

## M. Sc. Sem-IV (Polymers Unit-IV)

### Conducting Polymer (Polypyrrole and Bipolaron)

#### INTRODUCTION

Solids show a wide range of electrical conductivities from  $10^{-20}$  to  $10^7$   $\text{ohm}^{-1} \text{m}^{-1}$ . On the basis of electrical conductivity, the solid can be broadly classified into three types:

##### 1. Conductors

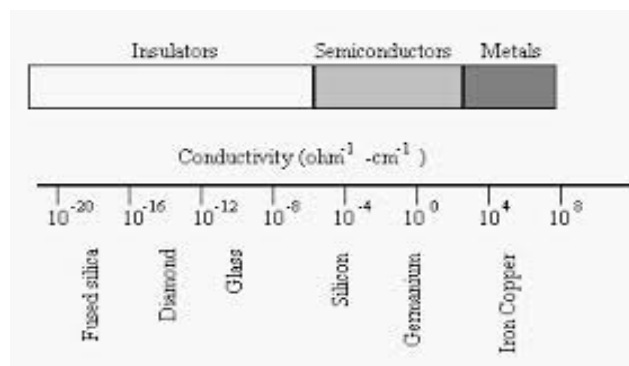
The solids which have conductivities in order of  $10^4$  to  $10^7$   $\text{ohm}^{-1} \text{m}^{-1}$ . Metals are good conductors of electricity.

##### 2. Insulators

Solids which have very low conductivity in the range  $10^{-20}$  to  $10^{-10}$   $\text{ohm}^{-1} \text{m}^{-1}$ . For example, wood, rubber, sulfur, phosphorus etc.

##### 3. Semiconductors

Their conductivity is in between conductor and insulator up to the order of  $10^{-6}$  to  $10^4$   $\text{ohm}^{-1} \text{m}^{-1}$ .



#### Electrical Conductivity

Solids can conduct electrical charge due to the motion of electrons and the positive holes (electronic conductivity) or because of the motion of ions (ionic conductivity). The reason for electrical conductivity of metals is the motion of electrons and it increases by increasing the number of participating electrons in the process of conduction.

Pure ionic solids, in which conduction occurs only through the ionic motion, are termed as insulators. The defects in crystal structure increases the conductance property of semiconductor and more so with insulator. The electrical conductivity of metals, insulators and semiconductors can be explained in terms of Band Theory.

#### Band theory

This is based on molecular orbital theory. The molecular orbitals are formed by overlapping of atomic orbitals and the number of molecular orbitals formed are equal to the number of atomic orbitals which take part in overlapping.

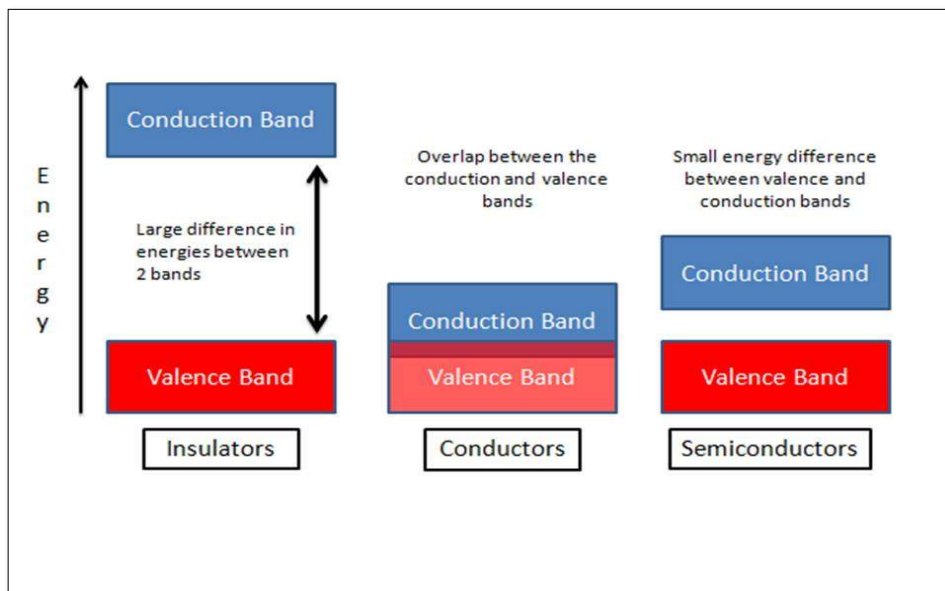
In the case of metals, the atomic orbitals are very close in energy so they form a large number of molecular orbitals which are very close in energy. This set of molecular orbitals is called band which is of two types.

