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Electrical Transport Studies in PPy/SnO_2 Composites

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Abstract: *A set of conducting polymer composites, PPy-SnO_2 were prepared by chemical oxidative polymerization technique using an anhydrous ferric chloride (Fecl$_3$) as an oxidizing agent. The effect of temperature on DC conductivity of the samples has been measured. Conductivity was found to be in the order of 10^{-3} to 10^{-4} ($\Omega^{-1}m^{-1}$) and exhibited semiconducting behavior with respect to temperature. Data has been analyzed using Mott's Small polaron hopping and Variable range hopping models. And relevant results are reported. Activation energies for conduction 94and density of states at Fermi level were determined. Activation energy was found to be in the order of a meV. It is for the first time PPy-SnO_2 composites were investigated for temperature variation of conductivity and conduction mechanisms probed thoroughly.*

Keywords: *Polymers, Tin oxide, Polypyrrole, Conductivity.*

1. Introduction

Tin oxide (SnO_2) has become the important functional material due to its large band gap and excellent optical and electrical properties. It can be used as transparent electrode in thin-film solar cells, liquid crystal displays, smart windows and anodes for lithium batteries [1–8].

Manjunath et al. [9] have synthesized conducting SnO_2/polyaniline (PANI) composites by chemical deposition technique and found that the AC conductivity and dielectric properties depend strongly on the wt% of SnO_2 in polyaniline. Shao et al. [10] have successfully synthesized SnO_2-based composite coaxial nanocables with multiwalled carbon nanotube and PPy via a simple one-pot chemical route. These nanostructures measured high conductivity, and effectively suppressed mechanical stress and prevent aggregation of SnO_2 nanoparticles, leading to the improvement in the electrochemical utilization and cycling stability of SnO_2 during Li-storage reaction.

DC Conductivity increased with increase of fluence and conduction mechanism followed a one dimensional variable-range hopping model. AC conductivity also increased with increase of ion fluence and obeys correlated barrier-hopping model [11]. PPy is known to be capable of storing electrical charges. The stored electrical charges can be recovered upon demand and that is why PPy can be considered as a good candidate for super-capacitor application [12–15]. Han and Lu [16] reported the electrical conductivity of the graphite oxide/polypyrrole composites. The conductivity was found to be 7 S cm−1. Yuan and his group [17] reported synthesis and characterization of SnO_2/PPy composites for lithium-ion battery where, nanosize PPy particles were uniformly coated onto the surface of the SnO_2 powder. These composites demonstrated significant improved charge storing capacity and cycle durability compared to bare SnO_2 electrode. Significant modifications in synthesis for PPy/G composites were suggested through electrochemical polymerization of PPy with various dopants [18–20]. De and his co-workers [21] reported the effect of temperature on DC conductivity of the PPy/FeO_3 nanocomposites. Kalpana and co-workers [22], fabricated electrochemically the polypyrrole/activated carbon composite electrodes and studied as an active electrode material in electrochemical super-capacitors.

Increase in hardness and strength and exhaustment in electrical, optical and physical properties of the polymers have been reported [23–26]. Inview of this, an attempt has been made by the authors to study conductivity as a function of temperature in PPy-SnO_2 composites and the results of which are analysed and presented in this manuscript.

2. Experimental

Analytical grade Pyrrole, Tin oxide and ferric chloride were used and prepared Pyrrole. Pyrrole solution of 0.1M was prepared by dissolving 5ml of Pyrrole in 100 ml of double distilled water. This solution was taken in a beaker and placed in an ice tray mounted on magnetic stirrer. Pre-cooled 0.3M ferric chloride anhydrous (oxidizing agent) solution was added drop-wise to Pyrrole solution. The mixture was stirred continuously for 5 hours by maintaining temperature of the solution to be below 276K. The Greenish black precipitate was filtered and dried in a furnace maintained at 373K. The yield of the polypyrrole was 5g [27].

PPy-SnO_2 composites were prepared by mixing different weight percentages of SnO_2 with polypyrrole powder. The weight percentages of SnO_2 considered for making PPy-SnO_2 composites are 10%, 30%, 40% and 50%. The composites are labeled as PS1, PS2, PS3 and PS4 respectively. PPy-SnO_2 powder were made into pellets of 1 cm diameter and 3mm thickness in a hydraulic press. The silver paste was applied to the two large surfaces of pellets to act as electrodes.

