© 2018 IJSRSET | Volume 4 | Issue 1 | Print ISSN: 2395-1990 | Online ISSN : 2394-4099
Themed Section : Engineering and Technology

Study of DC Conductivity of Polypyrrole doped with SnO_2 Nanocomposites

R M Agrawal*[1], T S Wasnik[2] , K B Raulkar[2] , G T Lamdhade[2]

[1]Department of Physics, Shri RLT College of Science, Civil Lines Road, Akola, Maharashtra, India

[2]Department of Physics, Vidyabharti Mahavidyalaya, C. K. Naidu Road, Amravati, Maharashtra, India

ABSTRACT

The nanocomposites of PPy-SnO_2 were prepared by chemical oxidative polymerization technique using an anhydrous ferric chloride ($FeCl_3$) as an oxidizing agent and it was characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), Fourier transform infrared (FTIR). The samples are prepared in the form of thick films by screen printing method. The effect of temperature on DC conductivity of the samples has been measured and the conductivity of sample PS3 (60 % PPy + 40 % SnO_2) was found to be maximum amongst all the prepared samples. Activation energy was found to be 0.1062 eV.

Keywords: PPy-SnO_2 nanocomposites, DC conductivity.

I. INTRODUCTION

Recently, the conducting polymers are important materials emerging with lot of applications in various fields. To improve the quality and applicability the research in the field of such polymers with some modification of existing polymers has been carried out. Some of these modifications involve preparing hybrid materials in which organic materials and inorganic oxides or salts of different metals, viz. SnO_2, ZnO, MgO etc. [1]. The most widely studied conducting polymers are polypyrrole, polyaniline, polythiophene etc. Additionally, PANI can coordinate with metal ions, giving the multi-metallic system and also preparation of nanocomposite materials with other polymers. PPy is one of the most interesting conducting polymers since it is easily deposited from aqueous and non-aqueous media, very adherent to many types of substrates, and is well-conducting and stable. Electrochemical polymerization produces thin films with a thickness of few micrometers on an electrode surface, while a chemical oxidation yields fine-grained materials [2-4]. 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 [5-8].

The present study deals with the synthesis & characterization of PPy/SnO_2 composites and evaluation of dc conductivity for different wt. % of SnO_2 in PPy nanocomposites with an intention to know the effect of SnO_2 doping. The characterization of the composites has been done by SEM analysis techniques.

II. EXPERIMENTAL

A. Synthesis of SnO_2 nanoparticles.

All the chemicals used in this study were of GR grade purchased from Sd-fine, India (purity 99.99%). In preparation of SnO_2, 2g (0.1 M) of stannous chloride dehydrate ($SnCl_2.2H_2O$) is dissolved in 100 ml water. After complete dissolution, about 4 ml ammonia solution is added to above aqueous solution with magnetic stirring. Stirring is continued for 20 minutes. White gel precipitate is immediately formed.

It is allowed to settle for 12 h. Then it is filtered and washed with water 2-3 times by using de-ionized water. The obtained precipitate were mixed with 0.27g carbon black powder (charcoal activated). The obtained mixer is kept in vacuum oven at 70ºC for 24 h to obtain a dried powder. Then this dry product was crushed into a fine powder by grinder. Now the obtained product of fine nanopowder of SnO_2 was calcinated at 700ºC up to 6 h in the auto-controlled muffle furnace (Gayatri Scientific, Mumbai, India.) so that the impurities from products will be completely removed.

B. Synthesis of Polypyrole (PPy)

The Py monomer, anhydrous iron (III) chloride ($FeCl_3$) and methanol were used as received for synthesis of PPy. The solution of 7 ml methanol and 1.892 g $FeCl_3$ was first prepared in round bottom flask. Then 8.4 ml Py monomer was added to ($FeCl_3$ + methanol) solution with constant stirring in absence of light. The amount of Py monomer added to the solution (1/2.33 times of $FeCl_3$) was in such a way to get maximum yield. The resulting black precipitates are filtered and washed with copious amount of distilled water until the washings are clear. PPy so obtained is dried by keeping in oven at 600ºC for 3 h. The synthesized material was characterized by using XRD, SEM.

