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Variable Range Hopping Mechanism of Electrical Transport in Polyaniline-Succinic Acid Nanocomposite

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ABSTRACT

Polyaniline-succinic acid nanocomposite has been prepared by a simple chemical method. It follows variable range hopping mechanism of electrical transport. A positive magnetoconductivity is obtained and it can be explained with forward interference model of electrical transport.

Keywords: Polyaniline, Succinic acid, Electrical transport

I. Introduction

Nanomaterials have excellent electronic properties and these interesting properties are being used in various electronic devices [1-2]. Nanomaterials of conducting polymers are very interesting in application point of view. Conducting polymers have extended π-conjugation with single- and double-bond alteration along the polymer chain. They are semiconductors with low charge carrier mobility. Conductivity of these polymers can be increased by way of doping [3-4]. It shows interesting tunable properties like electrical, magnetic, optical, and chemical properties. Hence these conducting polymers are widely used in different technological applications like electromagnetic interference (EMI) shielding, rechargeable batteries, electrodes, light emitting diodes, sensors, corrosion protection coatings, and microwave absorption [5-10]. Polyaniline is a conducting polymer which can be used as a dielectric medium. Preparation of polyaniline from aniline, a very cheap monomer, is very simple and its environmental and thermal stability is very good in comparison to other conducting polymers. Its conductivity is also very high compare to others and it exhibits good electrical, optical, magnetic and chemical properties [11-13]. Hence we have taken polyaniline in this investigation.

2. Sample preparation and experimental technique

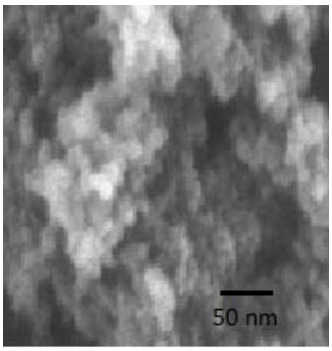
2.1. Synthesis

Aniline (MERCK) has been distilled for two times under reduced pressure to get a colourless distillate. Ammonium peroxodisulphate (APS, MERCK), succinic acid and acetone required for this investigation is taken from local market. We have prepared the sample in a very simple chemical route. Equal volume of 1mM aniline solution is mixed with 1 mM succinic acid solution. Ice cooled 0.5 M APS solution is added drop wise

under continuous magnetic stirring. A green coloured solution is obtained which is left in refrigerator at rest for 24 hours to complete the polymerization process. A solid mass is obtained on centrifugation at 10000 rpm for an hour. It is washed with acetone and double distilled water to remove monomer, oligomers and excess oxidant until the filtrate become colourless. Samples are dried in an oven at 30^0C for overnight. For the comparison purposes we have prepared three samples using 0, 1, 5 and 10 mM succinic acid solution and they are marked as S_0, S_1, S_5 and S_{10} respectively.

2.1. Characterization:
Morphology of samples is obtained by using a Scanning electron microscope (SEM). The phase identification is performed by Rigaku mini-flex-II desktop X-ray diffractometer (XRD) with nickel filter Cu k_α radiation (λ = 1.54 Å) in 2θ range from 20 to 90^0. Standard four-probe method has been used to measure the dc conductivity and it is measured in the temperature range 77≤ T ≤ 300K in presence and absence of magnetic field using pellet of individual samples.

3. Result and discussion
3.1. Structural characterization
Granular morphology is seen from the SEM micrograph of Fig.1. Grains are well resolved and almost circular in shape. Diameter of the grains observed from the micrograph is in the range of 50-60 nm. Room temperature XRD analysis is done to predict the crystal structure. Fig.2 shows XRD pattern. The spectrum shows no characteristic peak excluding a hump near 2θ = 25.5^0 which indicates amorphous nature of polyaniline. No characteristic peak is observed in composite, but increase in intensity is observed.



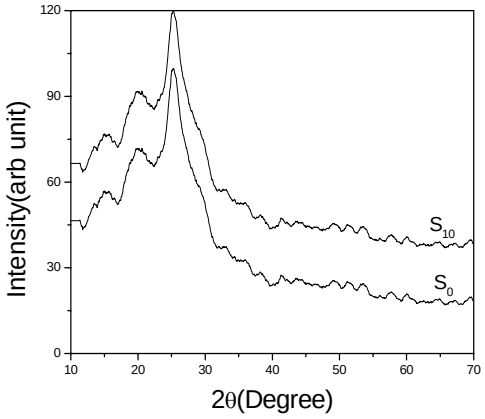


Figure1: SEM micrograph

Figure 2: XRD pattern

3.2. Electrical Transport Mechanism
Direct current resistivity of the samples is investigated within the temperature range 77≤ T ≤ 300K. Room temperature resistivity decreases with doping. Resistivity ratio ρ_r [=ρ(77K)/ρ(300K)] is found to be higher with the in S_{10} and its

value varies in between 29.6 to 1770.0. The increase in efficiency of the charge transfer between the polymer chains and succinate anion with increase in the temperature significantly decreases the resistivity. The variation of resistivity ρ(T) with increasing temperature without magnetic field is shown in Fig.3. All the samples are behaving like a semiconducting material i.e. there is a decrease in resistivity with increasing temperature. In general, the variation of resistivity with temperature can be explained in terms of Mott's variable range hopping theory [14]. According to this theory, resistivity becomes

