1.1 Introduction

Polymer is a large molecule (macromolecule) composed of repeating structural units connected by covalent chemical bonds. The word is derived from the Greek words (poly), meaning manyand (meros), meaning parts [1]. For a long time, polymers were considered as nonconductors of electricity and were used as insulating materials for example, metal cables arecoated in plastic to insulate them [2]. It was a breakthrough, therefore, when Shirakawa found in 1971 that acetylene can be polymerized to give a free standing film with promising mechanical properties [3] and when, some what later, MacDiarmid and Heager [4] showed that polyacetylene becomes conducting by exposing it to oxidizing agents like iodine or arsenpentafluoride(AsF)[5] and its conductivity can be increased by 13 orders of magnitude to $l0^3$ to 10^4 S/cm . These findings initiated a lot of fundamental investigations, and gave rise to the development of a new class of materials, which combine the typical properties of plastics with electrical conductivity of metals.

1.2 Conducting Polymers

Polymers that are made by filling conducting materials such as carbon black,metal flakes, or metalized fibers by chemical and electrochemical synthesis methods arecalled conducting polymers.[6]The properties of polymers such as strength,elasticity, plasticity and toughness often compare withthose of metals and offer a lot of very importantadvantages over the latter, normally light weight, greaterworkability and economy. The important fundamentalproperty which distinguishes metals from polymers is theirvery high electrical conductivity of the order of10^4-10^6(Ohm)cm^{-1}[7]. Polymers have generally very highresistivity with conductivity around 10- 14 cm^{-1}andthis low electrical conductivity has led to widespreaduse of polymers as electrical insulators [8-9]. In spite ofthe low inherent conductivity of polymers, severalattempts were made

by researches to make them electricallyconducting.Conducting polymers so far developed fall into twodistinct groups. The first generation conducting polymerswere made by incorporating conductive filler or additivesinto the normally insulating polymer **.**

The major practical function of the polymer matrix inthese composites is to serve as a 'glue' to hold theconductive elements together in a solid entity. Theconductive filler which are the cause of electricalconduction are evenly dispersed in the polymer matrix.Kusy and Turner [10],and latter Bhattacharya et al. [11]reported the use of 6-10 weight % metallic powder as theconductive fillers, for moderate conductivity. They proposedthat the enhanced conductivity at comparativelylower loading of metallic powder is due to the formationof hexagonal ring structure of the metal powder in thepolymer matrix. But.these composites cannot be regardedas conducting polymers because the polymers present insuch composites are non-conducting. These types of polymersare not used as electrical conductor but used mostlyin electromagnetic interference shielding applications.The conductivity of these polymers varies as a function ofcharge incorporated in the polymer, and for charges upto20% by weight of the polymers, the conductivity rangesbetween $10^{-6}$and 10^{-1} (Ohm) cm^{-1}. The concentration of thecharge(metallic powders) cannot be increased beyond thislimit because then the charged polymers lose the mechanicalproperties of the host polymer and become lessuseful[12]. The second generation conducting polymers themselvesconduct electric current without the agency of anyadditives. The delocalized electron cloud and/or nonbondingelectrons provide the conduction path in the chainof molecules in these polymers.Most important is that the conducting polymers offered the promise ofachieving the most recent generation of polymers: materials which exhibit the electricaland optical properties of metals or semiconductors and which retain the

attractivemechanical properties and processing advantages of polymers.Conducting polymers are classified into two ways depending upon

- Nature of polymer and dopant (Figure 1.1)

- Conduction mechanism (Figure 1.2)

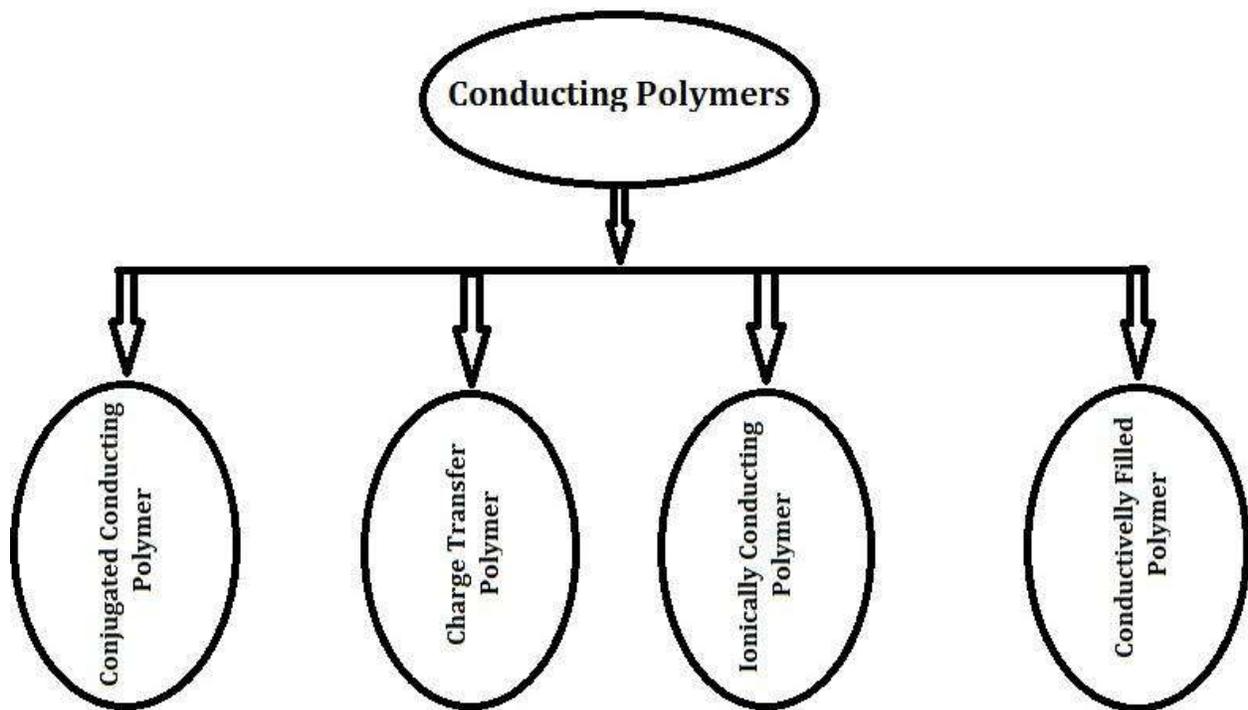## 1.2.1 Classification based on Nature of Polymer and Dopant

Figure 1.1: Classification of conducting polymers based on nature of matrix anddopant

The conductively filled conducting polymers were first made in 1930 for theprevention of corona discharge. The potential uses for conductively filled polymershave since been multiplied due to their ease of processing, good environmentalstability and wide range of electrical properties. Being a multi-phase system innature, however, their lack of homogeneity and reproducibility has been an inherentweakness for conductively filled polymers. Therefore, controlling the quality

ofdispersion to obtain homogeneous conducting polymer composites is criticallyimportant. The report of electrical conductivity in ionic polymers in 1975 (Wright, 1975)attracted considerable interest. Since then, various ionically conducting polymers orpolymer electrolytes have been prepared for a wide range of applications rangingfrom rechargeable batteries to smart windows. Polymer electrolytes are also highlyprocessable. The ionic conduction mechanism requires the dissociation of oppositeionic charges and the subsequent ion migration between coordination sites, whichare generated by the slow motion of polymer chain segments. Consequently,polymer electrolytes normally show a low conductivity and high sensitivity tohumidity. They often become electrically non-conducting upon drying.

The discovery of electrical conductivity in molecular charge transfer (CT)complexes in the 1950s (Akamatuet al., 1954) promoted the development ofconducting CT polymers, and led to subsequent findings of superconductivity withmolecular CT complexes in 1980 (Jerome et al., 1980) and with fullerene in (Iqbalet al., 1986). The conductivity in CT complexes arises from the formation of appropriate segregated stacks of electron donor and acceptor molecules and a certaindegree of charge transfer between the stacks. A desired crystal structure is,therefore, essential for good conductivity in the molecular CT complexes. However,the resultant materials are often brittle and unprocessable. To overcome thisproblem, attempts have been made to attach electron donor and/or acceptor moietiesonto polymer backbones to produce charge transfer polymers with goodprocessability and stacking properties.Along with all of the activities described above, various conjugated polymershave been synthesized during the past 25 years or so which show excellent electricalproperties (Skotheimet al., 1986). Owing to the delocalization of electrons in acontinuously overlappedπ-orbital along the polymer backbone, certain conjugatedpolymers also possess interesting optical and magnetic properties. These

unusualoptoelectronic properties allow conjugated polymers to be used for a large numberof applications, including protecting metals from corrosion, sensing devices,artificial actuators, all-plastic transistors, non-linear optical devices and lightemittingdisplays. Due to the backbone rigidity intrinsically associated with thedelocalized conjugated structure, however, most unfunctionalizedconjugatedpolymers are intractable (i.e. insoluble, infusible and brittle). Some of them are evenunstable in air[13-17].

