration of protein.

7.4 New plastic resin finds home in electronics industry

The new biodegradable resin is made with polylactic acid (PLA) processed from cornstarch. This is already used to make cups and blister packaging, as well as bottles, carpet, shirts, films, and wraps. Using PLA to manufacture an electronic product. Specifically, the resin will be employed in the body casing and some internal parts. Carbon is stored in plant starches, which can be broken down into natural plant sugars. The carbon and other elements in these natural sugars are then used to make PLA, the Nature Works building block. The goal of industries is to make the production and disposal of electronic products more sustainable. Developing bio-derived and bio-degradable plastics for the electrical and electronic sector is being undertaken.

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Chapter - 6
SOLAR CELLS

G. Magesh

1. Introduction

The International Energy Agency says the world will need almost 60% more energy in 2030 than in 2002, and fossil fuels will still meet most of its needs. We depend on oil for 90% of our transport, and for food, pharmaceuticals, chemicals and the entire bedrock of modern life. But oil industry experts estimate that current reserves will only last for about 40 years. Views vary about how much more will be found or made economically viable to use. Particularly among the various countries the growth in demands for India will be the highest at 134% (Fig.1). This shows that there is an urgent need to develop an alternative for oil which should also be renewable. One of the most promising options is to utilize solar energy and produce electricity from it. This process is lot more advantageous because it does not involve greenhouse gases like CO_2.

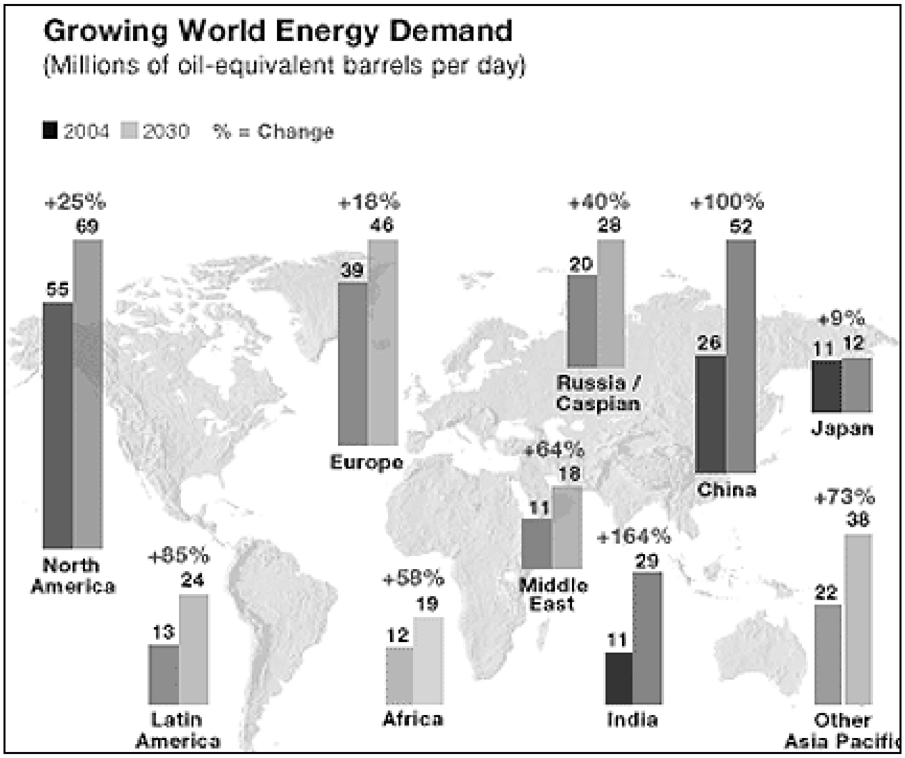

Fig. 1. Energy demand projections for the various regions in the world

2. Solar cell

Solar cells (as the name implies) are designed to convert (at least a portion of) available light into electrical energy. They do this without the use of either chemical reactions or moving parts.

The development of the solar cell stems from the work of the French physicist Antoine-César Becquerel in 1839. Becquerel discovered the photovoltaic effect while experimenting with a solid electrode in an electrolyte solution; he observed that voltage developed when light fell upon the electrode. About 50 years later, Charles Fritts constructed the first true solar cells using junctions formed by coating the semiconductor selenium with an ultrathin, nearly transparent layer of gold. Fritts's devices were very inefficient, transforming less than 1 percent of the absorbed light into electrical energy.

By 1927 another metal-semiconductor-junction solar cell, in this case made of copper and the semiconductor copper oxide, had been demonstrated. By the 1930s both the selenium cell and the copper oxide cell were being employed in light-sensitive devices, such as photometers, for use in photography. These early solar cells, however, still had energy-conversion efficiencies of less than 1 percent. This impasse was finally overcome with the development of the silicon solar cell by Russell Ohl in 1941. In 1954, three other American researchers, G.L. Pearson, Daryl Chapin, and Calvin Fuller, demonstrated a silicon solar cell capable of 6-percent energy-conversion efficiency when used in direct sunlight. By the late 1980s silicon cells, as well as those made of gallium arsenide, with efficiencies of more than 20 percent had been fabricated. In 1989 a concentrator solar cell, a type of device in which sunlight is concentrated onto the cell surface by means of lenses, achieved an efficiency of 37 percent due to the increased intensity of the collected energy. In general, solar cells of widely varying efficiencies and cost are now available.

Even though the research in solar is around 80 years old, the development of commercial viable solar cells is at a very crucial stage now. The development of commercial solar cells with more than 20% efficiency under direct sunlight is the ultimate goal now. This is leading to intense research being conducted in this field at present.

3. Functioning of solar cells

The solar cells that you see on calculators and satellites are photovoltaic cells or modules- a group of cells electrically connected and packaged in one frame. Photovoltaic (photo = light, voltaic = electricity) cells convert sunlight directly into electricity. Once used almost exclusively in space, photovoltaics are used more and more in less exotic ways. They could even power your house.

3.1. General mechanism

Photovoltaic (PV) cells are made of special materials called semiconductors such as silicon, which is currently the most commonly used. Basically, when light strikes the cell, a certain portion of it is absorbed within the semiconductor material. This means that the energy of the absorbed light is transferred to the semiconductor. The energy knocks electrons loose, allowing them to flow freely.

PV cells all have one or more electric fields, which act to force electrons freed by light absorption to flow in a certain direction. This flow of electrons is a current, and by placing metal contacts on the top and bottom of the PV cell, we can draw that current off to use externally. For example, the current can power a calculator. This current, together with the cell's voltage (which is a result of its built-in electric field or fields), defines the power that the solar cell can produce.

That's just the basic process,. We can study in detail about the mechanism involved in solar cell using one of the types of solar cell i.e. single crystalline silicon solar cell. It should be always kept in mind that there are various other semiconductor materials which are used in solar cell in place of silicon. Not only a single material but a combination of more than one semiconductor is also used.

3.2 Functioning of single crystalline silicon solar cell

Pure silicon is a poor conductor of electricity because none of its electrons are free to move about as electrons are in good conductors like copper. Instead, the electrons are all locked in the crystalline structure. Silicon in a solar cell is modified slightly so that it becomes a semiconductor and will work as a solar cell.

These cells have silicon with impurities - other atoms mixed in with the silicon atoms, changing the way things work a bit. We usually think of impurities as something undesirable, but in this case, the cell wouldn't work without them. These impurities are actually put there on purpose. When an atom with lower valency like boron is added as impurity the resulting silicon is p-type. When an atom with higher valency like phosphorous is added the resulting silicon is n-type. Both these can conduct electricity at room temperature.

In the solar cell the p-type and n-type silicon are always in contact with each other. Remember that every PV cell has at least one electric field. Without an electric field, the cell wouldn't work, and this field forms when the n-type and p-type silicon are in contact. Suddenly, the free electrons in the n-side, who have been looking all over for holes to fall into, see all the free holes on the p-side, and there's a mad rush to fill them in. Before now, the silicon was all electrically neutral. The extra protons in the phosphorous balanced our extra electrons out. The missing protons in the boron balanced our missing electrons (holes) out. When the holes and electrons mix at the junction between n-type and p-type silicon, however, that neutrality is disrupted. But all the free electrons and holes will not be neutralized. Right at the junction, however, they do mix and form a barrier, making it harder and harder for electrons on the n-side to cross to the p-side. Eventually equilibrium is reached, and we have an electric field separating the two sides. This field acts as a diode, allowing (and even pushing) electrons to flow from the p-side to the n-side, but not the other way around. It's like a hill - electrons can easily go down the hill (to the n-side), but can't climb it (to the p-side). A schematic representation of the diode is shown in Fig. 2.

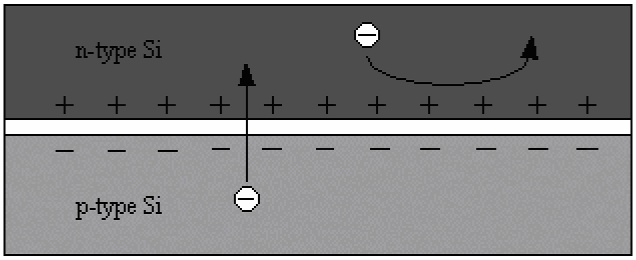

Fig. 2. The p-n junction before irradiation with light

Now, when light, in the form of photons, hits the cell, its energy frees electron-hole pairs. Each photon with enough energy will normally free exactly one electron, and results in a free hole as well. If this happens close enough to the electric field, or if they happen to wander into its range of influence, the field will send the electron to the n-side, and the hole to the p-side. This causes further disruption of electrical neutrality, and if we provide an external current path, electrons will flow through the path to their original side (the p-side) to unite with holes the electric field sent there, doing work for us along the way. The electron flow provides the current, and the cell's electric field causes a voltage. With both current and voltage, we have power, which is the product of the two. The process taking place on irradiation in a solar cell is shown in Fig. 3.

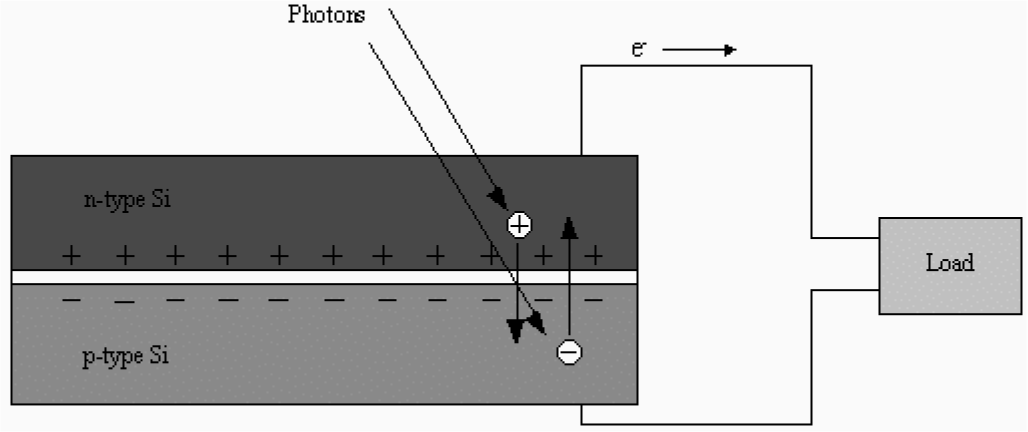

Fig. 3. Operation of a solar cell

4. Components of solar cell

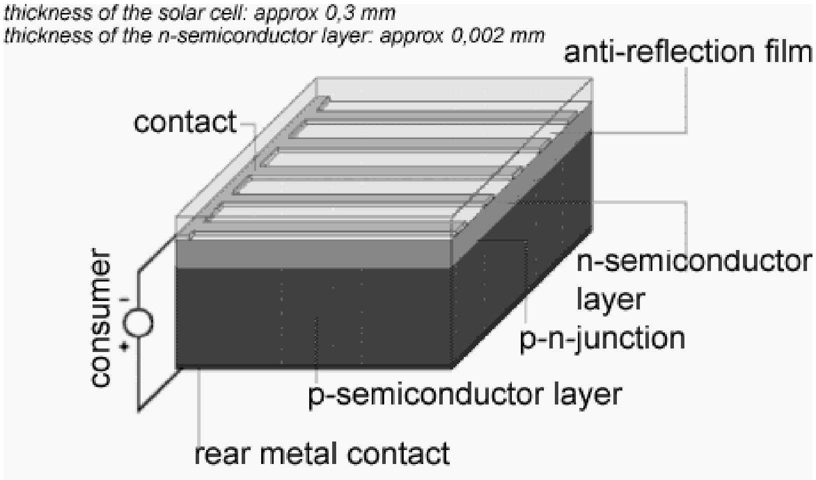

Fig. 4. Schematic representation of the actual solar cell

In addition to the above mentioned semiconductor which is called as the absorber in semiconductor technology. Fig. 4 shows the schematic of the actual solar cell. The remaining components are explained further.

4.1. Electrical contacts

Electrical contacts are essential to a photovoltaic cell because they bridge the connection between the semiconductor material and the external electrical load, such as a light bulb. The back contact of a cell, *i.e,* on the side away from the incoming sunlight *i.e* is relatively simple. It usually consists of a layer of aluminum or molybdenum metal. But the front contact, on the side facing the sun, *i.e* is more complicated. When sunlight shines on the photovoltaic cell, a current of electrons flows all over its surface. If we attach contacts only at the edges of the cell, it will not work well because of the great electrical resistance of the top semiconductor layer. Only a small number of electrons would make it to the contact.

To collect the maximum current, one must place contacts across the entire surface of a photovoltaic cell. This is normally done with a "grid" of metal strips or "fingers." However, placing a large grid, which is opaque, on the top of the cell shades active parts of the cell from the sun. The cell's conversion efficiency is thus significantly reduced. To improve the conversion efficiency, we must minimize these shading effects. Another challenge in cell design is to minimize the electrical resistance losses when applying grid contacts to the solar cell material. These losses are related to the solar cell material's property of opposing the flow of an electric current, which results in heating the material. Therefore, in designing grid contacts, we must balance shading effects against electrical resistance losses. The usual approach is to design grids with many thin, conductive fingers spreading to every part of the cell's surface. The fingers of the grid must be thick enough to conduct well (with low resistance), but thin enough not to block much of the incoming light. This kind of grid keeps resistance losses low while shading only about 3% to 5% of the cell's surface.

Grids can be expensive to make and can affect the cell's reliability. To make top-surface grids, we can either deposit metallic vapors on a cell through a mask or paint them on via a screen-printing method. Photolithography is the preferred method for the highest quality, but has the greatest cost. This process involves transferring an image via photography, as in modern printing. An alternative to metallic grid contacts is a transparent conducting oxide (TCO) layer such as tin oxide (SnO_2). The advantage of TCOs is that they are nearly invisible to incoming light, and they form a good bridge from the semiconductor material to the external electrical circuit. TCOs are very useful in manufacturing processes involving a glass superstrate, which is the covering on the sun-facing side of a PV module. Some thin-film PV cells, such as amorphous silicon and cadmium telluride, use superstrates. In this process, the TCO is generally deposited as a thin film on the glass superstrate before the semiconducting layers are deposited. The semiconducting layers are then followed by a metallic contact that will actually be the bottom of the cell. The cell is actually constructed "upside down," from the top to the bottom. But the construction technique is not the only thing that determines whether a metallic grid or TCO is best for a certain cell design. The sheet resistance of the semiconductor is also an important consideration. In crystalline silicon, for example, the semiconductor carries electrons well enough to reach a finger of the metallic grid. Because the metal conducts electricity better than a TCO, shading losses are less than losses associated with using a TCO. Amorphous silicon, on the other hand, conducts very poorly in the horizontal direction. Therefore, it benefits from having a TCO over its entire surface.

4.2. Antireflective coating

Since, silicon is a shiny gray material and can act as a mirror, reflecting more than 30% of the light that shines on it. To improve the conversion efficiency of a solar cell, and to minimize the amount of light reflected the semiconductor material should capture as much light as possible to use in freeing electrons. Two techniques are commonly used to reduce reflection. The first technique is to coat the top surface with a thin layer of silicon monoxide (SiO). A single layer reduces surface reflection to about 10%, and a second layer can lower the reflection to less than 4%. A second technique is to texture the top surface. Chemical etching creates a pattern of cones and pyramids, which capture light rays that might otherwise be deflected away from the cell. Reflected light is redirected down into the cell, where it has another chance to be absorbed.

5. Cell to module

In order to make the appropriate voltages and outputs available for different applications, single solar cells are interconnected to form larger units. Cells connected in series have a higher voltage, while those connected in parallel produce more electric current. The interconnected solar cells are usually embedded in transparent Ethyl-Vinyl-Acetate, fitted with an aluminum or stainless steel frame and covered with transparent glass on the front side.

The typical power ratings of such solar modules are between 10 W peak and 100 W peak. The characteristic data refer to the standard test conditions of 1000 W/m² solar radiation at a cell temperature of 25° Celsius. The manufacturer's standard warranty of ten or more years is quite long and shows the high quality standards and life expectancy of today's products.

6. Types of silicon solar cells

One can distinguish three cell types according to the type of crystal: monocrystalline, polycrystalline and amorphous. To produce a monocrystalline silicon cell, absolutely pure semiconducting material is necessary. Monocrystalline rods are extracted from melted silicon and then sawed into thin plates. This production process guarantees a relatively high level of efficiency.

Table 1. Efficiencies of various silicon based solar cells

Material	**Level of efficiency in % Lab**	**Level of efficiency in % Production**
Monocrystalline Silicon	approx. 24	14 to17
Polycrystalline Silicon	approx. 18	13 to15
Amorphous Silicon	approx. 13	5 to7

The production of polycrystalline cells is more cost-efficient. In this process, liquid silicon is poured into blocks that are subsequently sawed into plates. During solidification of the material, crystal structures of varying sizes are formed, at whose borders defects emerge. As a result of this crystal defect, the solar cell is less efficient. If a silicon film is deposited on glass or another substrate material, this is a so-called amorphous or thin layer cell. The layer thickness amounts to less than 1µm (thickness of a human hair: 50-100 µm), so the production costs are lower due to the low material costs. However, the efficiency of amorphous cells is lower than that of the other two cell types. Because of this, they are primarily used in low power equipment (watches, pocket calculators) or as facade elements. Table 1 shows the efficiencies of various silicon based solar cells.

7. Thin film technology

The various thin-film technologies currently being developed to reduce the amount (or mass) of light absorbing material required in creating a solar cell. This can lead to reduced processing costs from that of bulk materials (in the case of silicon thin films) but also tends to reduce energy conversion efficiency, although many multi-layer thin films have efficiencies above those of bulk silicon wafers.

7.1. Crystalline thin-film silicon

The first considerations concerning thinner silicon wafers for solar cells were made by Wolf and Lofersky, while simulating the ideal parameters for record high efficiencies. They pointed out that with decreasing cell thickness the open circuit voltage increases due to the reduced saturation current which again is a result of a decreasing geometry factor. The first theoretical work on light trapping in silicon layers suggested a lambertian back reflector as a simple but efficient structure.

7.1.1. The basic components of a crystalline silicon thin-film solar cell (c-SiTFC)

The linking feature of all c-SiTFC approaches is the underlying substrate needed as a mechanical support due to the reduced thickness of the active silicon layer of typically 5–50 µm. The substrate consists either of low quality silicon or of foreign materials such as glass, ceramics or graphite. The choice of the substrate material determines the maximum allowed temperature for solar cell processing and therefore nearly all c-SiTFC approaches can be assigned to one of the three categories: (1) high-temperature approach; (2) low-temperature approach; and (3) transfer techniques, which are described below.

7.2. Other promising materials for thin film solar cells

Other than silicon there are various other materials which are showing promising efficiencies. They are Copper Indium Diselenide (CIS), Copper Indium Gallium

Diselenide (CIGS), Cadmium Telluride(CdTe) and Gallium Arsenide(GaAs). An efficiency of 19.5 % has been achieved in the lab scale using CIGS based solar cells.

7.2.1. Cadmium Telluride (CdTe)

Cadmium telluride is an efficient light-absorbing material for thin-film solar cells. Compared to other thin-film materials, CdTe is easier to deposit and more suitable for large-scale production. Despite much discussion of the toxicity of CdTe-based solar cells, this is the only technology (apart from amorphous silicon) that can be delivered on a large scale, as shown by First Solar and Antec Solar. There is a 40 megawatt plant in Ohio (USA) and a 10 megawatt plant in Germany. First Solar is scaling up to a 100 MW plant in Germany.

The perception of the toxicity of CdTe is based on the toxicity of elemental cadmium, a heavy metal that is a cumulative poison. Scientific work, particularly by researchers of the National Renewable Energy Laboratories (NREL) in the USA, has shown that the release of cadmium to the atmosphere is lower with CdTe-based solar cells than with silicon photovoltaics and other thin-film solar cell technologies.

7.2.2 Cadmium Indium Gallium Diselenide (CIGS)

CIGS are multi-layered thin-film composites. The abbreviation stands for copper indium gallium selenide. Unlike the basic silicon solar cell, which can be modelled as a simple p-n junction (see under semiconductor), these cells are best described by a more complex heterojunction model. The best efficiency of a thin-film solar cell as of December 2005 was 19.5% with CIGS. Higher efficiencies (around 30%) can be obtained by using optics to concentrate the incident light. The use of gallium increases the bandgap of the CIGS layer as compared to CIS thus increases the voltage. In another point of view, gallium is added to replace as much indium as possible due to gallium's relative availability to indium. Approximately 70% of Indium currently produced is used by the flat-screen monitor industry. Some investors in solar technology worry that production of CIGS cells will be limited by the availability of indium.

Producing 2 GW of CIGS cells (roughly the amount of silicon cells produced in 2006) would use about 10% of the indium produced in 2004. For comparison, silicon solar cells used up 33% of the world's electronic grade silicon production in 2006! Nanosolar claims to waste only 5% of the indium it uses. As of 2006, the best conversion efficiency for flexible CIGS cells on polyimide is 14.1%. That being said, indium can easily be recycled from decommissioned PV modules. The recycling program in Germany would be one good example to follow. It also highlights the new regenerative industrial paradigm: "From cradle to cradle". Selenium allows for better uniformity across the layer and so the number of recombination sites in the film are reduced which benefits the quantum efficiency and thus the conversion efficiency.

Table 2. Comparison efficiency of CdTe and CIGS based solar cells

Material	**Bandgap (eV)**	**Cost per watt (\$/W)**	**Efficiency (Lab) (%)**	**Efficiency (Com) (%)**
CdTe	1.56	0.6	16.4	11
CIGS	1.02 – 1.68	0.57	19.5	14

7.2.3 Copper Indium Diselenide (CIS)

$$\begin{pmatrix}Cu\\Ag\\Au\end{pmatrix}\begin{pmatrix}Al\\Ga\\In\end{pmatrix}\begin{pmatrix}S\\Se\\Te\end{pmatrix}_2$$

Fig. 5. Possible combinations of I III VI group elements having photovoltaic effect

The materials based on CuInSe2 that are of interest for photovoltaic applications include several elements from groups I, III and VI in the periodic table. These semiconductors are especially attractive for thin film solar cell application because of their high optical absorption coefficiency and versatile optical and electrical characteristics which can in principle be manipulated and tuned for a specific need in a given device. CIS is an abbreviation for general chalcopyrite films of copper indium selenide (CuInSe2), CIGS mentioned above is a variation of CIS. While these films can achieve 13.5% efficiency, their manufacturing costs at present are high when compared with a silicon solar cell but continuing work is leading to more cost-effective production processes. A manufacturing plant was built in Germany by Würth Solar. It was inaugurated in October 2006. Full production is expected by end of 2006. There are more plans by AVANCIS and Shell in a joint effort to build another plant in Germany with a capacity of 20 MW. Honda in Japan has finished its pilot-plant testing and is launching its commercial production. In North America, Global Solar has been producing pliable CIS solar cell in smaller scale since 2001. Apart from Daystar Technologies and Nanosolar mentioned in CIGS, there are other potential manufacturers coming on line such as Miasole using a vacuum sputtering method and also a Canadian initiative CIS Solar attempting to make solar cells by low cost electroplating process.

6.7.2.4 Gallium arsenide (GaAs) multijunction

High-efficiency cells have been developed for special applications such as satellites and space exploration. These multijunction cells consist of multiple thin films produced using molecular beam epitaxy. A triple-junction cell, for example, may consist of the semiconductors: GaAs, Ge, and GaInP2. Each type of semiconductor will have a characteristic band gap energy which, loosely speaking, causes it to absorb light most efficiently at a certain color, or more precisely, to absorb electromagnetic radiation over a portion of the spectrum. The semiconductors are carefully chosen to absorb nearly all of the solar spectrum, thus generating electricity from as much of the solar energy as possible. GaAs multijunction devices are the most efficient solar cells to date, reaching as high as 29% efficiency. They are also some of the most expensive cells per unit area (up to US\$40/cm^2).

6.8. Dye-sensitized cells

Nano-crystalline dye-sensitized solar cells are based on the mechanism of a fast regenerative photoelectrochemical process. The main difference of this types of solar cells compared to conventional cells is that the functional element, which is responsible for light absorption (the dye), is separated from the charge carrier transport itself. In the case of the n-type semiconductor TiO_2 (band gap 3.2 eV), this results in a working cycle starting with the dye excitation by an absorbed photon at the TiO_2/electrolyte interface and an electron injection into the TiO_2. The injected electrons may migrate to the front electrode (a transparent TCO glass) and can be extracted as an external current. The dye is subsequently reduced by a redox electrolyte, based on an organic solvent and the redox couple iodide/triiodide. The major advantage of the concept of dye sensitization is the fact that the conduction mechanism is based on a majority carrier transport as opposed to the minority carrier transport of conventional inorganic cells. Thus, impure starting materials and a simple cell processing without any clean room steps are permitted, yet resulting in promising conversion efficiencies of 7–11% and the hope of a low cost device for photoelectrochemical solar energy conversion. The most important issue of the dye-sensitized cells is the stability over the time and the temperature range which occurs under outdoor conditions.

6.9 Organic solar cells

Besides dye-sensitized solar cells, which may be considered as organic/inorganic hybrid cells, other types of organic solar cells have currently become of broader interest. These cells can be divided roughly into molecular and polymer organic solar cells or into flat-layer systems and bulk heterojunctions. Extremely high optical absorption coefficients are possible with these materials, which offer the possibility for the production of very thin solar cells (far below 1 mm) and therefore only very small amounts of needed materials. Considering the fact that light-emitting films of plastic materials have been realized there is a chance to achieve photovoltaic conversion also in such materials.

Only modest solar conversion efficiencies of up to 1% were reached until 1999 but efficiencies then increased rapidly. With molecular flat-layer systems based on molecular organic single crystals made of iodine- or bromine-doped pentacene, efficiencies of up to 3.3% under AM1.5 illumination have been reported at Lucent Technologies. Nearly the same value was reported with improved bulk heterojunctions (interpenetrating network) of conjugated polymers and fullerene derivatives. Before these cells become practical, which at the moment looks still far away, the efficiency will have to be increased further. Also, long-term stability and protection against environmental influences are significant challenges.

6.10 Concentrating photovoltaics (CPV)

Concentrating photovoltaic systems use a large area of lenses or mirrors to focus sunlight on a small area of photovoltaic cells. If these systems use single or dual-axis tracking to improve performance, they may be referred to as Heliostat Concentrator Photovoltaics (HCPV). The primary attraction of CPV systems is their reduced usage of semiconducting material which is expensive and currently in short supply. Additionally, increasing the concentration ratio improves the performance of general photovoltaic materials and also allows for the use of high-performance materials such as gallium arsenide. Despite the advantages of CPV technologies their application has been limited by the costs of focusing, tracking and cooling equipment. On October 25, 2006, Australia announced it would construct a solar plant using this technology to come online in 2008 and be completed by 2013. This plant, at 154 MW, would be ten times larger than the largest current photovoltaic plant in the world.

6.11. Surface structuring to reduce reflection loss

For example, construction of the cell surface in a pyramid structure, so that incoming light hits the surface several times. New material: for example, gallium arsenide (GaAs), cadmium telluride (CdTe) or copper indium selenide ($CuInSe_2$).

6.12. Tandem or stacked cells

In order to be able to use a wide spectrum of radiation, different semiconductor materials, which are suited for different spectral ranges, will be arranged one on top of the other.

6.13. Natural limits of efficiency

In addition to optimizing the production processes, work is also being done to increase the level of efficiency, in order to lower the costs of solar cells. However, different loss mechanisms are setting limits on these plans. Basically, the different semiconductor materials or combinations are suited only for specific spectral ranges. Therefore a specific portion of the radiant energy cannot be used, because the light quanta (photons) do not have enough energy to "activate" the charge carriers. On the other hand, a certain amount of surplus photon energy is transformed into heat rather than into electrical energy. In addition to that, there are optical losses, such as the shadowing of the cell surface through contact with the glass surface or reflection of incoming rays on the cell surface. Other loss mechanisms are electrical resistance losses in the semiconductor and the connecting cable. The disrupting influence of material contamination, surface effects and crystal defects, however, are also significant.

Single loss mechanisms (photons with too little energy are not absorbed, surplus photon energy is transformed into heat) cannot be further improved because of inherent physical limits imposed by the materials themselves. This leads to a theoretical maximum level of efficiency, i.e. approximately 28% for crystal silicon.

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Chapter 7
IONIC LIQUIDS

C. M. Janet

1. Introduction

An ionic liquid (IL) is a recently emerged new class of solvents which often exist as fluid at room temperature. They consist entirely of ionic species. In a broad sense, the term includes all molten salts, for instance, sodium chloride at temperatures higher than 800 °C. Today, however, the term "ionic liquid" is commonly used for salts whose melting point is relatively low (below 100 °C). In particular, the salts that are liquid at room temperature are called room-temperature ionic liquids or RTILs. They have many fascinating properties which make them of fundamental interest to all chemists, since both the thermodynamics and the kinetics of reactions carried out in ionic liquids are different to those that take place in conventional molecular solvents and also the chemistry is different and unpredictable at our current state of knowledge.

Designing of IL can be done by varying two components, they are anions and cations. Either the solvents can be designed with a particular end use in mind or to possess a particular set of properties. Hence the term designer solvents have been assigned to the ionic liquids.

The first room-temperature ionic liquid $[EtNH_3][NO_3]$ (m.pt. 12 °C) was discovered in 1914 , but interest did not develop until the discovery of binary ionic liquids made from mixtures of aluminum (III) chloride and *N*-alkylpyridinium or 1, 3 dialkylimidazolium chloride. In general, ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt and hence the melting point will be lower. Ionic liquids come in two main categories, namely simple salts (made of a single anion and cation) and binary ionic liquids (salts where equilibrium is involved). For example, $[EtNH_3][NO_3]$ is a simple salt whereas mixtures of aluminum (III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species.

Being advantageous over conventional organic solvents, ILs have attractive physicochemical properties such as negligible vapor pressure even at elevated temperatures, excellent thermal and chemical stability, high ionic conductivity up to 0.1 S cm^{-1}, high mobility, high heat capacity, cohesive energy density, low toxicity and non-flammability. Furthermore, as the physicochemical properties of ILs strongly depend on the species of cation and anion and the length of the lateral alkyl groups on the heterocyclic rings, alternation of the anion or the length of the alkyl groups allows fine tuning of the physico chemical properties such as viscosity, solvation, catalytic activity, hydrophobicity, density and melting points. For example, the melting points of ionic liquids are a function of the alkyl chain length and depending upon the chain length it can form liquid crystalline phases. Another important property that changes with structure is the miscibility of water in these ionic liquids. This behavior can be of substantial benefit when carrying out solvent extractions or product separations, as the relative solubilities of the ionic and extraction phase can be adjusted to make the separation as easy as possible. Cations are normally big bulky and asymmetric accounting for the low melting points. The anion contributes more to the overall characteristics of the IL and determines the air and water stability.

Many classes of chemical reactions, such as Diels-Alder reactions and Friedel-Crafts reactions, can be performed using ionic liquids as solvents. Recent work has shown that ionic liquids can serve as solvents for bio-catalysis. The miscibility of ionic liquids with water or organic solvents varies with side chain lengths on the cation and with choice of anion. They can be functionalized to act as acids, bases or ligands and have been used as precursor salts in the preparation of stable carbenes. Because of their distinctive properties, ionic liquids are attracting increasing attention in many fields, including organic chemistry, electrochemistry, catalysis, physical chemistry, and engineering for instance magnetic ionic liquid.

IL are environmentally friendly alternatives to organic solvents for liquid-liquid extractions, catalysis, separations and electrochemistry. IL will reduce or eliminate the related costs, disposals requirements, and hazards associated with volatile organic compounds. The ability to fine tune the properties of the IL medium will allow replacing the specific solvents in a variety of different processes.

Room temperature ionic liquids

We are also always on the look out for new potentially environmentally benign separation media. One such possibility is the class of solvents known as room temperature ionic liquids. Room temperature ionic liquids consist of bulky and asymmetric organic cations such as 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, N-methyl-N-alkylpyrrolidinium and ammonium ions. A wide range of anions is employed, from simple halides, which generally inflect high melting points, to inorganic anions such as tetrafluoroborate and hexafluorophosphate and to large organic anions like bis-trifluorsulfonimide, triflate or tosylate. There are also many interesting examples of uses of ionic liquids with simple non-halogenated organic anions such as formate, alkylsulfate, alkylphosphate or glycolate. As an example, the melting point of 1-butyl-3-methylimidazolium tetrafluoroborate or **[bmim] [BF_4]** with an imidazole skeleton is about -80 °C, and it is a colorless liquid with high viscosity at room temperature.

It has been pointed out that in many synthetic processes using transition metal catalyst; metal nanoparticles play an important role as the actual catalyst or as a catalyst reservoir.

It also been shown that ionic liquids (ILs) are an appealing medium for the formation and stabilization of catalytically active transition metal nanoparticles. More importantly, ILs can be made that incorporate co-ordinating groups, for example, with nitrile groups on either the cation or anion (CN-IL). In various C-C coupling reactions catalyzed by palladium catalyst, it has been found the palladium nanoparticles are better stabilized in CN-IL compared to non-functionalized ionic liquids; thus enhanced catalytic activity and recyclability are realized.

Advantages of IL

Due to their non-volatility, effectively eliminating a major pathway for environmental release and contamination, ionic liquids have been considered as having a low impact on the environment and human health, and thus recognized as solvents for green chemistry. However, this is distinct from toxicity, and it remains to be seen how 'environmentally-friendly' ILs will be regarded once widely used by industry. Research into IL aquatic toxicity has shown them to be as toxic as or more so than many current solvents already in use. Available research also shows that mortality isn't necessarily the most important metric for measuring their impacts in aquatic environments, as sub-lethal concentrations have been shown to change organisms' life histories in meaningful ways. According to these researchers balancing between zero VOC emissions, and avoiding spills into waterways (via waste ponds/streams, etc.) should become a top priority. However, with the enormous diversity of substituents available to make useful ILs, it should be possible to design them with useful physical properties and less toxic chemical properties.

With regard to the safe disposal of ionic liquids it has been reported that the use of ultrasound to degrade solutions of imidazolium-based ionic liquids with hydrogen peroxide and acetic acid to relatively innocuous compounds is already practiced.

Despite their low vapor pressure many ionic liquids have also found to be combustible and therefore require careful handling. Brief exposure (5 to 7 seconds) to a flame torch will ignite these IL's and some of them are even completely consumed by combustion.

Ionic liquids are highly solvating, non-coordinating medium in which a variety of organic and inorganic solutes are able to dissolve. They are outstanding good solvents for a variety of compounds, and their lack of a measurable vapour pressure makes them a desirable substitute for VOCs. Ionic liquids are attractive solvents as they are relatively inexpensive to manufacture.

The key point about ionic liquids is that they are liquid salts, which means they consist of a salt that exists in the liquid phase and have to be manufactured, they are not simply salts dissolved in liquid. Usually one or both of the ions is particularly large in the case of ionic liquids. The low degree of symmetry of the cation will result in IL having a reduced lattice energy and hence with lower melting points. Special conditions are not usually required when carrying out reactions in neutral ionic liquids. For example, there is often no need to exclude water, or to carry out the reaction under an inert atmosphere. This, combined with the ability to design the ionic liquid to allow for easy separation of the product, makes reactions in ionic liquids extremely straightforward to carry out. Moreover, processes in ionic liquids do not require strictly anhydrous conditions or an inert atmosphere to carry out the reaction. This makes the whole reaction sequence easier, cheaper, and less time consuming to perform.

Disadvantages of IL

Extracting the chemical product from the ionic liquid in pure form can pose a problem. Water soluble compounds can easily be extracted with water and distillation can be used to separate compounds with high vapour pressure, however higher temperatures would be required to extract chemical products with low vapour pressures which will most likely result in the decomposition of the chemical product. Moisture sensitivity and the difficulty of separation of products containing heteroatoms are the difficulties encountered while using Ionic liquids.

Examples for typical IL cations

Cations such as substituted imidazoliums, substituted pyridiniums

Examples of an alkylpyridinium cation is shown below:

Examples of dialkylimidazolium cations are shown below:

N-butyl pyridinium, 1-alkyl 3 –methylimidazolium cations

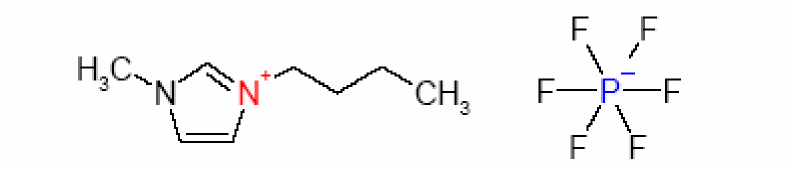
Examples for IL anions

Anions as borates, phosphates and halides and others Less common anions include: Triflate, Nonaflate, Bis trifylamide, Trifluoro acetate, Hepta fluoro butanoate etc.

