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Study on DC Conductivity of PPy-ZnO Nanocomposites

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Abstract

In the present work, the nanocomposites of PPy-ZnO were prepared by chemical oxidative polymerization technique using an anhydrous ferric chloride (FeCl_3) as an oxidizing agent. The prepared samples were characterized via XRD and SEM (Scanning electron microscope) to determine the crystal size and porosity, respectively. Using, screen printing technique, thick films of the samples were fabricated. At room temperature and stepwise increasing temperature, dc conductivity of the samples had been measured and it was found that sample PZ2 has smallest average crystalline size 99.40 nm.

DC conductivity measurement showed nearly linear variation of $\ln(i)$ versus $\ln(V)$, exhibiting ohm's law being obeyed on logarithmic scale. Maximum value of current density, $1.261 \times 10^{-5} \text{ A/m}^2$ for PZ2 (70% PPy + 30%ZnO) sample was obtained from schottky plot, at 400 K. Thus PZ2 sample is best among the prepared samples and its activation energy recorded to be 0.1106 eV.

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1.0 Introduction

Now a day, conducting polymers are class of polymer that possesses high-quality tuneable electrical conductivity. But they are chemically sensitive and have poor mechanical property; on the other hand, nanomaterials exhibit good mechanical properties. Thus, because of good mechanical orientation, oxides nanoparticles showed best utility thereof. Such properties of nanocomposites are strongly dependence of polymer concentration. Separation of nanoparticles in polymer matrix has large effect on the polymers properties [1]. As PPy has good electrical conductivity and good ion-exchange capacity, it is most studied conducting polymer. PPy can be prepared in different forms such as powder, films, colloidal particles and composites in micro and nano sizes [2-5]. Nanoparticles of PPy are prepared by various path such as chemical or electrochemical [6] with organic or inorganic metals. Low conducting polymers have many applications in the fabrication of insulators and dielectrics [7-8].

The present study deals with the synthesis, characterization of Zn/PPy composites and evaluation of dc electrical conductivity for different weight percentages.

2.0 Experimental

2.1 Synthesis of ZnO Nanoparticles

In the present work, chemicals used are of GR grade with purity 99.99%. Zinc acetate dehydrate $Zn(O_2CCH_3)_2(H_2O)_2$, sodium hydroxide, Methanol and de-ionized water was used during reaction. For the preparation, Zinc Oxide (ZnO) 0.2M Zinc Acetate dehydrates dissolved in 100 ml de-ionized water was kept for 15 min and then added with NaOH (0.02 M) solution. After the mixing the solution was kept under constant magnetic stirring for 15 min. and then again it was grinded for 30 min. The white precipitate produced was allowed to wash with de-ionized water and methanol many times so as to remove by-products. Watt-man filter paper was used to filter the product. The obtained white paste was kept in vacuum oven for 4 h at 80°C. Then this dry product was crushed into a fine powder by using grinding machine and finally this fine nano-powder of ZnO was calcinated at temperature 800°C for 6 h.

2.2 Synthesis of Polypyrole (PPy)

Iron (III) chloride ($FeCl_3$), methanol and Py monomer were taken in pure forms for synthesis of PPy sample [10]. 1.892 g $FeCl_3$ was taken in fine power form and it was mixed with 7 ml methanol solution in round bottom flask. Then 8.4 ml Py monomer was introduced to ($FeCl_3$ +methanol) solution with constant vigorous stirring in dark. The amount of Py monomer introduced to the solution (1/2.33 times of $FeCl_3$) was in such a way to get peak yield. The resulting black precipitates were filtered and cleaned with copious amount of distilled water until the washings are clean and clear. The obtained PPy was powdered by putting in oven at 600°C for 3 h.

2.3 Preparation of Pellets

Initially, for the preparation of pellets the synthesised material ZnO, and PPy were mixed with different weight percentage in pure and composite forms (Table 1). The pellets of different series of ZnO-PPy nano-powder were prepared by using electrically operated automatic press machine (KBr Press) at load of 5 tons / cm^2 for 0.5 h. All the pellets were heated at 150°C for 0.5 h. These pellets were polished and then electrodes were formed with the help of conductive silver paint on their edges. Again pellets were sintered for the drying the silver paint at 100°C for half an hour.

