Synthesis, characterization and temperature studies on the conductivity of AlCl$_4^-$ ion doped polypyrrole

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Synthesis of free standing conducting polypyrrole film using room temperature melt as the electrolyte is reported. We also report variation in the contribution of ionic conductance with temperature of the polymer film by four probe method and electrochemical properties like diffusion coefficient and ionic mobility of AlCl$_4^-$ doped polypyrrole film. An attempt has been made to arrive at the stability of charge carrier concentration over a temperature range of 295 to 350 K under vacuum. The film was characterized by optical techniques and scanning electron micrography. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Among the conjugated conducting polymers, polypyrrole is non toxic and is obtained as a free standing film by a simple electrochemical polymerization with a wide practical applications [1–6]. The electronic conductivity of PPy can be switched between the conducting and the insulating states through doping and undoping cycles. The electronic conductivity around 10^3 S/cm has been achieved by doping with ordered small counter anions that are coplanar with respect to polymer chains [7–10]. Hence polypyrrole has been used as a cathode material in lithium batteries [11–14]. Actually PPy is a mixed type of conducting polymer via both electronic and ionic mechanisms. However both the components must be characterized in practical use. As shown in the literature [15–17], many methods have been provided to measure the ionic transport number and the ionic mobility in the solid polymer electrolyte (SPE). Kato *et al.* [18] studied the temperature dependence of the ionic transport numbers of Li$^+$ by means of the combination of the complex impedance and potentiostatic polarization measurements of the crosslinked polyethylene oxide (PEO). Chandra *et al.* [19] observed that the polymeric system, PEO + AgNO$_3$, shows mixed (ionic + electronic) conduction. Nevertheless, no available methods can be used in distinguishing between ionic and electronic conductances of conducting polymers.

In this work, we have synthesized conducting polypyrrole in the presence of room temperature melt as the electrolyte and characterized using spectroscopic and morphology studies. We have studied the d.c conductivity as a function of temperature for polypyrrole films and thereby arriving at electrical properties like ionic mobility, diffusion coefficient and charge carrier density due to the dopant ion in the oxidized form. This ionic conductivity contributes preferentially to the bulk conductance.

2. Experimental
2.1. Reagents

Anhydrous aluminum chloride (98% Sigma Aldrich) recrystallized cetyl pyridinium chloride (98% Sigma Aldrich) and vacuum distilled pyrrole (99% Sigma Aldrich) were used. Each time the aluminium chloride was sublimed before use.

2.2. Preparation of electrolyte

Cetyl pyridinium chloride (33%) and aluminum chloride (67%) were mixed together thoroughly inside a dry box to get a highly viscous liquid (melt). The proportion of aluminum chloride is always maintained to be higher than cetyl pyridinium chloride to get the acidic melt. This viscous melt is dissolved in diethylether (solvent) to reduce the viscosity.

2.3. Electrochemical polymerization

The electro polymerization of pyrrole was carried out by potentiodynamic technique using EG & G PARC Model175 universal programmer and Tacussel bi-pad type potentiostat with BBC-GOERZ METRAWATT SE790 model recorder at room temperature. A three compartment sealed glass electrochemical cell was used with platinum sheet as the working electrode and platinum wire was used as the counter electrode. A high purity aluminum wire was used as the reference

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electrode. The electro deposition of PPy was carried out by sweeping potential at 50 mV/sec in the potential range of 0 and 1.1 V vs. Al wire from the 0.1 M electrolyte prepared by adding the room temperature melt in pyrrole. Black, homogeneous films were obtained readily at electropolymerization time within 15–30 min. In order to avoid any contact with oxygen in air, the samples were dried and transferred in a dry vessel with nitrogen atmosphere to investigate the conductivity of the system.

2.4. Characterization
The characterization of PPy film was carried out under anhydrous condition by spectroscopic methods and scanning electron micrograph.

2.4.1. Electronic spectral studies
UV spectra of the electrode surface were recorded on Cary 500 scan UVVIS-NIR spectrophotometer using high alumina pellet as reference in the range 200 nm to 1500 nm.

2.4.2. Vibrational spectral studies
FTIR spectra were recorded using Perkin Elmer Paragon −500 FTIR spectrophotometer using KBr pellets in the region between 400 and 4000 cm^{-1}.

