DC Conductivity Studies of PPy/ZnO Composites

Tanveer Fatima, T. Sankarappa* and R. Ramanna
Department of Physics, Gulbarga University, Gulbarga, Karnataka – 585106, INDIA

Available online at: www.isca.in
Received 21st September 2015, revised 3rd October 2015, accepted 13th October 2015

Abstract

Samples of conducting polypyrrole (PPy) and Polypyrrole/ZnO composites were synthesized through chemical oxidative polymerization method using an anhydrous ferric chloride ($Fecl_3$) as an oxidizing agent. DC conductivity as a function of temperature as has been measured and data analyzed using Small polaron hopping and Variable range hopping theories. Activation energies for conduction and density of levels at Fermi energy were determined. Conductivity was found to be in the order of 10^{-3} ($\Omega^{-1}m^{-1}$) and exhibited semiconducting behavior with respect to temperature. Activation energy was found to be in the order of a meV. It is for the first time PPy-ZnO nanocomposites were investigated for temperature variation of conductivity and conduction mechanisms probed thoroughly.

Keywords: Conducting polymers, Polypyrrole, Nanocomposite, Electrical transport.

Introduction

Electronically conducting polymers have been used as artificial metals because they can act as substitutes for metals and semiconductors in electrical and electronic devices and at the same possessing the mechanical properties of polymers[1]. The widely exploited properties of conducting polymers in technological and commercial applications are their thermally withstanding capacity, bio-compatibility, electrical conductivity, switching capability between conducting-oxidized and insulating-reduced state[2-4].

Polypyrrole (PPy) is a most investigated conducting polymer because of its sizable electrical conductivity, ion-exchange capacity, hydrophobic nature etc. PPy can be synthesized in the form of powder, films, colloidal particles and composites in micro and nano sizes as mentioned in literature[5-8].

Now days, polymer-inorganic hybrid nanocomposites have been receiving extensive attention due to their innumerable applications in various fields. As mentioned in reference[9], the translucent conducting materials of the type zinc oxide (ZnO) and titanium dioxide (TiO_2) have advantages of non-toxicity, low price, chemical sustainability and feasibility of their being doped with variety of ions. Among these, zinc oxide (ZnO) has been greatly used in the fabrication of PPy hybrid materials[10]. The dc electrical resistivity was found to be increased with increasing temperature in PPy-ZnO composites which indicated semiconducting nature[11]. In polymer composites[12], electrical conductivity got reduced for low concentrations of ZnO ie., for 10% and that was attributed to the deterioration in the compactness of polymer. Moreover, for ZnO concentrations of 20% and 30%, conductivity was found to be increased and that was understood to be due to improvement in the packing of the polymer chains. For 40% of ZnO, conductivity decreased by two orders. This may be due to the composite transforming completely into an amorphous state and in that charge transport take place among localized states near Fermi level. The conductivity of polypyrrole room temperature has been reported to be 4.9 x10^{-4} S/cm [13]. It has been reported[14] that PPy nanoparticles are highly porous in sol form, exhibit good conductivity and can be effectively dispersed due to their large surface area for reactions. There are many reports on the studies of electrical conductivity in polypyrrole[15-18] but, very few have attempted to understand conduction mechanisms operated in polypyrrole nanoparticles. In view of this, an attempt has been made by us to study temperature variation of conductivity in PPy-ZnO composites and probe conduction mechanisms.

Material and Methods

Analytical grade Pyrrole, Zinc oxide and ferric chloride have been used to prepare Pyrrole. Pyrrole solution of 0.1M was prepared by dissolving 5ml of Pyrrole in 100 ml of double distilled water and the same has been placed in an ice tray and, magnetically stirred. Pre-cooled 0.3M ferric chloride anhydrous (oxidizing agent) solution was added drop by drop 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 of Polypyrrole was filtered and dried in a furnace maintained at 373K[19]. The yield of the polypyrrole was 5g.

PPy-ZnO composites were prepared by mixing different weight percentages of ZnO with polypyrrole powder. The weight percentages of ZnO considered for making PPy-ZnO composites are 20%, 30%, 40% and 50%. The composites are labeled as PZ1, PZ2, PZ3 and PZ4 respectively.