3.0 Results and Discussion

3.1 X-Ray Diffraction

XRD pattern of polypyrrole (PPy) and its composites are as shown in Fig. 1 and Fig. 2 respectively. XRD pattern of PPy manifested amorphous nature of PPy. At 27° broad peak occurred which is the characteristics of amorphous nature of polypyrrole. Broad peak resulted by scattering of X-Rays from polymer chains at the interplaner spacing. The maximum intensity position of amorphous also depends on monomer to oxidant ratio [9].

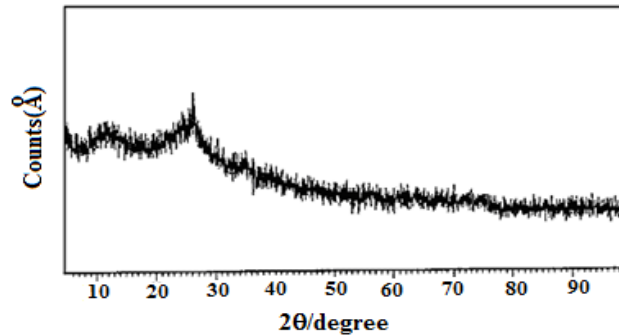


Fig. 1: XRD pattern of PPy

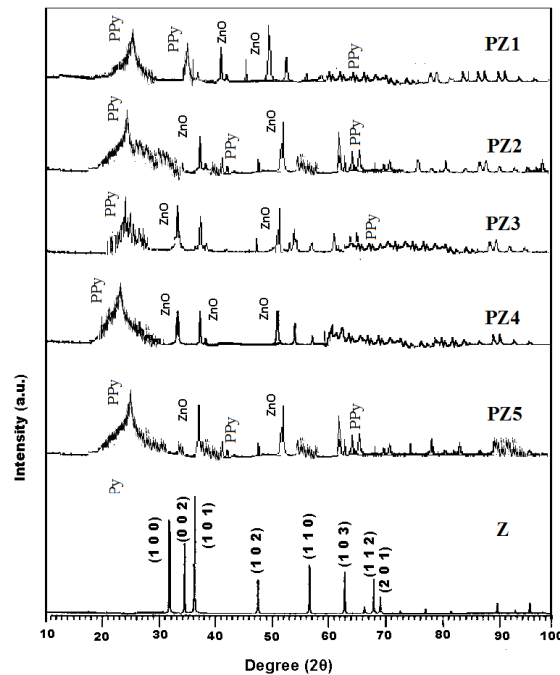


Fig. 2: XRD of PPy and ZnO composites

Table 1: Sample Codes

Sr. No.	Pure Sample and composites	Codes
1	Pure Polypyrrole	P
2	80 % ppy + 20 % ZnO	PZ1
3	70 % ppy + 30 % ZnO	PZ2
4	60 % ppy + 40 % ZnO	PZ3
5	50 % ppy + 50 % ZnO	PZ4
6	40 % ppy + 60 % ZnO	PZ5
7	Pure ZnO	Z

From XRD pattern of composites, it is observed that average crystallite size of 70PPy:30ZnO composition is least (99.40 nm) as compared to other compositions and pure PPy and hence 70PPy:30ZnO composition (PZ2) has large active area which tends to increase the conductivity of PZ2 sample.

3.2 SEM Analysis

The surface morphology of polypyrrole and composites of PPy and ZnO materials were studied by SEM and its pictures are shown in Figs. 3-9.

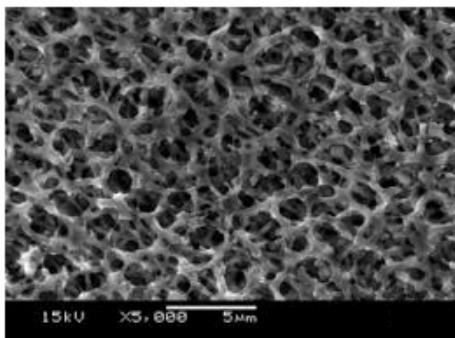


Fig. 3: SEM of P (pure PPy)

