Journal of Materials and Electronic Devices 3 (2024) 42-45

A simple test for the occurrence of the 1D- variable hopping conduction mechanism (VRH) in semiconducting polymers

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Semiconducting polymers have unusually strong temperature of dependence of electrical conductivity. It is evaluated that this strong temperature dependence is due to one-dimensional variable hopping conductivity (1D-VRH) in the conducting polymers. The VRH depends on chemical structure of polymer studied and hopping is formed by the one or three dimensional diffusion between intermolecules in polymers. The experimental data obtained from dielectric constant supports the 1D-VRH theory, i.e. the fact that the dielectric constant increases linearly with increasing temperature is evidence for VRH.

Keywords: *Conducting polymer, hopping conductivity, transport*

Submission Date: 29 July 2024
Acceptance Date: 31 August 2024

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1. Introduction

Electrically conducting polymers, recently described by the Nobel Laureate Alan J.Heeger as the ‘fourth generation of polymeric materials, have provided an alternative to traditional intrinsically conducting materials such as carbon black and metallic particulates [1]. Conductive polymers possess a wide range of electrical conductivity values from insulating to highly conducting. The conducting polymers are candidate materials for applications in the fields such electronic and optical devices [2-9]. It is important to determine conduction mechanism of conducting polymers. However, with significant advances in conductivity, in the point of view that the transition of charge between chains of polymers is essential in the transport. Charge carriers preferably tunneling or hopping along the molecules because of good overlapping may be suggested. In the charge transport mechanism, there are two basic models such as intermolecular and intramolecular conduction processes. The intramolecular process between chains may be provided hopping conduction and this process is characterized low and high activation energy for conduction. Such a system remains essentially 1D as long as the intermolecular conduction is weaker intramolecular conduction process. The movement of charge carriers in conducting polymers occurs via jumps among one-dimensional conducting regions. For this reason, the effect of temperature on conductivity is important for investigating the nature of charge transportation in polymers. In this work it is discussed the temperature dependence of variable range hopping conductivity in conducting polymers and the results compare with the experimental data. Thus, it will be found evidence for the three dimensional hopping conductivity in conducting polymers with electrical and dielectric measurements.

2. Variable hopping conducting in two and three dimensional

In the variable range hopping (VRH) process [10-12], it becomes favorable for an electron to jump from one

localized state to another where there is an overlap of the wave functions. The difference in the eigenenergies is compensated by the absorption or emission of phonons. When the temperature is low enough so that carriers cannot be excited into one of the allowed bands, in which carriers hop from occupied to unoccupied sites which are located within the band dap. Such a hopping mechanism may occur when the density of localized states is high enough to allow a non-negligible overlap of the individual wave functions. It is assumed all electronic states to be localized with phonon assisted transitions between them. The hopping rate w,, from one state j to the other i, including Fermi occupation numbers p,, is given by the formula[13],

$$w_{ij}\, p_j(2-p_i) = \nu \exp(-2 f_{ij})$$

$$f_{ij} = \frac{|\varepsilon_i - \varepsilon_j| + |\varepsilon_j - \varepsilon_f| + |\varepsilon_i - \varepsilon_F|}{4kT} + \frac{|r_i - r_j|}{L_{loc}} \qquad (1)$$

where εi; and rj, are random energies and position vectors of states, LLoc is the localization radius, ν is the characteristic phonon frequency.

2.1. Two dimensional hopping conductivity

The hopping motion is effectively confined to two dimensions and the variable range hopping conductivity is expressed by equation [14],

$$\sigma_{dc}(T) = \sigma_o \frac{h\nu}{2\pi k T_o} \left(\frac{T_o}{T}\right)^{2/3} exp\left[-\left(\frac{T_o}{T}\right)^{1/3}\right] \qquad (2)$$

where To and σo are

$$\sigma_o = \left(\frac{2\pi e^2}{h}\right) \text{ and } T_o = \frac{1}{kN(E_F)L_{Loc}^2} \qquad (3)$$

The Debye losses in VRH regime [15]

$$\sigma_{ac} = \sigma_o \frac{\hbar\omega}{kT_o^2} T\, ln(\nu/\omega)^4 \qquad (4)$$

$$\varepsilon(\omega \to 0, T) = \varepsilon_o\left(1 + \frac{T}{T_o} ln(\nu/\omega)^5\right)$$

where εo is attributed to the polarization of single localized states. The second term in Eq.5 is due to charge exchange the pairs of close states. The static dielectric constant is found to be [16]

$$\sigma_o = \varepsilon_o T_o$$

$$\varepsilon(\omega \to 0, T) = \varepsilon_o\left(\frac{1}{kN(E_F)L_{Loc}^2}\right)^{2/3} T^{2/3} \qquad (5)$$

The dielectric constant in Eq.5 increases linearly with temperature. This temperature corresponds to the extension of a space that becomes accessible for electrons with thermal activation.

