Chapter 1

Introduction

In the sophisticated language ‘material science technology’ normally expressed by means of ceramics or crystalline materials, glasses or non–crystalline materials, polymers or long molecular chain materials and metals or cohesively bonded materials. [1]

1.1 Polymers

Polymers are defined as macromolecules composed of one or more chemical units (monomers) that are repeated throughout a chain. In Greek ‘poly’ means ‘many’ and ‘mer’ means ‘units’ [2-3]. A polymer is like a thread joins many coins punched through the centre, in the end we get a string of coins, the coins would be the monomers, and the chain with the coins would be the polymer. The basic part of a polymer are the monomers, the monomers are the chemical units that are repeated throughout the chain of a polymer, e.g. polyethylene monomer is ethylene, which is repeated x times along throughout the chain. Number of polymers, such as starch and proteins, occur obviously and have been used by human being. In reality, the body of man itself is partly created from polymer substance, such as the keratin of his hair and nails and strapping coiled beauty of the deoxyribonucleic acid (DNA) found in the every nucleus of the body cells. Now days, the material made of polymers finds multifarious uses starting from common household utensils, automobiles, furniture, etc to space the aircraft, biomedical and surgical operation. [4-5]

1.2 Historical development of polymers

Natural resins and gums were us various unique properties of the natural polymers have attracted the interest of researchers about a century ago and they were classed as ‘colloids’ to distinguish from crystalline material. The concept gradually changed with the improvement of researchers in synthetic polymer.

Polyethylene glycol was synthesized in 1860. Its structure was studied and was related to high molecular weight. Styrene and isoprene were polymerized in 1839 and 1879, respectively. To these polymers, cyclic structures held together by partial valences. [6-8]
Goodyear and Macintosh discovered the process of vulcanization of natural rubber in 1839. Cellulose derivatives were discovered by Hyatt in 1868. His product celluloid found application in the production of explosive and synthetic fibers. A team of scientists namely Cross, Bevan, Beadle and steam from England discovered viscose rayon fibers (1893-1898). Purely synthetic plastic was discovered by Baekeland (U.S.A). In 1907 belonging to the family of phenol formaldehyde resins is still a major industrial important. Cellulose acetate fibers were discovered in 1924. Alkyd resins and polyvinyl chloride was discovered in 1926 to 1927, respectively.

The first landmark in polymer science was reached in 1920, when Staudinger (Germany) put forth macro-molecular hypothesis. He proposed long chain formulae for polystyrene, rubber and polyoxy methylene. Carothers synthesized and characterized polymers and his analysis corroborated the macromolecular view point \[9-11\] In the middle of nineteenth century, brought out other discoveries, for example Neoprene (1931), polyvinyl acetate (1936), polystyrene, Buna S, Buna N (1937), nylon-66 (1938), melamine-formaldehyde resins (1939), butyl rubber (1940) were the important discoveries. \[12-15\]

During the period of World War II, Flory explained the mechanism for chain-reaction polymerization. Flory postulated that the ends of the long chain molecule consist of normal satisfied valence structure, which made possible the study of the presence and nature of end group by chemical method. \[16-20\]

During forties, the discoveries of polyethylene (1941), silicones, polyurethanes, styrene-butadiene rubber (World War II), epoxy resins (1947) aqueous biphasic systems (ABS) polymers (1948), polyester fibers (1950), and acrylic fibers (1948-1950) was prepared.

In the forties, Zeigler give to the science of polymer by his coordination complex polymerization. Natta explained the tactility in polymers and Swarc put up this research on interface poly condensation. This led to the development of high density polyethylene, polypropylene and polycarbonates were discovered in 1957, synthetics-poly isoprene and cis-polybutadiene in 1959 and ethylene rubber in 1960. \[17\]
In the sixties, Nuclear Magnetic Resonance (NMR) spectroscopy was useful to the polymer structure study. Phenoxy resins and polyimide resins were discovered in 1962. Polysulphones, styrene butadiene block co-polymer was discovered in 1965. The investigate for new plastic is an continuous process and new uses for the existing ones are constantly being developed so that the industry is always in a state of change. Billmeyer described the sequential progress of plastic materials.

