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 πολυ (poly), meaning ‘many’; and μέρος (meros), meaning ‘parts’ [1]. Discovery of polymers has given a new dimension to the present era. Polymers are known so far as a class of heat sensitive, flexible, electrically insulating amorphous materials. Polymers possess a wide range of properties from soft like fur to hard like diamond. Polymers are typically utilized in electrical and electronic applications as insulators where advantage is taken of their very high resistivity.

Polymers have been considered as insulators as they found many applications due to their insulating properties. So far, any electrical conduction in polymers which is generally due to loosely bound ions was mostly regarded as an undesirable phenomenon [2]. However, emerging as one of the most important materials in the twentieth century, the use of polymers move from primarily passive materials such as coatings and containers to active materials with useful electronic, optical, energy storage and mechanical properties. Although conducting polymers are known as new materials in terms of their properties, the first work describing the synthesis of a conducting polymer was published in the nineteenth century. In 1862, Henry Letheby prepared polyaniline by anodic oxidation of aniline, which was conductive and showed electro-chromic behavior. Research interest in the development of conducting polymers such as polyaniline, polypyrrole, polythiophene, polyphenylene, etc. has increased tremendously during the last decade due to their high electrical conductivity and good environmental stability [3]. Due to their good processability, low specific weight and resistance to corrosion and
exciting prospects for the polymers fabricated into electrical wires, films or electronic devices, these materials have attracted the interest of both industrial and academic researchers in domains ranging from Chemistry to Solid State Physics. The close interaction between scientists from various backgrounds has been a significant factor in the rapid development of the field of conducting polymers. There is a long history of successful development, which came from the enormous contributions of numerous people in the discovery of conducting polymers [4]. The development of conducting polymers became one of the most promising field with the accidental discovery of intrinsically conducting polymer polyacetylene by Alan J. Heeger, Hideki Shirakawa and Alan G. MacDiarmid in 1977, for which they were awarded the Nobel Prize in Chemistry, 2000 and this development of conducting polymers is a grand recognition of the “dawn of the new plastic age” [5]. The subsequent discovery by Alan Heeger and Alan MacDiarmid that the polymer would undergo an increase in conductivity of 12 orders of magnitude by oxidative doping quickly opened up new avenues in Materials Physics and Chemistry.

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 are called conducting polymers. The conductivity of these polymers is provided by the filler material and the function of the polymer matrix is to hold the material together in one piece. These conductive composites often replace metals when light weight, tough and corrosion resistance materials are required for the applications. However, a considerably high concentration of the conducting filler is required to achieve acceptable levels of
electrical conductivity, thus, giving rise to poor mechanical properties in these composites. Conductivity in these materials is not an inherent property of the polymer chains but a property of the material as a whole.

The discovery of conducting polymers and the ability to dope these polymers over the full range from insulator to metal was particularly exciting because it created a new field of research on the boundary between Chemistry and Condensed-matter physics [6].

Perhaps most important is that the conducting polymers offered the promise of achieving the most recent generation of polymers: materials which exhibit the electrical and optical properties of metals or semiconductors and which retain the attractive mechanical 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 and dopant](image)
In conjugated polymers, the long chain carbon compounds contain alternate single and double bonds that leads to one unpaired electron per carbon atom [7]. In charge transfer polymers, the orbital on adjacent molecules are overlapped to form continuous one-dimensional bands. The charge carriers in this system are provided by the electron transfer between the electron donors (D) and acceptor (A) molecules. In case of ionically conducting polymers, the conductivity arises from the ion migration between coordination sites repeatedly generated by the local motion of polymer chain segments [8]. Therefore, a desirable polymer host must possess: a) electron-donating atoms or groups for the coordinate bond formation with cation, b) low bond rotation barriers for an easy segmental motion of the polymer chain, and c) an appropriate distance between coordinating centers for multiple inter-polymer bonding with cation. Ionically conducting polymers or polymer electrolytes represent a relatively new class of solid ionics.

In the case of conductively filled polymers, the conductivity is introduced through the addition of the conducting components in various polymer materials including both amorphous and crystalline polymers which can be made electrically conducting.
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 of conducting fillers in the insulating polymer matrix. Commonly, various materials such as conductive carbon black, graphite flakes, fibers, metal powders etc. are used as conductive fillers. These fillers are loaded in the common insulating polymers, which have been used as major matrix, like PC, PET, PP, PVC, HDPE, Nylon etc. to get conducting polymer composites or master batches. Because the conductivity is introduced through the addition of the conducting components, various polymer materials including both amorphous polymers can be made electrically conducting. The electrical conductivity of the polymer is decided by the volume fraction of the filler. A transition from insulating to non-insulating behavior is generally observed when volume fraction of conductive filler in the mixture reaches a threshold of about 25%.

These are the materials exclusively used as the commercial conducting polymers. These are used as semiconducting layers in high voltage applications, EMI shielding materials, etc.
To get sufficient conductivity, filler loading of more than 20% is required. This higher addition of these rigid fillers will cause a drastic increment of melt viscosity, which causes serious processing problems. Moreover, these fillers also affect the properties of finished products like aesthetics, brittleness, poor finish, etc. Hence, there is need to develop process where an alternative material or blend can be prepared preferably from conducting polymers.

1.2.2.2 Organometallic Polymeric Conductors

These types of conducting materials are obtained by adding organometallic groups to polymer molecules. In this type of materials, the d-orbital of metal may overlap with p-orbital of the organic structure and thereby increases the electron delocalization. The d-orbital may also bridge adjacent layers in crystalline polymers to give conducting property to it. Metallophthalocyanines and their polymers fall in this class of polymeric material [9]. These polymers have extensively conjugated structures. The bridge of transition metal complexes forms one of the stable systems exhibit intrinsic electrical conductivities without external oxidative doping.

![Figure 1.3: Structure of Polyphthalocyanines](image.png)
Polyferrocenylene is also an example of this type of polymer which is shown in Figure 1.3. These materials possess strong potential for future applications such as antistatic foils, molecular wires and fibers in xerography.

1.2.2.3 Polymeric Charge Transfer Complexes

Polymeric Charge Transfer Complexes (CTC) is formed when acceptor molecules are added to the insulating polymers. There are many charge transfer complexes reported in the literature, e.g. CTC of tetrathiafulvalene (TTF) with bromine, chlorine etc [10]. The reason for high conductivity in polymeric charge transfer complexes and radical ion salts are still somewhat obscure. It is likely that in polymeric materials, the donor – acceptor interaction promotes orbital overlap, which contributes to alter molecular arrangements and enhances electron delocalization.

1.2.2.4 Inherently Conducting Polymers

Intrinsically conducting polymers (ICP), more commonly known as “Synthetic Metals” [11] are organic polymers that possess high electrical, magnetic and optical properties of a metal while retaining the mechanical properties, processability etc. commonly associated with a conventional polymer. Research in the field of inherently conducting polymer started nearly four decades ago when Shirakawa and his group found drastic increase in the electrical conductivity of polyacetylene films when exposed to iodine vapor [12]. In 1975, the first papers on the novel metallic polymer, poly (sulfur-nitrile), $(SN)_x$ appeared in the literature. That event heralded the dawn of a new era of conducting polymers.

The most common examples of intrinsically / inherently conducting polymers are Polyacetylene, Polyaniline, Polypyrrole, Polythiophene, Polyphenylene, Poly (phenylene-
vinylene) etc. Figure 1.4 shows some of the conjugated polymers, which have been studied as intrinsically conducting polymers.

![Conjugated Polymers Diagram]

**Figure 1.4: Examples of conjugated polymers**

The unique electronic properties of these polymers are due to the presence of \( \pi \)-electrons and the wave functions of which are delocalized over long portions of polymer chain when the molecular structure of the backbone is planar [13]. Therefore, it is necessary that there are no torsion angles at the bonds, which would decrease the delocalization of the \( \pi \)-electron system [14]. The essential features of the delocalized \( \pi \) -electron system, which differentiates a typical conjugated polymer from a conventional polymer with \( \sigma \) - bonds are as follows:
Introduction

- Band gap $E_g$ (electronic band gap) is small (~ 1 to 3.5 eV) with corresponding to low excitations and semiconducting behavior.
- The polymer molecules can be easily oxidized or reduced through charge transfer reactions with atomic or molecular dopant species.
- Net charge carrier mobility in the conducting state is large enough and because of this, high electrical conductivity is observed.
- Quasi-particles, which under certain conditions, may move relatively freely through the material [15, 16].

