Dielectric Properties of Polythiophene-CoO Composites

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Abstract
Polythiophene has been prepared by oxidation process. Polythiophene-CoO composites were prepared by mechanical mixing of PTh and CoO in different weight percentages. Dielectric properties as a function of temperature from 300K to 425K and frequency in the range from 50Hz to 3MHz have been measured. Dielectric constant decreased with increase in frequency and increased with increase in temperature. Dielectric loss decreased with increase in frequency and increased with increase in temperature. Using dielectric data, ac conductivity has been determined. Conductivity was found to be in the order of $10^{-6}$ (Ω·m$^{-1}$) and it increased with increase in temperature. The temperature variation of conductivity has been analyzed using Mott’s polaron hopping model. Activation energy for conduction has been determined. Activation energy was determined to be in the order of meV and it has decreased with increase in frequency and CoO content. Similar results have been reported for polyaniline and cobalt doped phthalocyanine.

Keywords
Polythiophene, nanocomposites, conductivity, polaron hopping, activation energy.

INTRODUCTION
Conjugated conducting polymers have attracted much attention in research due to their optical, electrical and thermal properties [1-3]. Among organic conductive polymers, polythiophene (PTh) and its derivatives have been of special interest because of its easy preparation and specific properties such as environmental stability, higher conductivity and photoconductivity [4-5]. Conducting polymers can be doped suitably to have either semiconducting or normal conductor behaviour in them. Nano composites of conducting polymers have attracted much as they are proposed to be used in drug delivery, conductive paints, rechargeable batteries etc. Also over conducting polymer and metal oxide nano composites emerged as a new class of materials as they exhibit properties which are different from their pure forms [6-11]. The cobalt oxide has got scientific and technological importance [12-14]. Cobalt oxide is used as a supercapacitor electrode [15]. The conductivity of PTh-Zno composites were measured to be of the order of $10^{-4}$ Ω/m by chemical oxidative method [6]. Polyaniyne – cobalt nanocomposites have been synthesized by hydrothermal method and their conductivity increased with increasing amounts of cobalt nanoparticles [11]. The room temperature (25°C) conductivity of polypyrrole-TeO$_2$ and PTh-TeO$_2$ composites have been reported to be $1 \times 10^{-5}$ Ωcm$^{-1}$ and $2 \times 10^{-5}$ Ωcm$^{-1}$ respectively [16]. In these composites conductivity have been observed to have increased by $10^3$ to $10^6$ orders of magnitude compared to their pure PPy and PTh. PPy-V$_2$O$_5$ composites of different wt% in the range from 10 to 50 wt% were prepared at 0°C by chemical oxidative method. The room temperature conductivity plots of PPy- V$_2$O$_5$ composites at 100kHz revealed that the addition of vanadium oxide nanoparticles decreases conductivity up to 10% of V$_2$O$_5$ and there after remains same up to 50%. The ac conductivity of pure PPy increases constantly with frequency and PPy- V$_2$O$_5$ composite showed constant conductivity up to the frequency of $10^5$ Hz and thereafter increased steeply [17]. Literature survey up to now revealed that PTh-CoO nano composites have not been investigated by anyone for dielectric properties and ac conductivity as a function of frequency and temperature. Therefore, we report on dielectric results obtained for PTh-CoO nanocomposites. AC conductivity has been determined using dielectric data. Frequency and temperature dependence of dielectric and conductivity data has been thoroughly analyzed.

2. EXPERIMENTAL
PTh was prepared at 323K using analytical grade Thiophene, Ferric chloride, Methanol and Chloroform as starting materials. Homogenous aqueous solution of thiophene was prepared. Aqueous chloroform and ferric chloride solution was added drop wise to the PTh solution. Then the mixture magnetically stirred for 24 hours and then filtered. The resultant black precipitate was washed with chloroform and then with methanol. During this process the precipitate becomes brown which indicated the formation of Polythiophene. The powder was dried and grinded [16, 19]. The PTh-CoO composites were prepared by mixing Polythiophene and analytical grade CoO in different wt% defined as (PTh)$_{100-x}$,(CoO)$_x$, where x= 5%, 10%, 15%, 20% and 25% and labelled as PTh-CO1, PTh-CO2, PTh-CO3, PTh-CO4 and PTh-CO5 respectively. Powders of the composites were prepared into pellets of suitable size in a hydraulic press. Silver paste was attached on two large surfaces of the pellets. Capacitance, C, and dissipation factor, tanδ, were measured as function of frequency and temperature in the range from 50Hz to 3MHz and 300K to 423K respectively. These measurements were carried out in a precession impedance analyser (Wayne Kerr makes Model No. 6500B). Temperature was measured using Chromel-Alumel thermo- couple with accuracy of ± 1K.