C. Preparations of films

The thick films were prepared by using screen printing techniques. Initially, for the screen printing the thixotropic paste was formulated by mixing the sintered fine powder of pure and composite nano powder of SnO_2 and PPy in different weight percentage with a solution of ethyl cellulose (as 10% temporary binder) in a mixture of organic solvent such as butyl cellulose, butyl carbitol acetate and turpineol. The ratio of inorganic to organic part was kept as 75:25 in formulating the paste. The paste was then used to prepare thick films of pure and composite materials of SnO_2 and PPy and it was screen printed on a glass substrate. The prepared films were dried at 90-100ºC in oven for 1 h, so that all the organic materials (in the form of binders) and organic impurities can be evaporated from prepared films. For the surface conductance measurement, the electrodes of silver paint were formed on adjacent sides of the films and again, the films were subjected to heating at 70ºC for 15 minutes for drying the silver paint. The series of samples are as shown in table 1.

Table 1

S.N.	Nano composites	Sample Code
1.	Pure Polypyrrole	P
2.	80 % PPy + 20 % SnO_2	PS1
3.	70 % PPy + 30 % SnO_2	PS2
4.	60 % PPy + 40 % SnO_2	PS3
5.	50 % PPy + 50 % SnO_2	PS4
6.	40 % PPy + 60 % SnO_2	PS5
7.	30 % PPy + 70 % SnO_2	PS6
8.	20 % PPy + 80 % SnO_2	PS7
9.	Pure SnO_2	S

III. RESULTS AND DISCUSSION

A. XRD (X-ray Diffraction)

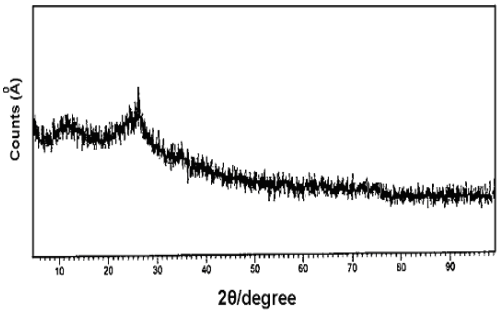

Figure. 1. XRD of pure PPy

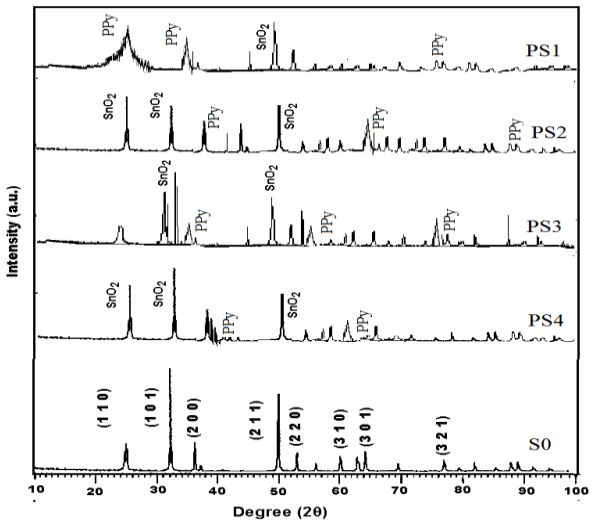

Figure.2. XRD of all composites sample

X-Ray diffraction pattern of pure polypyrrole (PPy) and their composites are as shown in figure (1 and 2). The pure PPy exhibited that, it was amorphous in nature. The broad peak occurred at 24^0 and it is characteristics of amorphous nature of polypyrrole. The broad peak occurs due to the scattering of X-rays from polymer chains at the interplaner spacing. The maximum intensity position of amorphous also depends on monomer to oxidant ratio. The X-ray diffraction patterns of composites of PPy, SnO_2 and pure SnO_2, calcinated at 200°C. Main peak, in case of pure SnO_2, is observed at 26.6° and this peak corresponds to the plane (1 1 0) of SnO_2 in tetragonal structure (JCPDS Card No.3-1114) with 100% intensity and the average crystalline size by using Scherer's formula was found to be 147.31 nm [9,10]. All the peaks are for the composites materials for molar weight percentage of various samples that are perfectly matched.