The electrical and optical properties of these materials depend on the electronic structure and basically on the chemical nature of the repeating units. The electrical conductivity is proportional to both the density and drift mobility of the charged carriers. The carrier drift mobility is defined as the ratio of the drift velocity to the electric field and reflects the ease with which carriers are propagated. To enhance the electrical conductivity of polymers, an increase in the carrier mobility and the density of the charge carriers is required [17].

Intrinsically conducting polymers have important applications in molecular electronics, electrical displays, electromagnetic shielding, printed circuit boards, rechargeable batteries, optical computers, variety of sensors and actuators, ‘smart’ structures in electronic devices, artificial nerves, drug release systems, antistatic clothing and inducting exchange membranes [18-22]. One of the remarkable features of ICPs is that it is possible to control conductivity of these polymers over a wide range from insulating to metallic by proper doping, addition of fillers and by intercalating these
polymers into different inorganic host materials such as Y$_2$O$_3$ [23], TiO$_2$ [24], TaS$_2$ [25], CdPS$_3$ [26], V$_2$O$_5$ [27], MoO$_3$ [28] and FeOCl [29].

1.3 Conjugated Conducting Polymers

Conjugated conducting polymers are the organic compounds that have an extended ($\pi$) orbital system and conjugated carbon system [30]. The conjugated polymers in their undoped, pristine state are semiconductors or insulators. As such, the energy gap can be $> 2$ eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophene, polyacetylene only have a low electrical conductivity of around $10^{-10}$ to $10^{-8}$ Scm$^{-1}$. The conductivity of these conjugated polymers can be controlled by the process of doping which may be carried out through a chemical route, electrochemical route or photochemical route and is characterized by charge transfer from dopant to polymer or from polymer to dopant [31]. On doping these conjugated polymers show very high conductivity similar to metals. Even at a very low level of doping (< 1 %), electrical conductivity increases several orders of magnitude up to values of around $10^{-1}$ Scm$^{-1}$. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around $10^2$-$10^4$ Scm$^{-1}$ for different polymers. Highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of around $8 \times 10^4$ Scm$^{-1}$ [32]. Although the $\pi$ - electrons in polyacetylene are delocalized along the chain, pristine polyacetylene is not a metal. Polyacetylene has alternating single and double bonds which are 0.145 nm and the longer bond length is 0.135 nm, respectively. Upon doping, the bond alteration is diminished and conductivity increases. [33-38].
The most exciting applications of these polymers are in television sets, cellular telephones, automotive dashboard displays and artificial cockpit displays, Light emitting devices, solar cells, light-weight batteries, light emitting diodes (LEDs), polymer actuators, corrosion protection agents, sensors and molecular electronic devices [39, 40].

Amongst the family of conducting polymers Polypyrrole (PPy) is one of the most promising electrically conducting polymers.

1.3.1 Structure and Properties

1.3.1.1 Conjugation

Table 1.1 lists the repeat units and conductivities for some common conjugated polymers [41]. As can be seen in Table 1.1, the conjugated structure with alternating single and double bonds or conjugated segments coupled with atoms providing $p$-orbitals for a continuous orbital overlap (e.g. N, S) seems to be necessary for polymers to become intrinsically conducting.

This is because just as metals have high conductivity due to the free movement of electrons through their structure; in order for polymers to be electronically conductive they must possess not only charge carriers but also an orbital system that allows the charge carriers to move. The conjugated structure can meet the second requirement through a continuous overlapping of $\pi$-orbital along the polymer backbone. Due to its simple conjugated molecular structure and fascinating electronic properties, polyacetylene has been widely studied as a prototype for other electronically conducting polymers [42].
Table 1.1: Structure and conductivity of some conjugated conducting polymers

<table>
<thead>
<tr>
<th>Polymer (Conductivity discovered)</th>
<th>Structure</th>
<th>Energy gap (eV)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacetylene and analogues</td>
<td><img src="image" alt="Polyacetylene" /></td>
<td>1.5</td>
<td>10³ – 1.7×10⁵</td>
</tr>
<tr>
<td>Polyacetylene (1977)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polypyrrole (1979)</td>
<td><img src="image" alt="Polypyrrole" /></td>
<td>3.1</td>
<td>10² – 7.5×10³</td>
</tr>
<tr>
<td>Polythiophene (1981)</td>
<td><img src="image" alt="Polythiophene" /></td>
<td>2.0</td>
<td>10 – 10³</td>
</tr>
<tr>
<td>Polyphenylene and analogues</td>
<td><img src="image" alt="Polyphenylene" /></td>
<td>3.0</td>
<td>10² – 10³</td>
</tr>
<tr>
<td>Poly(paraphenylene) (1979)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(p-phenylene vinylene) (1979)</td>
<td><img src="image" alt="Poly(p-phenylene vinylene)" /></td>
<td>2.5</td>
<td>3 – 5×10³</td>
</tr>
<tr>
<td>Polyaniline (1980)</td>
<td><img src="image" alt="Polyaniline" /></td>
<td>3.2</td>
<td>30 – 200</td>
</tr>
</tbody>
</table>

1.3.1.2 Doping

The conjugated polymers are either electrical insulators or semiconductors, since most organic polymers do not possess intrinsic charge carriers. These polymers can become highly conductive by the insertion or injection of electrons. Such a process of structural modification is called ‘doping’. The required charge carriers may be provided by partial oxidation (p-doping) of the polymer chain with electron acceptors (e.g. I₂, AsF₅) or by partial reduction (n-doping) with electron donors (e.g. Na, K). Through such
a doping process, charged defects (*e.g.* polaron, bipolaron and soliton) are introduced in the polymer chain, which could then be available as the charge carriers. In the case of I2-doped \textit{trans}-polyacetylene, it was estimated that nearly 85% of the positive charge is delocalized over 15 CH units to give a positive soliton. In fact, the insulator-to-metal transition in conjugated polymers is not so simple, and the way in which charges can be stabilized on the polymer chains and the nature of the charge transport process are still a matter of debate.

During the doping process, an organic polymer, either an insulator or semiconductor having small conductivity, typically in the range of $10^{-10}$ to $10^{-5}$ S cm$^{-1}$, is converted to a polymer which is in a ‘metallic’ conducting regime ($1$ to $10^4$ S cm$^{-1}$). The highest value reported to date has been obtained in iodine-doped polyacetylene ($> 10^5$ S cm$^{-1}$). Conductivity of other conjugated polymers reaches up to $10^3$ S cm$^{-1}$. The dopant concentration 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 electrons associated with the polymer backbone changes. All conducting polymers, *e.g.* PPy, PANI, PT etc. undergo p or n-redox doping by chemical or electrochemical process. p-doping was first discovered by treating \textit{trans}\textsubscript{-(CH)$_x$} with an oxidizing agent such as iodine.

- **Photo doping**: When \textit{trans}\textsubscript{-(CH)$_x$} is exposed to radiation of energy greater than its band gap, electrons are promoted across the gap and polymer undergoes photodoping.
• **Non-redox doping**: In this type of doping, the number of electrons associated with the polymer backbone does not change during the doping process, but merely the rearrangement of the energy levels occurs. The emeraldine base form of PANI was the first example of the doping of an organic polymer to a highly conductive 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 without chemical modifications during the process of doping. Ex: I₂, Br₂, AsF₂, Na, K, H₂SO₄, FeCl₃.

- **Ionic dopants** are either oxidized or reduced by an electron transfer with the polymer and the counter ion remains with the polymer to make the system neutral. Ex: LiClO₄, FeClO₄.

- **Organic dopants** are anionic dopants, generally incorporated into polymers from aqueous electrolytes during anodic deposition of the polymer. Ex: CF₃COOH, CF₃SO₃Na.