Room Temperature Ionic Liquids

PF_6- for moisture stable water immiscible IL

BF_4- for moisture stable, but water miscible IL



Naming of IL can be done in the following way, including Cation Cation Anion Anion names in the respective order. For example, the following ionic liquid is named as 1-butyl-3-methylimidazolium hexafluorophosphate.

Chloroaluminate Ionic liquids

Acidic or basic IL can be obtained through varying the concentration of the following species

$Al_2Cl_7^- + Cl^- \rightarrow 2\ AlCl_4^-$

Acidic basic neutral

Large electrochemical windows are possible for both chloro and bromo ionic liquids. Basic haloaluminate in molten state preclude salvation and solvolysis of metal ion species. But they are moisture sensitive.

Applications:

Applications as solvents in

1. Catalysis
2. Synthesis
3. Electrochemistry
4. Separations

Recent activities in room temperature ionic liquids as solvents include:

Supercritical – CO_2 stripping after extraction, preparation of conducting RTIL, Ionic liquid polymer gel electrolytes, catalytic hydrogenation reactions, electrochemistry in RTIL, butene dimerisation, benzene polymerization, two phase separations, Friedel crafts regioselective alkylation and organometallic synthesis.

1. Catalysis

Reactant	**Arene**	**Product**	**Yield (%)**
Ferrocene	Benzene	$Fe(C_5H_5)(C_6H_6)$	53
Ferrocene	Toluene	$Fe(C_5H_5)(C_6H_5Me)$	64
Ferrocene	Naphthalene	$Fe(C_5H_5)(C_{10}H_8)$	53

IL can function both as catalyst and solvent. In a series of arene exchange reactions on ferrocene an acidic $[bmim]^+$ chloroaluminate IL was used where $[Al_2Cl_7]$- is the active

Lewis acid. Lower yields observed for the solid arenes are eliminated in the case of RTIL.

2. Synthesis

Unique solvent effects may enhance the reaction rates in synthesis. Product selectivity can be enhanced by the nature of the anionic species.

Solvent	**Conversion (%) Pent-1-ene**	**Yield (%)**		**TOF (mol/min)**
		Pentane	**Pent-2-ene**	
Acetone	99	38	61	0.55
[bmim][SbF_6]	96	83	13	2.54
[bmim][PF_6]	97	56	41	1.72
[bmim][BF_4]	10	5	5	0.73

3. Electro Chemistry

Unique features of chloroaluminate ionic liquids include a large electrochemical window, although these anions are moisture sensitive. Possible applications include low cost and recyclable electrolytes for batteries, photochemical cells and electroplating. BF_4^- and PF_6^- ionic liquids have been developed as moisture stable electrolytes.

4. Separations

IL based method is a simple method for separations due to their water immiscibility. Ex: Pd (II) complexes in [bmim][BF_4] catalyze hydro dimerization of 1,3-butadiene. After the reaction, almost 97 % of the catalyst can be retained in the ionic liquid phase. RTIL is used as best alternatives to volatile organic solvents for liquid-liquid extractions. Benzene and derivatives partition to [bmim][Pf_6] from aqueous phase and may be selective. For example, *para* - hydroxyl benzoic acid and phthallic acid are soluble in [bmim] [BF_4] at a pH less than 2 where as aniline is soluble in the same IL at a pH greater than 10.

5. **Food science**

The application range of ionic liquid also extends to food science. For instance, [bmim]Cl (1-Butyl-3-methylimidazolium Chloride) is able to completely dissolve freeze dried banana pulp and the solution with an additional 15 % DMSO lends itself to Carbon-13

NMR analysis. In this way the entire banana compositional makeup of starch, sucrose, glucose, and fructose can be monitored as a function of banana ripening.

Future aspects of IL research:

As the green chemistry and IL originates at a single point, better utilizations for the social needs require a joint progress rather than their complimentary development. Insufficient knowledge in ionic liquids and the ignorance of its implications made this field empty without using its capabilities. Hence it is necessary to accumulate full information corresponding to IL for combinatorial development such as comprehensive tocxicity data, physical properties database, various existing chemistry, comparators for direct comparison of IL and other traditional solvents, industrial input into a research agenda, economic synthetic pathways and also a wider availability.

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Chapter - 8
FUEL CELLS

T. Meialagan

1. Introduction

In today's society there is an enormous demand for energy. Environmental concerns necessitate that new energy sources must be efficient and have zero (or very low) emissions. The fuel cell is an emerging technology that can meet these demands. A fuel cell is defined as an electrochemical device that can continuously convert chemical energy into electrical energy. Much like a battery, a fuel cell produces electrical energy. However, unlike a battery, the reactants are continuously supplied and products are continuously removed. Hence, a fuel cell does not store energy. Typically, hydrogen is the fuel consumed at the anode; oxygen (usually from air) is consumed at the cathode. In an acid electrolyte, the cell reactions are as follows:

Anode: $H_2 \longrightarrow 2\,H^+ + 2\,e^-$

Cathode: $O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$

The main advantage a fuel cell has over heat engines is that they are theoretically more efficient and produce no noxious emissions. Also, fuel cells operate very quietly, reducing noise pollution. Because of these advantages, fuel cells are being developed for numerous commercial and military applications, such as automobiles, portable electronic devices, mobile and stationary power generation.

Sir William Grove invented fuel cells around 1839. But it is only in the last 40 years, since the commercial fuel cell systems were applied in space technology, that their properties are highly desirable for specific applications. Because the efficiency of electrochemical energy conversion by fuel cells is high, the interest has lead to an intensive development of components and of better cell designs. Therefore it can be expected that performance will improve significantly in the near future.

There are, however, several hurdles that must be overcome before fuel cells can become a commercially viable technology on a large scale. Cost is one such factor. The required catalyst, membrane and cell hardware (e.g. bipolar plates) are expensive, resulting in a very high initial cost. Also, hydrogen storage requires a large (weight and volume) storage system. This reduces the operational range of portable fuel cell devices. There is much research for better ways to store hydrogen. In particular, storing hydrogen in carbon nanotubes and metal hydrides has received a great deal of attention recently.

1.2 How does a fuel cell works?

The basic physical structure or building block of most fuel cells consists of an electrolyte layer in contact with porous anode and cathode electrodes on either side. All fuel cells have similar basic operating principle. The input fuel is catalytically reacted (electrons removed from the fuel) in the fuel cell to create an electric current. The input fuel passes over the anode is catalytically split into electrons and ions. Air/oxygen passes over the cathode is reduced by the electrons which are generated at anode and passed on to the cathode by external circuit. At cathode, the ions which are formed at anode and transported to cathode through the electrolyte, combine with the oxide ions and generate the oxidized product. If the fuel happens to be hydrogen, then water is formed.

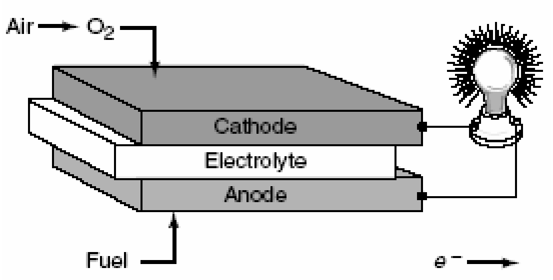


Fig.1. Schematic of a fuel cell

1.3 The Promise of Fuel Cells

Compared to internal combustion engines, fuel cell has an efficient conversion process. The internal combustion engine is less efficient due to the conversion of chemical energy into thermal energy and then thermal energy to mechanical energy. If cars were powered by electricity generated from fuel cell, there would be no combustion involved.

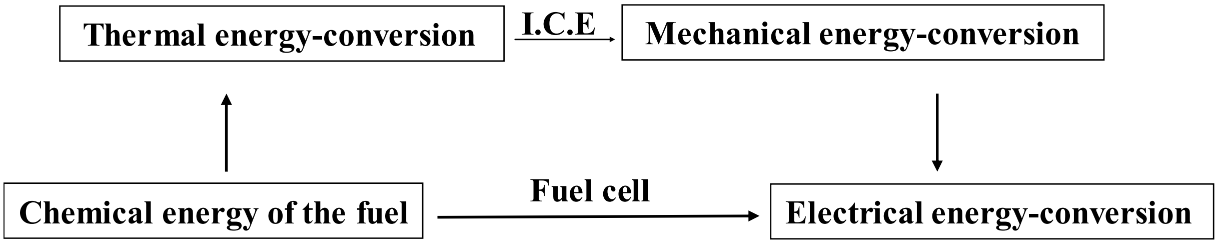


Fig 2. Direct energy conversion with Fuel cells in comparison to conventional internal combustion engine (ICE)

Fuel cells have many applications that make them attractive when compared with the existing conventional energy conversion technologies, namely:

(i) Promise of high efficiency
(ii) Promise of low or zero emissions
(iii) Simplicity
(iv) No moving parts and promise of long life
(v) Quiet
(vi) Fuel and size flexibility

Because of their attractive properties, fuel cells have already been developed and come into widespread commercial use through three main applications: transportation, stationary power generation and portable applications.

2. Thermodynamical and kinetic aspects of electrochemical energy transformation

The energy storage and power characteristics of electrochemical energy conversion systems follow directly from the thermodynamic and kinetic formulations for chemical reactions as adapted to electrochemical reactions.

2.1. Thermodynamics

The basic thermodynamic equations for a reversible electrochemical transformation are given as

$$\Delta G = \Delta H - T\Delta S$$

where ΔG is the Gibbs free energy, or the energy of a reaction available for useful work, ΔH is the enthalpy, or the energy released by the reaction, ΔS is the entropy, and T is the absolute temperature, with $T\Delta S$ being the heat associated with the organization/disorganization of materials. The terms ΔG, ΔH, and ΔS are state functions and depend only on the identity of the materials and the initial and final states of the reaction.

Effect of temperature on free energy change (Gibbs–Helmholtz equation) is given by

$$\Delta G = \Delta H + T(\partial(\Delta G)/ \partial T)_p$$

or

$$(\partial(\Delta G/T)/ \partial T)_p = - \Delta H/T^2$$

Effect of pressure on free energy change is given by

$$(\partial(\Delta G)/ \partial P)_T = \Delta nRT/P$$

The maximum electrical work (W_{el}) obtainable in a fuel cell operating at constant temperature and pressure is given by the change in Gibbs free energy (ΔG) of the electrochemical reaction:

$$\Delta G = -nFE \quad \text{----} \ (1)$$

and

$$\Delta G^o = -nFE^o \ \text{----} \ (2)$$

where n is the number of electrons transferred per mole of reactants, F is the Faraday constant, being equal to the charge of 1 equiv of electrons, and E is the voltage of the cell with the specific chemical reaction; in other words, E is the electromotive force (emf) of the cell reaction. The voltage of the cell is unique for each reaction couple. The amount of electricity produced, nF, is determined by the total amount of materials available for reaction and can be thought of as a capacity factor; the cell voltage can be considered to be an intensity factor. The usual thermodynamic calculations on the effect of temperature, pressure, etc., apply directly to electrochemical reactions. Spontaneous processes have a negative free energy and a positive emf with the reaction written in a reversible fashion, which goes in the forward direction. The van't Hoff isotherm identifies the free energy relationship for bulk chemical reactions as

$$\Delta G = \Delta G^o + RT \ln(Q); \ Q = A_P/A_R$$

where R is the gas constant, T the absolute temperature and Q is the term dependent on the activity of reactants (A_R) and products (A_P).

Combining eq (1) and (2) with the van't Hoff isotherm, one obtain the Nernst equation for electrochemical reactions:

$$E = E^o - RT/nF \ln(Q)$$

According to the Nernst equation for hydrogen-oxygen reaction, the ideal cell potential depends on the cell temperature, pressure of reactants, etc. The impact of temperature on the ideal voltage, E, for the oxidation of hydrogen is shown in Fig. 3.

At a given temperature, the ideal cell potential can be increased by operating at higher reactant pressures, according to the equation

$E = E^0 + (RT/2F) \ln [P\ H_2/P\ H_2O] + (RT/2F) \ln [P^{1/2}\ O_2]$

and improvements in fuel cell performance have, in fact, been observed at higher pressures.

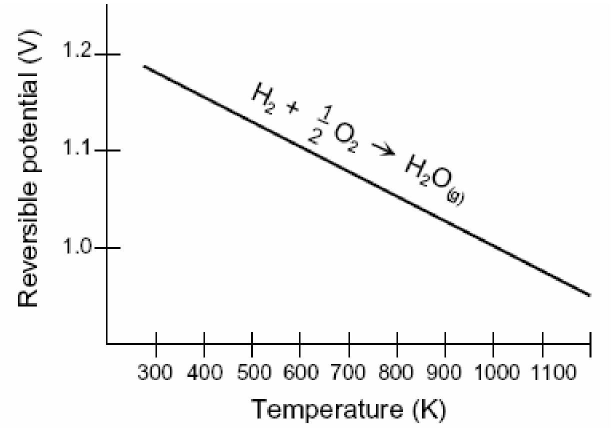


Fig.3. H_2/O_2 fuel cell ideal potential as a function of temperature

2.2. Kinetics

Thermodynamics describe reactions at equilibrium and the maximum energy release for a given reaction. Useful work (electrical energy) is obtained from a fuel cell only when a reasonable current is drawn, but the actual cell potential is decreased from its equilibrium potential because of irreversible losses. Figure 4 shows a typical voltage-current (E - I) discharge curve for a fuel cell with an open-circuit voltage E_{oc}. The overpotential $\eta = (E_{oc} - E)$ reflects the resistive IR losses due to the surface reaction kinetics, the resistance to transport of the working ion, H^+ or O^{2-} between the reductant and the oxidant reactive sites, and the resistance to diffusion of the oxidant and/or reductant to the catalytic sites and their products away from these sites. At low currents, the performance of a fuel cell is dominated by kinetic losses. These losses mainly stem from the high overpotential of the reactions occurred at anode and cathode. At intermediate currents, ohmic losses arise from ionic losses in the electrodes and separator, although contact and electronic resistances can be important under certain operating conditions. At high currents, mass transport limitations become increasingly important. These losses are due to reactants not being able to reach the electrocatalytic sites. Typically, oxygen is the problem due to flooding of the cathode by liquid water, but protons and electrons can also cause mass-transfer limitations.

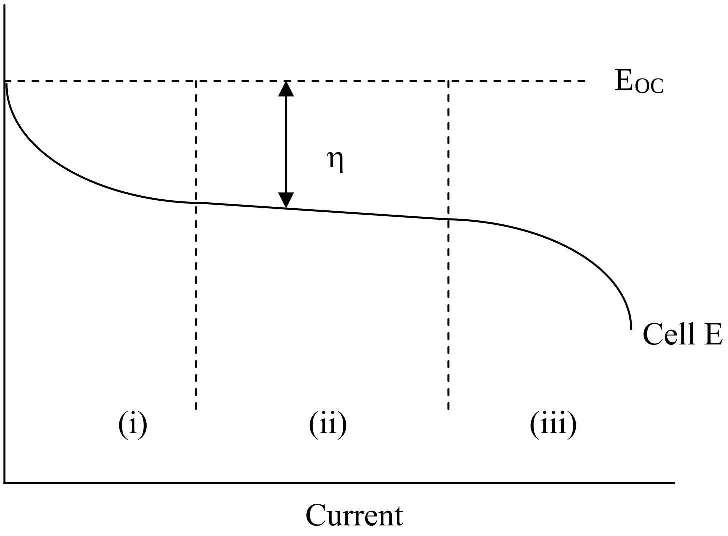


Fig.4. Typical polarization curve for a fuel cell: voltage drops due to: (i) surface reaction kinetics; (ii) electrolyte resistance; and (iii) reactant/product diffusion rates

At low current densities (i_o < 1 mA cm^{-2}), electrodes gives a larger R_{tr} and therefore overpotential, η should be greater than 400 mV (at room temperature). An extremely active electrocatalyst is needed to overcome this initial voltage drop in the E versus current discharge curve. The goal of fuel cell developers is to minimize the polarization so that Ecell approaches Eoc. This goal is approached by modifications to fuel cell design (improvement in electrode structures, better electrocatalysts, more conductive electrolyte, thinner cell components, etc.). For a given cell design, it is possible to improve the cell performance by modifying the operating conditions (e.g., higher gas pressure, higher temperature, change in gas composition to lower the gas impurity concentration). However, for any fuel cell, compromises exist between achieving higher performance by operating at higher temperature or pressure and the problems associated with the stability/durability of cell components encountered at the more severe conditions.

2.3. Fuel cell efficiency

The ideal or maximum efficiency of an electrochemical energy converter depends upon electrochemical thermodynamics whereas the real efficiency depends on electrode kinetics. The thermal efficiency of an energy conversion device is defined as the amount of useful energy produced relative to the change in stored chemical energy (commonly referred to as thermal energy) that is released when a fuel is reacted with an oxidant.

$$\varepsilon = \text{Useful energy}/\Delta H$$

In the ideal case of an electrochemical converter, such as a fuel cell, the change in Gibbs free energy, ΔG, of the reaction is available as useful electric energy at the temperature of the conversion. The ideal efficiency of a fuel cell, operating irreversibly, is then

$$\varepsilon = \Delta G/\Delta H$$

The most widely used efficiency of a fuel cell is based on the change in the standard free energy for the cell reaction, for example,

$$H_2 + ½\, O_2 \rightarrow H_2O\ (l)$$

given by

$$\triangle G^o = G^o_{H_2O} - G^o_{H_2} - ½\, G^o_{O_2}$$

where the product water is in liquid form. At standard conditions of 25 ^{o}C (298 K) and 1 atmosphere, the chemical energy (ΔH) in the hydrogen/oxygen reaction is 285.8 kJ/mole, and the free energy available for useful work is 237.1 kJ/mole. Thus, the thermal efficiency of an ideal fuel cell operating reversibly on pure hydrogen and oxygen at standard conditions would be:

$$\varepsilon_{ideal} = 237.1/285.8 = 0.83$$

The efficiency of an actual fuel cell can be expressed in terms of the ratio of the operating cell voltage to the ideal cell voltage. The actual cell voltage is less than the ideal cell voltage because of the losses associated with cell polarization and the iR loss. The thermal efficiency of the fuel cell can then be written in terms of the actual cell voltage,

$$\varepsilon = \text{Useful energy}/\Delta H = \text{Useful power}/(\Delta G/0.83)$$
$$= (\text{Volts}_{actual} \text{ x Current})/(\text{Volts}_{ideal} \text{ x Current}/0.83)$$
$$= 0.83\ (\text{Volts}_{actual})/(\text{Volts}_{ideal})$$

As mentioned, the ideal voltage of a cell operating reversibly on pure hydrogen and oxygen at 1 atm pressure and 25 ºC is 1.229 V. Thus, the thermal efficiency of an actual fuel cell operating at a voltage of E_{cell}, based on the higher heating value of hydrogen, is given by

$$\varepsilon_{ideal} = 0.83 \text{ x } E_{cell}/E_{ideal} = 0.83 \text{ x } E_{cell}/1.229 = 0.675 \text{ x } E_{cell}$$

A fuel cell can be operated at different current densities, expressed as mA/cm^2 or A/ft^2. The corresponding cell voltage then determines the fuel cell efficiency. Decreasing the current density increases the cell voltage, thereby increasing the fuel cell efficiency. The trade-off is that as the current density is decreased, the active cell area must be increased to obtain the requisite amount of power. Thus, designing the fuel cell for higher efficiency increases the capital cost, but decreases the operating cost.

2.4 Choice of Fuels

The technical characteristics, economic feasibility and infrastructure requirements of PEFC electric engines are impacted greatly by the fuel chosen, with large difference between these impacts for the fuels that are presently being considered for transportation applications: hydrogen, methanol, and gasoline or related petroleum distillate fuels.

Table 1. Chemical and Electrochemical Data on Various Fuels

FUEL	**ΔG^0, kcal/mol**	**E_0 theor (V)**	**E_0 max (V)**	**Energy density (kWh/kg)**
Hydrogen	-56.69	1.23	1.15	32.67
Methanol	-166.80	1.21	0.98	6.13
Ammonia	-80.80	1.17	0.62	5.52
Hydrazine	-143.90	1.56	1.28	5.22
Formaldehyde	-124.70	1.35	1.15	4.82
Carbon monoxide	-61.60	1.33	1.22	2.04
Formic acid	-68-20	1.48	1.14	1.72
Methane	-195.50	1.06	0.58	-
Propane	-503.20	1.08	0.65	-

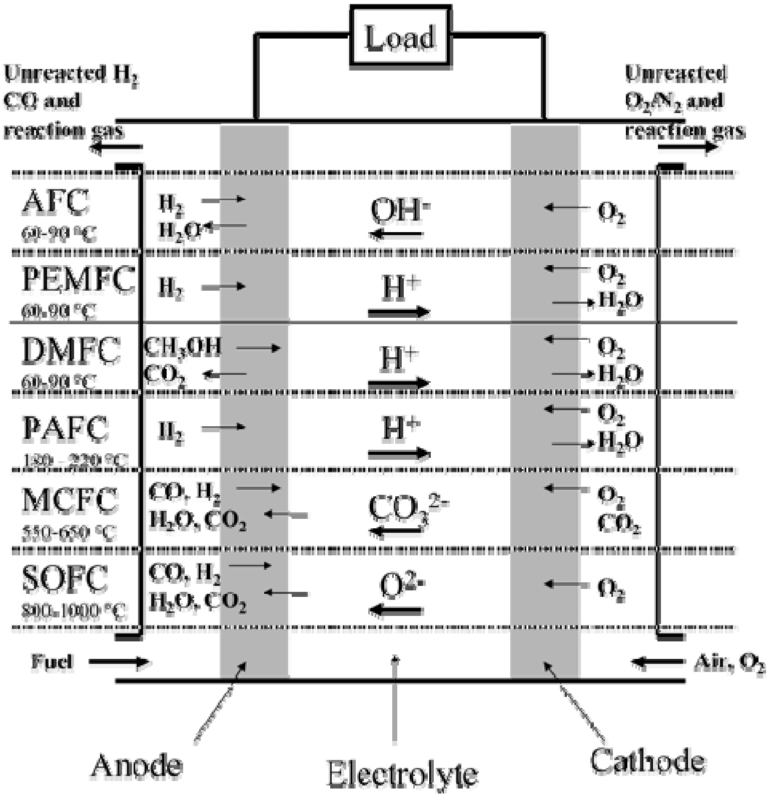
Hydrogen Fuel has the highest energy density, but lack of fuel infrastructure, bulky storage system and safety concerns have motivated fuel cell developers to look for alternative fuel. Indeed, Toyota, Daimler-benz, Ford and other leading developers have shifted their initial emphasis from hydrogen to methanol. Methanol is the only practical carbonaceous fuel that has significant electrochemical reactivity at fuel cell electrodes in the temperature range of interest for portable applications.

It is seen from the Table 1. that hydrogen is the most promising fuel because of its maximum energy density and the maximum voltage that can be derived which is closer to the theoretical value. However, the use of hydrogen as fuel is always associated with the complexity in storing and handling which drive one to reflect on an alternative fuel. Electrochemists are challenged to use a fuel, which is easily transportable and easily converted into energy from the liquid state. Next to hydrogen, methanol is the favourable fuel from the aspects of cost, efficiency, availability, existence in liquid state, stability, oxidizing ability, and electrical yield per gram of fuel. Though methanol has lower energy density than hydrogen, it is attractive over other fuels which pose problems. For instance ammonia has a limitation not only in its storage and handling but also the maximum voltage that can be derived is lesser than that of either hydrogen or methanol; Hydrazine has higher theoretical cell voltage than all the other fuels, but it exhibit the problem of self decomposition leading to the mixed potential and therefore the experimental value obtained will not be truly accounted for by the complete electrochemical combustion of the fuel. Since the other fuels such as formaldehyde, carbon monoxide and formic acid are already in their partially oxidized form, the power density derived from them will be practically lower than other fuels. The use of hydrocarbon such as methane, propane and their higher homologues required reformation to be effectively used as fuels. Carbon monoxide resulting from reforming of hydrocarbons acts as a poison for anode electrocatalysts in low temperature fuel cells, and its removal from the fuel source is a challenging task. Other potential contaminants such as sulphur containing compounds may pose further and new requirements for catalysts and their development. Methanol can be electro-oxidized at a fuel cell anode either directly or indirectly. If used indirectly, methanol is initially reformed to give hydrogen in a high temperature step. The reactor required to accomplish this, however, both lowers practical power densities and rises the inherent thermal signature of the overall power source system. As a consequence, there are strong incentives for developing fuel cells that directly oxidize methanol as a fuel in their anodic compartments.

It is therefore, desirable to use a fuel, which is easily transportable and easily converted into energy from the liquid state. What is needed, therefore, is the will to enter markets of fuel cell developers and manufacturers to combat the anticipated increase in energy demand.

3. Classification of Fuel Cells

Fuel cells are generally classified according to the type of electrolyte and the operating temperature. The most common types of fuel cells, characterized by the electrolyte are listed in Fig 5.



AFC : Alkaline Fuel Cells
PEMFC: Proton Exchange Membrane Fuel Cells
DMFC: Direct Methanol Fuel Cells
PAFC: Phosphoric acid Fuel Cells
MCFC: Molten Carbonate Fuel Cells
SOFC: Solid Oxide Fuel Cells

Fig. 5. Types of fuel cells.

The characteristic features of various types of fuel cells are shown in Table 2.

The heart of the fuel cell is membrane electrode assembly (MEA). The important components and their tasks are given in Table 3. A significant problem is the control of the interface at the junction of the reactant phase, the electrolyte medium, and the catalyzed conducting electrode, the so-called “three-phase boundary”, where the electrolyte, electrode, and reactant all come together. A stable three-phase boundary is critical to good performance and long operation. Therefore, the porosity and the wetting behavior with electrolyte and the electrode surface must be precisely adjusted.

Table 2. Characteristic features of various fuel cells

Electrochemical device	Operating temp (K)	Electrolyte	Charge carrier	Electrolyte state	Fuel for cell	Oxidant for cell
Alkaline fuel cell (AFC)	333-423	45% KOH	OH^-	Immobilized liquid	Hydrogen	O_2/Air
Phosphoric acid fuel cell (PAFC)	453-493	H_3PO_4	H^+	„	Hydrogen	O_2/Air
Proton exchange membrane fuel cell (PEMFC)	333-353	Ion exchange membrane (e.g., Nafion)	H^+	Solid	Hydrogen	O_2/Air
Direct methanol fuel cell (DMFC)	333-353	„	H^+	Solid	Methanol	O_2/Air
Molten carbonate fuel cell (MCFC)	923-973	Alkali carbonate mixture	CO_3^{2-}	Immobilized liquid	Hydrogen	O_2/Air
Solid oxide fuel cell (SOFC)	1073-1273	Yttria-stabilized zirconia	O^{2-}	Solid	Hydrogen	O_2/Air

The electrodes have to be gas (or liquid) permeable and therefore possess a porous structure. The structure and content of the gas diffusion electrodes is quite complex and requires considerable optimization for the practical application. The functions of porous electrodes in fuel cells are: 1) to provide a surface site where gas/liquid ionization or de-ionization reactions can take place, 2) to conduct ions away from or into the three phase interface once they are formed (so an electrode must be made of materials that have good electrical conductance), and 3) to provide a physical barrier that separates the bulk gas phase and the electrolyte. A corollary of first one is that, in order to increase the rates of reactions, the electrode material should be catalytic as well as conductive, porous rather than solid.

Table 3. MEA (Membrane electrode assembly) components and their tasks

MEA component	Task/effect
Anode substrate	Fuel supply and distribution (hydrogen/fuel gas) Electron conduction Heat removal from reaction zone Water supply (vapour) into electrocatalyst
Anode catalyst layer	Catalysis of anode reaction Ion conduction into membrane Electron conduction into substrate Water transport Heat transport
Proton exchange membrane	Ion conduction Water transport Electronic insulation
Cathode catalyst layer	Catalysis of cathode reaction Oxygen transport to reaction sites Ion conduction from membrane to reaction sites Electron conduction from membrane to reaction sites Water removal from reactive zone into substrate Heat generation/removal
Cathode substrate	Oxidant supply and distribution (air/oxygen) Electron conduction towards reaction zone Heat removal Water transport (liquid/vapour)

The catalytic function of electrodes is more important in lower temperature fuel cells and less so in high temperature fuel cells because ionization reaction rates increase with temperature. It is also a corollary that the porous electrodes must be permeable to both electrolyte and gases, but not such that the media can be easily "flooded" by the electrolyte or "dried" by the gases in a one-sided manner.

Porous electrodes are key to good electrode performance.

The reason for this is that the current densities obtained from smooth electrodes are usually in the range of a single digit mA/cm^2 or less because of rate-limiting issues such as the available area of the reaction sites. Porous electrodes, used in fuel cells, achieve much higher current densities. These high current densities are possible because the electrode has a high surface area, relative to the geometric plate area that significantly increases the number of reaction sites, and the optimized electrode structure has favorable mass transport properties. In an idealized porous gas fuel cell electrode, high current densities at reasonable polarization are obtained when the electrolyte layer on the electrode surface is sufficiently thin so that it does not significantly impede the transport of reactants to the electroactive sites, and a stable three-phase (gas/electrolyte/electrode surface) interface is established. When an excessive amount of electrolyte is present in the porous electrode structure, the electrode is considered to be "flooded" and the concentration polarization increases to a large value.

The porous electrodes used in low-temperature fuel cells (AFC, PAFC, PEMFC and DMFC) consist of a composite structure that contains platinum (Pt) electrocatalyst on a high surface area carbon black and a PTFE (polytetrafluoroethylene) binder. Such electrodes for acid and alkaline fuel cells are described by Kordesch et al [2]. In these porous electrodes, PTFE is hydrophobic (acts as a wet proofing agent) and serves as the gas permeable phase, and carbon black is an electron conductor that provides a high surface area to support the electrocatalyst. Platinum serves as the electrocatalyst, which promotes the rate of electrochemical reactions (oxidation/reduction) for a given surface area. The carbon black is also somewhat hydrophobic, depending on the surface properties of the material. The composite structure of PTFE and carbon establishes an extensive three-phase interface in the porous electrode, which is the benchmark of PTFE bonded electrodes.

In MCFCs, which operate at relatively high temperature, no materials are known that wet-proof, are retains porous structure against ingress by molten carbonates. Consequently, the technology used to obtain a stable three-phase interface in MCFC porous electrodes is different from that used in PAFCs. In the MCFC, the stable interface is achieved in the electrodes by carefully tailoring the pore structures of the electrodes and the electrolyte matrix ($LiA1O_2$) so that the capillary forces establish a dynamic equilibrium in the different porous structures. In a SOFC, there is no liquid electrolyte present that is susceptible to movement in the porous electrode structure, and electrode flooding is not a problem. Consequently, the three-phase interface that is necessary for efficient electrochemical reaction involves two solid phases (solid/electrolyte/electrode) and a gas phase. A critical requirement of porous electrodes for SOFC is that they are sufficiently thin and porous to provide an extensive electrode/electrolyte interfacial region for electrochemical reaction.

The essential criteria for a better electrode material are:

- high electronic conductivity
- high adsorption capacity of reactant and oxidant
- chemical and structural stability under the conditions employed in devices i.e., operating temperature, wide range of partial pressures of reactant and oxidant, concentration of electrolyte
- chemical and thermomechanical compatibility to electrolyte and interconnector materials
- high ionic conductivity
- ability to decompose the intermediate species formed during the oxidation/reduction process
- tolerant to contaminants e.g., halide ions, NO_x, CO_x, SO_x
- low cost of materials

Oxygen reduction reaction (ORR), which is a common cathodic reaction to all the fuel cell devices, has been studied over the years because of its fundamental complexity, great sensitivity to the electrode surface, and sluggish kinetics. The sluggish kinetics of ORR under the conditions employed in electrochemical devices is due to the low partial pressure of oxygen in air, slow flow rate of oxygen (i.e., less residence time for oxygen molecules on active sites) under ambient conditions. The main disadvantage in this important electrode reaction is the exchange current density (j_o) value in the region of

10^{-10} A/cm^2 in acidic medium and 10^{-8} A/cm^2 at 298 K in alkaline solution which is lower than the j_o value of anodic reaction (10^{-3} A/cm^2) in all the electrochemical devices. Hence (from the equation $\eta = RT/nF \ln(j/j_o)$) the oxygen reduction reaction usually contributes considerably to the overpotential and therefore results in a low efficiency in the functioning of electrochemical energy devices using air as oxidant. Understanding and exploitation of electrocatalysis for this reaction is needed more than any other reactions in electrochemical devices. Oxygen undergoes a two-step indirect reduction reaction. On most of the electrocatalysts, oxygen reduction takes place by the formation of high energy intermediate, H_2O_2 followed by further reduction to H_2O. The stable H_2O_2 intermediate is undesirable, as it lowers the cell voltage and H_2O_2 attacks and corrodes the carbonaceous electrode material commonly used. Better catalysts are needed to speed the decomposition of H_2O_2 to reduce its impact on the overall reaction. Similarly, a catalyst can enhance the fuel dissociation rate at the anode. In order to obtain maximum efficiency and to avoid corrosion of carbon supports and other materials by peroxide, it is desired to achieve a four electron reduction. Finding suitable electrocatalysts that can promote the direct four electron reduction of oxygen molecule is an important task.

The characteristic features, advantages and limitations of various types of fuel cells are given below.

4. Alkaline fuel cells (AFCs)

The first commercial fuel cell systems were the AFCs that became available in the 1950s. AFCs were used to power the Apollo spacecrafts and are currently used in the Space Shuttles. The electrolyte in AFCs is a concentrated KOH solution. For low temperature applications (60-90 °C) the KOH concentration is 35-50 wt%. To achieve optimum performance of AFCs with KOH concentrations of 85 wt% the operating temperature was increased to 200 °C. These high temperature cells are also operated at high pressures (4-6 atm) to prevent the electrolyte solution from boiling.

Pure H_2 and O_2 are input as the fuel and oxidizer in an AFC. The gas diffusion electrodes are constructed of porous carbon and are doped with Pt to catalyze the oxidation and reduction reactions. The anodes contain 20% Pd in addition to the Pt and the cathodes contain 10% Au and 90% Pt. For higher temperature operations, Ni catalysts are also used. Ni is used for the inter connectors in an AFC stack. The AFC operates at up to ~1 A/cm^2 at 0.7 V.

The mobile ions in the system are the OH^- ions in the alkaline solution that are transported from the cathode, where reduction of O_2 occurs, to the anode, where oxidation of H_2 occurs. Water is produced at the anode. The following reactions define the operation of AFCs:

At anode: $H_2 + 2\ OH^- \rightarrow 2\ H_2O + 2\ e^-$

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

Cell reaction: $H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O$

Although AFCs have the highest electrical efficiency of all fuel cell systems (60% LHV), they are extremely sensitive to impurities. The presence of N_2 and impurities in the gas streams substantially reduce the cell efficiency. The presence of even small amounts of CO_2 is detrimental to the long-term performance of AFCs because K_2CO_3 forms and inhibits gas diffusion through the carbon electrodes. The small amounts of CO_2 in air (~300 ppm) preclude the use of air as the oxidant in an AFC. This restriction limits the use of these fuel cell systems to applications such as space and military programs, where the high cost of providing pure H_2 and O_2 is permissible. Because pure gases are used, AFCs can generate pure, potable water for consumption during space missions.

5. Phosphoric acid fuel cells (PAFCs)

Other than the AFCs, PAFCs are closer to commercialization than other fuel cell systems. The two intended commercial uses for PAFCs are 1) distributed power using reformed natural gas as a fuel; and 2) for small-scale, on-site cogeneration. Air is used as the oxidant. In contrast to the AFC, PAFCs are tolerant of CO_2 because concentrated phosphoric acid (H_3PO_4) is used as the electrolyte. Compared to other inorganic acids, phosphoric acid has relatively low volatility at operating temperatures of 150-220 °C. Protons migrate from the anode to the cathode through 100% H_3PO_4 that is immobilized in a SiC-poly(tetrafluoroethylene) matrix. Electrodes are made of platinized, gas permeable graphite paper. The water produced at the cathode is removed with the excess O_2 and the N_2. PAFCs have demonstrated excellent thermal, chemical, and electrochemical stability compared to other fuel cell systems. PAFCs are defined by the following reactions:

At anode: $H_2 \rightarrow 2\ H^+ + 2\ e^-$

At cathode: $\frac{1}{2}\ O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O$

Cell reaction: $H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O$

To optimize the ionic conductivity of the electrolyte, operating temperatures are maintained between 150-220 °C at pressures ranging from atmospheric to ~8 atm. Reduction of oxygen is slower in an acid electrolyte than in an alkaline electrolyte, hence the need for Pt metal in the electrodes to help catalyze the reduction reactions. CO poisoning of the Pt electrodes is slower at PAFC operating temperatures than at lower temperatures so up to 1% CO in the fuel gas produced during the reforming process can be tolerated. At lower temperatures CO poisoning of the Pt in the anode is more severe. Currently, Pt based materials were used as anode and cathode. The anode operates at nearly reversible voltage with ~0.1 mg/cm^2 catalyst loading. The cathode requires a higher catalyst loading of ~1 mg/cm^2 of catalyst. PAFCs are already semicommercially available in container packages (200 kW) for stationary electricity generation. Hundreds of units have been installed all over the world.

