SYNTHESIS & CHARACTERISATION OF POLYMER COMPOSITE

Submitted in the partial fulfilment of requirement for the degree of

Master of Technology

in

Material Science& Metallurgical Engineering

Submitted by

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CERTIFICATE

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ACKNOWLEDGEMENT

Aparts from the efforts of me, the success of my project depends largely on the encouragement and guidelines of many others. I take this opportunity to express my gratitude to the people who has been instrumental in the successful completion of this project.

On submission of my thesis, I would like to express my esteemed sense of gratitude of my guides Dr. Kulvir Singh (Associate Prof. School of Physics and Material Science) and Dr. M.L. Singla (Prof. & Ex. Scientist 'G') for their inspiration, encouragement and support through the work for their appreciation, suggestion, constructive criticism and providing me good concepts during my scientific endeavor.

I am greatful to Dr. O.P. Pandey professor and Head of School of physics and Material science for his encouragement and execution of thesis work.

I would like to express my deep sense of guide to Dr. Pawan Kapur, Director C.S.I.O. for permitting me to work in the organization and to supplement my knowledge for successful completion of my dissertation work.

I am also greatful to Mrs. Suman singh (Scientist) for providing guidance throughout the process of my work. I am thankful to the whole staff of MRD for there ever valuable guidance.I would like to express my deep greatfulness to my parents and family who, in my ways encouraged me and provided me moral support.

Parul Nanda

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LIST OF ABBREVIATIONS

PPy	Polypyrrole
ITO	Indium Tin Oxide
FTIR	Fourier Transformed Infrared Spectroscopy
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
CV	Cyclic Voltammetry
PPy-FeCN	Composite of polypyrrole and Ferrocyanide

ABSTRACT

Present thesis focuses on the electrochemical synthesis of polypyrrole and its composites with ferri-cyanide and gold nanoparticles. The composite films were studied for their morphology, thermal properties, and electrochemical properties. Morphology of pyrole-FeCN composite was studies using Scanning electron microscopy (SEM).Polypyrole surface showed algal surface which further changed into grain like structure after the formation of its composite with FeCN. FTIR studies of PPy-FeCN composite showed that prominent peaks of polypyrole got shifted. Cyclic voltametric studies of PPy-FeCN composite showed the presence of oxidation peak of pyrole at 0.9 V as well as redox couple of Fe^{+2}/Fe^{+3}. TGA studies of polypyrole showed huge weight loss (49.30%) up to a temperature of 520^0 C which is due to the degradation of polypyrrole. But in polypyrrole-FeCN composite degradation of polypyrrole occurs at temperature of 600^0 C because due to the formation of composite its strength increases. After that there is a change of weight upto 900^0 C corresponding to the decomposition of FeCN molecule.

In case of PPy-AuNP composite, morphology has been studied using TEM. TEM image clearly showed the presence of square shaped gold nanoparticles in polymer matrix which are entrapped during the electrochemical polymerization of pyrole.Electrochemcial characterization showed the presence of

reduction peak of gold at 0.9 V as well as an oxidation peak of pyrole at 0.95 V. Impedance studies showed that PPy-AuNP composite has less charge transfer resistance as compared to polypyrole. The characteristic FTIR peaks of PPy-AuNPs are found to shift to higher wave number.

CHAPTER1

INTRODUCTION TO CONDUCTING POLYMERS AND ITS COMPOSITE

1.1 HISTORY OF CONDUCTING POLYMERS

Historically, polymers have been considered as insulators and found application areas due to their insulating properties. Infact, so far, any electrical conduction in polymers which is generally due to loosely bound ions was mostly regarded as an undesirable fact [1]. 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 optical, electronic energy storage and mechanical properties. Indeed, discovery and study of conducting polymers have already started this development [1,3]. Electrically conducting polymers are defined as materials with an extended system of conjugated carbon-carbon double bonds (Figure 1.1) [4]. They are synthesized either by reduction or oxidation reaction, which is called doping process, giving materials with electrical conductivities up to 10^5 S/cm. Conducting polymers are different from polymers filled with carbon black or metals, since the latter are only conductive if the individual conductive particles are mutually in contact and form a coherent phase [5]. 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 nineteeth century. In 1862, Henry Letheby prepared polyaniline by anodic oxidation of aniline, which was conductive and showed electrochromic behaviour.

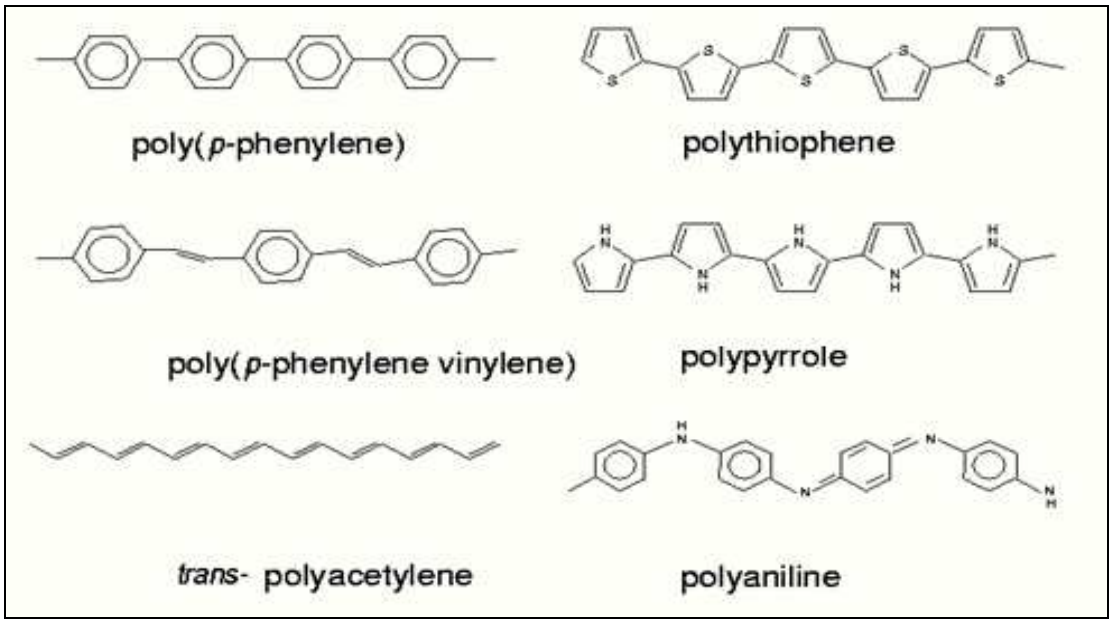


Figure 1.1 Some examples for conducting polymers

However, electronic properties of so called aniline black were not determined [1,3]. In 1958, Natta et al. synthesized polyacetylene as a black powder which was found to be a semiconductor with conductivity in the range of 10^{-11} to 10^{-3}S/cm, depending on the process conditions of the polymer [1]. In 1977, drawing attention on "conducting polymers", the first intrinsic electrically conducting organic polymer, doped polyacetylene, was reported. Intrinsically conducting polymers are a different class of materials than conducting polymers, which are a physical mixture of a non-conductive polymer with a conducting material such as metal or carbon powder [2].

1.2 THEORY OF CONDUCTING POLYMERS

Conductive polymers or more precisely intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have conductivity range either in metals or in semiconductors [6]. The biggest advantage of conductive polymers is their processability. Conductive polymers are also plastics, which are organic polymers. Therefore, they can combine the mechanical properties (flexibility, toughness, malleability, elasticity, etc.) of plastics with high electrical conductivity. Furthermore these properties can be fine-tuned using the proper methods of organic synthesis [7].

Conducting polymers are conjugated (have alternating single and double bonds), having extended delocalised [pi]-bonds (orbitals) along the polymer backbone. It is the [pi]-orbital delocalisation (single-double bond alternation) that facilitates the electron mobility and charge transport within the conducting polymer chain. By contrast, traditional polymers, such as polyethylene and polypropylene, are essentially made up of [sigma]-bonds where all valence electrons are bound in fully saturated chemical bonds and as a result there are no mobile electrons that can participate actively in electron transport (electrical conduction).

From the perspective of technological importance, conducting polymers can be grouped into six main families: aniline, pyrrole, thiophene, phenylvinylene, acetylene, and phenylene--and their derivatives.

1.3 PRINCIPLES OF ELECTRICAL CONDUCTION

1.3.1 BAND THEORY

The electronic properties of any material are established by its electronic structure. The most reasonable explanation of electronic structure of materials is achieved by the band theory. According to quantum mechanism the electrons of an atom can only have specific or quantized energy levels. However, in the lattice of a crystal, where the atoms are closely spaced, the energy levels form bands. The highest occupied electronic levels constitute the valence band and the lowest unoccupied levels constitute the conduction band. Depending on how the bands are filled, the electrical properties of conventional materials are determined. When bands are completely filled or empty no conduction is observed. If the band gap is narrow, at room temperature, thermal excitation of electrons from valence band to conduction band gives rise to conductivity which is the case of classical semiconductors. When the band gap is wide, thermal energy at room temperature is insufficient to excite electrons across the gap and the solid is an insulator. In conductors, there is no band gap since the valence band overlaps the conduction band and hence their high conductivity (Figure 1.2) [1].

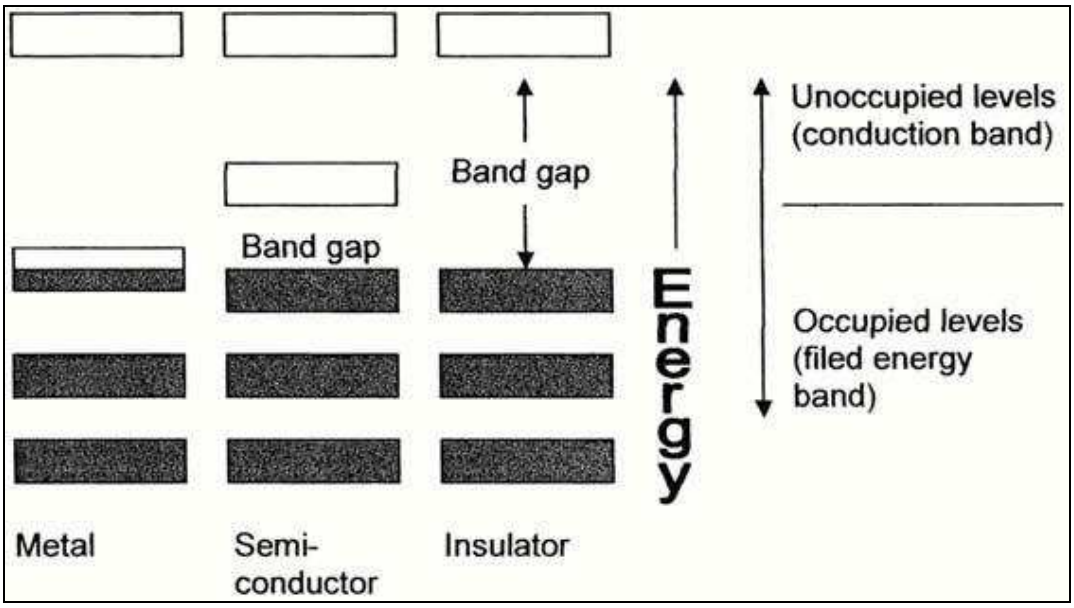


Figure 1.2 Band theory

1.3.2 DOPING PROCESS

Doping process is basically the process that transforms insulating polymers(e.g., polyacetylene, conductivity 0.1 S/cm) to excellent conductors (Figure 1.3) [8]. Doping is achieved by formation of charge-transfer complexes by electron donors such as sodium or potassium (n doping, reduction) or by electron acceptors such as I_3 , AsF_5 , or $FeCl_3$ (p doping, oxidation). As a result of the process the doped polymer backbone becomes negatively or positively charged with the dopant forming oppositely charged ions (Na^+, K^+, I^{3-}, I^{5-}, AsF^{6-}, $FeCl^{4-}$). Application of an electric potential results in motion of counterions in and out which enables to switch the polymer between the doped, conductive state and the undoped, insulating state (Figure 1.4) [5].