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3. RESULTS AND DISCUSSIONS

Dielectric properties

Using the measured capacitance and dissipation factor, the dielectric constant and dielectric loss were determined for all the composites, using the expression given in [18]. Fig. 1 shows the variation of dielectric constant, $\varepsilon'$, with frequency for all the five composites. From this figure, we can note that $\varepsilon'$ decreases gradually with frequency up to 70 KHz and becomes constant for higher frequencies for all the samples. Dielectric loss factor, $\varepsilon''$ variation with frequency for all the five composites is plotted in Fig. 2. $\varepsilon''$ varied with frequency in the same fashion as that of $\varepsilon'$. Moreover, the dielectric loss factor also depends on the number of other factors such as stoichiometry [20]. The temperature variation of $\varepsilon'$ for PTh-CoO composites is depicted in Fig. 3. In this figure, we see that $\varepsilon'$ increases with temperature. Similar nature of variation of $\varepsilon'$ with temperature has been observed for the remaining composites. The change in $\varepsilon'$ with temperature for PTh-CO3 is shown in Fig. 4. Similar behaviour of $\varepsilon''$ with temperature has been observed for the remaining composites.

Electrical Conductivity

Conductivity, $\sigma$, has been determined using dielectric data using the following equation [21].

$$\sigma_{dc} = \varepsilon'' \omega \varepsilon_0$$

Where $\varepsilon_0$ is free space permittivity which is equal to $8.85 \times 10^{-12}$ Fm$^{-1}$. Conductivity variation with temperature for different frequencies for the composite PTh-CO1 is shown in Fig. 5.

Fig 1. Dielectric constant, $\varepsilon'$ versus ln(f) for PTh-CO nanocomposites at the temperature of 323K.

Fig 2. Dielectric loss, $\varepsilon''$ versus ln(f) for PTh-CO nanocomposites at the temperature 323K.

Fig 3. Dielectric constant, $\varepsilon'$ versus ln(f) for PTh-CO3 nanocomposites for different temperatures.
It can be seen in Fig. 5 that conductivity increases with increasing temperature indicating semiconducting type of behaviour. It also increased with increasing frequency [13]. All the present composites behaved in the same way. Conductivity variation with entire range of temperature increased is found to be within the same order of magnitude i.e., $10^{-4}$ $(\Omega^{-1}m^{-1})$.

Conductivity variation with CoO content for two different frequencies at temperature of 313K is shown in Fig. 6. From Fig. 6, it is clear that conductivity increases with increasing cobalt oxide content. This result reveals that more number of polarons (electrons) are getting added to the conducting pool in the composites as the cobalt oxide content is increased. Also, conduction mechanism in these composites appeared to be getting expedited with increasing frequency. This could be due to the fact that increase in frequency enhances polaron hopping frequency.

The temperature variation of conductivity has been fit to an expression derived by Mott originally for Small Polaron Hopping (SPH) in noncrystalline semiconductor solids. As there are no good theories for explaining conduction mechanism in conducting polymers and their composites, we use Mott’s SPH model. According to this model, the conductivity is given by [22],

$$\sigma = \sigma_0 \exp \left\{ \frac{E_a}{k_B T} \right\}$$

Where $E_a$ is the activation energy for small polaron hopping.

The plots of $\ln(\sigma T)$ versus $(1/T)$ were made as per Eqn. (2) for the composite PTh-CO2 and shown in Fig. 7. The linear lines were fit to the data in the high temperature region where the data appeared linear. The slopes were used to determine the activation energy, $E_a$.

Activation energy, $E_a$ versus CoO content determined for the present composites for different frequencies are plotted in Fig. 8.

**Fig 4.** Dielectric loss, $\varepsilon''$ versus $\ln(f)$ for PTh-CO3 nanocomposites for different temperatures.

**Fig 5.** Temperature dependence of electrical conductivity of PTh-CO1 composite nanoparticles at different frequencies.
Fig 6. Conductivity versus wt % of CoO in PTh-CO nanocomposites for two different frequencies at T=313K.

Fig 7. Plots of $\ln(\sigma T)$ versus $(1/T)$ for PTh-CO2 composite for four different frequencies. Solid lines are linear fits as per Mott’s SPH model.

Fig 8. Activation energy versus wt. % of CoO for PTh-CO nanocomposites at two Different frequencies.

From Fig.8, it can be noted that $E_a$ decreases with increase in frequency and CoO content. It may be attributed to the decrease in scattering rate of polarons with increase in CoO content. Similar results have been reported for polyaniline doped with camphor sulphonic acid and blended with tetrameric cobalt phthalocyanine and polyaniline-Co:O$_4$ [23, 12].

4. CONCLUSIONS

Polythiophene has been synthesized at 323K by chemical method. Nanoparticles of Polythiophene-CoO (PTh-CO) composites were prepared by mechanical mixing of Polythiophene and CoO in different weight percentages. Dielectric properties as a function of temperature and frequency have been measured over wide ranges. Dielectric constant
decreased with increase in frequency and increased with temperature. Dielectric loss decreased with increase in frequency and increased with temperature. Using dielectric data, conductivity has been deduced. Conductivity was found to increase with increase in temperature and frequency and this may be due to the fact that conduction process is made relatively easy by the presence of CoO content. By employing Mott’s Small Polaron Hopping Model expression for conductivity, activation energy has been obtained. Activation energy was found to be decreased with increase in frequency and CoO content and it may be attributed to the decrease in the scattering rate of polarons with increase in CoO content.

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REFERENCES