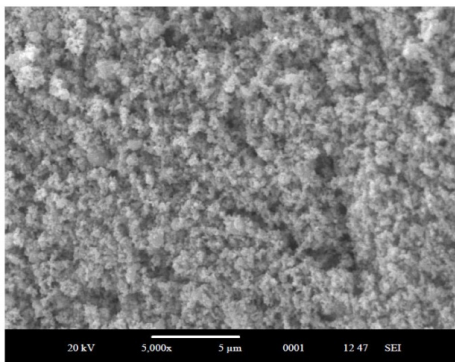


Fig. 4: SEM of PZ1 (80 % PPy + 20 % ZnO)

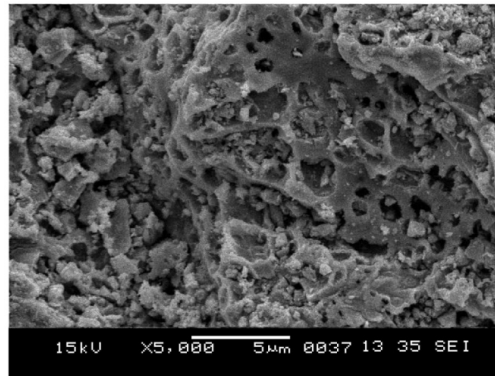


Fig. 5: SEM of PZ2 (70 % PPy + 30 % ZnO)

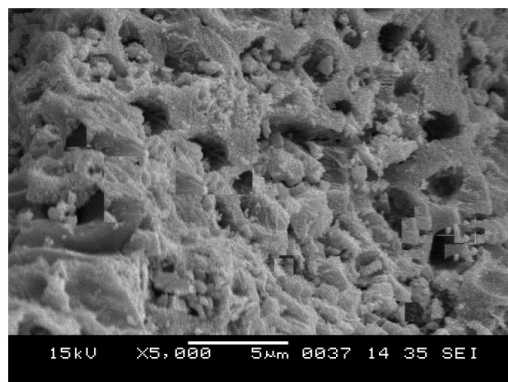


Fig. 6: SEM of PZ3 (60 % PPy + 40 % ZnO)

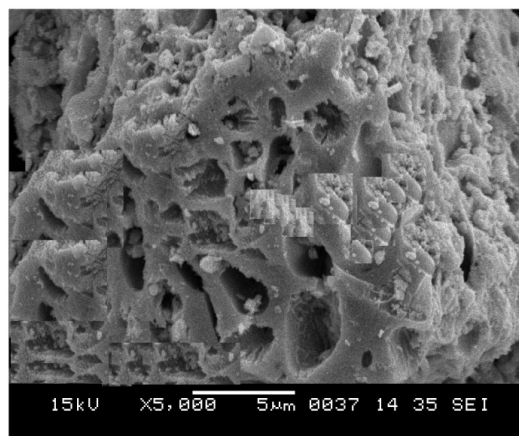


Fig. 7: SEM of PZ4 (50 % PPy + 50 % ZnO)

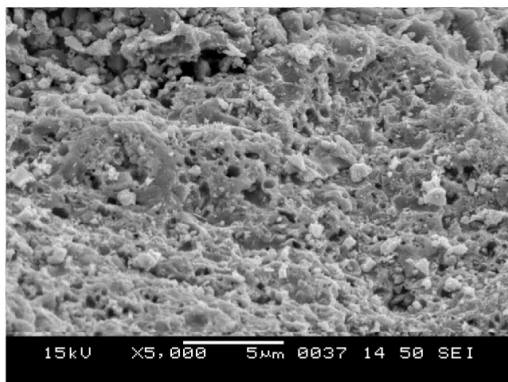


Fig. 8: SEM of PZ5 (40 % PPy + 60 % ZnO)

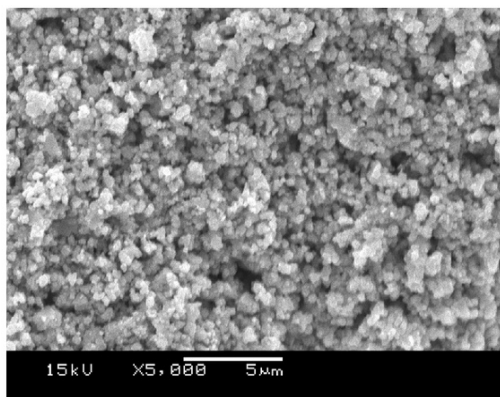


Fig. 9: SEM of Z (pure ZnO)

From the SEM photos, it is observed that in every inch of the region, number of pores was different and an average numbers of pores were taken for comparative study. From every photo, porosity was calculated for one inch square area. From figures, it is found that number of porosity of PZ2 sample is more among samples [10]. Conductivity increases as for the ions and charges surface area is large because of large porosity. Because of the large surface area due to high porosity, collision frequency decreases and obstacle for the flow of ions and charges becomes less. This enhances the charges mobility and tends to increase electrical conductivity.