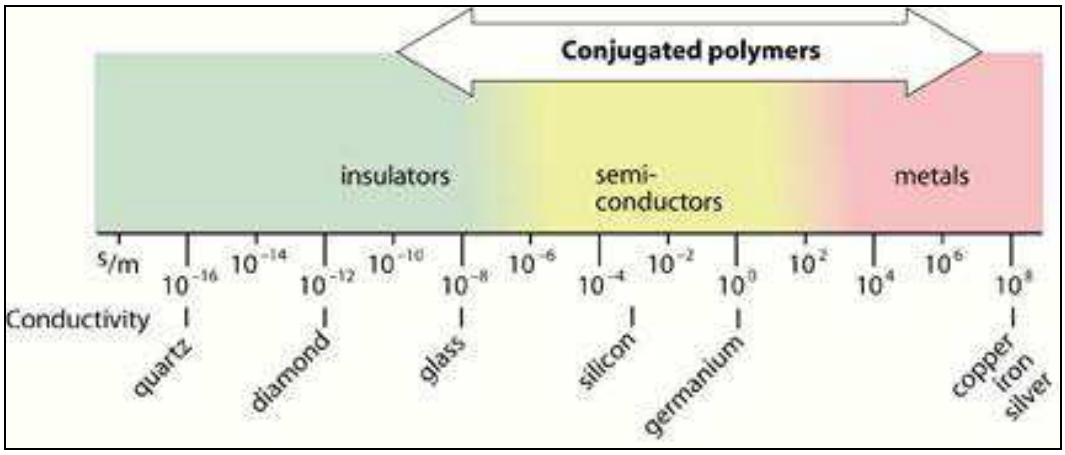


Figure 1.3 Conductivities of insulator, semi-conductors, metals and Conjugated polymers

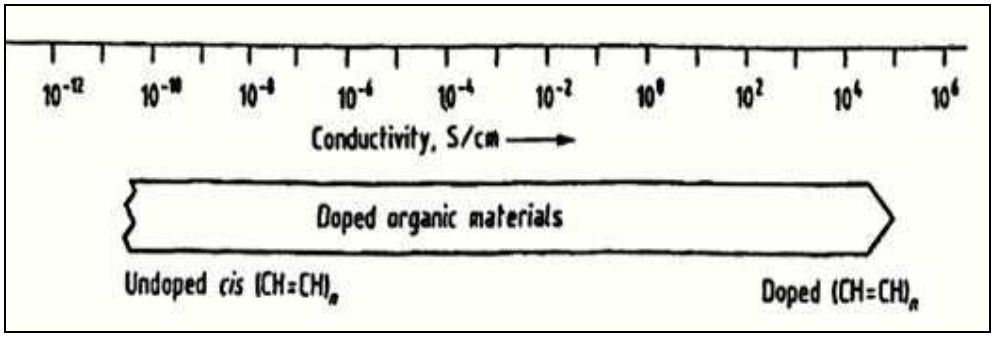


Figure 1.4 Conductivity of doped and undoped organic materials

1.3.3 POLARON AND BIPOLARON MODEL

The band theory is insufficient to explain the electrical conduction in electrically conducting organic materials such as polyphenylene, polyacetylene or polypyrrole where the charge-carrying species (electrons or holes) are spinless. Although the mechanism is not fully understood, conduction by polarons and bipolarons is now thought to be the dominant mechanism of charge

transport in organic materials. This concept is also used for explanation of the drastic deepening of color changes produced by doping. A polaron which is a term used in solid-state physics is defined as a radical cation that is partially delocalized over several monomer units (e.g. in a polymer segment) where a bipolaron is a diradical dication. Doping level determines formation of polaron and bipolarons. Low doping levels gives rise to polarons, whereas higher doping levels produce bipolarons. Both polarons and bipolarons are mobile and can move along the polymer chain [5]. In order to explain the doping process, the oxidative doping of polypyrrole is described in Figure 1.5. The process begins when an electron is removed from the p-system of the backbone by the dopant producing free radical and a spinless positive charge. Due to local resonance of the charge and the radical, the radical and cation are coupled to each other. This combination of a charge site and a radical is called a polaron. This could be either a radical cation or radical anion. This creates a new localized electronic states in the gap, with the lower energy states being occupied by a single unpaired electrons. The polaron state of polypyrrole are symmetrically located about 0.5 eV from the band edges. Upon further oxidation the free radical of the polaron is removed, creating a new spinless defect called a bipolaron. This is of lower energy than the creation of two distinct polarons. At higher doping levels it becomes possible that two polarons combine to form a bipolaron. Thus at higher doping levels the polarons are replaced with bipolarons. The bipolarons are located symmetrically with a band gap of 0.75 eV in the case of polypyrrole [9].

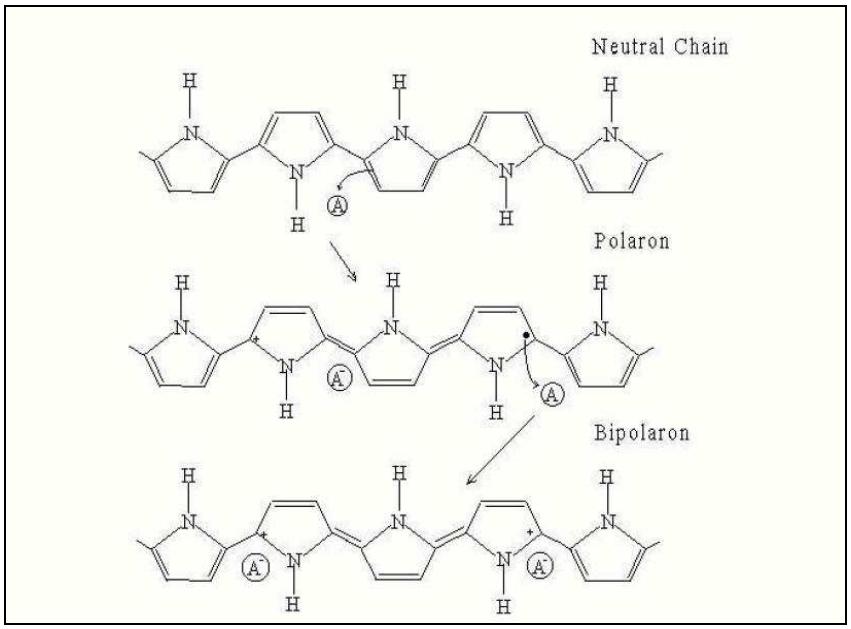


Figure 1.5 Oxidative doping of polypyrrole

Continuous doping eventually forms continuous bipolaron bands. Their band gap also increases as newly formed bipolarons are made at the expense of the band edges.For a very heavily doped polymer the upper and the lower bipolaron bands merge with the conduction and the valence bands respectively to produce partially filled bands and metallic like conductivity (Figure 1.6) [9].

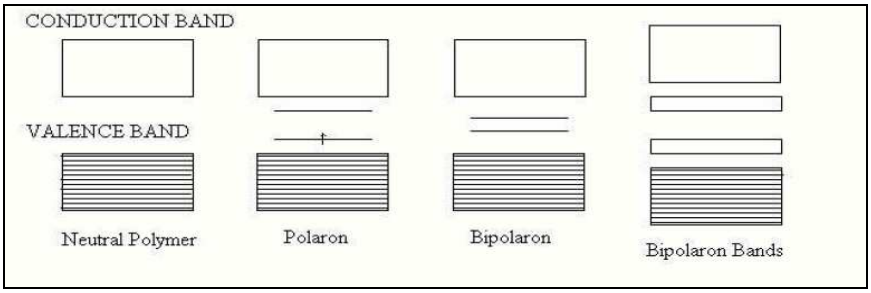


Figure 1.6 Band theory of conducting polymers

1.4 SYNTHESIS METHOD

Conducting polymers are generally synthesized via chemical or electrochemical polymerization process. These process are discussed in detail in the following section:

1.4.1 CHEMICAL POLYMERISATION

Chemical polymerization afford bulk polymer, usually in the form of a powder that require further processing for practical applications such as casting from an organic solvents. Hence chemically prepared polymers are generally unsuitable for electrode reaction. Chemical polymerization is typically carried out with relatively strong chemical oxidants like ammonium peroxydisulfate, ferric ions,permanganate or bichromate anions or hydrogen peroxide. These oxidants are able to oxidize the monomers in solution, leading to the formation of cation radicals. These cation radicals further react with other monomers or n-mers , yielding oligomers or insoluble polymer.

1.4.1 ELECTROCHEMICAL POLYMERISATION

The product of electrochemical polymerization is a film that adheres well to the electrode surface. Electrochemically prepared conducting polymers exhibit good electrochromic properties. The electrochemical synthesis of conducting polymers first demonstrated with polypyrrole has been enhanced in the development of this field [10]. Using this approach, semiconducting polymers have been obtained from a wide variety of monomers including thiophene, furan, carbazole, aniline, indole, azulene and polyaromatic monomers such as pyrene and fluoranthene.

1.5 POLYPYRROLE

Polypyrrole (PPy) is a chemical compound formed from a number of connected pyrrole ring structures. For example a tetrapyrrole is a compound with four pyrrole rings connected. Methine-bridged cyclic tetrapyrroles are called porphyrins. Polypyrroles are conducting polymers of the rigid-rod polymer host family, all basically derivatives of polyacetylene. Polypyrrole was the first polyacetylene-derivative to show high conductivity.

Polypyrrole is considered among the most promising conductive polymers due to its stability and ease of conversion between conducting and insulating forms. Despite many interesting applications the use of polypyrrole is limited because difficulty in processing. Several reports have been published on the synthesis of polypyrrole-metal nanocomposites. The sensing and catalytic abilities of the polypyrrole composites are significantly better than those for polymer alone [11].

Polypyrroles are also called pyrrole blacks or polypyrrole blacks. Polypyrroles also exist naturally, especially as part of a mixed copolymer with polyacetylene and polyaniline in some melanins. In 2006, scientists from Brown University published work on a fast-charging and discharging battery chemistry based on polypyrroles .There are current studies into the medical applications of polypyrroles: A current study suggests that polypyrroles may be used for testing the blood lithium levels of patients being treated for bipolar disorder.

Polypyrrole is also being investigated in low temperature fuel cell technology to increase the catalyst dispersion in the carbon support layers and to sensitize cathode electrocatalysts as it has been inferred that the metal electrocatalysts (Pt, Co, etc) when coordinated with the nitrogen in the pyrrole monomers show enhanced oxygen reduction activity

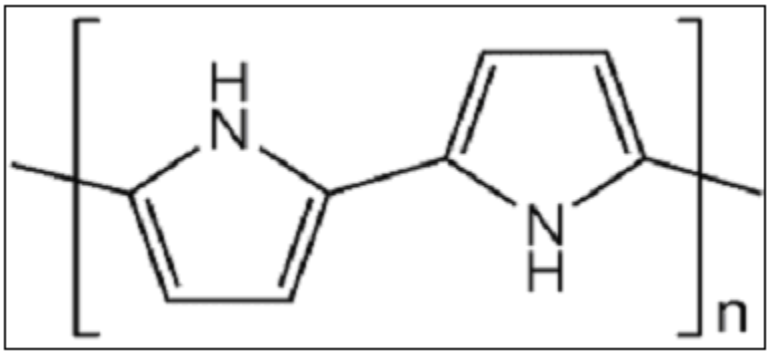


Figure 1.7 Structure of polypyrrole.

1.5.1 SYNTHESIS OF POLYPYRROLE

Polypyrrole and many of its derivatives can be synthesized via simple chemical or electrochemical methods [12]. Photochemically initiated and enzyme-catalyzed polymerization routes have also been descibed but less developed. Different synthesis routes produce polypyrrole with different forms; chemical oxidations generally produce powders, while electrochemical synthesis leads to films deposited on the working electrode and enzymatic polymerization gives aqueous dispersions[13]. Electrochemical polymerization method is utilized extensively for production of electroactive/conductive films. The film properties can be easily controlled by simply varying the electrolysis conditions such as

electrode potential, current density, solvent, and electrolyte. It also enables control of thickness of the polymers. Electrochemical synthesis of polymers is a complex process and various factors such as the nature and concentration of monomer/electrolyte, cell conditions, the solvent, electrode, applied potential and temperature, pH affects the yield and the quality of the film. Thus, optimization of all of the parameters in one experiment is difficult. In contrast, chemical polymerization does not require any special instruments, it is a rather simple and fast process. Chemical polymerization method involves oxidative polymerization of pyrrole monomer by chemical oxidants either in aqueous or non-aqueous solvents or oxidation by chemical vapour deposition in order to produce bulk polypyrrole as fine powders [14].

Iron (III) chloride and water are found to be the best oxidant and solvent for chemical polymerization of pyrrole respectively regarding desirable conductivity characteristics.

