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Temperature dependence of *dc* conductivity in polyaniline-metal halide composites

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Polyaniline (PANI) and its metal halide composites of trivalent metal ions of Ni and Co have been synthesized with various compositions (0, 50, 100 M%) by chemical oxidative polymerization technique with ammonium peroxydisulphate in aqueous hydrochloric acid medium. *I-V* characteristics of these materials at room temperature as well as function of temperature (313-393K) have been studied. The temperature and composition dependence of *dc* conductivity for these materials has been investigated. The dependence of conductivity on temperature is suggestive of the metallic nature of the composites and shows positive temperature coefficient of resistance. The variation of electrical conductivity in the composition shows the lowest conductivity for Co-Ni (50-50) over the values obtained for Ni (100) and Co (100) separately. This interesting result can be explained on the basis of bonding of cobalt and nickel with polyaniline matrix during their polymerization.

Keywords: Polyaniline, Metal halide composites, *dc* Conductivity

IPC code: G01R

1 Introduction

The conducting polymers have emerged as a novel class of materials of current research interest worldwide. They have electrical properties of semiconductors and at the same time, the processing advantages and mechanical parameters of polymers. Among the conducting polymers, polyaniline (PANI) and its derivatives have attracted much interest because of their higher environmental, thermal and chemical stability along with high conductivity[1]. The electrical conductivity of PANI can be influenced both by the oxidation level of main polymer chain and degree of protonation.

Extensive work has been reported in literature about the doping with protonic acid in PANI to improve its electrical conductivity[2]. These studies have established that the macromolecular structural, morphological and electrical properties of PANI are dependent on the nature of dopant ion inserted into the polymer[3]. Although inorganic metal ions bearing negative charge can fulfill the requisites of dopant for PANI, this concept of doping still remains unexploited and studies on this aspect are scarce. The polymer metal composite opens a new field for the development of advance material in science and technology[4]. The doping effect of metal halides of Co and Ni with different molar ratio and their impact on the electrical characteristics of PANI have been investigated.

PANI-metal halide composite of trivalent metal ions of Ni and Co were synthesized by chemical oxidative polymerization. The *I-V* characteristics of these composites at room temperature and also as a function of temperature (313-393K) have been studied.

2 Experimental Details

In the present work, PANI composites doped with Ni and Co were prepared by redox polymerization of aniline using ammonium peroxydisulphate $[(NH_4)_2S_2O_8]$ as an oxidant. For this synthesis, double distilled aniline (.01M) was dissolved in pre-cooled HCl (1M) and metal halide (MX) solution according to stoichiometry. This solution was mixed thoroughly with the help of stirrer for one hour. A calculated amount of ammonium peroxydisulphate (.01M) was dissolved in HCl (1M) pre-cooled to 0°C. Now this aqueous solution of ammonium peroxydisulphate was added to the stirred solution of aniline metal halide solution dissolved in HCl. The temperature of this

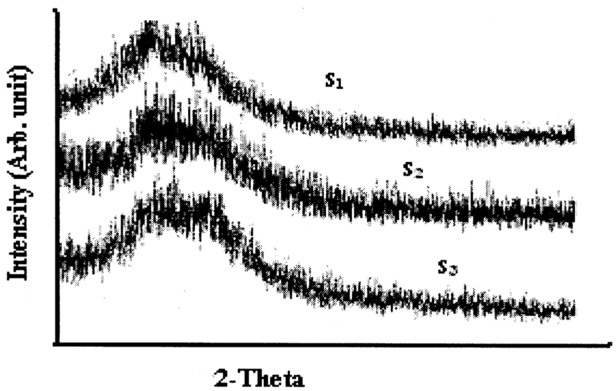

Fig. 1—XRD patterns of all samples.

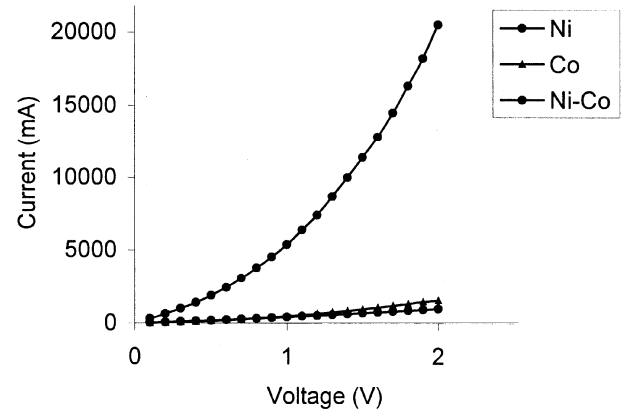

Fig. 2—*I-V* characteristics of different composition at room temperature.

