STM JOURNALS

Journal of
Polymer & Composites

ISSN: 2321-2810 (Online)
ISSN: 2321-8525 (Print)
Volume 12, Special Issue 6, 2024
DOI (Journal): 10.37591/JoPC

https://journals.stmjournals.com/JOPC/

Research JoPC

Investigation of Electronic Transport in Li_2O and ZnO Nanoparticles Containing Polypyrrole Systems

Rajshekar. L. Madival[1], Suresh Patnaik Pakki[2], B. Simhachalam[3], Prashantkumar. M[4*] , Vinay. V. Kannur[5], N. Nagaraja[6], Y. T. Ravikiran[7], V. Harshavardhan[8], S. K. Alla[9,]

Abstract

Polypyrrole systems having nanocrystalline ZnO and Li_2O with different compositions (PPy50 + Li_2Ox + ZnO(50-x), where x = 0, 2, 4, 6, 8, and 10) have been produced by ball milling. compositions of the type The temperature-dependent DC conductivity of each sample was determined in the temperature range of 313 K to 363 K. The conductivity studies show that Polaron hopping was the conducting mechanism in the material composites. The weight proportion of Li_2Ox + ZnO (50-x) NPs was discovered to increase the conductivity and activation energy of the PPy, indicating that the hopping distance between the charged particles is reduced, improving the metallic character and charge carrier particle density.

Keywords: Polypyrrole, composites, nanoparticles, dc conductivity

***Author for Correspondence**
Prashantkumar. M pacificmg@gmail.com

[1]Assistant Professor, Department of Physics, Rao Bahadur Y Mahabales warappa Engineering College, Ballari, Karnataka, India
[2]Assistant Professor, Department of Physics, Aditya Institute of Technology and Management, K Kotturu, Tekkali, Srikakulam, Andhra Pradesh, India
[3]Assistant Professor, Department of Physics, Surya Teja Degree College, Kasibugga, Palasa, Andhra Pradesh, India
[4]Associate Professor, Department of PG Studies and Research in Physics, Government College (Autonomous), Kalaburagi, Karnataka, India
[5]Assistant Professor, Department of Physics, Rao Bahadur Y Mahabaleswarappa Engineering College, Ballari, Karnataka, India.
[6]Assistant Professor, Department of Physics, Rao Bahadur Y Mahabaleswarappa Engineering College, Ballari, Karnataka, India.
[7]Associate Professor, Department of PG Studies and Research in Physics, Government First grade College, Holalkere, Karnataka, India.
[8]Associate Professor, Department of Physics, CMR Technical Campus, Hyderabad, Telangana, India.
[9]Associate Professor, Department of Physics, Aditya Institute of Technology and Management, K Kotturu, Tekkali, Srikakulam, Andhra Pradesh, India

Received Date: March 19, 2024
Accepted Date: June 13 , 2024
Published Date: September 27, 2024

Citation: Rajshekar. L. Madival, Suresh Patnaik Pakki,B. Simhachalam, .Prashantkumar. M,.Vinay. V. Kannur,.N. Nagaraja, Y. T. Ravikiran, , V. Harshavardhan, .S. K. Alla. Investigation of Electronic Transport in Li_2O and ZnO Nanoparticles Containing Polypyrrole Systems. Journal of Polymer & Composites. 2024; 12(Special Issue 6): S88–S95.

INTRODUCTION

Corrosion protection layers, electrodes for batteries and capacitors, energy storage devices, sensors and electrocatalysts are produced by semiconductor polymers drawn attention to scientists and engineers in recent years [1-2]. Polymers are typically assumed to be non-conducting [3]. Conjugated polymers with two bonds display semiconducting characteristics [3]. When properly doped, polypyrrole possesses semiconducting characteristics [3]. The use of conducting polymers and their typical representative are indicators of their properties [4]. A selective metal oxide doping causes augmentation of conductivity of poly-conjugated polymers from 10^{-10} S/m to 10^{-5} S/m [5-8]. Improved fabricability and other PPy characteristics have recently been the focus of study [9–11].

Conducting polymers using nanofillers enhance the conducting qualities of composite composites [12]. ZnO nanoparticles (NPs) serve as reinforcement fillers in PPy and other polymers [13-14]. Non-toxic, cheap, efficient absorbent and size dependent electrical and optical characteristics, ZnO NPs have attracted a lot of interest as a semiconductor recently [15-19]. ZnO NPs have been discovered to be easily generated in metals

and have a wide range of applications in the electronic and medical industries [20]. The host materials' electrical and mechanical characteristics are improved by the second of the nanocomposite's metal and organic components, while the mechanical properties are improved by the first [21].