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

- **Metal Oxide dopants** are known for their electron donor property. The oxygen atoms of the metal oxide contain lone pairs of electrons which help localization of charge in the polymeric chain, leading to the enhancement of conductivity of the host polymer. Ex: CeO₂, TiO₂, SnO₂, WoO₃, CoO₃.
1.3.2 Band Theory

According to band theory, the electrical properties of direct gap inorganic semiconductors are determined by their electronic structures, and the electrons move within discrete energy states called bands. By analogy, the bonding and anti-bonding π-orbital of the $sp^2$ hybridized π-electron materials (e.g., polyenes) generate energy bands, which are fully occupied (σ-band) and empty (σ*-band). The energy band that results from the bonding orbital of a molecule is known as the valence band, while the conduction band is as a result of the anti-bonding orbital of the molecule. The width of individual bands across the range of energy levels is called band width. The valence band (VB) represents the highest occupied molecular orbital (HOMO) and the conduction band (CB) represents the lowest unoccupied molecular orbital (LUMO) [43]. The gap between the highest filled energy level and lowest unfilled energy level is called band gap ($E_g$). This band gap represents a range of energies which is not available to electrons, and this gap is known as the ‘band gap’, ‘energy gap’, or ‘forbidden gap. The level of electrons in a system which is reached at absolute zero is called the Fermi level [44]. The size of the energy band gap depends on extend of delocalization and the alternation of double and single bonds. Moreover the size of the energy band gap will determine whether the conducting polymer is metal, semiconductor or insulator [45]. Combining the concepts explained in both atomic and molecular orbital theory, the electronic properties of metals, semiconductors, and insulators can be differentiated with reference to the energy band gap as shown in Figure 1.5 below.
Electrons must have certain energy to occupy a given band and need extra energy to move from the valence band to the conduction band. Moreover, the bands should be partially filled in order to be electrically conducting, as neither empty nor full bands can carry electricity. Owing to the presence of partially filled energy bands, metals have high conductivities. The energy bands of insulators and semiconductors, however, are either completely full or completely empty. For instance, most conventional polymers have full valence bands and empty conduction bands, which are separated from each other by a wide energy gap. In contrast, conjugated polymers have narrower band gaps and doping can change their band structures by either taking electrons from the valence band (p-doping) or adding electrons to the conduction band (n-doping).

When an electron is added (removed) to the bottom of the conduction band (from the top of the valence band) of a conjugated polymer (Figure 1.6 a), the conduction (valence) band ends up being partially filled and a radical anion (cation), commonly termed as a polaron [46], is created (Figure 1.6 b).
Figure 1.6: Schematic representation of the formation of (a) polyene, (b) polaron, (c) bipolaron and (d) soliton pair on a trans-polyacetylene chain by doping

The formation of polarons causes the injection of states from the bottom of the conduction band and top of the valence band into the band gap. A polaron carries both spin (1/2) and charge (±1e). Addition (removal) of a second electron on a chain, already having a negative (positive) polaron, results in the formation of a bipolaron (spinless) through dimerization of two polarons, which can lower the total energy (Figure 1.6 c). In conjugated polymers with a degenerate ground state (i.e. two equivalent resonance forms), like trans-polyacetylene, the bipolarons can further lower their energy by dissociating into two spin less solitons at one-half of the gap energy (Figure 1.6 d). Solitons do not form in conjugated polymers with non-degenerate ground states, such as in polypyrrole, polythiophene and polyaniline. The population of polarons, bipolarons or solitons increases with the doping level. At high doping levels, the localized polarons,
bipolarons or solitons near to individual dopant ions could overlap, leading to new energy bands between and even overlapping the valence and conduction bands, through which electrons can flow.

1.4 Conducting Polymer: Polypyrrole

1.4.1 Introduction

Among the conducting polymers, *polypyrrole* has drawn considerable attention due to its high conductivity, simple preparation, stability and good mechanical and electrochemical properties.

*Pyrrole* is a heterocyclic aromatic organic compound, a five-member ring with the formula $C_4H_4NH$ [47]. Substituted derivatives are also called pyrrole. For example, $C_4H_4NCH_3$ is $N$-methylpyrrole. Porphobilinogen is a tri-substituted pyrrole, which is the biosynthetic precursor to many natural products [48]. Pyrrole is a component of more complex macro cycles, including the porphyrins of heme, the chlorins, bacteriochlorins chlorophyll, and porphyrinogens [49]. The structure of polypyrrole is shown in following Figure 1.7.

![Chemical structure of Polypyrrole](image)

*Figure 1.7: Chemical structure of Polypyrrole*

Polypyrrole exhibits a wide range of surface conductivities ($10^{-3} \text{Scm}^{-1} < \sigma < 100 \text{Scm}^{-1}$) depending on the functionality and substitution pattern of the monomer and the nature of the counter ion or dopant [50]. However, the principal problems with the
practical utilization of conducting polymers like polypyrrole include its poor mechanical properties like brittleness and low processability [51]. Blending insulating polymers is an attractive route to improve their mechanical properties without losing their conductivity [52].

There are many potential applications in the electronic and electro-chromic devices [53, 54], secondary batteries [55-57], capacitors [58, 59], light emitting diodes [60, 61] and enzyme electrodes [62-64]. There are other potential application areas of polypyrrole such as chip-in-chip connector, microwave shielding and corrosion protection [65]. Apart from these, polypyrrole is widely used in sensor applications because they provide stable and porous matrix for the gas component and also facilitates the e-transfer process [66]. Also, polypyrrole offers a new class of materials in biological and biomedical applications including biosensors [67]. These composites can also be used in the low k – dielectric materials above $10^3$ Hz.

Polypyrrole can be synthesized either by oxidative chemical polymerisation [68, 69] or by electrochemical oxidation in aqueous or organic solutions [70].

1.4.2 Chemical Synthesis

Since the first electrochemical preparation of polypyrrole by Dall’Olie et. al., considerable improvement in the mechanical properties has been achieved. These improvements stem from the work of Diaz and Hall [71], who showed that the mechanical properties of polypyrrole toluenesulfonate were significantly superior to other forms of polypyrrole. In many respects, the mechanical properties of these films are comparable to regular insulating polymers or carbon-loaded polymers of similar conductivity. The mechanical properties of these polypyrrole toluenesulfonate films can
be improved even further by growing them on vitreous carbon electrodes [72, 73]. These electrodes permit the use of high voltages and high currents, which allows growth of thick films in relatively short times.

Hotta et. al. [74] have shown that films of polypyrrole hexafluoroarsenate grown at elevated temperatures from tetrabutylammonium hexafluoroarsenate solutions in dimethylsulfate, have improved mechanical properties. Recently, Lindsey and Street [75] have demonstrated that polypyrrole can be deposited within the matrix of several swellable polymers to form a conducting composite. For instance, polypyrrole sulfate can be electrochemically deposited from an aqueous electrolyte solution into a polyvinyl alcohol film which has been spun on to a metal electrode and then partially cross linked to reduce its solubility while still permitting to swell.

Figure 1.8(a-c) shows an outline of the polymerization scheme for pyrrole. The mechanism for polymerization can be deduced from several observations. First, a radical cation produced by the initial oxidation of pyrrole dimer, makes an electro-philic attack on a neutral molecule [76]. The coupling of two radical is favored over electro-philic attack, since the electrochemical polymerization reaction occurs only when the potential applied to oxidize the polymer species present at the electrode surface is essentially zero. Second, the amount of charge consumed during polymer formation has an initial linear time dependent and is independent of pyrrole concentration during constant potential electrolysis [77]. The evidence indicates that the entire electrochemical reaction occurs at the electrode surface. Third, the dimer bipyrrrole, the trimer and the polymer oxidize more readily than pyrrole monomer, itself and thus are in an oxidized state during polymerization [78].
Therefore coupling is believed to occur between digomer radical cation, and pyrrole radical cation at the electrode surface. Probably, the growth of polypyrrole chains terminates when the ends of the growing chains becomes sterically blocked [79].

Recently, polypyrrole has become one of the most attractive conductive polymers. There are 3 methods generally used to prepare polypyrrole, they are (i) Chemical polymerization in solution [80], (ii) Chemical vapor deposition (CVD) [81] and (iii) Electrochemical polymerization [82].
Nowadays, the preparation of conductive composite by chemical oxidative polymerization has been developed, since this method is easier and more effective. In the preparation of polypyrrole composite, pyrrole monomer is polymerized by chemical oxidative polymerization using oxidant such as ammonium per sulfate within host polymer solution. In this method, the distribution between polypyrrole and host polymer is good, and thus electrical conductivity and mechanical properties increases. But two phases are basically immiscible, and phase separation still exists between each phase. If the miscibility of these blends is enhanced between two phases, the electrical properties will be enhanced due to the decrease of interfacial tension between them [83, 84].