1.3 Classification of polymers

Polymers include a large number of materials of high molecular weight. Polymers have dissimilar chemical structures, physical properties, mechanical behaviour, thermal characteristics, etc. Polymers can be broadly separated into two classes–natural polymers and synthetic polymers. Polymers found in nature (mostly from plant and animal) are natural polymers, and polymers synthesized in a laboratory or industry are synthetic polymers.

1.3.1 Natural polymers

The polymers obtained from nature (plants and animals) are called natural polymers. These polymers are very essential for life. Natural polymers contain starch, cellulose, polysaccharides, proteins, nucleic acid and natural rubber. Starches are polymers of glucose i.e. starch molecule consist of several hundreds of glucose molecules connected together. Cellulose is also a polymer of glucose. It's made by using the plant from glucose produced through photosynthesis. Similarly, protein is get as a result of polymerization of amino-acid. Protein, a long-chain polymer, sometime long cross-linked, is composed of 20-1000 amino acid in a highly organized arrangement. Another very significant natural polymer is rubber. It is a polymer consisting of repeat unit of the hydrocarbons normally known as isoprene (2-methyl 1, 3-butaaidiane).

1.3.2 Synthetic polymers

Synthetic polymers are artificial polymers. Most of the synthetic polymers are long-chain organic molecules surround thousands of monomer units, such as polyethylene, polystyrene, polyvinyl chloride (PVC), Bakelite, nylon and Dacron.
1.4 Conducting polymers

Polymers are traditionally regarded as electrical insulators; hence any conduction of electricity is regarded as an undesirable property. However, a new class of polymers known as intrinsically conducting polymers or electro active conjugated polymers has emerged during the past two decades. These novel materials with interesting and unanticipated properties have attracted the whole scientific community including polymer and synthetic chemists, material scientists, organic chemists as well as theoretical and experimental physicists. They exhibit interesting electrical and optical properties. The conduction of electricity in conducting polymers is due to the occurrence of delocalized molecular orbital.

1.4.1 History of conducting polymers

About 46 years ago, carbon based polymers were strictly referred as insulators. The trend has been changed after the discovery of conducting polymer. Conducting polymers are practically newer class of polymers. The metallic property of conducting polymer was first time reported in 1977 after the discovery of electrically conducting polyacetylene (PA). The consequence of the discovery of PA, the scientists concerned in this discovery were awarded the Nobel Prize in the year 2000 in chemistry. As like PA, there are many other key conducting polymers were made-up, synthesized and studied their variety of properties. The most frequent conducting polymers are polypyrrole (Py), polythiophene (PTh), polyaniline (PANI), etc. All these conducting polymers show a range of applications viz. a sensors, super capacitor, electro ceramic devices, corrosion inhibitor, polymeric batteries, etc. Such wide range application of these polymers just indicates that modification of properties is predominant by changing the monomer, or dopant included into the conducting polymer. [39]

1.4.2 Types of conducting polymers

The conducting polymers are broadly classified into following groups such as (a) Intrinsically / inherently conducting polymer (ICP), (b) Conducting polymer composites and (c) Ionically conducting polymer.

1.4.2.1 Intrinsically conducting polymer (ICP)

Intrinsically conducting polymers are also known as synthetic metals, because these organic polymers have electrical, electronic, and optical properties, which are the frequent properties of metal. The behaviour of metallic nature of conducting
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polymer can be obtained during mechanical properties, processability, etc. Polyacetylene, polypyrrole, polythiophene, polyaniline etc. are the examples of ICPs. The list demonstrate below (Fig.1) is the ICPs, which are acting as conjugated polymers (CPs). \[40\]