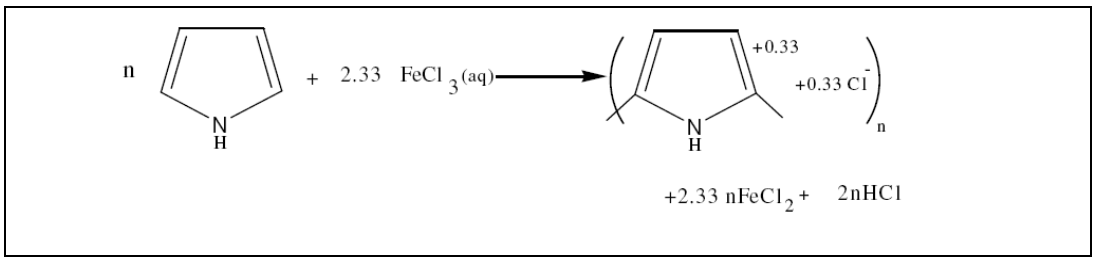


Figure 1.8 Chemical polymerization of polypyrrole

1.6 APPLICATIONS OF CONDUCYING POLYMER

1.6.1 GENERAL APPLICATIONS

Conductive polymers show large-scale applications due to their light weight and easy processability. They have been known to work as antistatic materials. In addition to this these materials can also be used in commercial displays and batteries, however the basic hinderance to use these materials extensively is manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process. Literature also suggests that conducting polymer can be used in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide [15]. Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly, provide fresh air to this field with their higher surface area and better dispersability.

1.6.2. ELECTROLUMINESCENCE

Electroluminescence is light emission stimulated by electrical current. In organic compounds, electroluminescence has been known since the early 1950s, when Bernanose and coworkers first produced electroluminescence in crystalline thin films of acridine orange and quinacrine [16]. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some

cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using Organic LEDs, solar panels, and optical amplifiers[16].

1.6.3. STABLE CONDUCTING POLYMER ANDELECTROCHROMIC DEVICES

In the development of long-lived electrochemical devices based on conducting polymers, the electrolyte plays an extremely important role. Good electrolytes should have high ionic conductivity, large electrochemical windows, excellent thermal and chemical stability, and negligible evaporation rates. Room temperature ionic liquids are good electrolyte candidates that meet these requirements. On the other hand, conducting polymers possess desirable physical properties for electrochemical devices such as light weight, low cost, good redox capability, good processability, mechanical flexibility, and high charge capacity. In the present work, we combined the unique properties of ionic liquid electrolyte with those of conducting polymers to fabricate high performance and long lifetime electrochromic devices. More specifically, we have explored the application of ionic liquids are: a) electrochemical synthesis of thin transparent films of conducting polymers (e.g., polypyrroles, polythiophenes, and polyanilines); b) in the electrochemical characterization of conducting polymer thin films; and c) in the fabrication of stable conducting polymer electrochemical devices including electrochromic windows and numeric displays. An excellent

lifetime of 1,000,000 cycles for the electrochromic devices has been achieved without change in the performance of the device.

The Ionic Liquid Electrochromic Display (ILECD) changes its color and transparency when an appropriate voltage is applied. The essence of the devices is shown in Figure 1.9. It consists of two conducting polymer (also referred to as p-conjugated polymers) thin films deposited onto the surface of ITO glass electrodes, with an ionic liquid electrolyte "sandwiched" in between them. The use of room temperature ionic liquids as the electrolyte is the key enabling-technology leading to commercial viability. The applied voltage induces redox reactions in the polymers, which changes their color and transparency [17].

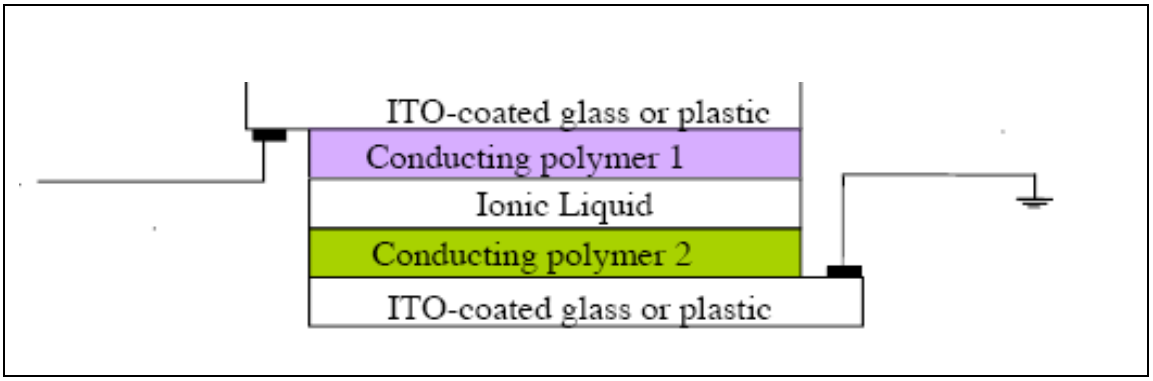


Figure 1.9 Ionic liquid electrochromic device.

1.7 NANOCOMPOSITES

Nanomaterials and nanocomposites have always existed in nature and have been used for centuries. However, it is only recently that characterization and control of structure at nanoscale have drawn intense interest for research and these materials start to represent new and exciting fields in material science.

A nanocomposite is defined as a composite material where at least one of the dimensions of one of its constituents is on the nanometer size scale [4] . In other words, nanocomposites can be considered as solid structures with nanometer - scale dimensional repeat distances between the different phases that constitute the structure. These materials typically consist of an inorganic (host) solid containing and an organic component or vice versa. They can consist of two or more inorganic/organic phases in some combinational form that at least one of the phases or features is in the nanosize.

In general, nanocomposite materials can exhibit different mechanical, electrical, optical, electrochemical, catalytic, and structural properties than those of each individual component. The multifunctional behavior for any specific property of the material is often more than the sum of the individual components.

CHAPTER 2

LITERATURE REVIEW

Among the conjugated polymers, polypyrrole (PPy) is the most representative one for its easy polymerization and wide application in gas sensors, electrochromic devices and batteries. Polypyrrole can be produced in the form of powders, coatings, or films. It is intrinsically conductive, stable and can be quite easily produced also continuously. The preparation of polypyrrole by oxidation of pyrrole dates back to 1888 and by electrochemical polymerization to 1957. However, this organic p- system attracted general interest and was found to be electrically conductive in 1963.

Chen et al. [18] studied that the polypyrrole is an important conducting polymer with high electrical conductivity and appropriate environmental stability.Conducting polymers are important materials emerging with lot of applications in various fields .Research in the field of such polymers aims mainly at some suitable modifications of existing polymers so that their applicability can be improved. Some of these modifications involve preparing hybrid materials in which the organic materials and inorganic oxides or salt of different materials,viz. SnO_2,Ceo_2,V_2O_5,TiO_2,fly ash composites etc are combine in some special fashion with the conducting polymers to give rise to the composites. In almost all the cases some specific nature of association between the two components has been observed and reported.

Kivelson et al. [19] studied that the electrical transport in polymeric materials has become an area of increasing interest in research because these materials possess a great potential for solid state devices. Moreover the composite of conducting polymer have attracted considerable interest in recent years because of their numerous applications in variety of electric and electronic devices. It has been found that such composites can exhibit some novel properties and better mechanical properties than pure conducting polymer. Polypyrrole has been regarded as one of the most studied conducting polymers.

S.Goel and A.Gupta synthesized polypyrrole samples of different nanodimensions and morphologies by time dependent interfacial polymerization reaction. Pure chloroform was used as solvent for pyrrole and ammonium persulphate dissolved in HCl was used as the oxidizing solution. The polymerization occured in the interface of organic and aqueous phases and polypyrrole was formed as thin layer on the interface. Morphology study of polypyrrole nanoparticles was done by scanning electron microsopy and transmission electron microscopy [20].

Yang Liu and Ying Chu synthesized polypyrrole nanoparticles through microemulsion polymerization. Alcohol-assited microemulsion polymerization was performed in order to adjust the inner structure of polypyrrole nanoparticles for polymerization SDS was used as the surfactant, water was used as the solvent and aqueous solution of $NH_4S_2O_8$ was used as the oxidant.

Characterisation of polpyrrole was done by FT-IR and morphology study was performed by SEM and TEM [21] .

Hongxia Wang and Tong Lin synthesized polypyrrole nanoparticles by oxidation of pyrrole with ferric chloride solution during microemulsion polymerization process.Dodecyltrimethyl ammonium bromide (DTAB) was used as the surf actant. Particle characaterisation was per formed by using FTIR, elemental analysis, UV-VIS spectra and SEM. Variation of particle size from about 50 to 100, 100 to 200 nm with the change in surfactant concentration was reported [22].

Xinyu Zhang and Sanjeev K. Manohar synthesized narrow pore-diameter polypyrrole nanotubes. The synthesis was performed by chemical oxidative polymerization of pyrrole using $FeCl_3$ oxidant and V_2O_5 nanofibers as the sacrificial template producing microns long electically conducting polypyrrole nanotubes having 6 nm average pore diameter [23].

M.R. Karim and C.J. Lee synthesized polypyrrole by radiolysis polymerization method.Conducting PPy was synthesized by the in situ gamma radiation-induced chemical oxidative polymerization method.This method was reported to provide a highly uniform polymer morphology [24].

Polypyrrole (PPy)/Al_2O_3 nanocomposites were prepared by chemical polymerization of pyrrole in the presence of Al_2O_3 nanoparticles using iron trichloride ($FeCl_3$) as an oxidant. The obtained nanocomposites were characterised by Fourier transform infrared spectroscopy, Raman spectroscopy,

scanning electron microscopy and thermal gravimetric analysis. Upon exposure to an electromagnetic wave in the X-band ranging from 8 to 12 GHz, PPy/ Al_2O_3 composite was shown to be an effective electromagnetic absorbent. More than 53% of the incident microwave radiation was absorbed after passing through a thick composite coated textile [25].

Maria Omastova and Ivan Chodak prepared conductive polypropylene/polypyrrole composites using the method of chemically initiated oxidative modification of polypropylene particles in suspension by pyrrole. In order to prepare the composite, polypropylene particles were dispersed in water-methanol mixture and $FeCl_3$ was added to be used for chemical oxidation. Addition of pyrrole started formation of polypyrrole particles in polypropylene suspension. The electrical and rheological properties of the composite were compared with polypropylene/polypyrrole composite prepared by melt mixing of pure polypropylene with chemically synthesized polypyrrole and with polypropylene/carbon black composites also prepared by melt mixing. Elemental analysis verified presence of polypyrrole in polypropylene matrix .The conductivity studies show that even a very small PPy amount present in composites results in a significant increase in conductivity. Processing conditions are observed to have a great effect on electrical conductivites of composites.The composite prepared by sintering PP particles covered with PPy shows about 7 orders of magnitude higher conductivity than the composite prepared by melt mixing of pure polypropylene with chemically synthesized polypyrrole whereas the

conductivity of sintered PP/PPy composites is comparable to that of PP/Carbon black composite.The PP/CB and injection molded PP/PPy composites exhibit similar flow properties. However, for compresion molded PP/PPy composites a considerable increase of complex viscosity was observed [26].

Jürgen Pionteck and Maria Omastova prepared an electrical-conducting polypropylene/polypyrrole (PP/PPy) composite by chemical oxidative modification reaction of pyrrole on the surface of PP particles in suspension. For comparison, another type of composite was prepared by mixing coated PP particles with noncoated PP particles.Both composites were processed with injection and compresion molding. Beter mechanical properties were achieved by injection molded composites compared to that of compression molded ones. However, compression molded composites exhibit beter antistatic behaviour and electrical conductivity. XPS studies proved that the PP in the PP/PPy powder is almost totally covered with PPy. Prevention of the outflow of PP melt by PPy layer as heating to 200°C without shear was proved by hot-stage optical microscopy studies.The investigation of mechanical properties and melt viscosities of PP/PPy composites shows that PPy structure was almost completely destroyed by injection molding whereas compression molded composites exhibits presence of PPy networklike structure [27].

Miroslava Mravcakova and Maria Omastova prepared polypropylene/montmorillonite/polypyrrole (PP/MMT/PPY) composites by oxidative polymerization of pyrrole in the presence of dispersed polypropylene and montmorillonite particles in aqueous solution of an anionic surfactant, dodecylbenzenesulfonic acis (DBSA), or in water /methanol solution. The composites are compared with PP/PPy blends prepared by melt mixing. WAXS study showed the intercalation of PPy into galleries of MMT in PP/MMT/PPy composites. Rheology and conductivity studies showed that using DBSA as surfactant during PPy polymerization changed the gallery structure of MMT and stabilized the structure also during following processes. The conductivity of compression molded PP/MMT/PPy composites were found to be $10^{-5}S^{-1}$cm already at 4,8% PPy content.However, due to destruction of the conductive shell of PPy particles during melt mixing, the PP/PPy blends exhibited lower conductivity [28].