Nanocrystalline ZnO sensors and Li_2O based energy storage components have been developed due to their unique electrical and electronic properties [22-29]. Utilization of polymers which are produced by in-situ polymerization process as fillers have reported [30-31].

Lithium oxide and ZnO NPs are both often utilized as dopants. Lithium oxide is used to implant ZnO NP crystallite clusters, whereas ZnO NPs are used to decorate PPy amorphous structures [11]. In addition to offering superior electrical, chemical, and mechanical qualities for industrial production [32-33]. as well as application in sensors and lithium-ion batteries [34-35]. the mechanical mixing procedure is appropriate for large-scale production.

The goal of this study is to determine the effect of incorporating ZnO NPs and bulk Li_2O into pristine PPy matrix in varied compositions. Polypyrrole nanocomposites with nanocrystalline ZnO particles and Li_2O (PPy50 + Li_2O*x* + ZnO (50-*x*), where *x* = 0, 2, 4, 6, 8, and 10) have been synthesized and the samples of various compositions are referred as HC0, HC2, HC4, HC6, HC8, and HC10.

EXPERIMENTAL DETAILS

Metal oxide nanoparticles, Ammonium Persulphate (APS) and Acetone purchased from Sigma Aldrich. Pyrrole, a doubly distilled monomer, is polymerized in situ in a beaker with a 0.3 M concentration of ammonium persulphate (APS). The beaker is held in place by a magnetic stirrer. In 100 ml of water, 0.6 M ammonium persulphate is added. APS is gradually dissolved in 0.3 M Polypyrrole. The obtained precipitate was washed several times with deionized water and dried. The byproduct was heated to 373 K in a muffle furnace, yielding 2.25 g of black Polypyrrole powder, which was then considered 100%.

A mechanical vibration mill (Make: Techno search instrument Mumbai, India) used to produce the polymer composites. The milling was done for 15 – 20 min and wt.% of metal oxides varies for different samples [36]. Further, each sample composite was added to an agate mortar and thoroughly hand mixed in presence of acetone. Crushing the powder with an 80 MPa hydraulic press resulted in pellets with varying weight percentages. The pellets were 10 mm in diameter and about 2 mm in thickness.

By applying silver paste onto two major surfaces of the HC pellet, the electrical contacts have been established. The DC conductivity of these nanocomposites as a function of temperature, in the temperatures of 313 K and 463 K, has been measured using two-probe method (SES Make Instruments, Roorkee, India) [34–35]. The current flowing through samples were measured using a digital Pico ammeter. A temperature control unit with a Chromel Alumel thermocouple and a high-quality PID Controller with a maximum temperature range of 200 °C was used to measure the temperature of the sample. The conductivity was determined for all the composites using the formula $\sigma = \frac{1}{p}$ where resistivity $p = \frac{RA}{d}$, d is the thickness, A is the surface area and R is the resistance of the sample. The predicted conductivity inaccuracy was estimated to be between 2 and 3%. Scanning Electron Microscope Model-EVO-18 Special Edison Zein Germany drew sketches of the sample morphologies (Flow chart 1).

RESULTS AND DISCUSSIONS

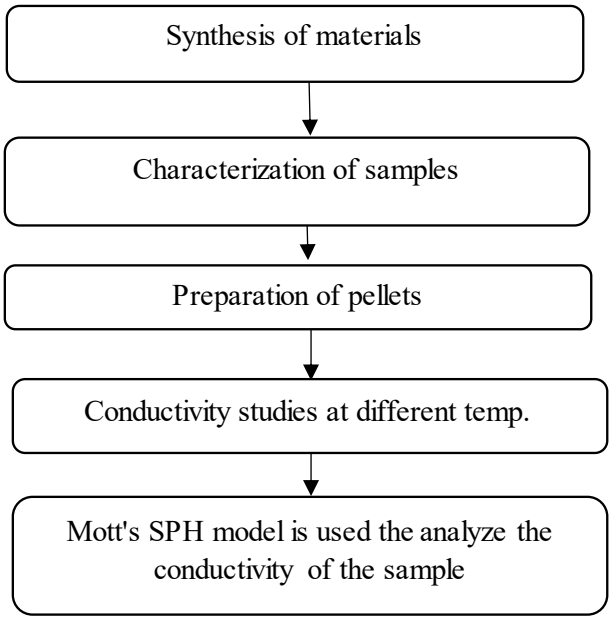
Sem Analysis

The analysis of the SEM micrographs confirmed the hexagonal crystal structure of the present ZnO nanocrystallites (Figures. 1a to f). These figures also depict that the ZnO NPs are embedded into the amorphous structure of PPy. The increase in weight percentage ZnO NPs in the ratio (0, 2, 4, 6, 8 & 10)

