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Investigation of nonlinear electrical properties of ZnO/PPy nanocomposite and its application as a low-voltage varistor

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ABSTRACT

The present study reports the electrical characteristics of a low voltage ZnO/Polypyrrole nanocomposite varistor which was fabricated as a thin disk based on zinc oxide with different weight percentages of polypyrrole as additive using a cold pressing method. Current-voltage characteristics and nonlinear coefficients of the ZnO/Polypyrrole nanocomposite thin disks were studied in direct current mode. Results showed good varistor behavior of prepared ZnO/Polypyrrole nanocomposite. According to the results, ZnO/Polypyrrole nanocomposite thin disk varistors can be utilized to preserve circuits from 35 V up to 350 V over voltages. I-V characteristics of nanocomposite samples showed that by increasing zinc oxide content from 98.52% to 99.01%, the breakdown voltage of ZnO/Polypyrrole nanocomposite varistor increased whereas its nonlinear coefficient decreased. However, more increase in ZnO content of nanocomposite caused to the reduction of its breakdown voltage and increase of nonlinear coefficient. The results obtained from SEM micrographs indicated that by increasing ZnO content, both the grain numbers and their morphologies are changed which is caused the different effects in the grain boundaries, I-V characteristics, and varistor properties of nanocomposites. As a very important result, in this experimental work, an ideal varistor with sufficient low breakdown voltage and acceptable high nonlinear coefficient was obtained.

1. Introduction

With the rapid development of microelectronic devices, their protection against transient over voltages and the suppression of sudden surge have become more important issues [1,2]. On the other hand for lengthening the service life of devices and decreasing energy expenditure, the necessity of their operation at low voltages is expressed. An effective way to reach this purpose is to use the variable resistors and voltage stabilizers which are named as varistors. Limiting undesirable voltages repeatedly without destroying is the main function of varistors that can be caused by their highly non-linear current-voltage characteristics. The miniaturization of electrical circuits and devices induces the construction and application of low voltage varistor [3]. There are several ways to achieve low voltage varistors which have some advantages as well as some disadvantages. Adding of different additives, decreasing the thickness and increasing the grain size of usual varistors can lead to the production of low voltage varistors with low breakdown voltage, but they may have some disadvantages such as decreasing of absorption energy which can cause damage to the varistor operation [4]. Compositing of the inorganic metal oxide with organic polymers is another method to produce low voltage varistors [5]. In recent years, conducting polymer nanocomposites containing semiconductor nanoparticles have attracted great attention owing to their potential applications in a variety of fields such as electrical and optical devices [6,7]. These materials have both properties of polymers such as easy processing and flexibility as well as desired characteristics of inorganic materials such as high surface to volume ratio and high surface energy [8]. The incorporation and compositing of inherently conducting polymers with semiconductors is a powerful way to improve and enhance the properties of each constituents toward individual components and can cause to synergetic and complementary effects [9]. Different semiconductors have been utilized in the fabrication of composite varistors. Among them, zinc oxide (ZnO) is the most potential material due to its easy synthesis, non-toxicity, good environmental friendly features. ZnO has wide application potential in diverse areas such as light emitters, gas sensors and solar cells [10,11].

Conducting polymers are π-conjugated materials that display adjustable electrical conductivity, high electron affinity, low energy optical transitions, and low ionization potential. Polypyrrole is one of the most stable members of the conducting polymers that has been

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extensively used in various fields because of its low cost, ease of synthesis, environmental stability, high catalytic activity, and outstanding optical and electrical properties, so it has been subjected to several studies [12–14]. Most of conventional and traditional varistors are in the ceramic form based on zinc oxide. In this state, achieving of a low voltage varistor is difficult because of low permittivity of zinc oxide [15]. As it was mentioned before, one method to attain a low voltage varistor is the preparation of a polymeric varistor by using a conducting polymer. There are a few reports on the construction and application of polymeric composite varistors which have been included by the high concentration of a semiconductor filler [16]. It has been shown that polymer composites such as ZnO-polyaniline/polyvinyl alcohol [5], gallium arsenide-polyaniline/polyethylene [17] and Si-polyaniline/polyethylene [18] can be used as low voltage varistors.

The varistor effect originates from non-ohmic characteristics of current-voltage behavior of semiconductors such as zinc oxide. In general, I-V characteristic of materials is expressed by the empirical relation $I = kV^{\alpha}$ where α is the non-linearity coefficient, which is an important parameter in manufacturing of an ideal varistor, k is a constant of proportionality, I is the current and V is the voltage [19]. The non-ohmic behavior of a ZnO-based varistor arises from its inter-granules junctions. The presence of PPy chains in the grain boundaries of ZnO grains causes to a p-n junction effect which leads to the production of a varistor phenomenon. Different parameters are important in the manufacturing of an ideal varistor such as breakdown voltage, and nonlinear coefficient. The breakdown voltage of a varistor depends on both the numbers of grain boundaries between the electrodes and the average current of the grain boundaries [20,21]. The p-n junction between n-type semiconductor and p-type conducting polymer may play the important role in I-V characteristics of ZnO/conducting polymer varistor. The electric behavior of varistors can be interpreted by their microstructure as a set of back-to-back zener diodes. The present investigation is devoted to the preparation and utilization of the ZnO/PPy nanocomposites in the construction of polymeric nanocomposite varistors. In this paper, the current-voltage characteristics of prepared polymer nanocomposite varistors are studied to evaluate their electrical properties including breakdown voltage, nonlinear coefficient and potential barrier height.

