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Conductivity Studies on Polythiophene-CoO Nano-Composites

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ABSTRACT

Polythiophene (PTh) was prepared at 323K by oxidation method using ferric chloride as an oxidizing agent. PTh-CoO composites were prepared by mixing PTh and CoO in different amounts. XRD studies on these composites revealed peaks corresponding to CoO structure. Using these peaks, grain sizes were estimated and they were found to be of few nanometers. SEM image of pure CoO showed nano size grains. Whereas, SEM images of PTh-CO composites exhibited nano size grains and some tubular structure. DC conductivity has been measured in the temperature range from 300K to 425K. Conductivity has been analyzed using polaron hopping models and activation energy was determined. Activation energy was found to be the fraction of a meV for all the composites. With increase in CoO content, E_a decreased. Densities of states of charge carriers at Fermi level were determined.

1. Introduction

Conducting polymers are important materials due to their unique properties which are useful for various applications. Among these organic materials, polythiohene (PTh) and its derivatives have attracted much attention as they can be easily prepared and have good stability, and show higher conductivity [1-5]. The conductivity of these materials can be tuned by doping.

Dopant anion plays important role in polymerization [6-9]. PTh has been successfully combined with different metal nanoparticles and produced nanocomposites. Nanocomposites possess physical, chemical and biological properties which are very special can be used in making quantum electronic devices, magnetic recording materials, sensors, battereies etc [10-12]. Cobalt oxide has got scientific and technological importance [13-15]. Cobalt oxide is used as a super capacitor electrode [16]. The room temperature conductivity of PTh-Zno composites was found to be of the order of 10-4 Ωm^{-1} [11]. Hydrothermally made polyaniline–cobalt nanocomposites showed increasing trend in conductivity with increasing amounts of cobalt nanoparticles [17]. Polypyyrole-V_2O_5 composites showed decrease in conductivity upto 10% of V_2O_5 and remained constant for higher concentration of V_2O_5 [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} [19]. The room temperature conductivity values of polypyrrole-TeO_2 and PTh-TeO_2 composites are reported to be 1 x 10-5 Ωcm^{-1} and 2 x 10^{-2} Ωcm^{-1} respectively [20]. In these composites, conductivity has been observed to have increased by 103 orders of magnitude compared to their pure PPy and PTh .The composites, 2PTh-V_2O_5 and PTh-2V_2O_5 which were made by chemical oxidative method were studied for electrical conductivity. Later composite gave conductivity an order of magnitude higher than the former [21]. Here, we report our conductivity studies on PTh-CoO composites in the temperature range from 300 to 425K.

2. Experimental Methods

Analytical grade thiophene, ferric chloride, methanol and chloroform were used as starting materials in the preparation of PTh. Aqueous solution of thiophene was prepared and stirred. Aqueous chloroform and ferric chloride solution were added drop wise to the homogeneous PTh solution. The mixture was magnetic stirred for 24 hours and the black precipitates became brown indicating the formation of Polythiophene [20, 22]. The powder was dried and grinded. The synthesis was carried out at 323K. The PTh-CoO composites nanoparticles were prepared by mechanical mixing of prepared polythiophene and adding analytical grade CoO in different amounts defined as $(PTh)_{100-x}$ $(CoO)_x$, where x= 5%, 10%, 15%, 20% and 25% and are labelled as PTh-CO1, PTh-CO2, PTh-CO3, PTh-CO4 and PTh-CO5 respectively.

Samples they were subjected to XRD studies using X'Pert Pro X-Ray diffractrometer. To observe surface structure, the SEM images were recorded using JEOL- JSM-6360 Scanning Electron Microscope.

The compressed pellets of the composites were made under hydraulic pressure of 5 ton load. The pellets were annealed at 373K. Electrical conductivity has been measured in the temperature range from 300K to 425K in a Danbridge resistance Bridge (DB 502). The bridge applies suitable amount of voltage V, across the pellet and measures current, I, through it. The resistivity, ρ, has been determined using the expression,

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

Where A is surface area and l the thickness of the pellet. On inputting A and l values DB502 itself calculated ρ. Conductivity, σ=1/ρ was calculated. Chromel-Alumel thermo-couple was used to measure temperature with accuracy of ± 1K. The errors on σ were estimated to be within 2%.

3. Results and Discussion

3.1 X-Ray Diffraction

A typical XRD pattern obtained for pure PTh and PTh-CO5 composite are shown in Figs. 1 and 2.

No sharp peaks can be observed in Fig. 1 which indicate amorphous nature of PTh. XRD patterns reported for PTh made by others also revealed amorphous nature [20, 23].

The (Fig. 2) reveals peaks at 2θ = 18.98, 31.26, 36.84, 44.80, 59.36 and 65.22 corresponding to d = 4.67 Å, 2.85 Å, 2.43 Å, 2.02 Å, 1.55 Å and 1.42 Å respectively.