3. Results and Discussion

The conductivity of PPy-SnO_2 composites were measured by two probe method in the temperature range from 300K to 423K. The variation of DC conductivity with temperature for composite PS1 is shown in Fig.1. The DC conductivity of pure PPy increased with doping of SnO_2 exhibiting semiconductor characteristics. Rest of the composites showed similar temperature behavior.

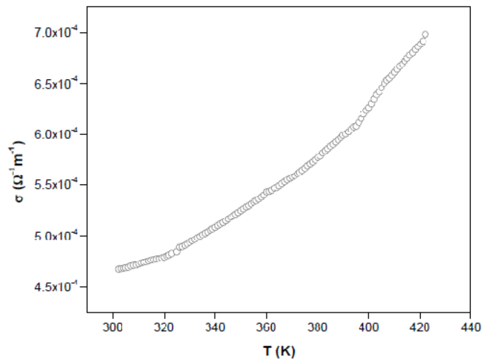

Fig1. *Temperature dependence of electrical conductivity, σ of PS1*

It is observed that at 422K the conductivity is increased from 0.698143 X 10^{-3} $\Omega^{-1}m^{-1}$ to 1.9791 X 10^{-3} $\Omega^{-1}m^{-1}$ as doping concentration of SnO_2 increased from 10 to 40 % as shown in Fig.2. This may be attributed to the doping of SnO_2 which maximizes the number of carriers. The highest number of carriers can be linked with the delocalization effect of doping process and formation of the polarons or bipolarons in the composite structure, thus enhancing the conductivity of composite [28-31]. At higher ($\geq$ 40 %) content of SnO_2, the conductivity decreases. This decrease in conductivity may be due to the accumulation of charge carrier [32]. When PPy is doped with SnO_2 the charge carriers form nonlinear configurations, consequently conductivity does not change substantially. The nonlinear formation may be more in the case of heavy doping of 50% of SnO_2 doping than 40% doping [33].

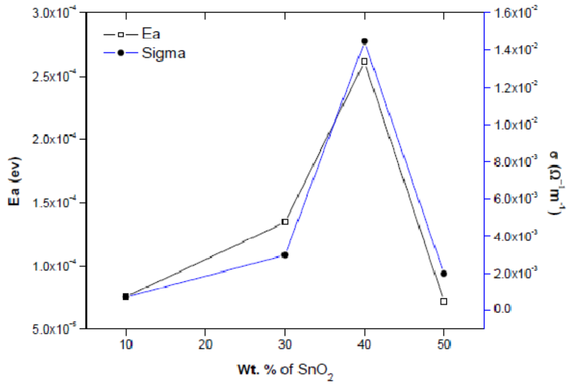

Fig2. *Conductivity at 422K versus SnO_2 contents in PPy/SnO_2 composites.*

The temperature variation of conductivity of the composites has been fit to conductivity expression due to Mott's Small polaron hopping (SPH) derived for noncrystalline semiconductors. As per our knowledge there is no good theory to understand conduction mechanism in polymers. That is why, here SPH model has been employed. According to this model, the conductivity in the non-adiabatic regime is given by [34, 35].

$$\sigma = \frac{\sigma_0}{T}\exp\left[-\frac{E_a}{K_B T}\right] \qquad (1)$$

Where, σ_0 is the pre exponential factor and E_a the activation energy for small polaron hopping. The plots of ln(σT) versus (1/T) were plotted as per Eqn. (1) for all the composites and shown in Fig. 3. 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 and they are tabulated in table 1.

