Volume : 2 | Issue : 4 | Apr 2013 • ISSN No 2277 - 8179

Research Paper

AC Conductivity study of Polyaniline – CeO_2 Composites

Physics

KEYWORDS : ac conductivity, AC Conductivity, Polyaniline, CeO_2

Sangshetty Kalyane Department of Physics, BKIT Bhalki ,Karnataka India-585328

ABSTRACT

Insitu polymerization of aniline was carried out in the presence of CeO2 to synthesize Polyaniline - CeO2 composites by chemical oxidation method. The PANI/ CeO2 composites have been synthesized with various compositions viz., 10, 20, 30, 40 and 50 Wt. % of CeO2 in PANI. The AC conductivity was studied in the frequency range 102–107 Hz at room temperature. It is observed that, ac conductivity is maximum for 40wt% of CeO2 in PANI. The dimensions of CeO2 particles in the matrix have a greater influence on the conductivity values.

1. Introduction

In recent years electrical and optical properties of conducting polymers synthesized by electrochemical polymerization have been studied in great detail. Considerable attention has been paid to the polymers of five membered heterocycles such as Polyaniline, polythiophene and polyacetalene, since they can substitute for conductors and semiconductors in a wide variety of electric and electronic devices. The features of conducting polymers such as reversibility, availability in film form and good environmental stability enhance their potential use for practical applications. One of the most widely studied conducting polymers. polyaniline, can be obtained chemically or electrochemically. The electrochemical polymerization of PANI has been extensively studied as it is easily obtained in the form of free standing films, and has good environmental stability and conductivity.

The electrical transport in polymeric materials [16-17] has become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices. Conducting polymer composites with some suitable compositions of one or more insulating materials led to desirable properties. These materials are especially important owing to their bridging role between the world of conducting polymers and that of nanoparticles. For application of conducting polymers, knowing how these conducting polymers composite will affect the behavior in an electric field is a long – standing problem of great importance. The discovery of doping in conducting polymer has led to further dramatic increase in the conductivity of such conjugated polymers to values as high as 105 S Cm-1.

2. Experimental

2.1.Materials and Methods

Ammonium persulphate (NH4)2S2O8, Hydrochloric acid (HCl) and Cerium oxide (CeO2) used were of AR grade. Doubly distilled water and aniline is used as a solvent and a monomer. Polyaniline is prepared by oxidative method and Polyaniline composites were prepared by insitu polymerization method with dispersion of CeO2 in polyaniline.

2.2. Synthesis of Polyaniline/ CeO2 Composites

Aniline was dissolved in 1m HCl to form polyaniline (PANI). Cerium oxide was added to PANI solution with vigorous stirring to keep the Cerium oxide suspended in the solution. To this reaction mixture, 0.1M of ammonium persulphate [(NH4)2S2O8], which acts as an oxidant, was added slowly with continuous stirring for 4-6 hours at 0-5OC. The precipitated powder recover was vacuum-filtered and washed with deionizer water. Finally, the resultant precipitate was dried in an oven for 24 hours to achieve a constant weight. In the similar manner pure PANI is prepared without adding Cerium oxide.

PANI/ CeO2 composites were prepared in weight percent ratio in which the concentration of dysprosium oxide (10, 20, 30, 40 and 50%) was varied. The test samples to be used were prepared in pellet form of diameter 10mm and thickness 3mm by applying pressure of 7t using Pye-Unicam dye. The contacts for these composites were made using silver paste as electrodes on both sides.

AC conductivity measurements were carried out at room temperature over the frequency range 102-107Hz using the Hiokie LCR Q meter.

3. Results and Discussion

Figure1

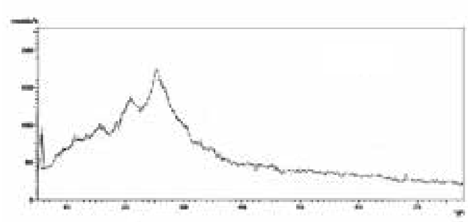

Figure 1(a). X – Ray diffraction pattern of Polyaniline

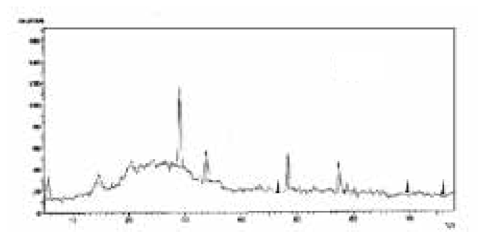

Figure.1(b) X – Ray diffraction pattern of Polyaniline – CeO2 composite (50 wt %)