The extreme property of conjugated polymers is the existence of $\pi$ electrons, which are delocalized over a long portion of the chain. The structure of conducting polymer is planar. It is essential that, there should not be the force check angles due to which, the possibility of delocalization of $\pi$ electrons is decreases. \[41\]

Fig.1. (a) Polyethylene dioxythiophene (PEDOT), (b) Polypyrrole (c) polythiophene (d) polyacetylene and (e) polyaniline

1.4.2.2 Conducting polymer composites

Materials like metals, metal sulfide and metal oxide are included in polymer matrix or vice a versa to form polymer nanocomposites, which shows interesting properties and applications.
1.4.2.3 Ionically conducting polymer

Ionically conducting polymers is the complex of polymer and metal salts, where polymer chain acts as a function of ligands. [42] The typical example of ionically conducting polymer is nafion.

Among the existing conducting polymers, polyaniline has attracted lots of attention in recent few years because of its superior properties over others. The major advantages of PANI are discussed below in detail.

1.5 Polyaniline

Polyaniline is largely popular because of ease synthesis, uniform conduction mechanism and superior environmental stability in the presence of oxygen and water. [43] Polyaniline was first time reported in the year 1862 by Letheby [44] after 100 years, it was reported in the year 1970 in three oxidation states. [45]

It is an intrinsically conductive polymer located in the subgroup of ionic electro active polymers (EAPs). It is a flexible polymer with similar characteristics to semiconductors. Advantages include its fairly low cost, simple production process and the compound’s stable conductive form. Disadvantages include little electrochemical strain, insolubility in the majority solvents and infusibility, which makes it inappropriate for melting processes. [46] However, solubility has been enhanced with the use of new solvents, such as dimethyl urea and N-methyl-2-pyrrolidone (NMP). Since, polyaniline undergoes decomposition upon heating above its critical temperature; synthesis was finished in its solution form. In general, polyaniline characteristically has relatively low strain (1−2 %), actuation stress in the range of 2−4 megapascals (MPa) and a conductivity of approximately 103 S/cm. [47] The common synthesis methods of polyaniline in various nanostructures forms are exposed in detail. [48]

1.5.1 Different classes of polyaniline

Polyaniline mostly exist in three different forms both salt and base versions of leucoemeraldine, emeraldine and pernigraniline. Leucoemeraldine is completely oxidized, emeraldine is half-oxidized and half-reduced and pernigraniline is fully reduced. The manufacture of polyaniline fibers would be rather easy if processing could be attain with the most preferred oxidation state and emeraldine salt (PANI-ES). However, the insolubility of polyaniline -ES, the only conductive form of polyaniline
requires a different approach to processing. Hence, the total process engages the translation of emeraldine base to leucoemeraldine base and eventually to emeraldine salt.

The increase in conductivity is reached by introduction the PANI in a doping bath, where ion move takes place. In the case of PANI, protonic acid doping engages the accumulation of protons to the polymer backbone. The resulting positive charge is balanced by negatively charged anions move from the doping bath, which is an aqueous and an acidic solution. Protonation also introduces a delocalization of a radical cation, termed a polaron. A polaron is fundamentally a charge carrier with a surrounding field of polarization. An enhancement in the doping levels is accompanied by the formation of a bipolaron, which is a pair of polarons. This formation reduces the abovementioned band gap between the valence band and the conduction band, making actuation possible.\[49]\ In the case of PANI, improved levels of doping are accompanied by an raise in conductivity, at the expense of fiber tenacity. Therefore, PANI must be subjected to a most favorable level of doping in order to achieve an appropriate balance between conductivity and tenacity. Structure of PANI can be obtainable by following general way as.\[40\]

![structure_of_pani]

1.5.2 Nanostructure forms of polyaniline

A nanostructure is an object of intermediate size between microscopic and molecular structures. Conducting polymer nanostructures have received increasing attention in both fundamental research and various application fields in recent years. Compared with bulk conducting polymers, conducting polymer nanostructures are expected to display improved performance in energy storage devices because of the unique properties which arises from their nanoscale size: high electrical conductivity, large surface area, short path lengths for the transport of ions, and high electrochemical activity. It was reported that nanostructures of polyaniline shows attention in the present time in nanoscale electronic and molecular devices. Nanostructures of polyaniline are in a controllable diameter, length and conductivity.
There are a variety of nanostructure forms of polyaniline including nanoparticles, nanofibers, nanotubes, nanospheres etc. The important forms are discussed below.

