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Frequency and Temperature dependence studies in PTh-V_2O_5 composites

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Abstract

By oxidation method, Polythiophene (PTh) has been prepared. Composites were prepared by mixing Polythiophene and V_2O_5 in different weight percentages. Their phases were confirmed by XRD and SEM studies. Dielectric properties and AC conductivity were measured over broad range of frequency and temperature. Conductivity varied with temperature is the semiconductor fashion. Dielectric constant and loss both were found to decrease with increase in frequency and increased with increase in temperature. Conductivity variation with temperature has been analysed in terms of small polaron hopping theory of Mott.

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

Introduction

The conducting polymers have been of great importance as this exhibit unique optical, electrical, chemical and thermal properties. Among these polymers, polythiohene (PTh) received, attention due to its high conductivity and thermal stability[1-4]. The conductivity of these materials can be tuned by doping. Dopant anion palys important role in polymerization[5,6]. Polymer nanocomposites are considered to be hybrid. Nano composites of polymers are used in drug delivery, conductive paints, betteries etc[7-13]. Vanadium oxides are polyfunctional materials and shows metal semiconductor transition. V_2O_5 is used an active electrode in a rechargeable lithium battery, elctro chromic devices, catalysts etc[14-19]. The conductivity of PTh-Zno composites were measured and found it to be order of 10^{-4} Ω/m[7]. The room temperature conductivity of polypyrrole-TeO_2 and PTh-TeO_2 composites have been reported to be 1 x 10^{-5} Ωcm^{-1} and 2 x 10^{-2} Ωcm^{-1} respectively[20]. In these composites, conductivity have been observed to have increased by 10^3 to 10^4 orders of magnitude compared to their pure PPy and PTh. PPy-V_2O_5 composites of different wt% in the range from 10 to 50 wt% were prepared by chemical oxidative method. The room temperature conductivity of these composites at 100 KHz revealed that the addition of vanadium oxide nanoparticle results in the decrease in conductivity up to 10% V_2O_5 and remain constant for higher amount of V_2O_5. The ac conductivity of pure PPy increased with frequency and PPy-V2O5 composite showed constant up to the frequency of 10^5 Hz and then increased steeply[16]. Polyaniline-V_2O_5 composites showed constant conductivity up to 10^5 Hz[17, 18]. DC conductivity of polyaniline-V_2O_5 composites of different wt% of V_2O_5 was found to change from 10^{-7} to 10^{-9} Ωcm^{-1}, attaining a maximum value for 30 of V_2O_5 [15]. Here, we present the result of dielectric results for PTh-V_2O_5 nanocomposites. AC conductivity has been determined using dielectric data. Frequency and temperature dependence of both dielectric data and conductivity data has been thoroughly analyzed.

Material and Methods

PTh was prepared at 323K using AR grade Thiophene, Ferric chloride, Methanol and Chloroform. Homogenous aqueous solution of thiophene was prepared. Chloroform and ferric chloride solutions were mixed drop by drop to the PTh solution. The mixture magnetically stirred for 24 hours and filtered. The precipitate so formed was washed with chloroform and then with methanol. In this process, the precipitate changed its colour to brown indicating the formation of Polythiophene .The powder was dried up and subsequently grinded[20,21]. The PTh-V_2O_5 composites were prepared by mixing Polythiophene and analytical grade V_2O_5 in different wt% defined as (PTh) 100-x $(V_2O_5)x$, where x= 5%, 10% and 15% labelled as PTh-VO1, PTh-VO2 and PTh-VO3 respectively. Powders were subjected to XRD and SEM studies. From these studies, it is confirmed that the grains in these composites are of nano size[22]. Powders of the composites were pressed into 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 impedence analyser (Wayne Kerr make Model No. 6500B). Temperature was sensed using Chromel-Alumel thermo- couple with the accuracy of ± 1K.

Results and Discussion

Dielectric properties: Using the measured capacitance and dissipation factor the dielectric parameters were determined for all the composites, using the expressions given in reference[23]. Figure-1 shows the variation of dielectric constant, ε' with frequency for all the three composites. From this figure, we note that, ε' decrease gradually with frequency upto 70 KHz and become constant for higher frequencies. Dielectric loss factor, ε'' variation with frequency for all the three composites is plotted in figure-2. ε" varied with frequency in the same fashion as that of ε'. Temperature variation of ε' for PTh-VO1 is shown in figure-3. In this figure, we see that ε' increases with temperature. Similar nature of variation of ε' with temperature has been observed for the remaining composites. The change in ε" with temperature for PTh-VO1 is shown in figure-4. Similar behaviour of ε" with temperature has been observed for the remaining composites.