Aside from the CO produced during hydrocarbon reforming, the concentration of other impurities must be low compared to the reactants and diluents. Sulfur gases (mainly H_2S and COS) that originate from the fuel gas can poison the anode by blocking active sites for H_2 oxidation on the Pt surface. Molecular nitrogen acts as a diluent but nitrogen compounds like NH_3, HCN, and NO_x are potentially harmful impurities. NH_3 acts as a fuel, however, the oxidant nitrogen compounds can react with the H_3PO_4 to form a phosphate salt, $(NH_4)H_2PO_4$. Unacceptable performance losses can occur if the concentration of this phosphate salt in the electrolyte increases above 0.2 mole%.

6. Proton exchange membrane fuel cells (PEMFCs)

PEM fuel cells are a serious candidate for automotive applications, but also for small-scale distributed power generation, and for portable power applications as well. PEMFCs contain a proton conducting ion exchange membrane as the electrolyte material. The membrane material is a fluorinated sulfonic acid polymer commonly referred to by the trade name given to a material developed and marketed by DuPont - Nafion®. The acid molecules are immobile in the polymer matrix; however, the protons associated with these acid groups are free to migrate through the membrane from the anode to the cathode, where water is produced. The electrodes in a PEMFC are made of porous carbon cloths doped with a mixture of Pt and Nafion®. The catalyst content of the anode is ~0.1 mg/cm^2, and that of the cathode is ~0.5 mg/cm^2. The PEMFC operates at ~1 A/cm^2 at 0.7 V.

PEMFCs use H_2 as the fuel and O_2 as the oxidant. The PEMFC is insensitive to CO_2 so air can be used instead of pure O_2 and reforming hydrocarbon fuels can produce the H_2. Thermally integrating fuel reformers with operating temperatures of 700-800 °C with PEMFCs that operate at 80 °C is a considerable challenge. The PEMFC is defined by the following reactions:

At anode: $H_2 \rightarrow 2\ H^+ + 2\ e^-$

At cathode: $\frac{1}{2}\ O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O$

Cell reaction: $H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O$

PEMFCs have received considerable attention lately as the primary power source in electric vehicles for several reasons. Since the electrolyte is a polymeric material, there is no free corrosive liquid inside the cell (water is the only liquid), hence material corrosion is kept to a minimum. PEMFCs are also simple to fabricate and have a demonstrated long life. On the other hand, the polymer electrolyte (Nafion®) is quite expensive and Pt loadings in the electrodes are quite high so the fuel cell cost is high. The power and efficiency of a PEMFC is also dependent on the water content of the polymer electrolyte, so water management in the membrane is critical for efficient operation. The conductivity of the membrane is a function of the number of water molecules available per acid site and if the membrane dries out, fuel cell power and efficiency decrease. If water is not removed from the PEMFC the cathode can become flooded which also degrades cell performance. For high temperature PEMFCs, polybenimidazole based membranes will be preferred.

The required moisture content of the membrane is what limits the operating temperature of a PEMFC to less than 120 °C. This temperature ensures that the by-product water does not evaporate faster than it is produced. Low operating temperatures equates to high Pt loadings in the electrodes to efficiently catalyze the oxidation and reduction reactions. The Pt content of the electrodes also necessitates that the CO content of the fuel gas be very low (< 5 ppm) because CO blocks the active sites in the Pt catalyst. Therefore, if a hydrocarbon reformer is used to produce H_2, the CO content of the fuel gas needs to be greatly reduced. This is usually accomplished by oxidation of CO to CO_2, using a water gas shift reactor, or using pressure swing adsorption to purify the hydrogen.

7. Direct methanol fuel cells (DMFCs)

The DMFC uses the same basic cell construction as for the PEMFC. It has the advantage of a liquid fuel in that is easy to store and transport. There is no need for the reformer to convert the hydrocarbon fuel into hydrogen gas. Methanol is the liquid fuel having high energy density (6.2 kWh/kg) among all the liquid fuels and next to hydrogen. The anode feedstock is a methanol and water mixture or neat methanol, depending on cell configuration. The DMFC is under development as a power source for portable electronic devices such as notebook computers and cellular phones. The pure methanol or a methanol-water mixture would be stored in a cartridge similar to that used for fountain pens. Refueling would involve the quick replacement of the cartridge. The reaction for the direct conversion of methanol has a similar voltage as for hydrogen.

DMFCs use CH_3OH as the fuel and O_2 as the oxidant. Due to the chemical similarity of water and methanol, the methanol has considerable solubility in the polymer membrane, leading to significant crossover from the anode side to the cathode side of the cell. On reaching the cathode, the methanol is oxidized. This significantly lowers the cathode voltage and the overall efficiency of cell operation. The typical DMFC yields ~0.5 V at 400 mA/cm^2 at 60 °C. The DMFC is defined by the following reactions:

At anode: $CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6\ e^-$

At cathode: $3/2\ O_2 + 6\ H^+ + 6\ e^- \rightarrow 3\ H_2O$

Cell reaction: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2\ H_2O$

The main disadvantage of the DMFC system is the relative low power density, which has to be significantly improved if the DMFC should be a viable alternative to the PEMFC plus reformer system. The lower cell performance of a DMFC is caused by the poor kinetics of the anode reaction. The oxidation reaction proceeds through the formation of carbon monoxide as an intermediate which strongly adsorbs on the surface of a Pt catalyst. Therefore, a potential, which is more anodic than the thermodynamic value, is needed to obtain a reasonable reaction rate. In contrast to the PEMFC, where it is mainly the cathode that is kinetically hindered, both electrodes of a DMFC suffer from kinetic losses. Consequently, numerous materials were studied to find an electrode material that displays an enhanced catalytic activity and therefore lower overpotentials towards the methanol oxidation. At present, the most active anode catalysts are based on Pt–Ru alloys. Ruthenium reduces the poisoning effect by lowering the overpotentials at the anode and thus increases considerably the catalytic activity of pure platinum. The platinum-ruthenium catalyst loadings for the anode are higher than for the PEMFC and are in the range of 1-3 mg/cm^2. Cathode catalysts are based on Pt and Pt alloys (Pt-M where M = Cr, Co, Fe and Ni).

8. Molten carbonate fuel cells (MCFCs)

MCFCs contain an electrolyte that is a combination of alkali (Li, Na, and K) carbonates stabilized in a $LiAlO_2$ ceramic matrix. The electrolyte should be pure and relatively free of alkaline earth metals. Contamination by more than 5-10 mole % of $CaCO_3$, $SrCO_3$, and $BaCO_3$ can lead to performance loss. Electrons are conducted from the anode through an external circuit to the cathode and negative charge is conducted from the cathode through the electrolyte by $CO_3{}^{2-}$ ions to the anode. Water is produced at the anode and removed with CO_2. The CO_2 needs to be recycled back to the fuel cell to maintain the electrolyte composition. This adds complexity to the MCFC systems. The oxidation and reduction reactions that define MCFC operation are as follows:

At anode: $H_2 + CO_3^{2--} \rightarrow H_2O + CO_2 + 2\ e^-$
$CO + CO_3^{2--} \rightarrow CO_2 + 2\ e^-$
Shift: $CO + H_2O \rightarrow H_2 + CO_2$
At cathode: $\frac{1}{2}\ O_2 + CO_2 + 2\ e^- \rightarrow CO_3^{2-}$
Cell reaction: $H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O$

MCFCs typically operate at temperatures between 600-700 °C providing the opportunity for high overall system operating efficiencies, especially if the waste heat from the process can be utilized in the fuel reforming step or for cogeneration. Operating temperatures higher than 700 °C lead to diminishing gains in fuel cell performance because of electrolyte loss from evaporation and increased high temperature materials corrosion. Typical operating parameters are ~150 mA/cm^2 at 0.8 V at 600 °C.

The high operating temperature of a MCFC system also provides for greater fuel flexibility; a variety of hydrocarbon fuels (natural gas, alcohols, landfill gas, syn gas from petroleum coke, coal and biomass, etc.) can be reformed to generate hydrogen for the fuel cell. The CO from biomass and coal gasification product gas and reformed hydrocarbons is not used directly as a fuel but when mixed with water vapor can produce additional hydrogen via the water-gas shift reaction. Oxygen or air is used as the oxidant. An attractive design incorporates an internal fuel reformer within the fuel cell eliminating the need for a separate fuel processor.

A higher operating temperature also means that less expensive materials can be used for the electrocatalysts in the electrodes; Pt is not required and Ni is used as the catalyst. The Ni in the cathode becomes oxidized and lithiated (from contact with the electrolyte) during initial operation of a MCFC so that the active material is Li-doped NiO. Unfortunately, NiO is soluble in molten carbonates leading to the possible dissolution of the cathode and dispersion of metallic nickel in the electrolyte, which can eventually short-circuit the electrodes. This is one of the materials issues that is being investigated to improve the long-term operability of MCFC systems. Recently, $LiCoO_2$ and Li_2MnO_3 were found to be alternative materials as cathode.

The anode contains Ni doped with 10% Cr to promote sintering. An external methane reformer is not needed in a MCFC system because the presence of Ni in the anode at MCFC operating temperatures is very effective for internal CH_4 reforming at the anode. Internal methane reforming can increase overall system efficiencies, but can also induce unwanted temperature gradients inside the fuel cell that may cause materials problems. Catalyst poisoning is also an issue if the sulfur content of the reagent gases is greater than 10 ppm, similar to all Ni-based fuel-reforming systems. Coke formation on the anode from fuel reforming can also be an issue.

9. Solid oxide fuel cells (SOFCs)

SOFC systems operate between 900-1000 °C, higher than any other fuel cell system. At these operating temperatures, fuel composition is not an issue because in the presence of enough water vapor and oxygen complete oxidation will be achieved, even in the absence of catalytic materials. High overall system efficiencies are possible with waste heat recovery. The electrolyte material in a SOFC is yttrium (8-10 mol%) stabilized zirconia

(YSZ). This material is a solid with a stable cubic structure and very high oxide conductivity at SOFC operating temperatures. The mobile O^{2-} ions migrate from the cathode to the anode where water is produced. The electrochemical reactions occurring in a SOFC system are as follows:

At anode: $H_2 + O^{2-} \rightarrow H_2O + 2\ e^-$

At cathode: $\frac{1}{2}\ O_2 + 2e^- \rightarrow O^{2-}$

Cell reaction: $H_2 + \frac{1}{2}\ O_2 \rightarrow H_2O$

Similar to the MCFC systems, the high operating temperatures of the SOFCs provides fuel flexibility without the need for expensive catalysts in the electrodes. The cathode in a SOFC consists of mixed oxides with a perovskite crystalline structure, typically Sr-doped lanthanum manganate ($LaMnO_3$). The anode material is a Ni cermet (ceramic and metal composite). It contains metallic Ni for catalytic activity in an YSZ support. The YSZ adds mechanical, thermal, and chemical stability, chemical and thermal compatibility between the anode and the electrolyte is not an issue. Like the MCFC systems, internal methane steam reforming at the Ni-based anode in the presence of water vapor is possible in SOFC systems. The cells operate at ~1 A/cm^2 at 0.7 V.

Overall, SOFC systems can tolerate impurities because of their high operating temperatures. Sulfur tolerances can be up to two orders of magnitude higher in SOFCs than in other fuel cell systems because of the high operating temperatures. Energy efficient, high temperature sulfur removal methods are used to lower the sulfur content of the gas to less than 10 ppm. At the same time, the high operating temperatures of SOFCs can cause considerable materials issues like material incompatibilities (thermal and chemical) and corrosion.

Significant research and development efforts have gone into technically and cost-effectively addressing materials issues in SOFC systems for commercial applications. This is reflected in the variety of designs for SOFC systems. There are three general types of designs for SOFC systems: tubular, bipolar monolithic, and bipolar planar. The bipolar designs have a bipolar plate that prevents reactant gases in adjacent cells from mixing and provides serial electrical interconnectivity between cells. The single cells are stacked with interconnectors, gas channels, and sealing elements in between. There are two types of tubular designs: seal-less and segmented cell in-series. A single cell in a tubular SOFC consists of a long porous YSZ ceramic tube that acts as a substrate. The cathode, followed by the electrolyte, and finally the anode are deposited on the outer surface of the tube. A portion of the tube is left with a strip of the cathode covered by the interconnector material to make the electrical connection. Individual tubes are arranged in a case and air flows inside the tubes while fuel flows around the outside of the tubes.

Developments in SOFC systems that operate at intermediate temperatures (550-800 °C) are currently receiving considerable attention. Reducing the operating temperature of SOFC systems is being pursued in an attempt to reduce the cost of these systems. Some of the benefits of a reduced operating temperature include: better thermal integration with fuel reformers and sulfur removal systems, reduced material issues such as less thermal stress and more material flexibility, lower heat loss, shorter time to achieve operating temperature, and less corrosion. Capitalizing on the benefits of lower SOFC operating temperatures is an area of continued and future research and development.

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Chapter - 9
NUCLEAR ENERGY OPTIONS

The **sun shall be turned into darkness**, and the moon into blood, before that great and notable day of the Lord come:

The Holy Bible (The Acts 2:20)

While **the sun**, or the light, or the moon, or **the stars**, be not **darkened**, nor the clouds return after the rain:

The Holy Bible (Ecclesiastes 12:2)

Introduction:

Clearly, energy security and energy independence are the two challenges ahead of any nation in this new millennium. The global appetite for energy is simply too great and recurring as well. There is an abrupt need to look something beyond incremental because the additional energy needed is greater than the total of all the energy currently produced. Energy sources are inevitable for progress and prosperity [1].

Energy is inevitable for the very sustenance of human life. There is an abrupt need for vast, unperishable, inexhaustible, long lasting and human friendly energy sources in view of the fast depleting fossil fuel based non renewable energy resources. In this regard can we think of Nuclear energy as a better option? Why? Why not? [2]

The two challenges for human society in the 21st century are the purposeful transition towards a sustainable energy future and also to ensure effective conservation of natural resources across the globe [3].

It has now become imperative to consider what the chances are for saving humanity from energy poverty through controlled power from the nucleus of the atom.

The issue of "*Nuclear Energy Options*" was and is a matter of unending debate with views diverging and opinions contradicting. This can be exemplified from the following two well known quotes:

"Lord, we are especially thankful for nuclear power, the cleanest, safest energy source there is. Except for solar, which is just a pipe dream." – Homer Simpson

"The nuclear power option - expensive, ineffective, unnecessary and problem-multiplying." – Professor Stuart White

It is generally argued that improving energy efficiency of conventional energy generation process and exploitation of renewable energy sources like wind energy and solar energy can be cheap option for green house gas reduction compared to nuclear energy. Further it appears that nuclear waste management (disposal), decommissioning and proliferation risks involved in Nuclear energy option multiply the existing problem.

The choice of Nuclear Energy hold great promise of inexhaustible energy for manifold applications that can quench human thirst satisfy the need if exploited with wisdom. But the same can be extremely disastrous leading to the destruction of life on earth if used ignorantly.

The July 2005 Indo-US Nuclear deal:

The issue of Nuclear energy gained vitality with the recent remarkable July 2005 Indo-US Nuclear agreement deal according to which the US government should adjust U.S. laws and policies to enable full civil nuclear energy cooperation and trade with India. But all is not good with the deal and the existing obstacles are clear, namely, lifetime fuel guarantees for Indian civilian reactors in return for perpetuity safeguards, the U.S. insistence on "fallback" bilateral safeguards in addition to IAEA (International Atomic Energy Agency) safeguards, the U.S. refusal to allow India to import components and technology for safeguarded reprocessing and enrichment activity, the U.S. refusal to allow reprocessing of spent fuel, India's IAEA safeguards agreement and the timing and nature of the Nuclear Suppliers Group's decision to amend its guidelines to allow commerce with India.

Irrespective of the afore mentioned hindrances it should be noted that India’s advancement in the exploitation of Nuclear energy is not dependent on the mercy of any foreign nation for we have already achieved self-reliance in this field and cooperation from external sources will only be an addition to our efforts in this direction harnessing nuclear energy. Break down of cooperation from other nations is no loss.

The first stage of India's nuclear power programme, presently consisting of 12 Pressurised Heavy Water Reactors (PHWRs), is completely in the industrial domain. As result of the consolidation of the entire work done in the last 50 years, we now have a clearly defined roadmap for future R&D and its commercialization. we have now succeeded in this very frontline technology in all its dimensions. We have different technologies for various applications, namely, Nuclear energy applications in agriculture, health, food security and so on. In addition we have contributed towards nuclear weapons ability in the country. India today is a country with nuclear weapons to ensure its long-term security. At the same time, we have domestic capability to guarantee long-term energy security in a manner that will help in preserving the environment and avoiding the adverse impact of climate change.

Thorium utilization – Indian context:

In Indian context owing to the availability of rich reserves of Thoria development and construction of breeder reactors is of paramount importance and it forms one of the key elements in solving our future energy needs.

Fortunately, India is blessed with natural wealth. Monazite has been used as the source of thorium up to the present time . The deposits are often coloured black by the presence of Magnetoite, or red by the presence of garnet. Monazite is characterized by its chemical stability. Solvent extraction process suits well for thorium separation and tributyl phosphate is a particularly promising solent. This extracts thorium and leavesth rare earths in the aqueous phase. India's vast thorium reserves amount to nearly one-third of world's thorium reserves. Effective utilization of the available vast thorium reserves for harnessing Nuclear energy for the benefit of mankind should be one of the worthy targets of the India's Nuclear Programme. Monazite is the potential source of Uranium. The Monazite has been eroded from igneous rocks and transported by streams to form alluvial deposits. The beach sand of the Indian Malabar and Coromandel coasts are very rich in Monazite and are estimated to contain upto 1,80,000 tons of Thorium in an easily extractable form. An important Thorium reserve further inland has been discovered also, in the state of Bihar; this is estsimated to contain over 3,00,000 tons of thorium at a concentration of over 10 percent. India has to fall back to its thorium reserves for energy security on a sustainable basis. Road map should be prepared for introducing Thorium (as ThO_2) in place of UO_2 in the blanket zone of FBR's (fast breeders reactors) at an appropriate growth level of installed nuclear power capacity in the second stage. One of the major tasks in hand is to start construction of the thorium fuel based 300 MWe Advanced Heavy water reactor (AHWR). Other large scale deposits of Monazite occur in Brazil, Taiwan, Ceylon and the USA.

Focus Areas:

Very recently while addressing an important conference Shri.Bhattacharjee, Director, BARC , focused on the following issues :

The primary mandates to improve the quality of life of our 1 billion plus population are :

i. To provide energy security by way of generating safe, reliable eco-friendly and economical nuclear power.

ii. Enhance use of radio isotopes and radiation technology in non-power sector for health care, nuclear agriculture and food preservation and industrial applications.

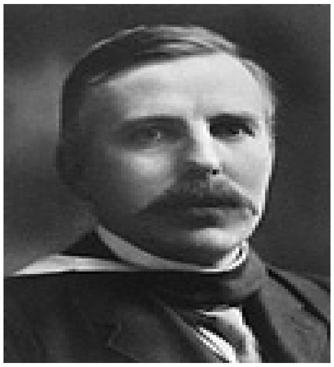
Plans are on the way to induct nuclear energy as primary energy source in the near future i.e., nuclear energy as some of heat for variety of applications such as compact high temperature reactor for small unattended power packs for electricity generation in remote areas that are not connected to the grid systems or for the production of hydrogen from H_2O using thermochemical means as an environment friendly alternative to hydrocarbon fuels for our transportation sector or even for refinement of low grade coal and oil deposits to high grade fossil fuel.

Nuclear Technology – Scientific Contribution:

Very many scientists have toiled for years and offered sacrifices to generate fundamental knowledge related to Nuclear Science and Technology. It is inevitable that their efforts and achievements are rememberbed before start of any preliminary discussion on Nuclear Energy options.

Stalwarts in the field of Nuclear Science:

Ernest Rutherford, (1871-1937), Great Britain:

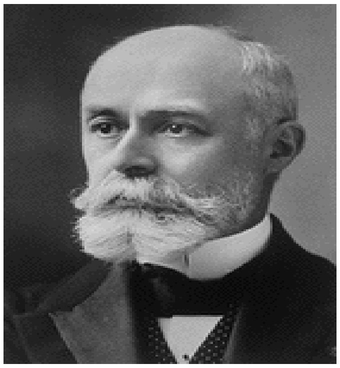


Ernest Rutherford was awarded the Nobel prize in Chemistry 1908 for his investigations into the disintegration of the elements, and the chemistry of radioactive substances. He was the first to postulate the concept of Nucleus which is one of the greatest contributions to science. He was the first to deliberately transmute one element into another. In 1989 he reported the existence of alpha and beta rays in uranium radiation and indicated some of their properties. In 1910 his investigations into the scattering of alpha rays and the nature of the inner structure of the atom which caused such scattering led to the postulation of his concept of "nucleus". According to him practically the whole mass of the atom and at the same time all positive charge of the atom is concentrated in a minute space at the centre.

Niels Henrik David Bohr, 1885-1962, Denmark:

Niels Bohr was awarded the Nobel prize in Physics 1922 for his contribution in the investigation of the structure of atoms and of the radiation emanating from them. He succeeded in working out and presenting a picture of atomic structure. He proposed liquid drop model for Nuclear structure. This particular model permitted the understanding of the mechanism of nuclear fission.

Antoine Henry Becquerel, 1852 – 1908, Paris:



Discovered Radioactivity

Awarded the Nobel prize in Physics, 1903

Becquerel was born in Paris on 15th December, 1852. In 1982 he was appointed as Professor of Applied Physics in the Department of Natural History at the Paris museum. Becquerel's earlier work was related to polarization of light, the phenomenon of phosphorescence and the absorption of light by crystals.

In 1896, Henri Becquerel observed the blackening of a photographic plate placed unintentionally close to a uranium preparation. This has led to the serendipitous discovery of radioactivity. The phenomenon was then wholly incomprehensible and subsequently led to series of other spectacular discoveries. The new results thus obtained formed the basis of modern concepts and the birth of Nuclear Science. Marie Sklodowska Curie, a Polish pupil of Becquerel, proposed the name radioactivity. Becquerel was awarded the Noble prize for Physics in 1903 for his discovery of spontaneous radioactivity. Pierre and Marie Curie shared the Noble prize with Becquerel for their study of the Becquerel radiation.

Marie Sklodowska Curie , 1867-1934, Poland:

1903 Nobel Prize in Physics

1911 Nobel Prize in Chemistry

Discovered elements radium and polonium

Coined term "Radioactivity"

Marie Curie was born in Warsaw on 7th November, 1867. Her early researches, together with her husband Pierre Curie, were often performed under difficult conditions, with poor laboratory arrangements. Pierre and Marie Curie observed naturally occurring pitch blend to be many more times radioactive than expected as per the uranium content. They were right in their comprehension that some unknown element far more radioactive than uranium must be present in naturally occurring pitch blend. Knowing fully well, the road ahead it dark and gloomy, they determined to go ahead with the faith in their reasoning in spite of the very fact the no financial support existed. The Curies attempted to isolate the mysterious element. They worked in a shed with a simple electroscope developed by Pierre himself for differentiating the 'active' fraction from the rest. Their agonizingly prolonged toil was not in vein and they succeeded in separating and isolating not one but two new intensely radioactive elements from the bismuth and barium fractions. The former was named Polonium, after Marie's native country and the other Radium (1898). The isolation of these elements present in no more than some mg in a tonne of the ore, is not only a remarkable triumph of their prediction, but a chemical engineering achievement unparalleled in the history of Science. Together with her husband, Madam Curie was awarded Nobel prize for Physics in 1903 for their study into the spontaneous radiation discovered by Becquerel. In 1911 she received the second Nobel prize for Chemistry in recognition to her work in radioactivity.

Madam Curie was held in high esteem and admiration by Scientists throughout the world.

Irene Joliot - Curie, 1897-1956, France:

Discovered Artificial Radioactivity
1935 Nobel Prize in Chemistry

Irene Curie was born on 12th September, 1897 in Paris. She was the daughter of Pierre and Marie Curie. In 1926 she was married to Frederic Joliot. Her Doctoral studies were focused on the alpha rays of Po. She carried out important work along with her husband Frederic on natural and artificial radioactivity, transmutation of elements. Soon after the discovery of the neutron, in a series of experiments, Irene and Frederic Joliot-Curie studied the effects of bombarding light elements like B, Al and Mg with high energy alpha particles from Po. They observed anomalies when Al^{27} is bombarded with α particle ($_2He^4$). In all the cases they observed the emission of neutrons and positrons. From the considerations of the conservation of mass and charge the recoil product should be the light isotope of Phosphorous (P^{30}) which was not know at the time (the natural element being monoisotopic P^{31}). Also, the moment the α source was removed, the emission of neutrons stopped. But the emission of positrons continued over well measurable periods. The intensity of the positron emission was observed to decay exponentially with time. The half-life was found to be 3 minutes. Thus a true artifical radioactive source is found (P^{30}) for the first time. Other immediate studies were Mg^{24} and B^{10} which resulted in the formation of radioisotopes Si^{27} and N^{13}. The the toiling efforts of Irene and Frederic Jaliot-Curie resulted in the synthesis of P^{30}, Si^{27} and N^{13}, the first three radioisotopes prepared artificially. Now radioactivity is no longer restricted to few naturally occurring elements as Ra, U and Th. Radioisotopes find diverse applications in research, medicine, agriculture and industry. She shared the Nobel prize in Chemistry for 1935 with Frederic Joliot in recognition of their synthesis of new radioactive elements.

Lise Meitner, 1878-1968, Austria:

Most significant woman scientists of the 20th century

Discovered the element Protactinium (91)

First to explain the theory of Nuclear fission

Germany's first woman Physics professor

Artificial element 109 named in her honour

Lise Meitner was born on 27th October, 1968 in Austria. She studied Radioactivity and Nuclear Physics. In 1917, Lise Mitner and Otto Hahn discovered the first long-lived isotope of the element Protactinium. In 1923, she discovered the cause of the emission of electron from surfaces with 'signature' energies. (Auger effect). With the discovery of the neutron by James Chadwick in 1932 speculation arose in the scientific community that it might be possible to create elements heavier than Uranium in the laboratory. A scientific race began between Ernest Rutherford in Britain, Irene Joliot – Curie in France, Enrico Fermi in Italy, and the Meitner-Hahn team in Berlin. None suspected that this research would create in nuclear weapons.

James Chadwick , 1891-1974, Great Britain:

The Nobel prize in Physics 1935 for the discovery of Neutron – An epoch making discovery.

Chadwick prepared the way towards the fission of U-235 leading to the creation of the atomic bomb.

Chadwick proved the existence of neutrons which constitute one of the elementary particles of atom apart from proton and electron. It is present inside the nucleus. Neutron is devoid of any charge and so it need not overcome any electric barrier (electric forces present in heavy nuclei) offered by heavy atoms. As a result neutrons can penetrate and split the nuclei of even the heaviest elements.

Enrico Fermi, 1901-1954, Italy:

The Nobel prize in Physics 1938

Evolved the theory of ß-decay, 1934

First to device and design an atomic pile

Enrico Fermi was born in Rome on 29th September 1901. He was awarded the Nobel prize in Physics 1938 for his demonstrations of the existence of new radio active elements produced by neutron irradiation and for his related discovery of nuclear reactions brought about by slow neutrons. He evolved the β-decay theory in 1934. He demonstrated that nuclear transformations occur in almost every element subjected to neutron bombardment. He saw the possibility of emission of secondary neutrons and of a chain reaction. He has proceeded to work with tremendous enthusiasm which ultimately led to the atomic pile and the first controlled nuclear chain reaction.

Glenn Theodore Seaborg, 1893-1981, USA:

The Nobel prize in Chemistry 1951

G. T. Seaborg was born in Rome on 29th September 1901.

He was co-discoverer of Plutonium and all further transuranium elements through element 102. Seaborg and his colleagues are responsible for the identification of more than 100 isotopes of elements through out the periodic table.He was awarded Nobel prize in Chemistry for the discovery of the transuranic elements.

Homi J Bhabha, 1909 – 1966, India:

Homi Jehangir Bhabha is the Architect of India's Nuclear Programme. He is an outstanding scientist and a brilliant Engineer. Bhabha was indeed a perfectionalist. This worthy son of Mother India was born on 30th October, 1909.

In the words of the inventor of Cloud Chamber C.T.R. Wilson: “Scientist, engineer, master-builder and administrator, steeped in humanities, in art and music, Homi was a truly complete man."

The name 'Meson' now used for a class of elementary particles (new particle found in cosmic radiation with a mass intermediate between that of electron and the proton), was infact suggested by Bhabha. He established two great research institutions namely the TIFR and BARC and from this we can know how great visionary he was.

To remember his own views about life let us look at a quote of Bhabha.

"I know quite clearly what I want of my life. Life and my emotions are the only things I am conscious of. I love the consciousness of life and I want as much of it as I can get. But the span of one's life is limited. What comes after death no one knows. Nor do I care. Since, therefore, I cannot increase the content of life by increasing its duration, I will increase it by increasing its intensity. Art, music ,poetry and every thing else that consciousness I do have this one purpose - increasing the intensity of my consciousness of life." Unfortunately Bhabha died prematuredly in a suspicious air crash on Mount Blanc on 24th January, 1966. It was indeed an irreparable loss to the Nation as a whole.

A. P. J. Abdul Kalam, (1931 -), India:

Avul Pakir Jainulabdeen Abdul Kalam, the most distinguished scientist of India was born on 15th October, 1931 at Rameswaram in Tamil Nadu. He got specialized in Aeronautical Engineering from Madras Institute of Technology. He mastered himself in missile launch vehicle technology. He led to the weaponisation of strategic missile systems and the Pokhran – II nuclear tests which made India a nuclear weapon state. He took up a mission to ignite the young minds for national development by meeting high school students across the country. Dr. Kalam became the 11th president of India. He received the highest civilian award Bharat Ratna in the year 1997.

India's Nuclear Polocy:

Our policy is based on complete disarmament and no first use. India has always stood for nuclear non-proliferation and its nuclear programme was meant for peaceful purposes in the field of energy for civil purposes, agriculture, medicine and research.

Nuclear Reactions:

Nuclei remain intact in a vast majority of chemical reactions. Some space should be devoted here for Alchemy and Alchemists since modern Chemistry has originated from Alchemy. Alchemy is as old as human civilization. The Greek word 'chemia' appeared in the fourth century. Later Arabic prefix 'al' was added to it. Thus the word Alchemy signifies art of chemistry in general. Alchemy was a mixture of mystical, speculative thought and practical laboratory techniques of chemistry and metallurgy. The main aim of Alchemists was the transformation of base metals in to silver and gold (artificial transmutation) which can in no way achieved by any of the known chemical reactions. Development and understanding of Nuclear Science made it possible to artificially transmute one element in to another. It is now known that a few nuclei under ordinary conditions, and all nuclei under special conditions, undergo changes leading to nuclear reactions. Such reactions in which nucleus of an itself undergoes spontaneous change or interact with other nuclei of lighter particles resulting new nuclei and one or more lighter particles are called nuclear reactions. There are striking differences between ordinary chemical reactions and nuclear reactions and the differences are summarized below.

i. Chemical reactions depend upon the number of extra electron while nuclear reactions are independent of the electrons but depend on the nature of the nucleus.
ii. Chemical reactions involve some loss, gain or overlap of outer orbital electron of the two reactant atoms. Nuclear reactions involve emission of some light particles (α, β, positron and few others) from the nucleus of the atom to form another element.
iii. The chemical reactivity of an element is dependent on the nature of the bond present in the concerned compound. Where as the nuclear reactivity of an element is independent of its state of chemical combination. For instance, radium whether present as such or in the form of its compound shows similar radioactivity.
iv. A chemical reaction is balanced only in terms of mass where as a nuclear reaction must be balanced in terms of both mass and energy.

v. The energy change occurring in nuclear reactions is very high as compared to that in chemical reactions. The energy involved in a chemical reaction is expressed in kcal/mole where as in nuclear reactions the energy is expressed in MeV per nucleus.

vi. The chemical reactions are dependent on temperature and pressure while the nuclear reactions are independent of external conditions.

Energy from Nuclear Fission:

Among several nuclear reactions known, for instance, nuclear fission, nuclear fusion, radioactive decay, artificial transmutation, photonuclear reactions, radiative capture, evaporation, spallation and many others, nuclear fission has the greatest practical significance and has been exploited to the greatest extent for energy related applications relative to other reactions.

The staggering amount of energy released during the process of fission is illustrated below with respect to the fission of ^{235}U caused by thermal neutrons where in the fission fragments are ^{95}Mo and ^{139}La. The exact mass numbers of reactants and products are shown below each of the reactants and products.

$_{92}U^{235} \quad + \quad _0n^1 \quad \rightarrow \quad _{42}Mo^{95} + {}_{57}La^{139} + 2\ _0n^1$ + energy

235.0439 + 1.0087 94.9057+ 138.9061+2.0174

236.0526 235.8292

Mass loss, $\Delta m = 0.2234$ amu

Fission energy = $931\ \Delta m = 208$ MeV

From where thing figure 931 suddently appeared? What is special about it?

The energy equivalent to 1 atomic mass unit (amu) is 931 MeV.

The mass of standard carbon atom ($_6C^{12}$) is taken to be 12 amu.

So, mass of $_6C^{12}$ atom = 12 amu

1 amu = 1/12 x mass of $_6C^{12}$ atom

1 mole = 12 g

6.023×10^{23} atoms = 12 g

1 atom = $12/6.023 \times 10^{23}$ g

1 amu = $1/12 \times 12/6.023 \times 10^{23}$ g

= 1.66×10^{-24} g = 1.66×10^{-27} kg

According to Einstein's mass-energy relation:

$E = mc^2$

E, energy in Joules

M, mass in kg

C, velocity of light in m/sec

$E = 1.66 \times 10^{-27} \times (2.99 \times 10^8)^2$ J

$1\ \text{eV} = 1.602 \times 10^{-19}$ J

$E = 1.66 \times 10^{-27} \times (2.998 \times 10^8)^2/1.602 \times 10^{-19}$ eV

$= 1.66 \times 2.998 \times 2.998 \times 10^8/1.602$

$= 9.3134 \times 10^8$ eV

$= 931.3$ MeV

This total energy of about 200 MeV is found to be distributed between the products of fission as follows:

Table 1. Energy from fission

Fission product	**Energy carried, MeV**
Light fragment Heavy fragment	100 67
2.5 neutrons each of 2 MeV energy	5
γ photons	12
β^- and neutrinos	16

Nuclear Fission:

Fission is a process in which a nucleus excited by a neutron or by other means breaks into two fragments of comparable sizes. A significant amount of matter of atomic nucleus is annihilated releasing the corresponding on a scale totally unknown before

The process of nuclear fission was discovered by Otto Hahn and F. Strassman in January 1939. It marked the beginning of the nuclear age. The discovery of neutron by James Chadwick in 1932 can be termed as the origin of experiments that resulted in the discovery of Nuclear Fission. Soon after the discovery of fission by Hahn and Strassman, Lise Meitner and O. R. Frisch developed a theory for the phenomenon. They porposed that upon neutron capture to a point of overcoming the force of surface energy, distortion of the excited nucleus takes place resulting in a splitting of the nucleus into fragments of comparable masses [4].

The reaction of nuclear fission is schematically shown in Fig. 1. Fission occurs when fissionable nucleus captures a neutron. The internal balance between neutrons and protons in the nucleus is upset and it splits into two lighter nuclei. On the average 2-3 neutrons are emitted. The mass of the resulting products is less than the sum of the masses of the original nucleus plus the captured neutron and the difference appears as energy according to Einstein's equation ($E=\Delta mc^2$, where Δm is the mass loss involved in a particular nuclear reaction, c is the velocity of light). If the released neutrons are captured by other fissionable nuclei more fission events occur. When the reaction becomes self-sustaining so that one fission triggers at least one more fission, the phenomenon is termed as a chain reaction.

If the amount of U-235 is small, most of the neutrons will escape from the surface and the reaction will stop. Therefore, a critical mass of metallic uranium is necessary in order to start and sustain a chain reaction. The critical mass of U-235 has been found to be between 1 to 100 kg.

The basic principle of an atomic bomb is the chain reaction. At the time of explosion two samples each of subcritical mass, but whose total mass exceeds the critical mass, are brought together by the use of ordinary explosives. Once these subcritical masses come together, a chain reaction starts releasing a large amount of energy. One gram of U-235 evolves upon fission about 2×10^7 kcal of energy.

Let us take the fissionable nucleus, U^{235}, as a specific example.

In general the fission reaction resulting from absorption of neutron by U235 can be written as shown below. The two fission fragments are lebelled as F_1 and F_2 to indicate that many possible ways of splitting do exist.

${}_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{A1}F_1{}^{Z1} + {}_{A2}F_2{}^{Z2} + \acute{\ddot{\upsilon}}{}_{0}n^{1} + \text{energy}$

When uranium isotope – 235 is bombarded with slow neutrons, U^{236} is formed by the capturing of neutron. The U^{236} being unstable break up into two fragments besides releasing two or three neutrons.

${}_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{92}U^{236} \rightarrow {}_{56}Ba^{141}\ (F_2) + {}_{36}Kr^{92}\ (F_1) + 2\text{-}3\ {}_{0}n^{1} + 200\ \text{MeV}$

${}_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{92}U^{236} \rightarrow {}_{54}Xe^{139} + {}_{38}Sr^{95} + 2\ {}_{0}n^{1} + 200\ \text{MeV}$

$_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{92}U^{236} \rightarrow {}_{54}Xe^{141} + {}_{38}Sr^{92} + 2\ {}_{0}n^{1}$ + 200 MeV

$_{92}U^{235} + {}_{0}n^{1} \rightarrow {}_{92}U^{236} \rightarrow {}_{52}Te^{137} + {}_{40}Zr^{97} + 2\ {}_{0}n^{1}$ + 200 MeV

As seen above the fission fragments (F1) and (F2) are not a unique pair but could be one of about 30 possible pairs such that the mass number of lighter fragments (F_1) ranges from about 85 to 105 and that of heavier fragments (F_2) from about 150 to 130.