2.4.3. Morphology—Scanning electron micrograph
Scanning electron micrographs were recorded at various magnifications using Hitachi-S-3000H SEM machine.

3. Conductivity measurements
The electronic conductivity measurements were carried out by four probe method using Keithley Model 2400 series Source meter and Keithley Model 2182 Nano voltmeter equipment under nitrogen atmosphere. The electrical contacts were made with a mercury drop between the polymer film and the four probes.

4. Results and discussions
4.1. Film appearance
The color of the PPy film depends on the thickness and varies from dark blue to black in doped state on the platinum substrate. The film turned to blue in the undoped state which was obtained by reversing the poles and making the film cathodic for one hour.

4.2. CV studies—Electrochemical polymerization of pyrrole by cyclic voltammetry
The growth of conducting polymer film has been a subject of intensive studies by various techniques to understand its various properties like ion transport and

optical studies. In principle the growth of the conducting polymer can be compared with electrodeposition of metals, the difference being that the former is an anodic reaction. The filming on an anode surface during electrolysis of a monomer in a suitable electrolytic medium occurs via oxidative generation of radical cations near the vicinity of an anode which on further coupling leads to precipitation of conducting polymer leading to a filming anode surface suggesting that particles are added one at a time to a cluster or aggregate of particles via random walk trajectories that is to say that competing growth of polymer on anode surface leads to formation of a cluster and can be considered as an alloy of macromolecule with counter ion giving it a distinct entity.

The electrodeposition reaction from solution phase is a transformation reaction thus there is a tendency in the system between order and disorder which results in thermodynamic fluctuations leading to the formation of an ordered phase.

The electrochemical polymerization of pyrrole to freestanding polypyrrole (PPy) film in room temperature melt is shown in Fig. 1. The growth is reflected by the increase in peak current. The color of the film was black. The electropolymerization of pyrrole to freestanding polypyrrole film in chloroaluminate room temperature melt medium was carried out by potentiodyanamic method. In the very first cycle of polymerization the peak appearing at 0.5 V corresponds to the oxidation of pyrrole to pyrrole radical cation. In subsequent cycles new oxidation peaks appear at 0.58 V indicating that these radical cations undergo further coupling and the peak current increases continuously with successive potential scans indicating the buildup of electroactive polypyrrole on the electrode surface. Though the peak potential of the peak observed in the first cycle is at 0.5 V (very broad: formation beginning around at 0.45 V), this suggests that even by keeping
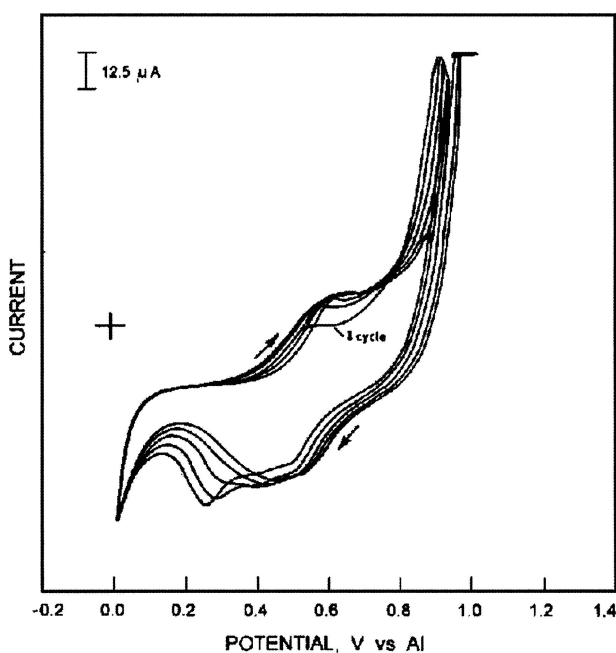

Figure 1 Electrochemical growth pattern of polypyrrole in the presence of chloroaluminate room temperature melt as the electrolyte, potential range –0.2 to 1.2 V vs. Al at sweep rate of 50 mV/sec.

the potential around this value can lead to formation of polymer at a slow growth rate, which is beneficial for obtaining a more ordered thin polymer film useful for electrochromic displays. Once the polymerization process is initiated it is influenced by the anion for the following factors:

- Adsorption of the anion on the electrode surface
- Redox potential of the anion
- The ionic charge
- The ionic size
- The hydration shell

Electrochemical studies reveal the influence of the counter anion on the peak potentials as well as on the polymer deposition rate indicating that the electron transfer and protonation processes are greatly influenced by the anion.