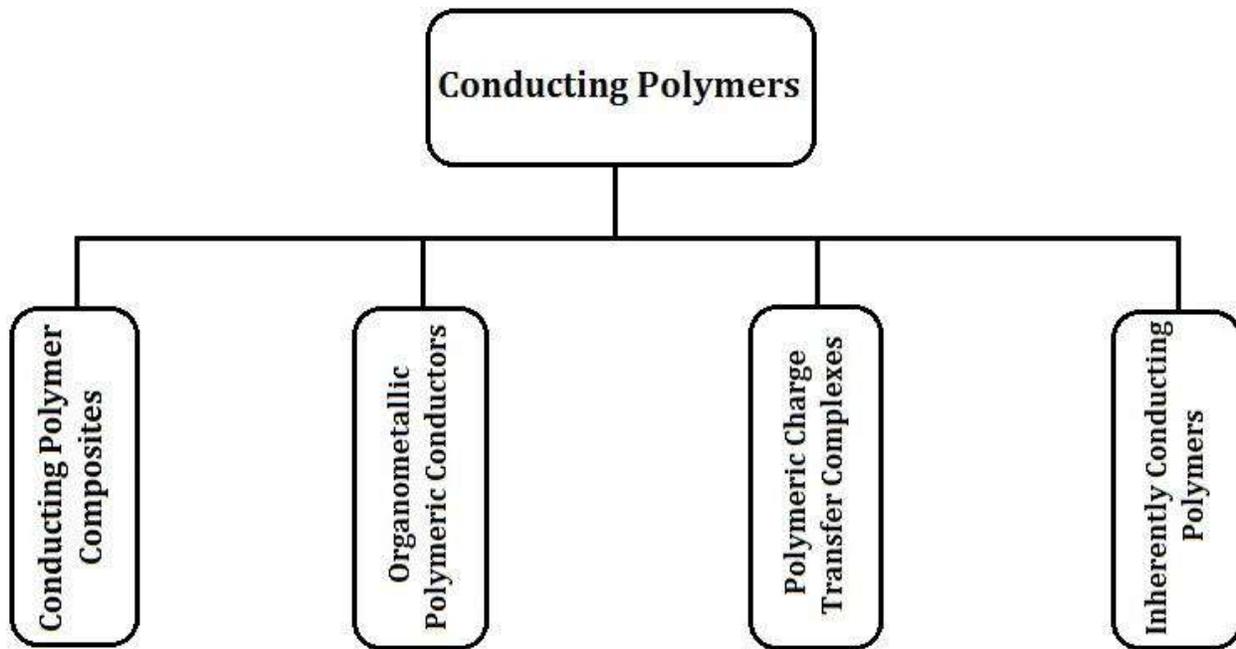## 1.2.2 Classification based on Conduction Mechanism

Figure 1.2: Classification of conducting polymers based on conduction mechanism

1.2.2.1 Conducting Polymer Composites

Conducting polymer composites are usually prepared by the addition ofconducting fillers in the insulating polymer matrix. Commonly, various materials such asconductive carbon black, graphite flakes, fibers, metal powders etc. are used asconductive fillers. These fillers are loaded in the common insulating polymers, whichhave been used as major matrix, like PC, PET, PP, PVC, HDPE, Nylon etc,to getconducting polymer composites or master batches. Because the conductivity isintroduced through the addition of the conducting components, various polymer materialsincluding both amorphous polymers can be made electrically conducting. The electricalconductivity of the polymer is decided by the volume fraction of the filler. A transitionfrom insulating to non-insulating behavior is generally observed when volume fraction ofconductive filler in the mixture reaches a threshold of about 25%.

1.2.2.2 Organometallic Polymeric Conductors

Organometallic polymers are made of over 40 elementsincluding main group of metals (Si or Ge), transitionmetals or rare earth elements in addition to the 10 elements(C, H, N, O, B, P, halides) which is found in organic polymers. Organometallic polymers are new materialswhich combine the low density and structural variationsand functional group varieties of organic materialswith electrical conductivity and the high temperaturestability features of inorganic compounds [18-19].Avariety of organometallic polymers have been synthesized.Some more important examples are as follows:Coordination polymers are polymers with covalentbonds in the repeating unit. Considerable work hasbeen done in this area. Among variety of applicationsof coordination polymers are thermally stable and conductingor semiconducting materials, and water basedcoatings which are environmentally friendly materialsin comparison with solvent based coatings.

1.2.2.3 Polymeric Charge Transfer Complexes

A charge transfer complex (CTC) consists of a "mixture"of an electron donating (D) moiety with an electron accepting (A) moiety. There must be some interaction of the orbitals of the two moieties, though the extent of this interaction may vary significantly. The two moieties can belong to the same molecule (intramolecular**CTC)** or to two different molecules (intermolecular CTC). The orbitals inter action usually requires a spatial proximity of the two moieties, andin this respect the intra and intermolecularcomplexes may not be that different. Intermolecular CTCs are known to form by appropriately bending a molecule to allow interaction between the electron-donor and the electron-acceptor parts**.** Probably the most important consequence of the CTC formation in "mixtures" of electron donors with electron-acceptors is (photoinduced) electron transfer. This phenomenon is the basis for a series of potential applications [20].

1.2.2.4 Inherently Conducting Polymers

Intrinsically conducting polymers (ICP), are more commonly known as "SyntheticMetals" Electricallyconducting polymers are of great interest because of potential applicationswhere they may replace metals and semimetals that require comparativelymore energy in processing. ICPs have electrical conductivity properties similarto inorganic semiconductors and as a result, are able to discharge static beforecharges reach unsafe levels. A need existed for novel electrically conductingpolymers with increased solubility, increased processability, and that can beprepared from inexpensive materials.The most common examples of intrinsically / inherently conducting polymers arePolyacetylene, Polyaniline, Polypyrrole, Polythiophene, Polyphenylene, Poly (phenylenevinylene) etc. Below Figure shows some of the conjugated polymers, which have beenstudied as intrinsically conducting polymers.Intrinsically conducting polymers have important applications in molecularelectronics, electrical displays, electromagnetic shielding,

printed circuit boards,rechargeable batteries, optical computers, variety of sensors and actuators, smartstructures in electronic devices, artificial nerves, drug release systems, antistatic clothingand inducting exchange membranes. One of the remarkable features of ICPs isthat it is possible to control conductivity of these polymers over a wide range frominsulating to metallic by proper doping [21-30].
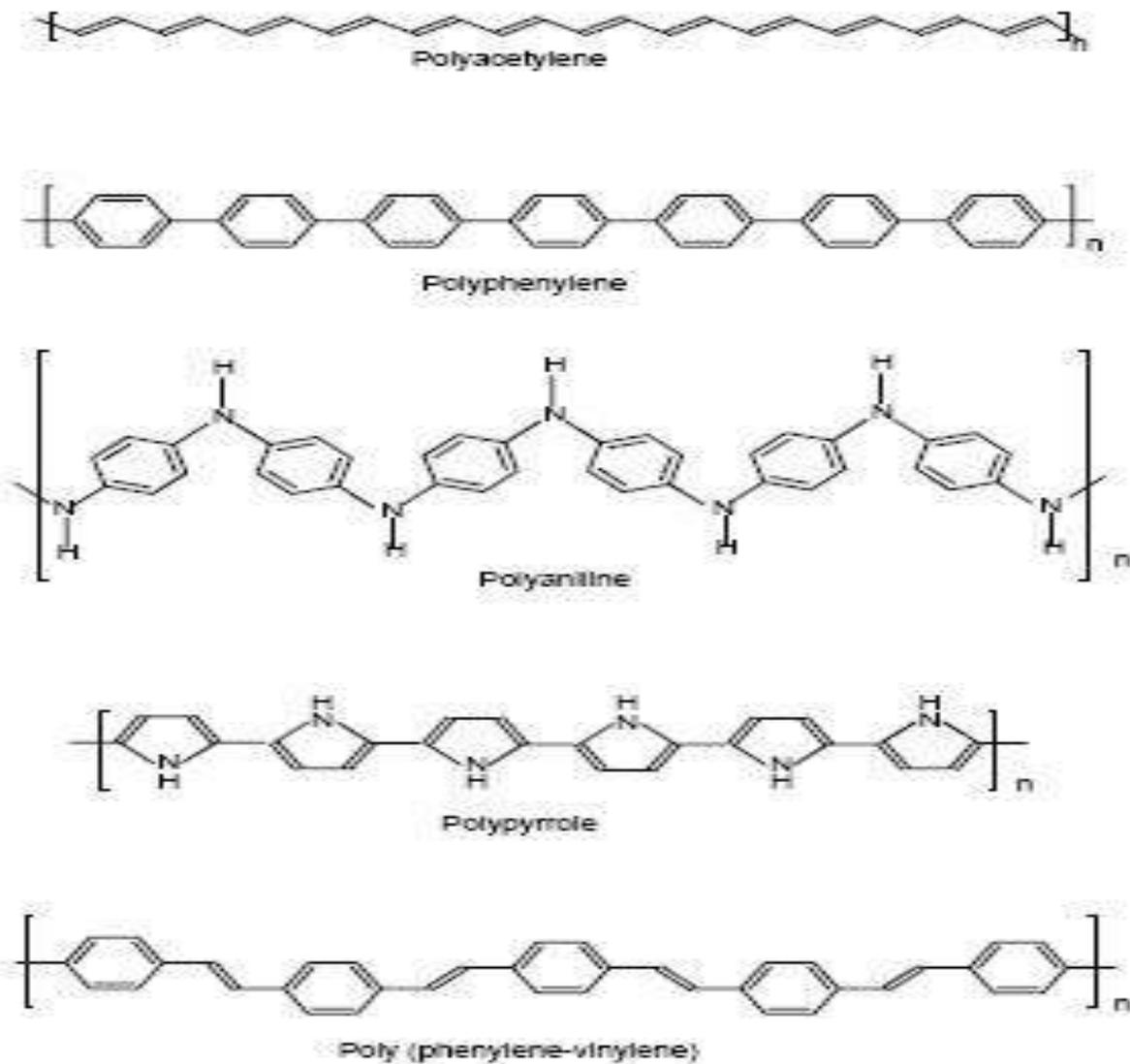
Polyacetylene

Polyphenylene

Polyaniline

Polypyrrole

Poly (phenylene-vinylene)

Figure1.3: Examples of conjugated polymers

1.3 Conjugated Conducting Polymers

Conjugated conducting polymers are the organic compounds that have anextended (π) orbital system and conjugated carbon system [31]. The conjugated polymersin their undoped, pristine state are semiconductors or insulators. As such, the energy gapcan be > 2 eV, which is too great for thermally activated conduction.