has yielded in a systematic and consistent structural change in the present composites. A granular morphology of the polypyrrole particle structures is measured from SEM images and found to be of the order of 200 nm.

The diameters of HC0, HC2, HC4, HC6, HC8 and HC10 respectively varied from 128.6 to 196.99 nm, 215.5 to 220.5 nm, 177.2 to 191.8 nm, 108 to 216.8 nm, 161.6 to 183.9 nm and 121.9 to 145 nm. This data confirms that with the increase in weight percentage of Li_2O into the composite there is a decrement in the size of particle.

The cluster of polypyrrole embedded ZnO NPs is observed in Figure 1a. There is agglomerated particle bounded to PPy as weight percentage of Li_2O is increased (Figure 1b - f). The observable voids may be attributed to weak interparticles interactions.



Flow chart 1. The steps involved in the process of synthesis, characterization of ZnO - LiO_2 Composite material.

Dc Conductivity Studies

The temperature dependent Conductivity is explained by Mott's small polaron hopping model. The high temperature activation energy was determined by applying Mott's small polaron hopping (SPH) model [37-39] according to the following equation,

$$\sigma T = \sigma o \exp(-Ea/(kB\ T)) \quad (4)$$

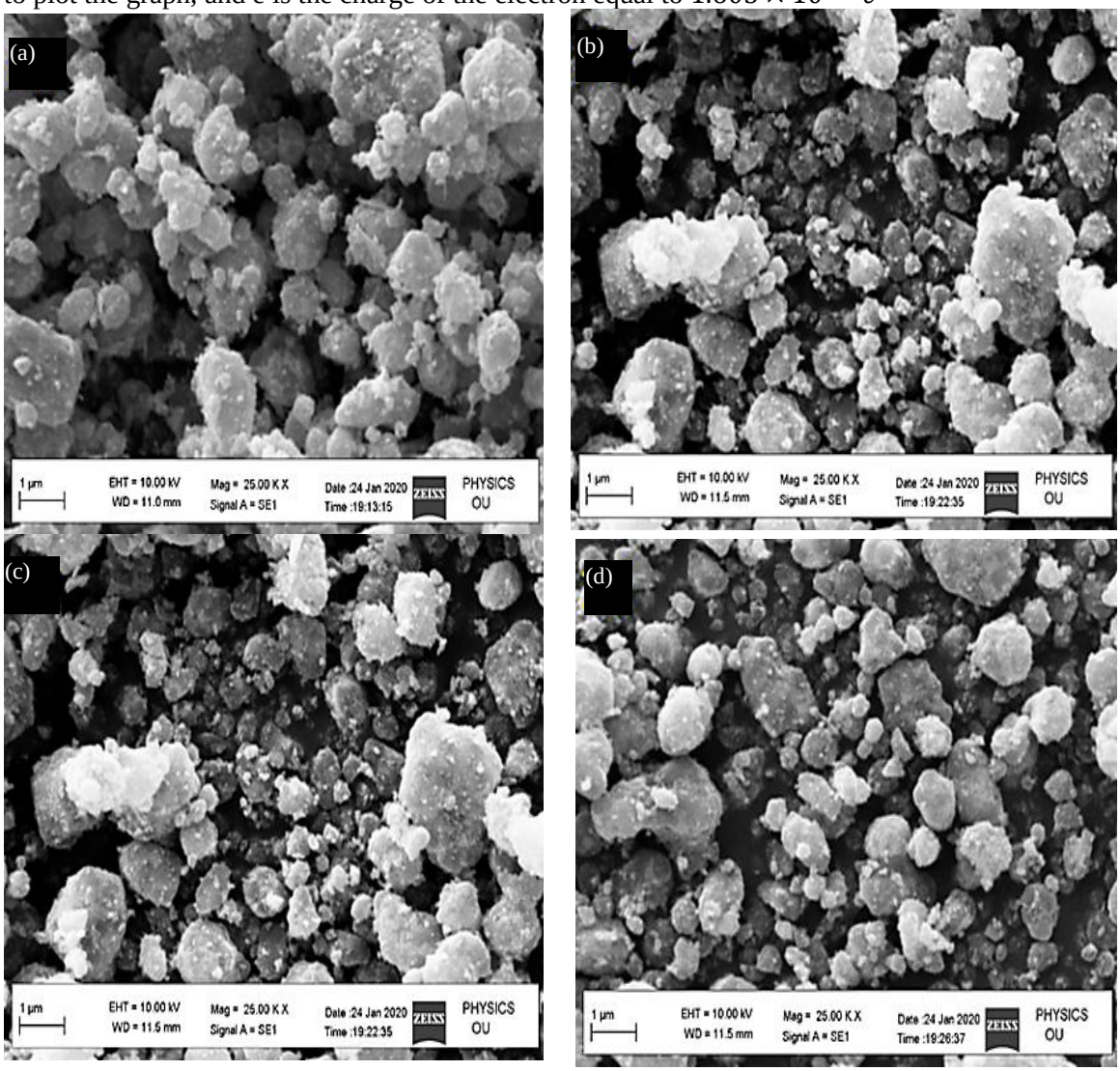
Where σ is the conductivity of the composites, σ_o is the pre-exponential factor and is constant, E_a is the activation energy, k_B is the Boltzmann's Constant, T is the absolute temperature of the samples.

