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An insight into the localization of charge carriers in conducting polyaniline by analyzing thermally stimulated depolarization signals

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Abstract

A dielectric relaxation mechanism, which is attributed to the localized motion of trapped polarons, has been recorded in conducting polyaniline by employing the thermally stimulated depolarization current technique. The signal was analyzed within the frame of the normal distribution in the activation energy value. The experimental dielectric relaxation results were manipulated in order to evaluate the length of the jump distance that the trapped polarons transfer along and the concentration of trap centers. The concentration of trapped carriers is calculated from two different viewpoints: the pair approximation that assumes phonon-assisted tunneling through the barrier separating two adjacent sites and the pinning model that considers the trapped polaron oscillating around its pinning point. Both models provide compatible results.

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1. Introduction

Conducting polyaniline is a promising polymer for technological applications, such as, electromagnetic shielding, anti-static coating, solid-state batteries, solar cells, electronic devices non-linear optics, etc. The electronic transport in conducting polymers has been the subject of theoretical and experimental investigation [1]. However, traps affect the electric charge transport in amorphous solids. A portion of the transferring entities is impeded within the bulk and is capable of performing localized motion. The application of an external electric field produces both dc conductivity and polarization (capacitance) phenomena. Preliminary investigations concerning the dielectric response of polyaniline, which is one of the representatives of the conducting polymers, protonated after treating with HCl showed that the presence of Cl^- at redox centers results in the spatial localization of polarons [2,3]. The result is an increase of the dielectric constant. In a recent work, we showed that the thermally stimulated depolarization current (TSDC) technique performed with blocking electrodes is capable of tracing the polarons' capture in deep traps. The scope of the present paper is to examine how the analysis of the TSDC signal or dielectric relaxation results can provide information in microscopic scale about the earlier-mentioned phenomenon.

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2. Theory

Mott and Davis [4] have described the localized motion of a hopping electron between two localized states at a distance R, by considering the relaxation time τ

$$\tau(T) = \nu_{\mathrm{ph}}^{-1} \exp(2\alpha R)\exp(W/kT) \tag{1}$$

where ν_{ph} is a typical phonon frequency, α the inverse localization length of the wave-function, W the effective activation energy and k denotes the Boltzmann's constant. The process occurs by multi-phonon assisted tunneling through the potential barrier separating two adjacent potential wells. By labeling

$$\tau_0 \equiv \nu_{\mathrm{ph}}^{-1} \exp(2\alpha R) \tag{2}$$

Eq. (1) takes the form of the Arrhenius law

$$\tau(T) = \tau_0 \exp(W/kT) \tag{3}$$

To a first approximation, τ_0 may be regarded as constant, or negligibly dependent on temperature in comparison with the strong exponential dependence on the inverse of the (absolute) temperature.

Assuming that the relaxation time, which governs the relaxation process, is an Arrhenius-type one (Eq. (2)), the TSDC is given by [5]

$$I(T) = \frac{S\Pi_0}{\tau_0}\exp\left[-\frac{W}{kT} - \frac{1}{b\tau_0}\int_{T_0}^{T}\exp\left(-\frac{W}{kT}\right)\mathrm{d}T\right] \tag{4}$$

where Π_0 is the initial polarization of the dielectric, S the surface sample area which is in contact with each one of the electrodes, b the heating rate and T_0 coincides to the liquid nitrogen temperature (LNT). The analysis of the TSDC signal provides the values of the activation energy W and the pre-exponential factor τ_0. W is understood as an 'effective' potential barrier. τ_0 evidences about the hopping distance R; Eq. (3) can be re-written as

$$R = \frac{1}{2\alpha}\ln(\nu_{\mathrm{ph}}\tau_0) \tag{5}$$

Pollak and Geballe [6] calculated the polarizability α_{p} within the so-called pair approximation

$$\alpha_{\mathrm{p}} = \frac{e^2R^2}{12kT} \tag{6}$$

The application of an electric field produces shifts the trapped charges transfer along a short distance R yielding an induced 'extended' dipole of mean length R. The polarization Π_0 is [7]

$$\Pi_0 = N\alpha_{\mathrm{p}}E_{\mathrm{p}} \tag{7}$$

where N is the (volume) density of traps and E_{p} is the intensity of the local polarization field. For samples of macroscopic dimensions, the local electric field coincides with the external electric field intensity [8]. Π_0 equals the electric charge Q produced during the depolarization (heating) stage in a TSDC experiment reduced to the sample-electrode surface area. The charge is obtained simply by graphical integration over the thermogram $Q = b^{-1}\int_{T_0}^{T_{\mathrm{f}}} I(T)\mathrm{d}T$, where b is the (constant) heating rate, T_0 denotes the temperature where the depolarization current appears initially and T_{f} is the end temperature of the TSDC band.