1.3.1 Structure and Properties

1.3.1.1 Conjugation

Table 1.1 lists the repeat units and conductivities for some common conjugatedpolymers [32] as can be seen in Table 1.1, the conjugated structure with alternatingsingle and double bonds or conjugated segments coupled with atoms providing π-orbitalsfor a continuous orbital overlap (e.g. N, S) seems to be necessary for polymers to becomeintrinsically conducting.This is because just as metals have high conductivity due to the free movement ofelectrons through their structure; in order for polymers to be electronically conductivethey must possess not only charge carriers but also an orbital system that allows thecharge carriers to move. The conjugated structure can meet the second requirementthrough a continuous overlapping of π -orbital along the polymer backbone. Due to itssimple conjugated molecular structure and fascinating electronic properties,polyacetylene has been widely studied as a prototype for other electronically conductingpolymers [33].
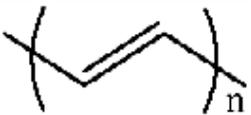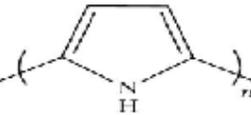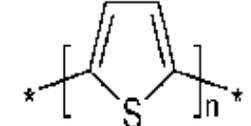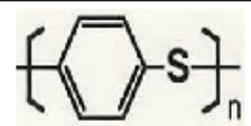
Polymer (Conductivity discovered)	Structure	Energy gap (eV)	Conductivity (S/cm)
Polyacetylene and Analogues Polyacetylene(1977)		1.5	$10^3 - 1.7 \times 10^5$
Polypyrrole (1979)		3.1	$10^2 - 7.5 \times 10^3$
Polythiophene (1981)		2.0	$10 - 10^3$
Polyphenylene and Analogues Poly(paraphenylene)(1979)		3.0	$10^2 - 10^3$
Poly(p-phenylene vinylene) (1979)		2.5	$3 - 5 \times 10^3$
Polyaniline (1980)		3.2	$30 - 200$
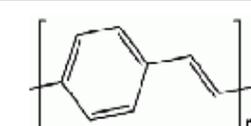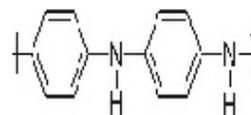
Table 1.1: Structure and conductivity of some conjugated conducting polymers

1.3.1.2 Doping

Since most organic polymers do not have intrinsic charge carriers, the requiredcharge carriers may be provided by partial oxidation (p-doping) of the polymerchain with electron acceptors (e.g. I_2, AsF_5) or by partial reduction (n-doping) withelectron donors (e.g. Na, K). Through such a doping process, charged defects (e.g.polaron, bipolaron and soliton) are introduced, which could then be available as thecharge carriers. In the case of I_2-doped trans-polyacetylene, it was

estimated thatnearly 85% of the positive charge is delocalized over 15 CH units to give a positivesoliton. In fact, the insulator-to-metal transition in conjugated polymers is not sosimple, and the way in which charges can be stabilized on the polymer chains andthe nature of the charge transport process are still a matter of debate. Nevertheless,the simple band theory can provide some useful information about the dopinginducedchanges in electronic structure.

During the doping process, an organic polymer, either an insulator orsemiconductor having small conductivity, typically in the range of 10^{-10} to 10^{-5} S/cm^{-1}, isconverted to a polymer which is in a „metallic" conducting regime (1 to 10^4 S/cm^{-1}). Thehighest value reported to date has been obtained in iodine-doped polyacetylene (> 10^5S/cm^{-1}). Conductivity of other conjugated polymers reaches up to 10^3 S/cm^{-1}. The dopantconcentration may be as high as 50%.The different types of doping are.

- **Redox doping**: It is the type of doping in which the number of electronsassociated with the polymer backbone changes. All conducting polymers, e.g.PPy, PANI, PT etc. undergo p or n-redox doping by chemical or electrochemicalprocess. p-doping was first discovered by treating trans- (CH)x with an oxidizingagent such as iodine.

- **Photo doping**: When trans-(CH)x is exposed to radiation of energy greater thanits band gap, electrons are promoted across the gap and polymer undergoes photodoping.

- **Non-redox doping**: In this type of doping, the number of electrons associatedwith the polymer backbone does not change during the doping process, butmerely the rearrangement of the energy levels occurs. The emeraldine base formof PANI was the first example of the doping of an organic polymer to a highlyconductive regime by non-redox type doping.

1.3.1.3 Doping Agents

Doping agents or dopant may be classified as:

- Neutral dopants are converted into negative or positive ions with or withoutchemical modifications during the process of doping. Ex: I_2, Br_2, AsF_2, Na, K,H_2SO_4, $FeCl_3$.

- Ionic dopants are either oxidized or reduced by an electon transfer with thepolymer and the counter ion remains with the polymer to make the system neutral.Ex: $LiClO_4$, $FeClO_4$.

- Organic dopants are anionic dopants, generally incorporated into polymers fromaqueous electrolytes during anodic deposition of the polymer. Ex: CF_3COOH,$CF3SO_3Na$.

- Polymeric dopants are functionalized polymer electrolytes containing amphiphilicanions. Ex: PVS, PPS, PS-co-MA.

- Metal Oxide dopants are known for their electron donor property. The oxygenatoms of the metal oxide contain lone pairs of electrons which help localization ofcharge in the polymeric chain, leading to the enhancement of conductivity of thehost polymer. Ex: CeO_2, TiO_2, SnO_2, WoO_3, CoO_3.

1.3.2 Band Theory

The electronic structures of metals, semiconductors and many solids may bedescribed in terms of band theory. The "chemical approach" to band theoryis to take molecular orbital theory, as it is usually applied to small, finite-sizedmolecules and to extend the treatment to infinite, three-dimensional structures.In the molecular orbital theory of diatomic molecules, an atomic orbital from anatom 1 overlaps with an atomic orbital on atom 2, resulting in the formation oftwo molecular orbitals (either ¾ orbitals or ¼ orbitals) that are delocalized overboth atoms. One of the molecular orbitals is "bonding" and has lower energythan that of the atomic orbitals.

At absolute zero temperature (0^0K), when the electrons all occupy the lowestavailable energy state, the energy in the middle of the highest occupied stateand the lowest unoccupied is the Fermi level [34]. This energy level separatesthe occupied from unoccupied electron levels. The corresponding energy is theFermi energy E_F. The location of the Fermi level in relation to the allowedenergy state is crucial in determining the electrical properties of a solid. Metals always have a partially filled free-electron band,so that the Fermi level corresponds to a level in the middle of the band and thismakes the metals electrical conductors. Semiconductors and insulators alwayshave completely empty electron bands at 0^0K. This means that the Fermi energylies between the bands, and consequently they are poor electrical conductors atambient temperatures.Most of the electronic properties of semiconductors can be described by referenceto the simplified energy band diagrams shown below. There are no partiallyfilled bands, just a filled valence band and an empty conduction band in a semiconductorat 0^0K. Therefore the Fermi level lies in the middle of the band gap.

Semiconductors can be divided into two groups: intrinsic and extrinsic semiconductors.

Intrinsic semiconductors are materials with relatively small band gaps. In thesecases, a number of electrons can be thermally stimulated across the band gap atroom temperature (300^0K) into the conduction band. Oncein the conduction band these electrons contribute to the electrical conductivity,as do the "holes" which are left behind in the valence band. When the temperature increases to a certain level, all the electrons in the donoror acceptor levels have been thermally promoted to the conduction or valenceband respectively. The concentration of extrinsic carriers attains its maximumvalue. At this stage the carrier concentration is independent of temperature andthe conductivity may show a gradual decrease with a further rise in temperaturedue to the mobility effect. This stage is called the "saturation" or "exhaustion". At still higher temperatures,

the energyprovided is sufficiently high so that the electrons in valence band are thermallyexcited to the conduction band, i.e., the intrinsic concentration of carriers exceedsthe extrinsic concentration. Both the concentration of carrier and the conductivityincrease sharply due to the exponential increase of charge carriers. When the semiconductor crystal is doped such that its intrinsic nature is modified, it is termed extrinsic. In an extrinsic semiconductor, the equilibrium number of free electrons and holes are no longer equal since a tool other than EHP(electron lone pair generation is used to create free carriers. Depending on the amount and type of impurity (or impurities) introduced, many electrical and optical properties of the semiconductor material may be modified or controlled to optimize desired behaviors or characteristics.