B. Scanning Electron Microscope (SEM)

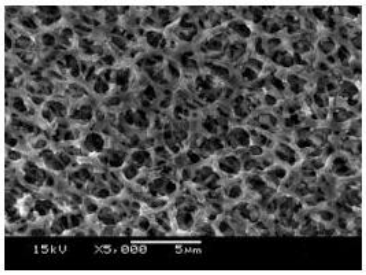

Figure. 3. SEM of Pure PPy

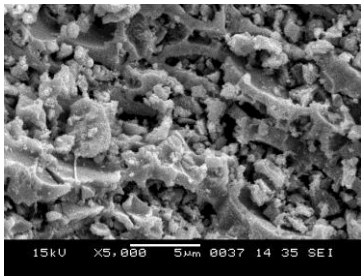

Figure. 4. SEM of PS3

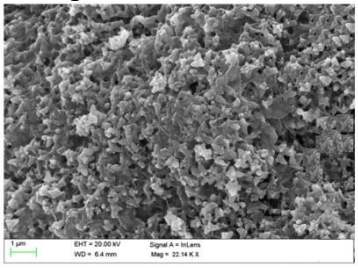

Figure. 5. SEM of Pure SnO_2

From the SEM photos, it is observed that in every inch of the region, number of pores was different and an average number of pores was taken for comparative study. From every photo, porosity was calculated for one inch region and listed in the tabular form. From above figures, it is found that number of porosity of 60PPy:40SnO_2 composition is more among the prepared and pure samples. Due to high porosity, available area for the flow of ions and charges is more and conductivity enhances. High porosity reduces the obstacle to the flow of charges and ions as collisions reduce (relaxation time increases) and charges mobility increases. This tends to high electrical conductivity.

C. DC Conductivity

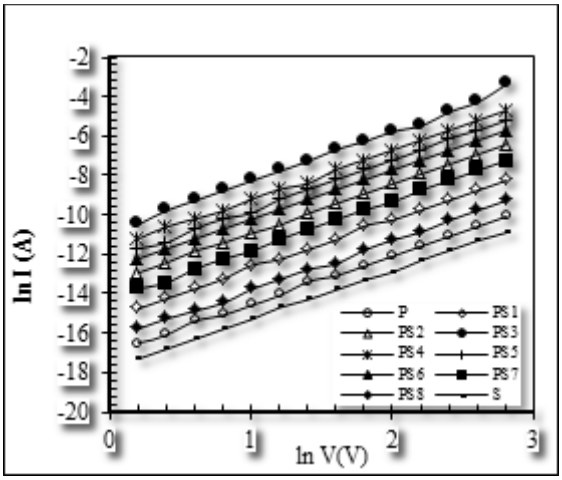

Figure. 6. DC conductivity of samples

The graph is plotted between lnI versus lnV at a constant temperature as shown in figure 6. As the doping percentage of SnO_2 in PPy increases, there is increases current with increase in voltage. It is maximum for PS3 sample (60%PPy + 40 % SnO_2) amongst the prepared samples. It is also manifested that, the nature of all the graphs is nearly straight line with constant slopes i.e. it obeys Ohm's law at temperature range 50°C to 350°C (linear ohmic material) on logarithmic scale [11].

D. Schottky Plots

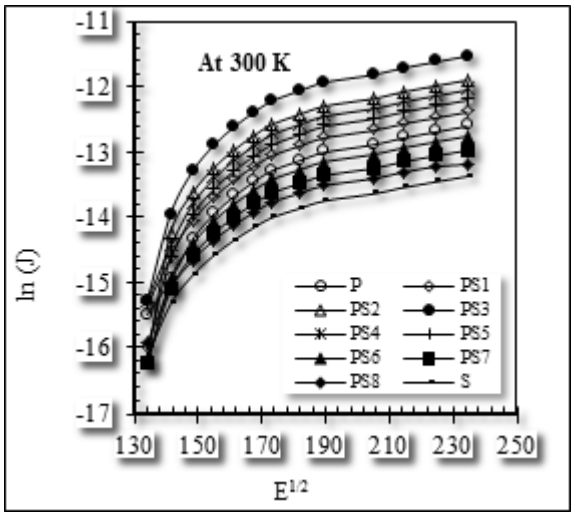

Figure. 7. Graph between Conductivity and $E^{1/2}$ at constant temperature

Then graphs are plotted between ln(J) and $E^{1/2}$ at temperatures 300 K, These graphs are known as Schottky Plots as shown in figure 7. It is observed that as electric field increases, current density increases more in the beginning and then shows saturation. Also ln(J) is maximum for PS3 sample, at constant temperature ln(J) increases. This also shows that with increase in doping of SnO_2 in PPy, ln(J) increases and becomes maximum for PS3. For sample PS3 the current density is $J = 9.8835 \times 10^{-6}$ A/m^2 which is minimum at temperature 300 K (room temperature).