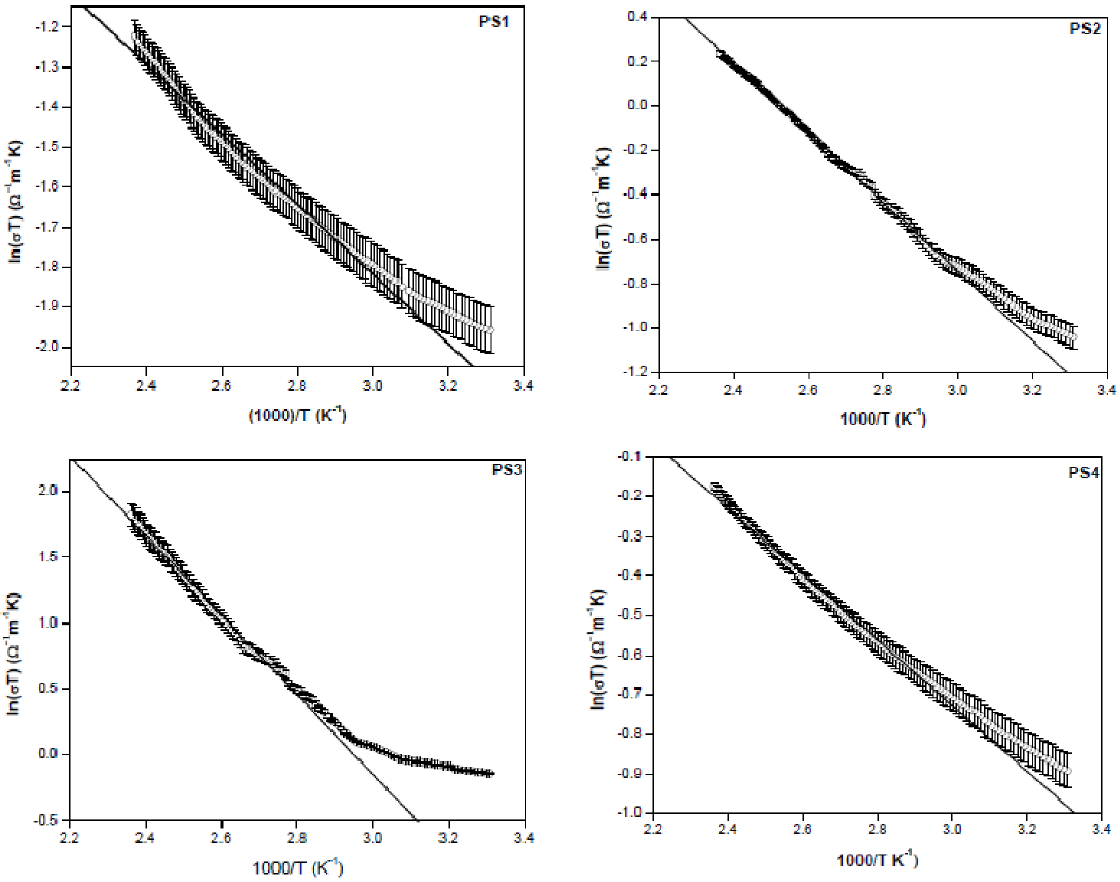

Fig3. *The plot of ln(σT) versus (1/T) as per SPH model of PS1, PS2, PS3 and PS4.*
Solid line is the linear line fit through data in high temperature region

It can be noted that E_a increases with weight % of SnO$_2$ up to 40% of SnO$_2$ thereafter decreases for higher content as shown in Fig 2. It is interesting to note that measured conductivity of all the four composites is greater than that reported for pure PPy nanoparticles [36].

Table1. *Activation energy, E_a, of PPy-SnO$_2$ composites.*

Systems	PS1-10%	PS2-30%	PS3-40%	PS4-50%
E_a (m eV)	0.075	0.134	0.261	0.071

The data deviated from SPH model has been fit to Mott's 3D VRH model. According to this model, the conductivity is given by

$$\sigma = A\exp\left\{-BT^{-\frac{1}{4}}\right\} \qquad (2)$$

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

Where, N(E_F) stands for density of states at Fermi level, v_0 the phonon frequency(=10^{13}H$_Z$) and $\alpha \approx 1.2$Å (Size of the monomer unit) [37, 38]. Mott's VRH has been used for analysing low temperature conductivity of polypyrrole and polythiophene [39]. The plots of ln(σ) versus ($T^{-1/4}$) were made according to this model for the present samples and shown in Fig. 4. The linear lines were fit through the data.

Density of states, $N(E_F)$ were determined using slope and recorded in Table 2. The $N(E_F)$ obtained are of the order of 10^{31} $eV^{-1}m^{-3}$ to 10^{34} $eV^{-1}m^{-3}$. These values of $N(E_F)$ are much more than that reported for elemental semiconductors and polymers [40]. We therefore conclude that though Mott's (VRH) model fit appeared to be good but the $N(E_F)$ values obtained are far off from the expected values and hence this model cannot be considered to be unsuitable for explaining the present data.