1.4 Polyaniline

1.4.1 Introduction

Polyaniline was first known in 1835 as "aniline black", a term used for anyproduct obtained by the oxidation of aniline. A few years later, Fritzchecarriedout the tentative analysis of the products obtained by the chemical oxidationof this aromatic amine. Subsequent investigators have verified theseresults, and similar observations have been made during the oxidation of aqueoushydrochloride acid solutions of aniline.The interest in polyaniline as an important conducting polymer has increasedsignificantly over the past decade, resulting in a number of review article publisheda few years ago [35-38]. At the same time, a number of groups looked atthe reaction conditions necessary to produce optimum equality polyaniline [39-41], but none of these studies the reaction at low temperatures. More recently,reports of high molecular weight polyaniline synthesized at temperatures of between-30°C and -40°C appeared, which used lithium chloride as an inert soluteto keep the reaction mixture mobile [42-45].These used either

a large molardeficit of ammonium persulfate oxidant to aniline, which gave a low yield of polymer,or electrochemical polymerization; but no attempts were made to assess thestructural quality of the polyaniline.The polyanilines, probably the earliest known synthetic polymer, [46-48], referto a large class of conducting polymers which have the following general formula.A large variety of derivatives can be prepared through substitution in the ringor on the N atoms. One of the special properties of polyaniline is that it canbe doped by protonic acids. Thus, the properties of the doped polymer can beturned by incorporating different dopant anions.It has been found that polyaniline can exist in three different, isolable oxidationstates at the molecular level [49]. They are the leucoemeraldine oxidationstate, the emeraldine oxidation state, and the pernigraniline oxidation state.Other oxidation states are the result of physical mixture of these oxidation states.

(i) **Leucoemeraldine base**: The fully reduced form of non-doped polyaniline. It is composed solely of reduced units as shown below:
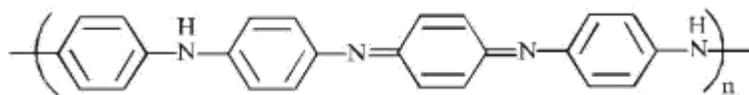

Figure1.4:Leucoemeraldine Base.

(ii)**Pernigraniline base**: The fully oxidized form of non-doped polyaniline. It iscomposed solely of oxidized base unite as shown below:
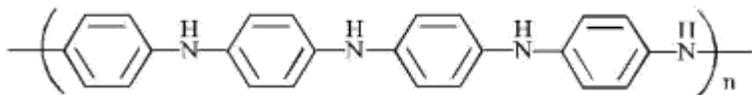
Figure1.5:Pernigraniline Base.

(iii)Emeraldine base: The intermediate oxidation state of polyaniline. It is composedof equal amounts of alternating reduced base and oxidized base units asshown below:
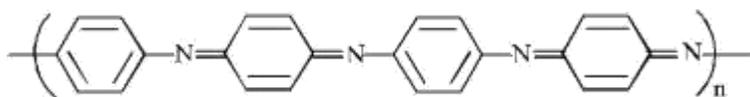

Figure1.6:Emeraldine Base.

The oxidation state of polyaniline can be precisely determined by volumetrictitration methods using $TiCl_3$ [50]. Several spectroscopic methods such as FTIR,Raman, and Uv-spectra can also provide qualitative information about the averageoxidation state of the polymer [51].

Methods of Synthesis

Polyaniline can be chemically or electrochemically synthesized by the oxidativepolymerization of aniline monomer in the presence of aqueous acid e.g., 1M HClsolution [52]. The formed polymer is called an emeraldine salt. For chemicalsynthesis, there are many different oxidizing agents, including: ammonium peroxydisulfate [52-53], hydrogen peroxide [54], ferric chloride [55] and ceric nitrate and sulfate [56-57]. Typically the ratio of oxidizing species to aniline has beenreported to be oxidant/aniline ~1.25 (a stoichiometric equivalent of oxidant)[58,59]. Other

chemical polymerization incorporate a stoichiometric deficiency ofthe oxidant with respect to aniline (oxidant/aniline ratio~0.25) [60].A typical chemical synthesis of polyaniline is carried out in aqueous 1M HClat a pH of >0 at temperatures between ~0°C and ~-4°C . It has also beenshown that higher molecular weight polyaniline (Mw>100,000) can be synthesizedwhen the polymerization is carried out at temperatures below -20°C [61-62]. Theneutral form of polyaniline, emeraldine base (EB), can be converted from thefully protonated emeraldine salt by deprotonation of the polymer with aqueousammonium hydroxide.

Polyaniline can also be synthesized electrochemically by the oxidation of anilineon an inert metallic (e.g., Pt) [63-64] electrode or on a piece of conducting Indium Tin Oxide (ITO) glass [65]. Electrochemical polymerization of anilinecan be carried out in acidic media by constant potential, constant current, andby repeatedly cycling the applied voltage between two pre-selected potentials. These polymerization methods offer the possibility of conveniently investigating various chemical and physical properties of polyaniline since spectroscopic techniquessuch as UV/Vis, EPR, Raman and FTIR may be investigated insitue.

1.4.2 Polymerization Mechanism

No matter whether polyaniline (PANI) is synthesized electrochemically or chemically,it is generally assumed that there is a close similarity in their polymerizationmechanism. In both cases, the polymerization process proceeds via the following mechanism. The first step is the formation of the radical cation by an electron transferfrom the 2s energy level of the aniline nitrogen atom, as shown in the Figurebelow

(a)   (b)   (c)   (d)
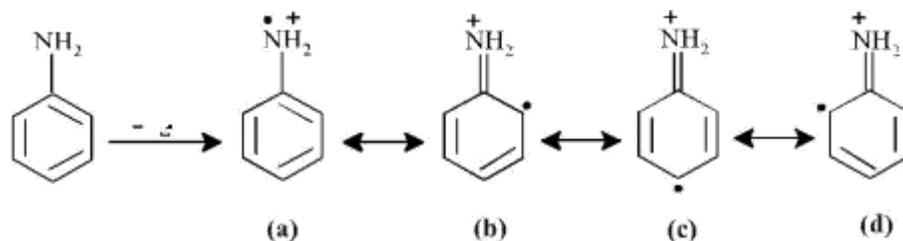
Figure1.7: The formation of the aniline radical cation and its different resonantstructures.

The formed aniline radical cation has several resonant forms, in which (c) is themore reactive one due to its important substituent inductive effect and its absenceof steric hindrance.The next step corresponds to the dimer formation by the so-called "head-totail"reaction between the radical cation and its resonant form (most probablyform (c) in acidic medium. Then the dimer is oxidized to form a new radicalcation dimer, as shown in Figure.

Figure 1.8: Formation of the dimer and its corresponding radical cation.

Next, the formed radical can react either with the radical cation monomer orwith the radical cation dimer to form, respectively, a trimer or a tetramer. If thiscontinues, similar to the above steps, the polyaniline (PANI) polymer is finallyformed as shown in Figure.
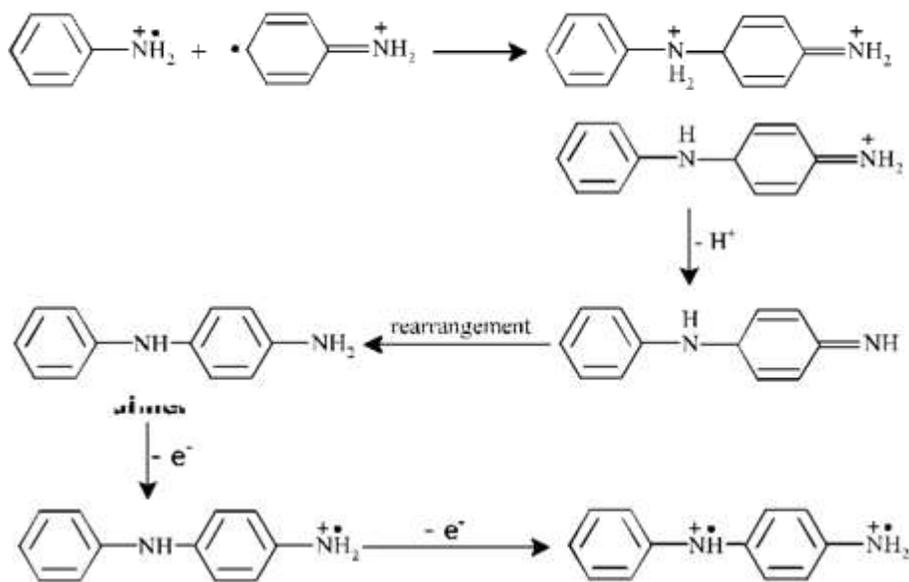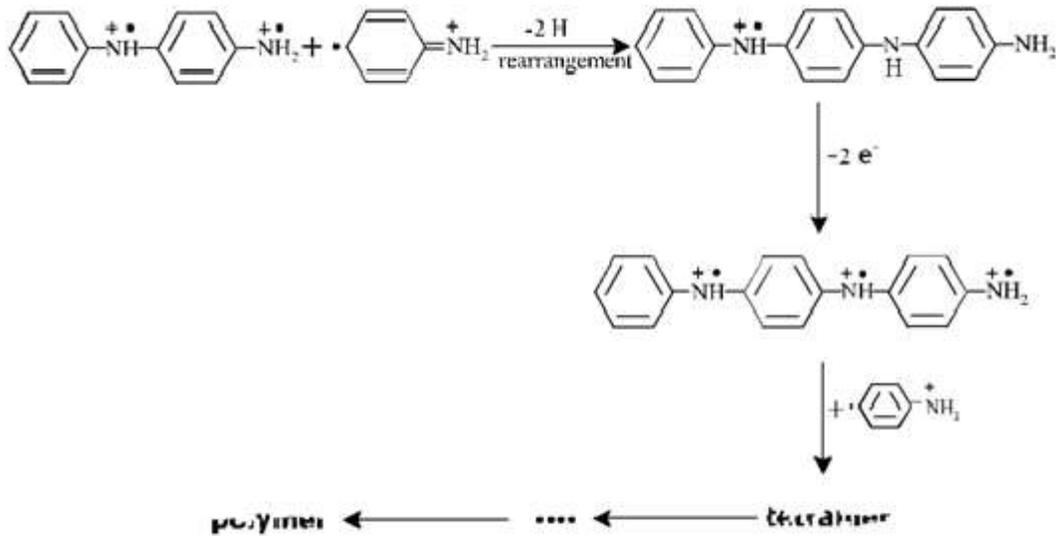

Figure1.9: One possible way of PANI polymer formation

At the end, it should be mentioned that beside idealized formation of p-coupledPANI chain in the reactions described above, some side reactions were also identifiedcoupling of aniline and its oligomers in "ortho" position;formation of benzidine groups ("tail to tail" coupling);chlorine substitution in aromatic ring (in systems with HCl and LiCl or NaCl);formation of N=N bonds (azo groups);[2] formation of N-CArgrafting bridges between chains;polymer hydrolysis (=O and -OH groups).All those reactions introduce undesirable elements to the structure of PANIand are considered as chain defects.