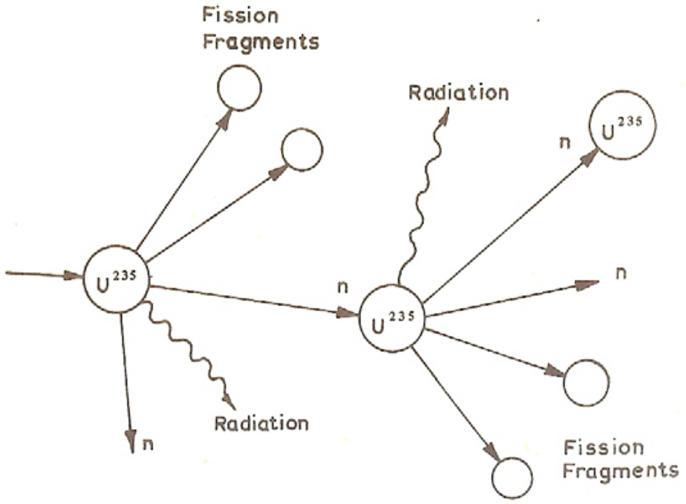


Fig. 1. Schematic of U^{235} fission [5]

Mechanism of Nuclear Fission:

In certain heavy elements like U and Pu absorption of a neutron results in the splitting of the nucleus in to two massive fragments. The sequence of events involved in the process are depicted in Fig. 2. As illustrative example the reaction of U-235 with neutron is considered. In stage A, the neutron approaches the U-235 nucleus. In stage B, the U-236 nucleus has been formed, in an excited state. The excess energy in some interactions may be released as a gamma ray. More frequently, the energy causes distortions of the nucleus into a dumbbell shape, as in stage C. The parts of the nucleus oscillate in a manner analogous to the motion of a drop of liquid. Because of the dominance of the electrostatic repulsion over nuclear attraction, the two parts can separate, as in stage D.

They are then called fission fragments, bearing most of the mass-energy released. They fly apart at high speeds carrying some 166 MeV of kinetic energy out of the total of around 200 MeV released in the whole process. As the fragments separate, they lose atomic electrons, and the resulting high-speed ions lose energy by interation with the atoms and molecules of the surrounding medium. The resultant thermal energy is recoverable if the fission takes place in a nuclear reactor. Also shown in the diagram are the gamma rays and fast neutrons that come off at the time of splitting.

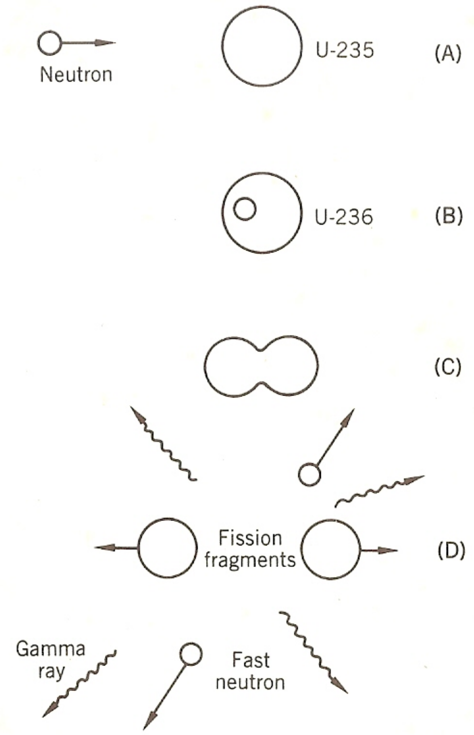


Fig. 2. The Fission Process [6]

Fission energy:

As in all radioactive decays, Nuclear Fission is also accompanied by mass loss and the liberation of corresponding amount of energy. The mass loss in nuclear fission comes to around 0.2 amu (atomic mass units) which is roughly 100 times greater than the mass loss observed in all other types of radioactive decay.

Nuclear reactors:

A nuclear reactor is a device designed to produce and sustain a long term controlled fission chain reaction. The words sustain and long term should be noted with some emphasis, since they indicate the fundamental difference between a nuclear reactor and an atomic bomb.

Fissioning of a gram of uranium yields approximately one million times as much energy as is released by the same quantity of uranium undergoing a chemical reaction , eg. oxidation. This comparison between nuclear energy and chemical energy is a major feature unique to nuclear reactors.

There is only one naturally occurring isotope which fissions readily. This is the isotope of uranium having an atomic weight of 235. It constitutes about 0.7% of natural uranium (balance U-238). There are two other fissionable isotopes of practical interest , Pu-239 and U-233 which can be produced as a result of neutron reactions with U-238 and Th-232 respectively.

Components and materials of Nuclear Reactors:

In brief, the lighter elements such as H, Be and C act as suitable neutron moderators. Most of the elements near the centre of the periodic table appear as fission products. The heavier elements are either potential nuclear fuels or are produced by neutron capture in the fuel during operation of a reactor. Many of the transition metals make suitable construction or container materials for nuclear reactors. Many elements such as fluorine, as UF6, find a unique application in the industry. An elaborate account of the components of the nuclear reaction are placed below:

The Fuel:

Special nuclear material (SNM) – Where does it come from?

SNM is defined by Title I of the atomic energy act of 1954 as Pu, U-233 or uranium enriched in the isotopes of U-233 or U-235. The definition includes any other material which the commission determines to be special nuclear material, but does not include source material.

U-233 and Pu-239 do not occur naturally. They can be formed in nuclear reactors and extracted from the highly radioactive spent fuel by chemical separation. U-233 can be produced in special reactors that use Thorium as fuel. Pu-239 can be produced in reactors using U-238 or U-235 fuel. Uranium enriched in uranium 235 is created by an enrichment facility. U-233 is an entirely man-made isotope. Its importance stems from the fact that it has a high cross section for fission by thermal neutrons. Its fission cross sections are comparable to that of the other fissile nuclides like U-235 and U-239. The precursor for U-233 is the widely occurring monoisotopic Th-232. India has an abundant supply of Th-232 in the form of rich monazite sand of kerala.

Plutonium – Why do world nations crave for this?

Plutonium (Pu) is strategically the most important element of the 20th century. It is entirely man-made atom by atom, first in μg and now in kg amounts and stockpiled in tones, in subcritical amounts.

$U^{238} + {}_0n^1 \rightarrow U^{239}$ (β decay) → Np^{239} (β decay) → Pu^{239} (α emitter, half life = 2.4×10^4 years) → U^{235}

Pu-239 is employed as nuclear fuel on account of its high neutron absorption cross section (cross section for fission by thermal neutrons). It is used as fuel in fast breeder reactor, where it is bred from U^{238}. It is used as an atom bomb element.

Uranium enrichment:

Three isotopes of uranium occur naturally and their relative abundances (in atomic percent) are as follows:

${}_{92}U^{234}$ (light weight atom) - 0.006%
${}_{92}U^{235}$ (middle weight atom) - 0.714%
${}_{92}U^{238}$ (heavy atom) - 99.28%

The fuel for nuclear reactors has to have a higher concentration of uranium-235 than exists in natural uranium ore. This is because U-235 is the key ingredient that starts a nuclear reactor and keeps it going. Normally, the amount of U-235 isotope is enriched from 0.7 % of uranium mass to 5 %. Several different processes are used to enrich uranium. The important methods among them being *Gas diffusion* and *Gas centrifuge*. Separation of U-235 from natural uranium is an outstanding example of isotope separation. The separation process relies upon the slight difference in the rate of diffusion through a membrane (Graham's law of diffusion) of the hexafluorides namely $U^{235}F_6$ and $U^{238}F_6$. Fortunately the situation is not complicated by the variation in the isotopic weights of fluorine since the only naturally occurring isotope of fluorine is F^{19}.

Gas diffusion method:

In the gaseous diffusion enrichment plant, the solid uranium hexafluoride (UF_6) from the conversion process is heated in its container until it becomes a liquid. The container becomes slightly pressurized as the solid melts. Because the container is not completely full UF_6 gas then fills the top of the container. The UF_6 gas is slowly fed into the plant's pipelines where it is pumped through special filters called barriers or porous membranes. The holes in the barriers are so small that there is barely enough room for the UF_6 gas molecules to pass through. The isotope enrichment occurs when the lighter UF_6 gas molecules (with the U-234 and U-235 atoms) tend to diffuse faster through the barriers than the heavier UF_6 gas molecules containing U-238. One barrier is not enough to do the job. It takes many hundreds of barriers, one after the other, before the UF_6 gas contains enough U-235 to be used in reactors. At the end of the process, the enriched UF_6 gas is with drawn from the pipelines and condensed back into a liquid that is poured into containers. The UF_6 is then allowed to cool and solidify before it is transported to fuel fabrication facilities where it is turned into fuel assemblies for nuclear power reactors.

Gas centrifugation method:

The gas centrifuge uranium enrichment process uses a large number of rotating cylinders in a series. These series of centrifuge machines, called trains. They are interconnected to form cascades. In this process, uranium hexafluoride (UF6) gas is placed in a rotating drum or cylinder and rotated at a high speed. This rotation creates a strong gravitional field so that the heavier gas molecules (with U-238) move toward outside (out let at the bottom) of the cylinder and the lighter gas molecules (containing U-235) collected closer to the centre. The stream that is slightly enriched in U-235 is withdrawn and fed into next higher stage, while the slightly depleted stream is recycled back into the next lower stage. Significantly more U-235 enrichment can be obtained from a single unit gas centrifuge than from a single unit gaseous diffusion barrier.

Moderator:

Material which helps the neutrons lose energy and keeps them in custody until they are relatively safe from capture by U-238 is known as moderator. It is obvious that the moderator must not absorb too many neutrons or the reaction will stop. Fast neutons released by fission are not as easy to catch as are slower neutrons, so we allow them to wander around in the moderator and reduce their energy to that corresponding to the ambient temperature. These neutrons are then in thermal equilibrium with the atoms or molecules of the moderator. Such neutrons are called thermal neutrons and have kinetic energies in the order of 0.025 eV, implying a speed of about 5000 mph. The probability that a U-235 nucleus will fission is about 300 times greater with a slow (thermal) neutron than with a fast neutron. In more technical terms, it can be stated that the fission cross-section of natural uranium increases from about 0.015 barn at a neutron energy of 1 MeV to 3.9 barn at thermal neutron energy. Thus to produce a neutron chain reaction in natural uranium it is necessary to add a moderating material which will slow down the neutrons by collision with the moderator nuclei. Suitable moderators are light and heavy water, carbon (graphite), beryllium, and beryllium compounds.

The most widely used moderators are heavy water (D_2O) and graphite. Light water can be used but it has high neutron absorption cross section compared to deuterium. When D_2O is moderator, since the neutron absorption cross section is low, the U-235 content of the fuel is correspondingly smaller.

Natural graphite has a density of 2.26 g/cc where as artificial graphite has a lower density of 1.6 – 1.7 g/cc. This lower density implies a comparatively high porosity. Unfortunately, this is a considerable disadvantage since the amount of surface available for oxidation reactions is increases.

Nuclear Reactors – Control:

Safety is given no less priority in the design and fabrication of the Nuclear reactors meant for a sustained chain reaction. In this regard, Control rods play a prominant role. It can be regarded as one of the poisons towards neutrons and these can be employed at the call of the situation. They have great capacity to absorb neutrons. They are arrestors of neutrons. The number of fissions occurring per second in the nuclear reactions and thus the chain reactions can be regulated by adjusting the position of these rods.

What materials can function as control rod poisons ?

What criteria a given material has to satisfy for it to be employed as a control rod ?

The major requirements that should be satisfied are. high neutron absorption, adequate strength, low mass (for rapid movement), corrosion resistance, stability under heat and radiation and satisfactory heat-trasfer properties.

The possible materials for control rods are :

Boron, Cadmium, Hafnium, Rare earths, Europium, Gadolinium, Samarium, Dysprosium, Erbium and Lutetium. Elements with relatively high thermal neutron absorption cross section are Cd (2400 barns), Boron (750 barns), Hafnium (115 barns), Iridium (440 barns), Mercury (300 barns), and mixtures of rare earths. Because Hafnium, Indium and the rare earths were quite expensive and Mercury presented engineering difficulties early emphasis was on Cd and B.

Unfortunately, neither of these, in elemental form , meets all the requirements. In more recent years, interest in Hf and the rare earths has greatly increased.

The Hafnium:

Hafnium is found associated with Zirconium in all its minerals, and is normally obtained by removing it from Zr. In general Hafnium is similar to Zr and Ti in its properties, corrosion resistance, fabrication etc. Unlike Zr, however, it is not sensitive to small amounts of impurities such as Nitrogen. Although the thermal neutron absorption cross section is relatively low, Hf is highly effetive as a control becasue of its large epithermal resonance-capture crosss section. The major advantage of hafnium over B and Cd is that is, doesn't need to be incorporated in some other materials, since it has more than adequate strength and stability in itself.

Coolants:

The heat produced in the reactor is extrated out by coolants. The heat can be used to convert water to high pressure steam which drives the turbine and the latter in turn drives the generator. Light water, CO_2, Helium and liquid sodium can be used as coolants.

Classification of Nuclear Reactors:

Depending on the purpose, neutron energy, moderator and coolant, fuel arrangement and structure materials reactors can be classified into various types the main purpose being power, research, breader and so on.

Depending on the energy of the neutron used to induce fission the reactors can be classified into either fast reactor or thermal reactors. In a fast reactor most of the neutrons are in the energy range of 0.1 – 1 MeV. The neutron remain at high energy because there is relatively little material present to cause them to slow down. In contrast, thermal reactor contains a good neutron moderating material. In these reactors, the bulk of the neutrons have energy in the vicinity of 0.1 eV.

Nuclear power plants:

The talk of building Nuclear power plants is reviving world over because of their low emissions of green house gases in the generation process. Nuclear energy is a way to generate heat using the fission process of atoms . A Nuclear power plant converts the heat into electricity. The purpose of a nuclear power plant is to produce or release heat and boil water. It is designed to produce electricity. It should be noted that while there are significant differences, there are many similarities between power plants and other electrical generating facilities. Uranium is used for fuel, in general, in nuclear power plants to make electricity. The main difference between a nuclear power plant and other kinds of power plants (coal, oil, gas) is that at a nuclear plant , the heat used to make the steam is produced by fissioning atoms. Fission is the splitting of atoms into smaller pieces, caused by neutrons. These smaller pieces (in crude terminology) strike other atoms, releasing energy. When this process continues it is called a chain reaction.

Broadly there are three types of nuclear power plant reactors, namely, burner reactors, converter reactors, and breeder reactors.

Both Pressurized water reactors and boiling water reactors are two types of light water reactors.

Breeder reactors:

Breeder reactors produce more fissionable material than they consume. Breeder fuel consists of a mixture of both fertile (U^{238} , Th^{232}) and fissile ((Pu^{239} , U^{233}) materials. The number of neutrons released is sufficient to propagate the fission reaction and to produce more fissionable materials (Pu^{239}) by the conversion of fertile isotopes to fissile isotopes.

Principle of breeding:

As seen above an appropriate mixture of Pu^{239}(U^{233}) and U^{238}(Th^{232}) should be employed as fuel in breeder reactors. Let us consider one such reactor. It is possible to create conditions such that out of the three neutrons released from the fission of each fissile atom (Pu^{239} or U^{233}) one of the neutrons is used up in propagating the fission chain by interacting with other fissile atom (Pu^{239} or U^{233}). At the same time the remaining two neutrons will be available for transmuting U^{238} or Th^{232} in to two new fissile atoms of Pu^{239} or U^{233} by the reactions shown below.

$_{92}U^{238} + {}_0n^1 \rightarrow {}_{92}U^{239}$ (β decay) $\rightarrow {}_{93}Np^{239}$ (β decay) $\rightarrow {}_{94}Pu^{239}$

$_{90}Th^{232} + {}_0n^1 \rightarrow {}_{90}Th^{233}$ (β decay) $\rightarrow {}_{91}Pa^{233}$ (β decay) $\rightarrow {}_{92}U^{233}$

These constitute two fissile atoms bred in the reactor, against one initially consumed. Thus natural uranium (U^{238}) or Th^{232} serves as a fertile source for breeding fissile atoms. There are two most common breeding cycles:

i. The Uranium cycle: In this the conversion of fertile U^{238} into fissionable Pu^{238} takes place. The uranium cycle uses high energy neutrons and is carried out in a fast reactor. In these reactors liquid sodium metal or pressurized helium is used as a coolant. No moderator is employed since the neutrons need not be slowed down.

ii. The Thorium cycle: In this the conversion of fertile Th232 into fissionable U^{233} takes place. The thorium cycle is analogous to the uranium cycle. But is works best in a thermal reactor.

Fertile U^{238} is abundant and inexpensive. It constitutes over 99% of naturally occurring uranium. It exists as large stock piles as a by-product of past uranium fuel-enrichment processing.

Fast breader reactors – Why are they needed?

Uranium keeps disappearing rapidly. The world reserves of uranium are by no means infinite. France, currently the largest producer of nuclear energy, anticipates a near total exhaustion of stocks of uranium in nature by about 2025 AD. It can be taken as a signal by other nations too to look for alternatives to uranium and conserve uranium stocks. World energy reserves can be extended very considerably by the use of Thorium. Natural thorium contains primarily the isotope ^{232}Th. This does not undergo fission with thermal neutron but it has an appreciable neutron absorption cross section to give Th-233, which then decays by beta particle emission through Protactinium to U-233 From a nuclear physics point-of-view, U-233 is the most desirable for use in thermal reactor systems. It is possible to build breeder reactors, for instance of the homogeneous aqueous type, which operate with U-233 fuel in the core and have a surrounding blanket of Th^{232} [7]. Thus there is a need for a fast breeder reactor which not only enables the extraction of 100 times more energy from uranium than via light water reactor (LWR), but manufacturers more fissile material (Pu-239) than it consumes (U-235). After removing the fission fragments, the plutonium isolated can be used as fresh fuel in a second reactor identical to the first.

Operation of Fast breader reactors in addition to resulting in enormous amounts of energy they yield Pu which is undoubtedly an asset.

Working of a fast breeder reactor:

For the sake of discussion let us consider a specific example of fast breeder reactor, namely the fast breeder test reactor at Kalpakkam, which is totally designed and fabricated in India. It being fast neutron reactor the fissile content of the fuel should be high in the range of 15-20 percent. Liquid sodium is used as coolent. The power output is 13 MW_e (Megawatt electrical). 70% PuC and 30 % UC in the form of sintered ceramic pellets encapsulated in stainless steel tubes is employed as fuel. Compared to oxide fuel , carbide fuel has higher heating rage and a higher breeding gain.

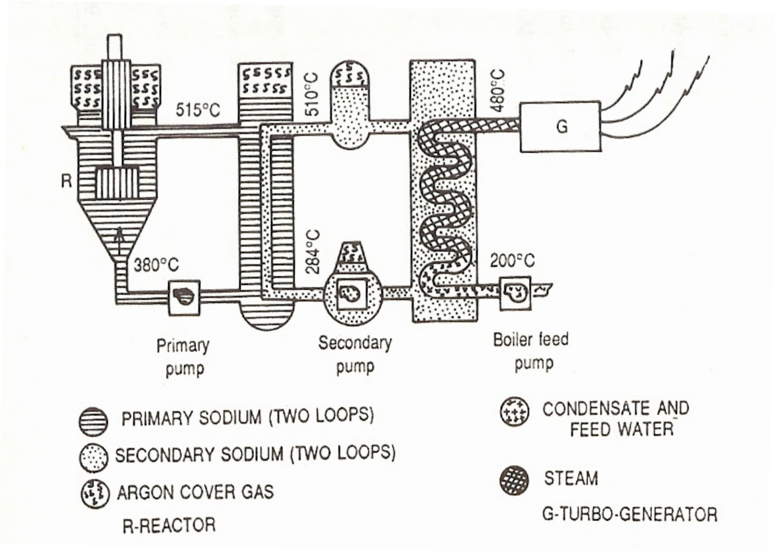


Fig. 3. The Fast Breeder Test Reactor [4]

It being a fast neutron reactor, there is no moderator and hence small size of the reactor core and a resulting much higher power density than in a thermal reactor of same power level. But far more efficient cooling system is needed. A liquid metal with high heat transference and compatible with the fuel and structural material should be circulated along the primary and secondary loops depicted in Fig. 3. In general low melting point metals like ^{7}Li and ^{23}Na were proved to be the best.

A sodium pump drives the liquid metal at 380 ºC into the reactor core from below. When the liquid leaves at the top at 515 ºC much heat would have been extracted from the reactor core. By this time Na^{23} becomes radioactive Na^{24} by (n, γ) reaction. Being radioactive the primary sodium is made to transfer the heat to a sealed second loop of sodium as an intermediate heat exchanger which remains non-radioactive. The two sodium pumps are of special design to keep circulating some 150 tons of molten sodium in the two mutually isolated loops. Thus the activity of the first loop is wholly contained therein. The heat from the secondary sodium loop is finally transferred to a boiler. The steam generated at 480 ºC and 125 kg/cm pressure drives a steam turbine to generate electricity. Thus the breeder reactor generates electricity.

Doubling time: The time needed to set up the second reactor is called the doubling time. In other words, the time required to double the inventory of fissionable material.

Nuclear Fusion:

A thermonuclear reaction in which nuclei of lighter atoms combine to form nuclei of heavier atoms accompanied by the release of large amount of energy is called a fusion reaction.

The Sun – Is the sun truly an inexaustable source of energy? How?
Can there be an artificial sun?

Truly the light is sweet, and a pleasant thing it is for the eyes to behold the Sun: ***The Holy Bible (Ecclesiastes 11:7)***

Fusion reactions are considered to be responsible for the endless (currently assumed) source of energy given out by the sun.

The sun keeps replenishing its energy because it is continuously supplied with atomic energy from nuclear reactions going on in the interior, where the temperature is of the order of 20 million degrees centigrade. The energy of the sun is supposed to arise from the following thermo-nuclear reactions:

$_{1}H^{1} + {}_{1}H^{1} \rightarrow {}_{1}H^{2} + e+ + \text{Energy}$

$_{1}H^{2} + {}_{1}H^{1} \rightarrow {}_{2}He^{3} + \text{Energy}$

$_{2}He^{3} + {}_{2}He^{3} \rightarrow {}_{2}He^{4} + 2\,{}_{1}H^{1} + \text{Energy}$

The net result of this reaction is the combination of four protons to produce one nucleus of helium ${}_{2}He^{4}$ as represented below:

$4\ {}_{1}H^{1} \rightarrow {}_{2}He^{4} + 2\ {}_{+}e^{0}$

4 x 1.008144 4.003873 2 x 0.000558 = 0.001116

4.032576 4.004989

Mass loss, Δm = 4.032576 – 4.004989

= 0.027587 amu

Energy released = 0.027587 x 931 MeV = 26.7 MeV

Controlled nuclear fusion:

In sharp contrast to fission, nuclear fusion process could not be controlled. The estimated amounts of deuterium in the water of the earth is 10^{17} pounds (1 kg = 2.2 pounds). Each pound of deuterium is equivalent to 2500 tons of coal in energy. So a controlled fusion reactor would provide a virtually inexhaustible supply of energy. Thus a great effort is being made to build such a reactor. Success in this direction is not too far [8].

Obstacles in exploiting fusion energy:

i. Fuel : Attempts should be intensified to separate deuterium from ordinary water. Production of tritium can also be attempted.

ii. The particles must be heated to temperatures ranging from 50 to 100 million degrees depending upon the particular reaction.

iii. The state of plasma must be present for a long enough time so as to allow a substantial portion of the nuclei present in it to undergo fission.

iv. Technology to harness the released energy to generate useful power also need to mature.

The energy released is 26.7 MeV for four protons. The heat produced in these thermonuclear reactions makes up the loss of heat by sun's radiation there by keeping the sun's temperature constant.

Fusion reactions are used to make hydrogen bomb (thermonuclear bomb). The technology of fusion bombs is different from that of fission bombs (atom bomb). Since very high temperature is required to initiate the fusion reaction of the type ${}_{1}H^{2} + {}_{1}H^{2} \rightarrow {}_{2}He^{4}$, an atomic bomb is used as a trigger [9].

Radio isotopes for Electricity:

Exploiting nuclear reactions such as Fission and Fusion are well heard. But since there is wide scope for the synthesis of new radioisotopes and also enormous number of radioisotopes have already been reported and also large amount of energy is released during the decay of the radioactive atom, attempts can be intensified to develop devices, atleast auxiliary power sources, (since the quantum of energy output is orders of magnitude lower than that derived from Fission and Fusion reactions) based on radioisotopes. An interesting example of power generation by using ^{90}Sr radioisotope is presented below:

The Strontium-Ninety Auxiliary Power (SNAP) developed in US is an efficient but auxiliary power source for charging batteries used in submarines, space craft, unmanned Arctic stations and in nuclear devices coupled to high frequency transmitters for continuous signaling of weather conditions. The 0.54 MeV β emitter 90Sr in the form of strontium titanate ($^{90}SrTiO_3$) is used in the device depicted in Fig. 4. The radioactive source is in a highly compact packing. The packing gets heated to temperatures of the order of 500 ºC. The device provides thermoelectric power through a large number of efficient thermojunctions. The cold junctions outside remain at temperatures around 50 ºC. ^{238}Pu (with half-life 87.7 year period) which is an α emitter with energy 5.4 MeV can also be used in place of ^{90}Sr.

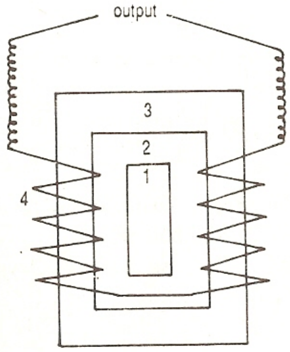


Fig. 4. Radioisotope ($^{90}SrTiO_3$) as a source of thermoelectricity
(Strontium-Ninety Auxilary Power) [4]
1 – Column of $^{90}SrTiO_3$, 2-Insulator, 3-Shielding, 4-Thermocouples

Such deivces are not risk free for enough care need to be taken such that no leak of encapsulation takes place.

Conclusion:

The work of construction should not stop for fear of destruction. Let us go ahead with the option of nuclear energy since the benefits and comforts derived there from out weight the frustrations and fears of peril.

Wisdom is better than weapon of war: but one sinner destroyeth much good.

The Holy Bible (Ecclesiastes 9:18)

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Chapter - 10
HYDROGEN ENERGY

L. Hima Kumar

Introduction

Energy is one of the most basic of human needs and is extremely crucial for continued human development. The accomplishments of civilization have largely been achieved through the increasingly efficient and extensive harnessing of various forms of energy to extend human capabilities and ingenuity. Providing adequate and affordable energy is essential for eradicating poverty, improving human welfare, and raising living standards worldwide. The global demand for energy is rapidly increasing with increasing human population, urbanization and modernization. The growth in global energy demand is projected to rise sharply over the coming years. The world heavily relies on fossil fuels to meet its energy requirements, fossil fuels such as oil, gas and coal. Presently employed energy systems will be unable to cope with future energy requirements, fossil fuel reserves are depleting, and predominantly the developed countries employ nuclear power. Fossil fuel and nuclear energy production and consumption are closely linked to environmental degradation that threatens human health and quality of life, and affects ecological balance and biological diversity. It is therefore clear that if the rapidly increasing global energy needs are to be met without irreparable environmental damage, there will have to be a worldwide drive to exploit energy systems that should not endanger the life of current and future generations and should not exceed the carrying capacity of ecosystems.

One of the most significant transitions in global energy systems is that of decarbonization, an increase in energy quality (Fig. 1). Considering the case of fossil fuels, the dominating energy resource over the course of human history, each successive transition from one source to another from wood to coal, from coal to oil has entailed a shift to fuels that were not only harnessed and transported more economically, but also had a lower carbon content and higher hydrogen content. It is also evident that at each step greater energy density is being achieved. The third wave of decarbonization is now at its threshold, with natural gas use growing fastest, in terms of use, among the fossil fuels. The next logical fuel in this progression is hydrogen. Its major drivers are technological advances, renewed concern about the security and price of oil and gasoline, and growing pressure to address local air pollution and climate change.

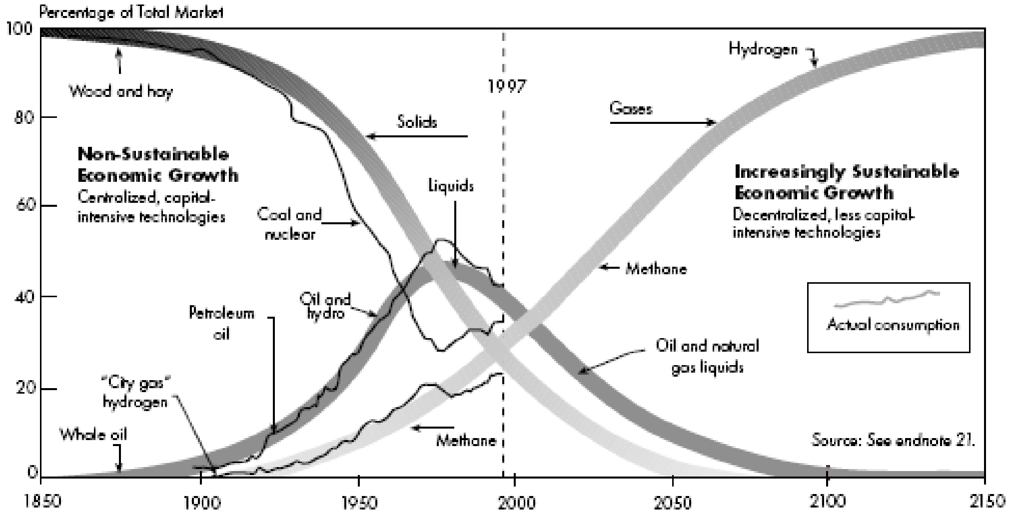

Fig. 1 Global energy systems transition, 1850 – 2150

Renewable energy sources that use indigenous resources have the potential to provide energy services with almost zero emissions of both air pollutants and greenhouse gases. Renewable energy sources such as solar energy, wind power, biomass and geothermal energy are abundant, inexhaustible and widely available. Renewable energy as the name implies is the energy obtained from natural sources such as wind power, solar energy, hydropower, biomass energy and geothermal energy. Renewable energy sources have also been important for humans since the beginning of civilization; Biomass, for example, has been used for heating, cooking and steam production; wind has been used for moving ships; both hydropower and wind have been used for powering mills to grind grains. Renewable energy resources are abundant in nature. They are presently meeting almost 13.5% of the global primary energy demands and are acknowledged as a vital and plentiful source of energy that can indeed meet entire world's energy demand. For the future of the worldwide energy supply three goals must be fulfilled: security in the energy supply, environmental protection and the utilization of energy sources that promote the economic growth of societies.

The so-called hydrogen economy is a long-term project that can be defined as an effort to change the current energy system to one which attempts to combine the cleanliness of hydrogen as an energy carrier with the efficiency of fuel cells (FCs) as devices to transform energy into electricity and heat. As an energy carrier, hydrogen must be obtained from renewable energy sources, which survive for long term and avoid/minimize CO_2 emissions.

Why hydrogen?

Hydrogen is the cleanest, sustainable and renewable energy carrier. Hydrogen is the simplest, lightest and most abundant element in the universe, making up 90% of all matter. It is made up of just one electron and one proton and is, therefore, the first element in the periodic table. In its normal gaseous state, hydrogen is odourless, tasteless, colourless and non-toxic.

Table 1. Properties of hydrogen compared to other fuel system

Property	**Unit**	**Hydrogen H_2**	**Methane CH_4**	**Gasoline $-(CH_2)n-$**
Lower heating value	kWh kg^{-1}	33.33	13.9	12.4
Self ignition temperature	K	858	813	498-774
Flame temperature	K	2318	2148	2473
Ignition limits in air	Vol %	4 - 75	5.3 - 15	1.0-7.6
Min. ignition energy	mW	0.02	0.29	0.24
Flame propagation in air	m s^{-1}	0.02	0.4	0.4
Explosion energy	kg TNT m^{-3}	2.02	7.03	44.22
Diffusion coefficient in air	cm^2 s^{-1}	0.61	0.16	0.05
Toxicity		No	No	High

Hydrogen burns readily with oxygen, releasing considerable amounts of energy as heat and producing only water as exhaust. Hydrogen is highly flammable with a high flammability range, burning when it makes up 4% to 74% of air by volume. It has high energy content by weight nearly three times that of gasoline. By contrast, hydrogen has a low energy density by volume at a standard temperature and atmospheric pressure. One gram of hydrogen gas at room temperature occupies about 11.2 liters of space. Storing the gas under pressure or at temperatures below -253º C, at which point it turns into a liquid, raises its volumetric density. In many ways hydrogen seems to be an attractive replacement for existing fossil fuel system by their properties as given in Table 1.

Hydrogen is a carrier of energy, not a source. It does not exist in a natural state on earth and must be manufactured using a hydrogen-rich compound such as water as the raw material. Once it is extracted, becomes a useful “feedstock”, or input, to a variety of industrial activities and sufficient to energize virtually all aspects of society, from homes to electric utilities to business and industry to transportation

Hydrogen production

Hydrogen can be produced from a variety of feed stocks. These include fossil resources, such as natural gas and coal, as well as renewable resources, such as biomass and water with input from renewable energy sources (*e.g.* sunlight, wind, wave or hydro-power). A variety of process technologies can be used, including chemical, biological, electrolytic, photolytic and thermo-chemical. Each technology is in a different stage of development, and each offers unique opportunities, benefits and challenges. Local availability of feedstock, the maturity of the technology, market applications and demand, policy issues, and costs will all influence the choice and timing of the various options for hydrogen production. An overview of the various feed stocks and process technologies is presented in Figure 2.

From fissile fuels

There are many industrial methods currently available for the production of hydrogen; almost all the hydrogen produced in the world today involves the steam reforming of fossil fuels using a nickel catalyst. At present, this is a proven, commercial technology

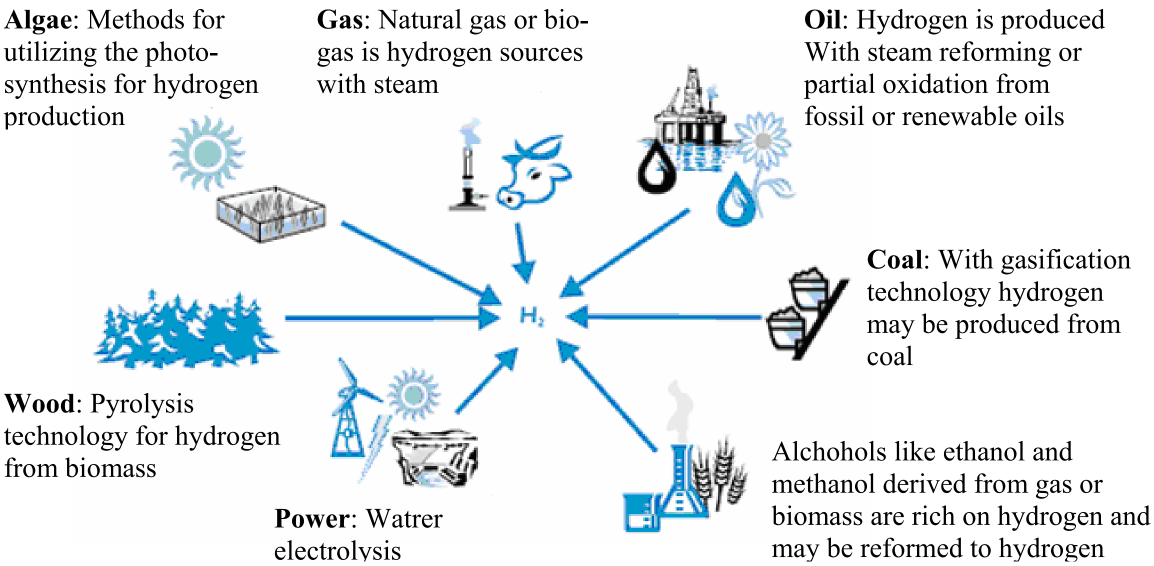

Fig. 2 various feed stocks and process technologies for hydrogen production

and is by so far the cheapest way of making hydrogen on a large scale. In most cases, natural gas (methane) is the raw material. ***Partial oxidation*** of methane is also used to produce hydrogen. The process involves, reacting the methane with oxygen to produce hydrogen and carbon monoxide, which is then reacted with water to produce more hydrogen and carbon dioxide.

Gasification of coal

Hydrogen can be produced from coal through a variety of gasification processes. Gasification of coal is the oldest technique for making hydrogen, and is still used in some parts of the world. Hydrogen production from coal is commercially mature, but it is more complex than the production of hydrogen from natural gas. The cost of the resulting hydrogen is also higher. But since coal is plentiful in many parts of the world and will probably be used as an energy source regardless, it is worthwhile to explore the development of clean technologies for its use.

Water electrolysis

Hydrogen production using water electrolysis (Water electrolysis is the process whereby water is split into hydrogen and oxygen through the application of electrical energy) is minimal today, because it requires large amounts of electricity, which is expensive. This technique is normally used only to produce hydrogen of very high purity, required in some industrial processes, or other products, such as chlor-alkali, with hydrogen as a by-product. But electrolysis could be used to produce small quantities of hydrogen close to the point of use; for example, at refuelling stations. To be economic, the electricity would need to be cheap. The environmental benefits of electrolysis-based hydrogen energy depend on how the electricity is produced. If it were generated from nuclear or renewable energy sources, such as wind, solar and biomass, electrolysis would produce carbon-free hydrogen. But large reductions in the cost of renewables-based electricity and nuclear power are needed to enable hydrogen produced by electrolysis to compete with conventional sources of energy on a large scale.