- **Valence band:** This is a band of lower energy

- **Conduction band:** The band of higher energy

The energy difference separating these two bands is called band gap or energy gap. These energy bands are separated by space where no energy is allowed in and are termed as forbidden bands. The top of available electron energy level at low temperature is called Fermi level.

- If the **valence band is partially filled** or it overlaps with higher energy or have unoccupied conduction band then the electrons can be excited from lower to higher energy level by supplying a very small amount of energy or applied electric field. Hence the metal conducts electricity and behaves as a **conductor**.
- If the **gap between the filled valence and unfilled conduction band is large** and it's not possible for electrons to jump from the valence to conduction band, then the substance has extremely low conductivity and behaves as an **insulator**.
- If the **gap between the valence and conduction band is small** and some electrons can jump from valence to conduction band, then the substance shows some amount of conductivity and behaves as a **semiconductor**.



**Fig 1. Band diagram showing difference of energy bands in conductors, semiconductors and insulators**

A **conductor** is an object or type of material that permits the flow of electric charges in one or more directions. For example, a wire is an electrical conductor that can carry electricity along its length.

In metals such as copper or aluminum, the movable charged particles are electrons. Positive charges may also be mobile, such as the cationic electrolyte(s) of a battery, or the mobile protons of the proton conductor of a fuel cell. Insulators are non-conducting materials with few mobile charges and support only insignificant electric currents. Conducting materials include metals, electrolytes, superconductors, semiconductors, plasmas and some nonmetallic conductors such as graphite and Conductive polymers.

**Conductive polymers** or, more precisely, **intrinsically conducting polymers (ICPs)** are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, *i.e.*, they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical

properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

Polyaniline was first described in the mid-19th century by Henry Letheby, who investigated the electrochemical and chemical oxidation products of aniline in acidic media. He noted that reduced form was colorless but the oxidized forms were deep blue.

The first highly-conductive organic compounds were the charge transfer complexes. In the 1950s, researchers reported that polycyclic aromatic compounds formed semi-conducting charge-transfer complex salts with halogens. In 1954, researchers at Bell Labs and elsewhere reported organic charge transfer complexes with resistivities as low as 8 ohms-cm. In the early 1970s, researchers demonstrated salts of tetrathiafulvalene show almost metallic conductivity, while superconductivity was demonstrated in 1980. Broad research on charge transfer salts continues today. While these compounds were technically not polymers, this indicated that organic compounds can carry current. While organic conductors were previously intermittently discussed, the field was particularly energized by the prediction of superconductivity following the discovery of BCS theory.

In 1963 Australians B.A. Bolto, D.E. Weiss, and coworkers reported derivatives of polypyrrole with resistivities as low as 1 ohm·cm. cites multiple reports of similar high-conductivity oxidized polyacetylenes. With the notable exception of charge transfer complexes (some of which are even superconductors), organic molecules were previously considered insulators or at best weakly conducting semiconductors. Subsequently, DeSurville and coworkers reported high conductivity in a polyaniline. Likewise, in 1980, Diaz and Logan reported films of polyaniline that can serve as electrodes.

