Temperature dependence of conductivity of polypyrrole doped with sulphuric acid

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Polypyrrole samples doped with sulfuric acid have been synthesized by using chemical oxidative polymerisation technique in different ways. The monomer mixed with acid (sample S\textsubscript{1}) and oxidant mixed with acid (sample S\textsubscript{2}) is characterized by XRD and FTIR spectroscopy. Electrical conduction in these doped samples are studied through the $I-V$ measurements at room temperature as well as function of temperature from 313 to 473 K. The $I-V$ characteristics for both the samples have been found to be linear but conductivity of sample S\textsubscript{2} is found to be higher. Temperature dependence of conductivity suggests a transition from semiconducting nature to metallic nature with increase in temperature. Activation energies for both the samples have been found to be in milli electron volt range, 96.76 meV and 116.72 meV for samples S\textsubscript{1} and S\textsubscript{2}, respectively.

**Keywords**: Conducting polymer, Electrical conduction, Temperature dependence, Activation energies

1 Introduction

Conducting polymer is one of the most promising functional materials. Many scientists have extensively investigated its synthesis and applications. Due to high electrical conductivity of conducting polymers, they have attracted lots of research interest and become popular basic materials for advanced applications such as plastic batteries, light emitting diodes, EMI shields, electro chromic displays devices, gas separation membranes, smart windows and sensors\textsuperscript{1-3}.

Polypyrrole is a relatively air stable organic conducting polymer with high electrical conductivity, good environmental, chemical and electrical stability and easy synthesis\textsuperscript{4-5}. The charge carriers of the polypyrrole are generally considered to be polarons and bipolarons stabilized by counter ions incorporated into the polymer during preparation. Therefore, conducting and physical properties of polypyrrole depend on the choice of the counter ion, often called dopants\textsuperscript{6}.

In this paper the temperature dependence of electrical conductivity of doped polypyrrole sample in bulk form with the variation in preparation techniques is studied.

2 Materials and Methods

2.1 Material preparation

Polypyrrole was prepared by oxidative polymerisation of double distilled pyrrole using ammonium persulfate, (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} as an oxidant. The polymerisation was performed at 0°C temperature with oxidant/monomer molar ratio 0.2. As a typical preparation, sample S\textsubscript{1} was synthesized by taking ammonium peroxydisulphate and sulfuric acid according to stoichiometry, dissolved in distilled water. Now this aqueous solution is added to the stirred solution of double distilled aniline dissolved in distilled water. The black precipitate resulting from the reaction is washed with distilled water and methanol and then dried under vacuum for 6-8 h\textsuperscript{7}.

Similarly, sample S\textsubscript{2} was synthesized by adding dropwise aqueous solution of ammonium peroxydisulphate to the stirred solution of double distilled aniline dissolved in distilled water. The black precipitate resulting from the reaction is washed with distilled water and methanol and then dried under vacuum for 6-8 h\textsuperscript{7}.

2.2 Characterization

X-ray diffraction patterns as shown in Fig. 1 of samples were taken at room temperature in order to study the structure of the material. The materials were found to be amorphous in nature.

However, hump is observed at low angle scattering for pure polypyrrole sample\textsuperscript{8}. This hump splits into two broad peaks from 10° to 30° with doping of H\textsubscript{2}SO\textsubscript{4} in pure polypyrrole\textsuperscript{9}. The FTIR spectra of polymer powder obtained in KBr pellet is shown in Fig. 2.

The band observed at various modes confirms the formation of polypyrrole and peak observed
at 1035 and 690 cm$^{-1}$ in H$_2$SO$_4$ doped PPy (S$_2$) are due to the symmetric stretching of sulphate group inferred the doping of polypyrrole with sulfuric acid$^{10}$.

2.3 Experimental techniques
The details about electrical measurements of I-V characteristics have been discussed earlier$^{11}$. The I-V characteristics were recorded in the temperature range of room temperature to 473 $K$.

