AC Conductivity and Dielectric Measurements of Bulk Tertracyanoquinodimethane

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Abstract: Electrical conductivity (AC and DC), dielectric constant $\varepsilon'$ and dielectric loss $\varepsilon''$ have been made for bulk tertracyanoquinodimethane (TCNQ) in the form of compressed pellet with evaporated ohmic Au electrodes have been investigated in the frequency range from 42 Hz to 5 MHz and in a temperature range (298-423 K). The frequency dependence of $\sigma(w)$ follows the Jonscher’s universal dynamic law with the relation $\sigma(w) = \sigma_{dc} + A w^s$, where $s$ is the frequency exponent. The DC conductivity shows an activation energy $DE = 0.285$ eV. The temperature behaviour of the frequency exponents shows that the correlated barrier hopping (CBH) model is well adapted to TCNQ semiconductor material. The dielectric constant, $\varepsilon'$, and dielectric loss, $\varepsilon''$, have been determined for bulk TCNQ both $\varepsilon'$ and $\varepsilon''$ decrease with increasing frequency and increase with increasing temperature.

Key word: Electrical Conductivity (AC and DC), Dielectric Constant $\varepsilon'$ and Dielectric Loss $\varepsilon''$

INTRODUCTION

In recent years, the study of the electrical conduction mechanism in organic compounds has been the subject of many theoretical and experimental investigations. The interest of this topic is stimulated by the applications of these compounds in the development of various modern and future technologies of solid-state devices. Moreover, the information on the electrical properties of materials is also necessary for determining the optimum conditions and for the analysis of electrical transport in these materials. Also, both direct current (dc) and alternating current (ac) measurements provide important information about the conduction process and the predominant charge transport mechanism within an organic material. These measurements are the major tools used for the study of ionic conduction in glasses, ceramics and organic materials (Boltcher CJF et al., 1978 and McCrum NG et al., 1967 and Komilla Suri et al., 2003). Among the organic materials, Tetracyanoquinodimethane (TCNQ) has attracted particular attention due to the development of micro and nanostructures to be used as active material in electron nano-devices (Cao G. et al., 2005). TCNQ is small organic molecule; the molecular structure is shown in Fig. 1. It has four cyano groups and all $\pi$ electrons are delocalized (Higo M. et al., 2001). It is a strong electron acceptor and forms a variety of charge-transfer complexes with inorganic and organic donors. The applications of TCNQ included switching devices (Oyamada T. et al., 2003) and sensors (Ho K.C. et al., 2003).

In the present work, the ac conductivity, dielectric constant and dielectric loss measurements have been performed TCNQ in bulk form. The temperature and frequency dependence of the electrical conductivity, the dielectric constants for TCNQ in the frequency range 42 Hz to 5 MHz and in the temperature range 298-423 K have been investigated and analyzed to determine some related parameters and predict the electronic conduction mechanisms.

2. Experimental Techniques:

The powder of TCNQ (99.7%) used in this study was purchased from Kodak, UK. The TCNQ were firstly compressed under a pressure of $\sim 2 \times 10^8$ N/m$^2$ in the form of a pellet. Secondly TCNQ pellet was sandwiched between two evaporated gold, Au, film electrodes which provide ohmic contacts to the sample. The resulting pellet has a diameter of $1 \times 10^{-2}$ m and thickness of $0.8 \times 10^{-3}$ m. The sample was placed in a holder specially designed to minimize stray capacitance. A programmable automatic RLC bridge, model Hioki 3532 Hitester, was used to measure the frequency $F$, impedance $Z$, the capacitance $C$, and the loss tangent (tan $\delta$) directly. The range of frequencies was 42 Hz-5 MHz. The temperature of the sample was measured by a thermocouple over a temperature range 298-423 K. The total conductivity was calculated from the following equation: $\sigma_t(w) = d/ZA_o$, where $d$ is the thickness of the sample and $A_o$ is the cross-section area. The dielectric constant, $\varepsilon_1$, was calculated from the equation: $\varepsilon_1 = dC/A_o \varepsilon_o$, where $\varepsilon_o$ is the permittivity of free space.