**In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa reported similar high conductivity in oxidized iodine-doped polyacetylene. For this research, they were awarded the 2000 Nobel Prize in Chemistry "for the discovery and development of conductive polymers."** Polyacetylene itself did not find practical applications, but drew the attention of scientists and encouraged the rapid growth of the field. Since the late 1980s, organic light-emitting diodes (OLEDs) have emerged as an important application of conducting polymers.

The demand for electrically conducting polymers as used in the electronics industry has in the past been met by using high loadings of conductive powders such as silver, gold and graphite (sometime as high as 80% by weight) with the polymer matrix<sup>1</sup>. There are, however, a number of disadvantages to this approach, including high cost and deterioration in other properties of the polymer. Intrinsically conducting organic polymers such as polyaniline, polypyrrole and polythiophene have been studied intensively during the last decade due to their high electrical conductivity, good environmental stability.

Among the conducting polymers known to date, ones based upon **PPy (polypyrrole)** have attracted special interest because of their high conductivity, their ease and high flexibility in preparation, their stability and good mechanical properties and Potential technological applications such as in electronic and electrochromic devices, counterelectrode in electrolytic capacitors, sensors, chromatographic stationary phases, light-weight batteries, membrane separation consequently, have attracted a great deal of attentions in recent years and this is currently one of the most active areas of research in polymer science and engineering at present.

## Synthesis

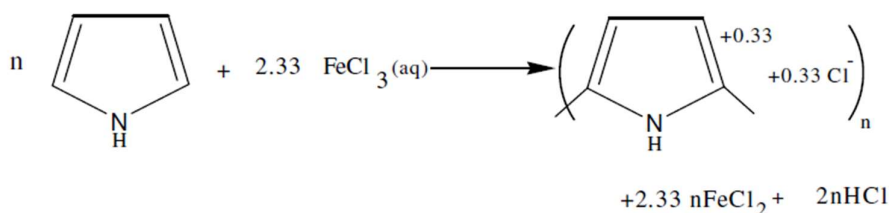
Polypyrrole and a wide range of its derivatives can be prepared by following methods:

1. Chemical method
2. Electrochemical method

## 1. Chemical method

Chemical polymerisation is a simple and fast process with no need for special instruments. Bulk quantities of polypyrrole (PPy) can be obtained as fine powders using oxidative polymerisation of the monomer by chemical oxidants in aqueous or non-aqueous solvents or by chemical vapour deposition. However, the use of chemical polymerisation limits the range of conducting polymers that can be produced since only a limited number of counterions can be incorporated. The chemical polymerisation of pyrrole appears to be a general and useful tool for the preparation of conductive composites and dispersed particles in aqueous media.

Iron (III) chloride has been found to be the best chemical oxidant and water is the best solvent for chemical polymerisation with respect to desirable conductivity characteristics. The overall stoichiometry resulting from chemical polymerisation of PPy with ferric chloride oxidant is shown in Figure 1.



**Figure 1.** Chemical polymerization of polypyrrole

During chemical polymerisation of pyrrole, electroneutrality of the polymer matrix is maintained by incorporation of anions from the reaction solution. These counterions are usually the anion of the chemical oxidant or reduced product of oxidant. For example, when  $\text{FeCl}_3$  or  $\text{Cl}_2$  are used as oxidants,  $\text{Cl}^-$  ion is incorporated as counterion or when  $\text{I}_2$  is used as oxidant,  $\text{I}_3^-$  ions are incorporated into the polymer matrix. It has been found that factors such as solvent, reaction temperature, time, nature and concentration of the oxidizing agent, affect the oxidation potential of the solution. These in turn influence the final conductivity of the chemically synthesized polypyrrole. Elemental analysis data has shown that the composition of polypyrrole prepared chemically is almost identical with that electrochemically prepared.

## 2. Electrochemical preparation

The electrochemical approach for making electroactive/conductive films is very versatile and provides a facile way to vary the film properties by simply varying the electrolysis conditions (e.g. electrode potential, current density, solvent, and electrolyte) in a controlled way. Or the variations in the properties of polymer can be made in the selection of the monomer or the electrolyte.