A graph was fitted to equation (4) and lnσ versus 1/T plotted for all the material composites using origin 8.5. The curve is linear at high temperature region and nonlinear at low temperature region.

The high temperature activation energy was calculated at linear portion of the curve by using estimated slope as follows

$$Ea = \frac{-100mk}{e} \quad (5)$$

E_a is high temperature activation energy, m is the slope of the linear portion of the line which was negative, k is Boltzmann constant and is equal to $138 \times 10^{-23} j/k$, 1000 was multiplication factor used to plot the graph, and e is the charge of the electron equal to $1.603 \times 10^{-19} c$



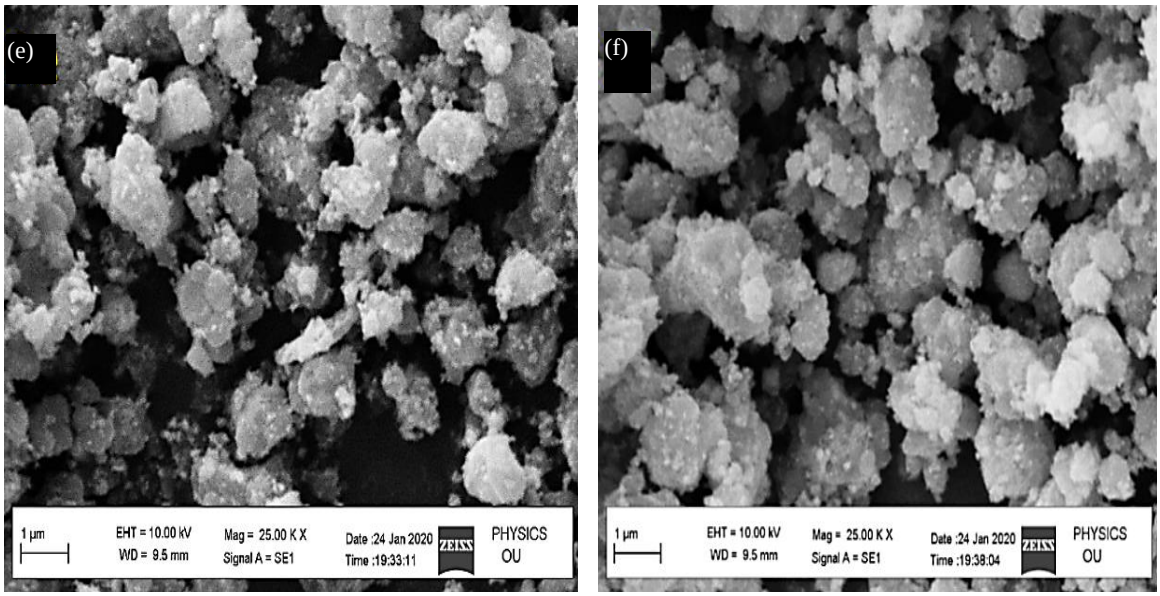


Figure 1. Showing SEM images of Figure 1 (a) HC0, (b) HC2, (c) HC4, (d) HC6, (e) HC8 and (f) HC10.