3 Results and Discussion
I-V characteristics of doped polypyrrole were recorded at different temperatures and are found to be linear as shown in Figs 3-4.

Under the influence of applied external field the localized (short range) motions of the trapped charges in the sample serve as effective electric dipoles$^{12}$, which contribute to the formation of polaron and bipolarons.

As the strength of the applied field increases the degree of such distortion increases, resulting in the increment of current. It is also observed that the current increases with the increase in temperature. Elevations in temperature lead to an increase in lattice vibration, which results in chain stretching. This stretching of polymer chain leads to an effective charge distribution all over the chain and increment in alignment of polymer chains with potential for longer conjugation length$^{13}$. This leads to intra and inter chain hopping of charge carriers which inturn increase the conduction. Therefore, in these bulk samples, charge transports involve both intra and inter chain contributions. From the measured I-V characteristics of these two samples, the values of electrical conductivities have been obtained at different temperatures as follows:

$$\sigma = \frac{(I \times L)}{(V \times A)} \quad \ldots(1)$$

where $I$ is the current, $V$ is the voltage, $L$ the thickness, and $A$ the cross-section area of the sample.

A comparative study of both samples suggests that the conductivity of sample S$_2$ is about $10^5$ times that of sample S$_1$, i.e conductivity of S$_2$ is higher as compared to S$_1$. Doping with sulfuric acid causes bond alternation from aromatic configuration to quinoid configuration, which is higher in energy and confines charge and spin density to a self localized structural deformation that is mobile along the chain$^{14}$. In sample S$_2$, more and more anions or radical ions are coupled to pyrrole units via local resonance. Hence, more and more number of quinoid rings are created along the polymer backbone. The distorted structures result into a widening of bonding and antibonding levels with larger gap, which is responsible for higher electrical conductivity of sample S$_2$. 

Fig. 1—X-ray diffraction pattern of pure and H$_2$SO$_4$ doped polypyrrole

Fig. 2—FTIR spectra of H$_2$SO$_4$ doped polypyrrole

Fig. 3—I-V characteristics of sample S$_1$
The electrical conductivity of both the samples has been determined in the temperature range 313 to 473 K explained using Arrhenius model\textsuperscript{12}.

\[ \sigma = \sigma_0 \exp \left[ -\frac{E_{ac}}{kT} \right] \quad \ldots \quad (2) \]

where \( \sigma_0 \) is the conductivity at room temperature, \( E_{ac} \) is the carrier activation energy and \( k \) is the Boltzmann constant.

Fig. 5 shows the temperature dependence of electrical conductivity of both the samples. The electrical conductivity of both the samples increases with temperature up to 433 K and then decreases with further increase in temperature. This suggests a transition from semiconducting to metallic nature with increase in temperature.

Plots of \( \ln(\sigma) \) versus \( 1000/T \) have been shown in Figs 6-7. The slope [equal to \( E_{ac}/1000k \)] of these plots provides information about activation energies \( E_{ac} \). Activation energies were found to be 96.76 meV and 116.72 meV for samples S\textsubscript{1} and S\textsubscript{2}, respectively.

It is an interesting fact that the activation energy of S\textsubscript{1} is smaller as compared to S\textsubscript{2}, but conductivity is large for S\textsubscript{2}. This is due to the creation of larger number of polarons and bipolarons in the sample and the availability of these contribute to the enhancement in the conductivity of the sample. With the increase in doping, formation of continuous bipolaron bands take place. The separation between these bipolaron bands increases at the expense of the band edges. For a very heavily doped polymer it is
conceivable that the upper and lower bipolaron bands will merge with conduction and valence band, respectively leading to a wider separation between these bands and hence such an inherent change leads to a higher value of activation energy.

4 Conclusions

Temperature dependence of conductivity of doped polypyrrole samples suggests a transition from semiconducting nature to metallic nature with increase in temperature. However, doping of sulfate ion into the monomer increases the conductivity more in comparison to doping along APS. With the increase of doping a wider separation of bipolaron band takes place, which in turn enhances the activation energy.

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