Furthermore, the electrosynthesis allows an easy control of the thickness of the polymers. Preparation of conducting polymers electrochemically is a complex process and the yield and quality of the resulting polymer films is affected by various factors. The nature and concentration of monomer/electrolyte, cell conditions, the solvent, electrode, applied potential and temperature, pH all have a strong effect on the electro-oxidation reaction and the quality of the film. It is therefore not easy to optimize all parameters in one experiment.

Among these different parameters, the counterion plays the most important role. In the electrochemical method the polymer is synthesized directly in its oxidised and doped state. Then can be removed in either its conducting or insulating form. The monomer is first dissolved in a salt solution (where the electrolyte is highly dissociated and which are slightly acidic) with low nucleophilicity and

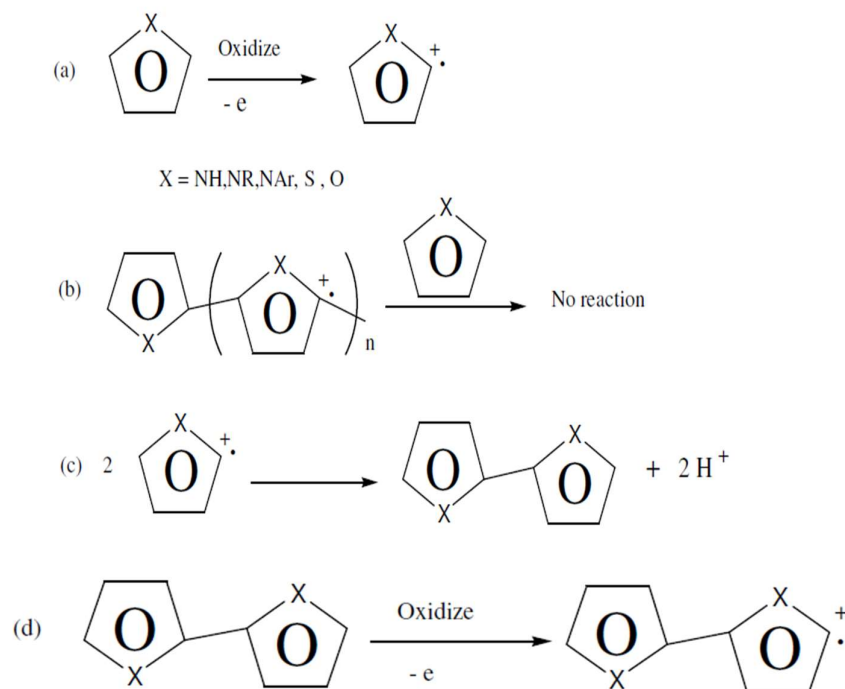
solution resistance. Application of a suitable potential ( $E = -0.65 \text{ V vs. Ag/AgCl}$ ) initiates the polymerization reaction. The oxidation potential used can be easily controlled and therefore the quality of the polymer can be optimized. Also because of the good solubility of pyrrole monomer in a wide range of solvents, pyrrole is easily electropolymerised in both aqueous and non-aqueous solvents.

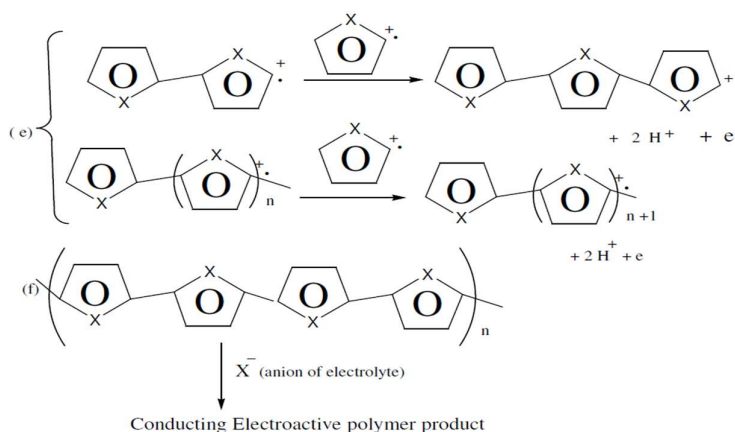
The polymerisation reaction is very complicated and the mechanism of electropolymerisation is still not fully understood.