solution was maintained at 3-4°C during mixing time. The dark green precipitate resulting from this reaction was kept in HCl solution for 24 hr. This precipitate was washed in distilled water and methanol until the green colour of filtrate disappears. The precipitate was then dried under dynamic vacuum for obtaining PANI composite in powder form[5]. As a typical preparation, sample S_1 (Co=100 M%) was synthesized by treating the aqueous solution of aniline, hydrochloric acid, and $CoCl_2$ taken according to the stoichiometry[6]. The resulting solution was stirred thoroughly and added to solution of ammonium peroxydisulphate. The precipitated composites were washed repeatedly with distilled water and methanol until the filtrate was colourless and then dried under dynamic vacuum. Similarly, samples S_2 (Co = 50M% and Ni = 50M%) and S_3 (Ni = 100M%) were synthesized using the same procedure by varying the quantities of Co and Ni according to the stoichiometry.

3 Characterization of Sample

X-ray diffraction patterns, as shown in Fig. 1 of all samples were taken at room temperature in order to study the structure of the material. The materials were found to be amorphous in nature with a big hump at low angles (10-30°), which confirms the homogenous nature of the samples.

The polymer composites were ground in a mortar pestle to obtain fine powder form. The pellets of thickness 1 mm and diameter 12 mm were prepared from these powdered materials by a pressure of 5 ton. *I-V* characteristics of the polymer composites were investigated at room temperature as well as in the temperature range (313-393K) for these pellets by Keithley electrometer/high resistance meter 6517A. In order to ensure proper contact between the electrodes and the sample, the pressure contact method was used[7]. Resistances were determined from the *I-V* characteristics at a constant voltage and converted into conductivity data using the dimensions of the pellet.

4 Results and Discussion

The *I-V* characteristics of PANI doped with metal Ni and Co with various compositions (0, 50, 100 M%) is shown in Fig. 2 at room temperature. For all samples S_1, S_2, and S_3, the current increases non-linearly with increasing voltage for low voltage range (0-2V) as shown in Fig. 2. This non-linear increase in current can be explained by the conduction mechanism of doped polymer metal composites. In the doping process, the insertion of metal ions into the conductive polymer system takes place over the bulk volume of the material rather then just at the surface and as a result, a very large amount of charge carriers are produced per unit volume. Also the conduction mechanism in conducting polymers is very different compared to intrinsic semiconductors[8]. Here the negative or positive charges initially added to the polymer chain upon doping do not simply begin to fill the rigid conduction or valence bands. In conducting polymers, there are no permanent dipoles. However, there exists random charge (polaron) trapping in the sample. Under the influence of applied external field, a strong coupling between electrons and phonons causes lattice distortions around the doped charge and hence charge (polaron) trapping results into strong one and their localized (short range) motion serves as an effective electric dipole. This leads to formation of

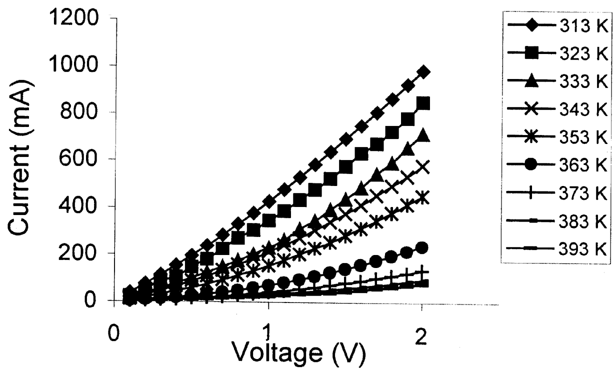

Fig. 3—Temperature dependence of *I-V* characteristics for Ni 100 M%.

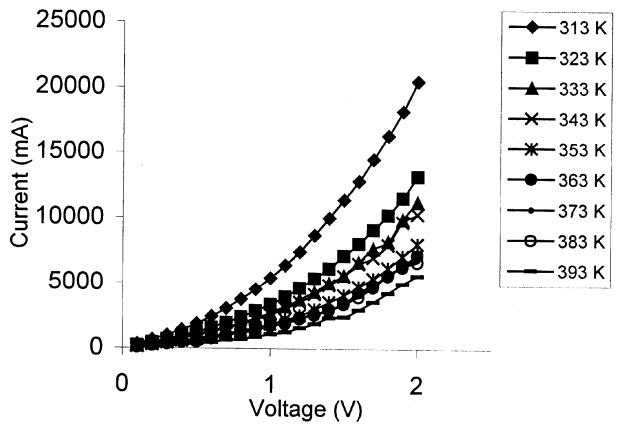

Fig. 4—Temperature dependence of *I-V* characteristics for Ni-Co 50-50 M%.

new quasi-particles such as solitons, polarons and bipolarons[9,10]. Here the charge transport is through these polarons and bipolarons. As the applied field increases the formation of polarons and bipolarons increases which contributes to the rapid increase in current with respect to applied voltage and we get non linear *I-V* curve.