Pure PPy and PPy-ZnO powder were made into pellets of 1 cm diameter and 3mm thickness in an hydraulic press by applying 3

Vol. **3(5),** 1-5, October **(2015)** *Res. J. Material Sci.*

tones of pressure. The conducting silver paste was applied on two large surfaces of the pellets to act as electrodes. The conductivity of Pure PPy and PPy-ZnO composites were measured in the temperature range from 302K to 423K by two probe method.

Results and Discussion

The change in conductivity with increase of temperature for pure PPy and composite PZ1 is shown in Figure-1. The conductivity of pure PPy increased with increasing temperature exhibiting semiconductor characteristics. Rest of the composites showed similar behavior.

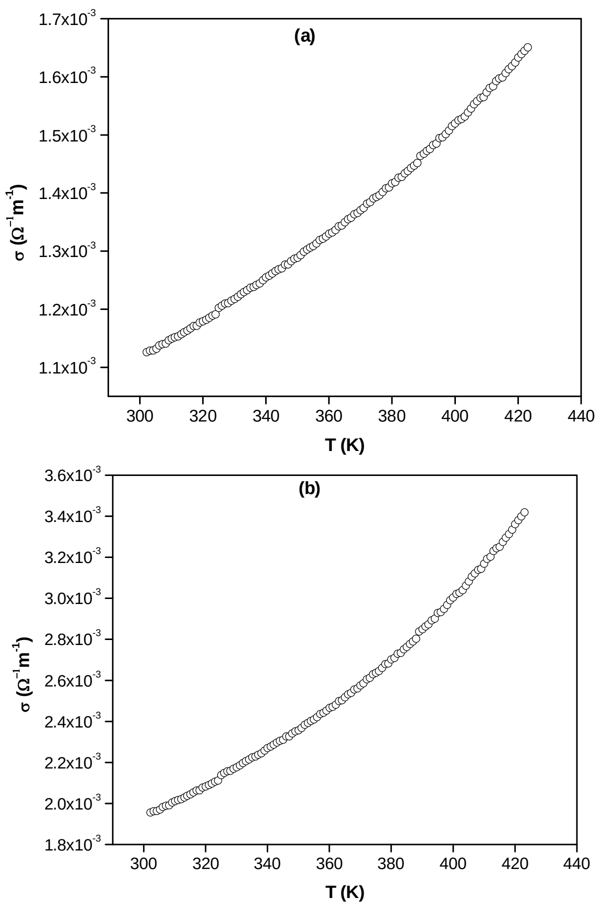

Figure-1
Temperature dependence of electrical conductivity, σ of (a) pure PPy and (b) PZ1

It is observed that conductivity of PPy–ZnO composites at room temperature increases from 1.955 X 10^{-3} $\Omega^{-1}m^{-1}$ to 5.28 X 10^{-3} $\Omega^{-1}m^{-1}$ as doping concentration of ZnO increased from 20% to 40% as shown in Figure-2. This may be due to increase in number of charge carriers with increase in doping of ZnO. The increase in the number of carriers with increase of ZnO content might be due to delocalization effect associated with doping process and that produces polarons and/or bipolarons in the composite structure which in turn enhance conductivity[20-23]. At higher (≥ 40 %) content of ZnO, the conductivity decreases. This decrease in conductivity may be due to the accumulation of charge carrier[24]. The charge carriers form nonlinear configurations in PPy when it is doped with ZnO. Consequently, conductivity does not change much. The degree of formation of nonlinear configuration may be more for ZnO doping of 50% than 40% [25].