### Mechanism of Electro-polymerization of polypyrrole

The generally accepted mechanism is that-

- i. In the first step the neutral monomer is oxidised to a radical cation.
- ii. Followed by aromatization and oxidation of the dimer.
- iii. As the dimer, on account of its greater conjugation, is more easily oxidised than the monomer under the given experimental conditions, it is immediately reoxidised to the cation.
- iv. Since the polymerisation reaction proceeds only when the potential is sufficiently high to oxidise the monomer, the coupling reaction must involve the coupling of two radical cations. Although most of their pyrrole units are linked at the a-a (or 2,5) positions, a significant number of the units are coupled through the a-b and b-b cross linkages, the less desirable 3,4 or 2,3 coupling contributes to the formation of soluble oligomers and reduces the conjugation length and lowers the conductivity (Figure 2).





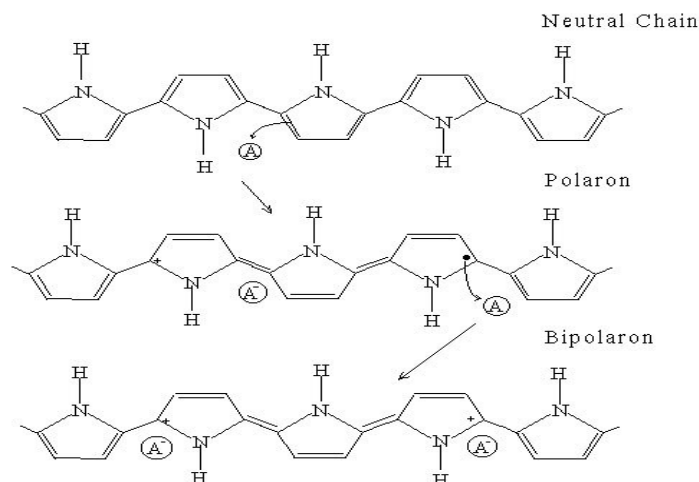
**Figure 2.** The accepted mechanism for electropolymerisation mechanism of polypyrrole or other aromatic heterocyclic monomers

### Electrical conductivity in polypyrrole

The electrical conductivity of PPy conductive polymers is one of the most important properties for analytical applications. PPy is a conducting polymer which has a nondegenerate conduction band in the ground state the **polaron and bipolarons are the dominant charge carriers in these polymeric conductors**. The mechanism of conduction in PPy has not been yet conclusively established because of the persistent structural disorder of the polymer. The most widely accepted view of conductivity in these systems involves **charge transport along the polymer chains, as well as hopping of carriers (holes, bipolarons, etc.)**.

Electrically conducting polymers are semiconductors with a filled valence band and an empty conduction band. These bands are separated by an energy gap. Doping of these polymers creates new bands in the energy gap, making it possible for the electrons to move to these new bands and increasing the conductivity of the materials. **In the reduced (undoped) form, PPy conducting polymers are insulators. Bipolarons (radical di- ions) showed in Figure 3, play a major role in the electronic and transport properties of conducting polymers.**

The bipolaron model has been shown to provide a coherent and unified picture of the properties of doped conducting polymers and the possibility of a small band gap has been pointed out. The positive charges created on the polymer backbone (commonly termed polarons) are the charge carriers for the electrical conduction (Figure 3).



**Fig-3 Proposed structure of polarons and bipolarons**

Their transport occurs via mobility along segments of conjugated polymer chain and the hopping of charges from chain to chain. The number of these charges contained in a material and their relative mobility controls the bulk electrical conductivity. A counterion (in this case an anion, typically termed a dopant anion) stabilizes the charge on the polymer but is not very mobile within the dry material. Thus, these polymers are truly electronic and not ionic conductors.

