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Charge Transport in Polyaniline Doped with 3-Nitro-1,2,4-triazol-5(4*H*)-one

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Summary: Polyaniline (PANI) base was protonated in aqueous solutions of an organic acid, 3-nitro-1,2,4-triazol-5(4*H*)-one (NTO). The temperature dependence of DC conductivity of PANI-NTO seems to correspond to the theory of variable range hopping (VRH) in three dimensions. The frequency dependence of AC conductivity also reflects the hopping nature of mobile charges. The activation energy for the polymers with protonation degree above 0.12 remains constant with increasing dopant concentration and DC conductivity. The value of this constant may correspond to the energy needed for the ionization of dopant counterion. The fit of the electric relaxation function to the stretched exponential function $\varphi(t) = \exp[-(t/\tau)^{\beta}]$ gives the stretch parameter β about 0.35, which shows that the distribution of relaxation times is broad and indicates a high inhomogeneity in the distribution of a dopant.

Keywords: charge transfer; charge transport; dielectric properties; disorder; polyaniline

Introduction

The electric properties of conducting polymers have been the topic of intensive study since the intrinsic conductivity in these materials was discovered[1]. Doping of PANI with organic or inorganic acids is used to create free or localized charges in a polymer medium. In this procedure, the conductivity of PANI increases by several orders[2], from ca. 10^{-10} to 10^{1} S cm^{-1}. PANI-NTO is a new type of material combining the properties of a conducting polymer, PANI, and the features of an explosive, NTO. Several mechanisms of charge transport were found in conducting polymers[1]. Despite high doping of a polymer, the charge carriers seem to be localized, so they should move in the material by hopping over or tunneling through the potential barriers between the localized states. Variable-range hopping[3] assumes that carriers tunnel through the energy barriers between the localized states by means of phonon thermal energy. 3D-VRH occurs in the

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disordered polymers with structures similar to amorphous semiconductors, where charges can choose an easiest hop in any direction. Quasi-1D VRH occurs in the polymers where charges move along the polymer chain, with sudden interchain hops[4]. In some cases, polymerization and protonation lead to creation of small conducting islands distributed in a non-conductive matrix. Then charges tunnel between these regions according to the charged-energy-limited tunneling (CELT) mechanism[5].

Experimental

PANI base was protonated in solutions of various NTO concentrations[6]. The protonation degree is defined as the molar ratio of NTO and PANI. Samples were dried and pressed into pellets 13 mm in diameter. DC and AC parameters were measured after vacuum deposition of gold electrodes (10 mm in diameter) on both sides of pelletized samples. The AC properties were measured in temperature range 100–320 K in the frequency range 20 Hz–5 MHz using precision LCR meters HP4284A and HP4285A. The temperature dependence of DC conductivity was measured in Kelvin configuration using a Keithley 2001 multimeter in temperature range 100–320 K.

Results and discussion

The temperature dependence of DC conductivity for the samples with different protonation levels is shown in Figure 1. Fitting the temperature dependence of DC conductivity showed the best agreement for the model of 3D VRH[3]

$$\sigma_{\mathrm{DC}} \propto \exp\left[-\left(T_0 / T\right)^{\gamma}\right] \tag{1}$$

with $\gamma = 1/4$. The frequency dependence of conductivity, $\sigma(\omega)$, measured at 215 K for the polymers with protonation degree from 0.02 to 0.23 is shown in Figure 2. The low-frequency limit of $\sigma(\omega)$ increases with increasing protonation degree with a simultaneous increase in characteristic or onset frequency ω_{c}. Below this frequency, the conductivity is almost constant, but beyond it increases with frequency. The approximate power law of AC conductivity $\sigma(\omega) \sim \omega^{s}$ [3] holds above ω_{c} with the exponent s ca. 0.65.

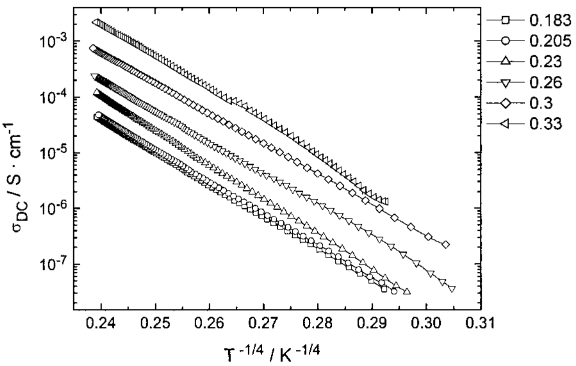

Figure 1. Temperature dependence of DC conductivity for polyanilines with different protonation degrees.

Fitting the frequency dependence of AC conductivity to the equations

$$\sigma(\omega) = \sigma_{\mathrm{AC}}(\omega) + \sigma_{\mathrm{DC}}(\omega)\,, \tag{2}$$

representing the total conductivity of a material, where σ_{DC} is the DC conductivity and

$$\sigma_{\mathrm{AC}}(\omega) \propto \omega \ln^{d+1}\left(\frac{\nu_{\mathrm{ph}}}{\omega}\right) \sim \omega^{s} \tag{3}$$

is the AC conductivity, we obtained values of $\nu_{\mathrm{ph}} = 10^{11}\ \mathrm{s}^{-1}$ for 3D-VRH ($d = 3$) and $\nu_{\mathrm{ph}} = 10^{8}\,\mathrm{s}^{-1}$ for quasi-1D VRH ($d = 1$). These values are independent of temperature. The latter value, corresponding to quasi–1D hopping, is too low in comparison with that known from literature ($\sim 10^{13}\ \mathrm{s}^{-1}$)[3]. This indicates that the 3D VRH takes place in these materials.