1.5.3 Polyaniline nanoparticles (NPs)
Preparation of different morphology of polyaniline nanostructures are time dependent. The variety of morphologies of polyaniline nanostructures can be controlled by the polymerization period. Nanoparticles (NPs) of polyaniline are illustrated in reference. [50]

1.5.4 Polyaniline nanofibers
One of the significant versions of polyaniline is in the form of nanofibers. The nanostructures, which are in the form of nanofibers have utmost aspect ratio and hence possess potential applications. Polyaniline nanofibers can be prepared by a variety of methods viz. oxidative chemical polymerization, electrochemical polymerization and electro-spinning polymerization methods. For the synthesis of polyaniline nanofibers [51] template methods were used and very a small number of methods are of template free. The template free methods are additional helpful as compared to with template as it involve more cost. In the synthesis of polyaniline nanofibers polymerization temperature, dopant, monomer concentration, mechanical disturbances and seeding strategy can influence the morphology. The uniform nucleation leads to formation of polyaniline nanofibers. The morphology of the polyaniline nanofibers are described in chapter 3.

1.5.5 Polyaniline nanospheres
Synthesis of polyaniline nanospheres is complicated as compared to polyaniline nanofibers. The development of nanofibers is more predominant than nanospheres at ambient situation. Due to the extra surface area polyaniline nanospheres are useful for optoelectronics and sensors. Polyaniline nanospheres are simply solvated due to the globular nature hence are preferable for spectroscopic study. The morphology of polyaniline nanospheres is given in reference. [52]

1.6 Nanomaterials
Today, nanomaterials shows an emerging, interdisciplinaty science that deals with the synthesis of polymer nanocomposites with scientific investigations. Overall, the nanomaterials has tremendous prospective in commercial and technological advances. The nanomaterials possess one or more dimensions of the order of 100
nanometer (nm) or less.\textsuperscript{[53-56]}

Fig. 2 Synthesis methods of nanoparticles (NPs)

1.7 Reduced graphene oxide (RGO)

Currently there is massive important in the physics, chemistry and material science concerning graphene and its allied materials. RGO is one of the allied materials. Single-layer graphite is known as graphene or graphene oxide (GO) and on reduction called as RGO.\textsuperscript{[57]} Graphene has been show to be a mounting superstar in the fields of material science, condensed matter physics and chemistry\textsuperscript{[58-60]} because of having surprising electronic, thermal, optical and mechanical properties.\textsuperscript{[60-63]} RGO morphology is described in chapter-3.

1.8 Polymer nanocomposites

In the field of nanotechnology, to develop the properties of polymer the nanoscopic materials are systematically dispersed in organic polymer matrix. The polymer with incorporation of nanoscopic materials is called as polymer nanocomposites.\textsuperscript{[64]} The polymer nanocomposites are the possible alternative for the conventional polymers due to the nanometre sizes and filler dispersion properties. The
organic polymer phase fills the nonporous of the composite inorganic materials providing outstanding mixing of the component phases in the nanocomposites. Synthesis and characterization of energetic polymer nanocomposites containing nanometre-size constituents are presenting a very active and exciting area to the researchers.