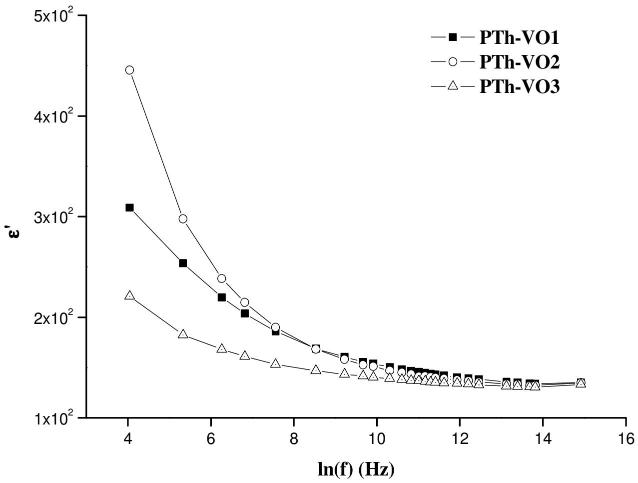

Figure-1
Dielectric constant, ε' versus ln(f) for PTh-VO nanocomposites at the temperature of 323K

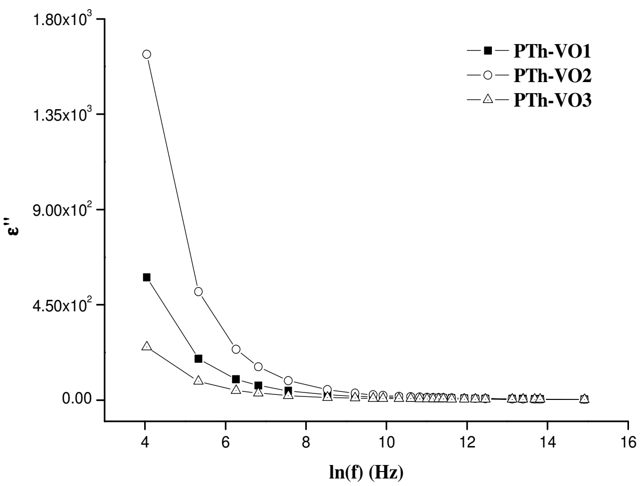

Figure-2
Dielectric loss, ε'' versus ln(f) for PTh-VO nanocomposites at the temperature of323K

Electrical Conductivity: Conductivity, σ, has been determined using dielectric data using the following equation [24].

$$\sigma_{ac} = \varepsilon'' \omega \varepsilon_o \quad (1)$$

Where: ε_o is free space permittivity which is equal to 8.85 x 10^{-12} Fm^{-1}. Conductivity variation with temperature for different frequencies for the composite PTh-VO2 is shown in figure-5.

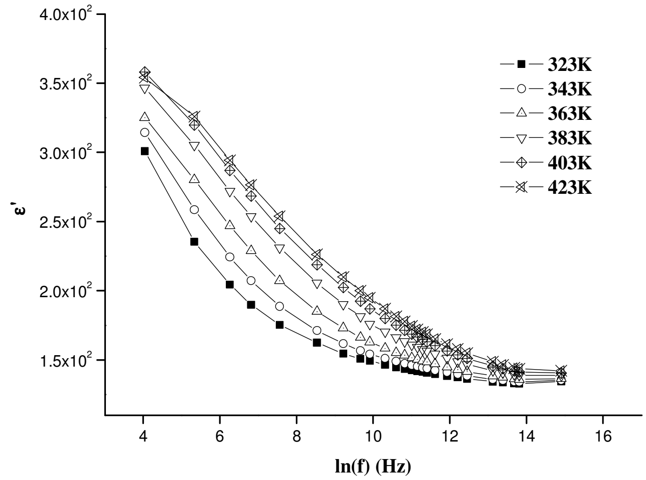

Figure-3
Dielectric constant, ε' versus ln(f) for PTh-VO1 nanocomposites for different Temperatures