3.3 DC Conductivity Measurement

Fig. 10 shows the variation of $\ln(i)$ versus $\ln(V)$ at constant room temperature, 300 K. From this figure, it is manifested that as the doping percentage of ZnO in PPy increases, $\ln(i)$ increases current with increase in $\ln(V)$. It is maximum for PZ2 sample (70%PPy + 30 % ZnO) amongst the prepared samples. It is also observed that, the nature of all the graphs is nearly straight line with constant slopes, exhibiting that obeys Ohm's law is obeyed on logarithmic scale.

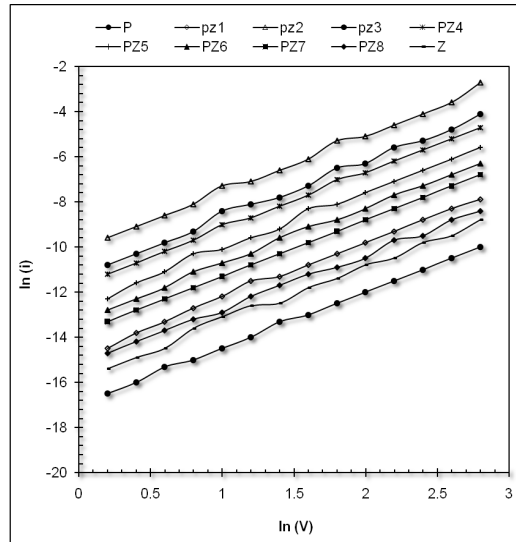


Fig. 10: Variation of $\ln(i)$ with $\ln(V)$ at room temperature (300K)

3.4 Schottky Plots:

Figure 11 shows the variation of $\ln(J)$ with $E^{1/2}$ at room temperature, 300K. The graph is known as Schottky plot and it is observed that as applied electric field E increases, $\ln(J)$ increases, speedily in the beginning and then slowly. It is also manifested that, for PZ2 composition, $\ln(J)$ is maximum. From Fig. 12, it is observed that, at optimum temperature i.e. 400 K, current density for PZ2 varies from $2.019 \times 10^{-6} \text{ A/m}^2$ (minimum) to $1.261 \times 10^{-5} \text{ A/m}^2$ (maximum). For all remaining samples, current density was low.