The electro active PPy is obtained only when the melt is acidic i.e. the proportion of aluminium chloride in the melt is more giving rise to the $AlCl_4^-$ anion which is the dopant responsible for the oxidation of pyrrole. The electro polymerization does not occur in the neutral or basic melts.

In the forward cycle during growth a well defined peak was observed at 0.58 V vs Al wire which is shifted to 0.6 V with increase in scan numbers and similarly in the reverse cycle 2 peaks were observed at 0.56 V which is shifted slightly to 0.55 V and at 0.4 V vs Al wire which is shifted to 0.2 V in the negative side. This shows that the polymerization reaction is reversible.

4.3. UV-VIS-NIR spectroscopic studies

The diffused reflectance UV-visible Near IR spectra of (a) doped and (b) undoped PPP are shown in Fig. 2.

The absorption peak observed between 350 and 390 nm is assigned to $\Pi–\Pi^*$ transition associated with benzenoid ring. The band due to cation radicals lie between 400 and 600 nm. The band observed near or more than 800 nm is due to the charge carriers. The tail of this band extends to the infra-red region indicating that the charge carriers are bipolarons or otherwise called as trapped excitons.

The first absorption peak around 0.7 eV (1264 nm) can be related to a transition from the valance band to the half filled polaron bonding level while the peak around 1.4 eV (882 nm) associated with the transition between bonding and antibonding polaron levels. The peak around 2.1 eV (457 nm) corresponds to the transitions from valance band to the antibonding polaron state. As the extent of oxidation increases, bipolaron formation increases. The bipolaron introduces the two states in the gap, at 0.75 eV above the valance band edge and 0.79 eV below the conduction band edge. However the bonding bipolaron state is empty, the presence of bipolarons leads to only two optical transitions in the gap which explains the appearance of absorption spectra at higher oxidation levels where the two intense bands within the gap are accounted for the two wide bipolaron bands. It is important to note that the gap between these bipolaron bands never goes to zero even at the highest doping levels achieved. Hence polypyrrole is never a metal.
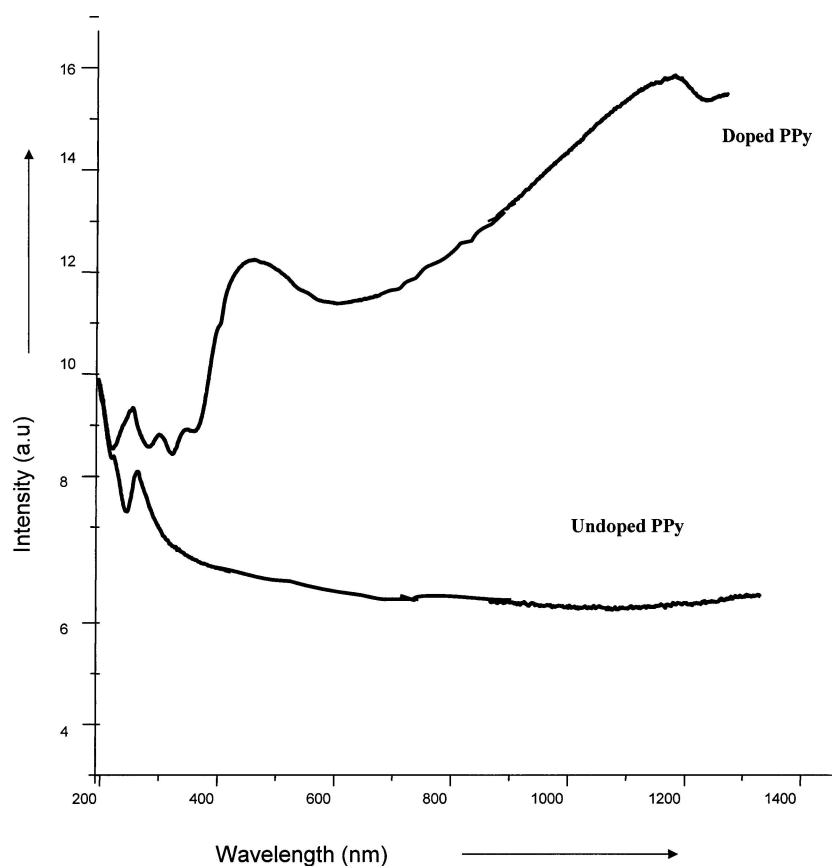

Figure 2 The diffused reflectance UV spectra of (a) doped and (b) undoped PPy using high alumina as reference in the range 200 to 1500 nm.