Eqs. (6) and (7) yield the density of trapped charge carriers

$$N = \frac{12kT\Pi_0}{E_{\mathrm{p}}e^2R^2} \tag{8}$$

The temperature $T_{\max}$ where the depolarization current reaches its maximum can take the place of T.

The concentration of trapped centers can be estimated in an alternative way: polarons and bipolarons are regarded as oscillating around a pinning point contributing to the dielectric constant of the material by a term [9–11]

$$\Delta\varepsilon = \frac{4\pi ne^2}{3\varepsilon_0 Vm^*\omega_0^2} \tag{9}$$

where n is the number of polarons per aniline ring, V the volume per ring, m^* the polaron effective mass and ω_0 is the polaron pinning frequency. However, the contribution $\Delta\varepsilon$ can be calculated from a TSDC experiment

$$\Delta\varepsilon = \frac{\Pi_0}{\varepsilon_0 E_{\mathrm{p}}} \tag{10}$$

From Eqs. (9) and (10) we get

$$n = \frac{\Pi_0}{E_{\mathrm{p}}}\frac{3Vm^*\omega_0^2}{4\pi e^2} \tag{11}$$

3. Experimental

The conductive samples of polyaniline were made from freshly distilled aniline (Merck) under vacuum polymerized in the presence of $FeCl_3$ (Merck) as oxidant in HCl acid–water solutions at pH 2.00 in an ice bath (aniline/oxidant = 1:1 mol/mol) under nitrogen atmosphere [12]. Disc shaped specimens 13 mm in diameter and about 1.5 mm thick were produced by pressing the powder in an IR press. The dc conductivity of the specimens depends on the conditions of their synthesis and in our case varied between 2 and 3 S/cm.

The specimen was separated from the standard metal electrodes of the measuring apparatus by a couple of thin teflon foils [14,15]. The TSDC experiments were performed inside a cryostat operating under a dynamic vacuum of about 10^{-1} Pa from the LNT to 420 K. The depolarization current was recorded by a Keithley 617 digital electrometer. The so-called metal–insulator–sample–insulator–metal (MISIM) configuration prevents the injection of charge carriers from the electrodes to the specimen and prohibits the dc conductivity of the specimen.

4. Results and discussion

The TSDC thermogram of conducting polyaniline is depicted in Fig. 1. The maximum of the TSDC peak is located at $T_m = 115.6$ K. The single relaxation time model (Eq. (3)) failed to simulate the experimental results. Instead, a normal distribution in the activation energy value around a central one W_0 was assumed to fit the TSDC signal [16]. The modified TSDC equation is

$$I(T) = \int_{-\infty}^{+\infty} f(W) I(T, W) \mathrm{d}W \tag{12}$$

where $I(T, E)$ is the non-distributed TSDC equation and $f(W)$ is the distribution function

$$f(W) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(W - W_0)^2}{2\sigma^2} \right] \tag{13}$$

where σ is the broadening parameter. We note that in the vast majority of insulating materials, Eq. (13) describes the relaxation process rather than Eq. (3) [16]. The theoretical curve (Eq. (12)) that best fits the experimental data points is determined by the following parameters: $W_0 = 0.243$ eV, $\sigma = 0.003$ eV and $\tau_0 = 2.51 \times 10^{-9}$ s.

4.1. Evaluation of the trapped polarn jump length

Protons are mostly cited in redox centers close to the nitrogen atoms of the polyaniline backbone. Talking about pinned polarons that do not contribute to the dc conductivity (i.e. long distance transport along the volume of the specimen), it is reasonable to assume that the wave-function is localized at distances compared with the dimensions of one ring. Therefore, the localization length should be about $\alpha^{-1} \approx 6.9$ Å [17]. A typical phonon frequency value is $\nu_{ph} \approx 10^{13}$ Hz. By replacing in Eq. (2), we get $R \approx 32.9$ Å, which indicates a localization of the trapped carriers along distances of about five aniline rings.

4.2. Evaluation of the trapped polaron concentration

A graphical integration of the $I(T)$ curve yields the charge released an the depolarization stage: $Q = 6.92 \times 10^{-11}$ C. The charge divided with the sample's surface area that is attached to one of the electrodes is identical to the polarization $\Pi_0 = 8.81 \times 10^{-7}$ C/m^2. The polarizing electric field intensity was $E_p = 9.98 \times 10^5$ V/m. The jump length of the trapped polarons $R \approx 32.9$ Å has been found in the preceding paragraph. By replacing these values into Eq. (8), the density of trapping sites *within the pair-approximation* is obtained: $N = 4.1 \times 10^{22}$ m^3. Recalling that the volume per aniline ring is $V = 125$ Å^3 [11], a trap concentration of 5 ppm aniline rings is obtained.