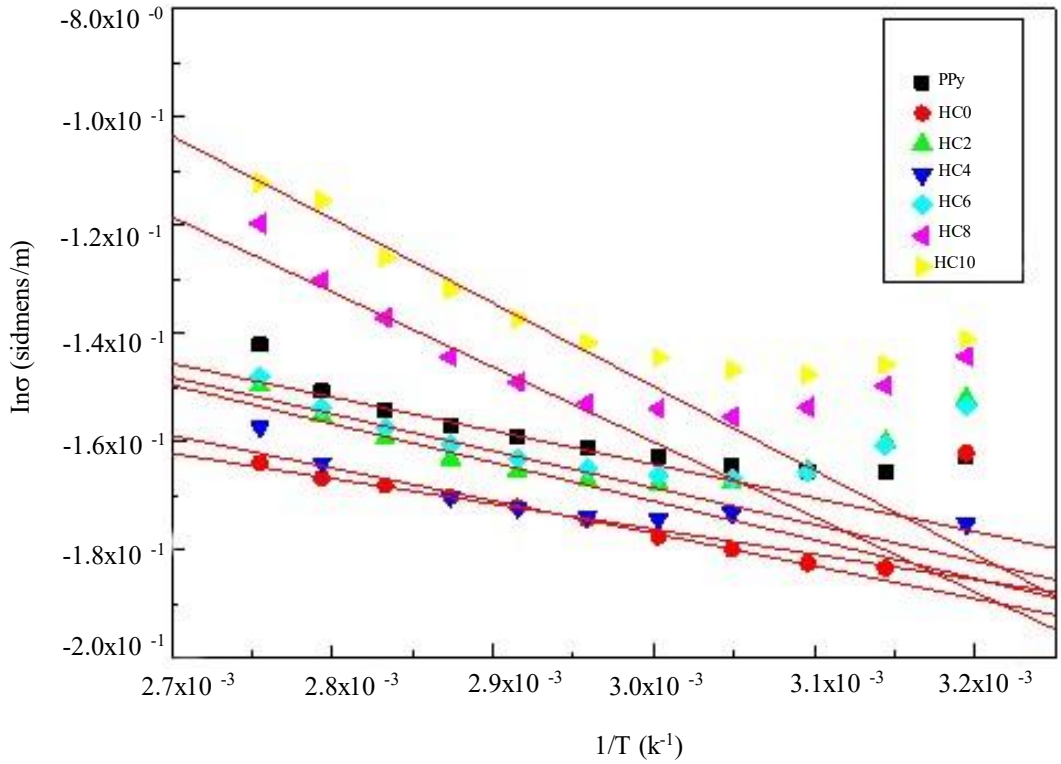


Figure 2. Showing ln σ versus 1/T conductivity of (Ppy, HC0, HC2, HC4, HC6, HC8, and HC10*)*.

The calculated activation energies for the material composites increases with increase weight percentage of ZnO NPs in Ppy. The calculated activation energy for different material composites at depicted in Table 1.

As shown in Table1, the observed conductivity for all PPy + Li_2O + ZnO NP composites at various temperatures ranges from 2.164 X 10^{-7} S/m to 9.135 X 10^{-8} S/m. The curve of conductivity at various temperatures for various weight percentages of Li_2O + ZnO NPs added in PPy was shown in Figure. 3.

The nano composites' conductivity increased nonlinearly with temperature and showed semiconducting behavior [37,38]. The addition of Li_2O + ZnO NPs increases the conductivity of ppy and indicates that the hopping distance between charged particles is decreasing, which improves the metallic character and charge carrier particle density [39]. The conductivity of composites improves as the concentration of Li_2O + ZnO NPs increases, depending on the loading of fillers [40-42].

In Figure.2, the deviation of dc conductivity curves in low temperature region is attributed to the variable range hopping of the polarons. The same can be analyzed in line with the Variable Range Hopping Theories due to N.F. Mott and N. Greaves.

Table 1. Showing Activation energy, wt% at different composites at temperature 313 and 363 K.