1.4.3 Properties and applications of Polyaniline

(i) Polyanilines electrical properties can be reversibly controlled by charge-transferdoping and protonation.

(ii) Polyaniline is environmentally stable and inert (noble) where stainless steelis corroded.

(iii) Polyaniline is applicable to electrical, electrochemical, and optical applications.

(iv) Polyaniline is currently used in cell phones and calculators, and other LCD technology etc.

1.5 Conducting Polymers in Sensors

Conducting polymers, such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) and theirderivatives, have been used as the active layers of gas sensors since early 1980s [66]. In comparisonwith most of the commercially available sensors, based usually on metal oxides and operated at hightemperatures, the sensors made of conducting polymers have many improved characteristics. Theyhave high sensitivities and short response time; especially, these feathers are ensured at roomtemperature. Conducting polymers are easy to be synthesized through chemical or electrochemicalprocesses, and their molecular chain structure can be modified conveniently by copolymerization orstructural derivations. Furthermore, conducting polymers have good mechanical properties, whichallow a facile fabrication of sensors.The conducting polymers mentioned in this review all refer to intrinsic conducting polymers. Theirmain chains consist of alternative single and double bonds, which leads to broad π-electronconjugation. Scheme 1 presents several typical conducting polymers used as the active layers in gassensors. However, the conductivity of these pure conducting polymers are rather low ($<10^{-5}S/cm^{-1}$). Inorder to achieve highly conductive polymers, doping process is necessary. The concept of doping is thecentral theme which distinguished conducting polymers from all other polymers [67]. Conductingpolymers can be doped by redox reaction or protonation, in which the latter is only applicable to PANI.In the development of long-lived electrochemical devices based on conducting polymers, the electrolyte plays an extremely important role. Good electrolytes should have high ionic conductivity, large electrochemical windows, excellent thermal and chemical

stability, and negligible evaporation rates. Room temperature ionic liquids are good electrolyte candidates that meet these requirements. On the other hand, conducting polymers possess desirable physical properties for electrochemical devices such as light weight, low cost, good redox capability, good processability, mechanical flexibility, and high charge capacity. In the present work, we combined the unique properties of ionic liquid electrolyte with those of conducting polymers to fabricate high performance and long lifetime electrochromic devices. More specifically, we have explored the application of ionic liquids in a) electrochemical synthesis of thin transparent films of conducting polymers (e.g., polypyrrole, polythiophene, and polyaniline) b) in the electrochemical characterization of conducting polymer thin films; and c) in the fabrication of stable conducting polymer electrochemical devices including electrochromic windows and numeric displays. An excellent lifetime of 1,000,000 cycles for the electrochromic devices has been achieved without change in the performance of the device.

Pi-conjugated electroactive and conducting polymers provide a range of properties potentially applicable to the aerospace industry,with conductivities ranging from 1 to 1000 S/cm, they are applicable to a range of EMI shielding applications. Material forms are accessible as powders for direct blending into composites, films which can be laid up in multi-layer prepregs prior to curing, and as conductive coatings on glass and polymer textiles. Especially highly conductive compositions can be considered for use in lightning strike protection. Solution processable compositions can be patterned and printed with potential utility in light-weight flexible electronics. The ability to electrically switch these polymers between redox states, in essence charged and neutral forms, provides a means for controllable conductivities and optical properties. Electrochromism (EC), changes in the absorption of electromagnetic radiation with electric field, shows these materials to be active from the UV, through the visible and infrared,

and even into the microwave region of the spectrum. Visible light can be used to provide color changing windows and surfaces, while IR EC provides a means for signature control.

1.6 Metal oxides

Metal oxides play a very important role in many areas of chemistry, physics andmaterials science.[68-72]. The metal elements are able to form a large diversity of oxidecompounds[73]. These can adopt a vast number of structural geometries with an electronicstructure that can exhibit metallic, semiconductor or insulator character. In technologicalapplications, oxides are used in the fabrication of microelectronic circuits, sensors,piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion,and as catalysts. In the emerging field of nanotechnology, a goal is to makenanostructures or nanoarrays with special properties with respect to those of bulk orsingle particle species[74-78] Metal Oxide nanoparticles can exhibit unique physical andchemical properties due to their limited size and a high density of corner or edge surfacesites. Particle size is expected to influence three important groups of basic properties inany material. The first one comprises the structural characteristics, namely the latticesymmetry and cell parameters13. Bulk oxides are usually robust and stable systems withwell-defined crystallographic structures. However, the growing importance of surfacefree energy and stress with decreasing particle size must be considered: changes inthermodynamic stability associate with size can induce modification of cell parametersor structural transformations[79-81] and in extreme cases the nanoparticle candisappear due to interactions with its surrounding environment and a high surface free energy. In order to display mechanical or structural stability, a nanoparticle must have alow surface free energy. As a consequence of this requirement, phases that have a lowstability in bulk materials can become very stable in nanostructures[82-

85].Among the transition metals oxides, aluminum oxide (Al_2O_3), zinc oxide (ZnO)[86], tin oxide (SnO_2) [87], tungsten oxide (WO3), titanium oxide (TiO2) [88], vanadiumoxide (V_2O_5), cerium oxide (CeO_2), iron oxide (Fe_2O_3), cobalt oxide (Co_3O_4) [89] etc. aremostly widely known oxides and industrially employed transition metal oxides since lastfifty years. These oxides have become important both scientifically and industriallybecause of their applications for sound and picture recording, data storage, humidity andgas sensors, conducting composite super capacitors, electrochromic display devices, etc.

In the present study the following transition metal oxides and Ferrite are used.

1) Nickel Oxide
2) Iron Oxide
3) Zinc Oxide
4) Zinc Ferrite

1.6.1 Nickel Oxide

Nickel oxide is the chemical compound with the formula NiO. It can be either agreen or black crystalline powder. The mineralogical form of NiO is bunsenite which isvery rare.NiO adopts the NaCl structure, with octahedral Ni and O2− sites as shown inFigure 1.10. The simple structure is commonly known as the rock salt structure. Likemany other binary metal oxides, NiO is often non-stoichiometric, meaning that the Ni:Oratio deviates from 1:10
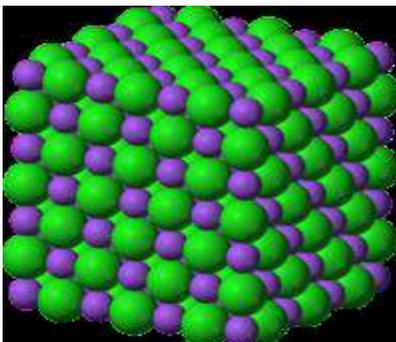

Figure 1.10: Crystal structure of NiO

NiO can be prepared by multiple methods. Upon heating above 400 °C, nickelpowder reacts with oxygen to give NiO. In some commercial processes, green nickeloxide is made by heating a mixture of nickel powder and water at 1000 °C, the rate forthis reaction can be increased by the addition of NiO [90].Nickel oxide has a range of applications such as:

1 Pigments for ceramic, glasses and glazes.

2Nickel oxide can be reacted with acids to form salts and other compoundse.g. nickel sulfamate for electroplating and nickel molybdate for hydrodesulfurization catalysts.

3Gold doped nickel oxide films can be used as transparent electrodes inoptoelectronic devices.

4 Nickel oxide is an anodic electrochromic material which has been widelystudied as counter electrodes with tungsten oxide in electrochromicdevices.some of the important properties of NiO. The molecular formula of nickel oxide is NiO,itscolour is green, molecular mass is 74.69g/mol and density is $6.67g/cm^3$.

1.6.2 Iron oxides

Iron oxides are chemical compounds composed of iron and oxygen. Altogether, there are sixteen known iron oxides and oxyhydroxides. Iron oxides and oxide-hydroxides are widespread in nature, play an important role in many geological and biological processes, and are widely used by humans, e.g., as iron ores, pigments, catalysts, in thermite and hemoglobin. Common rust is a form of iron(III) oxide. Iron oxides are widely used as inexpensive, durable pigments in paints, coatings and colored concretes. Colors commonly available are in the "earthy" end of the yellow/orange/red/brown/black range. Mostly used materials for the superparamagnetic core are iron oxides : magnetite Fe_3O_4 and maghemiteγ-Fe_2O_3.Both magnetite and maghemite have cubic

spinel structureMaghemite. Is formed by oxidation of magnetitecontains only trivalent Fe ions (91).

Its IUPAC name is iron (III) oxide, chemical formula γ-Fe_2O_3. It is Brownin color. Saturation magnetization of bulk material at 25^0 C is approximately 80 emu/g and its Crystal structure is similar to magnetite, but with vacancies in octahedral sites is due to oxidation of divalent iron ions.