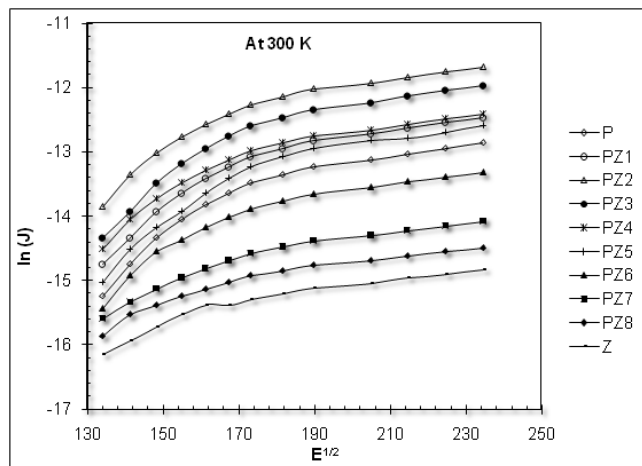


Fig. 11: Variation of $\ln(J)$ with $E^{1/2}$ at 300K

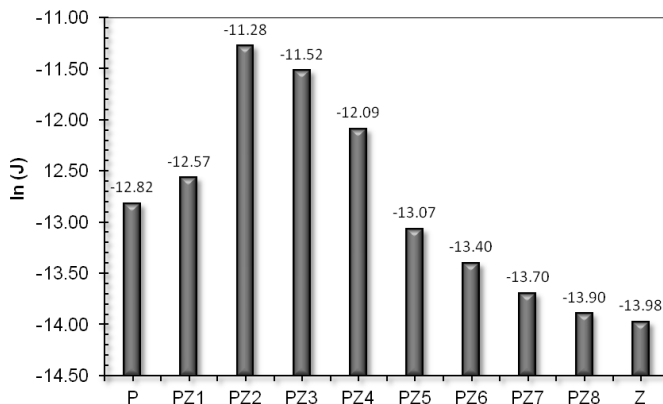


Fig. 12: Variation of ln(J) at 400 K temperature

3.5 Arrhenius Plot

It is seen from figure 13, that as temperature increases, $\ln(\sigma)$ increases. This variation is maximum for PZ2 sample and minimum for P sample. Due to increase of temperature, more and more charges in PZ2 samples become free and contribute to the conductivity and electrical conductivity increases. Slope of the PZ2 sample curve is maximum among the samples. As doping of ZnO in PPy increases, electrical conductivity increases and becomes maximum for 70%PPy + 30% ZnO sample (PZ2 sample) and further increase in doping of ZnO in PPy, conductivity decreases. This decrease may be due to collisions of more free charges with the vibrating local atoms in the sample as collision increases the obstacle to the motion of free charges.

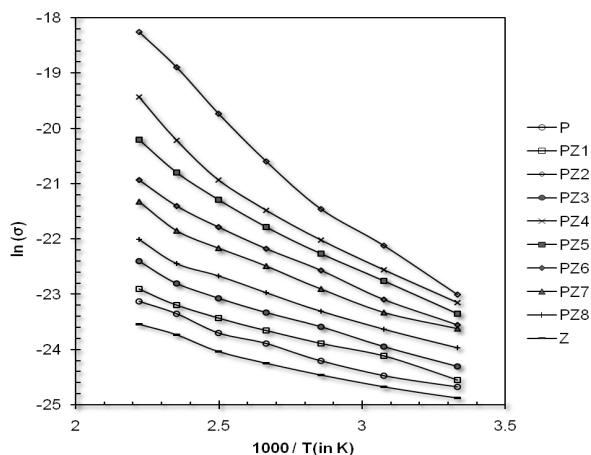


Fig. 13: Variation of ln(σ) with 1000/T(in K)

3.6 Activation Energy

Activation energy is given by, $E_a = -KT \times \text{Slope of graph from Arrhenius plot}$. Figure 14 manifested that activation energy of PZ2 sample is maximum among the samples and it is 0.1106 eV. This value is higher than other prepared samples.

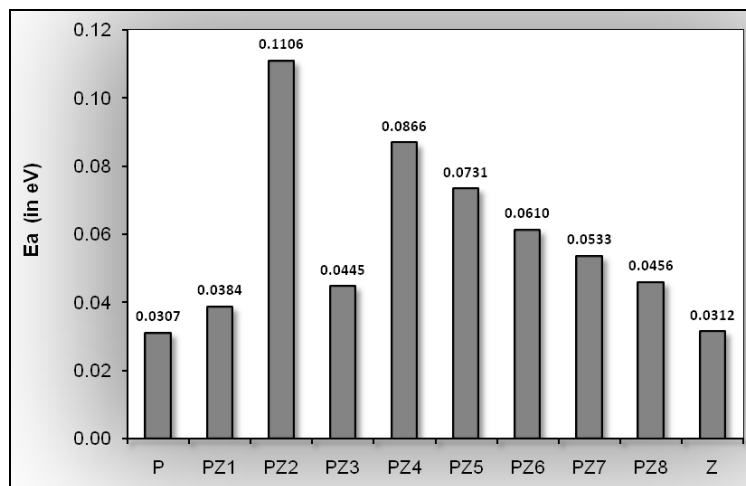


Fig. 14: Variation of $\ln(\sigma)$ with $1000/T$ (in K)

4.0 Conclusion:

Porosity of PZ2 sample was found to be more and its average crystalline size was found to be 99.40 nm, from XRD pattern. DC conductivity measurement showed nearly linear variation of $\ln(i)$ versus $\ln(V)$, exhibiting ohm's law being obeyed on logarithmic scale. Maximum value of current density, $1.261 \times 10^{-5} \text{ A/m}^2$ for PZ2 sample was obtained from schottky plot, at 400 K (shown in bar graph). Thus PZ2 sample is best among the prepared samples and its activation energy recorded to be 0.1106 eV.

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