Wt%	σ in S/m at 313K	σ in S/m at 363K	Energy activation (ev)
0	9.14 X 10^{-08}	7.56 X 10^{-08}	0.430
2	2.51 X 10^{-07}	3.18 X 10^{-07}	0.980
4	2.44 X 10^{-08}	1.46 X 10^{-07}	0.286
6	2.16 X 10^{-07}	3.73 X 10^{-07}	0.653
8	5.45 X 10^{-07}	6.35 X 10^{-06}	1.700
10	7.49 X 10^{-07}	1.36 X 10^{-05}	1.087

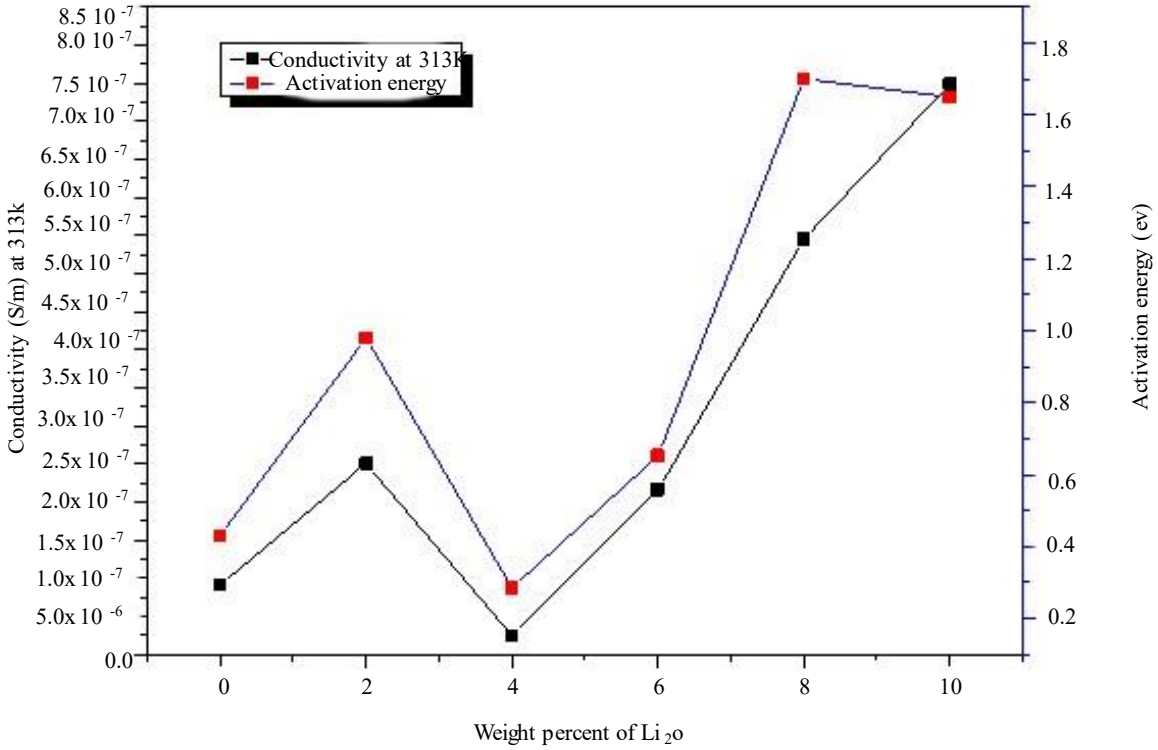


Figure 3. Showing dc conductivity and activation energy, E_{dc}, for different wt% at temp. 313K.

CONCLUSION

The novel Polypyrrole/ZnO NPs-Li_2O ternary composites were synthesized. The morphological changes due to the incorporation of Li_2O in the composites were studied using SEM technique. The DC electrical conductivity of the PPy/Zno- Li_2O composites was determined in the temperatures 313 and 363 K using two-probe method. SEM micrographs demonstrated that the agglomeration of particles enhanced for 10 wt.% sample in comparison with other samples. The dc conductivity increased with increase in the temperature. The variation of conductivity with temperature has been analyzed using

Mott's small polaron hopping model. As the weight percentage of Li_2O + ZnO NPs increased, the activation energy and conductivity also found to increase in the present composites.

Acknowledgements

One of the authors, Rajshekhar L Madival, acknowledges the experimental facilities he utilized at Department of Biotechnology, Gulbarga University, Kalaburagi & Govt. College (Autonomous), Kalaburagi, Karnataka State, India.