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RESULTS AND DISCUSSIONS

3.1. Dc Electrical Conductivity:

The temperature dependence of the dc electrical conductivity of TCNQ is shown in Fig. 2. Dc conductivity investigated in the temperature range (298-423 K) can be analyzed by the well-known Arrhenius equation:

\[ \sigma_{dc} = \sigma_0 \exp \left( \frac{DE}{k_B T} \right) \]  

where \( DE \) is the dc electrical activation energy, \( T \) is the absolute temperature, \( k_B \) is Boltzmann's constant and \( \sigma_0 \) is the pre exponential factor which including the charge carrier mobility and density of states. The value of \( DE \) was found to be 0.285 eV.

![Fig. 2: Temperature dependence of DC conductivity of TCNQ.](image)

3.2 Frequency and Temperature Dependence of Ac Conductivity:

The ac conductivity, \( \sigma_{ac} \), is obtained by subtracting the dc conductivity, \( \sigma_{dc} \), from the measured total conductivity according the following relation (S.R. Elliott., 1987 and N.F. Mott. et al., 1971 and A. Ben Rhaiem et al., 2009):

\[ \sigma_{ac}(w) = \sigma_{tot}(w) - \sigma_{dc}(w) \]  

where \( \sigma_{tot}(w) \) is the total electrical conductivity at a particular angular frequency \( w \) at a certain temperature. In this equation, the dc conductivity is taken to represent the ac conductivity in the limit \( w \rightarrow 0 \).

The frequency dependence of ac conductivity can be represented by a power law (R.D. Gould., 1986) as follows:

\[ \sigma_{ac}(w) = \Lambda w^s \]  

where \( \Lambda \) is constant, \( w \) is the angular frequency, \( w = 2\pi f \), and \( s \) is the frequency exponent.

![Fig. 3. shows the dependence of ac conductivity, \( \sigma_{ac} \), on frequency (42-5MHz) at different temperatures in the range 298-423 K. It is clear from the figure that \( \sigma_{ac} \) increases with the increasing of frequency. The frequency exponent, \( s \), can be calculated from the slope of the straight lines in Fig. 4 for high ranges of frequencies. At high frequencies the exponent \( s \) is decreases with increasing temperature as shown in Fig. 4.](image)
To determine the predominant conduction mechanism of the ac conductivity for the TCNQ sample, one can suggest the appropriate model for the conduction mechanism in the light of the different theoretical models correlating the conduction mechanism of ac conductivity with $s(T)$ behavior.

According to the correlated barrier hopping (CBH) model, values of $s$ decrease with increasing temperatures. This is in good agreement with the obtained results, as shown in Fig. 4. This model was applied for other different organic compounds (H. Hassib et al., 2008 and R.H. Chen et al., 2006 and A. Ghosh., 1990 and F. Yakuphanoglu et al., 2003). In this model, carrier motion occurs by means of hopping over the Coulomb barrier separating two defect centers. A Coulomb correlation between the charged defect centers results in the relaxation variable $W$ of the Coulomb barrier and the intersite separation $R$. This model, first developed by Pike (G.E. Pike., 1972) for single-electron hopping, and has been extended by Elliot (G.E. Pike., 1972) for simultaneous two electron hopping.
The frequency exponent $s$ for this model is given by

$$s = 1 - \frac{6k_B T}{W_m + k_B T \ln(w_m)}$$  \tag{4}$$

A first approximation of this equation gives the simple expression for the frequency exponent $s$:

$$1 - s = \frac{6k_B T}{W_m}$$ \tag{5}$$

To calculate the value of $W_m$ (the binding energy of the carrier in its localized sites), the values of $1-s$ were plotted versus temperature $T$, as shown in Fig. 4 for the investigated sample, and its slope used to calculate the binding energy $W_m$, which equals 0.25 eV. The binding energy $W_m$ is related to the maximum barrier height at infinite interstic separation, which is called the polaron binding energy.