Feifeng He and Mitsuru Omoto prepared conductive polypyrrole/polyurethane composite foam by vapor phase polymerization of pyrrole on polyurethne foam. $FeCl_2$ and $FeCl_3$ were used as oxidants.The study showed that increasing $FeCl_2$ / $FeCl_3$ ratio results in increasing conductivity despite decreasing polypyrole content.The result was explained as indication of higher density or structurally different PPy formation from those obtained by $FeCl_3$ alone. Low contents of PPy in the composite is also pointed out as an advantage for the mechanical propeties of the composite foam. It is concluded that the mixtures of the two iron chlorides are preferable to

$FeCl_3$ as oxidants for preparation of highly coductive composite foam. Also, it has been reported that lower reaction temperatures were preferable for higher conductivity.Regarding the mechanical properties, it is reported that the tensile strength and elongation of composite foam is comparable to those of pristine polurethane foam [29]. Functionalized polypyrrole film were prepared by incorporation of $(Fe(CN)_6)^{4-}$ as doping anion, during the electropolymerization of pyrrole onto a carbon paste electrode (CPE) in aqueous solution by using potentiostatic method. The electrochemical behavior of the $(Fe(CN)_6)^{3-}/(Fe(CN)_6)^{4-}$ redox couple in polypyrrole was studied by cyclic voltammetry and double step potential chronoamperometry methods. In this study, an obvious surface redox reaction was observed and dependence of this reaction on the solution pH was illustrated. The electrocatalytic ability of polypyrrole/ferrocyanide films modified carbon paste electrode (Ppy/FCNMCPEs) was demonstrated by oxidation of ascorbic acid. It has been found that under optimum condition (pH 7.00), the oxidation of ascorbic acid at the surface of such electrode occurs at a potential about 540 mV less positive than unmodified carbon paste electrode. The kinetic parameters such as electron transfer coefficient, α and catalytic reaction rate constant, k_h', were also determined by using various electrochemical approaches[30].

A biosensor is developed by co-entrapment of Purin Nucleoside Phosphorylase (PNP) and xanthine oxidase (XOD) and potassium ferrocyanide ($K_4Fe(CN)_6$ into polypyrrole (PPy) film via galvanostatic polymerisation of pyrrole. The optimum conditions for formation of the PPy-PNP-XOD-$Fe(CN)_6^{4-}$ film are 0.3 M pyrrole.

6.2 U mL^{-1} XOD, 49 U mL^{-1} PNP, 40 mM $K_4Fe(CN)_6$, polymerisation period of 200 sec and an applied current density of 0.5 mA cm^{-2}. The optimum potential for the amperometric biosensing of phosphate was 200 mV vs Ag/AgCl (3 M KCl) in 0.05 M barbitone buffer. The achievable linear concentration range was between 0.1 and 1 mM, while the minimum detectable amount was 10 μM [31].

The electrochemical determination of phenol at platinum electrodes modified with polypyrrole doped with ferricyanide is reported. The modified electrodes were prepared by electrochemical polymerization of pyrrole from aqueous solution by using cyclic voltammetry. The polypyrrole film has been deposited onto Pt electrode surface by potential cycling from (-0.2) V to +1.5 V at a scan rate of 0.1 V/s. The thickness of the polymeric film was controlled by the number of potential cycles. The resulted modified electrode is referred as to Pt/PPy-FeCN. After the deposition of the doped polymer film, the modified electrode was characterized in aqueous solution by using cyclic voltammetry and square wave voltammetry. The electrochemical oxidation of phenol at Pt/PPy-FeCN modified electrode has been investigated in aqueous solution of pH of 2 [32].

A novel nonenzymatic hydrogen peroxide (H_2O_2) sensor has been fabricated by dispersing copper nanoparticles onto polypyrrole (PPy) nanowires by cyclic voltammetry (CV) to form PPy-copper nanocomposites on gold electrodes. Scanning electron microscopy (SEM) was used to characterize the morphologies of the PPy nanowires and the PPy-copper nanocomposite. The reactivity of the PPy-copper nanocomposite towards H_2O_2 was characterized

by cyclic voltammetry and chrono amperometr y. Effects of applied potential, the concentrations of detection solution upon the response currents of the sensor were investigated for an optimum analytical performance. It was proved that the PPy-copper nanocomposite showed excellent catalytic activity for the reduction of hydrogen peroxide(H_2O_2) The sensor showed a linear response to hydrogen peroxide in the concentration range between 7.0×10^{-6} and 4.3×10^{-3} mol L^{-1} with a high sensitivity, and a detection limit of 2.3×10^{-6} mol L^{-1}. Ex periment results also showed that the sensor had good stability[33].

The electrocatalytic activity of core–shell Au $_{100-x}Ag_x$ (x = 15, 27, 46, and 60) bimetallic nanoparticles embedded in methyl functionalized sili cate MTMOS network towards the reduction of hydrogen peroxide was investigated by using cyclic vo ltammetry and chronoamperometric techniques. Core–shell Au/Ag bimetallic nanoparticles were characterized by absorption spectra and HRTEM. The MTMOS silicate sol–gel embedded Au_{73} Ag_{27} core–shell nanoparticles modified electrode showed better synergistic electrocatalytic effect towards the reduction of hydrogen peroxide when compared to mono- metal MTMOS-Au_{nps} and MTM OS-Ag_{nps} modified electrodes. These modified electrodes were studied np s n ps without immobilizing any enzyme in the MTMOS sol–gel matrix. The present study highlights the influence of molar composition of Ag nanoparti cles in the Au/Ag bimetallic composition towards the electro- catalytic reduction and sensing of hydrogen peroxide in comparison to monometal Au and Ag nanoparticles [34].

CHAPTER 3

CHACTERIZATION TECHNIQUES AND EXPERIMENTAL DETAILS

3.1 EXPERIMENTAL DETAILS

3.1.1 REAGENTS AND MATERIALS

Double distilled water was used throughout the studies.Potassium chloride ,potassium ferrocyanide , pyrrole , potassium nitrate,$HAuCl_4$. The available pyrrole monomer was distilled prior to use and rest of chemicals were used as such.

3.1.2 INSTRUMENRATION

Electrochemical polymerization of pyrrole and characterization of polypyrrole was carried out in 3 electrode cell compartment using electrochemical potentiostate. For polymerization of pyrrole indium-tin-oxide (ITO) glass was used as the working electrode, Platinum as a counter and Ag/AgCl as reference electrode. Further electrochemical studies were conducted on ITO/PPy, ITO/PPy/Fecn,ITO/PPy/Au were used as working electrodes. KNO_3 was used as electrolyte.

3.1.3 EXPERIMENTAL SET UP FOR THE ELECTROCHEMICAL POLYMERISATION OF PYRROLE FILM

In any electrochaemical synthesis of polypyrrole using a one electrode compartment cell it is important to choose a counter electrode reaction which does

not interfere film formation reaction at anode, for example, by giving rise to solvable reduction product, or unduly limiting the rate of film formation. These problem are avoided using a two compartment cell where the electrolyte can be separately choosen to optimize both the oxidation and reduction reaction. Single compartment cell consist the method uses a reference electrode, working electrode, and counter electrode which in combination are sometime reffered to as a three-electrode set up. Electrolyte is usually added to the test solution to ensure sufficient conductivity. The combination of the solvent, electrolyte and specific working electrode material determines the range of the potential.

Electrodes are static and sit in unstirred solutions during cyclic voltametry. This "still" solution method results in cyclic voltammetry's characteristic diffusion controlled peaks. This method also allows a portion of the analyte to remain after reduction or oxidation where it may display further redox activity. Stirring the solution between cyclic voltammetry traces is important as to supply the electrode surface with fresh analyte for each new experiment. The solubility of an analyte can change drastically with its overall charge. Since cyclic voltammetry usually alters any charge of the analyte it is common for reduced or oxidized analyte to precipitate out onto the electrode. This layering of analyte can insulate the electrode surface. For this and other reasons it is often necessary to clean electrodes between scans.

Common materials for working electrodes include glassy carbon,platinum, and gold. These electrodes are generally encased in a rod of inert insulator with a disk

exposed at one end. A regular working electrode has a radius within an order of magnitude of 1 mm. Having a controlled surface area with a defined shape is important for interpreting cyclic voltammetry results.

To run cyclic voltammetry experiments at high scan rates a regular working electrode is insufficient. High scan rates create peaks with large currents and increased resistances which result in distortions. Ultra microelectrodes can be used to minimize the current and resistance.

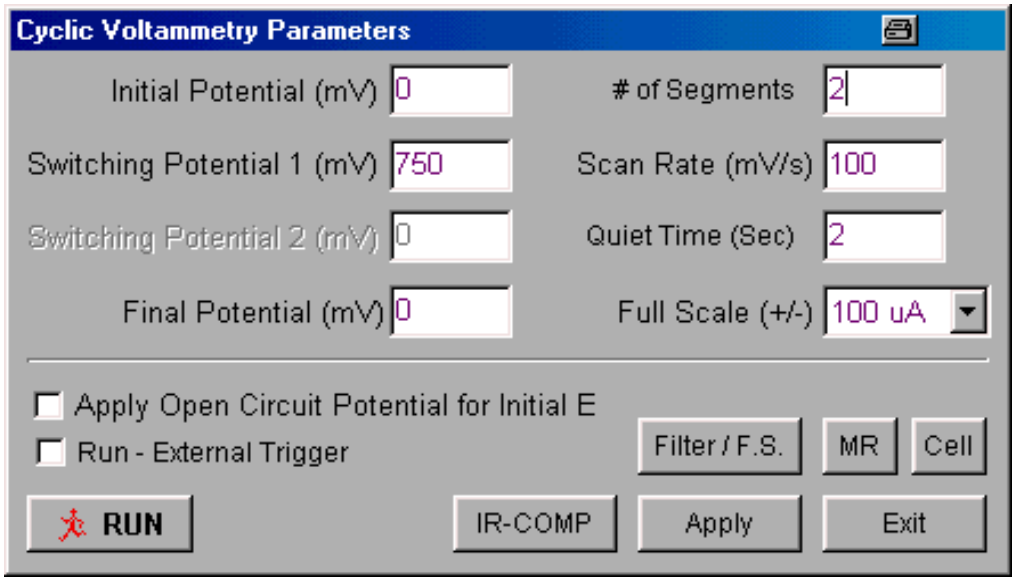
The counter electrode, also known as the auxiliary or second electrode, can be any material which conducts easily and won't react with the bulk solution. Reaction occurring at the counter electrode surface are unimportant as long as it continues to conduct current well. To maintain the observed current the counter electrode will often oxidize or reduce the solvent or bulk electrolyte.

Reference electrode may be hydrogen, Hg/Ag_2Cl_2 or Ag/AgCl(aq). However due to easiness and inert nature Ag/AgCl(aq)has been deployed as reference electrode

3.2 PROCEDURE USED

Electrochemical synthesis was carried out on electrochemical potentiostate under computer control indium-tin-oxide (ITO) coated on glass as working electrode,platinum foil as counter and Ag/AgCl as reference electrode. Polymerization was carried out at selected potentials, under variable time and with different electrolytes. The reaction solution consisted of 0.2 M of pyrrole and 0.1 M dopant concentration. Polypyrrole film deposited on ITO surface was

rinsed along with distilled water to remove any unbound monomer unit. These films were further characterized for their electrochemical behaviour /sensing capability for Nitrocompounds. Electrochemical studies was carried out at variable under potential etc.



Now various techniques used to characterize the material are discussed including;

Scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR) ,thermogravimetric analysis (TGA) and Electro Analytical Studies (Cyclic Voltammetry) which are characterized as below.

3.3 SCANNING ELECTRON MICROSCOPY

The first Scanning Electron Microscope (SEM) debuted in 1942 with the first commercial instruments around 1965. Its late development was due to the electronics involved in "scanning" the beam of electrons across the sample.