The electrical conductivity of PPy is the product of two important factors, the number of carriers (**e<sup>-</sup> or holes**) and charge carrier mobility. Higher mobilities will occur with more crystalline, better oriented, defect free materials. Increasing the doping level will increase the density of charge carriers. The conductivity decreases with falling temperature just like that of semiconductors. In contrast, the conductivities of typical metals, like silver, increase with falling temperature.

### **Factors Affecting Properties of Ppy**

#### ***(i) Effect of substrate***

- PPy films can be electropolymerised on a wide range of metal electrodes. Glassy carbon, platinum (Pt) and gold (Au) are mostly used.
- However, Indium-tin oxide (ITO) coated glass, Titanium (Ti), Aluminium (Al), mild steel, and brass, mercury, tin-oxide and silver have also been tried.
- In comparison with Pt electrode the oxidation potential of pyrrole is increased and current density reduced when Ti, Fe, or Al are used. This is a consequence of metal-oxide film formation which impedes electron transfer during electropolymerisation.
- Metals such as silver or aluminum, which oxidise more readily than the pyrrole monomer, would obviously not be a good choice.

#### ***(ii) Effect of dopant***

- The anion incorporated into the polymer (counterion) during synthesis has the greatest influence on the general properties of the polymer and the thermal stability.
- The as-formed polymers are molecular composites containing a cationic polymer backbone, with accompanying "dopant" anions for maintenance of charge neutrality. During electrochemical synthesis, as a result of simultaneous oxidation and polymerisation of the pyrrole monomer, the conducting form of the polymer with a delocalized positive charge on the p electron system is formed.
- Anions from the electrolyte solution in which the monomer has dissolved are incorporated into the polymer in order to achieve electroneutrality. The counterions used as supporting electrolytes in electropolymerisation should be very soluble in the monomer solution, chemically inert (toward the solvent or electrodes), electrochemically stable at the potential of monomer oxidation or reduction potential at the cathode.
- Therefore, easily oxidisable anions with a lower oxidation potential than the monomer, such as iodide or bromide, decrease the electropolymerisation efficiency or reduce the selectivity for film formation. The dopant is not necessarily the adopted supporting electrolyte anion, as other negatively-charged molecules, even with much larger size, can be incorporated into PPy matrix as dopant subsequently.
- In addition, the use of an aqueous deposition medium would also offer considerably larger selection of supporting electrolyte anions.

## Factors affecting electrical conductivity of polypyrrole

The electrical conductivity of the ppy films are strongly influenced by the preparation conditions such as:

- **Preparation method**

It has been indicated that highly conducting PPy films with an electrical conductivity higher than 500 S/cm have been prepared with the electrochemical method by selecting suitable polymerisation conditions. It has also been found that the preparation method also affects the properties of the produced films. For example, the use of a pulsed potential technique in the growth of ppy films leads to an enhancement in electrical conductivity.

- **Doping level**

It has already been found that the electrical conductivity and mechanical properties are also strongly influenced by the molecular structures of the dopant and the doping level. That is, the doped PPy film has high mechanical strength and conductivity, but its strength or conductivity decreases remarkably after un-doping.

- **Current density**

It has also been previously reported that with increasing current density, the surface of the polymer becomes rough which leads to inaccurate values for the film thickness. A decrease in conductivity at high current densities (high anodic potential) can also be caused by the reaction of nucleophiles, like H<sub>2</sub>O and/or OH<sup>-</sup> with the polymer backbone. This interrupts the conjugated structure and lowers the intrinsic conductivity of the polymer.

- **Synthesis temperature**

The electrical conductivity of the produced polypyrrole films are also affected by synthesis temperature. Polypyrrole synthesized at lower temperature exhibits longer conjugation length, structural order, fewer structural defects, and higher conductivity.