E. Arrhenius Plot

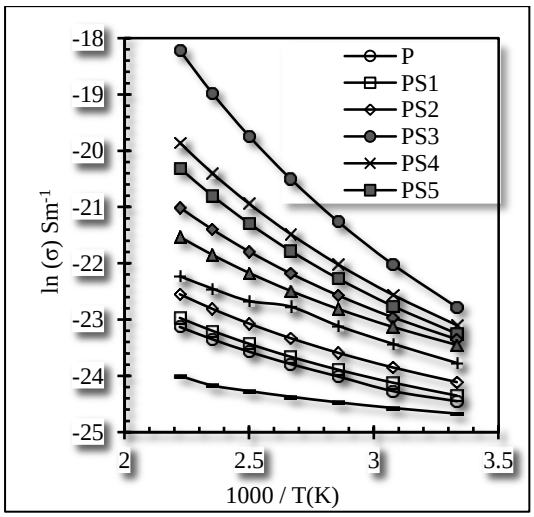

Figure. 8. Variation between ln(σ) and 1000/T(K) of all samples

The graph between ln(σ) and 1000/T(in K) is known as Arrhenius plot as shown in figure 8. It is observed that as temperature increases, ln(σ) increases. This variation is maximum for sample PS3. Due to increase of temperature, more and more charges in samples become free and contribute to the conductivity and electrical conductivity increases. As doping of SnO_2 in PPy increases, electrical conductivity increases and becomes maximum for 60%PPy + 40% SnO_2 sample (PS3 sample) and further increase in doping of SnO_2 in PPy, conductivity decreases. The value of activation energy of sample PS3 was found to be 0.1062 eV which is maximum among all the samples.

IV. CONCLUSION

The X-ray diffraction patterns of composites of PPy, SnO_2 and pure SnO_2, and it shows tetragonal structure and the average crystalline size is found to be 147.31 nm. The current–voltage (I–V) characteristics of the samples and its temperature dependence have been investigated in air at temperature 350°C. The linear nature of plots shows the semiconducting behavior and obeys Ohm's law and it is maximum for sample PS3. The value of activation energy of sample PS3 was found to be 0.1062 eV which is maximum among all the samples.

V. REFERENCES

[1]. A Bhattacharya, M. Ganguly, A De, S. Sarkar, , 1996, A new conducting nanocomposite-PPy-zirconium (IV) oxide, ,Materials Research Bulletin, vol. 31 (5), pp. 527 -530.

[2]. X Luo, A. Killard, M Smyth, 2007, Nanocomposite and Nanoporous Polyaniline , Conducting Polymers Exhibit Enhanced Catalysis of Nitrite Reduction, J. Chemistry-A European Journal, vol. 13 (7), pp. 2138 - 2143.

[3]. M Deepa, S Ahmad, K Sood, J Alam, S Ahmad, A Srivastava , 2007, Electrochromic properties of polyaniline thin film nanostructures derived from solutions of ionic

liquid/polyethylene glycol, J. Electrochimica Acta , vol. 52 (26), pp.7453 – 7463.

[4]. L Yang, Z Yang, W Cao , 2005,Fabrication of Stable Chiral Polyaniline Nanocomposite-Based Patterns, J. Macromolecular Rapid Communications, vol. 26(3), pp. 192 – 195.

[5]. G Dione, M Dieng, J Aaron, H Cachet, C. Cachet, 2007, "New composite electrodes made of polypyrrole and graphite: Construction, optimization and characterization" J. Power Sources , vol. 170, pp. 441-449.

[6]. K Ryu, Y Lee, K Han, M Kim, 2004 "The electrochemical performance of polythiophene synthesized by chemical method as the polymer battery electrode" , J. Mater. Chem. Phys., vol. 84, pp.380-384.

[7]. J Zang, S Bao, C Li, H Bian, X Cui, Q Bao, C Sun, J Guo, K Lian, , 2008, "Well-Aligned Cone- Shaped Nanostructure of Polypyrrole/RuO2 and Its Electrochemical Supercapacitor" J. Phys.Chem. C, vol. 112, pp. 14843-14847.

[8]. K Jurewicz, S Delpeux, V Bertagna, F Beguin, E Frackowiak, 2001, "Supercapacitors from nanotubes / polypyrrole composites" J. Chem. Phys. Lett., vol. 347, pp. 36-40.

[9]. K Persaud, 2005, Polymers for chemical sensing. Materials Today, vol. 8(4), 38-44.

[10]. Y Lu, G Shi, C Li, Y Liang, 1998, Thin polypyrrole films prepared by chemical oxidative polymerization, Journal of Applied Polymer Science, vol. 70 (11), pp. 2169 – 2172,.

[11]. B Josephine, V Jeseeentharani, V Teresita ,S Antony, 2013, "A Novel Nano Structured LaCaxCr1- xO3-δ for humidity sensors", International Journal of science and research (IJSR), vol. 2 (7), pp. 1691 -1701.