Gamma phase

γ-Fe_2O_3 has a cubic structure. It is metastable and converted from the alpha phase at high temperatures. It occurs naturally as the mineral maghemite. It is ferromagnetic and finds application in recording tapes, although ultrafine particles smaller than 10 nanometers are superparamagnetic. It can be prepared by thermal dehydratation of gamma iron(III) oxide-hydroxide, careful oxidation of iron(II,III) oxide. Another method involves the careful oxidation of Fe_3O_4. The ultrafine particles can be prepared by thermal decomposition of iron(III) oxalate.

Its properties are its molecular formula Fe_2O_3, Molar mass 159.69g,mol^{-1} ,Appearance,Red-brown solid
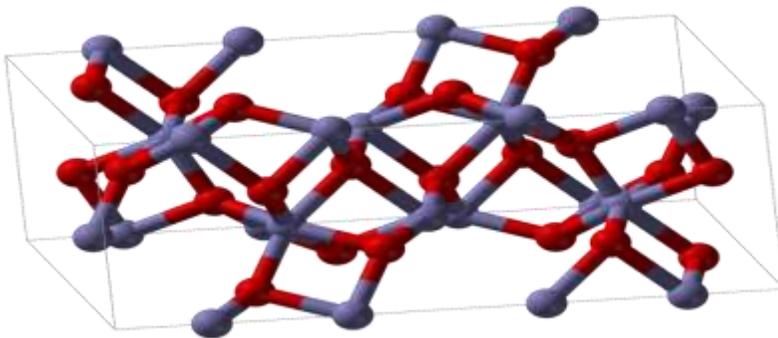

Figure 1.11: Crystal structure of Iron oxide

The two most commonly studied iron oxides have been magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are found naturally in the environment as particulate matter in air pollution and in volcanic eruptions. Either Fe_3O_4 (magnetite) or γFe_2O_3 (maghemite), particles can be generated as emissions from traffic, industry and power stations but can also be specifically synthesized chemically for a wide variety of applications .Various methods can be employed in their fabrication such as synthesis by water-in-oil microemulsion system, co-precipitation, reactions in constrained environments method, flow-injection synthesis and sonolysis Magnetic behavior is an important parameter in design and synthesizing of Superparamagnetic Iron Oxide NPs in order to maximally facilitate their imaging and therapeutic efficacy as these applications require high magnetization values. Although this can be accomplished by applying a maximum magnetic field acceptable under the clinical settings, the reaction conditions during the synthesis processes can be modulated to generate particle size with a large surface area, which in turn allows these particles to exhibit high magnetic .

1.6.3 Zinc oxide

ZnO is a versatile material that exhibits semiconducting, piezoelectric as well as pyroelectric properties. ZnO is a material that has a diverse range of nanostructures, whose configurations are far richer than any other known nanomaterials including carbon nanotubesZinc oxide is a group II-VI semiconductor that most commonly exhibits wurtzitestructure in its unstrained phase. It belongs to the C46v space group, also known asP63mc. At pressures above 8 GPa it undergoes a phase change to rocksaltstructure, It has also been shown to grow in zincblend phase as a thin film on GaAssubstrates[92].Electrical properties Zinc oxide (ZnO) has a wide direct band gap

(3.37 eV) and a relative large excitation binding energy (60 meV). Owing to its unique properties

wide band gap and large excitation binding energy, ZnO has the potential to be applied chemical

sensors, solar cells, luminescence devices etc. ZnO nanowires are also reported to have behaved

like a n-type semiconductor due to the presence of interstitial defects and vacancies [93- 97]. The

major roadblock of ZnO for widespread applications in electronics and photonics is its problems

with p-type doping. Quite a few p-type doping efforts have been reported like Ga and N co-

doping method which resulted in the formation of low resistivity (0.5 Ω/cm) p-type ZnO thin

films. Successful p-type doping for ZnO nanostructures will give a boost to their future prospects

in nanoscale electronics and in the field of optoelectronics. P-type and n-type ZnO nanowires can

serve as p-n junction diodes and LEDs. Field effect transistors (FETs) fabricated from them can

be used to make complementary logic circuits [98-102]. The Zinc oxide has the chemical

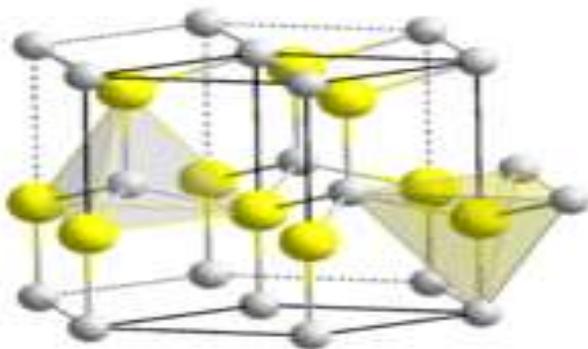formula ZnO,molecular mass 81.38g/mol, it is white solid and Crystal structure isWurtzite.

**Figure 1.12: Crystal structure of Zinc oxide**

1.6.4 FERRITES

Ferrites are chemical compounds with the formula AB_2O_4, where A and Brepresent various metal cations; usually including iron. Ferrites are a class ofspinels i.e. materials that adopt a crystal motif consisting of cubic closed packoxides with A cations occupying $1/8^{th}$ of the octahedral voids and B cationsoccupying half of the octahedral voids. For inverse spinel structure, half the Bcations occupy tetrahedral sites and both the A and B cations occupy the octahedral sites. Divalent, trivalent and quadrivalentcations can occupy the A andB sites and they include Mg, Zn, Fe, Mn, Al, Cr, Ti and Si.(103) .There are basically two varieties of ferrites: soft ferrite and hard ferrite.This is not a tactile quality but rather a magnetic characteristic. 'Soft ferrite'does not retain significant magnetism whereas 'Hard ferrite' magnetization isconsidered permanent. With the advent of 'spinel' ferrites [104], spin glassesand amorphous magnetic materials [105], a link between these emerging fieldsand 'rock' magnetism was established by Neel [106]. The termsantiferromagnetism and ferrimagnetism were introduced by Neel to explainthe properties of MnO and magnetite, Fe_3O_4, respectively. Explanation forantiferromagnetism behavior was proposed by Neel on the basis of thenegative inters atomic exchange coupling whereby the spins of neighboringatoms align antiparallel to each other. Thus, an antiferromangnetic materialconsists of two identical sublattices each of which is ferromagnetically orderedbut one is antiparallel to the other. For compounds exhibiting ferrimagnetism,the magnetic moments of the two sublattices are unequal; they do not cancelout but give rise to a net magnetic moment. Thus, ferrimagnetism can beconsidered as an uncompensated antiferromagnetism. The present dayclassification of materials is more elaborate and all different types of'magnetism' and their interrelationships have been discussed by Hurd [107].Naturally occurring magnetite is a weak 'hard' ferrite. 'Hard' ferrites possess amagnetism

which is essentially permanent. In time, man-made; 'hard' ferriteswith superior properties were developed but producing an analogous 'soft'magnetic material in the laboratory proved elusive. Spinel ferrites are important technological materials dueto their semiconducting and ferrimagnetic properties [108].Recently, ferrites due to their semiconducting behaviorhave been used as gas sensitive materials. A large numberof stoichiometric spinel ferrites, for example, $ZnFe_2O_4$, $NiFe_2O_4$, $CdFe_2O_4$, $MgFe_2O_4$, $CuFe_2O_4$, $CoFe_2O_4$, $NiZnFe_2O_4$, $MnZnFe_2O_4$, $MgZnFe_2O_4$, etc., have shown sensitivity to certaingases [109–114]. At the same time information about ferritegas sensors in comparison with single metal oxide gassensors is still limited and does not contain data about gassensing properties of complex or non-stoichiometric irondeficient or excess-iron spinel ferrite compounds, whichhave essentially different electrical properties.The conductivity in spinel ferrites is due to hopping ofcharge carriers (electrons or holes) between cations presentedby more than one valence state occupying the octahedralsites (115).

Zinc ferrites are a series of synthetic inorganic compounds of zinc and iron (ferrite) with the general formula of $Zn_xFe_{3-x}O_4$. Zinc ferrite compounds can be prepared by aging solutions of $Zn(NO_3)_2$, $Fe(NO_3)_3$, and triethanolamine in the presence and in the absence of hydrazine(116) or reacting iron oxides and zinc oxide at high temperature. Spinel (Zn, Fe) Fe_2O_4 appears as a tan-colored solid that is insoluble in water, acids, or diluted alkali(117). Because of their high opacity, zinc ferrites can be used as pigments, especially in applications requiring heat stability. For example, zinc ferrite prepared from yellow iron oxide can be used as a substitute for applications in temperatures above 350 °F (177 °C). When added to high corrosion-resistant coatings, the corrosion protection increases with an increase in the concentration of zinc

ferrite.(118). A recent investigation shows that the zinc ferrite, which is paramagnetic in the bulk form, becomes ferrimagnetic in nanocrystalline thin film format. A large room temperature magnetization and narrow ferromagnetic resonance linewidth have been achieved by controlling thin films growth conditions.

A site
(tetrahedrally coord.)

B site
(octahedrally coord.)

