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DC Conduction in Polythiophene Nanocomposites doped with V_2O_5

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Abstract

Polythiophene (PTh) has been prepared at 323K by an oxidation method using ferric chloride as an oxidizing agent. The Pth-VO composites were prepared by mechanical mixing of PTh and V_2O_5 in different wt%. PTh were confirmed to be amorphous in nature by XRD studies. XRD patterns of the composites indicate peaks corresponding to V_2O_5 structure. Using XRD peaks, grain sizes were estimated. They were found to be nanocrystalline. SEM image of pure V_2O_5 showed nano size grains and SEM images of PTh-VO composites exhibited nano size grains and some tubular structure. Temperature dependence of conductivity has been determined in the temperature range from 300K to 425K and found to be semiconducting type. Conductivity behaviour with temperature has been analyzed in view of Mott's small polaron and variable range hopping models. Activation energy, E_a for dc conduction was deduced and its value was found to be the fraction of an eV for all the samples. With increase in V_2O_5 content, E_a decreased and σ increased. Density of states of charge carriers at the Fermi level was determined.

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

Introduction

Conducting polymers are considered to be the most important semiconducting materials because of their fascinating chemical and physical properties useful for various applications[1]. Among the conducting polymers, polythiohene (PTh) and its derivatives have attracted much consideration because of their easy preparation, environmental stability, higher conductivity and photoconduction[2,3]. These materials can also be modified with different chemical groups to suit to specific applications by fast doping-undoping mechanism[4,5]. When PTh was combined with different inorganic materials such as metal nanoparticles, it produced nano-composites. Nano-composites exhibit unique physical, chemical and biological properties which in turn motivated to use these materials in several technological applications such as quantum electronic devices, magnetic recording, gas sensors etc[6,7]. Polythiophene is produced from the polymerization of thiophenes, a sulphur heterocycle, i.e. a linear chain of thiophene monomers that become conducting when electrons are added or removed from conjugated π-orbital[8-10]. There are several methods used for the synthesis of Polythiophene which include electrochemical and chemical method[11,12]. The process of synthesis and nature of the dopant anion play crucial role in the polymerization process and also they affect the properties.

V_2O_5 has been investigated by many authors due to its industrial importance to act as heterogeneous catalyst. V_2O_5 also plays the role of an active electrode in a rechargeable lithium battery[13]. The composites, PTh-V_2O_5 (2:1) and PTh-V_2O_5 (1:2) were prepared by chemical oxidative method and have been measured for electrical conductivity. Later composite gave conductivity an order of magnitude higher than the former[10]. PTh-TeO_2 and PTh–ZnO composites measured conductivity of the order of ~$10^{-4}\Omega/m$[7]. Polyaniline (PANI) and PANI- V_2O_5 composites exhibited electrical conductivity in the range from 2.48 x $10^{-11}\Omega/m$ to 3.58 x $10^{-8}\Omega/m$ and it increased with increase in V_2O_5 content[13]. Polypyyrole-V_2O_5 composites showed decrease in conductivity up to 10% of V_2O_5 and remained constant for higher concentrations of V_2O_5[14]. Here, we report our studies on synthesis of PTh and PTh-V_2O_5 composites and conductivity in the temperature range from 300 to 425K, as there are no reports on systematic study of electrical conductivity of Pth-V_2O_5 composites with variation in temperature and composition.

Methodology

PTh has been prepared using AR grade Thiophene, Ferric chloride, Methanol and Chloroform. Aqueous solution of thiophene was prepared and homogenised by constant magnetic stirring. Aqueous chloroform and ferric chloride solutions were added drop by drop to PTh solution. The mixture was continuously stirred for 24 hours and in that precipitate became brown which indicated the formation of Polythiophene[15, 16]. The powder was left for drying and then grinded. The synthesis was carried out at 323K. The PTh-V_2O_5 composites nanoparticles were prepared by mechanical mixing of prepared Polythiophene and adding analytical grade V_2O_5 in different weight percentages defined as $(PTh)_{100-x}$ $(V_2O_5)_x$, where x= 5%, 10%, 15%, 20% and 25% and are labelled as PTh-VO1, PTh-VO2, PTh-VO3, PTh-VO4 and PTh-VO5 respectively.