1.5 Potential Applications of Conducting Polymers

Conducting polymers have important applications in molecular electronics, electrical displays, electromagnetic shielding, printed circuit boards, rechargeable batteries, solid electrolytes and optical computers. Other potential applications of these conducting polymers are in chemical, biochemical and thermal sensors, artificial nerves, drug release systems, antistatic clothing, ion exchange membranes, corrosion protection, electromechanical actuators and ‘smart’ structures [85-87].

Interest in conducting polymers has its origin in the possible commercial applications of these materials. The commercial applications are based on the promise of a novel combination of light weight, processibility and electrical conductivity. Some of the conducting polymers can change their optical properties on applications of current or voltage and therefore may find useful applications as heat shutter and light emitting diode (LED).
But, problem hindering these wonderful applications is the poor processibility in these polymers. Improvement of the processibility will enable scientists and technologists to explore this to create a new looking world of conducting polymers. Much research is needed before many of the above application will become a reality. The stability and processability both need to be substantially improved if they are to be used in the market place. The cost of such polymers must also be substantially lowered. However, one must consider that, although conventional polymers were synthesized and studied in laboratories around the world, they did not become widespread until years of research and development had been done. Polymeric conductors with low density, good electrical conductivity coupled with low cost pose a serious challenge to the established inorganic semiconductor technology.

**Table 1.2: Group of applications of conducting polymers**

<table>
<thead>
<tr>
<th>Group – I</th>
<th>Group – II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electromagnetic shielding</td>
<td>Electrical displays</td>
</tr>
<tr>
<td>Electrostatic materials</td>
<td>Chemical and biochemical sensors</td>
</tr>
<tr>
<td>Conducting adhesives</td>
<td>Molecular electronics</td>
</tr>
<tr>
<td>Printed circuit boards</td>
<td>Rechargeable batteries</td>
</tr>
<tr>
<td>Artificial nerves</td>
<td>Drug release system</td>
</tr>
<tr>
<td>Antistatic clothing</td>
<td>Optical computers</td>
</tr>
<tr>
<td>Piezoceramics</td>
<td>Smart structure</td>
</tr>
<tr>
<td>Thermal sensors</td>
<td>Ion exchange membranes</td>
</tr>
<tr>
<td>Aircraft structures</td>
<td>Electromechanical actuators</td>
</tr>
</tbody>
</table>
There are two main groups of applications for these polymers as shown in Table 1.2. The first group utilizes their conductivity as its main property. The second group utilizes electro activity.

Some of the important applications of conducting polymers are discussed below.

**Conducting Polymers in Sensors**

The chemical properties of conducting polymers make them very useful for use in sensors. This utilizes the ability of such materials to change their electrical properties during reaction with various redox agents (dopants) or via their instability to moisture and heat. An example of this is the development of gas sensors. It has been shown that Polypyrrole behaves as a quasi ‘p’ type material. Its resistance increases in the presence of a reducing gas such as ammonia and decreases in the presence of an oxidizing gas such as nitrogen dioxide. The gases cause a change in the near surface charge carrier (here electron holes) density by reacting with surface adsorbed oxygen ions. Another type of sensor developed is a ‘biosensor’. This utilizes the ability of tri-iodide to oxidize polyacetylene as a means to measure glucose concentration. Glucose is oxidized with oxygen with the help of glucose oxidase. This produces hydrogen peroxide, which oxidizes iodide ions to tri-iodide ions. Hence, conductivity is proportional to the peroxide concentration, which is proportional to the glucose concentration.

**Conducting Polymers in Electrochromic Devices**

Conjugated polymers that can be repeatedly driven from insulating to conductive state electrochemically with high contrast in color are promising materials for electrochromic device technology. Conjugated polymers have an electronic band structure. The energy gap between valence band and the conduction band determines the
intinsic optical properties of the polymers. The color changes elicited by doping are due to the modification of the polymer band electronic structure. The electrochromic materials have been employed in large area display panels. In architecture, electrochromic devices are used to control the sun energy crossing a window. In automotive industry rear view mirrors are a good application for electrochromic system.

**Conductive Polymers in Aircraft Industry**

Modern planes are often made with lightweight composites. This makes them vulnerable to damage from lightning bolts. Coating aircraft with a conducting polymer can direct the electricity directed away from the vulnerable internals of the aircraft.

Polypyrrole has been approved for use in the U.S. Navy's A-12 stealth attack carrier aircraft for use in edge card components that dissipate incoming radar energy by conducting electric charge across a gradient of increasing resistance that the plastic material produces.

**Conducting Polymers as Catalyst**

Conducting polymers are expected to behave as redox catalyst as they exhibit redox property. Several reports have been found in literature on modification of conducting polymers and their use as catalyst for small organic molecules. Conducting polymers in their various oxidation states interconvert each other, which permits to construct redox cycle for catalytic reactions.

**Conducting Polymers inside the Human Body**

Due to the biocompatibility of some conducting polymers, they may be used to transport small electric signals through the body, i.e., act as ‘artificial nerves’. Perhaps,
modifications to the brain might eventually be contemplated. The use of polymers with electro active reaction has led to their use to emulate biological muscles with high toughness, large actuation strain, and inherent vibration damping. This similarity gained them the name "Artificial Muscles" and offers the potential of developing biologically inspired robots.

**Conducting Polymers as Antistatic Fabrics**

Another promising product incorporating conducting polymers is Contex® which is a fiber. The fiber is coated with a conductive polymer material called Polypyrrole and can be woven to create an Antistatic fabric. Antistatic fabrics are also being explored for possible application in clean room applications.

**Conductive Polymers for Medical Applications**

Suitable for a variety of applications, conductive thermoplastic compounds can satisfy the medical industry's need for miniaturized, high-strength parts. Most can withstand state-of-the-art sterilization procedures, including autoclave and many are certified for purity and pre-tested to minimize ionic contamination. Medical applications using conductive thermoplastics include:

- **Bodies for asthma inhalers.** Because the proper dose of asthma medications is critical to relief, any static ‘capture’ of the fine particulate drugs can affect recovery from a spasm.
- **Airway or breathing tubes and structures.** A flow of gases creates turboelectric charge or decay. A buildup of such charges could cause an explosion in high-oxygen atmospheres.
• Antistatic surfaces, containers, packaging to eliminate dust attraction in pharmaceutical manufacturing.

• ESD housings to provide Faraday cage isolation for electronic components in monitors and diagnostic equipment.

• ECG electrodes manufactured from highly conductive materials. These are X-ray transparent and can reduce costs compared with metal components.

• High thermal transfer and microwave absorbing materials used in warming fluids.

**Futuristic Applications of Conducting Polymers**

One of the most futuristic applications for conducting polymers is 'smart' structure. These are items, which alter themselves to make them better. An example is a golf club, which adapt in real time to persons' tendency to slice or undercut their shots. A more realizable application is vibration control. Smart skis have recently been developed which do not vibrate during skiing. This is achieved by using the force of the vibration. Other applications of smart structures include active suspension systems on cars, trucks and bridges; damage assessment on boats; automatic damping of buildings and programmable floors for robotics.

**1.6 Transition Metal Oxides**

Transition metal oxides are a fascinating class of materials due to their wide ranging electronic, chemical and mechanical properties. They are compounds composed of oxygen atoms bound to transition metals. They include insulators as well as (poor) metals. Often the same material may display both types of transport properties; hence a metal-insulator transition is obtained by varying either temperature or pressure. Transition metal oxides have a wide variety of surface structures which affect the surface
energy of these compounds and influence their chemical properties. They are commonly utilized for their catalytic activity and semi conductive properties. They are also frequently used as pigments in paints and plastics, most notably titanium dioxide. Transition metal oxides are used in a wide variety of technologically important catalytic processes. A number of transition metal oxides are also superconductors.

The majority of transition metal dioxides have the rutile structure and a few have perovskite structure as shown in Figure 1.9(a) and (b). Materials of this stoichiometry exist for Ti, Cr, V and Mn in the first row transition metal and for Zr to Pd in the second. The rutile structure is generated by filling half of the octahedral sites with cation of the hcp oxygen anion array [88, 89]. Few transition metals can achieve the +6 oxidation state in an oxide, so oxides with the stoichiometry MO$_3$ are rare [90].