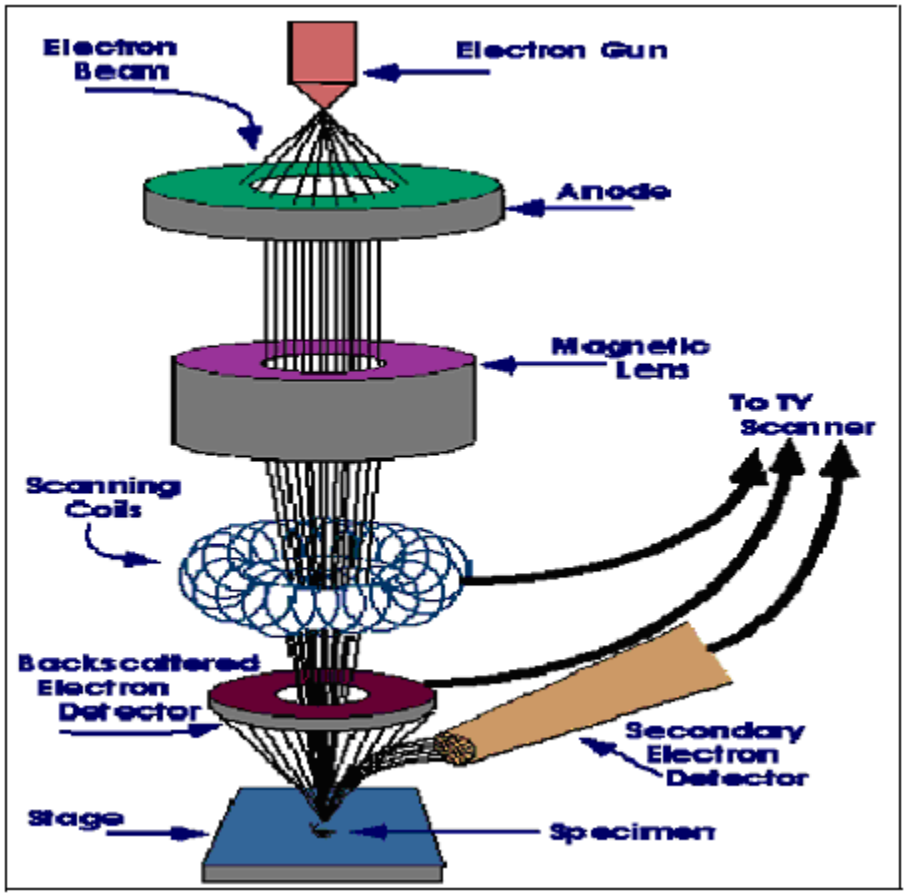


Figure 3.1 Working principle of SEM

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. The types of signals produced by an SEM include secondary electrons, back scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. These types of signal all require specialized detectors that are not usually all present on a single machine. The signals result

from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about 1 to 5 nm in size. Due to the way these images are created, SEM micrographs have a very large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. Here we have used SEM model no-HITACHI S-4300SE/N FE-SEM to take the images of the nanomaterials synthesized .

3.4 TRANSMISSION ELECTRON MICROSCOPY

TEM measurements were performed on a JEOL-1200EX TEM instrument operated at 120 kV. This instrument was used to see the smaller features of the composite material and the nanoparticles. The TEM micrographs were taken for the composite PANI/Au and Au nanoparticles.

For preparation of samples for TEM analysis, a portion of composite film was scratched and was dispersed in an ethanol solution and deposited on carbon-coated Cu-TEM grids. The film on the TEM grid was allowed to stand for some time to allow the liquid to evaporate. After drying, the specimen is transferred in the microscope column for imaging at different magnification and the electron diffraction patterns were recorded.

TEM images are formed using transmitted electrons (instead of the visible light) which can produce magnification details up to 1,000,00X with resolution better than 10 Å. The images can be resolved over a fluorescent screen or a

photographic film. Furthermore the analysis of the X-ray produced by the interaction between the accelerated electrons with the sample allows determining the elemental composition of the sample with high spatial resolution. At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging .

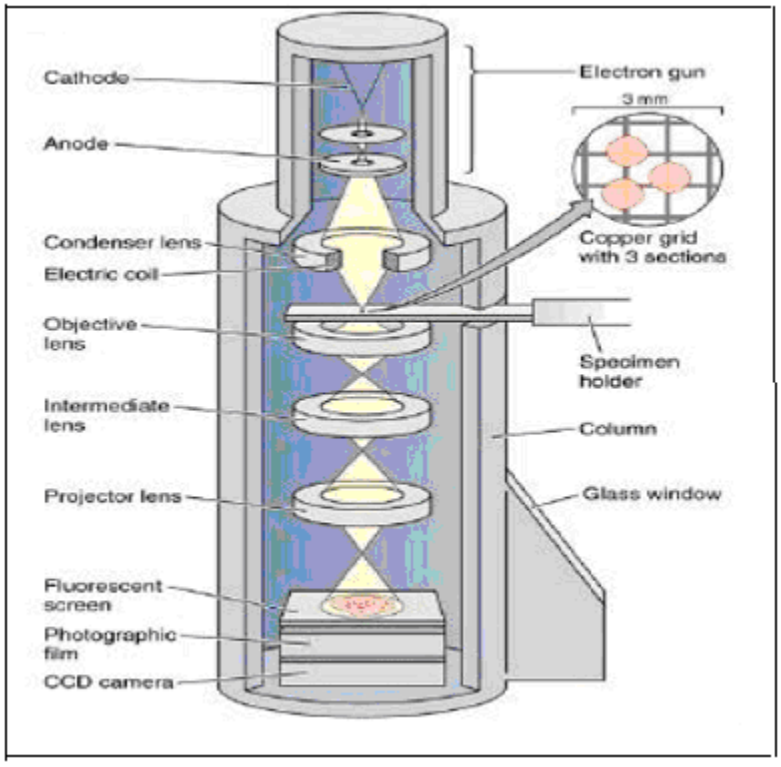


Figure 3.2 Working principle of TEM

3.5 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier transform infrared spectroscopy is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond there are several specific frequencies at which it can vibrate, According to quantum mechanics, these frequencies correspond to the ground state and several excited states. One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states, the light energy must exactly equal the difference in the energy between the two states. The energy corresponding to these transitions between molecular vibrational states is generally 1 to 10 kilocalories/mole which correspond to the infrared portion of the electromagnetic spectrum.

The Source: Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector). The Interferometer: The beam enters the interferometer where the “spectral encoding” takes place. The resulting interferogram signal then exits the interferometer.

The Sample: The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are unique characteristic of the sample, are absorbed. The Detector: The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal. The Computer: The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

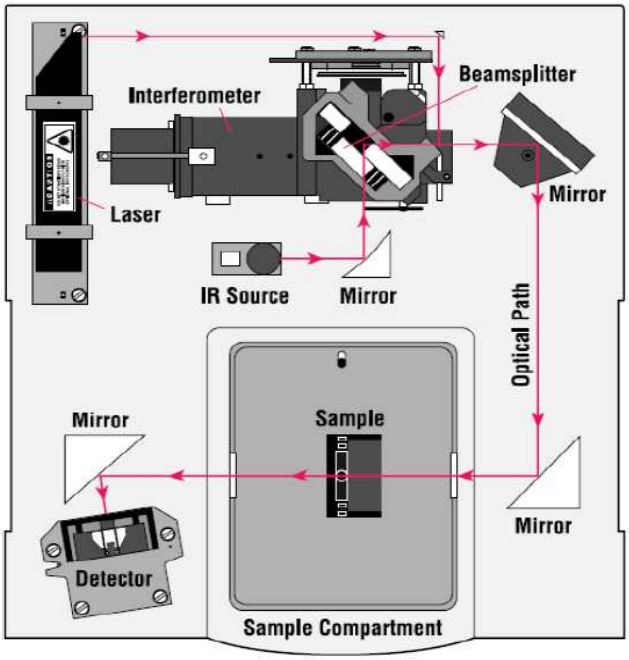


Figure 3.3 Schematic diagram describes working principle of FTIR

3.6 THERMOGRAVIMMETRIC ANANYSIS

Thermogravimetric analysis (TGA)/DSC will be used to determine the change in weight of the composites with increase in temperature and to estimate the amount

of polypyrrole in them. Basically the polypyrrole decomposes and vaporizes at a temperature of 420 ˚C and the weight loss of the sample at that temperature directly translates into the amount of polypyrrole in the composite. For analyzing samples that tend to lose weight during heating,the new Q600 technology provides improved DSC accuracy when the instantaneous weight than the initial sample weight is used in heat flow integration.

FIGURE 3.4 Thermal Analysis instrument

3.7 CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) has become an important and widely used electroanalytical technique in many areas of chemistry. It is rarely used for quantitative determinations, but it is widely used for the study of redox processes, for understanding reaction intermediates, and for obtaining stability of reaction products. This technique is based on varying the applied potential at a working electrode in both forward and reverse directions (at some scan rate) while monitoring the current. For example, the initial scan could be in the negative direction to the switching potential. At that point the scan would be reversed

and run in the positive direction. Depending on the analysis, one full cycle, a partial cycle, or a series of cycles can be performed.

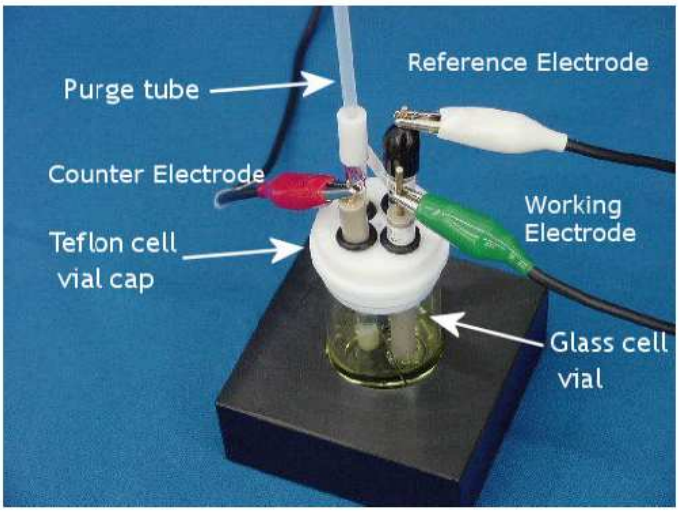


Figure 3.5 Working principle of cyclic voltammeter

The electrochemical cell, where the voltammetric experiment is carried out, consists of a working (indicator) electrode, a reference electrode, and usually a counter (auxiliary) electrode. In general, an electrode provides the interface across which a charge can be transferred or its effects felt. Because the working electrode is where the reaction or transfer of interest is taking place, whenever we refer to the electrode, we always mean the working electrode. The reduction or oxidation of a substance at the surface of a working electrode, at the appropriate applied potential, results in the mass transport of new material to the electrode surface and the generation of a current. Even though the various types of voltammetric techniques may appear to be very different at first glance, their fundamental principles and applications derive from the same electrochemical theory.

CHAPTER 4

RESULT AND DISCUSSION

4.1 CYCLIC VOLTAMMETRY

4.1.1 PREPARATION OF PPy-FeCN COMPOITE COATING

The PPY-FeCN composite has been synthesized by electrochemical polymerization from an aqueous solution containing pyrrole and 0.1 M $K_3[Fe(CN)_6]$ as supporting electrolyte. The resulted modified electrode is referred as to ITO/PPy-FeCN.

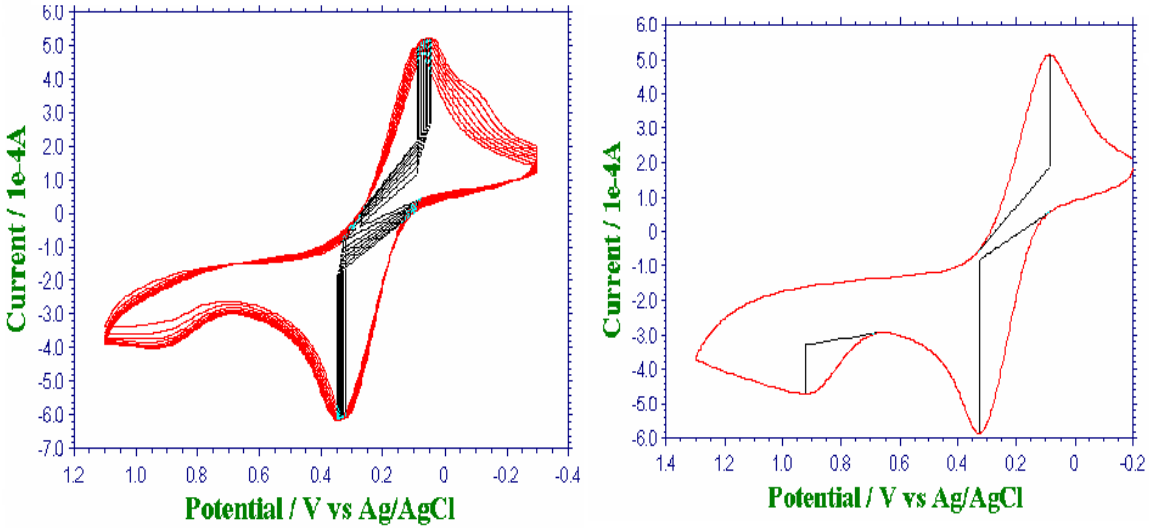


Figure 4.1 Polymerization of pyrole-FeCN composite in k3FeCN6+KCl solution (15 cycles & single)

Fig 4.1 shows the cyclic voltammograms recorded during the electrochemical polymerization of Py in the presence of potassium ferricyanide. The redox couple obtained at 0.34 V and 0.05 V corresponds to transition of Fe^{+2} to $Fe^{+3,}$ whereas an oxidation peak at 0.9 V corresponds to the oxidation of pyrole monomer thus resulting in its polymerization. In the initial cycles, system was not stable but after 3-4 cycles, system attained stability. Figure also shows that intensity of peak currents increased with increase in polymerization cycle thus indicating the continuous deposition of polymer composite. Due to the presence of ferricyanide ions, the organic polymer is doped with counterions from the electrolyte solution.