The structural information of the pure PTh and composites was obtained by subjecting the composite powders to the powder-XRD studies using X'Pert Pro X-Ray diffractrometer. Surface structure has been observed by collecting Scanning Electron Microscope (SEM) images.

The powders were pressed into pellets of appropriate size in a hydraulic press using a load of 5 tonnes. The pellets were annealed at 373K. DC conductivity has been experimentally measured for the temperature range from 300K to 425K making use of two point method in a high speed dc resistance bridge (Danbridge DB502). The bridge applies suitable amount of voltage V, across the pellet and measures the current, I, through it. The resistivity, ρ, has been determined using the expression,

$$\rho = \left(\frac{V}{I}\right)\left(\frac{A}{l}\right) \quad (1)$$

Where A is the surface area of the pellet and *l* is its thickness. On inputting A and l values DB502 itself calculated ρ. Using ρ the conductivity, σ=1/ρ was calculated. Temperature was measured using a Chromel-Alumel thermo- couple with accuracy of ± 1K. The errors on σ were estimated to be within 2%.

Results and Discussion

X-Ray diffraction studies: A typical XRD pattern obtained for pure PTH and the composite PTh-VO5 are shown in Figure-1 and Figure-2.

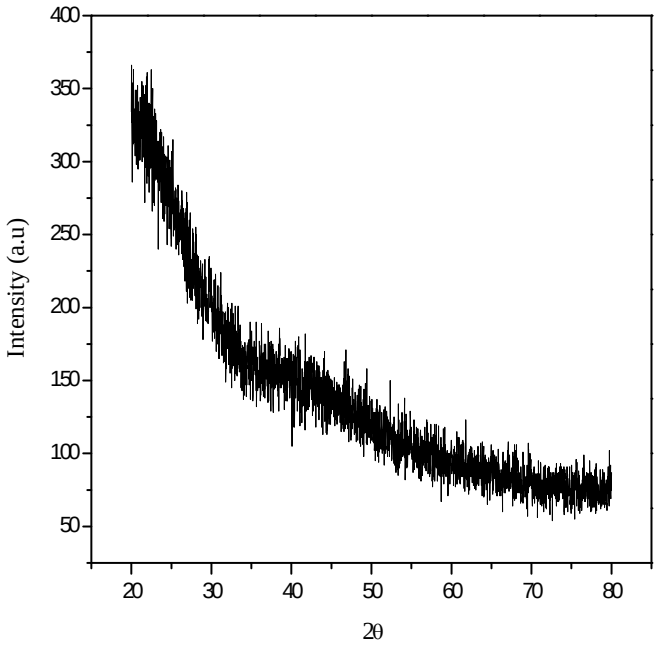


Figure-1
X-ray diffraction pattern of pure PTh

No sharp peaks can be observed in figure-1 which indicates amorphous nature of PTh. Similar XRD patterns was observed for PTh[15, 17]. The figure-2 reveals peaks at 2θ = 15.46, 20.38, 21.80, 26.21, 31.11, 32.46, 34.38, 41.31, 47.39, 51.27 and 55.69 corresponding to d = 5.72 Å, 4.35 Å, 4.07 Å, 3.39 Å, 2.87 Å, 2.75 Å, 2.60 Å, 2.18 Å, 1.91 Å, 1.78 Å and 1.64 Å respectively.