Figure 1.9: (a) Rutile structure (highly metallic) (b) Perovskite structure (highly insulating)

In rutile surfaces, the most common type of defect is oxygen vacancies. There are two types of oxygen vacancies, which result from either the removal of a bridging O$^{2-}$ ions or the removal of an in-plane O$^{2-}$ ion. Both of these will reduce the coordination of the surface cation [91, 92]. The bulk electronic band structure of transition metal oxides consists of overlapping 2p orbital from oxygen atoms, forming the lower energy, highly populated valence band, while the sparsely populated, higher energy conduction band consists of overlapping d orbital of the transition metal cation [93].
The electrical resistivity in oxide materials spans the wide range of $10^{-10}$ to $10^{20}$ Ω cm. We have oxides with metallic properties (e.g. RuO$_2$, RuO$_3$) at one end of the range and oxides with highly insulating behavior (e.g. BaTiO$_3$) at the other.

Among the transition metals oxides, aluminum oxide (Al$_2$O$_3$), zinc oxide (ZnO) [94], tin oxide (SnO$_2$) [95], tungsten oxide (WO$_3$), titanium oxide (TiO$_2$) [96], vanadium oxide (V$_2$O$_5$), cerium oxide (CeO$_2$), iron oxide (Fe$_2$O$_3$), cobalt oxide (Co$_3$O$_4$) [97] etc. are mostly widely known oxides and industrially employed transition metal oxides since last fifty years. These oxides have become important both scientifically and industrially because of their applications for sound and picture recording, data storage, humidity and gas sensors, conducting composite super capacitors, electrochromic display devices, etc.

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

- Nickel oxide (NiO)
- Niobium pentoxide (Nb$_2$O$_5$)
- Cerium oxide (CeO$_2$)

### 1.6.1 Nickel Oxide (NiO)

Nickel oxide is the chemical compound with the formula NiO. It can be either a green or black crystalline powder. The mineralogical form of NiO is ‘bunsenite’ which is very rare.

NiO adopts the NaCl structure, with octahedral Ni and O$^{2-}$ sites as shown in Figure 1.10. The simple structure is commonly known as the rock salt structure. Like many other binary metal oxides, NiO is often non-stoichiometric, meaning that the Ni:O ratio deviates from 1:1.
NiO can be prepared by multiple methods. Upon heating above 400 °C, nickel powder reacts with oxygen to give NiO. In some commercial processes, green nickel oxide is made by heating a mixture of nickel powder and water at 1000 °C, the rate for this reaction can be increased by the addition of NiO [98].

Nickel oxide has a range of applications such as:

- For making electrical ceramics such as thermistors and varistors e.g. ferrites (nickel zinc ferrite).
- Pigments for ceramic, glasses and glazes.
- Nickel oxide can be reacted with acids to form salts and other compounds e.g. nickel sulfamate for electroplating and nickel molybdate for hydrodesulfurization catalysts.
- Gold doped nickel oxide films can be used as transparent electrodes in optoelectronic devices.
- Nickel oxide is an anodic electrochromic material which has been widely studied as counter electrodes with tungsten oxide in electrochromic devices.
The following table shows some of the important properties of NiO.

**Table 1.3: Important properties of NiO**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>NiO</td>
</tr>
<tr>
<td>Appearance</td>
<td>Green crystalline solid</td>
</tr>
<tr>
<td>Molar mass</td>
<td>74.69 g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>6.67 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1,955 °C</td>
</tr>
</tbody>
</table>

1.6.2 Niobium Pentoxide (Nb₂O₅)

Niobium pentoxide is the inorganic compound with the formula Nb₂O₅. It is a colorless insoluble solid that is fairly unreactive.

It has many polymorphic forms all based largely on octahedrally coordinated niobium atoms [99, 100]. The form most commonly encountered is monoclinic H-Nb₂O₅ which has a complex structure, with a unit cell containing 28 niobium atoms and 70 oxygen, where 27 of the niobium atoms are octahedrally coordinated and one tetrahedrally [101]. The structure is shown in Figure 1.11.

Nb₂O₅ is prepared by hydrolysis of alkali-metal niobates and alkoxides and the fluorides using base. Such simple procedures afford hydrated oxides that are calcined. A method of production via sol-gel techniques has been reported hydrolyzing niobium alkoxides in the presence of acetic acid, followed by calcinations of the gels to produce the polymorphic form, T-Nb₂O₅ [102]. Nano-sized niobium pentoxide particles have been synthesized by LiH reduction of NbCl₅, followed by aerial oxidation as part of a synthesis of nano structured niobates.
Niobium pentoxide is used mainly in the production of niobium metal [103], but specialized applications include capacitors, lithium niobate and as a component of optical glasses [104]. It is the main precursor to all materials made of niobium, the dominant application being alloys.

The following table shows some of the important properties of Nb$_2$O$_5$.

**Table 1.4: Important properties of Nb$_2$O$_5$**

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>Nb$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearance</strong></td>
<td>White orthogonal solid</td>
</tr>
<tr>
<td><strong>Molar mass</strong></td>
<td>265.81 g/mol</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>4.60 g/cm$^3$</td>
</tr>
<tr>
<td><strong>Melting point</strong></td>
<td>1512 °C</td>
</tr>
</tbody>
</table>

1.6.3 Cerium Oxide (CeO$_2$)

Cerium oxide, also known as ceric oxide or ceria, is an oxide of the rare earth metal cerium. It is a pale yellow-white powder with the chemical formula CeO$_2$.

It has the cubic (fluorite) structure [105], containing 8 coordinate Ce$^{4+}$ and 4 coordinate O$^{2-}$ as shown in Figure 1.12. At high temperatures it can be reduced to a non-
stoichiometric, anion deficient form that retains the fluorite lattice, \( \text{CeO}_{(2-x)} \) where \( 0 < x < 0.28 \) [106].

Cerium oxide is formed by the calcination of cerium oxalate or cerium hydroxide. Powdered ceria is slightly hygroscopic and will also absorb a small amount of carbon dioxide from the atmosphere [107].

![Figure 1.12: Crystal structure of CeO₂](image)

Due to its fluorite structure, the oxygen atoms in a ceria crystal are all in a plane with one another, allowing for rapid diffusion as a function of the number of oxygen vacancies. As the number of vacancies increases, the ease at which oxygen can move around in the crystal increases, allowing the ceria to reduce and oxidize molecules on its surface. Undoped and doped ceria also exhibit high electronic conductivity at low partial pressures of oxygen due to reduction of the cerium ion leading to the formation of small polarons. Substituting a fraction of the ceria with gadolinium or samarium will introduce oxygen vacancies in the crystal without adding electronic charge carriers. This increases the ionic conductivity and results in a better electrolyte.
Introduction

It is used in ceramics, to sensitize photosensitive glass, as a catalyst and as a catalyst support, to polish glass and stones, in lapidary as an alternative to ‘jeweler’s rouge’. It is also used in the walls of self-cleaning ovens as a hydrocarbon catalyst during the high-temperature cleaning process.

The following table shows some of the important properties of CeO₂.

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>CeO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearance</strong></td>
<td>White or pale yellow solid</td>
</tr>
<tr>
<td><strong>Molar mass</strong></td>
<td>172.115 g/mol</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>7.215 g/cm³</td>
</tr>
<tr>
<td><strong>Melting point</strong></td>
<td>2400 °C</td>
</tr>
</tbody>
</table>

1.7 Introduction to Sensors

A sensor is a device that receives a signal or stimulus and responds with an electrical signal. The reason for the output of a sensor to be limited to electrical signals is related to the present development of signal processing, that is almost exclusively performed using electronic devices. Hence, a sensor should be a device that receives a physical, chemical or biological signal and converts it into an electric signal that should be compatible with electronic circuits. However, the stimulus can be mechanical, thermal, electromagnetic, acoustic or chemical in origin, while the measured signal is typically electrical in nature, although pneumatic, hydraulic and optical signals may be employed.

Sensor seems to have come from the word ‘sense’ given that usually sensor devices try to mimic human senses characteristics. In the biological senses, the output is also an electrical signal that is transmitted to the nervous system. Usually sensors are part
of larger complex systems, made by many other transducers, signal conditioners, signal processors, memory devices and actuators.