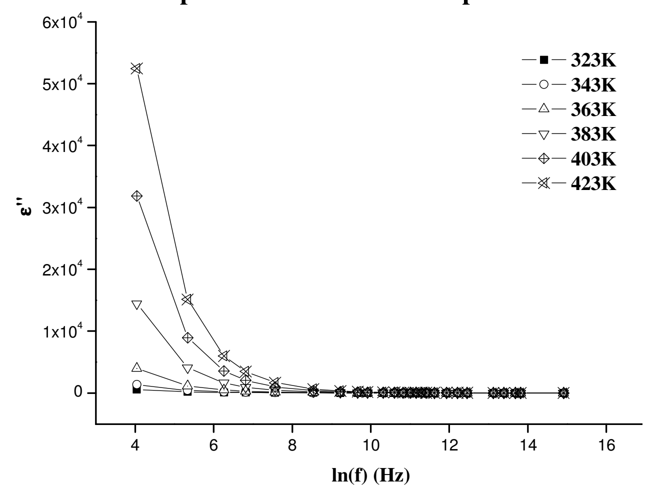

Figure-4
Dielectric loss, ε'' versus ln(f) for PTh-VO1 nanocomposites for different temperatures

It can be seen in figure-5 that conductivity increases with increasing temperature indicating semiconducting type of behaviour. It also increased with increasing frequency. Similar results have been reported for polyaniline doped with silver nanoparticles, polyaniline doped with cobalt and polyaniline doped with nickel oxide[25-27]. All the present composites behaved in the same way. Variation of conductivity of all the present composites was found to be within the same order of magnitude i.e, 10^{-4} ($\Omega^{-1}m^{-1}$).

Conductivity variation with V_2O_5 content for two different frequencies at temperature of 403K is shown in figure-6. From figure-6 it is clear that conductivity decreased with increasing V_2O_5 content.

The conductivity data as a function of temperature has been fit to the Mott Small Polaron Hopping (SPH) theory. This theory gave the conductivity expression as[28],

$$\sigma = \frac{\sigma_0}{T}\exp\left\{-\frac{E_a}{K_B T}\right\} \quad (2)$$

Where E_a the activation energy for small polaron hopping.

The plots of ln(σT) versus (1/T) were made as per eqnuation-2 for the composite PTh-VO2 and shown in figure-7. The linear lines were fit to the data in the high temperature region where the data appeared linear. Activation energy, E_a for ac conductivity was calculated using the slopes of the fit linear lines.

Activation energy, E_a versus V_2O_5 content determined for the present composites for different frequencies are plotted in figure-8.

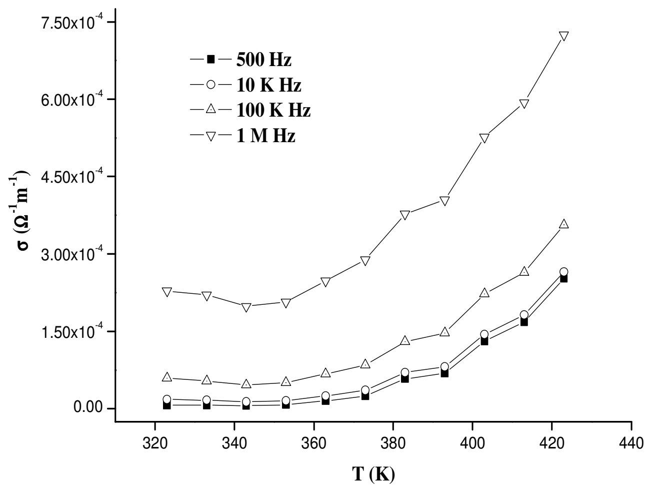

Figure-5
Temperature dependence of electrical conductivity of PTh-VO2 composite nanoparticles at different frequencies