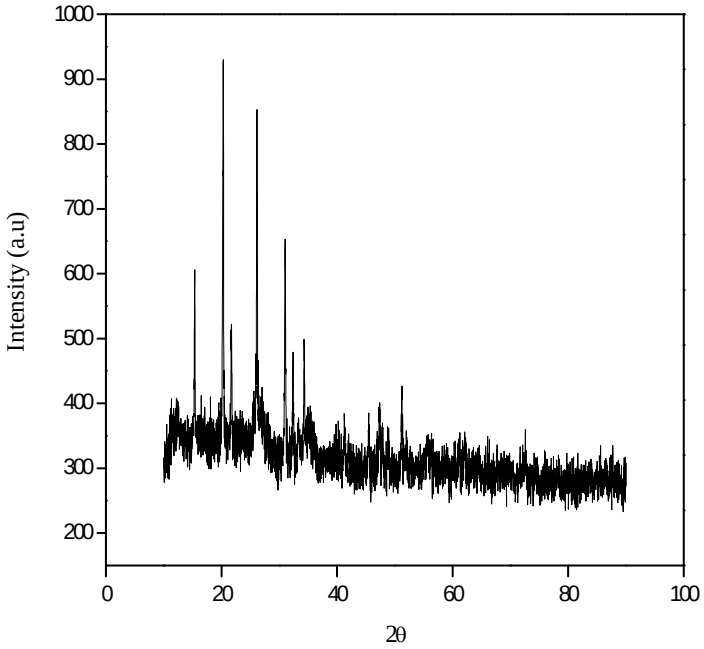
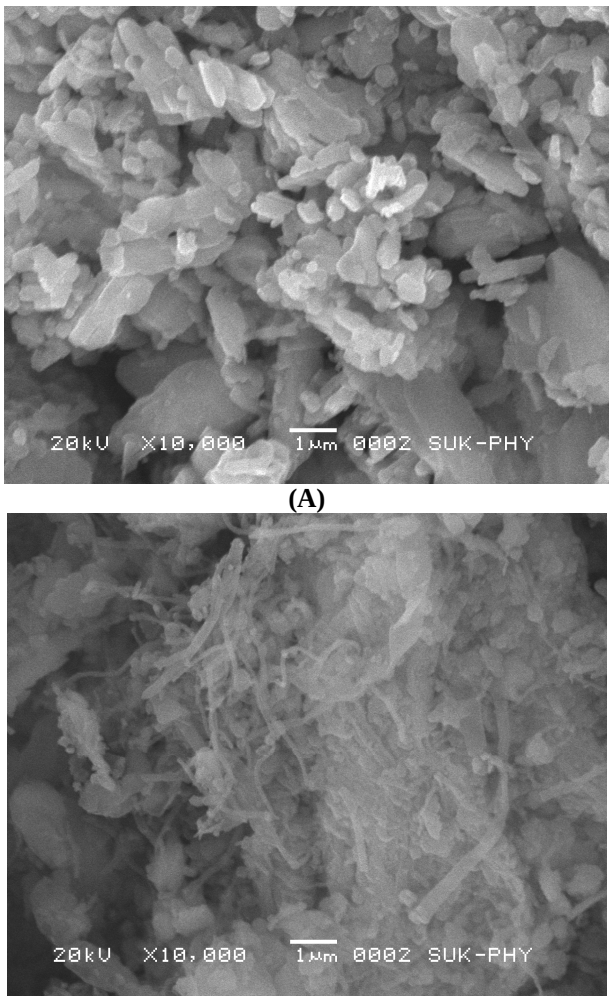


Figure-2
X-ray diffraction pattern of PTh-VO5 composites

Presently observed peak positions are comparable with those observed for pure V_2O_5[18-20]. Using peak widths and by following Scherer equation[21], the grain sizes were determined to be 72.13nm, 55.56nm, 60.33nm, 60.92nm, 42.29nm, 46.29nm, 53.82nm, 72.81nm, 94.16nm, 117.8nm and 89.00nm, respectively