### 1.9 Conducting polymer nanocomposites

Modern technologies constantly require new materials with special combination of properties. Many efforts have been completed in the last decades using novel nanoscience and nanotechnology knowledge in order to attain nanomaterials with determined functionality. One such category of nanomaterial is the conducting polymer nanocomposite, polymer matrices unbreakable with nano-scale fillers, which has shown improved optical, electrical and dielectric properties.\(^{[65-67]}\) Conducting polymer nanocomposites are materials in which nanoscopic particles, typically 1 -10 nm are dispersed in a conducting polymer matrix. The conducting polymer inorganic nanocomposite / inorgano-conducting polymer nanocomposites can be prepared by \emph{in-situ/ ex-situ} polymerization method.

Electrically conducting polymers, termed ‘fourth-generation polymeric materials, with their exceptional redox properties, when doped appropriately, may have electrical conductivities ranging from insulator to metallic.\(^{[68]}\) In the research of conductive materials. Two classes of polymer material viz. intrinsically conductive polymers (ICPs) and metallic nanoparticles filled polymer composites have been studied.\(^{[69,70]}\) They are significant promising materials with the potential of various applications, e.g. in static charge dissipation, electromagnetic shielding, light emitting diode (LED) displays, gas sensors, biosensors, pressure sensors, corrosion protection of metals, semiconductors, transistors, light weight batteries, etc. PANI has been broadly studied because of its stability and tunable electrical properties.\(^{[71]}\)

Inorganic nanoparticles of different nature and size can be combined with the conducting polymers, which forms to a host of nanocomposites with attractive physical properties and significant potential application.\(^{[72]}\) Now a day, the low carbon economy of sustainable and renewable resources has become a challenge due to climate change and the decreasing accessibility of fossil fuels. It is now necessary to develop new, low-cost eco-friendly energy conversion and storage systems. Advances have previously been made in energy storage, which includes super capacitors.
Conducting polymers (CP) such as polyaniline, polypyrrole, polythiophene, poly (3, 4-ethylene dioxythiophene) (PEDOT) etc. are the significant electrode materials in micro size for pseudo-capacitors compared with bulk conducting polymers. Conducting polymer nanostructures is expected to show enhanced performance in technological applications because of the exceptional properties, which arise due to nanostructures. Material chemists have made efforts to design and synthesize conducting polymer nanocomposites to understand high electrochemical performance.\[73\]

In current epoch, the conducting polymer nanocomposites (CPNCs) and their applications has seen important surge in research.\[74\] Polyaniline has been widely investigated by various research groups, mainly for the exploitation of its fascinating physico-chemical properties viz. high conductivity, humidity / gas sensing, redox, ion-exchange, excellent environmental stability and ease of preparation from general chemicals.\[75\] Recently, polyaniline in the form of different nanostructures has involved more attention as an exceptional material for supercapacitor irrespective of its stability.\[76\] However, the stability and electrochemical activity of polyaniline is extremely low, which needs additional improvement.

Particularly, transition metal oxides filled polyaniline nanocomposites have been attempted, which are more appropriate material for supercapacitor than pristine polyaniline. Polyaniline NCs can be prepared by just blending of polymers and other materials in the form of metal, oxides, sulfides etc.\[76,77\] As refer to earlier, polyaniline is an exceptional material for supercapacitor, but nanocomposites of polyaniline is still in the developing stage. Some transition metal oxides, such as ruthenium oxide (RuO₂), iridium oxide (IrO₂), magnese oxide (MnO₂), nickel oxide(NiO), tin oxide (SnO₂), iron oxide (Fe₂O₃), copper oxide (CuO), tungsten oxide (WO₃), vanadium pentaoxide (V₂O₅), titanium oxide (TiO₂) exhibits tremendous properties as pseudocapacitive electrode materials. These materials have some of serious boundaries.\[78-79\] Nanoparticles of transition metal sulfides based polyaniline nanocomposites also been reported. Molybdenum sulphide (MoS₂), tungsten sulphide (WS₂), silver sulphide (Ag₂S) and vanadium sulphide (VS₂) etc., have been successfully recognized as a new concept for supercapacitor.\[80-86\]

Recently, metal oxides, metal sulfides, graphene oxide, reduced graphene oxide (RGO) also been reported as an exceptional material for super capacitors.\[13-17\]
Some of the conducting polymer nanocomposites are discussed below, which are used for the energy devices. General steps involved in the synthesis of polyaniline - metal/ metal oxide/ metal sulfide nanocomposite is given below.