T A B L E I The major shifts of bands in FTIR spectra of doped PPy from virgin PPy, Fig. 3

Assignment of IR bands	
Undoped polypyrrole	Doped polypyrrole
$3421 \ cm^{-1}$ (NH str)	No band
$3100 \ cm^{-1}$ (C—H str)	Diminished band
$1535 \ cm^{-1}$ (C=C & C—C str)	$1529 \ cm^{-1}$
$1450 \ cm^{-1}$ (N—H str)	$1445 \ cm^{-1}$
$1295 \ cm^{-1}$ (C—H & N—H def)	$1290 \ cm^{-1}$
$1050 \ cm^{-1}$ (C—H def)	$1010 \ cm^{-1}$

Figure 4 Scanning Electron Micrograph of doped PPy film showing crystalline Structure.

Figure 3 FTIR spectra of doped (a) and undoped PPy (b) in the region $4000 \ cm^{-1}$ to $400 \ cm^{-1}$ in the KBr medium.
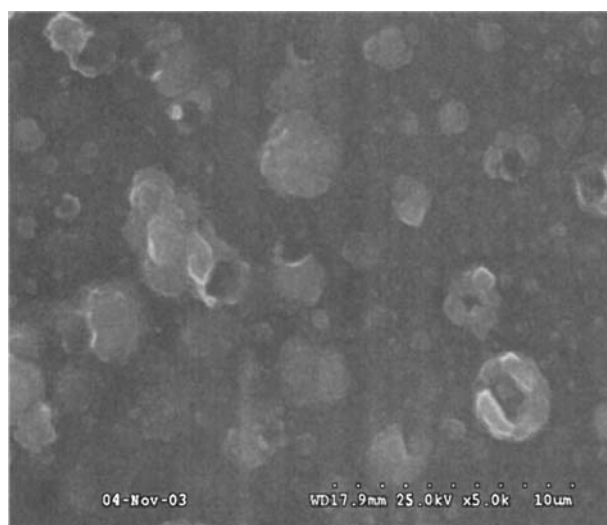
Figure 5 Scanning Electron Micrograph of undoped PPy film showing non-conducting dark portions.

4.4. FTIR spectroscopic studies of PPy film

Principal absorption bands observed in the IR spectra of doped and undoped polypyrrole are given in the Table I.

All the characteristic IR absorption bands due to polypyrrole are observed in doped PPy film with a slight shift in the position of absorption band. For example a band at $3400 \ cm^{-1}$ due to −NH stretching in neutral PPy vanishes in the doped form and $1529 \ cm^{-1}$ band due to C=C stretching has been observed at $1545 \ cm^{-1}$ in doped film. The spectrum of oxidized form of polypyrrole polymer does not show the NH or CH stretching because there is a strong electronic absorption. Fig. 3. shows the FTIR spectra for PPy films.

4.5. SEM pictures

Figs. 4 and 5 are the Scanning Electron Micrographs of doped and undoped PPy respectively. Fig. 4 shows that doped polymer has a regular hexagonal geometry (indicated by arrows). The study shows that the size of the largest hexagon is $3.5 \ \mu m$ and that of smallest is $2.5 \ \mu m$ and the undoped polymer has globular struc-
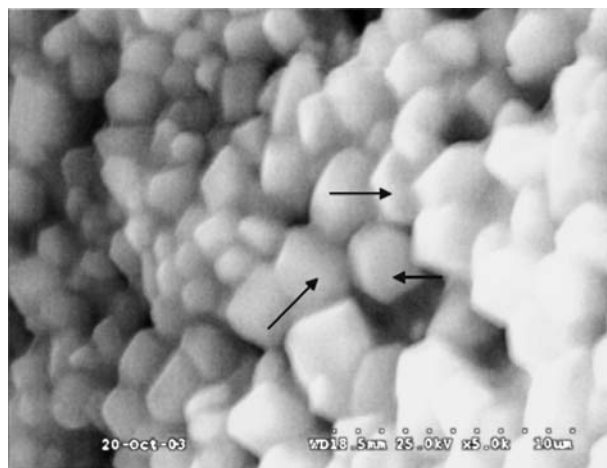
tures with particle size ranging from 0.85 to $14.7 \ \mu m$. The brightness of hexagon in an uniform way indicates the homogeneity of doping.