4.1.2 CV OF PPY-FeCN COMPOSITE

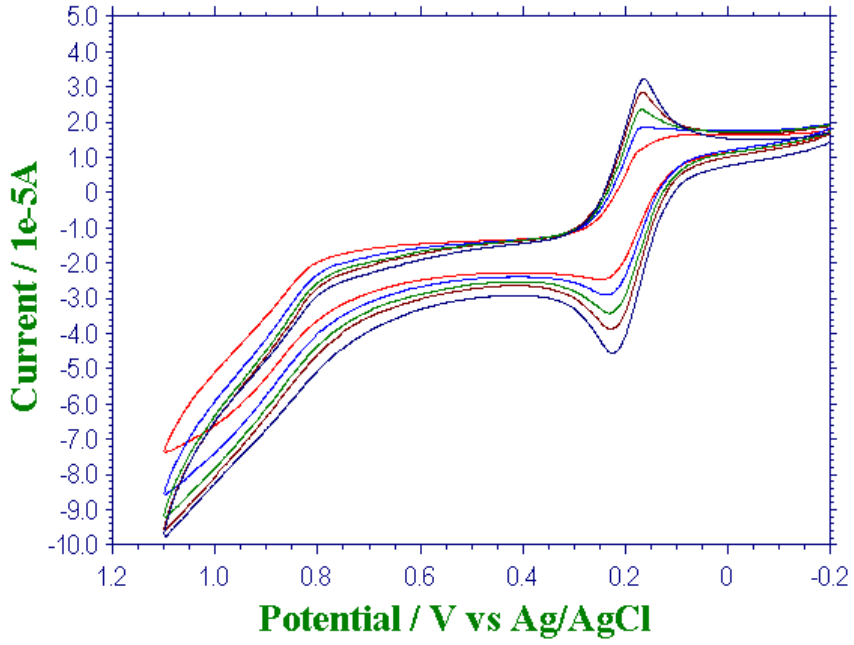


Figure 4.2 CV of PPy-FeCN composite in $FeCN_6$ solution, varied scan rate (0.02 to 0.12 V/s)

Fig 4.2 reports the cyclic voltammograms corresponding to potential cycles with varied scan rate. With increasing scan rate current also increases which indicate greater oxidation and reduction of PPy.

4.1.3 ELECTROCHEMICAL SYNTHESIS OF GOLD NANOPARTICLES

Gold nanoaprticles have been synthesized using electrochemical technique which involved applying reduction potential to initiate the reduction of auric acid in presence of KNO_3 which acted as reducing agent. Figure below shows the CV recorded during electrochemical synthesis of gold nanoparticles on platinum electrode. In KNO_3 solution no redox peak is observed and after addition of auric acid in the electrolyte, a reduction peak is obtained at 0.7 V which corresponds to the reduction of Au^{+3} to Au^{0}.

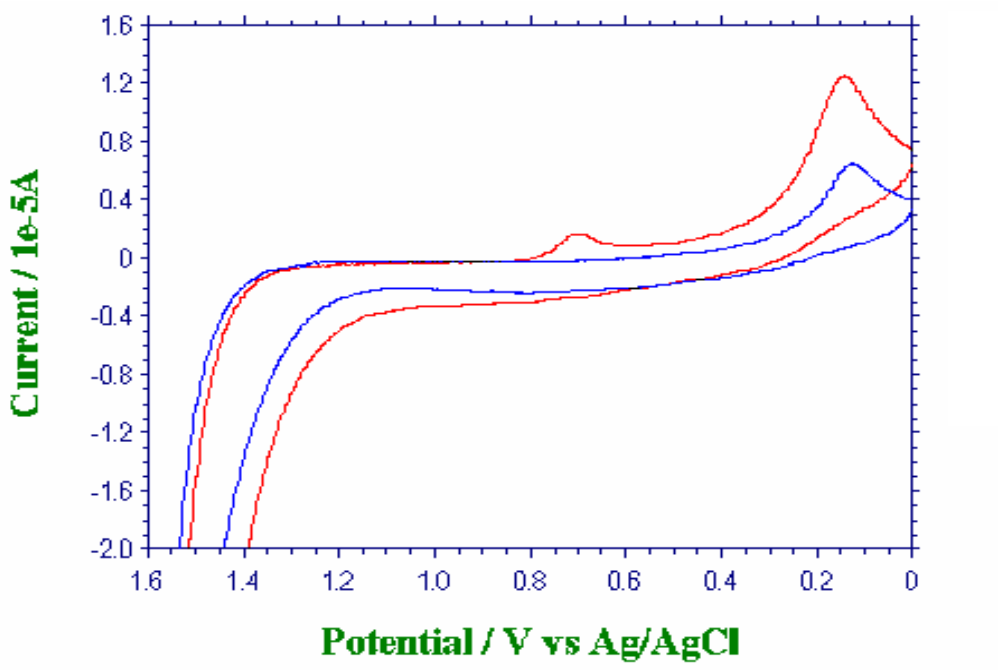


Figure 4.3 Bare Pt in KNO3 (blue) and polymerization of AuNPs on Pt electrode in (0.1 M) KNO3 solution

4.1.4 PREPARATION OF PPy-AuNP NANOCOMPOSITE

The nanocomposite has been prepared by electrochemical polymerization from an aqueous solution containing pyrrole and AuNP in KNO_3. The resulted modified electrode is referred as to Pt/PPY/AuNP. For PPY-AuNP nanocomposite, reduction peak of gold shifted to 0.9 V and pyrole got oxidized at approx 0.95 V. The identical applied potential facilitates the electrochemical synthesis of pyrole and its composite with gold nanoaparticles.

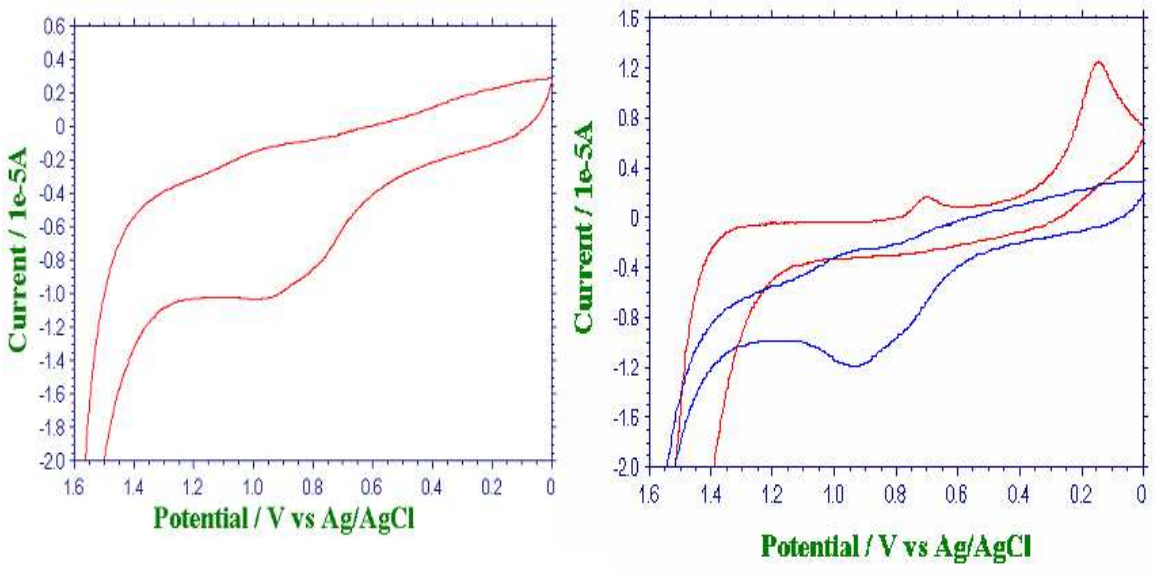


Figure 4.4 Polymerization of PPY-AuNP nanocomposite in (0.1 M) KNO_3 solution and overlay of polymerization curve for AuNPs (red) and PPY-AuNPs composite (blue).

4.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

4.2.1 FTIR OF POLYPYRROLE- POTASSIUM FERROCYANIDE COMPOSITE

In FTIR, the sample and KBr are taken in a ratio 1:100 (by weight mg) and grind together to make a pellet using a hand presser pellestier.The infrared absorption spectrum of polypyrrole film is shown in fig 4.5.The broad strong bands between 3440-3420 cm^{-1}corresponds to the absorption of N-H steching of polypyrrole. The frequency at 2923 cm^{-1} refers to stretching vibration of C-H bond. The absorption at 1626 cm^{-1} was assigned to the C=C ring stretching of pyrrole. The band at 1434 cm^{-1} is due to C-H vibrations. The band at 1050 cm^{-1} is due to in-plane deformation of C-H bond and N-H bond of pyrrole ring.

