International Journal of Scientific Research in Science and Technology
Print ISSN: 2395-6011 | Online ISSN: 2395-602X (www.ijsrst.com)
© 2021 | IJSRST | Volume 8 - Issue 1

Novel Synthesis and Characterization of PANi/ Sodium Superoxide Composites

R. V. Barde*[1], S. A. Waghuley[2]
[1*]Department of Physics, Govt. Vidarbha Inatitute of Science and Humanities, Amravati, India.
[2]Department of Physics, SantGadge Baba Amravati University, Amravati, India.

ABSTRACT
The sodium superoxide was prepared by heating sodium nitrate (NaNO3) in an oxygen-rich environment in a single step process. Using the Ex-situ technique the PANi/ NaO2 composites were prepared range from 5-20 w t %. The crystallinity and structure morphology of the samples were characterized by X-ray diffraction, Scanning electron microscopy. The peak positions appear in XRD pattern of as prepared Sodium superoxide exactly index to NaO2. The peaks of NaO2 are seen in XRD of PANi/a NaO2 composite suggests that NaO2 is present in the PANi matrix. The scanning electron microscope (SEM) shows that sample exhibit an irregular granular morphology.We investigate the DC conductivity of PANi/ NaO2 composites.Activation energy (EDC) is obtain from Arrhenius plots of temperature-dependent DC conductivity, and it is found to be 0.56 eV for 20 wt. % of NaO2.

Keywords : Superoxide, DC Conductivity, Arrhenius Plots.

I. INTRODUCTION

Conducting polymer has been broadly studied because of its various applications in gas sensors [1], batteries [2], light emitting diodes [3], solar cells. Polyaniline (PANi) is the most prominent polymer amongst the various polymers due to its unique properties like electrical properties, easy for synthesis, environmental stability, intrinsic redox reaction etc.[4] and various applications like rechargeable batteries [5], photovoltaic cell [6]. Polyaniline study shows that its chemical and physical properties mainly depend on the method of the preparation and the composition of the solution [7].The preferable formation of sodium superoxide (NaO_2) at the oxygen side is due to the transport limitation of gaseous oxygen through the electrolyte-filled cathode structure [8].It is known that, the sodium superoxide (NaO_2) can be formed as a stable and solid compound. One of the most convenient and delicate methods for studying the polymer structure is electrical properties.

Interest has arisen in organic and polymeric semiconductors, particularly because of their electro-photographic and solar cells applications. Many synthetic polymers like polyacetylene, polypyrrole, poly-carbazolete have been studied [9].

In this work, we synthesized PANi by using chemical route. The composite of PANi/NaO_2 was prepared by ex-situ approach. The as prepared samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscope (SEM).The DC electrical

conductivity is measured by using two probe techniques.

II. METHODS AND MATERIAL

PANi was chemically synthesized at room temperature by oxidative polymerization method. The suitable quantity of ammonium persulfate (1M) was dissolved in de-ionized water and subsequently kept for the magnetic stirring for 1 h. The aniline monomer was added in ammonium persufate solution in drop wise manner under constant magnetic stirring for 2h. The resultant product appears greenish black. The product was washed and filtered until it become colorless and dried it at 45 °C in an oven for 12 hr. The sodium superoxide was prepared by heating sodium nitrate in an oxygen-rich atmosphere using a single-step process. The PANi/ NaO_2 composites were prepared in wt. % stichometry by organic media using Ex-situ technique. The composites preparation range was fixed from 5-20 wt. %. The structural characterization of the samples performed by using Bruker D8 advance with Cu Kα radiation (λ = 1.5406A˚) is used to identify structure and phase purity of samples at room temperature. The pattern recorded with step height of 0.02º with scan rate 6.00. Scanning electron microscopy (SEM) was used for the determination of microstructure characterization by using JEOL Model JSM - 6390LV.In the present work films were fabricated by using screen printing technique. Conducting silver paste was deposited on both ends of thick film and DC electrical measurement of prepared samples was performed using two probe ceramic sample holder in temperature range 303-393 K.