Thermal decomposition of water

Direct decomposition of water to give hydrogen and oxygen occurs only at high temperatures above 4000 K. To reduce the temperature, other processes for high temperature splitting of water have been suggested. Even then, the splitting of water by thermo-chemical methods requires temperatures around 1500 K. The thermochemical cycles include the following: sulfuric acid–iodine cycle, hybrid sulfuric acid cycle, hybrid sulfuric acid–hydrogen bromide cycle, calcium bromide–iron oxide cycle (UT-3), and iron - chlorine cycle. Only, limited heat sources are available like nuclear reactor, which can provide the required high temperature. The main problem of this method is related to materials required for extremely high temperatures, recombination of the reaction products at high temperatures, toxicity of some of the chemicals involved and separation of hydrogen.

Biological or biochemical methods

The ***biological or biochemical methods*** for the production of hydrogen by splitting water have also been under investigation. Micro organisms are capable of producing H_2 via either fermentation or photosynthesis. Photo-biological production of hydrogen is based on two steps: photosynthesis and hydrogen production catalyzed by hydrogenases like algae and cyanobacteria. In biomass conversion processes, a hydrogen-containing gas is normally produced in a manner similar to the gasification of coal. However, no commercial plants exist to produce hydrogen from biomass. Currently, the pathways followed are steam gasification (direct or indirect), entrained flow gasification, and more advanced concepts such as gasification in supercritical water, application of thermo-chemical cycles, or the conversion of intermediates (*e.g.* ethanol, bio-oil or torrified wood). None of the concepts have reached a demonstration phase for hydrogen production.

Although the technology for production of hydrogen from renewable sources is well understood, it is currently not utilized for producing hydrogen in large quantities. Hydrogen produced from renewable energy sources is currently too expensive. Production of significant quantities of hydrogen using such methods would take considerable time and investment to develop, to allow capital costs to be reduced to a satisfactory level. However, in the long term, hydrogen offers a potential route for gaining energy independence from fossil fuels.

Hydrogen Storage

However hydrogen is produced, its widespread use will require large-scale infrastructure to transport, distribute, store and dispense it as a fuel for vehicles or for stationary uses. A range of storage technologies that address this problem; compressed gas, liquefied hydrogen, metal hydride, and carbon based systems are under development for stationary and onboard vehicle uses. Which choice is best depends on several factors: the application, the energy density needed, the amount to be stored and the time period of storage, the forms of energy available, maintenance requirements, and capital and operating costs. Hydrogen storage basically implies the reduction of the enormous volume of the hydrogen gas. In order to increase the hydrogen density in a storage system work must either be applied to compress hydrogen, or the temperature has to be decreased below the critical temperature.

For stationary systems, the weight and volume of the system used for hydrogen storage is not a key factor. However, for mobile applications, such as fuel cell electric vehicles or hydrogen-fuelled (internal combustion) cars, hydrogen storage system has to be compact, lightweight, safe and affordable. The US Department of Energy (DOE) Hydrogen Plan has set a standard for this discussion by providing a commercially significant benchmark for the amount of reversible hydrogen absorption. The benchmark requires system-weight efficiency (the ratio of stored hydrogen weight to system weight) of 6.5 weight % hydrogen and a volumetric density of 62 kg H_2/m^3, since a vehicle powered by a fuel cell would require more than 3.1 kg of hydrogen for a 500 km range. Fig. 3 shows that various storage options that meet the long-term needs. To reach the high volumetric and gravimetric density suitable for mobile applications, basically six reversible storage methods are known today : 1) high- pressure gas cylinders, 2) liquid in cryogenic tanks, 3) physisorbed on a solid surface e.g. carbon-nanotubes 4) metal hydrides of the metals or intermetallic compounds. 5) complex hydrides of light elements such as alanates and boranates, 6) storage via chemical reactions.

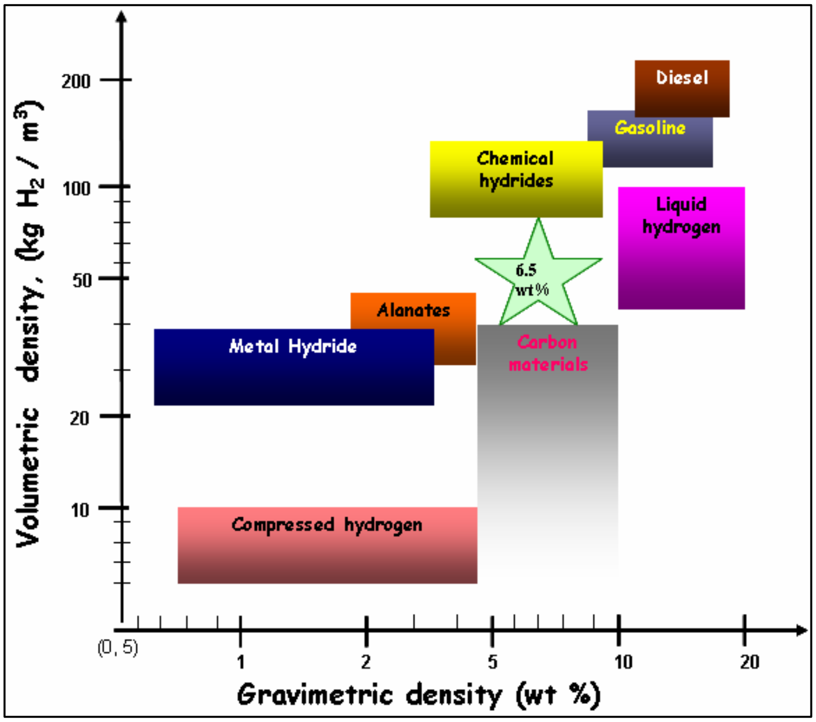

Fig. 3. Comparison of volumetric and gravimetric density of hydrogen with various storage media Compressed hydrogen gas

Gaseous hydrogen storage

The most common method to store hydrogen is as a compressed gas, either above or below ground or on board vehicles. With a compressed gas system, the hydrogen is typically compressed and stored in gas cylinders or spherical containers. For storing hydrogen on board vehicles, compressed hydrogen is the simplest and presently the cheapest method, requiring only a compressor and a pressure vessel. Its main obstacle is its low storage density. Higher storage pressures raise the cost, as well as safety issues.

Liquid hydrogen

As an alternative to compression, hydrogen can be liquefied for storage in stationary or onboard vehicle systems. Liquefaction takes place through a number of steps in which the hydrogen is compressed and cooled to form a dense liquid. The liquid hydrogen must then be stored at very low temperatures, below –250 °C. A major drawback with liquefied hydrogen storage is the high cost of liquefaction and the significant liquid “boil off”. Liquefying hydrogen gas also requires a large amount of electricity.

Solid hydrogen storage

Storage of hydrogen in solid materials has the potential to become a safe and efficient way to store energy, both for stationary and mobile applications. There are four main groups of suitable materials: carbon and other high surface area materials; H_2O reactive chemical hydrides; thermal chemical hydrides; and rechargeable hydrides.

Metal hydrides

Many metals and alloys are able to react spontaneously with hydrogen. These materials, either a defined compound or a solid solution, are designed as metallic hydrides. These are compounds that chemically bond the hydrogen in inter atomic lattice of a metal. The hydrogen is absorbed into the lattice through cooling and released through heating, with the temperature and pressure of these reactions depending on the particular makeup of the hydride. Hydrides are unusual in that they can draw in the hydrogen at or below atmospheric pressure, and release it at higher pressure when heated. Current drawbacks of metal hydrides are that they are heavy, the gravimetric hydrogen density is limited to less than 3 wt% of hydrogen, require energy to refill, and are comparatively costly.

Carbon nanostructures

Carbon-based systems are another strong hydrogen storage possibility in the early stages of development. Scientists are working to develop materials that can store significant amounts of hydrogen at room temperature, potentially a breakthrough that would enable the practical use of hydrogen run vehicles. Two types are being explored. Single walled carbon nanotubes, made up of molecule-sized pores and Graphite nanofibers, stacks of nanocrystals that form a wall of similarly small pores. Even though the price of the nanotubes and nanofibers is still high, they have a good potential in hydrogen storing and will remain as materials that are competitive for to be used in hydrogen storage processes.

Chemical hydrides

Chemical hydrides are also being considered for hydrogen storage on board vehicles. Hydrogen may also be stored chemically in alkali metal hydrides. There are many options in the alkali group like LiH, NaH, KH, CaH_2. But also complex binary hydride compounds like $LiBH_4$, $NaBH_4$, KBH_4, $LiAlH_4$ or $NaAH_4$ are of interest and have been proposed as hydrogen sources. None of these compounds can be found in nature. All have to be synthesized from metals and hydrogen.

Chemicals such as methanol or ammonia could also be used which has the advantage of an existing transport and storage infrastructure, a commercial technology, and relatively easy liquid and storage handling.

Hydrogen application

Residential and commercial applications:

Mixed with natural gas, hydrogen could be used in existing natural gas equipment. With no change to the devices up to 3 % volume of hydrogen can be added to the gas. More hydrogen requires modifications to the burners and other equipment of the consumer.

Industry

With proper adjustments all types of industrial natural gas burners can be fed with hydrogen. Hydrogen could then be used as natural gas for steam generation. However in order to maximize its energy efficiency, hydrogen is better used with fuel cells that produce simultaneously heat and electricity (cogeneration).

Internal combustion engines and fuel cells

The key to the hydrogen energy system is using the fuel economically in internal combustion engines, conventional combustion turbines, and fuel cells. Ongoing research on hydrogen-fueled ICEs is aimed at use in vehicles. Hydrogen is a good fuel for internal combustion (IC) engines and can improve efficiency by around 20% compared to the use of gasoline. Several companies, such as Alstom, Westinghouse and Mitsubishi are pursuing the use of hydrogen in gas turbines like those commercially established to run on natural gas. A more likely long-term approach will be to employ hydrogen to run fuel cells.

A fuel cell utilizes a chemical process to convert hydrogen (or a hydrogen-rich fuel) into electrical energy and heat. It can do so at high efficiency (not subject to limitations of the Carnot cycle), producing a non-fluctuating DC power output. Most fuel cells have high power densities (i.e. high power output per unit weight, volume, or area). There are six main types of fuel cell, distinguished by their different electrolytes and the different temperatures reached during operation. Fuel cells display high efficiency across most of their output power range whereas the internal combustion engine has a point of maximum operating efficiency. The fuel cell has a very flat characteristic and is generally more efficient at fractions of its rated power. As a consequence, the fuel cell will show even larger advantages over an IC engine during a drive cycle compared to continuous output tests.

The most commercially advanced version, the phosphoric acid fuel cell (PAFC) run generally on either natural gas or propane or direct hydrogen and have been purchased primarily for applications that produce both heat and power. Existing niche markets include landfills, wastewater treatment plants, industrial food processors, high-tech companies, banks, hospitals, and other facilities highly vulnerable to interruptions.

Two types of fuel cells must be operated at high temperatures, above 650 °C. These do not require expensive catalysts, and their waste heat can be captured and used to run turbines to increase overall efficiency to 60 percent or more, with the residual heat used for space and water heating. Alkaline fuel cells, the type used in the Apollo program, are being tested for commercial applications. Direct methanol fuel cells run on methanol without need of a reformer. The fuel cell that is attracting the most attention is the proton exchange membrane (PEM) fuel cell, used in the Gemini mission. This cell's membrane functions as an electrolyte through which protons pass, bonding with oxygen to form water. This leaves the electrons to move along an external circuit, creating an electrical current.

Future of hydrogen

Hydrogen has great potential as an environmentally clean energy fuel and as a way to reduce reliance on imported energy sources. Before hydrogen can play a bigger energy role and become a widely used alternative to gasoline, many new facilities and systems must be built. We will need facilities to make hydrogen, store it, and move it. We will need economical fuel cells. And consumers will need the technology and the education to safely use it. The realization of this hydrogen economy largely depends on the cooperation between the scientists for the development of new materials and technologists to design appropriate devices and reactors so that this alternate form of energy source can be utilized by mankind.

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Chapter - 11
ENERGY STORAGE

Ch. Venkateswara Rao

Introduction

What is energy storage?

Energy storage is the general method and specific techniques for storing energy derived from some primary source in a form convenient for use at a later time when a specific energy demand is to be met, often in a different location Energy storage involves methods and apparatus used to store heating, cooling, or power.

Why we need to store energy?

We seem to have an ever-increasing need for more energy. Both households and industries require large amounts of power. At the same time our means of production face new problems. International treaties aim to limit the levels of pollution, global warming prompts action to reduce the output of carbon dioxide and several countries have decided to decommission old nuclear power plants and not build new ones. Such development brings about the need to replace old energy production methods with new ones. While several are in development, including the promising but ever-so-distant nuclear fusion power, other production methods are already in commercial use. These often rely on the weather or climate to work, and include such methods as wind power, solar power and hydroelectricity in its many forms. These new sources of energy have some indisputable advantages over the older methods. At the same time, they present new challenges. The output of the traditional methods is easy to adjust according to the power requirements. The new energy sources are based more directly on harnessing the power of the nature and as such their peak power outputs may not match the power requirements. They may exhibit large fluctuations in power output in monthly or even annual cycles. Similarly, the demand can vary diurnally or annually. We need a way to buffer power, that is, store energy when excess is produced and then release it when production levels do not meet the requirements. Depending on how storage is distributed, it may also help the network withstand peaks in demand. Storing energy allows transmission and distribution to operate at full capacity, decreasing the demand for newer or upgraded lines. Storing energy for shorter periods may be useful for smoothing out small peaks and sags in voltage.

What are the methods available to store energy?

Energy can be stored in different ways. It can be stored electrochemical, electrical, mechanical and thermal manner.

Electrochemical energy storage devices – Batteries and Fuel cells

Electrical energy storage devices – Capacitors, Supercapacitors and Superconducting magnetic energy storage (SMES)

Mechanical energy storage devices - Compressed air energy storage (CAES), Flywheel energy storage, Hydraulic accumulator, Hydroelectric energy storage and Spring

Thermal energy storage devices - Cryogenic liquid air or nitrogen, Seasonal thermal storage, solar pond and Steam.

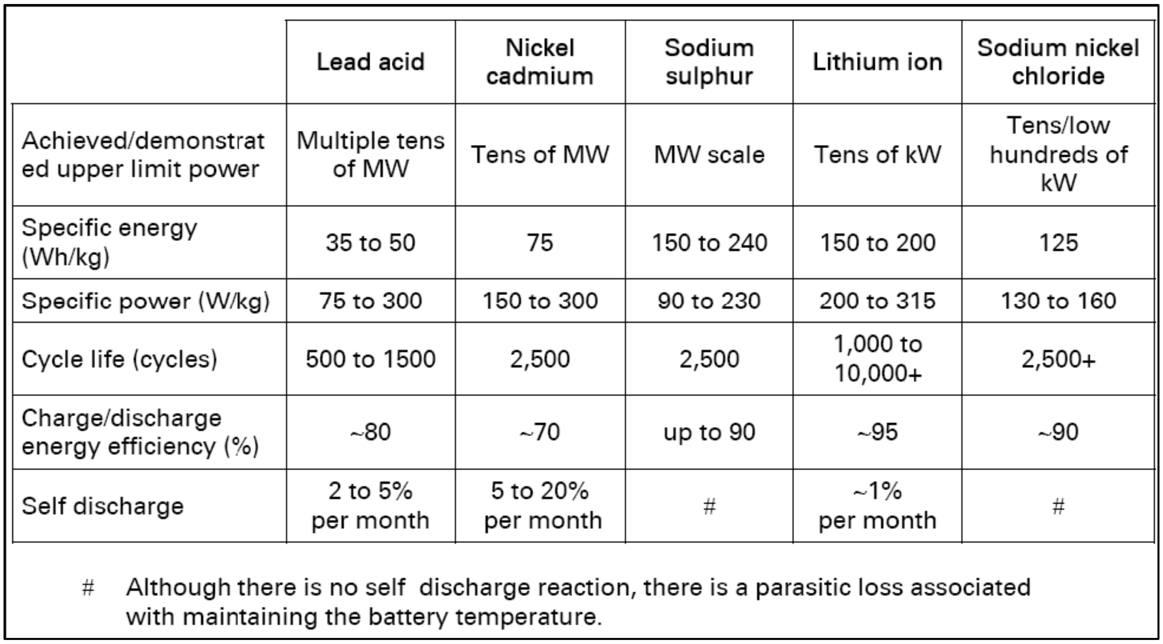
Electrochemical energy storage devices

Batteries:

The oldest and most established way of storing electricity is in the form of chemical energy in batteries. A battery comprises of one or more electrochemical cells and each cell consists of a liquid, paste, or solid electrolyte together with a positive electrode and a negative electrode. During discharge, electrochemical reactions occur at the two electrodes generating a flow of electrons through an external circuit. The reactions are reversible, allowing the battery to be recharged by applying an external voltage across the electrodes. Battery systems range from mature and reliable technologies, such as lead acid, which have been proven and developed over many years, to various newer designs which are at different stages of development, including sodium-sulphur and sodium nickel chloride based batteries. In recent years, new developments have been driven by the demands of consumer electronics, portable and transport applications, although there is increasing interest in the use of large scale batteries for utility energy storage applications.

Electrochemical approaches that are either in use and/or potentially suitable for utility scale battery energy storage applications include lead acid, nickel cadmium, sodium-sulphur, sodium nickel chloride and lithium ion. A summary of the performance characteristics of each of these battery systems is given in Table 1

Table 1. Performance characteristics of battery systems

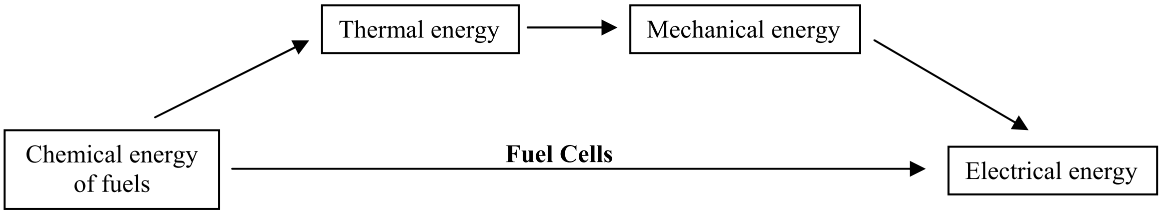


	Lead acid	Nickel cadmium	Sodium sulphur	Lithium ion	Sodium nickel chloride
Achieved/demonstrated upper limit power	Multiple tens of MW	Tens of MW	MW scale	Tens of kW	Tens/low hundreds of kW
Specific energy (Wh/kg)	35 to 50	75	150 to 240	150 to 200	125
Specific power (W/kg)	75 to 300	150 to 300	90 to 230	200 to 315	130 to 160
Cycle life (cycles)	500 to 1500	2,500	2,500	1,000 to 10,000+	2,500+
Charge/discharge energy efficiency (%)	~80	~70	up to 90	~95	~90
Self discharge	2 to 5% per month	5 to 20% per month	#	~1% per month	#

\# Although there is no self discharge reaction, there is a parasitic loss associated with maintaining the battery temperature.

Fuel cells:

An electrochemical cell in which the energy of a reaction between a fuel, such as liquid hydrogen, and an oxidant, such as liquid oxygen, is converted directly and continuously into electrical energy



Scheme 1. Direct energy conversion with fuel cells in comparison to conventional indirect technology

Typically, a process of electricity generation from fuels involves several energy conversion steps, namely:

1. combustion of fuel converts chemical energy of fuel into heat,
2. this heat is then used to boil water and generate steam,

3. steam is used to run a turbine in a process that converts thermal energy into mechanical energy, and finally

4. mechanical energy is used to run a generator that generates electricity.

A fuel cell circumvents all these processes and generates electricity in a single step without involving any moving parts. Such a device must be simpler, thus less expensive and far more efficient than the four-step process previously depicted. Fuel cells have many applications that make them attractive when compared with the existing conventional energy conversion technologies, namely:

(i) Promise of high efficiency
(ii) Promise of low or zero emissions
(iii) Simplicity
(iv) No moving parts and promise of long life
(v) Quiet

Because of their attractive properties, fuel cells have already been developed and come into widespread commercial use through three main applications: transportation, stationary power generation and portable applications.

How does a fuel cell works?

The basic physical structure or building block of most fuel cells consists of an electrolyte layer in contact with porous anode and cathode electrodes on either side. All fuel cells have similar basic operating principle. The input fuel is catalytically reacted (electrons removed from the fuel) in the fuel cell to create an electric current.

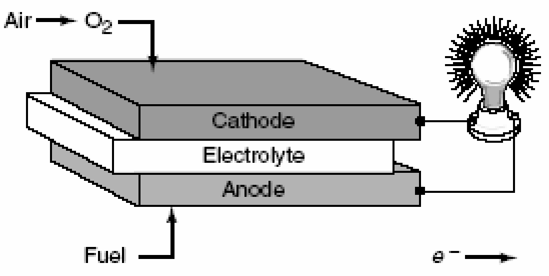


Fig. 1. Schematic of a fuel cell

The input fuel passes over the anode is catalytically split into electrons and ions. Air/oxygen passes over the cathode is reduced by the electrons which are generated at anode and passed on to the cathode by external circuit. At cathode, the ions which are formed at anode and transported to cathode through the electrolyte, combine with the oxide ions and generate the oxidized product. If the fuel happens to be hydrogen, then water is formed. A variety of fuel cells are in different stages of development. They can be classified by use of diverse categories, depending on the combination of type of fuel and oxidant, whether the fuel is processed outside (external reforming) or inside (internal reforming) the fuel cell, the type of electrolyte, the temperature of operation, whether the reactants are fed to the cell by internal or external manifolds. The characteristic features of various types of fuel cells are shown in Table 2.

Table 2. Characteristic features of various fuel cells

Electrochemical device	Operating temp (K)	Electrolyte	Charge carrier	Electrolyte state	Fuel for cell	Oxidant for cell
Alkaline fuel cell (AFC)	333-423	45% KOH	OH^-	Immobilized liquid	Hydrogen	O_2/Air
Phosphoric acid fuel cell (PAFC)	453-493	H_3PO_4	H^+	„	Hydrogen	O_2/Air
Proton exchange membrane fuel cell (PEMFC)	333-353	Ion exchange membrane (e.g., Nafion)	H^+	Solid	Hydrogen	O_2/Air
Direct methanol fuel cell (DMFC)	333-353	„	H^+	Solid	Methanol	O_2/Air
Molten carbonate fuel cell (MCFC)	923-973	Alkali carbonate mixture	CO_3^{2-}	Immobilized liquid	Hydrogen	O_2/Air
Solid oxide fuel cell (SOFC)	1073-1273	Yttria-stabilized zirconia	O^{2-}	Solid	Hydrogen	O_2/Air

Electrical energy storage devices

Capacitors and supercapacitors:

Capacitors store energy in an electrostatic field rather than as a chemical state as in batteries. No chemical reactions involved which means very long cycle life is possible. No limit on the cell voltage imposed by the "cell chemistry" as with galvanic cells. The terminal voltage is directly proportional to the State of Charge (SOC) which limits range of applicability somewhat.

Capacitors consist of two conductive parallel plates and separated by a dielectric insulator. The plates hold opposite charges which generate an electric field. Unlike in batteries where energy is stored in chemical form, capacitors store energy in the form of field.

The capacitance is defined as $\mathbf{C = (A/d)\, \varepsilon_r \varepsilon_0}$

where **A** is the area of the parallel plates **d** is the distance between them, ε_r is the relative permittivity or dielectric constant and ε_0 is the permittivity of free space (8.854×10^{-12} F/m).

The energy stored by the capacitor is given by $E = \mathbf{(1/2)\, C\, V^2}$

The energy density of supercapacitors can be four times more compared to the normal capacitor. The basic principle of energy storage in a supercapacitor is based on creating a charge-separated state in an electrochemical double layer. In this case, energy storage is based on the separation of charges in the double layer across the electrode/electrolyte interface. The positive electrode is electron deficient whereas the negative electrode contains a surplus of electrons. The energy (W) stored in a capacitor as a function of the voltage applied (U) and the capacity (C) is given by the equation : $\boldsymbol{W = CU^2/2}$.

Compared to conventional capacitors where a total capacitance of pF and mF is typical, the capacitance of and the energy density stored in the electrochemical double layer are high. In order to achieve a higher capacitance the electrode surface area is additionally increased by using porous electrodes with an extremely large internal effective surface. Combination of two such electrodes gives an electrochemical capacitor of rather high capacitance.

Electrochemical capacitors are used as back-up memory for electronic devices like VCR circuits, CD players, cameras, computers, clocks, clock radios, telephones and other electronic equipments. Electrochemical capacitors also used in hybrid electric vehicles in combination with batteries as their power density is higher than batteries for load leveling. Electrochemical capacitors in combination with batteries occupy less space and are light, have excellent cold weather starting and increased battery life. Other uses of electrochemical capacitors include regenerative breaking, unmanned monitoring units, uninterruptible power supplies (UPS), and high power lasers.

The supercapacitor has become available to the public. A commercial supercapacitor can hold 2500 farads, release 300 A of peak current with a peak voltage handling of about 400 V. The life-cycle of this supercapacitor is more than $1\text{x}10^6$ charge/recharge cycles.

Superconducting magnetic energy storage (SMES)

Superconducting magnetic energy storage (SMES) system is a device for storing and instantaneously discharging large quantities of power. It stores energy in the magnetic field created by the flow of DC in a coil of superconducting material that has been cryogenically cooled. These systems have been in use for several years to improve industrial power quality and to provide a premium-quality service for individual customers vulnerable to voltage fluctuations. The SMES recharges within minutes and can repeat the charge/discharge sequence thousands of times without any degradation of the magnet. Recharge time can be accelerated to meet specific requirements, depending on system capacity.

As an energy storage device, SMES is a relatively simple concept. It stores electric energy in the magnetic field generated by DC current flowing through a coiled wire. If the coil were wound using a conventional wire such as copper, the magnetic energy would be dissipated as heat due to the wire's resistance to the flow of current. However, if the wire is superconducting (no resistance), then energy can be stored in a “persistent" mode, virtually indefinitely, until required. Superconductors have zero resistance to DC electrical current at low temperatures so that ohmic heat dissipation is eliminated; hence the refrigerator is needed in the SMES to cool the coil.

The energy stored within the coil is given by $E = \frac{1}{2} \mathbf{LI}^2$

where L is the inductance of the coil, and I is the current passing through it. The volumetric energy density is given by $\mathbf{U_D = B^2/2\mu_o}$

SMES systems are environmentally friendly because superconductivity does not produce a chemical reaction. In addition, there are no toxins produced in the process. SMES can be used in enhancing transmission line capacity and performance. In a SMES system, energy is stored within a magnet that is capable of releasing megawatts of power within a fraction of cycle to replace a sudden loss in line power. The SMES recharges within minutes and can repeat the charge and discharge sequence thousands of times without any degradation of the magnet. Some SMES systems are designed to improve the power quality for critical loads and to provide carryover energy during voltage sags and momentary power outages. The system stores energy in a Superconducting coil immersed in liquid helium. It helps out overcome problems like sags, spikes, and voltage and frequency instabilities.

Mechanical energy storage devices

Compressed air energy storage (CAES):

In compressed air energy storage, off-peak power is taken from the grid and is used to pump air into a sealed underground cavern to a high pressure. The pressurized air is then kept underground for peak use. When needed, this high pressure can drive turbines as the air in the cavern is slowly heated and released; the resulting power produced may be used at peak hours. More often, the compressed air is mixed with natural gas and they are burnt together, in the same fashion as in a conventional turbine plant. This method is actually more efficient as the compressed air will lose less energy.

A CAES operates by means of large electric motor driven compressors that store energy in the form of compressed air in the mine. The compression is done outside periods of peak demand. As part of the compression process, the air is cooled prior to injection to make the best possible use of the storage space available. The air is then pressurized to about 75 bar. To return electricity to the customers, air is extracted from the cavern. It is first preheated in the recuperator. The recuperator reuses the energy extracted by the compressor coolers. The heated air is then mixed with small quantities of oil or gas, which is burnt in the combustor. The hot gas from the combustor is expanded in the turbine to generate electricity

CAES systems can be used on very large scales. Unlike other systems considered large-scale, CAES is ready to be used with entire power plants. Apart from the hydro-pump, no other storage method has a storage capacity as high as CAES. Typical capacities for a CAES system are around 50-300 MW. The storage period is also the longest due to the fact that its losses are very small. A CAES system can be used to store energy for more than a year. Fast start-up is also an advantage of CAES. A CAES plant can provide a start-up time of about 9 minutes for an emergency start, and about 12 minutes under normal conditions. By comparison, conventional combustion turbine peaking plants typically require 20 to 30 minutes for a normal start-up. If a natural geological formation is used (rather than CAS), CAES has the advantage that it doesn't involved huge, costly installations. Moreover, the emission of green house gases is substantially lower than in normal gas plants.

The main drawback of CAES is probably the geological structure reliance. There is actually not a lot of underground cavern around, which substantially limits the usability of this storage method. However, for locations where it is suitable, it can provide a viable option for storing energy in large quantities and for long times.

Flywheel energy storage

Kinetic energy storage systems operate on the basis of stored energy in a rotating mass which is converted from and to electrical energy via a motor/generator set. Such kinetic energy storage systems (or flywheel storage systems, as they are more commonly known) tend to fall into two discrete categories, namely conventional steel rotor systems or advanced composite machines. Flywheels have been used in steam boats and wind mills in the past as a method of transferring energy.

A flywheel is basically a spinning disc with a hole in the middle to be used for rotation. The technological developments, from the birth of the first flywheel for storing energy to the zero idling loss High critical Temperature Superconductor bearings (HTS) flywheel will be explored. Although there are some significant differences between the many types of flywheels, the idea behind them is simple. The applications of these flywheels will be explored, especially commercial applications.

The main applications of flywheels are to supply components and machines with high output voltages when there is a power surge or a shutdown. However, some companies are researching the use of flywheels in different fields. An example is the application of flywheels in starting and braking locomotives. Previously, chemical means of storing energy were used, but this involved heavy and bulky equipment. A flywheel is very practical for its light weight and high energy capacity. The energy is restored back into the flywheel using traction motors when the train moves down a slope. Flywheels have been introduced in the market of electric vehicles. A large amount of energy is needed to start an electric engine. Previously, cars used a chemical battery but it was not economical as it had a limited amount of charge/discharge cycle. The flywheel can be charged/discharged as many times as needed. Again, as with the locomotive, energy losses during braking can be minimized by storing excess energy and releasing it when accelerating.

Hydraulic accumulator:

Hydraulic accumulator is a pressure storage reservoir in which a non compressible hydraulic fluid is retained under pressure from an external source. Its main function is to store hydraulic energy and is necessary to make the energy available again to the system. A hydraulic accumulator is also referred to as the capacitance of the system.

The different types of accumulators include

(A) Dead weight type: The dead weight accumulator consists of a piston loaded with a dead weight and moving within a cylinder that exerts pressure on the hydraulic oil. The dead weight may be of some heavy material such as iron, concrete block, and scrap iron.

(B) Spring loaded type: Whether single-spring or multiple-spring type, the springs in this accumulator, act against a hydraulic piston forcing the fluid into the hydraulic system. A spring loaded accumulator consists of a cylinder body, a movable piston and a spring. The spring applies force to the piston. As fluid is pumped to it, the pressure in the accumulator is determined by the compression rate of the spring.

(C) Hydro-pneumatic type: The hydro-pneumatic accumulators are the most commonly used accumulators and apply force to the liquid by using a compressed gas that acts as the spring. It uses only dry nitrogen as there is a danger of exploding an air-oil vapor, in the case of compressed air. The different types of hydro-pneumatic accumulators used are:

1**.** Non-separator type, but not used due to possibility of foaming: It consists of a cylinder with hydraulic fluid and the charging gas with no separation between them. They are generally used on die casting machines or other similar places. They are always to be mounted vertically.

2. Piston: It consists of a cylinder body and a movable piston. The gas that occupies the volume above the piston is compressed as the cylinder body is charged with liquid.

3. Diaphragm: It consists of two metal hemispheres which are separated by flexible, synthetic rubber diaphragm. The storing action is effected by the compression of the volume of nitrogen enclosed in the diaphragm.

4. Bladder: It consists of a synthetic polymer rubber bladder like chloroprene, nitrile, etc. inside a metal (steel) shell. The bladder is filled with compressed gas. It responds quickly for receiving or expelling flow of oil. There is always a possibility of bladder failure that needs to be taken into consideration.

The hydraulic accumulators are applicable for hydraulic shock suppression is suitable for leakage compensation. The accumulators are the source of power during power failures. They aptly hold high pressure for long periods without keeping the pump running. They have wide applicability in large hydraulic presses, diesel engine starters, hydraulically operated hospital beds, farm machinery, landing gear mechanism on airplanes, hatch cover in ships, lifts, trucks, etc.

Hydroelectric energy storage:

Pumped storage hydroelectricity is a method of storing and producing electricity to supply high peak demands by moving water between reservoirs at different elevations. Pumped hydroelectric energy storage has been in use since 1929, making it the oldest kind of large-scale energy storage technology. In fact, until 1970, it was the only commercially available option for storing energy. Pumped hydroelectric stations are in active operation and new ones are still being built. Time has proven it to be an effective method for storing large amounts of energy. A pumped hydroelectic storage system consists of two large reservoirs located at different elevations. During peak demand, water is released from the upper reservoir. It drops downward through high-pressure shafts where it passes through turbines and ultimately pools up in the lower reservoir. The turbines drive power generators that create electricity. Therefore, when releasing energy during peak demand, a pumped hydroelectric storage system works similarly to traditional hydroelectricity. When production exceeds demand, water is pumped up and stored in the upper reservoir, ready to be released as needed.

Out of all large-scale energy storage methods, pumped hydroelectric storage is the most effective. It can store the largest capacity of electricity (over 2000 MW) and the period of storage is also among the longest; a typical plant can store its energy for more than half a year. Due to the rapid response speed, pumped hydroelectic storage systems are particularly useful as backup in case of sudden changes in demand. Partly due to the large scale and the relative simplicity of design, the operating cost per unit of energy is among the cheapest; the cost of storing energy can be an order of magnitude lower in pumped hydroelectic systems than in for example superconducting magnetic storage systems. Unlike hydroelectric dams, a pumped hydroelectic system has little effect on the landscape. It produces no pollution or waste.

However, the pumped hydroelectic storage system has its drawbacks too. Probably the most fundamental one is its dependence on specific geological formations. There have to be two large volume reservoirs along with sufficient amount of head for the building to be feasible. This is uncommon and often forces the location of the plants to be in remote places, like in the mountains, where construction is difficult and the power grid is not present. Although its operating cost is cheap, the capital cost of a pumped hydroelectric plant is massive, as it often involves building dams and enormous underground pipes. In terms of environmental issues, it disturbs the local habitat as the water level fluctuates daily. Also, the full amount of water has to be pumped up or down in one go, that is, the system must be `drained' completely before recharging, although elaborate planning could get around this.

Thermal energy storage devices

Cryogenic liquid air or nitrogen:

A liquid nitrogen economy is a hypothetical proposal for a future economy in which the primary form of energy storage and transport is liquid nitrogen. It is proposed as an alternative to liquid hydrogen in some transport modes and as a means of locally storing energy captured from renewable sources. An analysis of this concept provides insight into the physical limits of all energy conversion schemes.

Seasonal thermal storage:

A seasonal thermal store (also known as a seasonal heat store or inter-seasonal thermal store) is a store designed to retain heat deposited during the hot summer months for use during colder winter weather. The heat is typically captured using solar collectors, although other energy sources are sometime used separately or in parallel. Seasonal thermal storage can be divided into two broad categories: Low-temperature systems use the soil adjoining the building as a low-temperature seasonal heat store (reaching temperatures similar to average annual air temperature), drawing upon the stored heat for space heating. Such systems can also be seen as an extension to the building design (normally passive solar building design), as the design involves some simple but significant differences when compared to 'traditional' buildings. High-temperature seasonal heat stores are essentially an extension of the building's high voltage alternating current and water heating systems. Water is normally the storage medium, stored in tanks at temperatures that can approach boiling point. Phase change materials (which are expensive but which require smaller tanks) and high-tech soil heating systems (remote from the building) are occasionally used instead. For systems installed in individual buildings, additional space is required to accommodate the size of the storage tanks. In both cases, effective above-ground insulation / superinsulation of the building structure is required to minimise heat-loss from the building, and hence the amount of heat that needs to be stored and used for space heating.

Solar pond

A solar pond is large-scale solar energy collector with integral heat storage for supplying thermal energy. A solar pond can be used for various applications, such as process eating, water desalination, refrigeration, drying and solar power generation. The solar pond works on a very simple principle. It is well-known that water or air is heated they become lighter and rise upward e.g. a hot air balloon. Similarly, in an ordinary pond, the sun's rays heat the water and the heated water from within the pond rises and reaches the top but loses the heat into the atmosphere. The net result is that the pond water remains at the atmospheric temperature. The solar pond restricts this tendency by dissolving salt in the bottom layer of the pond making it too heavy to rise.

A solar pond has three zones. The top zone is the surface zone, or UCZ (Upper Convective Zone), which is at atmospheric temperature and has little salt content. The bottom zone is very hot, 70 – 85 °C, and is very salty. It is this zone that collects and stores solar energy in the form of heat, and is, therefore, known as the storage zone or LCZ (Lower Convective Zone). Separating these two zones is the important gradient zone or NCZ (Non-Convective Zone). Here the salt content increases as depth increases, thereby creating a salinity or density gradient. If we consider a particular layer in this zone, water of that layer cannot rise, as the layer of water above has less salt content and is, therefore, lighter. Similarly, the water from this layer cannot fall as the water layer below has a higher salt content and is, therefore, heavier. This gradient zone acts as a transparent insulator permitting sunlight to reach the bottom zone but also entrapping it there.