Fig. 3 General representation of synthesis of the PANI nanocomposites

1.9.1 Polyaniline–Metal Nanocomposites

The nanocomposites shows remarkable applications when they are in well organized structure present a new functional hybrid with synergistic properties over their single component counterparts. [87, 88] The fillers assist the reinforcement of polyaniline, which play a most important role in strengthening the properties. Homogeneous dispersion of the nanoparticles produces an ultra large interfacial area per volume between the filler and polyaniline. [89] The composites based on polyaniline and metals can be prepared in numerous ways. Some of the ways are easy blending of both components, [90, 91] the polymerization of aniline in the presence of preformed metal nanoparticles, [92] the deposition of metal on conducting polymer, [93, 94] the reduction of metal compounds with PANI [95–97] and the oxidation of aniline with metal compounds [98–100].

1.9.2 Polyaniline - Metal oxide Nanocomposites

polyaniline has been extensively investigated by different research groups, mostly for the exploitation of its attractive physico-chemical properties, such as high
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conductivity, humidity / gas sensing, redox, ion-exchange, outstanding environmental stability and ease of preparation from common chemicals. Recently, PANI in the form of different nanostructured has fascinated more attention as an important material for supercapacitor irrespective of its stability.

Owing to the matter of stability and activity of polyaniline, a number of other materials have been investigated for supercapacitor, mostly transition-metal oxides used for the synthesis of PANI NCs which are more appropriate material for supercapacitor than polyaniline.\cite{101}

1.9.3 The polyaniline metal sulfide nanocomposites

Polyaniline has been widely studied and synthesized for electronic applications.\cite{2} NPs of transition metal sulfides have been anchored into the polyaniline layer, because of different valence states, which are more helpful in a variety of applications.\cite{102,103} The nanomaterials viz. nanotube, fullerene-like nanostructure and graphene analogues shown huge potentials from the past decades.\cite{104-105}

There is an increasing interest in improvement of binary metal sulfide CPNCs by the scientific community. It is not easy to prepare binary / ternary metal sulfide alone in an H$_2$S atmosphere, because it requires high temperature due to which the bulk metal sulfide is obtained instead of nanomaterial.\cite{106-108} These sulfides are non-oxidizing and hence they are not appropriate for polymerization.

1.9.4 Polyaniline reduced graphene oxide nanocomposites

RGO has been synthesized via a simple chemical process, which has a potential to be used in a range of nanoelectronic devices. Several methods have been reported for the preparation of RGO viz. lithography, sonochemical and chemical vapor deposition (CVD).\cite{109} Controlled morphology of RGO has not yet been well studied due to different process parameters and steps involved in the synthesis. The CVD is one of the largely popular, powerful and well controlled method to synthesize required morphology and structures of RGO.\cite{109-117} But, the difficulty remains with CVD method as it yields poor quality RGO and also shows low electrochemical performance.\cite{111,113} Chemical methods were found to be economical and effective for producing RGO by chemical treatment from a variety of precursors. Therefore, chemical methods are more appropriate for synthesis of high-performance RGO and RGO based nanocomposites.\cite{118} The challenge remains with the preparation of high
quality crystalline RGO in great area single sheet and has not yet been determined completely.\[111\] However, the reduction of GO to RGO is not completed entirely by using hydrazine hydrate, which again shows the properties of GO. It is well known that the hydrazine hydrate is toxic, carcinogenic and unstable. Hence, it is necessary to search extremely efficient and eco-friendly reducing agent for the synthesis of the RGO. The conducting polymer like PANI, may be resolve the issues even though there is a weak attraction between RGO and PANI,\[119\] which is an effective way out over the harsh reducing agents.