SEM studies: The SEM images of the pure V_2O_5 and PTh-VO1 composites are shown in figures-3 (a) and (b). Agglomerated particles with micropores in between can be observed in Figure-3(a). In Figure-3(b), tubular structure along with grains can be observed. Here, grains may be due to V_2O_5 and tubular structure may be due to PTh in the composites. It may be noted that tubular structure of pure PTh has been reported to be the feature of the PTh particles synthesised at temperature 323K[16]. The average size of grains of pure V_2O_5 determined from Figure-3 (a) is 85nm, which is in the range of sizes obtained from XRD patterns. Average grain size of the grains determined from Figure-3(b) is 70nm. The average grain sizes determined for PTh-VO2, PTh-VO3, PTh-VO4 and PTh-VO5 are 63nm, 71nm, 83nm and 81nm respectively. These grain sizes indicate nanocrystalline nature of the PTh-VO composites.



(A)

(B)

Figure-3
SEM images of (a) pure V_2O_5 (b) composite PTh-VO1

Conductivity studies: Conductivity variation with temperature for the composite PTh-VO1 is shown in Figure-4. Conductivity increased with increasing temperature indicating semiconducting nature. Remaining composites of the present series behaved in the same way and, this result is in agreement with that reported for other similar systems[20, 22].

The measured room temperature conductivity for PTh-VO1, PTh-VO2, PTh-VO3, PTh-VO4 and PTh-VO5 composites are 8.147×10^{-7} $(\Omega m)^{-1}$, 6.555×10^{-7} $(\Omega m)^{-1}$, 7.262×10^{-7} $(\Omega m)^{-1}$, 9.779×10^{-7} $(\Omega m)^{-1}$ and 7.98×10^{-7} $(\Omega m)^{-1}$ respectively. These values are two orders of magnitude smaller than the reported values for pure PTh[16]. This implies that conductivity decreased with the incorporation of V_2O_5 in PTh. The decrease in conductivity with increase in V_2O_5 concentration up to 10% has been observed in Ppy – V_2O_5 composites[14]. However, increase in conductivity with V_2O_5 content has been observed in PANI-V_2O_5 composites[13]. The conducting data with temperature has been fit to Mott small polaron model derived equation.

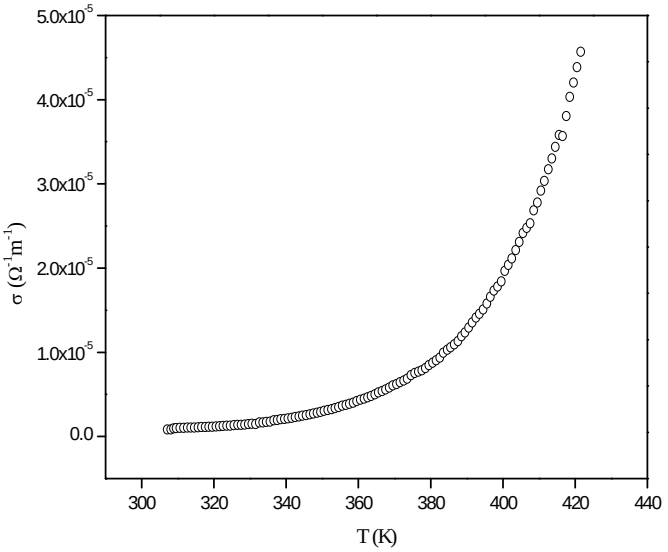


Figure-4
Temperature dependence of electrical conductivity of composite, PTh-VO1

According to this model, the conductivity in the non-adiabatic region is given by[23-24].

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

Where, E_a is the activation energy for small polaron hopping and σ_0 the pre-exponential factor.