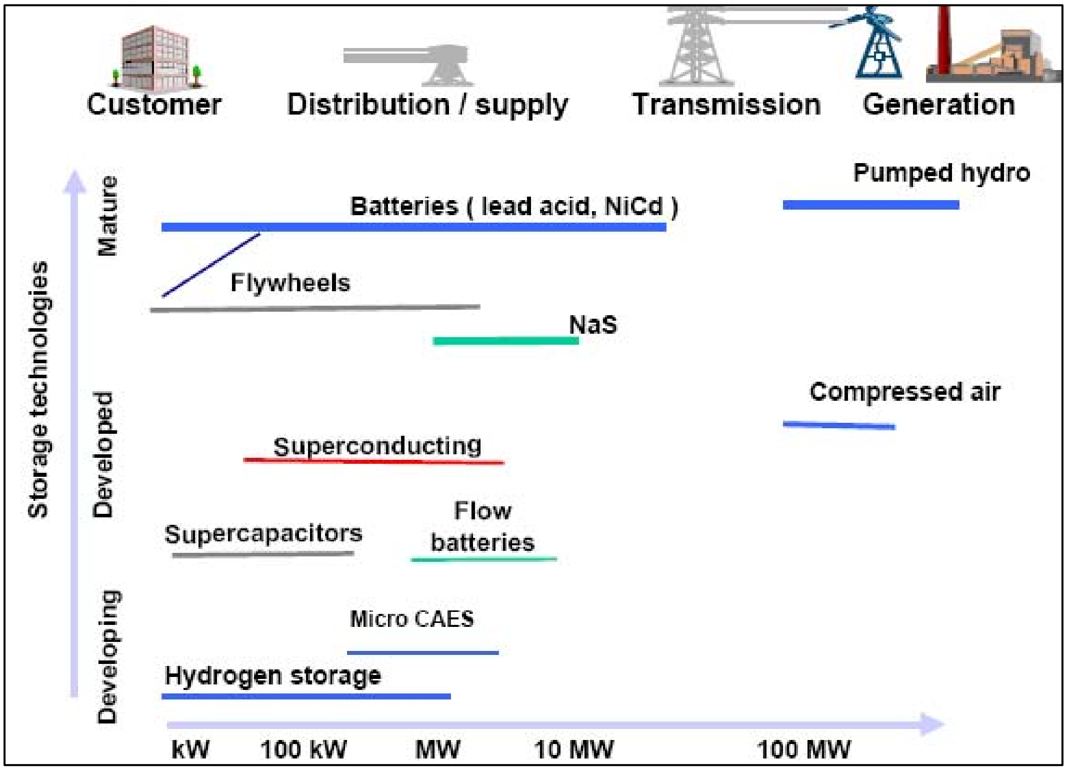


Fig. 2. Technical capability and commercial availability of energy storage types

The trapped (solar) energy is then withdrawn from the pond in the form of hot brine from the storage zone. Though solar ponds can be constructed anywhere, it is economical to construct them at places where there is low cost salt and bittern, good supply of sea water or water for filling and flushing, high solar radiation, and availability of land at low cost. The technical capability and commercial availability of several types of storage are shown in Figure 2.

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Chapter - 12
DIAGNOSIS AND DRUG DELIVERY

J. Rajeswari

1. Introduction

Accurate and early diagnosis as well as the effective treatment without side effects is the two prime factors on which the success of medicine depends on. Today, accurate diagnosis is made simple by the introduction of simple devices called as 'Lab on a Chip'. The limitations with chip technologies are incapability to detect low abundant targets. Increasing the signals at low abundance will be a good option to overcome this. This has been shown to overcome using bioconjugated nanoparticles on these chips. At present, 'Lab on a Chip' can be defined as devices or systems constructed using techniques inspired from nano-scale fabrication and the application of these chips range from diagnostics to drug delivery.

The development of new multidisciplinary branch, "Nanomedicine", discovery of miniaturized devices and sensors have revolutionized the field of medicine and human health. Nanomedicine includes biology, chemistry, physics, engineering and materials science. Nanomedicine may be defined as the monitoring, repair, construction and control of human biological systems at the molecular level, using engineered nanodevices and nanostructures. There are several reasons for attempting materials and devices in nanoscale for medicinal applications. The promise that nanotechnology brings is multifaceted, offering not only improvements to current techniques but also providing entirely new tools and capabilities. By manipulating drugs and other materials at the nanometer scale, the fundamental properties and bioactivity of materials can be altered. These tools can permit control over characteristics of drugs or agents such as solubility, blood pool retention times, controlled release over short or long durations, environmentally triggered controlled release or highly specific site-targeted delivery. Furthermore, by using nanometer-sized particles, the increased functional surface area per unit volume can be exploited in various ways.

Integration of nanotechnology into complex biological systems leads to detection and prevention of disease at the earliest stages of its development. Nanotechnology appears to bring a breakthrough in the field of medicine. They seem to be a suitable choice for the present day's need in medicine and biology. Their application to this field range widely from diagnosis, therapeutic applications, surgery and artificial implants. The unique optical, magnetic and electronic properties of nanomaterials enable them to be promising materials in all fields of medicine. Many biocatalysts such as enzymes or catalytic antibodies are available for performing a variety of synthetically important transformations or for bio-sensing applications. Glucose oxidase (GOD) is by far the most studied enzyme which catalyzes the oxidation of glucose by molecular oxygen and finds many applications in clinical analysis for the diagnosis of diabetes and in the food industry. Optical bio-sensors or amperometric biosensors have been extensively used in biosensors for the titration of glucose. A new kind of hybrid biosensor based on changes in enthalpy during the enzymatic oxidation of glucose recorded as a thermometric peak by a sensitive thermistor has been recently described in order to detect glucose in fruit juice, Coca Cola and human blood serum. Diseases can be linked to specific changes in the molecular processes of affected cells and tissues. When the cells are affected during disease, changes in the protein can be observed. Hence, there can be molecular signatures of disease. This helps in early detection and diseases. These signatures are sensitive to any one of the techniques such as fluorescence and magnetic field or can be detected using devices such as DNA and protein chips. All these emerging technologies and materials have led new strategies to monitor and maintain the health. In this chapter, we will discuss the current achievements in the field of nanomedicine for diagnosis and drug delivery.

2. Nanotechnology for medical diagnostics

There are several reports and ongoing research on the use of nanotechnology for early detection of several diseases. It has been proved that nanoparticles show a very high sensitivity towards the detection of target biomolecules even when they are present at a very low concentrations. Nanoparticles or nanotechnology based devices have been shown to be promising than the conventional materials or techniques in several aspects such as signal amplification, sensitivity, specificity and easy handling. Functionalized nanoparticles when conjugated with biomolecules have shown the ability to detect antibodies, proteins and damaged or disease cells by various methods. Few techniques based on nanoparticles or nanotechnology for diagnosis are discussed below. Nanoparticles possessing unique optical, electronic and magnetic properties have been demonstrated by several researchers as possible probes to detect biological species. Not only the minute size of nanocrystals comparable to biologically functional molecules, but also the ability to tune their biochemical properties by modifying their size, shape, and composition make these materials useful and optimized for the bio-medical purposes. Nanotechnology has the potential to bring dramatic improvement in the field of bio-medical sciences including detection, diagnosis, and therapeutic systems.

2. 1. Electrochemical biosensors

Biosensors are small devices employing biochemical molecular recognition properties as the basis for a selective analysis. The major processes involved in any biosensor system are analyte recognition, signal transduction, and readout. Due to their specificity, speed, portability, and low cost, biosensors offer exciting opportunities for numerous decentralized clinical applications, ranging from 'alternative-site' testing (e.g., physician's office), emergency-room screening, bedside monitoring, or home self testing. Such devices produce a simple, inexpensive and yet accurate and sensitive platform for patient diagnosis. The name electrochemical biosensor is applied to a molecular sensing device which intimately couples a biological recognition element to an electrode transducer. The purpose of the transducer is to convert the biological recognition event into a useful electrical signal. They use biological molecules, usually enzyme, antibody, or nucleic acid to recognize sample molecules of interest via hydrogen bonding, charge–charge interactions and other biochemical interactions to provide molecular information. The integration of biological systems and nanostructured materials requires information to be induced across the interface in a consistent and reproducible format. Recent advances in the field of nanotechnology and processing have resulted in solid-state biosensors offering unprecedented compatibility of inorganic materials with the chemical/biological agents, thus enabling stable, direct, and reproducible screening and detection. Amperometric and potentiometric transducers are most commonly used in conjunction with electrochemical biosensors. In potentiometric devices, the analytical information is obtained by converting the bio recognition process into a potential signal in connection to the use of ion selective electrodes (ISE). Amperometric biosensors operate by applying a constant potential and monitoring the current associated with the reduction or oxidation of an electroactive species involved in the recognition process. An amperometric biosensor may be more attractive because of its high sensitivity and wide linear range. Such miniaturization allows packing of numerous microscopic electrode transducers onto a small footprint of a biochip device, and hence the design of high-density arrays.

2. 1. 1. Detection of DNA hybridization and DNA damage

Electrochemical DNA hybridization biosensors rely on the conversion of the DNA base-pair recognition event into a useful electrical signal (Fig. 1). Electrochemical sensors have also shown to be extremely useful for detecting small damage to DNA induced by various chemical agents, enzymatic digestion, or ionizing radiation. Electrochemical biosensors use gold or silver nanoparticles for detecting the oxidation signal of electroactive DNA bases in the presence of DNA hybridization.

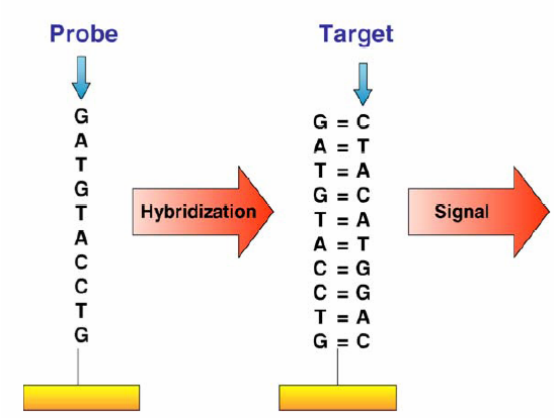

Fig. 1. Conversion of DNA base-pair event into an electric signal

One-dimensional (1D) nanostructures, such as semiconductor or conducting-polymer nanowires (NW), are extremely attractive for designing high-density protein arrays. Because of their high surface-to-volume ratio and novel electron transport properties, their electronic conductance is strongly influenced by minor surface perturbations (e.g., binding of biomolecules), The detection of specific base sequences in human, viral and bacterial nucleic acids is becoming increasingly important in the diagnosis of disease DNA biosensors based on nucleic acid hybridization processes are rapidly being developed towards the goal of rapid and inexpensive diagnosis of genetic and infectious diseases. an electrochemical biosensor for the voltammetric detection of DNA sequences related to the Hepatitis B virus (HBV) and TT virus (TTV) from polymerase chain reaction (PCR) amplified real samples has been reported.

2. 2. Fluorescent NP for biosensors and Biolabelling

Nanoparticles exhibit remarkable optical and electronic properties when compared to their bulk counterpart. Hence, they are found to be an excellent fluorescent probes for imaging, signaling, evolution and targeting of cells. This method of diagnosis relies on nanoparticles which have the capability of emitting color during absorption of light. The nanoparticles should be able to distinguish the presence and absence of biomolecules by producing characteristic color. This way they can function as labels or sensors for biomolecules. Fluorescent markers for diagnostic purposes exist in the markets from a long time but there are limitations associated with them. To overcome, fluorescent nanoparticles are being developed. Multi-color labeling of both fixed and living cells with fluorescent nanoparticles conjugated with biological ligands that specifically bind against certain cellular targets enables the recording of diffusion pathways in receptor cells. Uptake of nanoparticles into the vesicular compartments around the nucleus of cells can be used to label the cells so that their pathway and fate can be followed. The nanoparticles exhibit reduced photobleaching as compared to traditional dyes and are passed on to daughter cells during cell division, therefore allowing for much longer term observation. Colloidal gold nanoparticles have been found to strongly enhance the native signals of chemical constituents in cells. Surface Enhanced Raman Spectroscopy (SERS) relies on this signal magnification and serves as a tool for ultra-sensitive monitoring of the intracellular distribution of these chemicals. Colloidal gold biofunctionalized nanomodules also have potential for use in enzyme multi-sensors. Gold nanoparticles coated with proteins have been used to detect conformation changes in the attached proteins via observation of color changes in the solution.

2. 2. 1. Quantum Dots (QDs)

Quantum Dots (QDs) are one of the possible fluorescent nanoparticles for diagnostic applications. QDs are crystalline clumps of a few hundred atoms, coated with an insulating outer shell of a different material. They are spherical nanocrystals in 1-10 nm diameter. They are composed of atoms from group II-VI or III – V of the periodic table and are defined as particles with dimensions smaller than the excitation Bohr radius. When a photon of visible light hits such a minute particle, a quantum-physics reflect confines all the photon's energy to the crystal core before being emitted as an extraordinary bright fluorescence. The QDs absorb light at a wide range of wavelengths, but emit almost monochromatic light of a wavelength that depends on the size of the crystals. Larger QDs emit red light, whereas smaller crystals emit light at the blue end of the spectrum (Fig. 2). QDs fluorescence is so bright that it is possible to detect a cell carrying a single crystal. Quantum dots of semiconductor particles such as CdS and CdSe, whose electronic properties vary according to their particle size, are used as biolabels and biomarkers. Their water soluble nature and ability to conjugate with biological molecules make them a good choice as nanosensors. These Quantum dots can be tuned in size and composition to exhibit emission ranging from ultraviolet through visible region to near infrared. Hence, they can probe a variety of biological molecules. Quantum dots are advantageous over traditional dyes in terms of their stability. Quantum dots can withstand for a longer time, hence they can be used for long term observation of biological cells when compared to the traditional dyes.

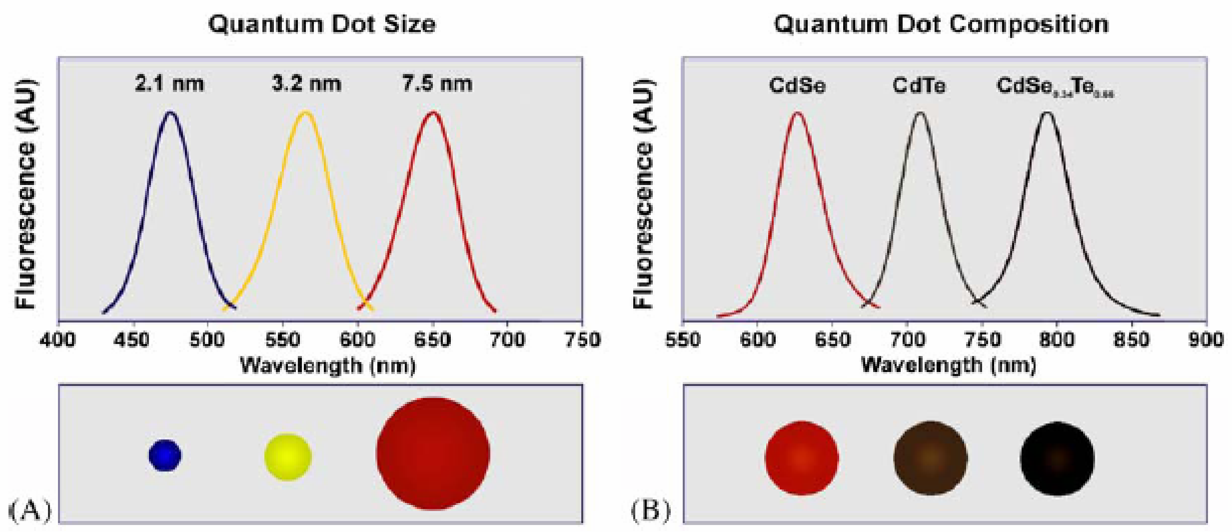

Fig. 2. Tuning of emission wavelength and color by particle size and composition

Several properties of quantum dots (QDs) make them suitable choice as fluorescent labels for biomolecules when compared to organic dyes.

(i) QDs exhibit narrow and symmetric emission peaks (FWHM typically 25-35 nm) whereas organic dyes show broad and unsymmetric emission peaks. Hence, QDs are suitable materials when simultaneous labeling and detection of multiple analytes are desired.

(ii) QDs have large molar absorptivities and high quantum yield

(iii) Quantum dots can withstand for a longer time, hence they can be used for long term observation of biological cells when compared to the traditional dyes. The rate of photodegradation is low for QDs.

Other than QDs, there is another type of fluorescent labels, wherein traditional luminescent dye tris(2,2-bipyridyl) dichlororuthenium (II) hexahydrate (Rubpy) is encapsulated into silica nanoparticles. By doing so, significant signal amplification has been observed as the high surface area silica nanoparticles can take in large number of luminescent dye inside its matrix. In addition to their high surface to volume ratio, dye silica nanoparticles have other advantages such as high intensity of fluorescent signal, excellent photostability due to exclusion of oxygen by silica encapsulation, efficient conjugation with biomolecules due to the easy modification of silica surface and also easy manufacturing process. Biomolecules such as streptavidin and avidin are conjugated to the silica surfaces of the nanoparticles. These systems were used in the area of imunocytochemistry where IgM – bearing cell surfaces are labeled using NPs. They exhibit red fluorescence. Dye doped silica nanoparticles have also been used in DNA microarrays which are used in genomics, drug discovery and clinical diagnosis. The common problem in such DNA microarrays is the difficulty in diagnosing low abundant targets. This has been overcome using nanoparticles modified DNA microarrays. Nanoparticles conjugated DNA microarrays showed intense fluorescence signals than the DNA microarrays without nanoparticles. Nanoparticles have also been shown to determine the DNA quantitatively as the fluorescence signals reflected the amount of DNA on the array. Protein microarrays have been used in protein expression, protein profiling and protein – protein interactions among others. Avidin nanoparticles showed specificity to the hIgG – biotin was spotted. These results show that the bioconjugated nanoparticles exhibit siginificant amplification of the analytical signal compared to the traditional dye as the amount of dye molecules are more in the nanoparticles than the conventional immunoassays. The nanoparticles can generate specific and high intensity fluorescent signals according to the antibody – antigen interaction, thus making it possible to detect bacterial or viral pathogens. The ultimate power of the fluorescent nanoparticles will emerge as a revolutionary tool for ultrasensitive detection of disease markers and infectious agents.

Some class of organophosphorous (OP) neurotoxins is extremely toxic to mammals and also they form chemical warfare agents. They are powerful inhibitors of esterase enzymes, such as acetyl and butyryl- cholinesterases or neurotoxic esterase which are involved in neurotoxins. Sensitive biosensors based on acetylcholinesterase (AChE) or butyryl cholinesterase (BChE) inhibition have been developed and used for OP agent detection. In inhibition based biosensors, the organophosphorus inhibits the active site of enzyme resulting in loss of enzyme activity and hence a decrease in sensor signal. There are several disadvantages. (1) any environmental or handling factors that cause loss of enzyme activity will result in false positive signals, (2) such sensors require baseline testing prior to sample application and lengthy sample incubation times to allow enzyme-analyte interaction (3) due to the irreversible nature of cholinesterase enzyme inhibition, inhibition-based sensors cannot be reused without regeneration of enzyme activity. A method based on gold nanoparticles has been developed to detect the presence of OP compound.

2. 3. Magnetic Nanoparticles

Magnetic nanoparticles are the other class of materials which find applications in frontiers of materials science including medical diagnosis. In addition to their high surface to volume ratio and quantum size effect, magnetic nanoparticles dramatically change some of the magnetic properties and exhibit superparamagnetic phenomena and quantum tunneling of magnetization, because each particles can be considered as a single magnetic domain. When bound to a suitable antibody, they are used to label specific molecules, cell populations, structures or microorganisms. Magnetic nanoparticles have been extensively studied for biomedical applications such as hyperthermia, magnetic resonance contrast enhancement and drug delivery. The magnetic field produced by the magnetic target molecules when conjugated to the antibody is measured as the signal and hence detected. The medical MRI (magnetic resonance imaging) relies on the relaxation properties of hydrogen nuclei in water and lipids. For MRI, iron oxide based nanoparticles and its related systems have been widely used. They consist of an inorganic core of iron oxide (magnetite Fe_2O_3, maghemite or other insoluble ferrites) coated with polymer such as dextran. Lumiren (silicon-coated iron oxide particles with diameter 300 nm) and Endorem (magnetite nanoparticles of 150 nm in diameter coated with dextran) are commercial names of Superparamagnetic nanoparticles.

Superconducting quantum interference device (SQUID) is a technique for specific, sensitive, quantitative and rapid detection of biological targets by using supermagnetic nanoparticles and a microscope based on a high transition temperature. In this technique, a mylar film to which the targets are bound is placed on the microscope alongside SQUID. A suspension of magnetic nanoparticles carrying antibodies directed against the target is added to the mixture in the well and 1-s pulse of magnetic field is applied parallel to the SQUID. In the presence of this aligning field, nanoparticles develop a net magnetization, which relaxes when the field is turned off. Unbound nanoparticles relax rapidly by Brownian rotation and contribute no measurable signal. Nanoparticles that are bound to the target on the film are immobilized and undergo a slowly decaying magnetic flux, which is detected by the SQUID.

Ferrofluids are colloidal solutions of iron oxide magnetic nanoparticles surrounded by a polymeric layer coated with affinity molecules, such as antibodies, for capturing cells and other biological targets from blood or other fluid and tissue samples. Ferrofluid particles are so small (25–100 nm in radius) that they behave in liquids as a solution rather than suspension. When the coated ferrofluid particles are mixed with a sample containing cells or other analytes, they interact intimately and completely. These properties enable the development of specialized reagents and systems with extremely high sensitivity and efficiency and capture. Recently, superparamagnetic iron oxide (SPIO) nanoparticles encapsulated within chitosan (polyglucosamine) were used to get the MRI images of the kidney of New Zealand white rabbit. PEG (polyethylene glycol) coated FeOOH nanoparticles were found to be potential material as tumor selective MRI contrast agents.

3. Drug Delivery

In the traditional drug delivery, the drug will be taken through the blood to the target of interest. The disadvantage of this conventional method is damage of other normal cells and normal organs by the drug since they will be toxic. This practice has been overcome by targeted drug delivery where the drug is delivered to the target without affecting any other organs and cells. In this aspect, there has always been considerable interest in developing biodegradable nanoparticles as drug delivery devices. The drug can be dissolved, entrapped, adsorbed, attached or encapsulated into the nanoparticle matrix. An ideal targeting system should have long circulating time, it should be present at appropriate concentrations at the target site and it should not lose its activity or therapeutic efficacy while in circulation. In this respect, nanomaterials have shown enhanced targeted drug delivery than the conventional drugs. Another important issue associated with the drug delivery systems are blood-brain barrier (BBB). The BBB is a unique membrane that tightly segregates the brain from the circulating blood. Delivery of drugs to the brain is a challenge and nanoparticles are proposed to deliver the drugs to brain effectively. Hence, they can be potential drug delivery system for neurological disorders. Nanomaterials of varying morphology such as nanoparticles, nanospheres or nanoencapsules can be used as drug delivery systems. Each form of the nanomaterials has its own characteristic drug releasing methodology. For example, nanocapsules are vesicular systems in which the drug is confined to a cavity surrounded by a polymer membrane, whereas nanosphere is matrix systems in which the drug is physically and uniformly dispersed (Fig. 3).

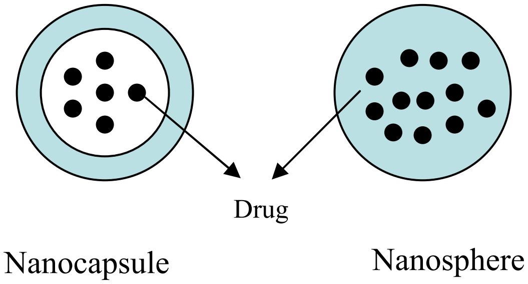

Fig. 3. Different forms of nano drug delivery systems

Drug delivery systems include nanoparticles, ceramic nanoparticles, micelles, polymeric micelles, dendrimers and liposomes. These systems are in general polymeric and nanosize. Ceramic nanoparticles such as organically modified silica nanoparticles entrapped with anticancer drug, 2-devinyl-2-(1-hexyloxyethyl) pyropheophorbide have been used to damage cancer cells.

3. 1. Various drug delivery systems

3. 1. 1 Nanoparticles

The advantages of using nanoparticles for drug delivery result from their interesting properties. Due to their small size, nanoparticles can penetrate through smaller capillaries and are taken up by cells, which allow efficient drug accumulation at the target sites. The use of biodegradable materials for nanoparticle preparation allows sustained drug release within the target site over a period of days or even weeks. Also, nanoparticles have the potential to overcome the Blood-Brain Barrier (BBB) which is a common problem in several drugs. Nanoparticles also protect the entrapped drug from gastrointestinal interferences. All these allow to reduction of dose and dosing frequency thereby reducing the side effects. Polymer nanoparticles such as PLGA (poly (lactide-co-glycolide)), PLA (polylactic acid) have been reported for sustained drug delivery of estradiol. There are reports of use of PLGA for gene therapy and protein delivery. Carbon nanotubes have also been used in cancer therapy. Carbon nanotubes carry small interfering RNA into the tumor cells where they not only silenced the target gene but also inhibited the prolifereation of cancer cells in vitro and suppressed tumor growth in mouse models.

3. 1. 2. Liposomes

Liposomes are vesicles made up of a lipid bilayer, resembling tiny cells with a cell membrane but nothing in the core. There are many different type of lipids with different head groups, different fatty acid chain lengths, and different melting temperatures (Tm). Hence, by manipulating the formulation of liposomes, they can be constructed to be temperature or pH sensitive to permit controlled release of their contents. Drug molecules can be encapsulated and solubilized within the bilayers. Certain proteins can be incorporated in the membrane of the liposome, which act as size- selective filters only allowing the diffusion of small solutes such as ions, nutrients and antibiotics. Thus, drugs encapsulated within a liposome ‘nanocage’ that has been functionalized with channel proteins, are effectively protected from premature degradation.

3. 1. 3. Micelles

Micellar systems are useful for the delivery of water insoluble drugs. Micelles have a fairly narrow distribution in the nanometer range and are characterized by their unique core shell architecture, in which hydrophobic segments are segregated from the aqueous exterior.

3. 1.4. Dendrimers

Dendritic architecture is one of the most pervasive topologies observed throughout biological systems at virtually all dimensional length scales. This architecture is found at the meter scale in tree branching and roots, on the centimeter and millimeter scales in circulatory topologies in the human anatomy such as lungs, kidney, liver, and spleen, and on the micrometer scale in cerebral neurons. The synthesis of dendrimers offers the opportunity to generate monodisperse, structure-controlled macromolecular architectures similar to those observed in biological systems. Dendrimers may be visualized as consisting of three critical architectural domains: (i) the multivalent surface, containing a larger number of potentially reactive/passive sites (nano-scaffolding), (ii) the interior shells (i.e., branch cell layers defined by dendrons) surrounding the core, and (iii) the core to which the dendrons are attached. The two latter domains represent well-defined nano-environments, which are protected from the outside by the dendrimer surface (nanoscale containers) in the case of higher generation dendrimers. These three domains can be tailored for a specific purpose, i.e., to function as a dendritic sensor, drug carrier, or as a drug. The high density of exo-presented surface functionalities makes the dendritic surface well-suited as a nano-scaffold where the close proximity of functional groups is important (polyvalency) or for receptor mediated targeting purposes. The interior is well-suited for host–guest interaction and encapsulation of guest molecules. Dendrimers are widely studied for its application as drug carriers for cancer therapy and for the delivery of DNA. Citric acid- polyethylene glycol- citric acid triblock dendrimers can function as drug delivery system for drugs such as 5-aminosalicylic acid, pyridine and mefenamic acid.

3. 2. Thermal ablation of cells using nanoparticles

3. 2. 1. Nanoshells

Nanoshells of gold core and silica shell have been used to demonstrate the damage of cancerous cells using their capability of converting optical energy to thermal energy. Manipulation of the thickness of the core and the outer shell permits these materials to absorb and scatter specific wavelengths of light across the visible and near-infrared (NIR) spectrum. This NIR light can penetrate several centimeters of human tissue without causing harm, because tissue chromophores do not absorb energy in the NIR range. Gold shells of 10 nm encasing a 110 nm silica core resonate in the NIR spectrum (800 nm); these wavelengths exhibit minimal optical absorption by, and consequently optimum penetration through, overlying tissues, with minimal attendant thermal injury. These nanoshells are extremely efficient in converting optical energy into heat. Direct injection of nanoshells into subcutaneous tumors in a mouse xenograft model resulted in temperature increases of ~37 °C greater than the surrounding normal tissue after ~6 min of exposure to 808 nm at 4 Watts/cm^2, associated with thermal damage to tumors.

3. 2. 2. Carbon nanotubes (CNT) and fullerenes

Carbon nanotubes when irradiated with NIR will heat up to 70 °C, this principle has been used to demonstrate the application of CNTs for cancer therapy. It has been demonstrated that folic acid adsorbed on carbon nanotubes allow specific binding to cancer cells. These tumor cells were destroyed upon NIR irradiation. Soluble derivatives of fullerenes such as C60—a soccerball– shaped arrangement of 60 carbon atoms per molecule show great promise as pharmaceutical agent. These derivatives, many already in clinical trials, have good biocompatibility and low toxicity even at relatively high dosages. Fullerene compounds may serve as antiviral agents (most notably against human immunodeficiency virus), antibacterial agents (Escherichia coli, Streptococcus, Mycobacterium tuberculosis), photodynamic antitumor and anticancer therapies, antioxidants and antiapoptosis agents as treatments for amyotrophic lateral sclerosis and Parkinson’s disease, and other applications most being pursued by C Sixty the leading company in this area.

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Chapter - 13
POLLUTION CONTROL

S. Chandravathanam

Introduction

Substances not naturally found in the air or at greater concentrations or in different locations from usual are referred to as 'pollutants'.

Pollution is the introduction of toxic substances arising mainly from human activities like, combustion of fossil fuels, domestic, industrial and agricultural waste generation, into the air, water or ground that are damaging to human health and ecosystems. Pollution is also the consequence of a natural disaster. But it accounts to very lesser extent and rate, to which nature can able to tolerate and recover. But the very fast industriallization and life style far encompassed the nature's recovery rate.

The major forms of pollution include:

- Air pollution, the release of chemicals and particulates into the atmosphere. Common examples include carbon monoxide, sulfur dioxide, chlorofluorocarbons (CFCs), and nitrogen oxides produced by industry and motor vehicles. Photochemical ozone and smog are created as nitrogen oxides and hydrocarbons react to sunlight.
- Water pollution via surface runoff and industrial wastewater discharges into the surface water sources.
- Increasing quantities of trash or garbages and biological solid wastes.
- Soil contamination with chemicals spill.
- Radioactive contamination, added in the wake of 20th-century discoveries in atomic physics.
- Noise pollution, which encompasses roadway noise, aircraft noise, industrial noise as well as high intensity sonar.
- Light pollution, which includes light trespass, over-illumination and astronomical interference.
- Thermal Pollution, with the drastic change of temperature of natural water bodies.

Air Pollution

In the past, only those in large cities had to worry about the air they breathed. Most took for granted that clean, fresh air would always be available. But today, nearly everyone on earth breathes a cocktail of poisons that is nearly worse than the tailpipe of a car. There are many substances in the air which may impair the health of plants and animals (including humans), or reduce visibility. These arise both from natural processes (like storm, volcanic eruptions, etc.) and human activity.

Pollutants can be classified as either primary or secondary. Primary pollutants are substances directly produced by a process, such as ash from a volcanic eruption or the carbon monoxide gas from a motor vehicle exhaust. Secondary pollutants are not emitted. Rather, they form in the air when primary pollutants react or interact themselves. An important example of a secondary pollutant is ground level ozone, one of the many secondary pollutants that make up photochemical smog. Some pollutants may be both primary and secondary. That is, they are both emitted directly and formed from other primary pollutants.

Primary pollutants produced by human activities include:

- oxides of sulfur, nitrogen and carbon.
- organic compounds, such as hydrocarbons (fuel vapours and solvents)
- particulate matter, such as smoke and dust
- metal oxides, especially those of lead, cadmium, copper and iron
- chlorofluorocarbons (CFCs)

Secondary pollutants include some particles formed from gaseous primary pollutants. For example compounds in photochemical smog, such as nitrogen dioxide, ground level ozone and peroxyacetyl nitrate (PAN).

The six main air pollutants are called as ‘Criteria air pollutants’ and are common throughout the globe. These pollutants can injure health, harm the environment and cause property damage. The six criteria pollutants are Carbon monoxide, Lead, Nitrogen dioxide (one of several Nitrogen oxides), Ozone (formed from precursor Volatile organic compounds), Particulate Matter and Sulfur dioxide.

Carbon monoxide (CO)

Carbon monoxide (CO) is a colorless, odorless and poisonous gas produced by incomplete burning of carbon in fuels. When CO enters the blood stream it reduces the delivery of oxygen to the body's organs and tissues. Health threats are most serious for those who suffer from cardiovascular disease. Exposure to elevated CO levels can cause impairment of visual perception, manual dexterity, learning ability and performance of complex tasks. 77% of the nationwide CO emissions are from transportation sources. Other major CO sources are wood burning stoves, incinerators and industrial sources.

Lead (Pb)

Lead (Pb) is a widely used metal that, once released to the environment, can contaminate air, food, water, or soil. Exposures to even small amounts of lead over a long time can accumulate to reach harmful levels. Harmful effects may therefore develop gradually without warning. Short-term exposure to high levels of lead may also cause harm. Lead can adversely affect the nervous, reproductive, digestive, cardiovascular blood-forming systems, and the kidney. In men, adverse reproductive effects include reduced sperm count and abnormal sperm. In women, adverse reproductive effects include reduced fertility, still-birth, or miscarriage. Children are a sensitive population as they absorb lead more readily and their developing nervous system puts them at increased risk for learning disabilities.

Lead gasoline additives, non-ferrous smelters, and battery plants are the most significant contributors to Pb emissions into the atmosphere. In 1993 transportation sources contributed 33% of the annual emissions, down substantially from 81% in 1985. Total Pb emissions from all sources dropped from 20,100 tons in 1985 to 4,900 tons in 1993. The decrease in Pb emissions from cars and trucks shifting to lead-free gasoline accounts for essentially this entire decline.

Nitrogen dioxide (NO_2)

Nitrogen dioxide (NO_2) is a brownish, highly reactive gas that is present in all urban atmospheres. NO_2 can irritate the lungs, cause bronchitis and pneumonia, and lower resistance to respiratory infections. The major mechanism for the formation of NO_2 in the atmosphere is the oxidation of nitric oxide (NO), which is produced by most combustion processes.

Nitrogen oxides (NO_x)

Nitrogen oxides (NO_x) include various nitrogen compounds like nitrogen dioxide (NO_2) and nitric oxide (NO). These compounds play an important role in the atmospheric reactions that create ozone (O_3) and acid rain. Individually, they may affect ecosystems, both on land and in water. NO_x forms when fuels are burned at high temperatures. The two major emission sources are transportation vehicles and stationary combustion sources such as electric utility and industrial boilers.

Ozone (O_3)

Ozone (O_3) is the major component of smog. Although O_3 in the upper atmosphere is beneficial because it shields the earth from the sun's harmful ultraviolet radiation, high concentrations of O_3 at ground level are a major health and environmental concern. The reactivity of O_3 causes health problems because it damages lung tissue, reduces lung function and sensitizes the lungs to other irritants. Scientific evidence indicates that ambient levels of O_3 not only affect people with impaired respiratory systems, such as asthmatics, but healthy adults and children as well. Exposure to O_3 for several hours at relatively low concentrations has been found to significantly reduce lung function and induce respiratory inflammation in normal, healthy people during exercise.

O_3 is not usually emitted directly but is formed through complex chemical reactions in the atmosphere. Precursor compounds like volatile organic compounds (VOC) and oxides of nitrogen (NOx) react to form O_3 in the presence of sunlight. These reactions are stimulated by ultraviolet radiation and temperature, so peak O_3 levels typically occur during the warmer times of the day and year.

Particulate matter (PM)

Particulate matter (PM) is a mixture of particles that can adversely affect human health, damage materials and form atmospheric haze that degrades visibility. PM is usually divided into different classes based on size, as total suspended matter (TSP), PM-10 (particles less than 10 microns in aerodynamic diameter) and PM-2.5 (particles less than 2.5 microns). In general, the smallest particles pose the highest human health risks. PM exposure can affect breathing, aggravate existing respiratory and cardiovascular disease, alter the body's defense systems against foreign materials, and damage lung tissue, contributing to cancer and premature death. Individuals with chronic obstructive pulmonary or cardiovascular disease, asthmatics, the elderly and children are most sensitive to the effects of PM.

Particulate matter (PM) includes dust, dirt, soot, smoke and liquid droplets directly emitted into the air by sources such as factories, power plants, cars, construction activity, fires and natural windblown dust. Particles formed in the atmosphere by condensation or the transformation of emitted gases such as SO_2 and VOCs are also considered as particulate matter.

Sulfur dioxide (SO_2)

High concentrations of sulfur dioxide (SO_2) affect breathing and may aggravate existing respiratory and cardiovascular disease. Sensitive populations include asthmatics, individuals with bronchitis or emphysema, children and the elderly. SO_2 is also a primary contributor to acid rain, which causes acidification of lakes and streams and can damage trees, crops, historic buildings and statues. In addition, sulfur compounds in the air contribute to visibility impairment in large parts of the country.