1.9.5 Metal –Metal oxide nanocomposites (Binary oxides)

Polymorphic forms of lithium vanadium oxide (LVO) nanotubes (NTs) have the characteristic properties and now extensively used in electronic applications.\[120\] The operating properties and applications of electronic devices depend not only on the oxidation state of vanadium, but also on its structure. The silver- lithium vanadium oxide nanocomposites have also been used as energy storage devices.

The conducting polymers like polyaniline have been tested for various electrochemical devices especially for supercapacitor. The polyaniline along with metal/ metal oxide/ metal sulfide etc. in the form nanocomposite also been tested for supercapacitor. The polyaniline in the form of nanocomposite shows enhanced specific capacitance as compare to polyaniline alone.

The energy stowage in such a type of nanocomposite shows much more electrostatic attraction and quick faradaic processes (pseudo-capacitance). It has been also shown that metal/ metal oxide/ metal sulfide plays the role of a perfect backbone for homogeneity. It is familiar that polyaniline is mechanically weak; hence, the metal/ metal oxide/ metal sulfide preserve material from automatic changes throughout long cycling. Apart from excellent conducting and mechanical properties, the presence of metal/ metal oxide/ metal sulfide also improves the charge transfer that assists a high charge/discharge rate. It is also notable that such type of polyaniline -metal/ metal oxide/ metal sulfide composite does not need any binding substance that is a chief practical benefit.\[101,121\]

1.10 Supercapacitor

The storage of electrical energy through a double layer charging and faradic processes or combination of both the device is known as supercapacitor. The stored quantity of energy is usually less and will be provided very quickly when
supercapacitor is ready to supply power rather than energy. Supercapacitor convey by different terms viz. ‘double-layer capacitor’, “ultra capacitor”, ‘power capacitor’, ‘gold capacitor’, ‘power cache’ or ‘electrochemical double-layer capacitor’.\textsuperscript{[121-125]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{supercapacitor_construction.png}
\caption{Construction of supercapacitor}
\end{figure}

1.11 Double layer capacitance

According to the intrinsic principles of charge storage and discharge in supercapacitors, there are two kinds of capacitance viz. double-layer and pseudocapacitance. The double layer capacitance involves non-faradic process, whereas pseudocapacitance involves a periodic process. The double layer obtained on separation of ionic charges (or electronic charges) arises at interfaces between solids and ionic solutions, especially in colloids, metal electrodes and semiconductors. An amassing of charges ($\Delta q$), of contrasting sign takes place across boundaries to an extent that is dependent on the potential of electrode ($\Delta V$) (related to the potential alteration built up across an interface).
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This consequences in a capacitance \( C = \Delta q / \Delta V \) or \( d(\Delta q) / d(\Delta V) \), which is referred to as the ‘double-layer’ capacitance. Charge storage in accurate double-layer capacitors is solely electrostatic in nature (separation of ion and electron charges) with no chemical reaction is involved. Consequently, charging and discharging is extremely reversible and takes place practically instantaneously. Sometimes double layer also known as Helmholtz layer. \(^{[126]}\)

1.11.1 Theory of double layer capacitance- supercapacitor

A charged layer appears at the interface between metal and an electrolyte. The ions created the charge on electrolytes, whereas on conductor by electrons or holes. For creating electrical neutrality the other layer having opposite charges should be formed.

In the Fig. 5 it was shown that in the viscous electrolyte the flat potential is obtained at the edges it is relatively more so that the static resistance increases. It is expressed by a variety of theories as explain below.

(A) Double Layer capacitance: Helmholtz model I

This is the simplest model of charge distribution in between metal–electrolyte interface. The ions are in solution having some distance from metal. The rate of diffusion is infinite. The model was proposed by Helmholtz in 1970. The negative potential is presented by \( U = \Phi_{\text{Metal}} \) and the electrolyte potential is presented by \( U = \Phi_{\text{solution}} \). The same number of negative ions has left the solvent to collect on the positive electrode. In the electrolyte remains "paires" negative and positive ions which are not used at the interface to insure the potential difference \( \Phi_{\text{Metal}} - \Phi_{\text{Solution}} = Q / C \). The ions form a compact mono-layer on the surface at a distance of about 1 nm. This distance is considered as the layer thickness. It depends on the ion size and voltage.