- **Solvent**

By a treatment of PPy with NaOH solution the conductivity of all PPys drops with time. This effect can be reversed if the sample is treated with HCl. This may be due to the stabilization of charge carriers (polarons or bipolarons). The doped ppy chain undergoes a deprotonation process in aqueous basic media (with pK<sub>a</sub> in the range 9-11), which causes a profound change in its electronic structure (probably the formation of quinoid structure) leading to de-doping and a low conductivity of 10<sup>-5</sup> S/cm known as chemical compensation. It has been shown that after exposure to sulphuric acid solution, the PPy films shrank, became hard, somewhat brittle and weaker. Sodium hydroxide, treatment also caused severe embrittlement of the films. Scanning electron microscopy (SEM) investigations of PPy has also showed that the surface morphology of the ppy changes with base or acid treatment.

## Electroactivity of PPy

- The electroactive behavior of the film is unique because it is an example of a redox polymer reaction which is accompanied by a change in the electrical properties of the film from an insulator to an electrical conductor involving both electron and ion transport within the film.
- Owing to the high conductivity and thermal stability of PPy the conducting polymer, the electroactive nature or the switching properties of PPy have been utilized as the basis of most proposed applications such as **sensors, separation devices and rechargeable batteries**.
- Reduction-oxidation processes in polypyrrole conducting polymers involves mass and resistance changes as well as electron transitions, and this makes these materials very different



from other redox systems in electrochemistry in which only electrons are involved during reduction and oxidation processes.

- Oxidation of pyrrole yields a charged polymer film with incorporated anions. During the following reduction, electroneutrality can be maintained either by expulsion of these anions or by incorporation of cations. The pyrrole units have positive charges, which are balanced by anions. When a sufficient negative potential is applied to the polymer, the anions are expelled (undoping), thus reducing it to the neutral state.
- Conversely, when a positive potential is applied to oxidize the neutral film (doping), the anions are taken up. The counter ion can be released, e.g. by applying a negative potential. Release can be specifically controlled, offering interesting possibilities for active counter ions of medical significance that can be incorporated into ppy. The properties or characteristics of the PPy films can therefore be modified with regard to the nature of its dopant or counter ion.
- The dopant anions (small size) in the PPy film can be exchanged relatively easily with electrolyte anions in aqueous solutions during potential sweeping. The anion exchange processes offer an alternative chemical route for the preparation of some conductive and anion specific PPy complexes. However, the anion exchange processes do not result any significant alteration of the basic structure of the polymer. It has also been found that in the case of immobilized polymeric dopants such as anionic polyelectrolytes or large surfactant anions, the incorporated dopant or counterion is not released during electrochemical reduction of the polymer and the electroneutrality of the polymer is conserved by the penetration of the electrolyte cation into the PPy matrix. Consequently, in contrast to PPy doped with small anions, where the anions move during switching, the electrochemistry of PPy/polyanion composites involves cation transport.
- The polyanions become trapped within the polypyrrole matrix due to their large size and, perhaps more importantly their entanglement with the polypyrrole chain. Consequently, this increases the stability and mechanical strength of the film. The extent to which anions leave during reduction or cations are taken in depends upon the identity of counterion and the solvent that is used. The contribution of both processes to the overall charge transport has been found to depend strongly on the formation potential during polymerisation. The redox process of PPy formed at +1.0 V vs. Ag/AgCl is accompanied by a change in mass, which can be interpreted by simultaneous transport of anions and cations. A lower formation potential leads to a separation of the charge transport in either an anion or cation dominated region.
- The mass transport processes which are necessary for the electrochemical activity of polymer coated electrodes are strongly dependent on: the morphology of the polymer matrix and the conditions of film preparation, the nature of counterion, solvent, thickness, type of the electrode, film conditioning in the solution, and the doping anion's solubility in the solvent and also by the history of electrochemical treatments in different electrolyte solutions.
- It has been shown that PPy can be used as a redox electrode in the potential range where it is conducting. The PPy electrodes should not be used at potentials more positive than +1.0 V due to overoxidation of the polymer, which would result in irreversible loss of the electrochemical activity. In polypyrrole, anodic overoxidation is an irreversible intrinsic redox reaction as shown in Figure 4.