III. RESULTS AND DISCUSSION

XRD Analysis

Fig. 1 shows the XRD pattern of as prepared Sodium superoxide. The peak positions appear in pattern exactly index to NaO_2 according to JCPDS reference card No. 01-077-0207 [10]. The XRD patterns for pure PANi and PANi/NaO_2 composites are shown in fig. 2(a–e), respectively, which shows changes from amorphous to semi-crystalline state. Fig. 2(a) shows the XRD pattern for pure PANi, as PANi is inherently amorphous and hence there are no sharp peaks for pure PANi. The broad diffraction peak is the characteristic peak of the PANi, which can be attributed to the periodicity parallel and perpendicular to the polymer chain respectively [11]. The peaks of NaO_2 are seen in XRD of PANi/NaO_2 composites shown in fig. 2(b-e), along with some other peaks. However, intensity of (200) and (222) peaks are suppressed in the PANi/NaO_2 composites compared to XRD of pure NaO_2. This suggests that NaO_2 is present in the PANi matrix and presence of PANi has influenced the preferred orientation of NaO_2 grains to some extent. However, these peaks are slightly shifted from their respective standard positions, which may be due presence of PANi matrix. The calculated values of d-spacing (D), inter-chain separation (R) and crystallite size (T) corresponding to the highest intense crystalline peak of PANi/NaO_2 composites are mention in Table 1.

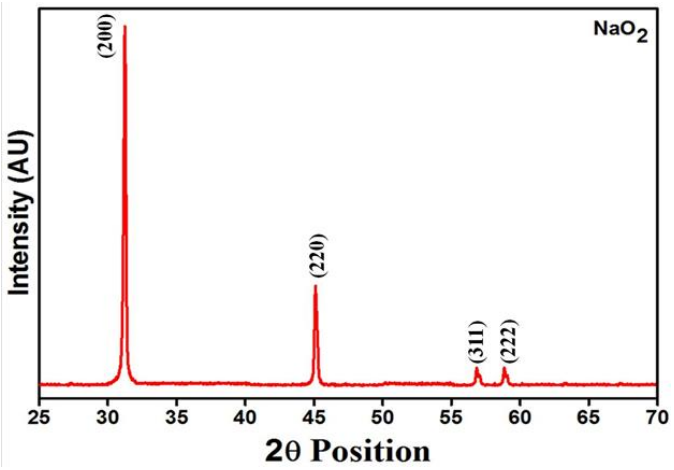

Fig. 1. XRD of Sodium Superoxide (NaO_2).

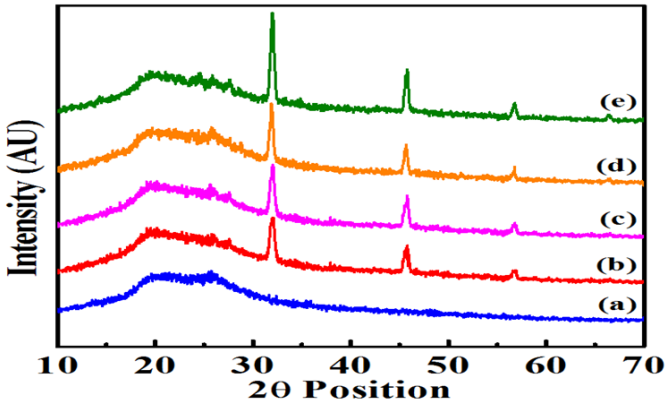

Fig. 2. XRD of (a) Pure PANi, (b) 5 wt. %, (c) 10 wt. %, (d) 15 wt. % and (e) 20 wt. % PANi/NaO_2.

PANI/NaO_2 Sample	D (A°)	R (A°)	T (A°)
5 Wt. %	5.02	3.14	91.80
10 Wt. %	5.18	3.24	107.94
15 Wt. %	6.99	4.37	137.35
20 Wt. %	5.53	3.46	160.95

Table.1. The d-spacing (D), inter-chain separation (R) and crystallite size (T) corresponding to the highest intense crystalline peak of PANi/NaO_2 composites.