5. Conductivity studies and electrical properties

The room temperature conductivity of the free standing polypyrrole film was 132 S/cm. Fig. 6 shows the dependence of d.c conductivity on temperature for PPy film doped with tetrahedral chloroaluminate ($AlCl_4^-$) ion. The curve indicates that the thermally activated conductivity increases for the PPy film and finally attains saturation. Fig. 7 gives the dependence of ionic mobility and diffusion coefficient of PPy film on temperature. They are in concordance with the conductivity graph. These investigations confirmed the quality of PPy film and their thermal stability upto 350 K. From the above calculations we have arrived at the charge carrier concentration of the doped PPy system. It was found that the charge carrier concentration remained unchanged throughout the temperature range from 295 to 350 K.

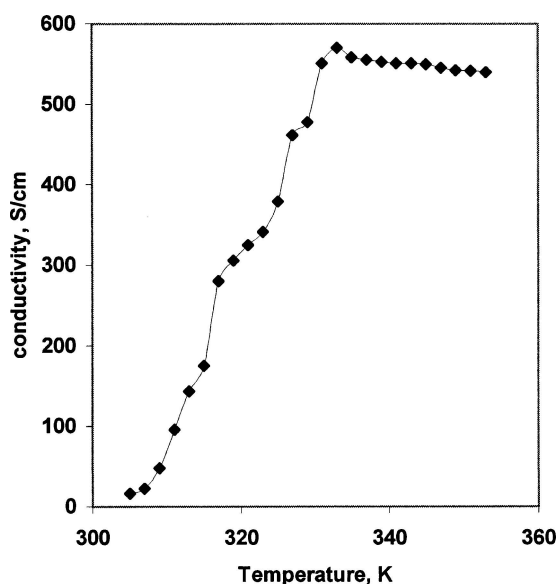| Temperature	Charge carrier concentration
305	3.9389×10^{21}
310	3.937×10^{21}
315	3.933×10^{21}
320	3.926×10^{21}
325	3.9357×10^{21}
330	3.9359×10^{21}
335	3.940×10^{21}
340	3.9356×10^{21}
345	3.9342×10^{21}
350	3.936×10^{21}

Figure 6 Temperature dependence of d.c conductivity of polypyrrole film.
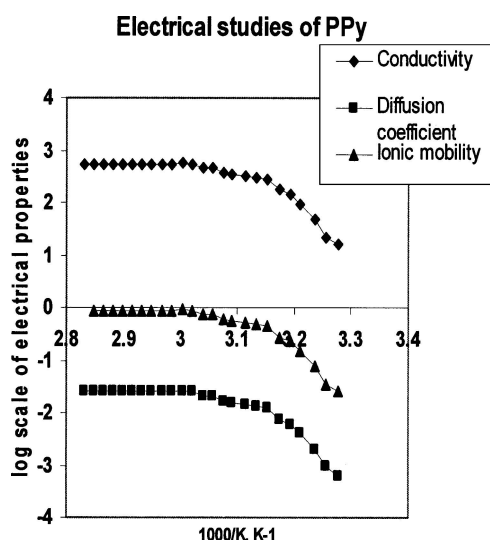

Figure 7 Temperature dependence of ionic mobility and diffusion coefficient in concordance with conductivity of polypyrrole film.

This states that the dopant is not decomposed in this range of temperature and also shows that the extent of doping is high. Only the mobility of $AlCl_4^-$ anion attains saturation and consequently the conductivity. Table II gives the charge carrier concentration evaluated at various temperatures.

6. Conclusion

High conductivity PPy films were synthesized electrochemically using room temperature melt as electrolyte. The conductivity variations with increase of temperature were studied using four probe technique and finally arrived at the electrical properties of PPy. The charge carrier concentration in the polymer film was found to be constant throughout the temperature range.

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