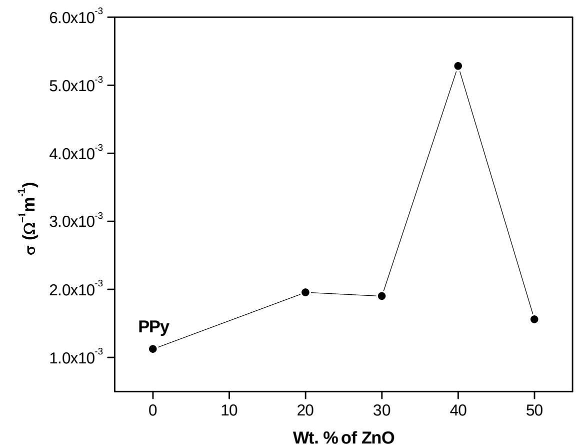

Figure-2
Conductivity versus ZnO concentration for PPy/ZnO composites

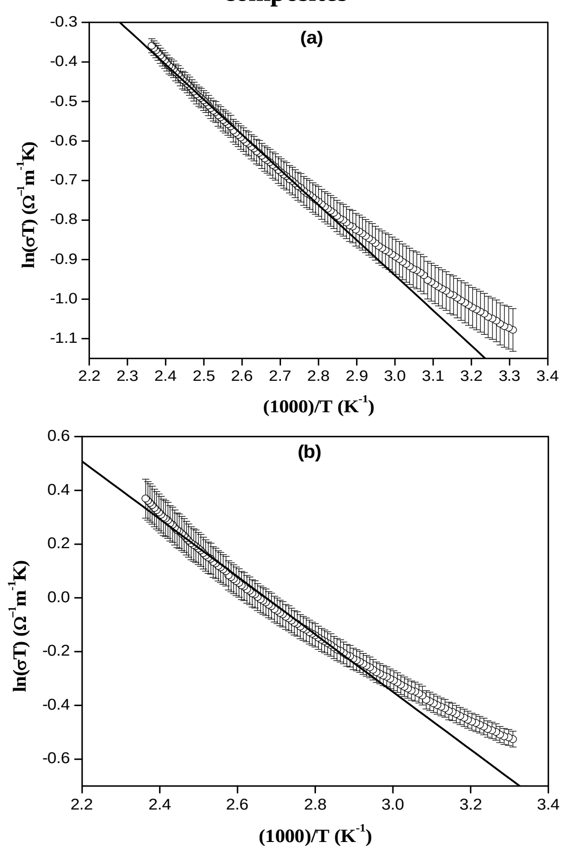

Figure-3
Plots of ln(σT) versus $(T)^{-1}$ as per SPH model (a) Pure PPy and (b) PZ2. Solid lines are the straight line fits in high temperature region

The temperature variation of conductivity of the composites has been fit to the expression due to Mott's Small polaron hopping (SPH) in noncrystalline semiconductors. It can be noted that there exist no good quantitative theory for explaining conduction mechanism in polymers. That is why, here SPH model has been employed. According to this model[26,27], the conductivity is given by,

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

Where, σ_0 is the pre exponential factor and E_a the activation energy for small polaron hopping. The plots of ln(σT) versus $(T)^{-1}$ for pure PPy and PZ1 are depicted in Fig. 3(a) and (b) respectively. The linear lines were fit at high temperature where linearity came into view. The activation energy, E_a was determined using slope.

Activation energy, E_a with weight % of ZnO in PPy-ZnO composites are tabulated in table-1. It is seen that E_a increases with weight % of ZnO nanoparticles except for PZ3. It is interesting to note that presently measured conductivity of all the four composites is greater than that reported for pure PPy nanoparticles in reference[28].

Table-1
Activation energy, E_a, of PPy and PPy-ZnO nanoparticle systems

Samples	PPy	PZ1-20%	PZ2-30%	PZ3-40%	PZ4-50%
E_a (meV)	0.076	0.092	0.097	0.075	0.240

Mott's 3-dimensional VRH model has been utilized for analyzing data deviated from SPH fit. Mott's VRH has been previously used by others[29,30] for understanding temperature dependence of conductivity of polypyrrole and polythiophenes. According to this model, the conductivity is given as[31,32],

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

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

Where, $N(E_F)$ defines density of levels at Fermi energy, v_0 the phonon frequency($=10^{13}$ H_Z) and α≈1.2Å (Size of the monomer unit). The plots of ln(σ) against $(T^{-1/4})$ were sketched as per this model for PPy and PZ1 composite as shown in figure-4. The straight lines were fit to the data.