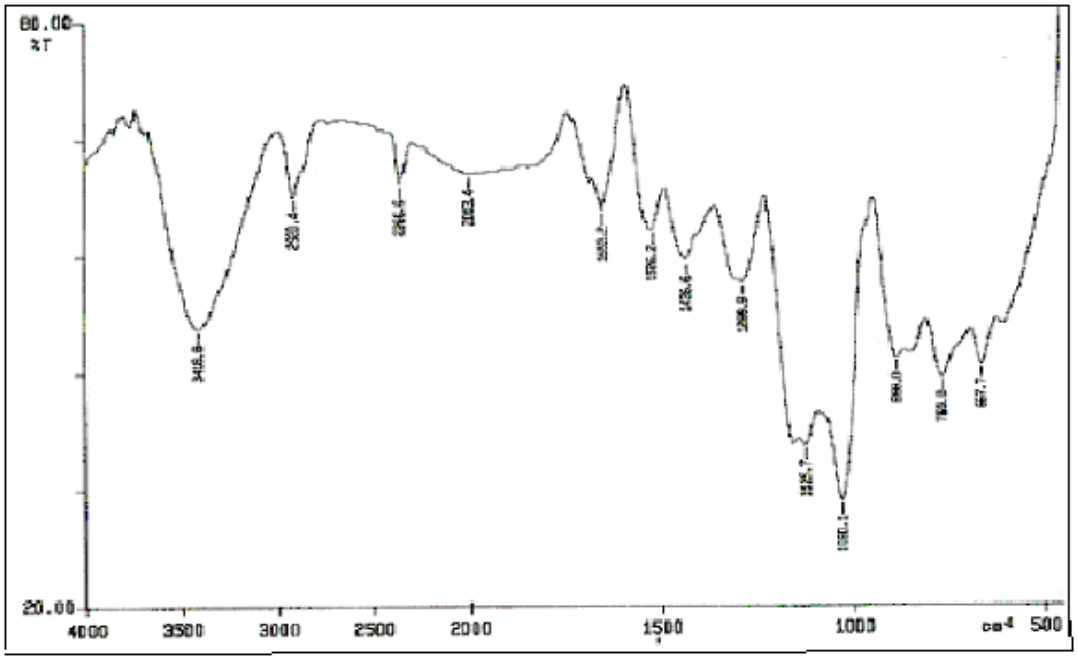


Figure 4.5 FTIR Spectrum of PPy in KCl

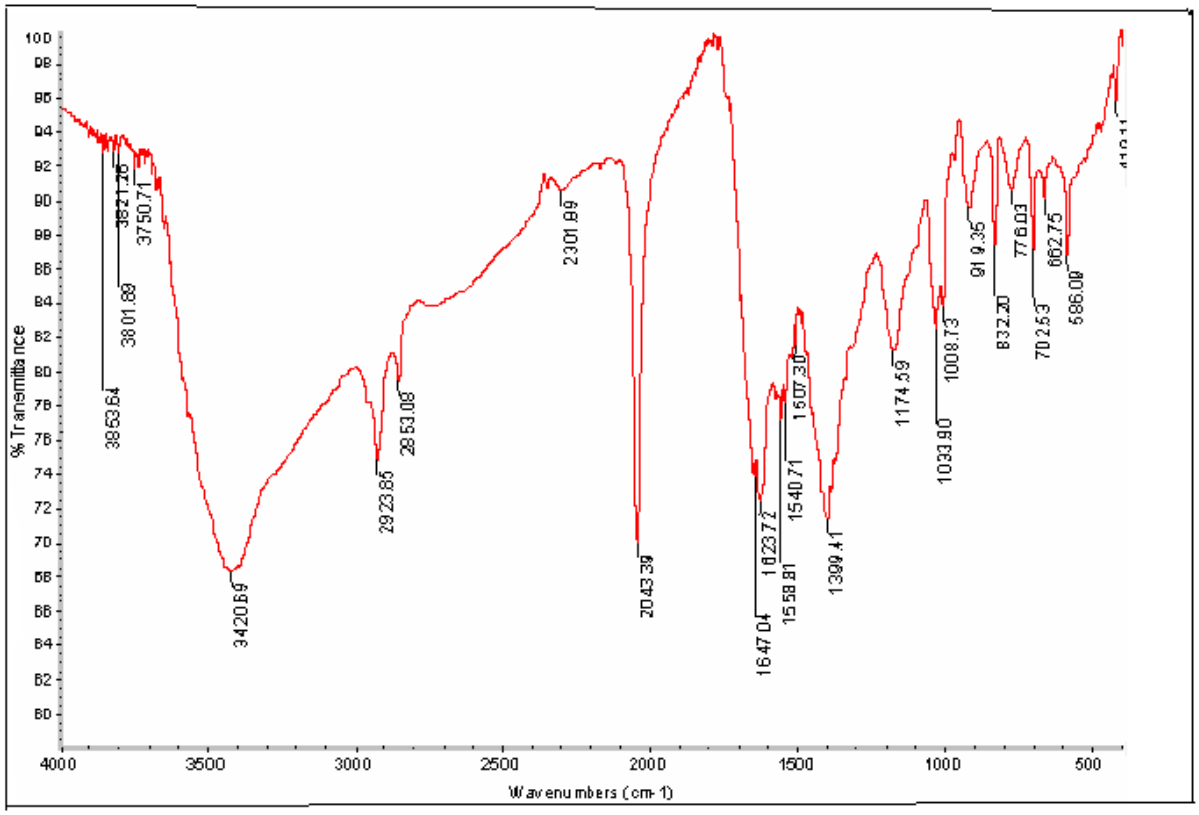


Figure 4.6 FTIR Spectrum of PPy/FeCN composite.

But in the infrared absorption spectrum of polypyrrole-potassiuum ferrocyanide composite film shows small shift in bands due to the formation of composite. The presence of a band at 2043 cm^{-1} is due to –CN srteching.

4.2.2 FTIR OF PYRROLE/AuNP NANOCOMPOSITE

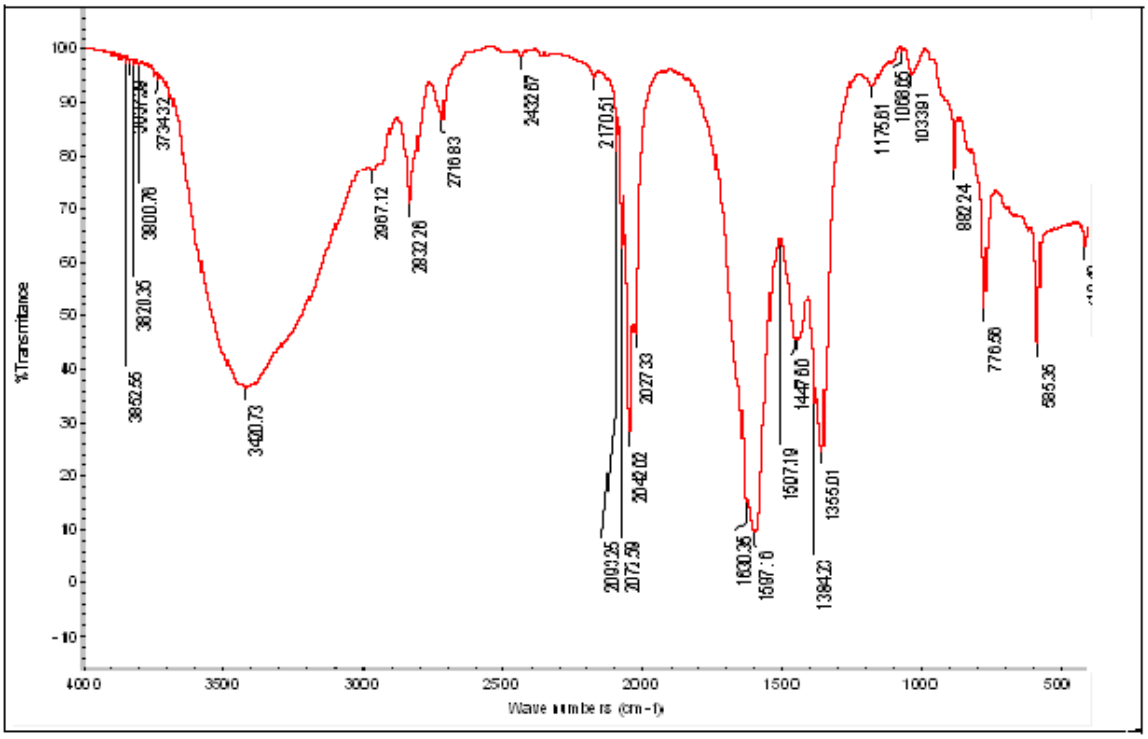


Figure 4.7 FTIR of Polypyrole in KNO_3

The infrared absorption spectrum of polypyrrole and polypyrrole/AuNP composite film is shown in fig 4.7 and 4.8 respectively. In fig 4.7 the broad strong bands between 3440-3420 cm^{-1} corresponds to the absorption of N-H steching of polypyrrole. The frequency at 2952 cm^{-1} refers to stretching vibration of C-H bond. The absorption at 1630 cm^{-1} was assigned to the C=C ring stretching of pyrrole. The band at 1384 cm^{-1} is due to C-H vibrations. The band at 1033 cm^{-1} is due to in-plane deformation of C-H bond and N-H bond of pyrrole ring. The corresponding bands showed shift in bands after the formation of composite of pyrole and gold nanoaparticles.

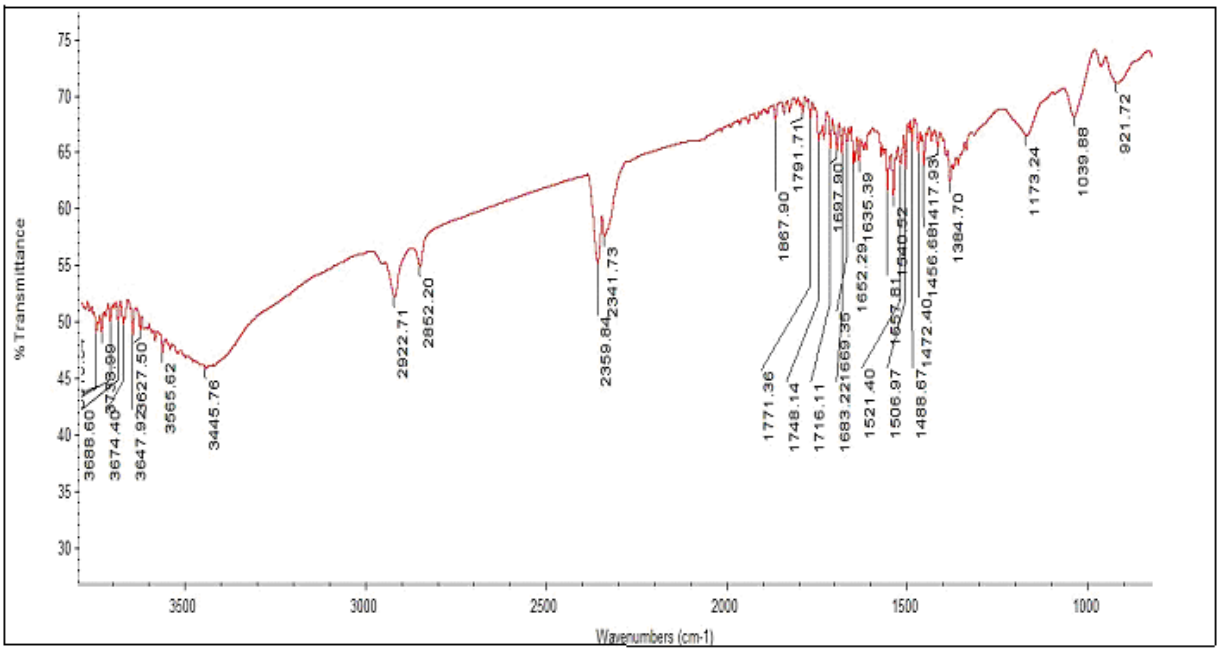


Figure 4.8 FTIR of pyrrole/AuNP in KNO_3

4.3 TRANSMISSION ELECTRON MICROSCOPY

In Transmission electron microscopy, the sample is prepared as per procedure and analysed through the TEM. The fig 4.9 shows the TEM images of polypyrrole/AuNP Nananoparticles. It is clear from the image that shape of particles are rectangular ,the average size of the particles lies between 80-100 nm. The dark images show that nanoparticles are solid in structure.These TEM images shows that gold is entrapped in the matrix of polypyrrole.

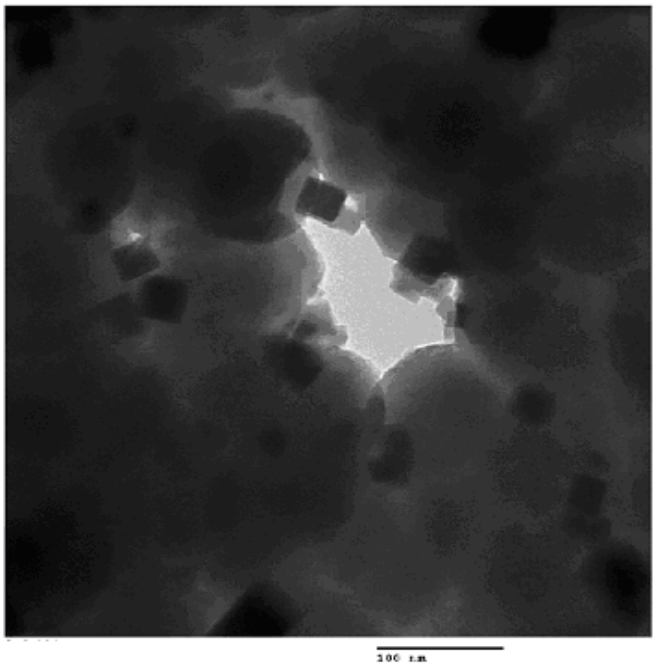


Figure 4.9 TEM image of polypyrrole/AuNP nanocomposite

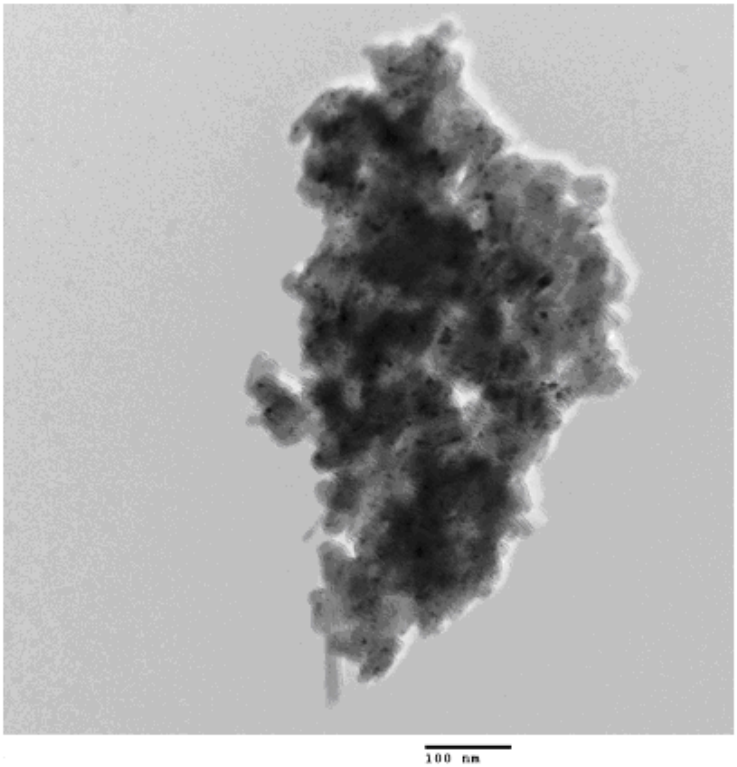


Figure 4.10 TEM image of polypyrrole/AuNP nanocomposite

4.4 SCANNING ELECTRON MICROSCOPY

In scanning electron microscopy, the study of surface morphology of polypyrrole/FeCN is done (fig 4.11).The surface morphology of polypyrole showed algal like surface with some globules on its surface. After the formation of composite with FeCN, algal surface changed into grain like structure, which might be due to engulfment of FeCN molecules into the algal surface.