These observed peak positions are comparable with those observed for pure cobalt oxide nanoparticles [24, 25]. Using peak widths and by following Scherer equation [26], the grain sizes were determined as 27.06

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nm, 10.21 nm, 18.58 nm, 13.47 nm, 19.39 nm and 22.19 nm, for PTh-CO1, PTh-CO2, PTh-CO3, PTh-CO4 and PTh-CO5 respectively.

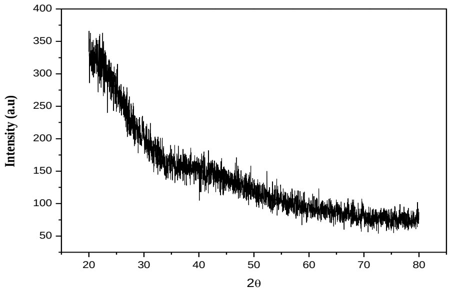


Fig. 1 X-ray diffraction pattern of pure PTh.

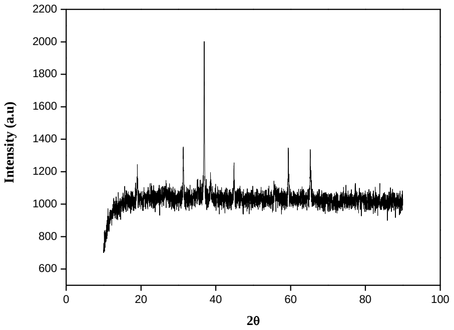
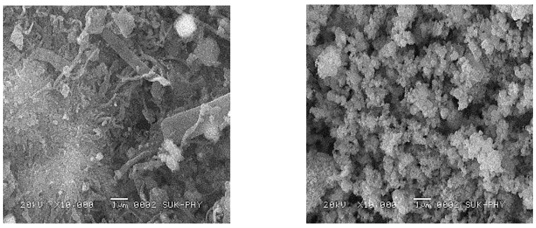


Fig. 2 X-ray diffraction pattern of and PTh-CO5 composites.

3.2 SEM

The SEM images of pure CoO and PTh-CO1 composite are shown in Figs. 3(a) and 3(b) respectively. Fig. 3(a) shows nanoparticles agglomerated with micropores in between. In Fig 3(b), tubular structures along with grains can be observed. Here, grains may be due to CoO 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 synthesised at temperatures above 323K [22], and no such features were observed in [20]. The average sizes of pure CoO in SEM image shown in Fig. 3(a) is determined to be 24nm which is in the range of sizes obtained from XRD patterns. Average grain size determined on SEM images shown in Fig. 3(b) are 48nm. The average grain sizes determined for PTh-CO2, PTh-CO3, PTh-CO4 and PTh-CO5 are 72 nm, 63 nm, 50 nm and 59 nm respectively.



(a) (b)

Fig. 3 SEM images of (a) pure CoO (b) PTh-CO1 composite

3.3 Conductivity

Conductivity versus temperature plot for all the PTh-CO composites is shown in Fig. 4. Conductivity increased with increasing temperature indicating semiconducting nature. All the present composites behaved in the same fashion. [26, 27]. Variation of conductivity with wt% of CoO has not followed any systematic trend.

The measured room temperature conductivites for PTh-CO1, PTh-CO2, PTh-CO3, PTh-CO4 and PTh-CO5 composites are 1.16 x10-7 Ωm^{-1}, 1.18 x10-7 Ωm^{-1},, 1.15 x10-7 Ωm^{-1},, 1.206 x10-7 Ωm^{-1} and 1.879 x10-7 Ωm^{-1}, respectively. These conductivities values are two orders of magnitude smaller than those measured for pure PTh [22]. This implies that conductivity decreased with the incorporation of CoO with PTh. The temperature variation of conductivity has been fit to conductivity expression derived by for small polaron hopping (SPH) in noncrystalline semiconducting solids. According to this model, the conductivity in the non-adiabatic region is given by [26, 28, 29],

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

Where σ_o is the pre exponential factor and E_a the activation energy for small polaron hopping.

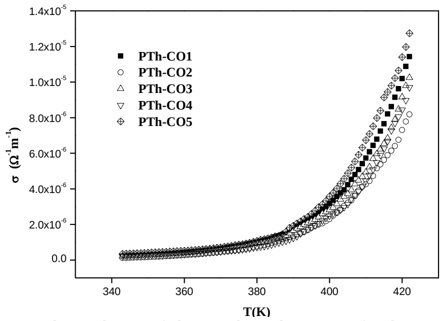


Fig. 4 Temperature dependence of electrical conductivity of PTh-CO composite.

The plots of ln(σT) versus (1/T) were made as per Eqn. (2) and shown in Fig. 5. The linear lines were fit to the data in the high temperature region where the data appeared linear. The slopes were used and activation energy, E_a Was calculated.