The electrical conductivity is maximum for sample S_3 (Ni = 100 M%) followed by S_1 (Co = 100 M%) and the lowest conductivity is obtained for S_2 (Ni = 50 M%, Co = 50 M%). Electronic configurations of Ni (z = 28) and Co (z = 27) are [Ar]$3d^8 4s^2$ and [Ar] $3d^7 4s^2$. In polyaniline matrix, nitrogen has one pair of electrons and when metal is doped in matrix, a bond formation between metal (Ni and Co) and nitrogen takes place[11]. This bond formation is responsible for the increased value of electrical conductivity of the composites (S_3 and S_1) doped with Ni and Co. Also Ni shows more metallic character than Co hence S_3 is more conductive than S_1. For sample S_2 (Ni=50M%, Co = 50M%), the probability of formation of metallic bond between Ni and Co is much higher than the bond formation between metal (Ni, Co) and nitrogen of PANI matrix. This metallic bond between Ni and Co forms complexes hence the free charge carriers responsible for charge transport are less available in PANI matrix, which results as the lowest conductivity for sample S_2. Figures 3-5 show the temperature dependence of *I-V* characteristics for composites S_1, S_2 and S_3 in temperature range (313-393K).

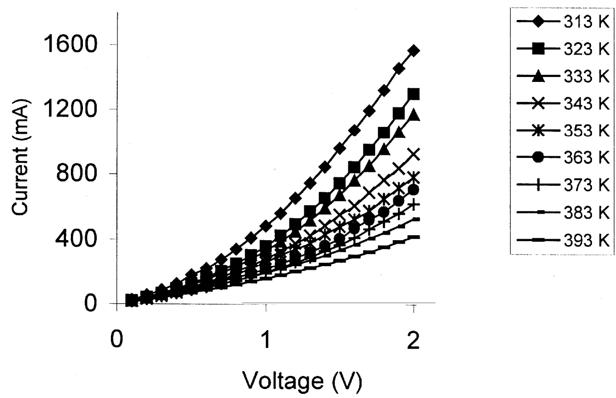

Fig. 5—Temperature dependence of *I-V* characteristics for Co 100 M%.

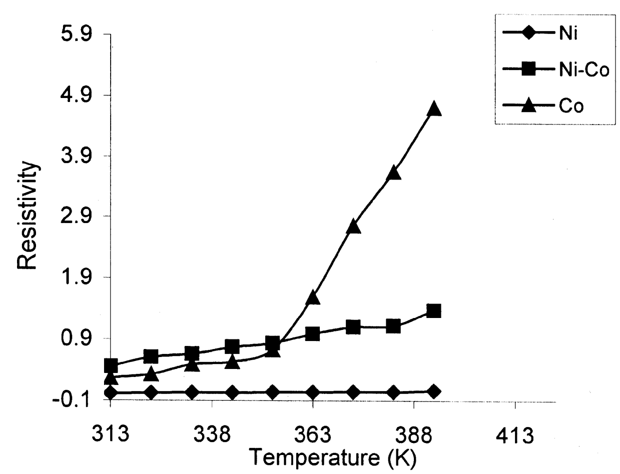

Fig. 6—Temperature dependence of resistivity for different composition.

Figure 6 shows the temperature dependence of resistivity for different composition and at a constant voltage the temperature dependence of these composites is suggestive of metallic nature and show positive temperature coefficient of resistance. This can be attributed to the thermally activated carriers.

At high temperatures, imperfections occur in polymer matrix because of dislocation of ions or ion vacancies in the lattice and due to this defects are always present. As the temperature increases, the free charge carriers associated with metal ion and the thermal vibrations of the sample structure contribute to increase the resistance of the sample.

In PANI-metal halide composites, the bonding between metal ion and nitrogen is not very strong and thermal activation energy due to rise in temperature breaks this bond. Hence, the electron phonon interaction which is responsible for formation of polarons and bipolarons is strongly affected and the number of these charge carriers decreases which is responsible for decrease in conductivity with temperature.

5 Conclusion

PANI composites doped with different concentration of (Co and Ni) were synthesized by chemical method. The *dc* electrical properties of these materials are indicative of metallic nature for PANI composites doped with metal. However, doping of single metal into the conducting polymer increases the conductivity more in comparison to binary doping with two metals.

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