$$\rho(T) = \rho_0 \exp\left(\frac{T_{Mott}}{T}\right)^{\gamma} \quad (1)$$

where ρ_0 is a constant, $T_{Mott} = \frac{24}{\pi k_B N(E_F) L_{loc}^3}$ is the characteristic Mott temperature which depends on the hopping barrier, electronic structure and energy distribution of the localized states, K_B is the Boltzman constant, $N(E_F)$ is the density of states at the Fermi level and γ is the VRH exponent. The dimensionality of the conducting medium con be obtained by the relation $\gamma = \frac{1}{1+d}$ for three, two and one dimensional system value of γ becomes ¼, 1/3 and ½ respectively. A three dimensional hopping mechanism (γ =¼) is observed from the variation of lnρ with $T^{-1/4}$ in Fig.3, Resistivity of the samples varies linearly with temperature. The value of Mott characteristic temperature (T_{mott}) has been calculated from the slopes of the graph which varies between 2.8 x 10^8 and 3.5 x 10^8 K. The value of T_{mott} is less in case of pure polyaniline than the nanocomposite. As the extent of succinic acid is increased, T_{mott} increases indicating localization of the electronic wave functions into the smaller regions.

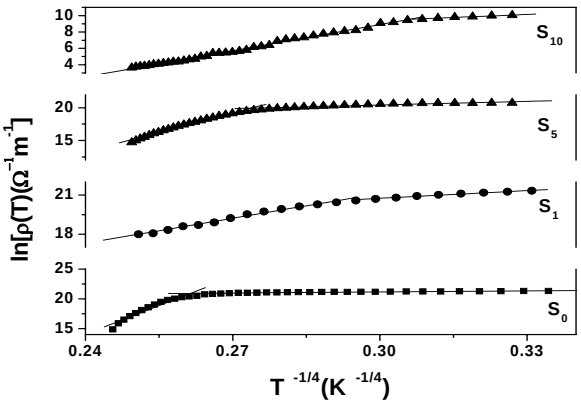


Figure 3: Variation of resistivity with temperature

The variation of the resistivity under a varying magnetic field up to 1Tesla has been investigated within a temperature range of 77≤ T≤300K. Conductivity increases upon increasing the magnetic field. The increase in conductivity under the influence of magnetic field can be thus explained in terms of forward interference model [15-17]. The forward interference among random paths between two sites spaced at a distance equal to optimum hopping distance explains the positive magneto conduction. According to this model, the conductivity ratio σ(B)/σ(0) can be written as.

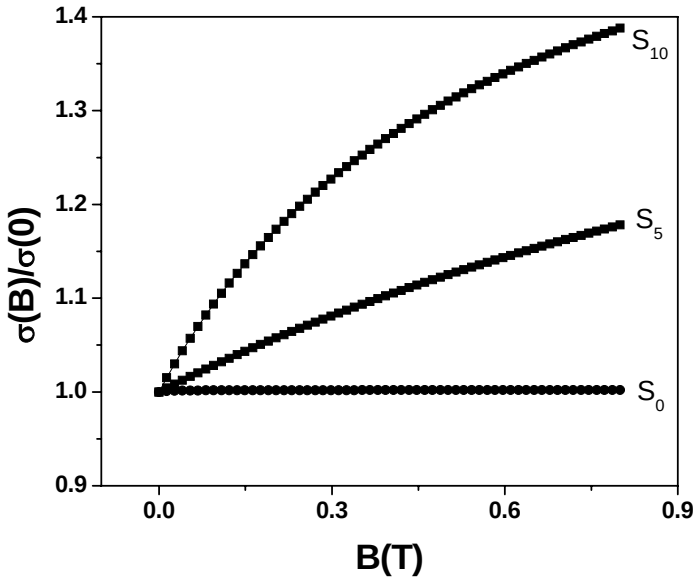


Figure 4: Variation of σ(B)/σ(0) with varying magnetic field

$$\frac{\sigma(B,T)}{\sigma(o/T)} = 1 + \frac{C_{sat} B / B_{sat}}{1 + B / B_{sat}} \qquad (2)$$

where B_{sat}=0.7(h/e) $(8/3)^{3/2}$ $(1/L_{oc}^2)$ $(T/T_{mott})^{3/8}$ and C_{Sat} is a temperature independent parameter. The variation of σ(B,T)/σ(0,T) with varying magnetic field is shown in Fig.4. The different points in Fig.4 are the experimental data, while the solid lines represent the theoretical best fits obtained from Eq.(2), taking C_{sat} and L_{ioc} as the fitting parameters and T_{mott} obtained from Eq.(1). The value of L_{loc} at different temperatures varies from 10 nm to 25 nm. All the samples are behaving in a similar manner. From the relation R_{hop}=(3/8) $(T/T_{moH})^{1/4}L_{ioc}$ average hopping length is calculated for different samples which varies from 0.05 nm to 0.3 nm. With increasing temperature, the average hopping length increases due to

which, there is an enhancement of magnetoconductivity with increasing temperature.

4. Conclusion

The dc conductivity of all the samples follows a simple 3-dimensional hopping type of charge conduction mechanism. The dc magnetoconductivity of all the samples were positive at room temperature and can be explained in terms of orbital magnetoconductivity model.

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