Sulfur dioxide (SO_2) is released primarily from burning fuels that contain sulfur (like coal, oil and diesel fuel). Stationary sources such as coal and oil fired power plants, steel mills, refineries, pulp and paper mills, and nonferrous smelters are the largest releasers.

Volatile organic compounds (VOC)

VOC emissions form O_3 through complex chemical reactions with oxides of nitrogen (NOx) in the presence of sunlight. Ozone is a respiratory toxicant. The class of VOCs includes many specific chemicals, which may also cause adverse health effects in their own right (such as cancer or reproductive toxicity).

VOCs are emitted from diverse sources, including automobiles, chemical manufacturing facilities, drycleaners, paint shops and other commercial and residential sources that use solvent and paint.

Table 1. Major air pollutants and their associated health hazards

Name of pollutant	**Health impacts**
RSPM	Respiratory illness, including chronic bronchitis and asthma; heart diseases.

SO_2	Heart diseases; respiratory problems including pulmonary emphysema, cancer, eye burning, headache, etc.
NO_2	Lung irritation, viral infection, airway resistance, chest tightness, etc.
SPM	Pneumoconiosis, restrictive lung diseases, asthma, cancer, etc.
Benzene	It causes immunotoxicity, carcinogenicity, asthma, anemia, unconsciousness etc.
Ozone	Impaired lung function, chest pains, coughing, irritation of eyes, nose etc.
CO	CO poisoning cause cherry lips, unconsciousness, death by asphyxiation etc.
Lead	It causes decreased hemoglobin synthesis, anemia, damage the nervous and renal (kidney) systems etc.

RSPM - Respirable suspended particulate matter

SPM - Suspended particulate matter

Table 1 describes the health impacts of main air pollutants and Table-2 gives a measure of major air pollutants present in few Indian cities.

Table 2. Measure of air Pollution in few Indian cities

CITY	PARTICULATE POLLUTION		GAS POLLUTION	
	RSPM ($\mu g/M^3$)	SPM ($\mu g/M^3$)	SO_2 ($\mu g/M^3$)	NO_2 ($\mu g/M^3$)
Ahmedabad (Ashram Road)	-	443	2	30
Bangalore (J.C. Road)	-	204	11	16
Chandigarh (Sector 7)	-	318	7	22
Chennai (T. Nagar)	-	141	12	8
Delhi (Lajpat Nagar)	-	426	12	26
Guwahati (Silpukhuri)	-	-	-	-
Hyderabad (Sr. Nagar)	-	219	5	19

Kolkata (Shyam Bazar)	-	89	5	31
Lucknow (Dalibagh)	-	357	10	26
Mumbai (Colaba)	-	280	8	9

National Ambient Air Quality Standard (For Residential area)

RSPM	Respirable Suspended Particulate Matter	200 µg/M^3
SPM	Suspended Particulate Matter	200 µg/M^3
SO_2	Sulphur-di-Oxide	80 µg/M^3
NO_2	Nitrogen-di-Oxide (Oxides of Nitrogen)	80 µg/M^3

Effects of Air Pollution

There are several well-known effects of air pollution. Few of these include smog, acid rain, the greenhouse effect, and holes in the ozone layer. Each of these problems has serious implications for our health and well being as well as for the whole environment.

Smog is a type of large scale outdoor pollution is a combination of smoke and fog. It is caused by chemical reactions between pollutants derived from different sources, primarily automobile exhaust and industrial emissions. In the 1950s a new type of smog, known as **photochemical smog**, was first described. Photochemical smog is the chemical reaction of sunlight, nitrogen oxides (NOx) and volatile organic compounds (VOC's) in the atmosphere, which leaves airborne particles (called particulate matter) and ground-level ozone.

Photochemical smog is a noxious mixture of air pollutants including nitrogen oxides, such as nitrogen dioxide, ozone, volatile organic compounds (VOCs), peroxyacetyl nitrates (PAN) and aldehydes (R'O). All of these chemicals are usually highly reactive and oxidizing.

Depending on the geographical location, temperature, wind and weather factors, pollution is dispersed differently. However, sometimes this does not happen and the pollution can build up to dangerous levels. A **temperature inversion** occurs when air close to the earth is cooler than the air above it. Under these conditions the pollution cannot rise and be dispersed. Cities surrounded by mountains also experience trapping of pollution. An inversion can lead to pollution such as smog being trapped close to the ground, with possible adverse effects on health. An inversion can also suppress convection by acting as a cap.

Another consequence of outdoor air pollution is **acid rain**. When a pollutant, such as sulfur dioxide combines with droplets of water in the air, the water (or snow) can become acidified. The effects of acid rain on the environment can be very serious. It damages plants by destroying their leaves, poisons the soil, and changes the chemistry of lakes and streams.

Table 3. Warming Potential of the greenhouse gases

Greenhouse Gas	Concentration	Warming Potential compared to CO_2	Lifetime in Atmosphere (Years)
Carbon dioxide (CO_2)	370 ppm	1	5 – 200
Methane (CH_4)	1720 ppb[a]	23	12
Nitrous oxide (N_2O)	314 ppb[a]	300	114
Chlorofluorocarbons (CFCs)	ppt[a] level	4000 - 8000	5 - 100

[a] ppb is thousand fold lower concentration than ppm and ppt is million fold lower than ppm.

The **Greenhouse Effect,** also referred to as global warming, is the trapping of heat by the greenhouse gases and causes the increase of global temperature. It is generally believed to come from the build up of carbon dioxide gas in the atmosphere, which is produced when fuels are burned. Plants convert carbon dioxide back to oxygen, but the release of carbon dioxide from human activities is higher than the world's plants can process. The situation is made worse since many of the earth's forests are being removed, and plant life is being damaged by acid rain. Thus, the amount of carbon dioxide in the air is continuing to increase. This buildup acts like a blanket and traps heat close to the surface of our earth. Other greenhouse gases include methane and NOx. The greenhouse effect due to these gases far exceeds that of CO_2 (Table-3) but in terms of quantity CO_2 far exceeds other greenhouse gases. Changes of even a few degrees of temperature of the globe will affect us all through changes in the climate and the possibility of melting of polar ice caps. (One of the consequences of polar ice cap melting would be a rise in global sea level, resulting in widespread coastal flooding.). Long term rising levels of atmospheric carbon dioxide also cause slight increases in the acidity of ocean waters and the possible effects of this on marine ecosystems.

Ozone depletion is another result of air pollution. Chemicals released by our activities affect the stratosphere (10 – 30 Km from the earth's surface), one of the atmospheric layers surrounding the earth. The ozone layer in the stratosphere protects the earth from harmful ultraviolet (UV) radiation from the sun. Release of chlorofluorocarbons (CFC's) from aerosol cans, cooling systems and refrigerator equipments remove some of the ozone in the stratosphere, causing "holes" in this layer and allowing the UV radiation to reach the earth. Ultraviolet radiation is known to cause skin cancer and has damaging effects on plants and wildlife.

Indoor Air Pollution

Many people spend large portion of time indoors (as much as 80-90% of their lives). For these reasons, some experts feel that more people suffer from the effects of indoor air pollution than outdoor pollution. There are many sources of indoor air pollution. Tobacco smoke, cooking and heating appliances, and vapors from building materials, paints, furniture, etc. cause pollution inside the buildings.

The extent to which an individual is harmed by air pollution usually depends on the total exposure to the damaging chemicals, i.e., the duration of exposure and the concentration of the chemicals must be taken into account. Air pollution can affect our health in many ways with both short-term and long-term effects. Examples of **short-term effects** include irritation to the eyes, nose and throat, and upper respiratory infections such as bronchitis and pneumonia. Other symptoms can include headaches, nausea, and allergic reactions. Short-term air pollution can aggravate the medical conditions of individuals with asthma and emphysema. **Long-term health effects** can include chronic respiratory disease, lung cancer, heart disease, and even damage to the brain, nerves, liver, or kidneys. Continual exposure to air pollution affects the lungs of growing children and may aggravate or complicate medical conditions in the elderly.

Hazardous air pollutants

Hazardous air pollutants, also known as **Toxic air pollutants**, are those pollutants that are known or suspected to cause cancer or other serious health effects such as reproductive effects or birth defects or adverse environmental effects. Examples of toxic air pollutants include benzene, which is found in gasoline; perchlorethlyene, which is emitted from some dry cleaning facilities; and methylene chloride, which is used as a solvent and paint stripper by a number of industries. Examples of other listed air toxics include dioxin, asbestos, toluene, PAHs (Polycyclic aromatic hydrocarbons), PCBs (Polychlorinated biphenyls), and metals such as cadmium, mercury, chromium, and lead compounds. In addition to exposure from breathing air toxics, some toxic air pollutants such as mercury can deposit onto soil or surface waters, where these are taken up by plants and ingested by animals and are eventually magnified up through the food chain.

Toxics essentially include all air pollutants other than the criteria pollutants, i.e., NO_x, SO_x, CO, Pb, PM and O_3. Most air toxics originate from human made sources, including mobile sources (e.g., cars, trucks, buses) and stationary sources (e.g., factories, refineries, power plants), as well as indoor sources (e.g., paints, shoe polish, cleaning solutions etc.).

Air Pollution Episodes

The worst short term civilian pollution crisis was in India, the **1984 Bhopal Disaster**. Leaked industrial vapors from the Union Carbide factory, belonging to Union Carbide, Inc., U.S.A., killed more than 2,000 people outright and injured anywhere from 150,000 to 600,000 others, some 6,000 of whom would later die from their injuries. The United Kingdom suffered its worst air pollution event when the December 4th **Great Smog of 1952** formed over London. In six days more than 4,000 died, and 8,000 more died within the following months. An accidental leak of anthrax spores from a biological warfare laboratory in the former USSR in 1979 near **Sverdlovsk** is believed to have been the cause of hundreds of civilian deaths. The worst single incident of air pollution in the

United States of America occurred in **Donora, Pennsylvania** in late October, 1948, death of about 80 people and over 7,000 injured due to the accumulation of pollutants caused by air inversion.

Pollution Prevention

Both indoor and outdoor pollution need to be controlled and/or prevented.

Various regulatory measures have been put on as a result of the breaking of air pollution episodes. United States Congress passed the Clean Air Act in 1963, the Air Quality Act in 1967, the Clean Air Act Extension in 1970, and Clean Air Act Amendments in 1977 and 1990. The Air (Prevention and Control of Pollution) Act – 1981, 1982 and the amendment Act 1987 are few of the important legislative measures taken in India towards air pollution control. The regulatory agencies play an essential role in reducing and preventing air pollution in the environment.

Air Pollution Control

The following items are commonly used as pollution control devices by industry or transportation devices. They can either destroy contaminants or remove them from an exhaust stream before it is emitted into the atmosphere.

Particulate control is done through Mechanical collectors (dust cyclones, multicyclones), Electrostatic precipitators, Fabric filters (baghouses) and Particulate scrubbers.

NOx control is done through Low NOx burners, Selective catalytic or non-catalytic reduction, NOx scrubbers, Exhaust gas recirculation and Catalytic converter (also for VOC control).

VOC abatement is by Adsorption systems, such as activated carbon, Flaring, Thermal and catalytic oxidizers, Biofilters, Absorption (scrubbing) and Cryogenic condensers.

Acidic Gas/SO_2 control is through Wet or dry scrubbers and Flue gas desulfurization.

Water Pollution

The giant lakes of water or aquifers are either quickly drying up or being left undrinkable from pollution. The United Nations predicts that by 2050 the entire world’s usable freshwater will be gone! In Tirupur, Tamil Nadu, 737 textile units consume around 90 million liters or 7,500 tanker loads of water every day. The unregulated mining of water has sent groundwater levels plummeting to below 800 feet.

Water pollution is a large set of adverse effects upon water bodies such as lakes, rivers, oceans, and groundwater caused by human activities. Although natural phenomena such as volcanoes, storms, earthquakes, etc. also cause major changes in water quality and the ecological status of water, these are balanced by nature with time. But man made activities and industriallization are causing to increase the pollutants in alarming rate so that nature cannot balance with its slow phase.

Table 4. Physico-chemical parameters and their significance of water pollution

Parameters	**Health Hazards**
Color	The presence of inorganic and organic impurities imparts colour to the water, decreasing consumer acceptance. Sometimes, the impurities may be toxic.
pH	A measure of relative acidity of the water. It is useful in assessing the corrosivity of water to plumbing.
Alkalinity	The amount of bicarbonate, the major anion in water, is related to pH and causes corrosion.
Acidity	Not a pollutant, in water it neutralises hydroxyl ions
Turbidity	A measure of clarity of water. If turbidity is high, there may be chances of water born diseases
Solids (dissolved, suspended, total)	These provide a measure of the suspended solids that can be separated with a filter and the dissolved salts that are present in water.
Conductivity	A measure of total dissolved minerals in water. A change in conductivity or unusual ratio of conductivity to hardness may signal presence of contaminants
Hardness	A measure of the amount of calcium and magnesium. Hardness is a measure of the capacity of water to precipitate soap. This is particularly important if water softening is considered

Dissolved Oxygen	This is a measure of dissolved oxygen in water. Decreased levels of dissolved oxygen in water affect the life in the waterbodies
Chemical Oxygen Demand	Indicates the amount of O_2 required to oxidise the carbonaceous matter. COD taste is widely employed as a means to measure the pollutional strength of domestic and industrial waste
Bromide	Chlorination of water that contains bromide ion may produce bromate ion as an undesirable disinfection by-product. Bromate ion is a carcinogen and nephrotoxin
Chloride	An indicator ion that if found in elevated concentration, points to potential contamination from septic systems, fertilizer, landfills, or road salt
Fluoride	Excessive levels of fluoride causes fluorosis, a mottling of the surface of the teeth
Nitrate	Nitrate in drinking water can cause blue baby syndrome in infants under six months old. Blue baby syndrome, or methemoglobinemia, are common symptoms of nitrate contamination. Nitrate contamination in drinking water may also increase cancer risk, because nitrate is endogenously reduced to nitrite and subsequent nitrosation reaction give rise to N- nitroso compounds; these compounds are highly carcinogenic and can act systematically
Nitrite	These serve as an indicator of the potential presence of other contaminants, such as pesticides or trace organic chemicals from septic system effluents
Phosphate	Excessive consumption of phosphorus may lead to osteoporosis and poor bone maintenance
Sulfate	Ingestion of water containing high levels of sulfate may be associated with Diarrhoea, and other gastrointestinal disorders. Of particular concern are groups in the general population (i.e. infants and transients) that may be at greater risk from the laxative effects of sulfate when they

	switch abruptly to drinking water with high sulfate concentrations
Calcium	Water with high calcium content is undesirable for various household uses such as washing, bathing and laundering, because of consumption of more soap and other cleaning agents
Magnesium	Mg has diuretic, cathartic and laxative effects if it is present in high concentrations

Water pollution has many causes and characteristics. Increases in nutrient loading may lead to eutrophication. Organic wastes such as sewage impose high oxygen demands on the receiving water leading to oxygen depletion with potentially severe impacts on the whole aquatic eco-system. Industries discharge a variety of pollutants in their wastewater including heavy metals, organic toxins, oils, nutrients, and solids. Discharges can also have thermal effects, especially those from power stations, and these too reduce the available oxygen. Silt-bearing runoff from many activities including construction sites, deforestation and agriculture can inhibit the penetration of sunlight through the water column, restricting photosynthesis and causing blanketing of the lake or river bed, in turn damaging ecological systems. Pollutants in water include a wide spectrum of chemicals, pathogens, and physical chemistry or sensory changes. Many of the chemical substances are toxic. Pathogens can obviously produce waterborne diseases in either human or animal hosts.

Sources of water pollution

The sources of water pollution is divided into ‘point source’ or ‘non-point source’ depending on the nature of the source from which the pollutant is discharged. If the pollutant is dischared from single identifiable source like the outlet pipes of industrial facilities or wastewater treatment facilities, is called a point source pollutant. A non-point source pollutant is one whose source is much harder to identify precisely like the surface runoff from cultivating land. Some of the principal sources of water pollution are discharge of poorly treated or untreated sewage, industrial discharge of chemical wastes and byproducts, surface runoff containing pesticides or fertilizers, surface runoff from construction sites, discharge of contaminated and/or heated water used for industrial processes, acid rain caused by industrial discharge of sulfur dioxide (by burning high-sulfur fossil fuels) and excess nutrients added by runoff containing detergents or fertilizers.

There are a variety of secondary effects stemming not from the original pollutant, but a derivative condition. Some of these secondary impacts are:

- Silt bearing surface runoff can inhibit the penetration of sunlight through the water column, hampering Photosynthesis in aquatic plants.
- Thermal pollution can induce fish kills and invasion by new thermophyllic species

Effects of Water Pollution

Few of the well known effects of water pollution are, conditions such as Hypoxia or Dead zone, Eutrophication and oil spilling in the surface waters.

Fig. 1 Still frame from an underwater video of the sea floor. The floor is covered with crabs, fish, and clams apparently dead or dying from oxygen depletion

Hypoxia or **oxygen depletion** is a phenomenon that occurs in aquatic environments as dissolved oxygen (DO molecular oxygen dissolved in the water) becomes reduced in concentration to a point detrimental to aquatic organisms living in the system. Dissolved oxygen is typically expressed as a percentage of the oxygen that would dissolve in the water at the prevailing temperature and salinity (both of which affect the solubility of oxygen in water; see oxygen saturation and underwater). An aquatic system lacking dissolved oxygen (0% saturation) is termed anaerobic, **anoxic or Dead zone**; a system with low DO of concentration, in the range between 1 and 30% DO saturation is called **hypoxic**. Most fish cannot live below 30% DO saturation. A "healthy" aquatic environment should seldom experience DO between 30 and 80%.

Eutrophication is caused by the increase in an ecosystem of chemical nutrients, typically compounds containing nitrogen or phosphorus. It may occur on land or in water. Eutrophication is frequently a result of nutrient pollution such as the release of sewage effluent into natural waters (rivers or coasts) although it may also occur naturally in situations where nutrients accumulate. When an aquatic ecosystem experiences an increase in nutrients, species such as algae experience a population increase (called an algal bloom). Algal blooms limit the sunlight available to bottom-dwelling organisms and cause wide variation in the amount of dissolved oxygen in the water. Oxygen is required by all respiring plants and animals and it is replenished in daylight by photosynthesizing plants and algae. Under eutrophic conditions, dissolved oxygen greatly increases during the day, but is greatly reduced after dark by the respiring algae and by microorganisms that feed on the increasing mass of dead algae. When dissolved oxygen levels decline to hypoxic levels, fish and other marine animals suffocate. As a result, creatures such as fish, shrimp, and especially immobile bottom dwellers die off. In extreme cases, anaerobic conditions ensue, promoting growth of bacteria such as Clostridium botulinum that produces toxins deadly to birds and mammals. Zones where this occurs are known as dead zones.

Oil spill

Studies of the Exxon Valdez oil spill, 1989 have shown that the environmental damage caused by oil spills can be greater than that was previously thought. It was clear that the impacts to marine life can be evident at less than one part per billion petroleum hydrocarbons. The lighter fractions of petroleum, such as benzene and toluene, are more toxic, but are more volatile and evaporate quickly. Heavier components of crude oil, such as polynuclear aromatic hydrocarbons (PAHs) appear to cause the most damage; while they are less toxic, they persist in the environment much longer than volatile components. A heavy oil spill across the shore blankets rock-pools etc, preventing gas exchange and eliminating light as well as directly leaching toxins into the water; it can also become mixed deeply into pebble, shingle or sandy beaches, where it may remain for months or even years. Well-weathered heavy oil on intertidal rocks doesn't retain serious toxicity, for example, it will be grazed off by limpets without apparent ill-effect.

Seabirds are adversely affected as the oil penetrates and opens up the structure of their plumage, so they become chilled, lose the ability to fly, and lose their buoyancy in water. They are thus unable to feed normally, but ingest the oil as they attempt to preen. They will almost inevitably die unless rescued and professionally cleaned.

Water Treatment

There are numerous processes that can be used to clean up waste waters depending on the type and extent of contamination. Most wastewater is treated in industrial scale wastewater treatment plants (WWTPs) which may include physical, chemical and biological treatment processes.

Sewage treatment, or **domestic wastewater treatment**, is the process of removing contaminants from wastewater, both runoff and domestic. It includes physical, chemical and biological processes to remove physical, chemical and biological contaminants. Its objective is to produce a wastestream (or treated effluent) and a solid waste or sludge also suitable for discharge or reuse back into the environment.

Typically, sewage treatment involves three stages, called **primary**, **secondary** and **tertiary treatment**. First, the solids are separated from the wastewater stream. Then dissolved biological matter is progressively converted into a solid mass by using indigenous, water-borne bacteria. Finally, the biological solids are neutralized and disposed of or re-used. The treated water may be disinfected chemically or physically (for example by lagooning and micro-filtration). The final effluent can be discharged into a stream, river, bay, lagoon or wetland, or it can be used for the irrigation of a golf course, greenway or park. If it is sufficiently clean, it can also be used for groundwater recharge.

Primary treatment

Primary treatment is to reduce oils, grease, fats, sand, grit, and coarse (settleable) solids. This step is done entirely with machinery, hence given the name mechanical treatment.

Screening

In the mechanical treatment, the influx (influent) of sewage water is screened to remove all large objects that are deposited in the sewer system, such as rags, sticks, condoms, sanitary towels (sanitary napkins) or tampons, cans, fruit, etc. This is most commonly done with a manual or automated mechanically raked screen. This type of waste is removed because it can damage the sensitive equipment in the sewage treatment plant.

Sand and grit removal

This stage typically includes a sand or grit channel where the velocity of the incoming wastewater is carefully controlled to allow sand, grit and stones to settle but still maintain the majority of the organic material within the flow. This equipment is called a detritor or sand catcher. Sand, grit and stones need to be removed early in the process to avoid damage to pumps and other equipment in the remaining treatment stages. The sand and grit is sent to a landfill.

Sedimentation

Many plants have a sedimentation stage where the sewage is allowed to pass slowly through large tanks, commonly called "primary clarifiers" or "primary sedimentation tanks". The tanks are large enough that faecal solids can settle and floating material such as grease and oils can rise to the surface and be skimmed off. The main purpose of the primary stage is to produce a generally homogeneous liquid capable of being treated biologically and a sludge that can be separately treated or processed. Primary settlement tanks are usually equipped with mechanically driven scrapers that continually drive the collected sludge towards a hopper in the base of the tank from where it can be pumped to further sludge treatment stages.

Secondary treatment

Secondary treatment is designed to substantially decompose the biological content of the sewage such as are derived from human waste, food waste, soaps and detergent. The majority of municipal and industrial plants treat the settled sewage liquor using aerobic biological processes. For this to be effective, the biota require both oxygen and a substrate on which to live. There are number of ways in which this is done. In all these methods, the bacteria and protozoa consume biodegradable soluble organic contaminants (e.g. sugars, fats, organic short-chain carbon molecules, etc.) and bind much of the less soluble fractions into floc. Secondary treatment systems are classified as **fixed film** or suspended growth. Fixed-film treatment process including trickling filters and rotating biological contactors where the biomass grows on media and the sewage passes over its surface. In **suspended growth systems** such as activated sludge the biomass is well mixed with the sewage can be operated in a smaller space than fixed-film systems that treat the same amount of water. However, fixed-film systems are more able to cope with drastic changes in the amount of biological material and can provide higher removal rates for organic material and suspended solids than suspended growth systems.

Secondary sedimentation

The final step in the secondary treatment stage is to settle out the biological floc or filter material and produce sewage water containing very low levels of organic material and suspended matter.

Tertiary treatment

Wastewater may contain high levels of the nutrients nitrogen and phosphorus. Excessive release of these nutrients to the environment can lead to eutrophication, which can in turn encourage the overgrowth of weeds, algae, and cyanobacteria (blue-green algae) which further leads to hypoxic or anoxic contitions in water boby. In addition to causing deoxygenation, some algal species produce toxins that contaminate drinking water supplies. Separate treatment processes are required to remove nitrogen and phosphorus as it needs longer residential time than the oxidation of carbonaceous material in the secondary treatment.

Nitrogen removal

The removal of nitrogen is effected through the biological oxidation of nitrogen from ammonia (nitrification) to nitrate, followed by denitrification, the reduction of nitrate to nitrogen gas. Nitrogen gas is released to the atmosphere and thus removed from the water.

Phosphorus removal

Phosphorus can be removed biologically in a process called enhanced biological phosphorus removal. In this process, specific bacteria, called polyphosphate accumulating organisms, are selectively enriched and allowed to accumulate large quantities of phosphorus within their cells (up to 20% of their mass). When the biomass enriched in these bacteria is separated from the treated water, these biosolids have a high fertilizer value. Phosphorus removal can also be achieved by chemical precipitation, usually with salts of iron (e.g. ferric chloride) or aluminum (e.g. alum). The resulting chemical sludge is difficult to handle and the added chemicals can be expensive. Despite this, chemical phosphorus removal requires significantly smaller equipment than biological removal, is easier to operate and can be more reliable in areas that have wastewater compositions that make biological phosphorus removal difficult.

Disinfection

The purpose of disinfection in the treatment of wastewater is to substantially reduce the number of microrganisms in the water to be discharged back into the environment. The effectiveness of disinfection depends on the quality of the water being treated (e.g., cloudiness, pH, etc.), the type of disinfection being used, the disinfectant dosage (concentration and time), and other environmental variables. Cloudy water will be treated less successfully since solid matter can shield organisms, especially from ultraviolet light or if contact times are low. Generally, short contact times, low doses and high flows all militate against effective disinfection. Common methods of disinfection include ozone, chlorine, or ultraviolet light. Chloramine, which is used for drinking water, is not used in wastewater treatment because of its persistence.

Chlorination remains the most common form of wastewater disinfection due to its low cost and long term history of effectiveness. One disadvantage is that chlorination of residual organic material can generate chlorinated organic compounds that may be carcinogenic or harmful to the environment. Residual chlorine or chloramines may also be capable of chlorinating organic material in the natural aquatic environment. Further, because residual chlorine is toxic to aquatic species, the treated effluent must also be chemically dechlorinated, adding to the complexity and cost of treatment.

Ultraviolet (UV) light can be used instead of chlorine, iodine, or other chemicals. Because no chemicals are used, the treated water's taste is more natural and pure as compared to other methods. UV radiation causes damage to the genetic structure of bacteria, viruses, and other pathogens, making them incapable of reproduction. The key disadvantages of UV disinfection are the need for frequent lamp maintenance and replacement and the need for a highly treated effluent to ensure that the target microorganisms are not shielded from the UV radiation (i.e., any solids present in the treated effluent may protect microorganisms from the UV light).

Ozone (O_3) is generated by passing oxygen (O_2) through a high voltage potential resulting in a third oxygen atom (O) becoming attached and forming O_3. Ozone is very unstable, reactive and oxidizes most organic material it comes in contact with, thereby destroying many pathogenic microorganisms. Ozone is considered to be safer than chlorine because, unlike chlorine which has to be stored on site (highly poisonous in the event of an accidental release), ozone is generated onsite as needed. Ozonation also produces fewer disinfection by products than chlorination. A disadvantage of ozone disinfection is the high cost of the ozone generation equipment and the requirements for highly skilled operators.

Sludge treatment and disposal

The sludges accumulated in a wastewater treatment process must be treated and disposed of in a safe and effective manner. The purpose of digestion is to reduce the amount of organic matter and the number of disease causing microorganisms present in the solids. The most common treatment options include anaerobic digestion, aerobic digestion, and composting. In general, composting is most often applied to small scale applications followed by aerobic digestion and then lastly anaerobic digestion for the large scale municipal applications.

Treatment of industrial wastewater

Industrial sources of wastewater often require specialized treatment processes. Disposal of wastewaters from an industrial plant is a difficult and costly problem. Most petroleum refineries, chemical and petrochemical plants have onsite facilities to treat their wastewaters so that the pollutant concentrations in the treated wastewater comply with the local and/or national regulations regarding disposal of wastewaters into community treatment plants or into rivers, lakes or oceans.

Different types of contamination in wastewater require variety of strategies to remove the contamination.

Solids removal

Most solids can be removed using simple sedimentation techniques with the solids recovered as slurry or sludge. Very fine solids and solids with densities close to one pose special problems. In such case filtration or ultra-filtration may be required. Alternatively, flocculation may be used with the addition of alum salts or polyelectrolytes.

Oils and greases

Many oils can be recovered from open water surfaces by skimming devices. However, hydraulic oils and the majority of oils that have degraded to any extent will also have a soluble or emulsified component that will require further treatment to eliminate. Removal of dissolved or emulsifying oil using surfactants or solvents usually exacerbates the problem rather than solving it, producing a very difficult to treat wastewater.

Soft organics

Organic material of plant or animal origin is usually possible to treat using extended conventional wastewater treatment processes. Problems can arise if the wastewater is excessively diluted with washing water or is highly concentrated such as neat blood or milk. The presence of cleaning agents, disinfectants, pesticides, or antibiotics can have detrimental impacts on treatment processes.

Hard organics

Synthetic organic materials including solvents, paints, pharmaceuticals, pesticides, coking products can be very difficult to treat . Treatment methods are often specific to the material being treated. Methods include distillation, adsorption, vitrification, incineration, chemical immobilisation or landfill disposal. Some materials such as some detergents may be capable of biological degradation and in such cases, a modified form of wastewater treatment can be used.

Acids and alkalis

Acids and alkalis can usually be neutralised under controlled conditions. Neutralisation frequently produces a precipitate that will require treatment as a solid residue which may be toxic. In some cases, gasses may be evolved requiring treatment for the gas stream. Some other forms of treatment are usually required following neutralisation.

Waste streams rich in hardness ions as from de-ionisation processes can readily loose the hardness ions in a buildup of precipitated calcium and magnesium salts. This precipitation process can cause severe furring of pipes and can, in extreme cases, cause the blockage of disposal pipes. Treatment can be modified to concentration of de-ionisation waste waters and disposal to landfill or by careful pH management of the released wastewater.

Hazardous water pollution

Hazardous waste is waste that poses substantial or potential threats to public health or the environment and generally exhibits one or more of the following characteristics.

- ignitable (can catch on fire like petroleum distillates or organic solvents),
- corrosive (can cause grievous injury at the point of contact, i.e., skin, eyes or mouth; such as strong acids and alkalis and chlorine or hydrogen peroxide),
- reactive (can react violently with water, air or other substances, such as ethers which form explosive peroxides if stored for longer time, dynamite, gun ammunition or firecrackers) and
- toxic (can adversely affect the health of living organisms exposed to it, such as arsenic, cyanide, pesticides and metals like lead).

Toxic materials including many organic materials, metals (such as zinc, silver, cadmium, thallium etc.) acids, alkalis, non-metallic elements (such as arsenic or selenium) are generally resistant to biological processes unless very dilute. Metals can often be precipitated out by changing the pH or by treatment with other chemicals. Many, however, are resistant to treatment or mitigation and may require concentration followed by landfilling or recycling.

Many chemicals undergo reactive decay or change especially over long periods of time in groundwater reservoirs. For example chlorinated hydrocarbons such as trichloroethylene (used in industrial metal degreasing) and tetrachloroethylene (used in the dry cleaning industry) which are carcinogens themselves, undergo partial decomposition reactions, leading to new hazardous chemicals.

Reuse of Treated water

Treated wastewater can be reused as drinking water (Singapore), cooling water (in industry), in artificial recharge of aquifers, in agriculture (70% of Israel's irrigated agriculture is based on highly purified wastewater) and in the rehabilitation of natural ecosystems (Florida's Everglades).

Legislative Measures

The Water (Prevention and Control of Pollution) Act – 1974 and The Water (Prevention and Control of Pollution) Cess Act – 1977 and 1978 are few of the important legislative measures taken by the Indian government to control water pollution. Federal Water Pollution Control Amendments of 1972 and Amendments in 1977 (nothing but the Clean Water Act) of US are few of the well known leglative measures taken to curb the water pollution. Since the Clean Water Act was passed, water pollution has drastically decreased in US.

Solid waste

Solid waste can be broadly classified into

a) Household waste (generally classified as municipal waste),
b) Industrial waste (hazardous waste) and
c) Biomedical waste or infectious hospital waste

Municipal solid waste Management

Municipal solid waste consists of household waste, construction and demolition debris, sanitation residue, and waste from streets. This garbage is generated mainly from residential and commercial complexes. With rising urbanization and change in lifestyle and food habits, the amount of municipal solid waste has been increasing rapidly and its composition also is changing. In 1947 cities and towns in India generated an estimated 6 million tonnes of solid waste, but in 1997 it was about 48 million tonnes. Over the last few years, the consumer market has grown rapidly leading to products being packed in cans, aluminium foils, plastics, and other such non-biodegradable items that cause incalculable harm to the environment.

There are different categories of waste generated, each take their own time to decompose (as illustrated in the table below).

The large quantity of the municipal solid waste generated in the streets is getting collected and segregated on the basis of four broad categories;

- Biodegradable waste: food & kitchen waste, green waste, paper (can also be recycled).
- Recyclable material: paper, glass, bottles, cans, metals, certain plastics, etc.
- Inert waste: construction and demolition waste, dirt, rocks, debris.

- Domestic hazardous waste (also called "household hazardous waste") & toxic waste: medication, paints, chemicals, light bulbs, fluorescent tubes,spray cans, fertilizer and pesticide containers, batteries, shoe polish.

The most commonly used methods for waste disposal are Landfilling, Composting, Anaerobic Digestion and Incineration.

Table 5. Composition of urban solid waste in Indian cities (% by weight)

City	Paper	Metal	Glass	Textiles	Plastics*	Ash & dust	Organic	Others**
Chennai	5.90	0.70	-	7.07	-	16.35	56.24	13.74
Delhi	5.88	0.59	0.31	3.56	1.46	22.95	57.71	7.52
Kolkata	0.14	0.66	0.24	0.28	1.54	33.58	46.58	16.98
Bangalore	1.50	0.10	0.20	3.10	0.90	12.00	75.00	7.20
Ahmedabad	5.15	0.80	0.93	4.08	0.69	29.01	48.95	10.39
Mumbai	3.20	0.13	0.52	3.26	-	15.45	59.37	18.07

Source: Planning commission on "Urban Solid waste Management in India", GOI (1995)
*Includes rubber and leather
**Includes bones, stones and woody matter

A landfill, also known as a dump, is a site for the disposal of waste materials by burial and is the oldest form of waste treatment. Historically, landfills have been the most common methods of organized waste disposal and remain so in many places around the world. Modern, engineered landfills usually have physical barriers such as liners and leachate collection systems, and procedures to protect the public from exposure to the disposed wastes.

Composting is the controlled decomposition of organic matter. Rather than allowing nature to take its slow course, a composter provides an optimal environment in which decomposers like the aerobes, and the larger creatures such as ants, nematodes, and oligochaete worms can thrive. To encourage the most active microbes, a compost pile needs the correct mix of Carbon, Nitrogen, Oxygen (in the case of aerobic composting) and Water.

Table 6. The approximate life time of the litter materials

The type of litter we generate and the approximate time it takes to decompose	
Type of litter	Approximate time it takes to degenerate the litter
Organic waste such as vegetable and fruit peels, leftover foodstuff, etc.	a week or two.
Paper	10–30 days
Cotton cloth	2–5 months
Wood	10–15 years
Woolen items	1 year
Tin, aluminium, and other metal items such as cans	100–500 years
Plastic bags	one million years?
Glass bottles	undetermined

Anaerobic digestion (AD) is the harnessed and contained, naturally occurring process of anaerobic decomposition. An anaerobic digester is an industrial system that harnesses these natural process to treat waste, produce biogas that can be used to power electricity generators, provide heat and produce soil improving material. Increasing environmental pressures on waste disposal have increased the use of AD as a process for reducing waste volumes and generating useful byproducts. It is a fairly simple process that can greatly reduce the amount of organic matter which might otherwise end up in landfills or waste incinerators. Almost any organic material can be processed in this manner. This includes biodegradable waste materials such as waste paper, grass clippings, leftover food, sewage and animal waste. Anaerobic digesters can also be fed with specially grown energy crops to boost biodegradable content and hence increased biogas production. After sorting or screening to remove inorganic or hazardous materials such as metals and plastics, the material to be processed is often shredded, minced, or hydrocrushed to increase the surface area available to microbes in the digesters and hence increase the speed of digestion. The material is then fed into an airtight digester where the anaerobic treatment takes place.

Incineration is a waste treatment technology that involves the combustion of waste at high temperatures. In effect, incineration of waste materials converts the waste into heat (that can be used to generate electricity), sends gaseous emissions to the atmosphere, and makes residual ash.

Incineration has particularly strong benefits for the treatment of certain waste types in niche areas such as clinical wastes and certain hazardous wastes where pathogens and toxins must be destroyed by high temperatures. Incineration is particularly popular in countries such as Japan where land is a scarce resource.

Hazardous waste

Many types of businesses generate hazardous waste. Some are small companies that may be located in a community. For example, dry cleaners, automobile repair shops, hospitals, exterminators, and photo processing centers all generate hazardous waste. Some hazardous waste generators are larger companies like chemical manufacturers, electroplating companies, and oil refineries.

Remarks

Every day, earth becomes more and more polluted. Air pollution fills our lungs with deadly substances. Water pollution is rapidly eradicating what little freshwater we have left. Land pollution is causing once-fertile lands to become little more than deserts. And the earth is choking in the polluted filth produced by humanity. Pollution is gradually destroying our planet and is gradually killing us too. So it is the need of the hour for every individual to adapt to sustainable life style and industries to be more concerned about processes to be sustainable towards our ecosystem.