Density of states, $N(E_F)$, were determined using slope and the same are tabulated in table-2. The $N(E_F)$ values are of the order of 10^{31} $eV^{-1}m^{-3}$ to 10^{35} $eV^{-1}m^{-3}$. These values of $N(E_F)$ are larger than those reported for conventional semiconductors and polymers[33]. Therefore, we conclude that Mott's (VRH) model fit seems to be in good agreement with data but the $N(E_F)$ values derived from the fits are far off from the expected values and hence this model cannot be considered to be suitable for explaining the present data.

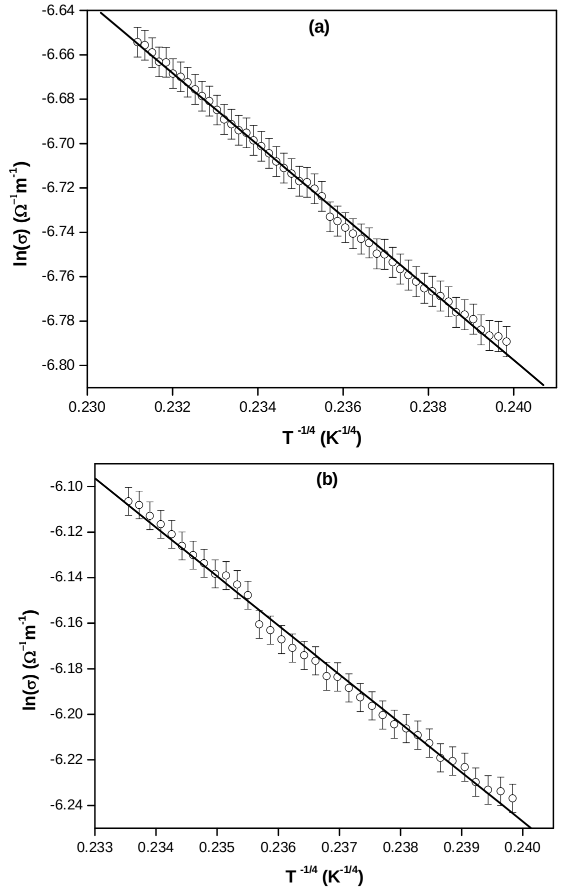

Figure-4
The plots of ln(σ) vs.$(1/T^{-1/4})$ for (a) Pure PPy (b) PZ1. Solid lines are the linear fits to the data

Table-2
Density of states at Fermi level, $N(E_F)$ for PPy-ZnO nanocomposites

Sample	PPy	PZ1-20%	PZ2-30%	PZ3-40%	PZ4-50%
$N(E_F)$ $(eV^{-1} m^{-3})$	5.01 X 10^{33}	2.64 X 10^{35}	1.79 X 10^{35}	2.69 X 10^{33}	5.49 X 10^{31}

Conclusion

Pure Polypyrrole and Polypyrrole/ZnO composites have been synthesized by chemical oxidation method. Temperature variation of dc resistivity has been investigated and it indicated semiconducting nature. Conductivity data analyzed using Mott's polaron hopping theories. Activation energy for conduction and density of levels of carriers at Fermi energy were 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.