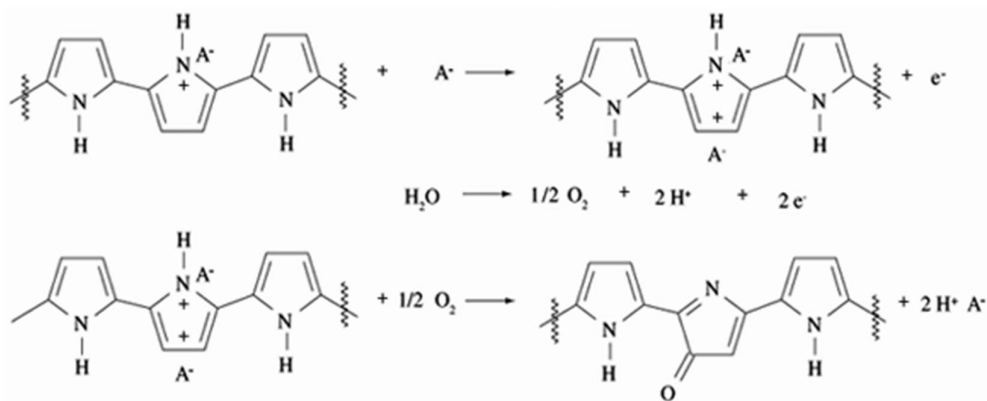


fig- 4 - Reactions that occur during the overoxidation of the PPy

The conjugation is interrupted and conductivity breaks down; hence the rechargeability of the polymer is lost. Higher electrochemical capacity of PPy films has been found in non-aqueous solvents under rigorous exclusion of oxygen and water<sup>85</sup>. Electroactivity of PPy's is also degraded by strong oxidative compounds when exposed to these chemicals. The electrochemical stability of PPy conducting polymers is also dependent on the pH of the Solution.

### General conclusions

Conducting polymers have more limited stability (environmental, thermal, chemical) than Conventional inert polymers due to the presence of dopant and their dynamic and Electroactive nature. The effect of the counterion on the intrinsic and extrinsic stability is More indirect; the effect of the anion might be to alter the crystallinity of the polymer/dopant System, the numbers of chemical defects, or extent of backbone oxidation. All of these may Affect the reactivity of the dopant/polymer system to the environment and its thermal Stability. Polypyrrole conducting electroactive polymers doped with aromatic sulfonates (mainly benzene or naphthalene sulfonates) as counterions produce flexible, and smooth Films that can be readily detached from working electrode as membrane with good Mechanical properties. The easily oxidizable organic or inorganic counterions were found That are not suitable for preparation of ppy as free-standing films. In addition, the electrolyte Should not have corrosive effect on the working electrode.

Electropolymerization of polypyrrole cep's is also limited to using high nucleophilic

Anions or substituents such as  $-\text{NH}_2$ . Preparation conditions were found that are very Important so that a small change in preparation conditions may lead to a big change in Properties of resulted polymer. The counterions used during preparation of polypyrrole films have the greatest effect on total properties of the resulted polymers. Thermal treatment at elevated temperatures affects the electrical conductivity and Electroactivity depending on the nature of the counterion incorporated during synthesis. The Changes are mostly an irreversible process. And the dopant anion has the greatest effect on Conductivity, electroactivity, mechanical, morphological, thermal and environmental and chemical stability of ppy conducting polymers. The most important factor in decay of Conductivity or electroactivity in air atmosphere is attributed to the chemical reaction of  $\text{O}_2$  with double bonds in conjugated system. The rate of thermal degradation of conductivity is Also very much dependent on temperature, atmosphere and duration of heating. The Conductivity decay of ppy polymer occurs much quicker in oxidative atmospheres, such as Air, as compared to inert atmospheres like nitrogen.