REFERENCES

1. Fatima T, Sankarappa T, Ashwajeet JS, Ramanna R. Structural and dielectric properties of PPy/ZnO composites. Int. J. Innov. Res. Sci. Eng. Technol. 2015; 2:206-13.
2. El-Gamal S, Ismail AM, El-Mallawany R. Dielectric and nano-scale free volume properties of polyaniline/polyvinyl alcohol nanocomposites. Journal of Materials Science: Materials in Electronics. 2015;26(10):7544-53.
3. Suhailath K, Ramesan MT. Temperature dependent AC conductivity, mechanical and different DC conductivity modeling of poly (butyl methacrylate)/samarium doped titanium dioxide nanocomposites. Journal of Materials Science: Materials in Electronics. 2017; 28:13797-805.
4. Friberg L, Nordberg GF, Vouk VB. Handbook on the Toxicology of Metals. Elsevier/North-Holland Biomedical Press, 335, The Netherlands; 1979.
5. Ratkovich A, Penn RL. Zinc oxide nanoparticle growth from homogenous solution: influence of Zn: OH, water concentration, and surfactant additives. Materials Research Bulletin. 2009; 44(5):993-8.
6. Akhoon SA, Rubab S, Shah MA. A benign hydrothermal synthesis of nanopencils-like zinc oxide nanoflowers. International Nano Letters. 2015; 5:9-13.
7. Yu D, Cai R, Liu Z. Studies on the photodegradation of Rhodamine dyes on nanometer-sized zinc oxide. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2004; 60(7):1617-24.
8. Curri ML, Comparelli R, Cozzoli PD, Mascolo G, Agostiano A. Colloidal oxide nanoparticles for the photocatalytic degradation of organic dye. Materials Science and Engineering: C. 2003; 23(1-2):285-9.
9. Chu SY, Yan TM, Chen SL. Characteristics of sol-gel synthesis of ZnO-based powders. Journal of materials science letters. 2000; 19(4):349-52.
10. Damonte LC, Zélis LM, Soucase BM, Fenollosa MH. Nanoparticles of ZnO obtained by mechanical milling. Powder Technology. 2004; 148(1):15-9.
11. Dai ZR, Pan ZW, Wang ZL. Novel nanostructures of functional oxides synthesized by thermal evaporation. Advanced Functional Materials. 2003; 13(1):9-24.
12. Vernitskaya, T.V., Efimov, O.N., Polypyrrole: a conducting polymer; its synthesis, properties and applications. Russian Chemical Reviews 1997; 66 (5): 443 – 457
13. Aldissi M, editor. Intrinsically conducting polymers: an emerging technology. Springer Science & Business Media; 2013.
14. Chaluvaraju BV, Ganiger SK, Murugendrappa MV. Synthesis, characterization and DC conductivity studies of polypyrrole/molybdenum trioxide composites. Polymer Science Series B. 2014; 56(6):935-9.
15. Inzelt G. Rise and rise of conducting polymers. Journal of Solid State Electrochemistry. 2011; 15:1711-8.
16. Bredas JL, Street GB. Polarons, bipolarons, and solitons in conducting polymers. Accounts of chemical research. 1985; 18(10):309-15.
17. Cheng Q, He Y, Pavlinek V, Li C, Saha P. Surfactant-assisted polypyrrole/titanate composite nanofibers: Morphology, structure and electrical properties. Synthetic Metals. 2008;158(21-24):953-7.
18. Behniafar H, Malekshahinezhad K. A unique path to reach thermostable polypyrrole/Pd microfibers via chemical oxidative polymerization. Colloid and Polymer Science. 2014;292:2083-8.