SEM Analysis

Fig.3 shows the SEM image of 20wt. % of PANi/ NaO_2. From the image it is observed that, the grains are high agglomerated and good interconnectivity between the particles. Such morphology helps the transportation of charge particles through the carbon back-bone of polymer chains [12]. The entire region of micrograph shows that sample exhibit an irregular granular morphology.

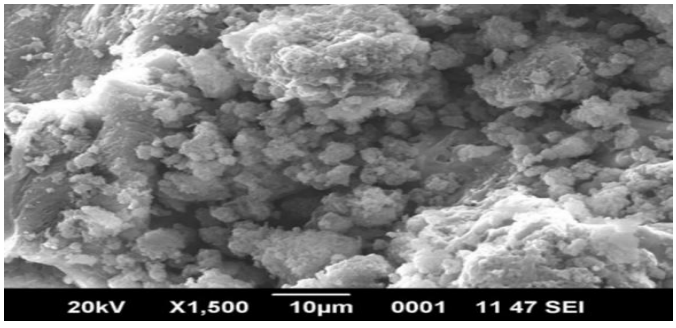

Fig. 3 SEM image of 20 wt. % of PANi/ NaO_2

DC Conductivity

Fig.4 shows a relation for the DC conductivity with temperature for different wt % of NaO_2. These values vary exponentially with temperature. The results show that the temperature-dependent conducting property of PANi, which can be caused by counter-ion mobility, has a positive effect. This is due to the alteration of the PANi/ NaO2 bulk morphology. It is noted that with temperature, the conductivity increases. The reason for the increase in the conductivity is attributed to the thermal energy at higher temperature to excite electrons to the conduction band. Such behavior can be expressed by the Arrhenius equation-[13]

$$\sigma_{DC} = \sigma_0 \exp\left(-\frac{E_{DC}}{KT}\right) \quad (1)$$

Where E_{DC} is the activation energy which is calculated from the least square straight line fitting of plots and listed in table 1and σ_0 is the pre-exponential factor.

The dependence on temperature of the DC electrical conductivity of the composites is similar to semiconducting behavior. The electrical conductivity of these composites increases with temperature in all these composites as the wt % of NaO_2 increases (fig. 5), and this exhibits a thermal electron process and a hopping process. The highest value of conductivity is found to be 1.59×10^{-7} S/cm for 20wt. % of NaO_2.

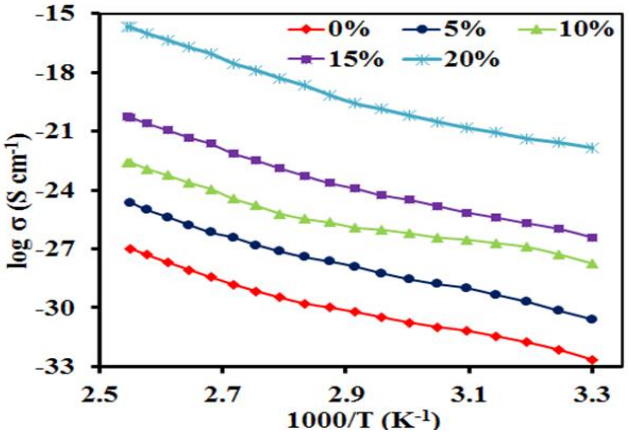

Fig. 4 Plot of DC conductivity of PANi/NaO_2 composites.

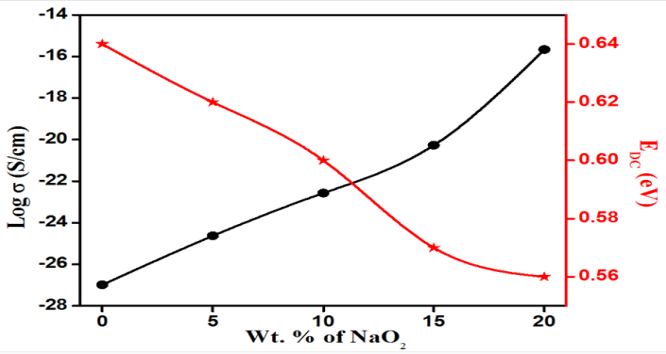

Fig. 5Variation of Log σ and E_{DC} with wt. % of NaO_2.