Oxygen
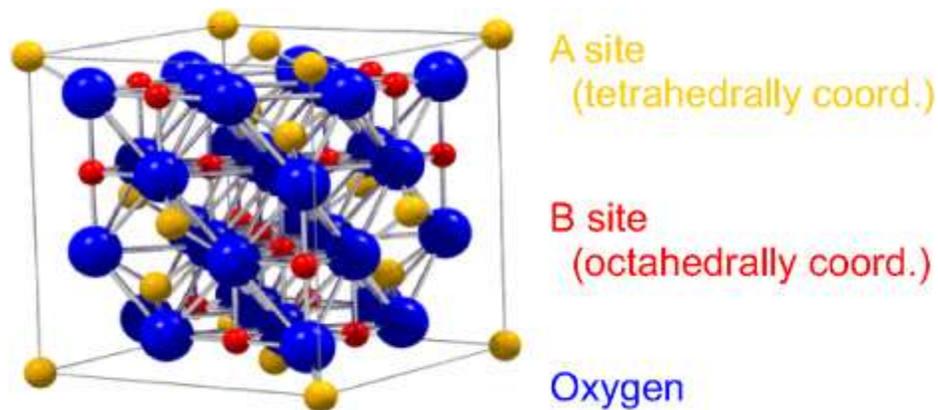
Zinc ferrite

1.7 Composite materials

A composite material can be definedas a combination of two or more materials thatresults in better properties than those of the individualcomponents used alone. In contrast tometallic alloys, each material retains its separatechemical, physical, and mechanical properties.The two constituents are a reinforcement and amatrix. The main advantages of composite materialsare their high strength and stiffness, combinedwith low density, when compared withbulk materials, allowing for a weight reductionin the finished part.The reinforcing phase provides the strengthand stiffness.

1.8 Classification of Composites

Composite materials are commonly classified at following distinct level:

The first level of classification is usually made with respect to the matrix constituent. The major composite classes include Organic Matrix Composites (OMCs), Metal Matrix Composites (MMCs) and Ceramic Matrix Composites (CMCs). The term organic matrix composite is generally assumed to include two classes of composites, namely Polymer Matrix Composites (PMCs) and carbon matrix composites commonly referred to as carbon-carbon composites.

1.8.1 Polymer-matrix composites

The wide range of processes used to produce reinforced plastics is partly new, and partly derivedfrom established methods of processing ordinary polymeric materials. The manner of combining fibresand matrix into a composite material depends very much on the particular combination in question andon the scale and geometry of the structure to be manufactured.

1.8.2 Metal-matrix composites

The basic attributes of metals reinforced with hard ceramic particles or fibres are improved strengthand stiffness, improved creep and fatigue resistance, and increased hardness, wear and abrasionresistance, combined with the possibility of higher operating temperatures than for the unreinforcedmetal (or competing reinforced plastics). These properties offer potential for exploitation in a range ofpump and engine applications.

1.8.3 Ceramic-matrix composites

Fabrication processes are complex and need to be carefully optimised because of the inevitablesensitivity of materials properties to microstructures controlled by processing conditions andinteractions. Much of the recent work on CMCs relatively familiar routes in attempting to reinforce glasses (like borosilicates) and glass-ceramics (likelithium

aluminosilicate or LAS and calcium aluminosilicate or CAS) with fibres such as the commercialNicalon and Tyranno varieties of silicon carbide(119-120).

1.9 Sensors

Sensor is a device that when exposed to a physical phenomenon (temperature, displacement, force, etc.)produces a proportional output signal (electrical, mechanical, magnetic, etc.). The term transducer isoften used synonymously with sensors. However, ideally, a sensor is a device that responds to a changein the physical phenomenon. On the other hand, a transducer is a device that converts one form ofenergy into another form of energy. Sensors are transducers when they sense one form of energy inputand output in a different form of energy. For example, a thermocouple responds to a temperature change(thermal energy) and outputs a proportional change in electromotive force (electrical energy). Therefore,a thermocouple can be called a sensor and or transducer.Many measuring and sensing devices, as well as loudspeakers, thermocouples,microphones, and phonograph pickups, may be termed transducers.Systems of sensors and transducers are constructed for a variety of applications includingsurveillance, imaging, mapping and target tracking. In some cases, the sensors providetheir own source of illumination and are referred to as active sensors. Passive sensors, onthe other hand, do not provide illumination and depend on variations of natural conditionsfor detection.

Active Sensors

Active sensors require the application of external power for their operation. This*excitation signal* is modified by the sensor to produce an output signal. They arerestricted to frequencies that can be generated and radiated fairly easily. This excludespart of the far infrared (above 3×10^{12}Hz), parts of the ultraviolet band and the gamma rayregion. However, inroads are being made into

these regions with the development ofTerahertz sources and detectors based on artificial photonic crystals.

Passive Sensors

Passive sensors directly generate an electric signal in response to a stimulus. That is, theinput stimulus is converted by the sensor into output energy without the need for anadditional source of power to illuminate the environment. The salient characteristics ofmost passive sensors are as follows:

• Do not emit radiation (or an excitation signal) as part of the measurement process.

• Rely on a locally generated or natural source of radiation (light from the sun), anavailable energy field (gravity) or even a chemical gradient

• Passive sensors can exploit EM radiation of any frequency in which some naturalphenomenon radiates and for which a detection mechanism exists. This canextend from ELF (below 3×10^3Hz) up to gamma rays (above 3×10^{19}Hz).

• They can exploit acoustic energy (vibration) from infrasound frequencies <1Hzfrom earthquakes or explosions up to the ultrasound(121).

1.9.1 Advantages of active and passive sensors

Passive Sensors arehavelow power requirement (long life),Cannot be detected (covert),Simple principles (sometimes),Good reliability due to simplicity,Field of view constrains observation,High angular resolution possible,Large variety.The advantage of Active sensors are ,Measurement requirements matched totransmitter characteristics,Range measurement by temporal correlation ,Radiation pattern constrains observation, High range and angle resolutions possible,Long range operation possible.

1.9.2 Gas sensors

Gas sensors have experienced a revolution similar to electronics, i.e., a decrease in size and power consumption. While at the beginning, resistive gas sensors were bulky and power consumption of a single device was typically a few hundred milliwatts, nowadays micromachined silicon technology has brought a dramatic decrease in size together with milliwatt power consumption. This has opened the possibility of developing portable analysers for many different applications such as alcoholmeters, fire detection units, carbon monoxide alarm monitors or analyzers for contamination within a fire, only to mention a few. The world market for resistive metal oxide gas sensors only was worth over 300 M € in 2011 with over 200 € M units sold. The technology favours the development of sensors with ever-decreasing size and power consumption. However, decreasing the size of the active area may lead to a decrease in sensitivity. Therefore, nanostructuring of the active layers has been the active and competitive area of research over the last few years. In particular, nanoscience and nanotechnology are enabling the explosion in the number of studies striving to overcome their drawbacks.

1.9.3 Metal oxide gas sensors

A generic chemical sensor is based on a sensitive layer that interacts with chemical or biological substances which are in contact with this layer and a transducer that converts the change in a chemical parameter into an electrical or optical signal, which can be measured. Gas sensors are a family within chemical sensors, where the chemical substance to be detected is present in the gaseous phase. There are different types of gas sensors depending of the sensing and transduction principles [122-123].MOX based gas sensors are semiconductor type and they are among the most studied. These sensors transduce a chemical signal into an easy-to-measure change in electrical resistance. The MOX sensors have been the subject of research for a few

decades.For resistive gas sensors, there are different parameters that can be monitored because they qualify the sensor performance. Some of these parameters are as follows:

- Conductance/Resistance: The most important parameter that is associated with this primary electrical property measured is to analyse gases.

- Base line: The conductance/resistance of the sensor in the reference or carrier gas, typically dry air.

- Sensitivity: The partial derivative of sensor response to gas concentration.

- Response time: The time taken to achieve 90 % of the final change in conductance. This parameter is used to determine practical applicability of a given sensor.

- Selectivity: The ratio between the response to a target gas and the response to interfering species .

- Stability: The chemical reaction at the surface of the sensor generates a long-term drift problem (poisoning). This problem can be minimised by a periodical calibration.

The porosity is one more important morphological parameter for the sensitivity, because if the material has a high porosity, the gas can enter into the material, and this results in an increase in the effective sensing area. The physical and chemical properties of the gas that has to diffuse within the pores of the sensing layer are of importance too and these parameters differ from gas to gas. The thickness of the sensing layer is another important parameter, in particular, if the sensing layer obtained is compact. Under these conditions it is possible to model the sensor resistance as two resistances in parallel, one in contact with the environment and another without the contact with the gas . Only the first resistance is a sensing resistance because it accounts for the sensor area that chemically interacts with the environment. On the other hand, the second resistance can be considered as a fixed resistance. The final variation of the resistance depends

on the ratio between the fixed resistance and the sensing resistance and the maximum sensitivity is obtained when the thickness of the fixed resistance tends to 0 (the value tends to ∞). Therefore, typical methods to increase the sensitivity of a metal oxide gas sensor is based on the reduction of the thickness of the layer with fixed resistance or the increase in film porosity. The deposition technique can affect the different factors that determine the final sensitivity of the sensor because it determines the crystal phase, porosity, grain size and thickness of the layer. Therefore, the deposition technique used is very important for determining the final gas sensing properties.[124-126].

A large number of different materials have their physical properties modified afterinteraction with a chemical environment such as ionic compounds (metal oxides), metals,polymers and supramolecular structures. Properties of the sensing materials, such asmolecular size, polarity, polarisability, and affinity, along with the matchingcharacteristics of the sensing material, govern the interaction.