Fig. 5 shows the ac conductivity $\sigma_{ac}(w)$ as a function of the reciprocal temperature $1000/T$ in the investigated temperature range at different frequencies for the TCNQ. From the figure, $\sigma_{ac}(w)$ increases linearly with increasing temperature. This may indicate that the ac conductivity is a thermally activated process it can be analyzed according to the well-known Arrhenius equation:

$$\sigma_{ac}(w) = \sigma^* \exp \left(\frac{-DE_{ac}}{kT}\right)$$ \tag{6}$$

where $\sigma^*$ is constant and $DE_{ac}$ is the activation energy for conduction. The obtained values of the ac activation energy for different frequencies are almost different between 0.21 and 0.298 ev.

Fig. 5: Variation of AC conductivity, $\sigma_{ac}(\omega)$, with temperature at different frequencies for TCNQ.

3.3. Dielectric Properties of TCNQ:

The dielectric relaxation studies are important to understand the nature and the origin of dielectric losses, which in turn, may be useful in the determination of the structure and defects in solids. The complex dielectric function for the investigated organic dye is expressed as (I.G. Austin et al., 1969 and C.T. et al., 1973).

$$\varepsilon^*(w) = \varepsilon'(w) + i\varepsilon''(w)$$ \tag{7}$$

where $\varepsilon'(w)$ and $\varepsilon''(w)$ are the dielectric constant and the dielectric loss respectively. The dielectric constant $\varepsilon'(w)$ and $\varepsilon''(w)$ were calculated in the range of frequency 42Hz-5MHz and temperature range 298-423k. Figs. 6 and 7 shows the variation of $\varepsilon'(w)$ and $\varepsilon''(w)$ with frequency at different temperatures, respectively. As seen in Figs. 6 and 7, $\varepsilon'(w)$ and $\varepsilon''(w)$ decrease with increasing frequency. This can be explained by means of the
Fig. 6: Variation of the dielectric constant $\varepsilon'(\omega)$ with frequencies at different temperature for TCNQ.

Fig. 7: Variation of the dielectric loss $\varepsilon''(\omega)$ with frequencies at different temperature for TCNQ.

dielectric polarization mechanism of the material. Dielectric polarization occurs as electronic, ionic, interfacial or dipolar polarization. Electronic and ionic polarizations are active in the high frequency range, while the other two mechanisms prevail in the low frequency range. When the frequency is increased, the dipoles will no longer be able to rotate sufficiently rapidly, so that their oscillations begin to lag behind those of the field. As the frequency is further increased, the dipole will be completely unable to follow the field and the orientation polarization stopped, so $\varepsilon'(\omega)$ decreases at a higher frequencies approaching a constant value due to the interfacial or space charge polarization only (Kurien S et al., 2006 and Anantha PS et al., 2005).

Figs. 8 and 9 shows the variation of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ with temperature at certain frequencies. Form the figure, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ increases with the increase in temperature and it exhibits strong temperature dependence at higher temperature and lower frequencies. The observed behaviour revealed that the TCNQ exists in the
form of molecular dipoles, which remain frozen at low temperature, while at high temperature the dipoles can rotate freely (J.M. Stevels., 1957) and increase the orientation polarization and hence increase in $\varepsilon'(\omega)$. The origins of the dielectric losses $\varepsilon''(\omega)$ is the conduction losses, dipole losses and vibrational losses.

**Conclusion:**

Electrical conductivity and dielectric properties of bulk, 7',8,8' tetracyanoquinodimethane was measured as a function of frequency range 42Hz-5M kHz and temperature range 298-423k in a compressed pellet, with evaporated ohmic Au electrodes. The ac conductivity $\sigma_{ac}(\omega)$ was found to vary as $\omega^s$ in the frequency At high range of frequency the frequency exponent, $s$, was less than unity and decreases with the increase in temperature indicating a dominant correlated barrier hopping (CBH) mechanism.
The temperature dependence of $\sigma_{ac}$ (w) showed a linear increase with increasing ac temperature. The calculated ac activation energy was found to decrease with increasing frequency. This may be indicated that the ac conductivity is a thermally activated process with activation energy 0.21-0.28eV. The dielectric constant, $\varepsilon'(w)$ and dielectric loss, $\varepsilon''(w)$ were found to decrease with increasing frequency and increase with increasing temperature.

REFERENCES