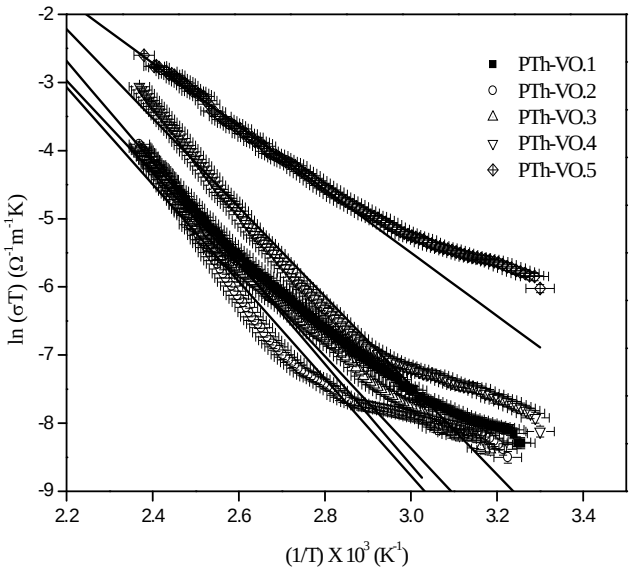


Figure-5
Plots of ln(σT) versus (1/T) for PTh-V_2O_5 composites. Solid lines are linear fits as per Mott's Eqn.(1)

The plots of ln(σT) versus (1/T) were made as per Equation (2) for all the composites and shown in Figure-5. Least square

linear lines were fit to the data in the high temperature region where the data appeared linear and slopes were extracted. Using slope of each line, activation energy, E_a of the corresponding sample has been estimated.

Variation of activation energy E_a, and conductivity at 400K as a function of wt% of V_2O_5 are plotted in figure-6. From the figure, it can be noted that E_a decreased and conductivity increased with increase of wt% of V_2O_5 content. In PANI-V_2O_5 composites, the conductivity increased with increase in V_2O_5 concentrations up to 40% [13].

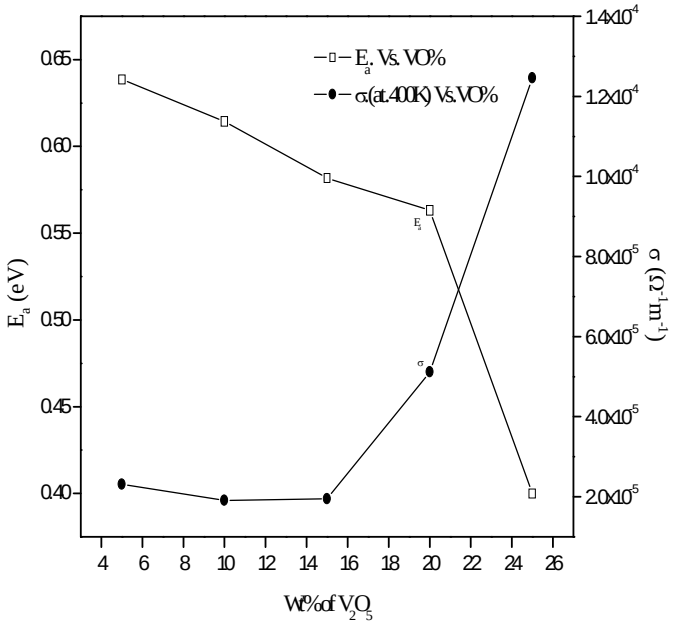


Figure-6
Variation of E_a and σ at 400K as a function of weight % of V_2O_5 in PTh-VO composites

Increase in conductivity with increase in V_2O_5 content may be due to the fact that conduction process is made relatively easy by the presence of V_2O_5 grains in between PTh tubes or grains. Decrease in E_a with increase in V_2O_5 concentration may be ascribed to the decrease in scattering rate of polarons with increase in V_2O_5 content. PANI and PANI- V_2O_5 composites conductivity increased with doping when compared to undoped sample[13].