There is an utmost need and desire for us to monitor all aspects of our environment in real time and this has been brought about by our increasing concerns with pollution, health and safety. There is also a desire to determine contaminants and analytes at lower and lower levels and one could say that the aim of all modern science is to lower the detection limits and to improve the accuracy and precision at those limits. Instrumentation has become so sophisticated that we are now able to detect chemicals in amounts smaller than we ever imagined a few years ago. Because of this desire and need of monitor, there is a tremendous energy and resources to develop sensors for a multitude of applications. The end result of all this research will one day provide us with portable, miniature, and intelligent sensing devices to monitor almost anything we desire.

Especially, research activity on chemical sensors is now flourishing throughout the world. Many papers of chemical sensors are being published in journals and read at domestic and international conferences. Although, various kinds of new devices and principles have been proposed not all of them have been commercially successful. Even scientifically fascinating and well-engineered devices sometimes find difficulty in the commercial market. Some of these encounter problems in the fact that, not just high performance but reasonable productions are required for a successful device. Moreover, new devices must be introduced at the right time to meet social needs.

Though there is successful development in the past decades, however, fundamental understanding of the sensor remains far from being satisfactory. There is increasing need of new sensors capable of detecting humidity, various toxic gases and
smell components. Trace gases sometimes at sub-ppm levels present in the environment or generated from food will be new target of detection in the near future. It is unlikely that such demands will be met easily by simple extension of the present trial and error approaches.

1.7.1 Types of sensors

Generally, sensors can be classified into many types based upon the applications, input signal, and conversion mechanism, material used in sensor, production technologies or sensor characteristics such as cost, accuracy or range. They are classified as follows:

- **Humidity sensors**: These are based on change in electrical properties of the material due to the absorption of water vapor. Hydrophilic polymers are used for resistance type humidity sensors, while hydrophobic polymers are preferred for capacitance type sensors.

- **Liquid and solid electrolyte-electrochemical sensors**: These are based on Faraday’s law. Because of the ionic nature, the ionic conductivity in the electrolytes for any current passing through it will carry a corresponding flux of matter. Therefore the measurement of pumping current provides an easy and accurate determination of the quantity of matter being transferred from one electrode to other.

- **Catalytic sensors**: In catalytic sensor, the gases react on a catalytic filament via an exothermic process. The resulting temperature increase is being monitored by a corresponding resistance change in the filament.
• **Electronic conductive devices-semiconductor sensors:** In these sensors, reversible reaction of the gas at the semiconductor surface results in a change of one of its electronic properties usually conductance.

• **Calorimetric sensors:** Detect change in temperature.

• **Optochemical sensors:** Chemical and biological changes are sensed in the form of optical signals.

• **Mass sensitive microbalance sensors:** Here gases are adsorbed on to a coated piezoelectric crystal. The resulting weight change causing a frequency shift from the fundamental.

• **Biosensors:** These sensors make the measurements on biological systems such as biologically based molecules, enzymes, amino acids, etc. as systems for improving selectivity of devices.

### 1.7.2 Gas Sensors

Gas sensor is a device that can change the concentration of an analyte gas into an electronic [108] or electrical signal [109]. A gas sensor is a chemical sensor that is operated in the gas phase. It is an important component of devices commonly known as ‘electric noses’ [110].

A gas sensor must possess at least two functions: (i) to recognize a particular gas and (ii) convert the output into measurable sensing signals. The gas recognition is carried out through the surface chemical processes due to gas-solid interactions. These interactions may be in the form of adsorption, or chemical reactions. Most of the gas sensors give an electrical output, measuring the change of current or resistance or capacitance.
The given signal can be related to the chemical environment it is exposed to. The response of a gas sensor to a single gas can be described as

\[ x = f_{\text{gas}}(c_{\text{gas}}) \]

where \( f_{\text{gas}} \) is a function (usually non-linear) and \( c_{\text{gas}} \) the concentration of the gas. The response is in most cases defined as the difference or ratio between the steady-state sensor response when exposed to the sample gas and the sensor response when exposed to a reference atmosphere (not sample gas). This is shown in Figure 1.13(a).

**Figure 1.13:** (a) Typical gas sensor response curve (b) Possible parameters to extract from a gas

The concentration-response relationship for most gas sensors approximately exhibits either saturated linear behavior, i.e. linear for low concentrations and saturated for higher concentrations, or logarithmic behavior. Other values containing information about the kinetics of the reactions can also be extracted from the sensor response, such as the derivatives and integrals over certain time intervals (Figure 1.13b).

Three important parameters when describing the response of a sensor are sensitivity; selectivity and stability. The sensitivity of the sensor towards a specific gas is, thus, defined as
The selectivity ($E$) of a single sensor is usually defined as the ratio of the sensitivity related to the gas concentration to be monitored in the linear region and the maximal sensitivity to all other interfering components. It is given by

$$E = \frac{\gamma_{\text{gas}}}{\max(\gamma)}$$

The stability of the sensor response is defined as the reproducibility of the sensitivity and selectivity as a function of time.

Most of the drawbacks of the commonly used gas sensing technologies come from their lack of stability. There are other demands to be met when producing gas sensors, such as short response time, good reversibility, low cost, small size and low power consumptions.

In order to achieve these requirements, it is important to have a clear view of how a gas sensor is made. It usually consists of two parts: the sensing material and the transducer. The sensing material interacts with the analyte, e.g. by adsorption/desorption or chemical reactions on the surface and/or the bulk of the material. The interaction changes some physical property or properties of the sensing material, such as the electrical conductivity or the mass, which can be detected using a transducer. The latter converts the variation of the physical properties, containing the chemical information, into an electrical signal. Different transducer principles can be used in chemical sensors, such as changes in conductivity as detected by the voltage drop over a series resistor, or changes in mass as detected by the shift in frequency of a resonator.
A schematic description of the working principle of either increase in resistance or decrease in resistance of solid-state gas sensors is represented in Figure 1.14.

![Figure 1.14: Working principle of sensor operation [111]](image)

When a sensing material is exposed to gas, then it interacts with the gas. This interaction may be by adsorption, desorption or chemical reactions on the surface or the bulk of the material. The interaction changes some physical properties of the sensing material, such as the electrical conductivity or the mass. The change in conductivity is detected by the voltage drop over a series resistor and a change in mass is detected by the shift in frequency of a resonator.

### 1.7.3 Need for Gas Sensors

A numerous luxury items have been brought by today’s society but with them series of problems like air pollution and emission of toxic gases have also been introduced to our society. The necessity to constantly monitor and control the gases emitted, sprouted the need for gas sensors. The various uses of gas sensors vary across a wide range from industrial to domestic applications; for example monitoring air pollution, chemical processes and exhaust from combustion engines. In recent years, several types of gases have been used in different areas of industries as raw materials. It becomes really important to control and monitor these gases, as there is a huge risk of
damage to property and human lives if a leak occurs. Certain gases are corrosive, explosive or can be toxic for human beings.

Currently, there are three categories in which gas monitoring is needed:

- For oxygen (O₂), in connection with the monitoring of breathable atmospheres and for the control of combustion.
- For flammable gases in air, in order to protect against the unwanted occurrences of fire or explosive limit, which is up to a few percent for most gases.
- For toxic gases in air, where the need is to monitor concentrations around the exposure limits which range from less than 1 ppm to several hundreds of ppm.

Therefore, we require gas sensors that can detect these gases continuously and effectively to avoid most of the problems.

The increasing demand is for better gas sensors with higher sensitivity and greater selectivity. Intense efforts are being made to find more suitable materials with the required surface and bulk properties for the use as gas sensors. Among the gaseous species to be observed are carbon monoxide (CO), carbon dioxide (CO₂), nitric oxide (NO), nitrogen dioxide (NO₂), hydrogen sulfide (H₂S), sulfur dioxide (SO₂), ozone (O₃), ammonia (NH₃), and organic gases such as methane (CH₄), propane (C₃H₈), liquid petroleum gas (LPG), and many others.