(a) & (b) shows the X-ray diffraction pattern of Polyaniline and Polyaniline – CeO2 composite with 50 wt % of CeO_2 in polyaniline. It is seen from figure 1 (a) & (b) that the cubic peaks of CeO2 indicates the crystalline nature of the composite. By comparing the XRD pattern of composite with that of CeO_2 (JCPDS No. 34-0394), the prominent peaks corresponding to 2 θ = 26.52 0, 33.51 0 and 59.58 0, are due to (111), (200), and (222) planes of CeO2. By comparing the XRD patterns of the composite and CeO2, it is confirmed that CeO2 has retained its structure even though it is dispersed in PANI during polymerization reaction. The peaks of CeO_2 after doping in PANI, are shifted slightly to higher values and also the peak of PANI at 270 has broadened this is due to dispersion of CeO_2 in PANI.

The IR spectra of pure PANI are shown in Fig. 2(a). The IR spectra of polyaniline – CeO2 composite (50 wt % of CeO2 in PANI) is shown in Fig. 2

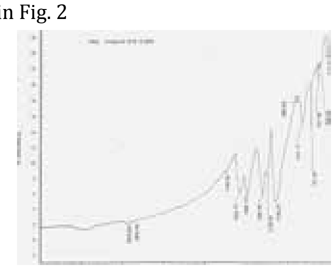

Figure : 2(b) FTIR spectra of PANI – CeO2 composite (50 wt%)

Volume : 2 | Issue : 4 | Apr 2013 • ISSN No 2277 - 8179

(b). The prominent peaks that are observed in polyaniline – CeO2 composite are 3437 cm-1, 2918 cm-1 2844 cm-1 1578 cm-1, 1486 cm-1, 1300 cm-1, 1134 cm-1, 899 cm-1, 831 cm-1, 707 cm-1, 646 cm-1, and 504 cm-1. By careful observation of IR the characteristic stretching frequencies are considerably shifted towards higher frequency side. The typical peaks are observed at 899 cm-1, 831 cm-1 646 cm-1 and 504 cm-1. The data suggest that, there is a Vander walls kind of interaction between the polymer chain and CeO2. This is further supported by the FTIR spectra of polyaniline / CeO_2 under reference.

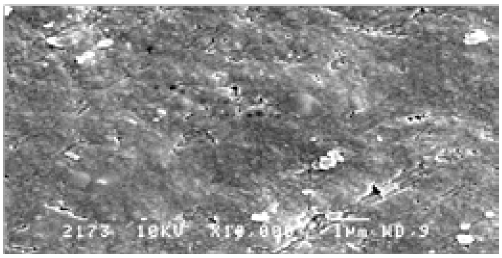

Figure 3(a): SEM Micrograph of Polyaniline

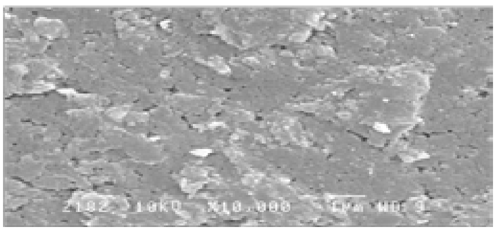

Figure 3(b): SEM Micrograph of Polyaniline CeO2 (50 wt %)

Figure. 3 shows the variation of ac conductivity as a function of frequency for polyaniline – CeO2 composites (different wt %). It is observed that in all the cases, σac remains constant up to around 104 Hz. There after conductivity increases for all the composites at different frequencies. The anomaly in the conductivity behavior of these composites is due to the variation in the distribution of CeO_2 in polyaniline. This behaviour is in agreement with earlier report.

The SEM micrograph of polyaniline & polyaniline – CeO_2 composite with 50 wt % of CeO2 in polyaniline is shown in figure 3.High magnification SEM image reveals the presence of CeO_2 particles uniformly distributed throughout the composite sample. A small variation in the particle dimensions of CeO_2 so dispersed in polyaniline has been observed. Also fibrillar morphology is observed in the composite. The contrast in the image is due to the difference in scattering from different surface areas as a result of geometrical differences between polyaniline and CeO2. Since structure property correlation plays a significant role, a correlation between dimension of CeO_2 used for composite preparation and its effect on electrical properties.

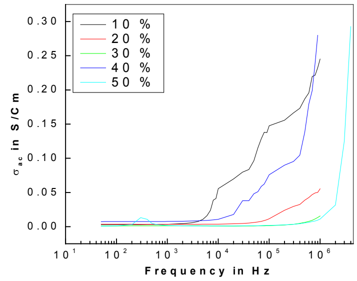

Figure 4(a): Variation of ac conductivity as a function of frequency for Polyaniline CeO_2 Composites

Figure. 4(a). Shows the variation of ac conductivity as a function of frequency for polyaniline – CeO_2 composites (different wt %). It is observed that in all the cases, σac remains constant up to around 104 Hz. There after conductivity increases for all the composites at different frequencies. The anomaly in the conductivity behavior of these composites is due to the variation in the distribution of CeO_2 in polyaniline. This behavior is in agreement with earlier report.