Variation of E_a as a function of wt% of V_2O_5 composites are plotted in Fig. 6. From the figure, it is clear that E_a decreased with increase of wt% of V_2O_5 content.

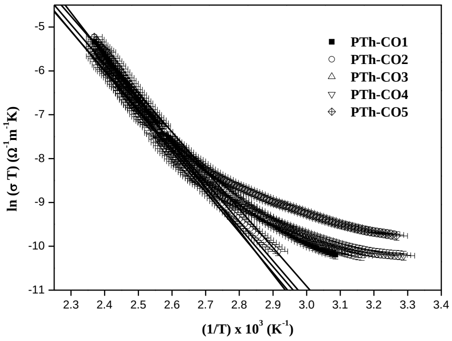


Fig. 5 Plots of ln(σT) versus (1/T) for PTh-CO composites. Solid lines are linear fits as per Mott's SPH model.

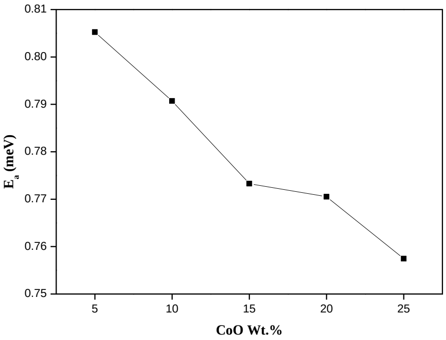


Fig. 6 Variation of E_a and σ at 400K as a function of weight % of V_2O_5 in PTh-VO composites.

Increase in conductivity with increase in CoO content may be due to the fact that conduction process become relatively easy by the presence of CoO grains in between PTh tubes or grains. Decrease in E_a with increase in CoO concentration may be attributed to the decrease in the scattering rate of polarons with increase of CoO content. Similar results have been reported for polyaniline doped with camphor sulphonic acid and blended with tetrameric cobalt phthalcocyanine and polyaniline-Co_3O_4 [13, 30].

The conductivity data deviated from SPH model line has been fit to Variable Range Hopping (VRH) model expression given by,

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

Where,

$$A = 4\left[\frac{2\alpha^3}{9\pi k_B N(E_F)}\right]^{\frac{1}{4}} \quad \text{and} \quad B = \left[\frac{e^2}{2(8\pi)^{\frac{1}{2}}}\right]v_0\left[\frac{N(E_F)}{\alpha k_B T}\right]^{\frac{1}{2}}$$

Here, N(EF) refers to density of states at Fermi level, υo is the phonon frequency (=1013 HZ) and α= 1.2 Å (size of the monomer unit) [31]. Mott's VRH model has also been used previously for understanding conductivity variation in polypyrrole and Polythiophene [23, 32]. The plots of ln(σ) versus (T-1/4) were made according to this model and shown in Fig. 7.

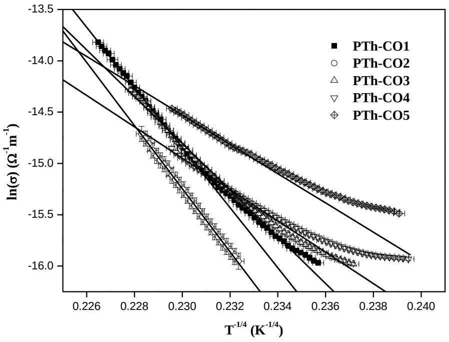


Fig. 7 Plots of ln(σ) versus (1/T-1/4) for PTh-CO composites. Solid lines are linear fits as per Mott's VRH model.

The linear lines were fit through the data. From the figure it can be noted that for each sample, still there is some data deviating from the fit line. Similar deviations of data from the VRH model fit have been reported previously also [22, 32-34].

Density of states at Fermi level N(E_F) of PTh-VO composites have been determined using the slopes and they are tabulated in Table.1. These N(E_F) values are in the range from 10^{28} eV^{-1} m^{-3} to 10^{30} eV^{-1} m^{-3}. These N(E_F) values appears to be high compared values reported for PPY-Ag composites [26].

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

Systems	PTh-CO1	PTh-CO2	PTh-CO3	PTh-CO4	PTh-CO5
N(E_F) (eV^{-1} m^{-3})	2.75 x 10^{28}	2.22 x 10^{28}	0.11 x 10^{30}	1.17x 10^{30}	1.87 x 10^{30}

4. Conclusion

Polythophene has been synthesised at 323K by chemical route. PTh-CoO composites were prepared by mechanical mixing of Polythiophene and CoO in different amounts. XRD patterns of the composites confirmed incorporation of CoO with PTh. SEM images of PTh-CO composites exhibited nano size grains and tubular structures. Changes in conductivity, with temperature revealed semiconducting nature. Activation energy for conduction has been determined by analysing data and using small polaron hopping model. E_a decreased with increase in CoO. The density of states of charge carriers at Fermi level were determined.

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