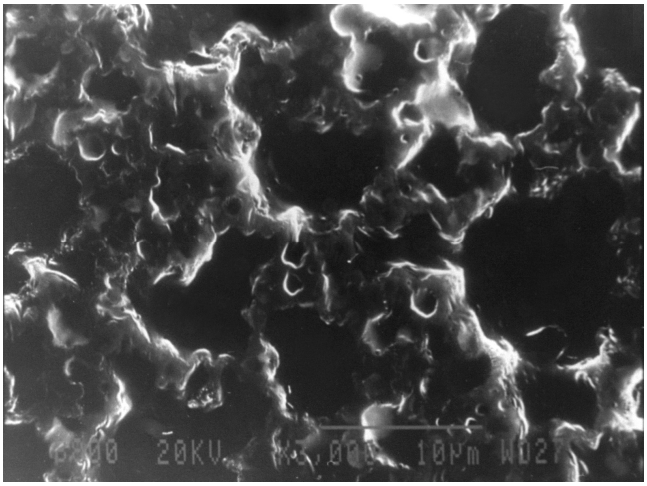


Figure 4.11 SEM of polypyrrole in KCL

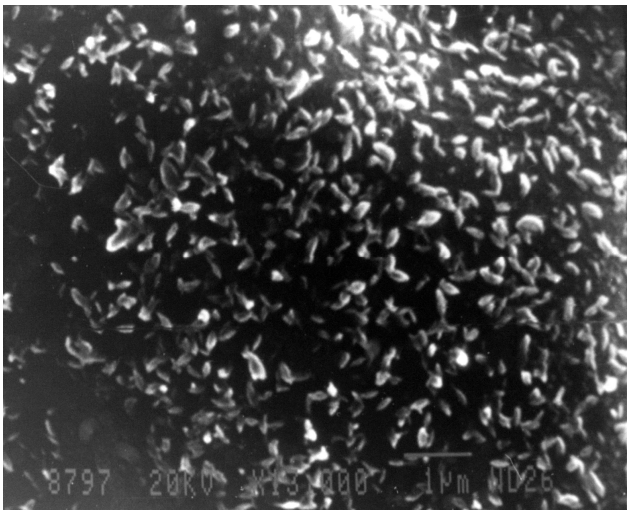


Figure 4.12 SEM of polypyrrole/FeCN

4.5 THERMOGRAMMETRIC ANALYSIS

4.5.1 TGA OF POLYPYRROLE-FeCN

The TGA plot of polypyrrole-FeCN composite was carried out in the presence of nitrogen from 30^0 C to 1000^0 C. For polypyrrole initially the huge loss of weight (49.30%) up to a temperature of 520^0 C is due to the degradation of polypyrrole and after that there is a degradation of solvent residue. But in polypyrrole-FeCN composite degradation of polypyrrole occurs at temperature of 600^0 C because due to the formation of composite its strength increases. After that there is a change of weight upto 900^0 C. It is due to the decomposition of FeCN.

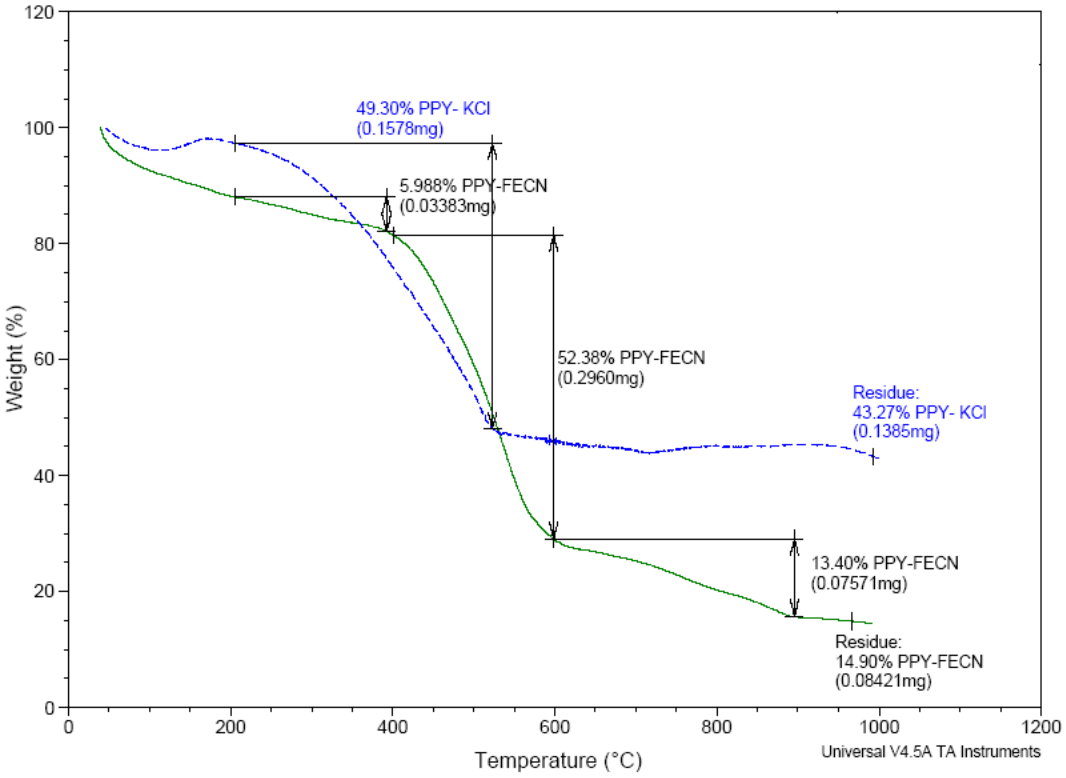


Figure 4.13 TGA of Polypyrole & Polypyrole-FeCN composite

4.5.2 TGA OF POLYPYRROLE-AuNP COMPOSITE

The TGA plot of polypyrrole-AuNP composite was carried out in the presence of nitrogen from 50^0 C to 700^0 C. Initial loss of weight up to a temperature of 180^0 C is due to the loss of moisture content. Thereafter weight loss upto 600 ^{0}C is due to the degradation of polymer backbone.

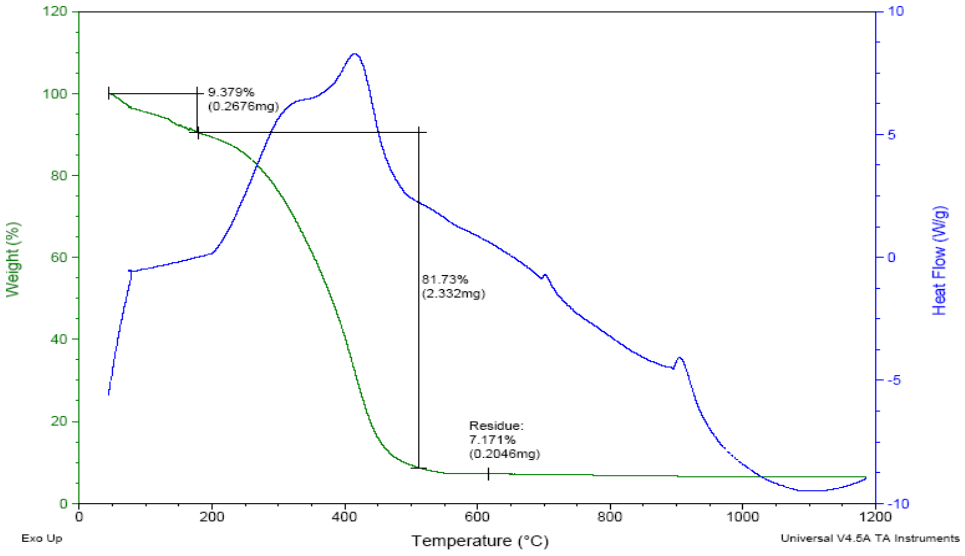


Figure 4.14 TGA of Polypyrole-AuNP composite

4.6 IMPEDENCE SPECTRA

Almost everyone knows about the concept of electrical resistance. It is a ability of a circuit element to resist the flow of electrical circuit. Like resistance, impedance is a measure of the ability of a circuit to resist the flow of current. For a poteniostated electrochemical cell, the input is the potential and the output is the current. Electrochemical cells are not linear. Doubling the voltage will not necessarily double the current. Electrochemical impedence is usually measured by applying an AC potential to an electrochemical cell and measuring the current

through the cell. The impedence is therefore expressed in terms of a magnitude,Z_0, and a phase shift, f.

The expression for Z (w) is composed of a real and a imaginary part. If the real part is plotted on the X axis and the imaginary part on the Y axis of a chart, we get a "Nyquist plot". Low frequency data are on the right side of the plot and higher frequencies are on the left. Impedence usually falls as the frequency rises.

Figure 4.15 shows Nyquist plot of impedance for bare platinum electrode, electrode with polypyrole, electrode with gold nanoparticles and electrode with PPy-AuNP nanocomposite. R_c value of bare Pt electrode (2.347 x 10^2) decreased after the polymerization of pyrole on it (2.053 x 10^2)which is attributed to the conducting behaviour of polypyrole. The value further decreased after the modification of Pt/PPy electrode with gold nanoaprticles (1.467 x 10^2). This result confirms the formation of PPy-AuNP nanocomposite.

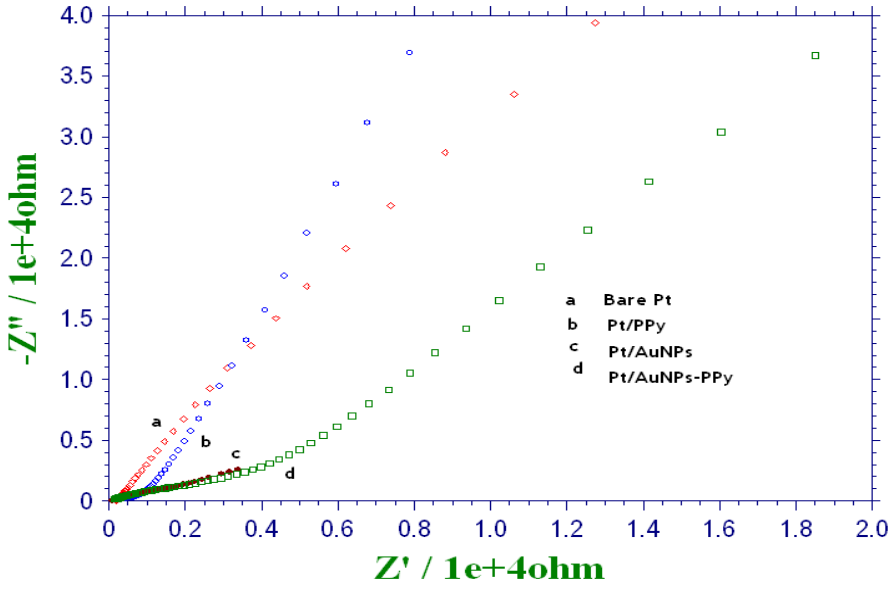


Figure 4.15 Impedence spectra of Bare Pt, Pt/PPy, Pt/AuNPs, Pt/AuNPs-PPy in 0.1 M FeCN-KCL

CONCLUSION

The thin films of PPy, PPy/FeCN and PPy/AuNPs composite are synthesized by Electrochemical polymerization. FTIR studies of PPy-FeCN and PPy-AuNPs composite showed that prominent peaks of polypyrole got shifted. Cyclic voltametric studies of PPy-FeCN composite showed the presence of oxidation peak of pyrole at 0.9 V as well as redox couple of Fe^{+2}/Fe^{+3}. TGA studies of polypyrole showed huge weight loss (49.30%) up to a temperature of 520^0 C which is due to the degradation of polypyrrole. But in polypyrrole-FeCN composite degradation of polypyrrole occurs at temperature of 600^0 C because due to the formation of composite its strength increases. After that there is a change of weight upto 900^0 C corresponding to the decomposition of FeCN molecule.

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