2. Experimental

2.1. Materials

Zinc chloride, pyrrole, 1- metyle- 2 pyrolidone (NMP), $FeCl_3.6H_2O$, methanol, ethanol and sodium hydroxide were purchased from Merck (Germany). Pyrrole monomer (C_4H_5N - Merck) was distilled and stored in the refrigerator dark environment at about 4 °C before use, since it is very sensitive to light and moisture.

2.2. Synthesis of ZnO nanoparticles

Zinc oxide nanoparticles were prepared by a co-precipitation method in which zinc chloride has been used as a parent source for Zn. 1 mol of $ZnCl_2$ was added to 50 mL of distilled water and the solution was stirred vigorously. The pH was adjusted to 10 by the addition of NaOH (1 M) drop wisely. Obtained white milky precipitate confirmed the progress of the reaction. Afterward the solution was dispersed in an ultrasonic bath for 5 h. The precipitate was collected by filtration and washed by mixture of distilled water and ethanol. The white powder was dried in oven at 60 °C for 24 h [22].

2.3. Synthesis of polypyrrole

The polypyrrole was synthesized by chemical polymerization of pyrrole in the presence of $FeCl_3.6H_2O$ as oxidizing agent. For the synthesis, distilled pyrrole monomer was added drop wise to the solution of oxidizing agent while stirring at 0 °C temperature. The monomer to oxidant ratio in polymerization media was 1:1.4. The polymerization progress was visually confirmed by the color change of solution from orange to black. After 5 h, stirring was stopped and the solution was filtered and rinsed by methanol to remove any impurities. The resultant residual was dried under vacuum at room temperature for 24 h and it was kept in a dark place [23,24].

2.4. Synthesis of ZnO/PPy nanocomposites

ZnO/PPy nanocomposite was synthesized by solvent mixing method. Different amounts of ZnO nanoparticles and PPy powder were separately dispersed in variant amounts of NMP as solvent. The dispersion was improved by the application of 30 W power ultrasound for 2 min for both solutions. The stirring of ZnO and PPy solutions was continued for more 1 h using magnetic stirrer. The solutions were mixed and the stirring was completed for 5 h to obtain a completely homogenous mixture. Finally, the ZnO/PPy nanocomposites was filtered and dried in an oven for 24 h at 60 °C. To evaluate the varistor effects and current-voltage response of the prepared ZnO/PPy nanocomposites, the nanocomposites powder was pressed into disks shape pellets with a 10 mm in diameter by 250 μm in thickness at a pressure of 60 MPa at room temperature. The prepared disks were checked for their observable qualities such as thickness uniformity and lack of any cracks by using an optical microscope. The pellets were placed between couple of copper electrodes with a diameter of 5 mm. Then circulating current was measured by applying DC voltage between two copper electrodes.

Furthermore, to determine the particle diameter of samples, the manual microstructure Distance Measurement software (Nahamin Pardazan Asia Co., Iran) was employed. The ultraviolet–visible (UV–Vis) spectra were recorded using a SPECORD 250 spectrophotometer (ANALYTIK JENAAG, Germany). To study the I-V properties of samples, two probe method (the samples are placed between two copper electrodes with the diameter of 6 mm) was utilized.

3. Result and discussion

3.1. Structural characterization

Fig. 1 shows the FTIR spectrum of polypyrrole. The characteristic peak of PPy related to the N-H stretching mode can be seen at 3428 cm^{-1} wavenumber. The peak at 2923 cm^{-1} is related to the stretching vibration mode of C–H bond. The peaks at 1540 cm^{-1} and 1446 cm^{-1} wavenumbers may be related to the C=C stretching vibration modes of the aromatic pyrrole ring vibrations. The peaks at

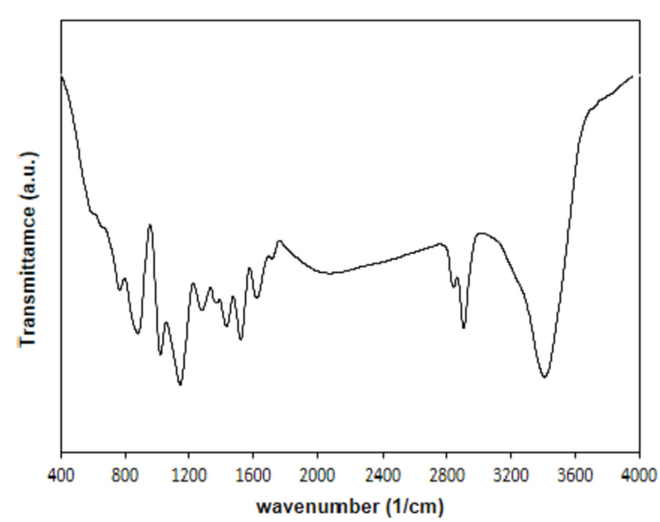

Fig. 1. FTIR spectrum of polypyrrole.