### 1.7.4 Classification of Gas Sensors

The gas detection is based on the fact that changes in gases atmosphere alters the properties of the sensing layer in the characteristic way, which is transformed into signal by the transducer. The sensing layer is optimized by the proper choice of the material and the signal transfer component by a suitable technology.
Gas sensors can be classified into different types based upon the changes in the properties of the sensing material. They can be classified into following types:

1) **Optical Gas Sensors**

In case of optical sensors, changes in the ambient atmosphere change the optical properties of the sensor element, e.g. optical thickness or adsorption which are measured by interferometers, optical waveguides, fibers etc. The sides or tips of the optic fibers (thickness, 2mm) are coated with a fluorescent dye encapsulated in a polymer matrix. Polarity alterations in the fluorescent dye, on interaction with the vapor, changes the dye’s optical properties such as intensity change, spectrum change, lifetime change or wavelength shift in fluorescence [112, 113]. These optical changes are used as the response mechanism for odour detection. Polyaniline-coated optical sensors have been used to detect ammonia at concentrations as low as 1 ppm and the linear dynamic range was between 180 and 18,000 ppm [114].

2) **Capacitive Gas Sensors**

Capacitive sensors respond by capacitive changes of the material, which are mostly detected through low frequency AC measurements.

3) **Mass Sensitive Sensors**

In case of mass sensitive sensors, the composition of the gas atmosphere affects the mass and hence the oscillating frequency is used in transducers like quartz microbalances, surface acoustic wave sensor etc. Surface acoustic wave sensor (SAW) is composed of a piezoelectric substrate with an input (transmitting) and output (receiving) interdigital transducer deposited on top of the substrate. The sensitive membrane is placed between the transducers and an AC signal is applied across the input transducer
creating an acoustic two dimensional wave that propagates along the surface of the crystal at a depth of one wavelength at operating frequencies. The mass of the gas sensitive membrane of the SAW device is changed on interaction with a compatible analyte and causes the frequency of the wave to be altered. Polymer-coated SAW devices have quite low detection limits, e.g. tetrachloroethylene, trichloroethylene and methoxyflurane have been detected at concentrations as low as 0.7, 0.6 and 4 ppm, respectively [115].

4) Conductance Sensors

Conductance sensors respond with the changes in resistance, which is normally determined by a 2 or 4- point probe resistance measurement e.g. metal oxide sensors, conductive polymer sensor, ionic conductors. Conducting polymer composites, intrinsically conducting polymers and metal oxides are three types of conductance sensors. The sensing material is deposited over two parallel electrodes, which form the electrical connections through which the relative resistance change is measured.

- **Metal Oxide Gas Sensors** - Many researchers have shown that the exposed gas molecules alter the properties of the metal oxide gas sensors [116]. The change in the property depends upon many factors like the microstructure of the sensing material, inherent properties of the base materials, surface areas, surfactants, temperature, humidity etc. The principle on which metal oxide gas sensors works is the change in resistance at high temperature due to interaction of gas molecules. Lot of research work has been carried out in recent years [117-122] to optimize the parameters of known metal oxides as well as to discover new materials.
Introduction

Semiconductor gas sensors were originally commercialized in Japan employing tin oxide as the sensitive component.

5) Electrochemical Gas Sensors

Electrochemical sensors operate by reacting with the gas and producing an electrical signal proportional to the gas concentration. A typical electrochemical sensor consists of a sensing electrode (or working electrode) and a counter electrode separated by a thin layer of electrolyte. Gas that comes in contact with the sensor first passes through a small capillary-type opening and then diffuses through a hydrophobic barrier and eventually reaches the electrode surface. The gas that diffuses through the barrier reacts at the surface of the sensing electrode involving either an oxidation or reduction mechanism. These reactions are catalyzed by the electrode materials specifically developed for the gas of interest. With a resistor connected across the electrodes, a current proportional to the gas concentration flows between the anode and the cathode. The current can be measured to determine the gas concentration. Because a current is generated in the process, the electrochemical sensor is often described as an amperometric gas sensor.

6) Catalytic Sensors

Potentially explosive mixtures of methane or other flammable gases, with air can be monitored by means of a catalytically active solid-state sensor. The device, often referred to as the ‘pellistor’, is essentially a catalytic micro calorimeter. It consists of a catalytic surface constructed around a temperature sensor and a heater, which maintains the catalyst at a sufficiently high temperature to ensure rapid combustion of any flammable gas molecules present. However, these sensors suffer from several problems,
including loss of sensitivity with time due to poisoning and burning out when exposed to high gas concentrations [123].

7) **Hetero-junction Gas Sensors**

Hetero-junction gas sensors are recently invented type of solid state gas sensors that can overcome some of these limitations of metal oxide gas sensors and show other desirable characteristics such as fast response and recovery, selectivity towards specific gases, good sensitivity etc. The junction width or potential barrier, which gets developed at the interface between two semiconductors changes by the influence of gas molecules. Thus the presence of the gas can be detected by hetero-junction devices specially liquefied petroleum gas (LPG), which is being widely used for domestic purpose. The region of hetero-junction is the interface between the two consisting semiconducting materials, which behaves like a p-n junction. Gases adsorbed on either side of the hetero-junction are oxidized at varying rates at the hetero-junction interface and influence its barrier characteristics. Hetero-junction sensors have fast response time, cross selectivity, improved sensitivity, reduced cost and important potential for miniaturization leading to low power consumption.

1.7.5 **Sensing Materials**

A large number of different materials have their physical properties modified after interaction with a chemical environment such as ionic compounds (metal oxides), metals, polymers and supramolecular structures. Properties of the sensing materials, such as molecular size, polarity, polarisability, and affinity, along with the matching characteristics of the sensing material, govern the interaction.
Two main types of interaction between the presence of gas and the sensing material are:

- Lock-and-key-type interaction, which usually consists of organic materials. They can be arranged either as a monolayer of the recognition molecules or as specific recognition sites in a polymeric matrix. Typical materials employed are cage-like molecules such as calixarenes [124].

- Chemical sensing with inorganic materials. Reactions at the surface and/or in the sensing material may lead to chemisorptions or catalytic reactions between the molecules present. Thus, the charge distribution, the carrier concentration or mobility in the sensing material might change [125].

Hydrocarbon gases are being used as fuel for domestic and industrial purposes. Domestic liquefied petroleum gas (LPG) and CO are combustible gases. They are potentially hazardous; increasing usage of liquefied petroleum gas (LPG) has increased the frequency of accidental explosions due to leakage. The toxic hazardous gases combine with hemoglobin very quickly and results in human death. People have been trying to detect them in its early stages to give alarm and perform effective suppression. Thus the requirements for reliable and sensitive gas detecting instruments have increased for safety at home and industry. Most of previous researches were focused on propane or butane gas sensor but little work has been done on LPG sensor. From the literature, it is inferred that presently available sensors have two major shortcomings, one, low sensitivity and two, its operation at a high temperature. One has to compromise with either the sensitivity or the operating temperature. A highly sensitive sensor mostly works at a very high operating temperature thus increasing the power consumption. On the other
hand, other sensors which operate at low temperature are not sensitive enough for trace
level detection of LPG [126]. To improve this problem, some researchers paid attention
to the study of signal analysis. Many reports showed that it was possible to discriminate
gases by evaluating the sensor response features [127].

1.7.6 Applications of Sensors

Gas sensors have found wide applications in industrial production, environmental
monitoring and protection, etc. [128, 129]. A variety of materials have been used for gas
sensing, which include electronic ceramics, oxide semiconductors, solid electrolytes, and
conducting polymers [130]. A gas sensor gives an electrical output, measuring the change in
property such as resistance or capacitance. Molybdenum oxide (MoO$_3$) which has similar
physical and chemical characteristics to WO$_3$ has recently drawn a lot of attention with
regard to its gas-sensing ability [131].

Recently, the controlled incorporation of molybdenum, tungsten, and vanadium
polyoxometallates into organic solid matrices has been attracting widespread interest in
materials science due to the prospects for developing new functional materials. Such
inorganic–organic hybrid films have been prepared by various methods, including ion
exchange reactions within the interlayer space of ammonium amphiphile bilayer films,
ion-complexing with ammonium amphiphile, electrostatic layer-by-layer self-assembly
and Langmuir–Blodgett deposition [132]. It should be emphasized here that
molybdenum, tungsten, and vanadium polyoxometallates are potential precursors for
MoO$_3$, WO$_3$, and V$_2$O$_5$, respectively, which are important gas sensor materials [133].
Sensors have a wide range of applications and are constantly being extended to new
areas. 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 the industrial processes, for human comfort, domestic purpose, in medical applications and in agriculture. Recently, there has been a considerable increase in the demand for humidity control in various fields such as air conditioning systems, electronic devices, tyre industries, sugar industries and drying processes for ceramics and food.