Table 2 Values of σ_{DC}, E_{DC} and Log σ_0 for PANi/ NaO_2 composites

Samples	σ_{DC} at R.T. (S/cm)	σ_{DC} at 393 K(S/cm)	E_{DC} (eV)	Log σ_0
0 wt. %	2.98×10^{-15}	1.9×10^{-12}	0.64	9.56
5 wt. %	1.2×10^{-13}	2.01×10^{-11}	0.62	6.05
10 wt. %	9.4×10^{-13}	1.3×10^{-10}	0.60	6.54
15 wt. %	6.5×10^{-12}	2.4×10^{-9}	0.57	0.22
20 wt. %	8.9×10^{-10}	1.59×10^{-7}	0.56	5.84

IV.CONCLUSION

The sodium superoxide was prepared by heating sodium nitrate (NaNO3) in an oxygen-rich environment in a single step process. Using the Ex-situ technique PANi/ NaO2 composites were prepared range from 5-20 wt %, with the interval of 5 wt. %. The peak positions appear in XRD pattern of as prepared Sodium superoxide exactly index to NaO_2. The peaks of NaO_2 are seen in XRD of PANi/NaO_2 composites suggests that NaO_2 is present in the PANi matrix and presence of PANi has influenced the preferred orientation of NaO_2 grains to some extent. The entire region of SEM shows that sample exhibit an irregular granular morphology. The DC conductivity shows Arrhenius-type temperature dependence. The electrical conductivity of these composites increases with temperature in all these composites as the wt. % of NaO_2 concentration is increased, and this exhibits a thermal electron process and a hopping process. ***The maximum value of conductivity and minimum value of*** activation energy ***are found to be in the range of*** 1.59×10^{-7} S/cm and 0.56 eV for 20 wt. % of NaO_2 ***at 393 K respectively.***

V. REFERENCES

[1]. H. Bai, G. Shi, Sensors, 7 (2007) 267-307.

[2]. Y. Chen, S. Zeng, J. Qian, Y. Wang, Y. Cao, H. Yang, X. Ai, ACS Appl. Mater. Interfaces, 6 (5) (2014) 3508-3512.

[3]. M. Kim, Y. S. Lee, Y. C. Kim, M. S. Choi, J. Y. Lee, Synth. Met., 161 (2011) 2318-2322

[4]. K.Gupta, P.C.Jana, A.K.Meikap, Synth. Met., 160 (2010) 1566-1573.

[5]. B.C.Dalai, I.N.Basmallick, S.Gosh, Indian J. of Chem. Tech., 15 (2008) 576-580.

[6]. S. Sonmezoglu, R. Tas, S. Akin, M. Can, App. Phys. Lett., 101 (2012) 253301

[7]. A. Rahy, D.J. Yang, Mater. Lett. 62 (2008) 4311-4314.

[8]. P. Hartmann, C. L. Bender, M.Vracar, A.K.Durr, A.Garsuch, J.Janek, P. Adelhelm, , Nature Mater., (2012) DOI: 10.1038/NMAT3486.

[9]. S.H.Deshmukh, D.K.Burghate, V.P.Akhare, V.S.Deogaonkar, P.T.Deshmukh, M.S.Deshmukh, Bull. Mater. Sci., 30(1) (2007) 51-56.

[10]. R. V. Barde, Preparation, characterization and CO2 gas sensitivity of Polyaniline doped with Sodium Superoxide (NaO2), Materials Research Bulletin, 73 (2016) 70–76.

[11]. S. Sultana, M. Z. Khan, K. Umar, M. Muneer, Electrical, Thermal, Photocatalytic and Antibacterial Studies of Metallic Oxide Nanocomposite Doped Polyaniline, J. Mater. Sci. Technol., 29(9) (2013) 795-800.

[12]. V.B. Chanshetty, K. Sangshetty, G. Sharanappa, Inter. J. Eng. Res. and Appl. 2 (2012) 611-616.

[13]. R. V. Barde, S. A. Waghuley, Transport and physical properties of V2O5–P2O5–B2O3 glasses doped with Dy2O3, J. Adv. Ceram., 2(3) (2013) 246–251.