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Chapter - 14
CHEMICALS PRODUCTION THROUGH ALTERNATE ROUTES

G. Magesh

1. Introduction

Increasingly, stringent environmental legislation has generated a pressing need for cleaner methods of chemical production, for instance, technologies that reduce or, preferably, eliminate the generation of waste and avoid the use of toxic and/or hazardous reagents and solvents. This trend toward green chemistry necessitates a paradigm shift from the traditional concept of process efficiency, which focuses exclusively on chemical yield, to one that assigns economic value to eliminating waste.

One more strategy is to dramatically substitute biochemicals for petrochemicals. In the last decade technological advances have lowered the cost of producing high quality products from plant matter while environmental regulations have raised the cost of manufacturing and using petroleum derived products. One of the examples in this case is the use of naturally available carbohydrates as raw materials for production of various chemicals. Attempts are being made to reduce carbon dioxide and naturally available carbonates to various hydrocarbons or its functionalized derivatives. Carbondioxide is widely available in atmosphere and its reduction will also reduce global warming since it is one of the greenhouse gases.

Thus the alternate routes of chemical production can be classified into three broad categories as
(i) routes which utilize alternate sources of energy
(ii) routes which involve alternate processes and technologies
(iii) routes which utilize sources other than petroleum as raw materials for chemicals

2. Alternate sources of energy

These processes utilize sources other than heat and electricity as the driving force for carrying out the reactions.

Various technologies involved in this category are

(i) Microwave assisted synthesis

(ii) Sonochemical assisted synthesis

(iii) Light assisted synthesis

2.1. Microwave assisted synthesis

It has long been known that molecules undergo excitation with electromagnetic radiation. This effect is utilized in household microwave ovens to heat up food. However, chemists have only been using microwaves as a reaction methodology for a few years. Some of the first examples gave amazing results, which led to a flood of interest in this novel technique (1).

The water molecule is the target for microwave ovens in the home; like any other molecule with a dipole, it absorbs microwave radiation. Microwave radiation is converted into heat with high efficiency, so that "superheating" becomes possible at ambient pressure. Enormous accelerations in reaction time can be achieved, if superheating is performed in closed vessels under high pressure; a reaction that takes several hours under conventional conditions can be completed over the course of minutes.

2.1.1. Thermal Vs. non thermal effects

Excitation with microwave radiation results in the molecules aligning their dipoles within the external field. Strong agitation, provided by the reorientation of molecules, in phase with the electrical field excitation, causes an intense internal heating. The question of whether a nonthermal process is operating can be answered simply by comparing the reaction rates between the cases where the reaction is carried out under irradiation versus under conventional heating. In fact, no nonthermal effect has been found in the majority of reactions, and the acceleration is attributed to superheating alone. It is clear, though, that nonthermal effects do play a role in some reactions.

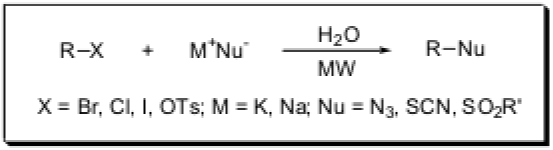
2.1.2. Is a home microwave suitable?

The microwave units specially designed for synthesis are often quite expensive. Unmodified microwave units suitable for domestic use are suitable in some cases. However, simple modifications (for example, a reflux condenser) can heighten the safety factor. High-pressure chemistry should only be carried out in special reactors with a microwave oven specifically designed for this purpose. A further point in favor of using more expensive apparatus is the question of reproducibility, since only these specialized machines can achieve good field homogeneity and in some cases can even be directed on the reaction vessel.

2.1.3. MW-assisted reactions in water, polyethylene glycol (PEG) and ionic liquids

Recent examples include the aqueous N-alkylation of amines by alkyl halides that proceed expeditiously in the presence of aqueous sodium hydroxide to deliver tertiary amines. The synthesis of N-azacycloalkanes, an important class of building blocks in natural products and pharmaceuticals, can be achieved by a simple, efficient, and environmentally friendlier alternative route using MW protocol. This double N-alkylation of primary amines readily assembles two C-N bonds in a S_N2-like heterocyclization sequence which cannot be fully realized under conventional heating conditions. The MW-assisted reaction proceeds in aqueous potassium carbonate and leads to the formation of a variety of five-membered heterocycles (e.g. isoindole, pyrazole and pyrazolidine) by condensation of amines or hydrazines with alkyl 1,3-dihalides or -ditosylates. Similarly, classical nucleophilic substitution reactions can be revisited in aqueous medium by reacting alkyl halides or tosylates with alkali azides to provide azides and thiocyanides in the absence of a phase transfer catalyst. The protocol can be extended to preparation of sulfones from sulfinate salts in aqueous medium. These MW-assisted ‘greener’ and expeditious chemical transformations circumvent the need for multi-step processes that use expensive metal catalysts and accommodate reactive functional groups because of mild reaction conditions, thus minimizing or eliminating the formation of byproducts. Selected reactions using polyethylene glycol (PEG), carbon dioxide, and ionic liquids as reaction media or catalysts have been accomplished, where recycling of catalysts have been demonstrated.

2.1.4. Microwave assisted organic transformations



Microwave-assisted synthesis of azides, thiocyanates, and sulfones has been developed that has proved to be a useful alternative which avoids the use of environmentally detrimental volatile chlorinated hydrocarbons (2) All the reactions with these readily available halides or tosylates have shown significant increase in reactivity, thus reducing the reaction times with substantial improvement in the yields. Various functional groups such as ester, carboxylic acid, carbonyl, and hydroxyl were unaffected under the mild reaction conditions employed. This method involves simple experimental procedures and product isolation which avoid the use of phase-transfer catalysts, and is expected to contribute to the development of greener strategy for the preparation of various azides, thiocyanates, sulfones, and other useful compounds(3).

2.2. Ultrasonic assisted synthesis

The normal range of hearing lies between 16 Hz and about 18 kHz whereas the ultrasound is considered to range from 20 kHz to 100 MHz. Ultrasound is best known for its use as the SONAR (acronym for "sound navigation and ranging") detection system (but notice that some sonars also use audible waves), as medical devices for diagnoses or treatment (5-10 MHz), and as jewels cleaning baths (20 kHz). Anyway, since more than one decade (the first international symposium in sonochemistry was held at Warwick University, UK, in 1986) there is also a real interest in the use of ultrasonic waves to promote organic reactions.

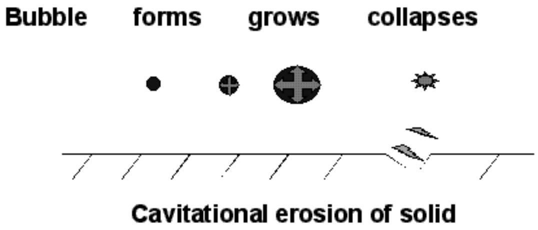


Fig. 1.Formation and collapse of cavitation bubble in a liquid medium

Indeed, it has been shown that at suitable frequencies (between 20 kHz to 1 MHz, but especially between 20 and 40 kHz, the frequencies generally used in the laboratories of chemistry) the propagation of ultrasound in a liquid is accompanied by the formation of cavitation bubbles. Those bubbles can expand suddenly and collapse violently releasing a large amount of energy which can be used to favour some chemical processes. Formation and collapse of cavitation bubble is represented in Fig. 1.

The theory is known as the "hot spot" and theoretical models predict that each cavitation bubble behaves as a microreactor ables to generate, in water, local temperatures of several thousand degrees and local pressure of several thousand atmospheres; at higher frequency - above 5 MHz - cavitation bubbles are not formed, thus explaining why ultrasound of such a power is safely used in medicine. Alternatively it has also been suggested that high speed stirring has a similar effect as sonication on a few heterogeneous reactions.

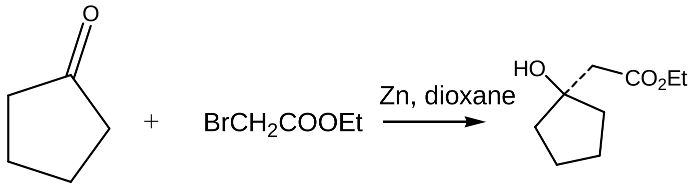
Ultrasound-promoted reactions can be performed by immersing a reaction vessel into an ultrasonic bath or by immersing an ultrasonic probe (horn) into a reaction medium. Reaction times decrease by a factor five to fifty for identical isolated yields.

Reactions which are carried out by ultrasound are:

(i) Organometallic Reactions
(ii) Condensations
(iii) Cycloadditions
(iv) Polymerizations

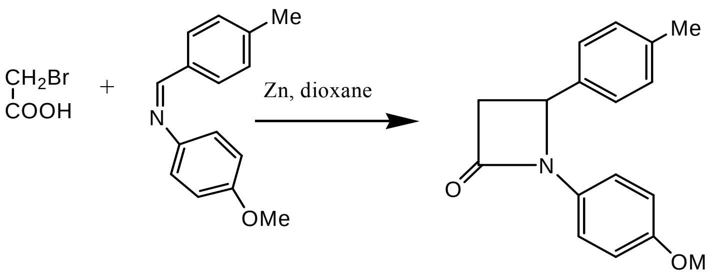
2.2.1. Reformatsky reaction

Reformatsky reaction which normally gives 50% yield and requires 12 hours to complete at 80°C can be carried out in 1h at room temperature with 97% yield under ultrasonic conditions.



US ,rt , 1h 97%

Stirred, 80 °C, 12 h 50%

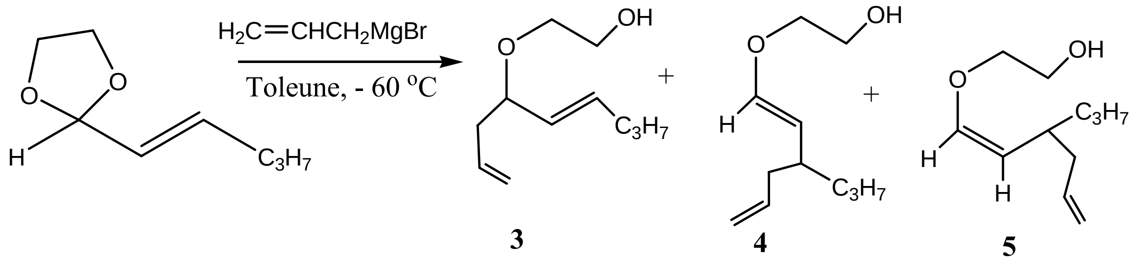


US 95%

Stirred, 60%

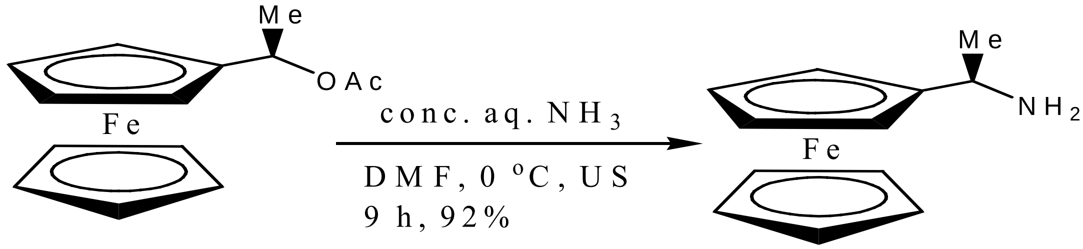
Some other ultrasonic mediated reactions are

Reactions using grignard reactions



Yield	US:100%	stirred: 17%
ratio **3**:(**4**+**5**)	85:15	84:16

Reactions using organometallic compounds



Without ultrasound, under optimal conditions, the maximum yield is 45%

2.3. Photoelectrochemical means of synthesis

Natural photosynthesis has evolved over a period of three billion years. It involves molecules combining with suitable macromolecules to carry out reactions with required efficiencies. Nature has been successful in synthesizing starch from water and CO_2. If mankind can synthesize molecules using sunlight as the energy source it will solve energy and environment related problems. The molecules or compounds include not only molecules like hydrogen from water but also the synthesis of other industrially important chemicals as well. It is also the desire to reduce carbon dioxide levels using photoelectrochemical means. There are plants which can convert CO_2 to hydrocarbons using only sunlight as the energy.

Light assisted reactions can be classified into two categories. They are

(i) Photochemical reactions

(ii) Photocatalytic reactions

2.3.1. Photochemical reactions

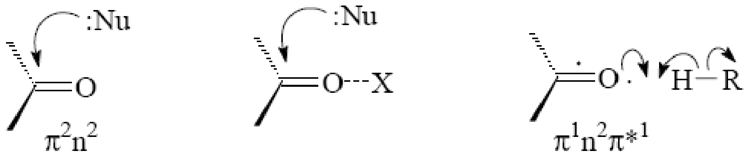
In the photochemical reactions, one or more of the reactants will absorb light and undergo the reaction using the light energy. Only reactants which can absorb light directly can undergo reaction.

Photoinitiated reactions are promising candidates for environment-friendly organic synthesis. The central issue of organic chemistry is to make quite stable organic molecules susceptible to reactions. This is obtained either by weakening a covalent bond (e.g., by complexation or adsorption on a catalyst surface) or by polarizing it (e.g., again by complexation or by forming a hydrogen bond) or by cleaving a covalent bond. The last choice is the one requiring more energy and more control of the medium, as typified by the deprotonation of a carbonyl or carboxyl derivative to form an enolate, probably the most largely used strategy for the formation of the carbon–carbon bond.

Photochemistry is different, since electronically excited states (see Scheme 1) differ from ground states not only for the high energy level, but also, and perhaps more importantly, for the dramatic change in the electronic distribution by which they are characterized as well as by the fact that such a change does not require the addition of a chemical reagent or—at least in principle—a special care of the medium. To take a simple example, a ketone is a weak electrophile, due to the polarization of the πC–O bond. As such, it reacts only with quite active (usually charged) nucleophiles. The electrophilicity can be increased by increasing the polarization (e.g., by complexation by means of a Lewis acid), and under these conditions weaker electrophiles add. However, electronic excitation brings about a more deep-seated change. The np* excited state is no more a C-electrophile (3 electrons now crowd in the π space) but the single electron remaining in the n_o orbital gives to this species a strong radical reactivity centered at the oxygen atom (see Scheme 1). Indeed, the typical reactions are fast (typical rates ≥ 1 X 10^6 $M^{-1}s^{-1}$) H-abstractions from a C–H bond or addition to an alkene, i.e., the same reactions that an alkoxy radical would give.

The mechanism of a normal nucleophilic reaction and light assisted reaction can be represented as follows

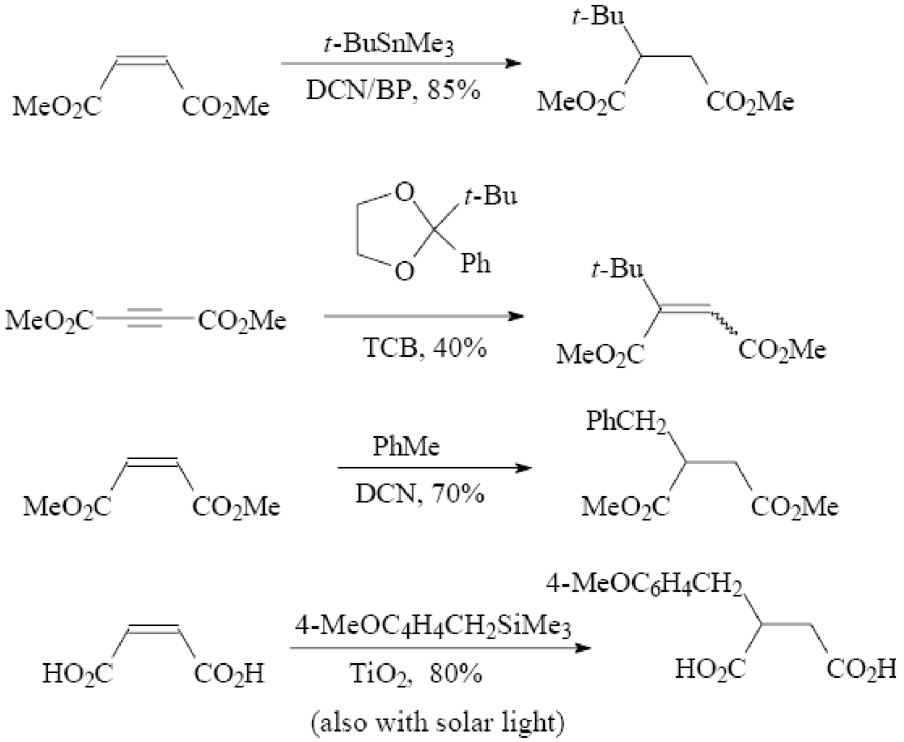
$$A + h\upsilon \rightarrow A^* \rightarrow \text{Products} \qquad (1)$$



Scheme 1

Importantly, such a change is obtained by the absorption of a photon, not by adding a reagent, and is relatively independent from the experimental parameters (temperature, medium characteristics, other reagents present). Therefore, the judicious choice of such parameters allows the direction of the reaction toward the desired target and gives to photochemical reactions an unparalleled versatility in every direction. This certainly includes a further control of the environmental compatibility and this must be added to the intrinsic advantage of such reactions, in which the maximum change of the reactivity is obtained through the minimum addition of reagents (in fact, none).

The reactivity of every excited state depends on its electronic structure and offers a real variety of novel chemical processes that can be used for synthesis (e.g., the above-mentioned radical reactions of the nπ* state of ketones, the geometric isomerization of alkenes, the rearrangement of some aromatics). The utility of photochemistry in key steps of organic synthesis has been demonstrated through many examples, including scaling up to reasonable amounts and industrial applications. Some other reactions assisted by light are given below.



2.3.2. Photocatalytic reactions

In the photocatalytic reactions a sensitizer will be involved in the reaction. The sensitizer will absorb light and transfers the energy to the reactants. In this way molecules which cannot absorb light can also be made to undergo reaction using light.

Some of the reactions which can be carried out photocatalytically were

(i) Oxidation of alcohols to carbonyl compounds

(ii) Oxidation of methane to methanol

(iii) Dehydrogenation reactions

(iv) Oxidation of benzene to phenol

(v) Oxidation of cyclohexane

(vi) Oxidation of light alkanes to oxygenated products

(vii) Oxidation of cyclic alkanes present in petroleum

(viii) Reduction of CO_2

(ix) Reduction of carbonates

(x) Reduction of N_2 to NH_3

(xi) Reduction of nitro compounds to amines

(xii) Hydrogenation reactions
(xiii) Production of hydrogen peroxide
(xiv) Isomerization reactions
(xv) Polymerization reactions

3. Alternate process and technologies

In this case alternate technologies were used both to reduce the waste as well as improving the efficiency of the reaction.

This category of reactions can be classified as

(i) Catalysis by solid acids and basis
(ii) Bifunctional and multifunctional catalysts
(iii) Asymmetric catalysts
(iv) Biocatalysis (Biotechnology)
(v) Green solvents for organic synthesis

3.1. Catalysis

In chemistry and biology, catalysis is the acceleration (increase in rate) of a chemical reaction by means of a substance, called a catalyst that is itself not consumed by the overall reaction. A catalyst provides an alternate route of reaction where the activation energy is lower than the original chemical reaction. Catalysts participate in reactions but are neither reactants nor products of the reaction they catalyze. An exception is the process of autocatalysis where the product of a reaction helps to accelerate the same reaction. They work by providing an alternative pathway for the reaction to occur, thus reducing the activation energy and increasing the reaction rate.

3.2. Catalysis by solid acids and bases

3.2.1. Solid acids

Conventional acid catalyzed reactions use acids like H_2SO_4 whose separation becomes difficult after the process is complete and thus the process becomes tedious and also pollutes the environment. Solid acid and base catalysts are appealing since the nature of acid and basic sites are known and their chemical behavior in acid and base catalyzed reactions can be rationalized by means of existing theories and models. It is possible to modify the acidic and basic properties of these materials by adopting various synthesis and post synthesis routes. In addition, it is possible to confirm these modifications by the available techniques. The main task of catalyst technologists is therefore to look for efficient and stable catalysts which are safe and eco-friendly.

Solid acids which are widely used to carry out organic reactions are

(i) Zeolites

(ii) Mesoporous materials like MCM and SBA

(iii) Alumina

(iv) Silica

(v) Heteropoly acids

(vi) Pillared clays

3.2.2 Base catalysis

Catalysis by solid bases has been less investigated though many interesting examples involving alkylation and condensation reactions can be found in the literature. The selective alkylation of catechol to veratrole with dimethyl carbonate has been reported over K-alumina. Base catalysts (alkali loaded zeolites) have been used in a number of condensation reactions such as aldol, knoevenagel and Michael condensations.

3.3 Bifunctional and mutilfunctional catalysts

Bifunctional catalysts are those which contain two types of active sites like acid and basic sites. Bifunctionality can function in a sequential mode or simultaneous mode. In the simultaneous mode, both the acid and base sites can interact with the substrate in such a way that the base pushes the electron pair to one part of the substrate, while the acid site pulls the electron pair from other part of the substrate. This can be classified as concerted mechanism for which the dehydration of 1-butanol on sodium doped alumina is a typical example. On the other hand in another variety of simultaneous mode, the acid sites and basic sites activate the substrates molecules and the activated substrates interact to yield the desired product. This can be called as go together mechanism and Tishchenko reaction of benzaldehyde on CaO is an example for this mechanism.

Successive interaction can be conceived in the reformation of methylcyclopentane (MCP) on silica-alumina and Pt/SiO_2 where dehydrogenation and isomerization occur successively on different sites. This concept of bifunctionality can have a variety of implications, like enhancement of reaction velocity, improvement in selectivity and also extending the life of the catalyst. Bifunctionality is often associated with reforming reactions.

This concept of active sites or bifunctionality has led to the concept of multifunctionality by which a variety of transformations can be carried out by the same catalytic system and thus lead to one pot synthesis of the desired products. It can also be possible that the multifunctionality can lead to many side or unwanted reactions together with the desired reaction.

3.4. Asymmetric catalysis

Asymmetric catalysis is the phenomenon whereby a chiral catalyst promotes the conversion of an achiral substrate to a chiral product with a preference for the formation of one of the mirror image isomers (enantiomers).

The demand for chiral compounds, often as single enantiomers, has escalated sharply in recent years, driven particularly by the demands of the pharmaceutical industry, but also by other applications, including agricultural chemicals, flavors, fragrances, and materials. Two-thirds of prescription drugs are chiral, with the majority of new chiral drugs being single enantiomers. Although the most obvious applications are bio-related, materials science also relies on the properties imparted by chirality, notably in chiral polymers and liquid crystals. This widespread demand for chiral compounds has stimulated intensive research to develop improved methods for synthesizing such compounds.

Historically, enantiomerically enriched compounds were generated either by chemical transformation of an enantiomerically enriched precursor, often derived directly or indirectly from nature's chiral pool, or by resolving an equimolar (racemic) mixture of the two enantiomers. Both of these approaches suffer from potentially severe drawbacks, the former in requiring stoichiometric amounts of a suitable precursor and the latter in typically yielding only up to 50% of the desired enantiomer.

Asymmetric catalysis, in which each molecule of chiral catalyst, by virtue of being continually regenerated, can yield many molecules of chiral product, has significant potential advantages over the older procedures. Indeed, enantiomerically pure compounds are produced in nature by such chirality transfer from enzymic catalysts. However, it was only relatively recently that such asymmetric catalysis, with enantiomeric excesses approaching 100%, was achieved with synthetic catalysts. A major breakthrough occurred in the early 1970s, when William Knowles and his colleagues at Monsanto demonstrated that rhodium complexes containing chiral phosphine ligands are able to catalyze the enantioselective addition of H_2 to one of the faces of a prochiral olefinic substrate generating a chiral C—H center with high enantioselectivity. This process was soon commercialized to produce the anti-Parkinson drug, L-dopa, followed over the next three decades by the development of many other commercial processes, as well as laboratory scale syntheses, to generate enantiomerically enriched compounds. In recognition of his achievement, Knowles shared the 2001 Nobel Prize in chemistry with Ryoji Noyori, also for work on asymmetric catalytic hydrogenation, and with K. Barry Sharpless for his work on asymmetric catalytic oxidation.

3.5. Biocatalysis (biotechnology)

Biotechnology in its broadest sense has been around for a long time, but the term has only been coined relatively recently. Although revolutionised by genetic engineering-techniques, biotechnology encompasses the pre-existing use of fermentation and enzyme extracts. A generally accepted working definition is: the use of microorganisms and enzymes to produce commercially useful biochemicals and other fine chemicals. Table 1 shows some of the mature biotechnological process.

Table 1. Details of established biotechnological processes

Mature Biotechnological Processes		
Product	***Process***	***Production m.tons/year***
L-Amino acids	fermentation/enzymes	hundreds
S-AMPA	microbial hydroxylation	100
6-APA	immobilized acylase	8,000

Aspartame	enzymic coupling	750
Cephalosporin C	fermentation	3,000
Clavulanic acid	fermentation	200
Ergot alkaloids	fermentation	25
S-alpha-Chloropropionic acid	isolated dehalogenase	1,200
Ephedrine	fermentation	500
Erythromycin	fermentation	2,000
D-(-)-Hydroxyphenylglycine	immobilized enzyme/whole cell	2,750*
17-alpha-Hydroxyprogesterone	immobilized hydroxylase	50
Lovastatin	fermentation	65
L-Phenylalanine	fermentation	8,500
Streptomycin	fermentation	1,750
Vitamin B12	fermentation	10

* Also made by chemical resolution (total volume: 3,500 metric tons)

14.3.5.1 The outlook

Biotechnology will continue to mature and new processes will be developed which take advantage of its benefits. Some older chemical processes will become obsolete and be replaced by newer technologies, some biotechnical others inspired by biotechnology.

Fermentation is an established technology for producing a wide range of chemicals and the yield and costs of fermentation products will continue to be improved by the application of biotechnology.

The use of industrial enzymes will increase as the isolates become more effective and the range of practical transformations they catalyze increases. Again biotechnology will greatly accelerate this development. By the turn of the century, the fine chemical industry will have come to terms with biotechnology and consultants will be addressing learned meetings on the opportunities presented by micromachines or some other new area of development.

3.6. Green solvents for organic synthesis

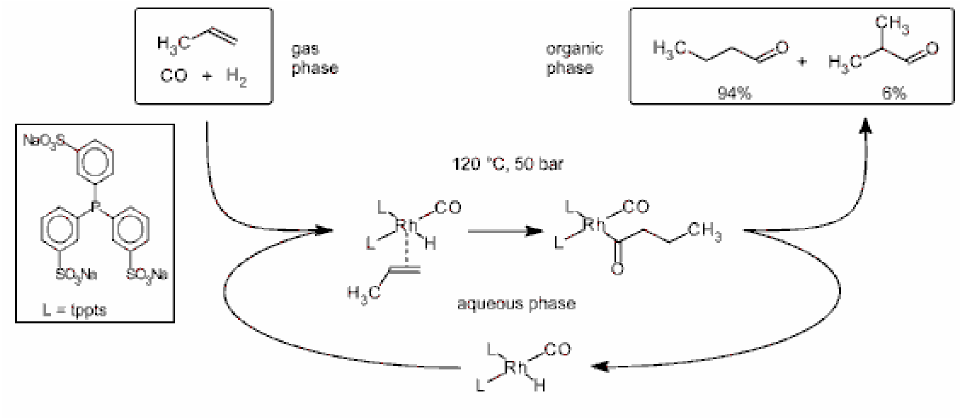
The growing awareness of the pressing need for greener, more sustainable technologies has focused attention on the use of atom efficient catalytic methodologies for the manufacture of fine chemicals and pharmaceuticals. Another aspect which is receiving increasing attention is the use of alternative reaction media that circumvent the problems associated with many of the traditional volatile organic solvents. The use of non-conventional reaction media also provides opportunities for facilitating the recovery and recycling of the catalyst. The use of alternative reaction media for green, sustainable organic synthesis is being widely studied. Liquid–liquid biphasic catalysis provides an industrially attractive method for the recovery and recycling of catalysts as an alternative to the more traditional solid heterogeneous catalysts. Various novel solvents like liquid–liquid biphasic catalysis— aqueous biphasic, fluorous biphasic, supercritical carbon dioxide, ionic liquids and various combinations thereof—were being studied. ‘‘The best solvent is no solvent’’ but if a solvent is needed then catalysis in aqueous biphasic systems is an industrially attractive methodology which has found broad application. Similarly, supercritical carbon dioxide is an interesting reaction medium in the context of green chemistry and catalysis in various mono- and biphasic systems involves this solvent. Fluorous biphasic systems and ionic liquids also have advantages in certain situations. The ultimate in clean catalytic technologies is to telescope multistep syntheses into one-pot in the form of catalytic cascade processes. Table 2 shows the E factor for the various chemical industries.

Table 2. E factor for various chemical industries

Type	**Tonnage**	**E factor = kg waste / kg product**
Bulk chemicals	10^4-10^6	<1 to 5
Fine chemicals industry	10^2-10^4	5 to > 50
Pharmaceutical industry	10-10^3	25 to >100

3.6.1. Aqueous biphasic catalysis

The best solvent is no solvent and if a solvent (diluent) is needed then water is preferred. Water is nontoxic, nonflammable, abundantly available and inexpensive. Moreover, owing to its highly polar character one can expect novel reactivities and selectivities for organometallic catalysis in water. Furthermore, this provides an opportunity to overcome a serious shortcoming of homogeneous catalysts, namely the cumbersome recovery and recycling of the catalyst. Thus, performing the reaction in an aqueous biphasic system, whereby the catalyst resides in the water phase and the product is dissolved in the organic phase, allows for recovery and recycling of the catalyst by simple phase separation. An example of a large scale application of this concept is the Ruhrchemie/Rhone-Poulenc process for the hydroformylation of propylene to n-butanal, which employs a water-soluble rhodium(I) complex of trisulfonated triphenylphosphine (tppts) as the catalyst. The mechanism involved in the Ruhrchemie/Rhone-Poulenc process is as follows.



Rhône-Poulenc/Ruhrchemie process for aqueous biphasic hydroformylation.

Other reactions which are carried out using aqueous biphasic catalysis are carbonylation of alcohols, cyanides, oxidations and synthesis of adipic acid.

3.6.2 Supercritical CO_2 as reaction medium

Other nonclassical reaction media have, in recent years, attracted increasing attention from the viewpoint of avoiding environmentally unattractive solvents and/or facilitating catalyst recovery and recycling. For example, supercritical carbon dioxide has been receiving increasing attention as an alternative reaction medium in recent years. Several features of scCO2 make it an interesting solvent in the context of green chemistry and catalysis. For carbon dioxide the critical pressure and temperature are moderate: 74 bar and 31 °C, respectively. Hence, the amount of energy required to generate supercritical carbon dioxide is relatively small. In addition, carbon dioxide is nontoxic, chemically inert towards many substances, nonflammable and simple depressurization results in its removal. It is miscible with, e.g. hydrogen, making it an interesting solvent for hydrogenation and hydroformylation (see below). Furthermore, the physical properties of scCO2, e.g. polarity, can be tuned by manipulation of the temperature and pressure. Although it is a greenhouse gas its use involves no net addition to the atmosphere; it is borrowed as it were. Its main uses are as a replacement for VOCs in extraction processes. For example it is widely used for the decaffeination of coffee where it replaced the use of a chlorinated hydrocarbon. The pre-existence of an established SCF extraction industry meant that the necessary equipment was already available.

Supercritical CO_2 is used as solvent for various reactions like hydrogenation, hydroformylation, oxidation and various biocatalysed reactions.

3.6.3. Fluorous biphasic systems

Fluorous biphasic catalysis was pioneered by Horvath and Rabai who coined the term ‘fluorous’ by analogy with ‘aqueous’, to describe highly fluorinated alkanes, ethers and tertiary amines. Such fluorous compounds differ markedly from the corresponding hydrocarbon molecules and are, consequently, immiscible with many common organic solvents at ambient temperature although they can become miscible at elevated temperatures. Hence, this provides a basis for performing biphasic catalysis or, alternatively, monophasic catalysis at elevated temperatures with biphasic product–catalyst separation at lower temperatures. A variety of fluorous solvents are commercially available (see Fig. 2. for examples), albeit rather expensive compared with common organic solvents (or water).

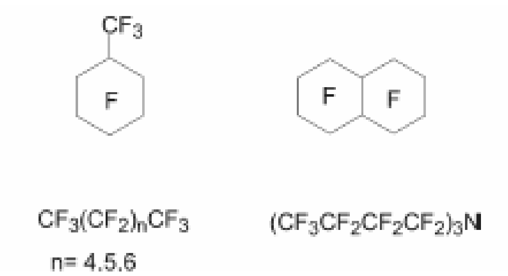


Fig. 2. Structures of some fluorous solvents

In order to perform fluorous biphasic catalysis the (organometallic) catalyst needs to be solubilised in the fluorous phase by deploying ‘‘fluorophilic’’ ligands, analogous to the hydrophilic ligands used in aqueous biphasic catalysis. This is accomplished by incorporating so-called ‘‘fluorous ponytails’’.

3.6.4 Ionic liquids

Ionic liquids are quite simply liquids that are composed entirely of ions. They are generally salts of organic cations, e.g. tetraalkylammonium, alkylpyridinium, 1,3-dialkylimidazolium, tetraalkylphosphonium (Fig.3). Room temperature ionic liquids exhibit certain properties which make them attractive media for performing green catalytic reactions. They have essentially no vapor pressure and are thermally robust with liquid ranges of e.g., 300 °C, compared to 100 °C for water. Polarity and hydrophilicity/hydrophobicity can be tuned by a suitable combination of cation and anion, which has earned them the accolade, ‘designer solvents’.

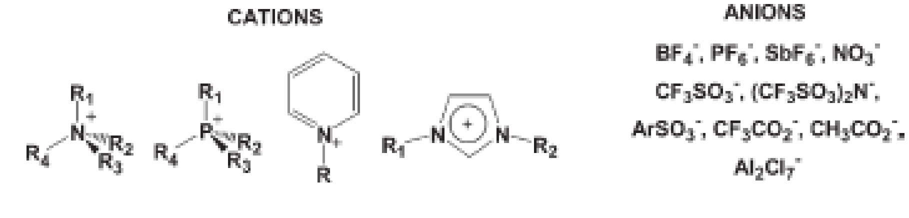


Fig. 3. Structures of common ionic liquids

Ionic liquids have been extensively studied in the last few years as media for organic synthesis and catalysis in particular. For example, the hydroformylation of higher olefins, such as 1-octene, was performed in ionic liquids.

4. Sources other than petroleum as raw materials

4.1. Carbohydrates as feedstock

The search is on for ways to marry the twin goals of economic development and environmental protection. One of the most promising strategies is to dramatically substitute biochemicals and other sources for petrochemicals. In the last decade technological advances have lowered the cost of producing high quality products from plant matter while environmental regulations have raised the cost of manufacturing and using petroleum derived products. The rebirth of a biological economy promises not only environmentally benign industries but a potential renaissance of rural America.

4.1.1. The past

Only a little more than 100 years ago most industrial products were derived from plant matter or, to a much lesser extent, from animals that fed on plant matter. Clothing was made from cotton or wool. Adhesives and glues were derived from corn and animal byproducts like bones and hides. Plant matter was the source of inks, paints, dyes, pharmaceuticals and most industrial chemicals. We read the word "synthetics" or "plastics" and immediately assume the product is made from petroleum. But the first commercial plastic, introduced in the 1880s, was actually made from cotton. Since cellulosic fibers comprise over 90 percent of cotton, the inventor dubbed the popular material, celluloid. In the 1920s, car radios were made from wood pulp derived plastics. The first film plastic is still available and also carries a name derived from its raw material: cellophane. The first synthetic fiber was cotton based rayon. Rayon is still a significant commercial fiber.

Today, 65 percent of our clothing is made from oil. Virtually all of our inks, paints, dyes, pharmaceuticals, plastics, and hundreds of intermediate chemicals are made from oil. The production of petroleum based plastics alone has expanded by more than 400 percent in the last two decades, to 30 million tons in 1990. Plastics are replacing glass, metals and paper in an ever expanding variety of products. Petroleum based products have even entered the food chain, with petrochemical based food dyes and, in some cases, petroleum derived vinegar.

4.1.2. The present

The biological economy substitutes biochemicals for petrochemicals. In the last decade a combination of technological advances and environmental regulation has opened up new markets for industrial products derived from plant matter.

The 20th century has been the age of the hydrocarbon. The 21st century should witness a rebirth of a carbohydrate economy. Living plants are again becoming attractive raw materials for manufacturers. The signs may be modest, but the conclusion is unmistakable. The pendulum is swinging back to a biological economy.

Some plastic bottles now are derived from a plastic manufactured by bacteria whose food is sugar. The colored ink sections of your local paper will more often than not contain vegetable oils, not mineral oil. Barbecue fluid may contain grain derived ethanol. Shampoo may contain vegetable oils and flower fragrances.

4.1.3. The benefits of a biological economy

A biological economy promises environmental and economic benefits. Environmentally, it benefits us by reducing our reliance on mining minerals and increasing our use of the stored chemical energy derived from sunlight, water, air and trace minerals in the soil. Economically, a biological economy benefits us by adding jobs and creating industries in poorer rural areas.

A biological economy must be based on sustainable cultivation and harvesting practices. The increased consumption of renewable materials must be matched by an increased commitment to agricultural techniques that preserve and enhance the quality of the soil.

Virtually all our non-energy, industrial product needs can be satisfied without expanding agricultural production. In fact, sufficient agricultural wastes exist to provide enough raw materials to displace almost all petrochemicals. Substituting biochemicals for petro-chemicals thus not only substitutes renewable materials for non-renewable materials but also finds uses for previously discarded materials.

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