Table2. *Density of states at Fermi level, $N(E_F)$ for PPy-SnO_2 Composites*

Sample	PS1-10%	PS2-30%	PS3-40%	PS4-50%
$N(E_F)$ (eV^{-1} m^{-3})	4.92 X 10^{34}	1.51 X 10^{33}	4.21 X 10^{31}	1.74 X 10^{34}

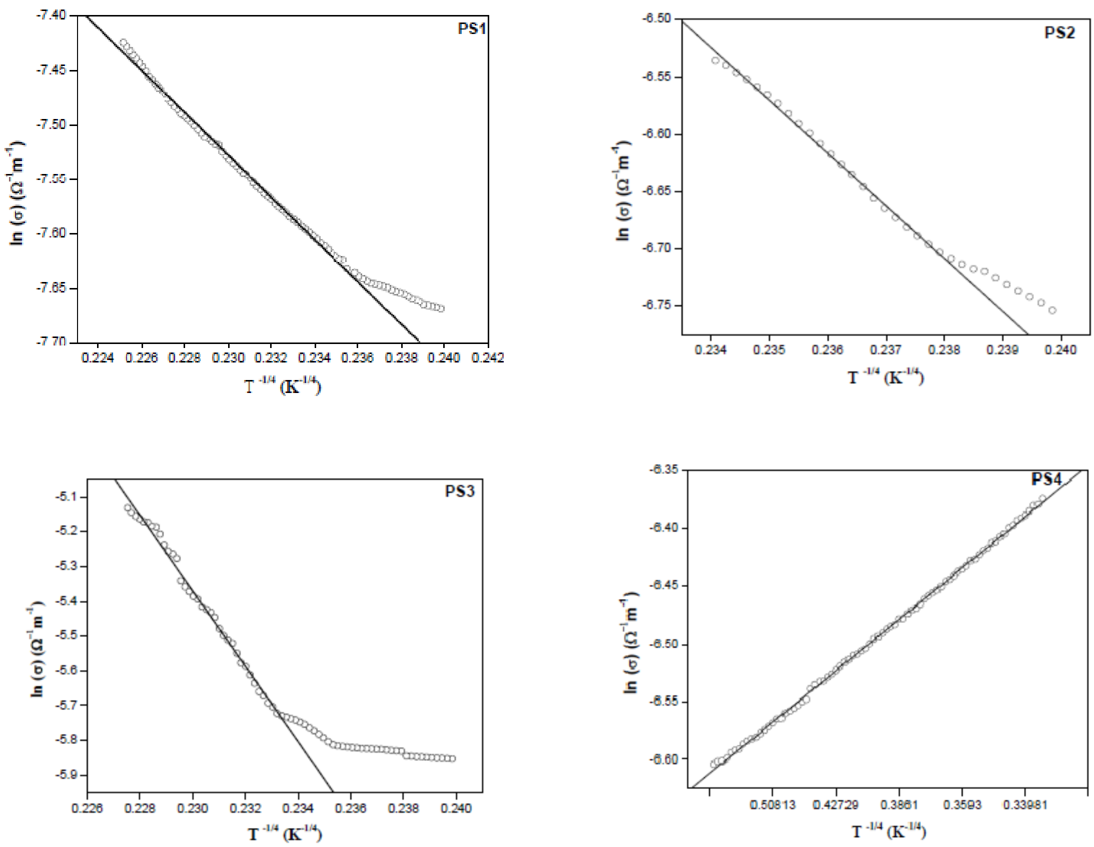

Fig4. *The plot of ln(σ) vs.($1/T^{1/4}$) for PPy-SnO_2 composites. Solid lines are the linear fits to the data.*

4. Conclusions

The PPy-SnO_2 Composites containing different weight percentage of SnO_2 have been synthesized by chemical oxidation method. Temperature variation of dc conductivity has been investigated and it revealed their semiconducting nature. Conductivity data was analyzed using Mott's polaron hopping models. Activation energy for conduction and density of states of carriers at Fermi level has been determined. It is confirmed that the charge transport in these systems is due to small polaron hopping at higher temperature and variable range hopping at lower temperatures.

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