(B) Double Layer capacitance: Gouy –Chapman Model II

This model can be explain on the basis of following laws and assumptions

- Thermal fluctuation
- Ions are still considered as point charges
- Boltzmann energy distribution law, \( N_i(x) = N_i \exp \left( - \frac{z_i e (\Phi(x) - \Phi_{\text{Solution}})}{kT} \right) \)
- Poisson electrostatic law \( \Delta \Phi(x) = - \frac{\rho(x)}{\varepsilon} \) with \( \rho(x) = \sum z_i e N_i(x) \)
- Diffuse ion distribution layer given by Fick law
In the above Boltzmann distribution equations, $N_i$ is the ion concentration in the electrolyte far from the interface, $z_i$ the number of charge of the ion, $e$ the electron charge. $k$ is Boltzmann constant and $T$ is the absolute temperature.

**Fig. 5 Double layer charges and potential**

This model combines Helmholtz compact layer model with a diffuse ion layer. Ions have a finite size with solvated shell.

Smaller the ion, stronger is the salvation. Cations are generally more solvated than anions, which requires a correction because of the capacitance over estimation.

**1.12 Pseudocapacitance**

Pseudocapacitance is related with electro sorption of ions or metal adatoms and particularly some redox processes which is apart from the double-layer capacitance.
Pseudocapacitance occurs due to the thermodynamic reasons, the charge \( q \), required for progression of an electrode process, e.g. electrosorption or redox conversion of an oxidized species to a reduced species in liquid or solid solutions and is a function of potential \( V \). So, the derivative of charge with respect to change in voltage \( \Delta q/\Delta V \) corresponds to a faradic capacitance (or pseudo capacitance). Thus pseudo capacitance can be related with either a redox reaction, for which potential is a logarithmic function of the ratio of activities of the oxidized species or with a process of progressive occupation of surface sites on an electrode by an under potential-deposited species. Pseudo capacitance arises, when the conducting polymer i.e. PANI is being charged. It loses electrons and becomes polycations, causing the anions in the solution to intercalate into the conducting polymer in order to maintain electro-neutrality. \(^{128}\)
1.12 Motivation of the work

Batteries and low temperature fuel cells are characteristically low power devices, whereas conventional capacitors may have a specific power of >106 W/Kg at very low specific energy. Supercapacitor fills the gap between batteries and conventional capacitors in terms of both specific energy and power i.e. they have a specific power as high as conventional capacitors and a specific energy close to that of batteries. Therefore, supercapacitor can get better battery performance in terms of power density when combined with batteries. In conclusion of this work, the supercapacitor is a promising alternative approach to meeting the growing power demands of energy-storage systems in general and in particular for portable electronic devices (digital).

Polyaniline nanocomposites are used as a model material to thoroughly investigate the synthesis, properties and applications of nanostructures of conjugated polymers. To begin, a conceptually new synthetic methodology is developed that readily produces high-quality, small-diameter nanofibers in great quantities. Next, the impact of this nanofibrillar morphology on the properties and applications of polyaniline is discussed. For example, it has been found that the nanofibers significantly improve the processability of polyaniline and its performance in many conventional applications involving polymer interactions with its environment.\textsuperscript{[129,130]} This leads to much faster and more responsive chemical sensors, new inorganic / polyaniline nanocomposites and ultra-fast non-volatile memory devices. Moreover, the extremely conjugated polymeric structure of polyaniline produces new nanoscale phenomena that are not accessible with current inorganic systems. As an example, the discovery of an enhanced specific capacitance, good responsive and recovery time that produces welding of the polyaniline with metal oxide, sulphide etc. are presented.
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