The concentration of trapped polarons is alternatively evaluated within the frame of the *pinning model* by using Eq. (11). The effective mass is $m^* \approx 60 m_e$, where m_e is the electron mass [13]. The pinning frequency ω_0 can take a typical phonon frequency value $\nu_{ph} \approx 10^{13}$ Hz. The values of the quantities Π_0, E_p and V were mentioned in the previous paragraph. By substituting into Eq. (11) we get $n = 5.2 \times 10^{-6}$ polarons per ring, or 5 ppm aniline rings.

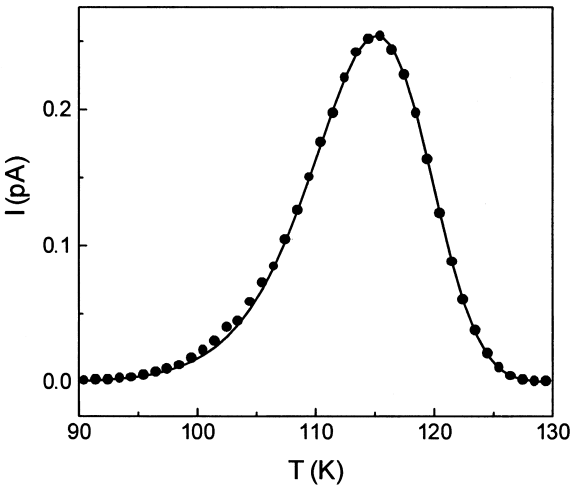

Fig. 1. The TSDC signal recorded in conducting polyaniline using the MISIM configuration (full circles). The line is the theoretical curve that fits best the experimental data points.

We observe that the two models yield the same concentration of trapped polarons. The pair-approximation demands an estimate for the localization length and requires knowledge of the value of τ_0. The latter results from time-consuming analysis of the TSDC signal. On the contrary, the pinning model directly gives the concentration of trapped polarons from the TSDC curve as it requires merely the graphical integration of the TSDC curve.

5. Conclusion

We have derived the appropriate formulation in order to interpret the TSDC and dielectric relaxation results concerning charge localization in amorphous media in microscopic scale. The system under consideration is conducting polyaniline, where charge trapping was observed by TSDC spectroscopy. The pre-exponential factor is related with the distance the trapped charges travel along when an external electric field is applied. The strength of the dielectric relaxation indicated the concentration of trapped carriers. Both the pair approximation and the pinning model provide compatible results. The improvement of conductive plastics is related with the minimization of charge-traps and the reduction of the subsequent relaxation phenomena. The methodology presented in this paper permits the quantitative characterization of conductive polymers by determining the concentration of trapped polarons from TSDC results.

References

[1] A.B. Kaiser, Rep. Prog. Phys. 64 (2001) 1.
[2] S. Sakkopoulos, E. Vitoratos, E. Dalas, Synth. Met. 92 (1998) 63.
[3] E. Dalas, S. Sakkopoulos, E. Vitoratos, Synth. Met. 114 (2000) 365.
[4] N.E. Mott, E.A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford, 1979, Chapter 215.
[5] C. Bucci, R. Fieschi, Phys. Rev. Lett. 12 (1964) 16.
[6] M. Pollak, T.H. Geballe, Phys. Rev. B 122 (1961) 1742.
[7] C. Kittel, An Introduction to Solid State Physics, Wiley, New York, 1976, Chapter 13.
[8] G. Nienhuis, J.M. Deutch, J. Chem. Phys. 55 (1971) 4213.
[9] F. Zuo, M. Angelopoulos, A.G. McDiarmid, A. Epstein, Phys. Rev. B 39 (1989) 3570.
[10] P.A. Lee, T.M. Rice, P.W. Anderson, Solid State Commun. 14 (1974) 703.
[11] N.J. Pinto, P.D. Shah, P.K. Kahol, B.J. McCormick, Solid State Commun. 97 (1996) 1029.
[12] C. Menardo, M. Nechtschein, A. Rousseau, J.P. Travers, Synth. Met. 25 (1988) 311.
[13] J.M. Ginder, A.J. Epstein, A.G. MacDiarmid, Solid State Commun. 72 (1989) 987.
[14] A.N. Papathanassiou, J. Grammatikakis, S. Sakkopoulos, et al., J. Phys. Chem. Solids 63 (2002) 1771.
[15] S. Sakkopoulos, E. Vitoratos, J. Grammatikakis, et al., J. Mater. Sci. 37 (2002) 2865.
[16] J. Vanderschueren, J. Gasiot, in: P. Braunlich (Ed.), Field Induced Thermally Stimulated Currents in Thermally Stimulated Relaxation in Solids, Springer, Berlin, 1979.
[17] J.M. Ginder, A.J. Epstein, Phys. Rev. B 41 (1990) 10674.