The conductivity data deviated from SPH model was considered under Mott's 3D Varible Range Hopping (VRH) model. According to this model conductivity is given by

$$\sigma = A\exp\left\{-BT^{-\frac{1}{4}}\right\} \quad (3)$$

Where $A = 4\left[\frac{2\alpha^3}{9\pi k_B N(E_F)}\right]^{\frac{1}{4}}$ and $B = \left[\frac{e^2}{2(8\pi)^{\frac{1}{2}}}\right]\nu_0\left[\frac{N(E_F)}{\alpha k_B T}\right]^{\frac{1}{2}}$

Here, $N(E_F)$ refers to density of states of the carriers at the Fermi level, υ_o the phonon frequency (=10^{13} H_Z) and α= 1.2 Å (size of the monomer unit)[25]. Mott's VRH model has also been used previously for understanding conductivity behaviour of pure polypyrrole and Polythiophene[26,27]. The plots of ln(σ) versus ($T^{-1/4}$) made as per this model are shown in Figure- 7.

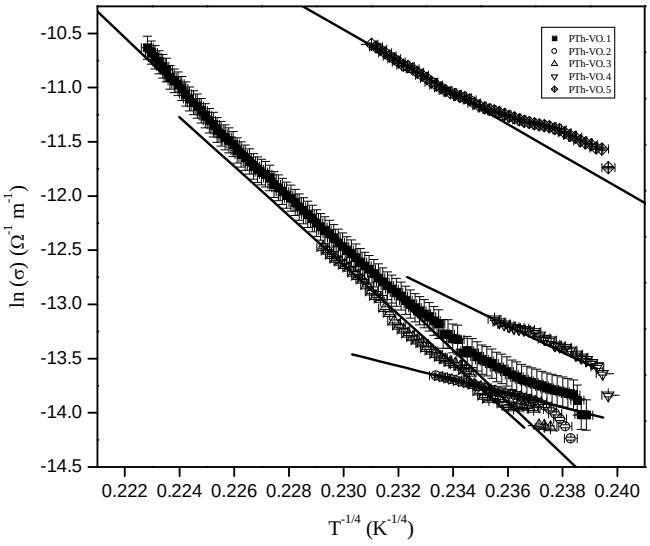


Figure-7
Plots of ln(σ) versus ($1/T^{-1/4}$) for PTh-VO composites. Solid lines are linear fits as per Mott's VRH Eqn.(3)

The linear lines were fit through the data. For each of the composite, only some range of data appeared to be in agreement with the model fit. The deviations of data from the VRH model fit below certain range of temperature have been reported previously in respect of other systems[16, 27-28].

Density of states of charge carriers at Fermi level, $N(E_F)$, of PTh-VO composites have been determined using slopes and are tabulated in table-1. $N(E_F)$ values are found to be in the range from 10^{28} $eV^{-1}m^{-3}$ to 10^{30} $eV^{-1}m^{-3}$. These $N(E_F)$ values high as, the values reported for PPY-Ag composites[18] were in the range from 10^{28} $eV^{-1}m^{-3}$ to 10^{30} $eV^{-1}m^{-3}$.

Table-1
Density of states at Fermi level $N(E_F)$, for PTh-VO composites

Systems	PTh-VO1	PTh-VO2	PTh-VO3	PTh-VO4	PTh-VO5
$N(E_F)$ (eV^{-1} m^{-3})	6.24 x 10^{28}	1.086 x 10^{30}	8.484 x 10^{28}	3.566 x 10^{30}	76.090x 10^{28}

Conclusion

i. Polythophene has been synthesised at 323K by chemical route. ii. Nanoparticles of Polythiophene-V_2O_5 (PTh-VO) composites were prepared by mechanical mixing of Polythiophene and V_2O_5 in different weight percentages. iii. The amorphous nature of PTh has been confirmed by XRD. XRD patterns of the composites exhibited peaks corresponding to V_2O_5. iv. SEM image of pure V_2O_5 showed nano size grains. Whereas SEM images of PTh-VO composites exhibited nano size grains and some tubular structure. v. Temperature variation of conductivity, σ, has been measured and found it to be semiconducting type. The temperature dependence of electrical conductivity has been analyzed using Mott's SPH and 3D VRH models. Activation energy, E_a, for conduction were determined. With increase in V_2O_5 content, E_a decreased and σ increased. vi. The density of states of charge carriers at Fermi level was determined.

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