1.9.4Applications of Sensors

Gas sensors have found wide applications in industrial production, environmentalmonitoring and protection, etc. [127- 128]. A variety of materials have been used for gassensing, which include electronic ceramics, oxide semiconductors, solid electrolytes, andconducting polymers [129]. A gas sensor gives an electrical output, measuring the change inproperty such as resistance or capacitance. Molybdenum oxide (MoO_3) which has similarphysical and chemical characteristics to WO_3 has recently drawn a lot of attention withregard to its gas-sensing ability [130].Recently, the controlled incorporation of molybdenum, tungsten and vanadiumpolyoxometallates into organic solid matrices has been attracting widespread interest inmaterials science due to the prospects for developing new functional materials. Suchinorganic–organic hybrid films have

been prepared by various methods, including ionexchange reactions within the interlayer space of ammonium amphiphile bilayer films,ion-complexing with ammonium amphiphile, electrostatic layer-by-layer self-assemblyand Langmuir–Blodgett deposition [131]. It should be emphasized here thatmolybdenum, tungsten, and vanadium polyoxometallates are potential precursors forMoO_3, WO_3, and V_2O_5, respectively, which are important as gas sensor materials [132].

Sensors have a wide range of applications and are constantly being extended to newareas. The following are some of the major areas of applications that can be identified.

- Humidity is one of the most common constituents present in the environment.Therefore, sensing and controlling humidity is of great importance in theindustrial processes, for human comfort, domestic purpose, in medicalapplications and in agriculture. Recently, there has been a considerableincrease in the demand for humidity control in various fields such as airconditioning systems, electronic devices, tyre industries, sugar industries anddrying processes for ceramics and food.

- Industrial hygiene has become very important because of the published healthhazards and related atmospheric pollution. The general public has becomemore sensitive to the various gases. As a result much effort is being focusedon producing relatively inexpensive sensors of medium sensitivity andselectivity to meet these needs.

- Another important area of application is in medical diagnosis of patients bymonitoring the humidity, oxygen and carbon dioxide concentration. Ourmedical applications include monitoring the environment for health hazardousgases and vapors including carcinogenic compounds not only within theconfines of industries associated with the use or production of such chemicalsbut also their spread through atmosphere by air movement.

Also, sensors ableto monitor the extent of contamination by all kinds of known or unknownmicro -organisms are expected to be in great future demand.

1.10 Literature Review

B. I. Nandapure et al studied the Magnetic and transport properties of conducting polyaniline/nickel oxide nanocomposites and nickel oxide nanoparticles dispersed in a polyaniline (PANI) which are prepared by an in-situ polymerization method The DC conductivity was studied in the temperature range from 30– 110°C. They found that the dimensions of fly ash in the matrix have a greater influence on the observed conductivity values[133].

B.M.Patil et al studiedAConductivity of Polyaniline – Nickel Oxide Composite and its Structural and morphology studies by FTIR and SEM. Further the ac conductivity was carried by two probe method. It is found that the conductivity increases with increase in frequency [134]

F. TUDORACHE et al Studied the polyaniline – iron oxides composites for gas detection Polyaniline iron oxides composites are found to be the most sensitive to acetone vapors and can be used as gas sensor. The higher value of specific surface of composites and a strong interaction between the polyanilineand metal oxide particles can explain the sensitivity values obtained for composite samples[135]

S. L. PATIL et al studied the fabrication of Polyaniline-ZnONanocomposite Gas Sensor,Polyaniline-ZnO nanocomposites were characterized for their structural as well as surface morphologies and there ammonia response was studied [136]

D.S. Dhawale, et al has carried out the liquefied petroleum gas (LPG) sensing for the p-polyaniline/n-ZnO thin film heterojunctions at room temperature LPG detection was fabricatedby electrodepositing polyaniline on chemical bath deposited ZnO film. The formation of diffusion free interface of heterojunction was confirmed from cross-sectional FESEM. The heterojunction sensor has quick and high response towards LPG as compared to N_2 and CO_2 and exhibited maximum response of 81% upon exposure of 1040ppm of LPG[137]

ManawwerAlam et al studied theOptical and Electrical Studies of Polyaniline/ZnO Nanocomposites forUV-Vis spectra of Pani/ZnOnanocompositewas investigate the optical behavior after doping the ZnO nanoparticle into the polymer matrix. The inclusion of ZnO nanoparticle gives rise to the red shift of π-π^* transition of Pani. The nanocomposite was found to be thermally stable upto 130°C and showed conductivity value of 3.0 x10^{-2} Scm^{-1}[138]

SYED KHASIM et al studied Synthesis, characterization and magnetic properties of polyaniline/ γ -Fe_2O_3 composites Conducting polyaniline/γ -Fe2O3 (PANI/FE) composites have been synthesized using an in situ deposition technique by placing fine-graded γ -Fe_2O_3 in a polymerization mixture of aniline. It is observed that the conductivity increases up to acomposition of 20 wt.% of γ-Fe_2O_3 in polyaniline and decreases thereafter. The initial increase in conductivity is attributed to the extended chain length of polyaniline, where polarons possess sufficient energy to hop between favourable sites. Beyond 20 wt.% of γ-Fe_2O_3 in polyaniline, the blocking of charge carrier hop occurs, reducing conductivity values[139]

Ramesh Patil et al studied Dielectric relaxation and ac conductivity of polyaniline–zinc ferrite composite The ac conductivity and dielectric properties are studied in the frequency range from 102 to 106 Hz.Theresultsofacconductivityshowa strong dependence on the weight percent of $ZnFe_2O_4$in polyaniline. At higher frequency, conductivity increases because of hopping of polarons from one localized states to another localizedstates. It is observed from the electrical conductivity studies thatthe 30wt.% of $ZnFe_2O_4$in the polymer matrix shows the enhancement of the conductivity of the polyaniline and their values arefound to be in the semiconducting range.[140]

Khened et al has studied on dc conductivity and LPG sensing behavior of PANi- CeO_2 composites. The conducting polyaniline-cerium oxide composites were prepared by insitu polymerization of CeO_2 in polyaniline. The dc conductivity studies show thermally activated behavior. The conductivity was found to increase with the increase in temperature indicating the semiconducting behavior of all the compositions. It was also found that on exposure of the composites to LPG, increase in resistance was observedwith the increase in gas concentration [141].

P. Raju et al studied the Preparation and characterization of Ni–Zn ferrite + polymer nanocomposites using mechanical milling method characterization of nanocomposites of Ni–Zn ferrite paraformaldehyde. These nanocomposites were prepared by using mechanical milling method and characterized by X-ray powder diffraction, scanning electron microscopy (SEM) and Fourier transform infrared spectrometer. The particle size estimated from SEM pictures for composites varies from 36 to 60 nm. From thestudies, it is observed that both the values of permittivityand permeability decrease with an increase in polymercontent. [142]

A. H. Elsayed et al studiedSynthesis and Properties of Polyaniline/ferrites Nanocomposites PANI/MFe$_2$O$_4$ nanocomposites (M = Fe$_2$+, Co$_2$+, Ni$_2$+, Mn$_2$+, and Zn$_2$+) were synthesized by in-situ precipitation method. The obtained samples were characterized .The XRD pattern of PANI/MFe$_2$O$_4$ nanocomposites and it was found that the Fe$_3$O$_4$, CoFe$_2$O$_4$, NiFe$_2$O$_4$,MnFe$_2$O$_4$ and ZnFe$_2$O$_4$ nanoparticles species in these nanocomposites are cubic spinel structure with lattice constant a = 8.32Å, 8.36Å, 8.42 Å, 8.49 Å, and 8.46 Å respectively they all have the size in range from 10 to13 nm[143]

Subhash B et al studied Nanocrystalline nickel ferrite reinforced conducting polyaniline nanocomposites Nanocrystalline nickel ferrite (NiFe$_2$O$_4$) powder of crystallite size 20 nm was synthesized by refluxing method . Electrically conductive polyaniline-nickel ferrite (PANI/NiFe$_2$O$_4$) nanocomposites have been synthesized by an in-situ polymerization of aniline monomer in the presence of as-prepared NiFe$_2$O$_4$ in different weight percentage (5%, 10%, and 15%)[144]

Guziewicz et al. studied electrical and optical properties of NiO films depositedby magnetron sputtering. Their work is concerned with the properties of NiO filmsfabricated by RF magnetron sputtering. Electrical and optical parameters of the films were characterized using Hall and transmittance measurements and they reported that the transmittance of NiO films strongly depends on deposition temperature and oxygen amount during sputtering [145].

Yu et al. made a comparative analysis of responses of thin films of various conducting polymers (polyaniline, polypyrrole and poly-3-methylthiophene) tothe vapors of polar and non-polar organic solvents were performed. The differences in the sensor response mechanisms of different COP films were most likely conditioned by the different nature of their doping, which was redox for PPy and acid base for PANI films[146]

1.11 Aim of the Study

The rapidly expanding fields of conducting polymer nanocomposites aregenerating many exciting new materials with novel properties. It is therefore, of immense significance to explore whether nanostructures of conducting polymers can lead to better performance in these already established areas, and whether reliable and scalable synthetic methods can be developed for the synthesis of conducting polymer composites in order to provide the base for both research and applications. The main objective of the present work is the quest of processibility, stability, and to understand charge transport mechanism in these conducting polymers.In this present study, Polyaniline is selected as a conducting polymer and the metal oxides such as Nickel oxide,Ironoxide,Zinc oxide and Zinc ferrite are used to make nanocomposites with Polyaniline. The author has tried to tailor the various electrical and sensing properties of Polyaniline and its nanocomposites. The composites were characterized with FTIR, XRD and SEM techniques to bring out the changes occurred due to doping. Studies on dc conductivity, acconductivity, and LPG gas sensing behavior were also done.

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