Industrial hygiene has become very important because of the published health hazards and related atmospheric pollution. The general public has become more sensitive to the various gases. As a result much effort is being focused on producing relatively inexpensive sensors of medium sensitivity and selectivity to meet these needs.

Manufacturing process monitoring and control has become very important especially for confined spaces such as chemical and fuel storage tanks and in particular on board of chemical and oil tankers.

Control of combustion processes where process monitoring have become an integral part of most manufacturing industries, including the wide spectrum of chemical industries and the high technology electronic industries. The objective also includes in addition to monitoring, to regulate the pollution at least to within compliance of the National Pollution laws (Control).

Fuel efficiency and pollution control of combustion processes require proper control of the ratio of fuel to oxygen or air in a jar or oil fires furnace in industrial and domestic installation or internal combustion engines. In the case
of exhaust gases, the detection of CO is also very important in addition to that of $O_2$. The main objective of the CO monitoring is to prevent the intoxication caused by incomplete burning in domestic combustion equipment.

- Another important area of application is in medical diagnosis of patients by monitoring the humidity, oxygen and carbon dioxide concentration. Our medical applications include monitoring the environment for health hazardous gases and vapors including carcinogenic compounds not only within the confines of industries associated with the use or production of such chemicals but also their spread through atmosphere by air movement. Also, sensors able to monitor the extent of contamination by all kinds of known or unknown microorganisms are expected to be in great future demand.

### 1.8 Literature Review

The structure and properties of polypyrrole films prepared by potentiostatic method have been compared to those prepared by the galvanostatic method by Hagiwara et al. [134].

Hauber et al. [135] studied the interaction between silver as an electrode material and the surface of polypyrrole films as a prototype material of stable conducting polymers by electron and electrical impedance spectroscopy. It is found that silver forms a stable interface on the two dimensional polypyrrole films. They have predicted that the stability is caused by the sequestering of Ag atoms in the two dimensional micro structure and by the formation of silver-polypyrrole compounds with metallic properties.

Suri et al. prepared nanocomposite pellets of iron oxide and polypyrrole for humidity and gas sensing by a simultaneous gelation and polymerization process. This
resulted in the formation of a mixed iron oxide phase for lower polypyrrole concentration, stabilizing to a single cubic iron oxide phase at higher polypyrrole concentration. Sensitivity to humidity increased with increasing polypyrrole concentration.

Kuwabata et al. [136] prepared charge discharge properties of V$_2$O$_5$-polypyrrole composites as positive electrode materials in rechargeable lithium batteries.

Lee et al. prepared electrically conducting composites by chemical oxidative polymerization using polypyrrole and polycarbonate or sulfonated polycarbonate in chloroform. The pyrrole was protonated and polymerized using iron (III) chloride [137].

Komilla et al. prepared nano composites of polypyrrole and iron oxide using simultaneous gelation and polymerization process. Varied amount of pyrrole monomer were added to a solution containing iron nitrate as precursor and 2-methoxy ethanol as solvent [138].

Chen et al. [139] presented a study on synthesis and characterization of pyrrole based chiral liquid crystals. The thermo tropic, electrochemical properties and polymerization of a series of N – substituted pyrrole monomers bearing mesogenic 4 – substituted azobenzenes attached as a pendent group via alkyl group, have been discussed by Y Chen et al. [140].

Muccillo et al. prepared nanosized powders of CeO$_2$ with controlled physical properties by the precipitation technique using ammonium hydroxide or oxalic acid as precipitating agent. The calcined precursors were studied by nitrogen adsorption to determine the specific surface area. The samples were characterized by XRD and SEM
techniques. It is shown that both precipitating materials may be used for the preparation of nanocrystalline powder (<10 nm) with high values of specific surface area [141].

Migahed et al. prepared conducting composites by oxidation polymerization of pyrrole interpenetrated in ethylene-vinyl alcohol copolymer. The oxidant used was iron (III) chloride. The conductivity was analyzed by the variable range hopping (VRH) model and the best results have been achieved for a one-dimensional model for charge transport in the present conducting composites. The morphology changes of the composite films were attributed to the synthesis conditions [142].

Murugendrappa et al. carried out the polymerization of pyrrole in the presence of fly ash (FA) to synthesize polypyrrole–fly ash composites (PPy/FA) by chemical oxidation method. The ac conductivity behavior has been investigated in the frequency range $10^2$–$10^6$ Hz. The dc conductivity was studied in the temperature range from 40–200°C. They found that the dimensions of fly ash in the matrix have a greater influence on the observed conductivity values [143].

Narsimha Parvatikar et al. studied the spectroscopic and electrical properties of polyaniline/CeO$_2$ composites and their application as humidity sensor. The change in resistance with respect to percentage relative humidity (% RH) is reported [144].

Vishnuvardhan et al. have studied the synthesis, characterization and ac conductivity of polypyrrole/Y$_2$O$_3$ composites. Frequency dependent dielectric loss, as well as variation of dielectric loss as a function of mass percentage of Y$_2$O$_3$ is also presented and discussed [145].

Synthesis, characterization and low frequency AC conduction of Polyaniline-niobium pentoxide composites were studied by Ravikiran et al. [146]. They reported that
three step decomposition patterns were observed for PANI and its composites. AC conductivity and dielectric response of the composites were investigated in the frequency range, $10^2$–$10^6$ Hz. AC conductivity obeyed the power law index, which decreased with increasing wt% of Nb$_2$O$_5$.

Hossein Eisazadeh synthesized Polypyrrole and its composites using FeCl$_3$ as an oxidant in aqueous and non-aqueous media. The effect of various solutions such as water, ethylacetate, acetonitrile, methylacetate, methanol, ethylmethylketone and surface active agents, poly (ethylene glycol) and poly (vinyl acetate) on the properties of product were studied [147].

The influence of Nb$_2$O$_5$ on density, molar volume, optical band gap and electrical conductivity of barium borate glasses has been reported Sonam et al. They found that the density and molar volume increases with increasing concentration of Nb$_2$O$_5$ [148].

Rui Wang et al. encapsulated NiO doped polypyrrole in mesoporous SBA-15. All of the synthesized samples were investigated as humidity-sensor materials at room temperature. The sensitivity mechanism was investigated by dc and ac analysis [149].

Yu et al. made a comparative analysis of responses of thin films of various conducting polymers (polyaniline, polypyrrole and poly-3-methylthiophene) to the 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 [150].

Suying Wei et al. prepared Polypyrrole-TiO$_2$ nanocomposite oxidative polymerization method with the effects of oxidant type and TiO$_2$ particle loading level on
the physiochemical properties of the PPy/TiO$_2$ nanocomposite were investigated. The frequency dependent dielectric constants of these nanocomposites were measured [151].

Guziewicz et al. studied electrical and optical properties of NiO films deposited by magnetron sputtering. Their work is concerned with the properties of NiO films fabricated 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 [152].

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 in situ polymerization of CeO2 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 observed with the increase in gas concentration [153].

Nalage et al. synthesized PPy-NiO hybrid nanocomposite thin-film sensor by spin-coating method on glass substrate. These sensors were used to study room temperature gas-sensing properties for oxidizing (NO$_2$, Cl$_2$) as well as reducing (NO$_2$, H$_2$S, NH$_3$) gases [154].

Polyacrylonitrile/Polypyrrole (PAN/PPy) composite is prepared by Ahmer et al. by sol-gel method. The temperature dependence of the DC electrical conductivity was measured on compressed pellets. The thermal stability of the composite material (HCl treated) in terms of dc electrical conductivity retention was studied under isothermal
conditions. The stability of the material (HCl treated) in terms of electrical conductivity retention was also monitored for five cycles for increasing temperatures. The composite material was found thermally and environmentally stable in terms of DC electrical conductivity retention [155].

1.9 Aim of the Study

The rapidly expanding fields of conducting polymer nanocomposites are generating 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, Polypyrrole (PPy) is selected as a conducting polymer and the metal oxides such as NiO, Nb$_2$O$_5$ and CeO$_2$ are used to make composites with PPy. The author has tried to tailor the various electrical and sensing properties of PPy and its composites. The composites were characterized with FT-IR, XRD and SEM techniques to bring out the changes occurred due to doping. Studies on dc conductivity, ac conductivity, dielectric properties and LPG gas sensing behavior were done.
Introduction

References


Introduction


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