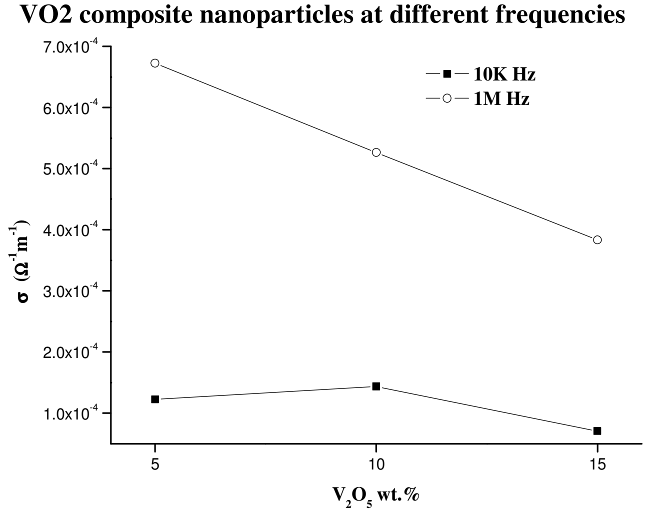

Figure-6
Conductivity versus wt % of V_2O_5 in PTh-VO nanocomposites for two different frequencies at T=403K

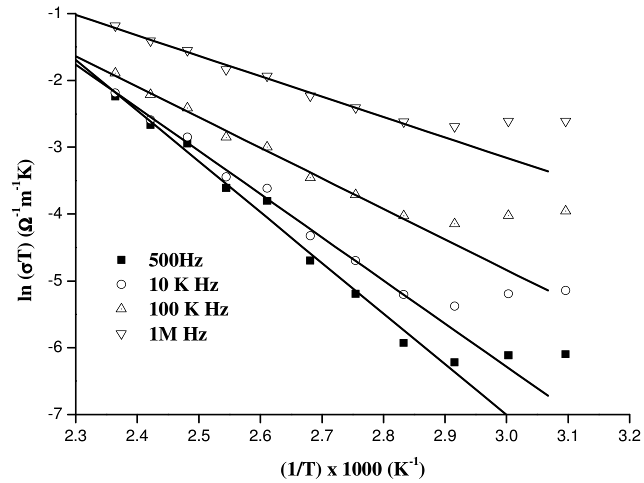

Figure-7
Plots of ln(σT) versus (1/T) for PTh-VO2 composite for four different frequencies. Solid lines are linear fits as per Mott's SPH model

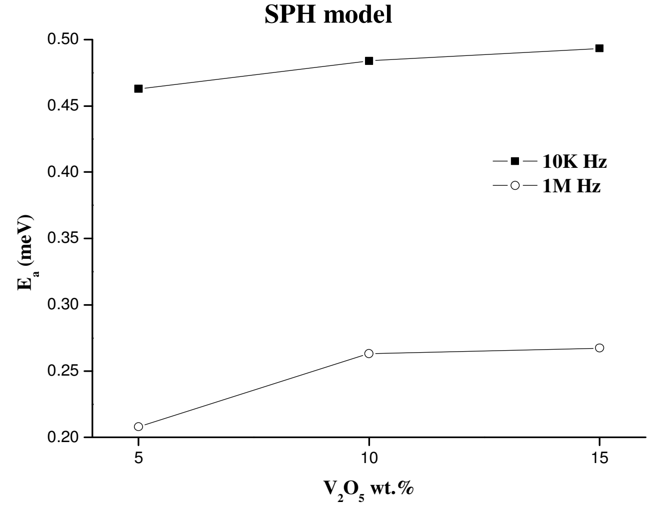

Figure-8
Activation energy versus wt. % of V_2O_5 for PTh-VO nanocomposites at two different frequencies

From the figure-8 one can note that E_a increases with increase of V_2O_5 content and decreased with increase of frequency. Increase in E_a with increase in V_2O_5 concentration may be that addition of V_2O_5 content to the PTh network contributes more to the scattering of polarons. Similar results have been reported for polyaniline doped with V_2O_5, polyanilinedoped with CeO_2 and polypyrrole doped with Ag[17,29,30].

Conclusion

Polythophene has been synthesised at 323K by chemical method. PTh-V_2O_5 composites were prepared by mixing Polythiophene and V_2O_5 in different weight percentages. The changes in dielectric properties with temperature and frequency were measured over broad ranges. Dielectric constant decreased with increase in frequency and increased with temperature. Dielectric loss decreased with increase in frequency and increased with temperature. Conductivity increased with increase of both temperature and frequency. By employing Mott's Small Polaron Hopping Model's conductivity expression, activation energy for ac conductivity has been obtained. Activation energy was found to be decreased with increase in frequency and increased with V_2O_5 content and it may be attributed to increase in the scattering rate of polarons with increase in V_2O_5 content.

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