Due to the high DC conductivity of the materials, representation of AC measurements in terms of dielectric permittivity is impossible, because the peak in ε'' is masked by the σ_{DC} contribution[7]. It was found that, in the case of conducting materials, it is convenient to present the results of AC measurements in terms of complex conductivity or complex modulus, which is the quantity reciprocal to complex permittivity $M^{*}(\omega) = 1/\varepsilon^{*}$. This quantity represents a Fourier transform[8]

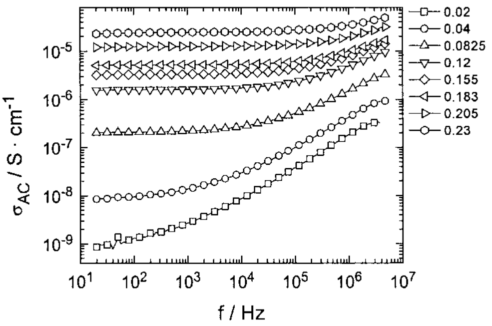

Figure 2. Frequency dependence of AC conductivity measured at 215 K for polyanilines with different protonation degree.

$$M^*(\omega) = M_\infty \left[1 - \int_0^\infty \left(- \frac{\mathrm{d}\varphi(t)}{\mathrm{d}t} \right) \exp(-\mathrm{i}\,\omega t)\,\mathrm{d}t \right] \tag{4}$$

of the decay function of electric field $\varphi(t)$, which in most cases can be presented in the form of Kolhrausch-Williams-Watts (KWW) function[8]

$$\varphi(t) = exp\left[-(t/\tau)^\beta \right] . \tag{5}$$

Figure 3 shows the frequency dependence of the imaginary part of electric modulus (points). The broad asymmetric curves indicate high disorder and broad distribution of relaxation times.

Fitting of the experimental plots to Equation (4) was made (Figure 3, full lines). Parameter β was found to have a constant value of 0.35 for all protonation degrees. This value correlates with the power exponent s characterizing this frequency behavior of AC conductivity $\beta + s \sim 1$[9]. Low β indicates broad distribution of relaxation times and high inhomogeneity of the distribution of dopant counterions.

Figure 4 shows the dependences of DC conductivity and activation energy on protonation degree. DC conductivity was measured at room temperature. The activation energy W was calculated from the temperature dependence of relaxation time τ, given by $\tau = \tau_0 \exp(W/kT)$, where τ_0 is the inverse phonon attempt frequency $\tau_0 = \nu_{\mathrm{ph}}^{-1}$.

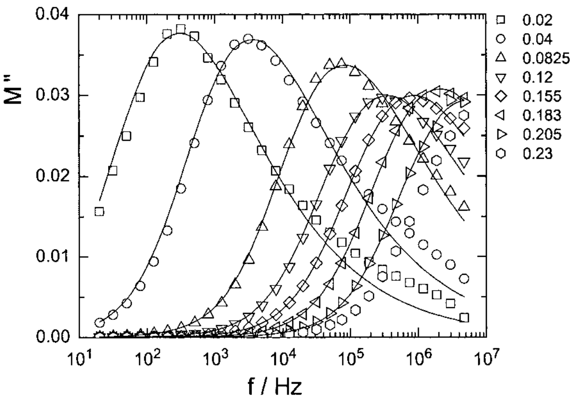

Figure 3. Frequency dependence of the imaginary part of complex electric modulus at 215 K for the polyanilines with protonation degree from 0.02 to 0.23. Full lines – fit to the KWW equation.

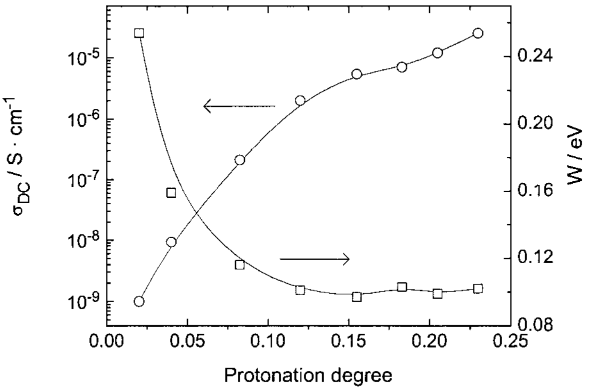

Figure 4. Dependence of activation energy W (circles) and DC conductivity σ_{DC} (squares) of polyanilines on the protonation degree (full lines – guide to eye).

At low concentrations of NTO, the activation energy and DC conductivity rapidly change. For the protonation degrees higher than 0.12, the activation energy of charge hopping remains constant, ~ 0.1 eV. In this region, DC conductivity increases slower than at low dopant concentrations. At low degrees of protonation, the decreasing activation energy is given by the increasing number of localized energy states and decrease in energy barriers between them. At high doping levels, the activation energy is defined by the energy required for the ionization of dopant[10], which is independent of the protonation degree. DC conductivity slowly increases due to increasing charge concentration.

Conclusions

Changing protonation degree is an effective method of controlling the electric properties of PANI. Conductance in PANI doped with NTO takes place *via* variable-range hopping among localized energy states, created during doping. The frequency dependence of AC conductivity indicates VRH in three dimensions; the onset frequency and activation energy increase with growing degree of protonation. Broadened and asymmetric $M''(\omega)$ plots indicate a highly disordered material. The low value of stretch parameter in the KWW function characterizes the broad distribution of relaxation times and high inhomogeneity of dopant distribution. The constant activation energy for samples with high degrees of protonation may correspond to the energy needed for the ionization of dopant counterion.

Acknowledgements

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