19. Lee DS, Lee DD, Hwang HR, Paik JH, Huh JS, Lim JO, Lee JJ. Characteristics of electrochromic device with polypyrrole and WO 3. Journal of Materials Science: Materials in Electronics. 2001; 12:41-4.
20. Ramesan MT, Nidhisha V, Jayakrishnan P. Facile synthesis, characterization and material properties of a novel poly (vinyl cinnamate)/nickel oxide nanocomposite. Polymer International. 2017; 66(4):548-56.
21. Ma X, Liu A, Xu H, Li G. Growth of ramification-like ZnO rods in the presence of polyaniline. Colloid and Polymer Science. 2007; 285:1631-5.
22. Huang J, Yang Z. Synthesis of ZnO/polypyrrole composites and an application in Zn/Ni rechargeable batteries. RSC Advances. 2014;4(37):19205-9.
23. Nguyen-Le MT, Lee BK. High temperature synthesis of interfacial functionalized carboxylate mesoporous TiO2 for effective adsorption of cationic dyes. Chemical Engineering Journal. 2015; 281:20-33.
24. Tajizadegan H, Torabi O, Heidary A, Golabgir MH, Jamshidi A. Study of methyl orange adsorption properties on ZnO–Al2O3 nanocomposite adsorbent particles. Desalination and Water Treatment. 2016; 57(26):12324-34.
25. Salem AN, Ahmed MA, El-Shahat MF. Selective adsorption of amaranth dye on Fe_3O_4/MgO nanoparticles. Journal of Molecular Liquids. 2016 ; 219:780-8.
26. Nassar MY, Mohamed TY, Ahmed IS, Samir I. MgO nanostructure via a sol-gel combustion synthesis method using different fuels: an efficient nano-adsorbent for the removal of some anionic textile dyes. Journal of Molecular Liquids. 2017;225:730-40.
27. Goel P, Choudhury N, Chaplot SL. Superionic behavior of lithium oxide Li_2O: a lattice dynamics and molecular dynamics study. Physical Review B. 2004;70(17):174307.
28. Keen DA. Disordering phenomena in superionic conductors. Journal of Physics: Condensed Matter. 2002; 14(32):R819.
29. Faisal M, Khasim S. Ku-band EMI shielding effectiveness and dielectric properties of Polyaniline-Y_2O_3 composites. Polymer Science Series A. 2014; 56:366-72.
30. Papageorgiou DG, Kinloch IA, Young RJ. Graphene/elastomer nanocomposites. Carbon. 2015; 95:460-84.
31. Dhingra M, Shrivastava S, Kumar PS, Annapoorni S. Polyaniline mediated enhancement in band gap emission of Zinc Oxide. Composites Part B: Engineering. 2013;45(1):1515-20.
32. Huang J, Yang T, Kang Y, Wang Y, Wang S. Gas sensing performance of polyaniline/ZnO organic-inorganic hybrids for detecting VOCs at low temperature. Journal of Natural Gas Chemistry. 2011; 20(5):515-9.
33. Zheng H, Ncube NM, Raju K, Mphahlele N, Mathe M. The effect of polyaniline on TiO 2 nanoparticles as anode materials for lithium ion batteries. SpringerPlus. 2016; 5:1-6.
34. Suryanarayana C, Norton MG, Suryanarayana C, Norton MG. X-rays and Diffraction. Springer US; 1998.
35. Li G, Liao X, Sun X, Yu J, He J. Preparation of conductive polypyrrole (PPy) composites under supercritical carbon dioxide conditions. Frontiers of Chemistry in China. 2007 ; 2:118-22.
36. Yasin SF, Zihlif AM, Ragosta G. The electrical behavior of laminated conductive polymer composite at low temperatures. Journal of materials science: Materials in electronics. 2005; 16:63-9.
37. Z. Jin, Y.X. Zhang, F.L. Meng, Y. Jia, T. Luo, X.Y. Yu, J. Wang, J.H. Liu, X.J. Huang, Facile synthesis of porous single crystalline ZnO nanoplates and their application in photocatalytic reduction of Cr(VI) in the presence of phenol, J. Hazard Mater. 276 (2014) 400–407.
38. Yadav, M.S., Singh, N. & Bobade, S.M. Zinc oxide nanoparticles and activated charcoal-based nanocomposite electrode for supercapacitor application. Ionics 24, 3611–3630 (2018).
39. Basavaraja C, Kim WJ, Thinh PX, Huh DS. Electrical conductivity studies on water-soluble polypyrrole–graphene oxide composites. Polymer composites. 2011 Dec;32(12):2076-83.

40. Prasad Sunkara, Kesavaulu Masula, Veerasomaiah Puppala, Yadgiri Bhongiri, Vijaykumar Pasala and Manohar Basude, Highly active zinc oxide-supported lithium oxide catalyst for solvent free Knoevenagel Condens, J. Chem. Sci. (2021)133:67.
41. R.Megha,Y.T.Ravikiran,S.C.VijayaKumari,H.G.Prakash,S.Manjunath,M.Revansidappa,M.Prashantkumar,S.Thomas;AC Conductivity studies in copper decorated and Zinc oxide embedded polypyrrole compositesnanoroda :interfacial effects: Material Science in semiconducyor processing Volume110, 104964.
42. Yiqiu Li, Yang Cao, Xiangxin Guo; Influence of lithium oxide additives on densification and ionic conductivity of garnet-type Li6.75La3Zr1.75Ta0.25O12 solid electrolytes, Solid State Ionics 253 (2013) 76–8.