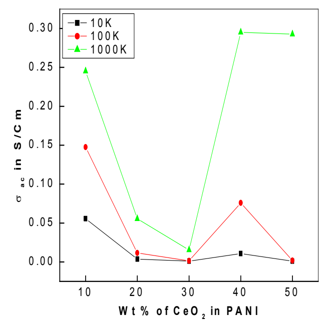

Figure 4(b): Variation of ac conductivity as a function of wt % for Polyaniline CeO2 at different frequencies

Figure. 4(b) shows the variation of σac as a function of wt% of CeO2 in polyaniline at three different frequencies and at room temperature. It is observed that in all the composites the conductivity decreases up to 30wt % of CeO_2 in polyaniline and then increases rapidly for 40 wt % and further decreases. This may be due to the trapping of charge carriers hop up to 30 wt % further increases in conductivity is due to the extended chain length of polyaniline which facilitate the hopping of charge carriers when the content of CeO_2 increases up to 40wt%.

4. Conclusion
Efforts have been made to synthesize PANI/ CeO_2 composites to tailor make their properties. The results of ac conductivity show a strong dependence on the wt. %. of CeO_2 in PANI.

5. Acknowledgement
It is the privilege for the author to express sincere thanks to staff of Physics Department, and Materials Science Department, Gulbarga University, Gulbarga for their kind support in experimental and conductivity measurments.

REFERENCE
1] A.F. Diaz, K.I. Castillo, T.A. Logan, V.Lec, J. Electroanal, Chem 129 (1981) 115. [2] G. Sotzing, J.R. Reynolds, P.J. Chem, Mater, 8 (1996) 882. [3] J.H. Borroughes, D.D.C. Bradley, A.R. Brown, R.N. marks, K.Mackay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature 347 (1990) 539. [4] D. Braun, A.J. Heeger, Appl. Phys. Lett 58 (1991) 1982. [5] F. Larmat, J.R. Reynolds, Synth. Met. 79 (1996) 229. [6] A. Rudge, I. Raistrick, S. Gottesfeld, J.P. Ferraris, Electrochim, dActa 39 (1994) 273. [7] F. Selampinar, L. Toppare, U. Akbulut, T. Yalcin, S. Suzer, Synth, Met 69 (1995) 109. [8] J.J. Miasik, A. Hooper B.C. Totield, J. Chem. Soc. Faraday Trans. 82 (1986) 117. [9] P.N. Bartlett, P.B.M. Archer. S.K. Lingchung, Sensors and Actuators 19 (1989) 125. [10] W. Schuhmann. C. Kranz, J. Huber, H. Wohlschlager, Synth. Met. 61 (1993) 31. [11] W. Schumann. Synth. Met. 41-43 (1991) 429. [12] F. Selampinar, U. Akbulut, M.Y. Ozden, L. Toppare, Biomaterials (1997) 64, [13]R. Singh, R.P. Tandon V.S. Panwar, S. Chandra, J. Appl, Phys. 64 (4) (1991) 2504. [14] S. Kivelson, Phys. Rev. Lett 46 (1981) 1344. [15] S.C. Raghavendra, S. Khasim, M. Revanasiddappa, M.V.N. Ambika Prasad, A.B. Kulkarni, Bull. Mater. Sci 26 (7) (2003) 733. [16] K.C. Patil, S.S. Manoharan, D. Gajapathy, in: P. Nicholas (Ed.), Hand Book of Ceramics and Composites, Synthesis and Properties, Vol. 1, Chereminision off Marcel and Pecker, Inc., New York and Basel. 1990, p. 461. [17] A. Goldman, Modern Ferrite Technology, Van Nostrand Reinhold, New YORK, 1990, p. 2. [18] N.W. Grimes, Phys. Tech. 6 (1975) 22. [19] M.V. Murugendrappa, M.V.N. Ambika Prasad, J. Appl. Polym. Sci., 41, (2006) 1364. [20] N.F. Mott E.A. Davis, Electron Process in Non- Linear Materials. [21] M. Raghu S.V. Subramanyam. Phys. Rev. B 43 (1991) 4236. [22] Margolis J M ,Conductive Polymers and Plastics(Chapman and Hall, New York)1989 [23] Friend R H, Conductive Polymers (Oxford)