References

1. Gade V.K., Shirale D.J., Gaikwad P.D., Kakde K.P., Savale P.A., Kharat H.J., Pawar B.H., Shirsat M.D., Synthesis and characterization of Ppy-PVS, P(NMP)-PVS and their co-polymer Ppy-P(NMP)-PVS films by galvanostatic method, *Int. J. Electrochem. Sci.*, **2,** 270–277 **(2007)**
2. Kassim A., Mahmud H.N.M.E., Yee L.M., Hanipah N., *Pac. J. Sci. Technol.***, 7 (2)** 105 **(2008)**
3. Zengin H. and Erkan B., Synthesis and characterization of polyaniline/silicon dioxide composites and preparation of conductive films, *Polym. Adv. Technol.*, **21,** 216–223 **(2010)**
4. Aisha Batool, Farah Kanwal, Muhammad Imran, Tahir Jamil and Saadat Anwar Siddiqi, Synthesis of polypyrrole/zinc oxide composites and study of their structural, thermal and electrical properties, *Synthetic Metals,* **161,** 2753– 2758 **(2012)**
5. Huiling Tai, Yadong Jiang, Guang Zhong Xie, Jun Shung Yu and Xuan Chen, Fabrication and gas sensitivity of polyaniline–titanium dioxide nanocomposite thin film, Sensors and Actuators **B25,** 644-650 **(2007)**
6. Nguyen Thi Le H., Garcia B., Deslouis C. and Le Xuan Q., Corrosion protection and conducting polymers: polypyrrole films on iron, *Electrochimical Acta***, 46,** 4259-4272 **(2001)**
7. Seandeera G.K.R., Kitamura T., Wada Y. and Yanagida S., Deposition of polyaniline via molecular self-assembly on TiO_2 and its uses as a sensitiser in solid-state solar cells, *Jour. of Photochem. and Photobiol. A: Chem.*, **164,** 61-66 **(2004)**
8. Au Ji Ru Son, Hoosung Lee and Bongjin Moon, Morphology and photoluminescence of colloidal polypyrrole nanoparticles, *Synth. Met.,* **157,** 597-602 **(2007)**
9. Ashokan S., Ponnuswamy V. and Jayamurugan P., Morphological, structural, functional effect and Comparative study of PPy with PPy/TiO2, and PPy/ZnO composite films by Nebulizer Spray coating Technique, *Journal of Applied Physics and Engineering,* **1(1),** 1–9 **(2015)**
10. Vivekchand S.R.C., Kam K.C., Gundiah G., Govindaraj A., Cheetham A.K. and Rao C.N.R., Electrical properties of inorganic nanowire–polymer composites, *J. Mater. Chem.,* **15,** 4922–4927**(2005)**
11. Chougule M.A., Sen S., Patil V.B., Facile and Efficient Route for Preparation of Polypyrrole-ZnO Nanocomposites: Microstructural, Optical and Charge Transport Properties, *Journal of Applied Polymer Science,* **125,** E541–E547 **(2012)**
12. Dalas E., Mougoyannis P. and Sakkopoulos S., Effect Of Zno Concentration On The Structure And Charge Transport In Conductive Polypyrrole/Zno X% W/W Composites With X = 10, 20, 30 And 40, *Rom. Journ. Phys.*, **58, 3–4,** 354–364, Bucharest, **(2013)**
13. Pallavi Mavinakuli, Suying Wei, Qiang Wang, Amar B. Karki, Sanjay Dhage, Zhe Wang, David P. Young, and Zhanhu Guo, Polypyrrole/Silicon Carbide Nanocomposites with Tunable Electrical Conductivity, *J. Phys. Chem. C,* **114,** 3874-3882 **(2010)**
14. Suri K., Annapoorni S., Tandon R.P., Rath C. and Aggrawal V.K., Thermal transition behaviour of iron oxide–polypyrrole nanocomposites, *Current Applied Physics,* **3, 2,** 209-213 **(2003)**
15. Sato K., Yamara M., Hagiwara T.H., Murata K. and Tokumoto M., Study on the electrical conduction mechanism of polypyrrole films, *Synth. Met.,* **40,** 35-48 **(1991)**
16. Spatz J.P., Lorentz B., Weishaupt K., Hochhima H.D., Menon V., Parthasarathi R., Martin C.R., Bechtold J. and Her P.H., Observation of crossover from three- to two-dimensional variable-range hopping in template-synthesized polypyrrole and polyaniline, *Phys.Rev.,* **B 50,** 14888-14892 **(1994)**
17. Maddison D.S. and Answorth J., Electrical Conductivity and Thermoelectric Power Of Polypyrrole With Different Doping Levels, *Synth. Met.,* **26,** 99-108 **(1988)**
18. Syed Abthagir P. and Saraswati R., Thermal stability of polypyrrole prepared from a ternary eutectic melt, *J. Materials Chemistry and Physics,* **92,** 21-26 **(2005)**
19. Murugendrappa M.V. and Ambika Prasad M.V.N., Chemical Synthesis, Characterization, and Direct-Current Conductivity Studies of Polypyrrole/γ-Fe_2O_3 Composites, *J. App. Poly. Sci.*, **103,** 2797 **(2007)**
20. Pawar S.G., Patil S.L., Chougule M.A., Raut B.T., Shashwati Sen and Patil V.B., Camphor sulfonic acid doped polyaniline–titanium dioxide nanocomposite: synthesis, structural, morphological, and electrical properties, *International Journal of Polymeric Materials,* **60,** 979–987, **(2011)**
21. Maminya YP., Davydenko VV., Pissis P. and Lebedev EV., Electrical and thermal conductivity of polymers filled with metal powders, *Eur Polym J,* **38,** 1887-1897 **(2002)**
22. Huang JC, Carbon black filled conducting polymers and polymer blends, *Adv Polym Technol,* **21(4),** 299–313 **(2002)**
23. Asif Ali Khan, Mohd. Khalid, Synthesis of Nano-Sized ZnO and Polyaniline-Zinc Oxide Composite: Characterization, Stability in Terms of DC Electrical