2.2. Three dimensional hopping conductivity

In 1968, Mott put forward the idea that this T-1/4 -hopping was due to variable range hopping (VRH) [11]. To explain the phenomena, it is started with ordinary hopping theory developed for the low-temperature transport of electrons localized in gap states of shallow donors in partly compensated crystals. Mott's analysis was as follows considering hops over a spatial distance, , and an energetic distance, ΔE, a carrier starting at the Fermi level finds on the average

$$n_s = \frac{4\pi}{3} \bar{R_o^3}\, N(E_F)\bar{\Delta E} \qquad (6)$$

sites. ns, must be at least in order to one site hop to. This criterion relates the average energy difference to the average hopping width,

$$\bar{\Delta E} = \frac{3}{4\pi N(E_F)\bar{R_o^3}} \qquad (7)$$

Optimizing the mean hopping frequency directly leads to an optimized hopping frequency,

$$\nu = \nu_o\, exp(-(T_o/T)^{1/4}) \qquad (8)$$

which shows the strange T1'4 law [17]. This is related to the dc conductivity,

$$\sigma_{dc}(T) = \sigma_o \frac{h\nu}{2\pi k T_o} \sqrt{\frac{T_o}{T}}\, exp\left[-\left(\frac{T_o}{T}\right)^{1/4}\right] \qquad (9)$$

where To and σo are

$$\sigma_o = \left(\frac{2\pi e^2}{h}\right)\frac{1}{L_{Loc}} \qquad T_o = \frac{1}{kN(E_F)L_{Loc}^3} \qquad (10)$$

The Debye losses in VRH regime [16]

$$\sigma_{ac} = e^2 kN(E_F)^2 T L_{Loc}^5\, ln(\nu/\omega)^5 \qquad (11)$$

$$\varepsilon(\omega \to 0, T) = \varepsilon_o\left(1 + \frac{T}{T_o} ln(\nu/\omega)^6\right) \qquad (12)$$

where εo is attributed to the polarization of single localized states. The second term in Eq.14 is due to charge exchange the pairs of close states. The static dielectric constant is found to be [16]

$$\sigma_o = \varepsilon_o T_o \quad (13)$$

$$\varepsilon(\omega \to 0, T) = \varepsilon_o (kN(E_F) L_{Loc}^3)^{-1} T^{1/2} \quad (14)$$

This equation shows that dielectric constant increases with temperature.

3. Implementation to conducting polymers

The observed temperature dependence of conductivity and the small mobility of current in the conducting polymers lead to the conclusion that charge transfer in variable fields predominates by means of the localized states with energy near the Fermi level. The temperature dependences of dc conductivity corresponds to the variable range hopping in semiconducting polymers are expressed as following relations

$$\sigma_{dc} = A exp[-(T_o / T)^{1/2}]$$

Experimental measurements of dc conductivity and dielectric constant in conducting polymers revealed that both are strongly dependent upon temperature according to Mott law. The one-dimensional variable hopping conductivity mechanism in conducting polymers was derived to be $\sigma_{dc} \alpha exp[-(T_o / T)^{1/2}]$ (Fig.l). It is suggested that one-dimensional hopping conductivity mechanism (1D-VRH) provides only the linear temperature dependence of dielectric constant, as shown in Fig. 1[16]. It is seen that the dielectric constant increase almost linearly with temperature and this temperature corresponds to the extension of a space that becomes accessible for electrons with thermal activation. The strong temperature dependence of dc conductivity takes place for in above 1D-VRH in the conducting polymers. This dependence shows the fact that in polymers system with dimensionality close to one the conductivity is controlled by the charge transfer between chains. Small changes of intermolecules connection with temperature cause large variations of conductivity. As a result, it is evaluated that experimental data obtained from dielectric constant supports the 1D-VRH theory, i.e. the fact that the dielectric constant increases linearly with increasing temperature is evidence for VRH .

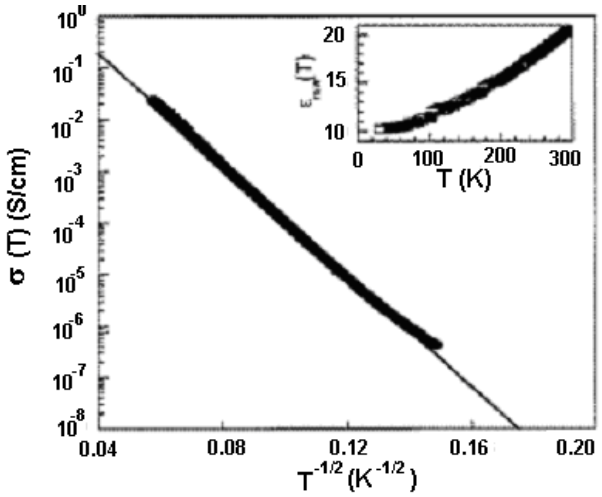

Fig.1. The variation of conductivity and dielectric constant of the sulfonated polyaniline with temperature [16].

6. Conclusion

In semiconducting polymers, the dependence of electrical conductivity on temperature and size has been investigated. Using experimental data obtained from the dielectric constant, it has been determined that the dielectric constant is caused by one- or three-dimensional diffusion between molecules in the polymers, depending on the chemical structure of the polymer, and that the dielectric constant increases linearly with increasing temperature. In our report, we provide a brief information about two and three dimensional hopping conductivity techniques which were commonly used for different applications.

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