Conductivity Retention and Application in Ammonia Vapor Detection, *Journal of Applied Polymer Science,* **117,** 1601–1607 **(2010)**

24. Chougule M.A., Khuspe G.D., Shashwati Sen and Patil V.B., Polypyrrole–ZnO nanohybrids: effect of CSA doping on structure, morphology and optoelectronic properties, *Appl. Nanosci.*, **3,** 423–429 **(2013)**

25. Shama Islam, Lakshmi G. B. V. S., Azher M. Siddiqui, Husain M. and Zulfequar M., Synthesis, Electrical Conductivity, and Dielectric Behavior of Polyaniline/V2O5 Composites, Hindawi Publishing Corporation, *International Journal of Polymer Science,* **2013, (2013)**

26. Mott N.F., Conduction in glasses containing transition metal ions, *J. Non-Cryst. Solids,* **1(1),** 1-17 **(1968)**

27. Praveenkumar K., Sankarappa T., Ashwajeet J.S., Ramanna R., Sujatha T., Jyoti Kattimani and Chandraprabha G., Conduction Mechanisms in Polypyrrole-Copper Nanocomposites, *Journal Of Nano- and Electronic Physics,* **7, 2,** 02043 **(2015)**

28. Praveenkumar K., Sankarappa T., Jyoti Kattimani, Chandraprabha G, Ashwajeet J.S., Ramanna R. and Sujata T., Electrical Conductivity in Polypyrrole Nano Particles, *ISJSET,* **17, 7,** 772 **(2014)**

29. Rawal I. and Kaur A., Effect of anion surfactant concentration on the variable hopping conduction in polypyrrole nanoparticles, *J. Appl. Phys.*, **115**, 043717-1–6 **(2014)**

30. Jyoti K., Sankarappa T., Ashwajeet J.S. and Ramanna R., Conductivity Studies on Polythiophene-CoO Nano-Composites, *Journal of Advanced Chemical Sciences,* **1(4)** 139–141 **(2015)**

31. Kiani G., Sheikhloie H. and Rostami A., Highly enhanced electrical conductivity and thermalstability of Polythiophene/single-walled carbon nanotubes nanocomposite, *Iran. Poly. Jour.*, **20(8)**, 623-632 **(2011)**

32. Othman N., Talib Z.A., Kassim A., Shaari A.H. and Liew J.Y.C., Electrical properties of polypyrrole conducting polymer at various dopant concentrations, *J. Fundamental Sci.*, **5,** 29-33 **(2009)**

33. Jyoti K., Sankarappa T., Praveenkumar K., Ashwajeet J.S., Ramanna R., Chandraprabha G.B and T. Sujatha, Structure and Temperature Dependence of Electrical Conductivity in Polythiophene Nanoparticles, *Int. Journal of Advanced Research in Physical Science (IJARPS),* **1(7),** 17-21, **(2014)**