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Original Scientific Paper

New Aspects of Variable-range-hopping Conductivity in Doped Polyaniline*

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Abstract. Temperature, T, dependence of the electrical conductivity, σ, of own-made polyaniline pellets, highly doped either by HCl or by dodecylbenzenesulphonic acid, is discussed. For the both dopants, a variable-range-hopping exponent 2/5 is found below $T^* \approx 200-250$ K. This result can be understood on the basis of a recent theory of Fogler, Teber and Shklovskii which takes into account Coulomb correlations in a three-dimensional system of chain-like conductors, predicting a power-law density of states for charge excitations around the Fermi energy. At $T > T^*$, the $\sigma(T)$ curves are steeper, implying a tendency towards nearest-neighbour hopping by a reduction of the average hopping length.

Keywords: doped polyaniline, electrical conductivity, hopping transport, Coulomb interaction

INTRODUCTION

Doped polyanilne (PANI) holds a prominent position among conducting polymers. Insulating, undoped PANI – where z reduced [–(C_6H_4)–(NH)–(C_6H_4)–(NH)–] and ($1 - z$) oxidised [–(C_6H_4)–N=(C_6H_4)=N–] units repeat – was made conducting in 1986 by a doping (protonation) in an aqueous HCl solution.[1] Numerous other acids can dope PANI similarly, for example dodecylbenzenesulphonic acid (DBSA)[2] or camphor-10-sulphonic acid[2,3] are nowadays frequently used. PANI is very stable both in its insulating and conducting forms, whereas its polymerisation and doping are simple and involve inexpensive chemicals.[4] This makes it suitable for a variety of scientific studies and technological applications. From the point of view of exploring processes behind the charge propagation in PANI (and other conducting polymers), a viable source of information is the $\sigma(T)$ characteristics as a function of doping, generally being of a form characteristic of variable-range hopping (VRH) of charge carriers. This transport mechanism is widespread among disordered systems[5,6] and results in $\ln\sigma = \text{const.} - (T_0 / T)^{\alpha}$, where $\alpha < 1$ and T_0 carry information on the underlying physics.

In this paper, we focus on a new aspect of VRH in polymers, *i.e.*, on an unambiguous experimental finding of $\alpha = 2/5$ both in HCl-doped and DBSA-doped PANI (PANI-HCl and PANI-DBSA, respectively) pellets pressed from the own-made polymer powder. This value of α was observed before in some other conducting polymers[7,8] but it was not understood. In 2004, Fogler, Teber and Shklovskii (FTS) presented a comprehensive VRH theory for chain-like systems, where $\alpha = 2/5$ appeared straightforwardly when Coulomb interactions were taken into account.[9] We identify conditions leading to $\alpha = 2/5$ in doped PANI, and discuss the applicability of the FTS model to our results.

MODELS OF ELECTRICAL CONDUCTIVITY IN DOPED POLYANILINE

Mobile charge in doped PANI is created by the protonation of the PANI backbone. We can concentrate on the symmetric and thermodynamically favoured form of undoped PANI, that is, the emeraldine base (PANI-EB) corresponding to $z = 1/2$, as the other ones are less stable and their fraction in the final material produced by the method used in this work is negligible. One mer of PANI-EB is shown in Figure 1(a). PANI-EB is not conducting because there are no free electron states – as shown by the dots that represent electrons (lone pair) on the N atoms. When an acid H^+A^- is brought in contact with the PANI-EB backbone, H^+ and the anion A^- are attracted toward the imine N atoms bonded to the quinone ring. This process eventually results in $(\text{PANI-H})^+A^-$, shown in Figure 1(b) for the full doping, with the protonated (formerly imine) amine N atoms.[10] The lone pair in PANI-EB is transformed

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Dedicated to Professor Boran Leontić on the occasion of his 80th birthday.

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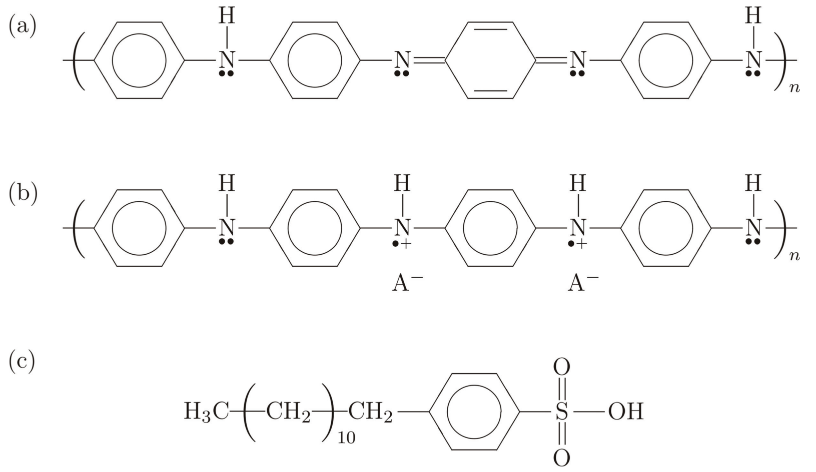

Figure 1. (a) One mer of PANI-EB. (b) One mer of fully protonated $(\mathrm{PANI\text{-}H})^{+}\mathrm{A}^{-}$. (c) DBSA molecule.

into an electron and a hole (+) in the protonated backbone, which can give rise to intrachain charge transport. The doping by HCl has so far been the most frequent and its consequences are best understood. On the other hand, technological interest in PANI-HCl has lessened, since there is no commercially useful solvent for PANI-HCl, *i.e.*, its processability is limited. A step forward is to find another dopant which would provide a good conductivity in combination with the solubility in a widely used solvent. A good choice seems to be DBSA, the molecule of which is shown in Figure 1(c). The sulphonic "head" can protonate the backbone while the hydrocarbon "tail" facilitates solubility in simple solvents (*e.g.*, chloroform, xylene, *m*-cresol) by a surfactant effect.[2]

Charge carriers resulting from the protonation propagate by the phonon-assisted VRH in a spatially random localisation potential, and this leads to

$$\sigma(T) \propto \exp\left[-\left(\frac{T_0}{T}\right)^{\alpha}\right]. \tag{1}$$

Although T_0 contains valuable information as well, α provides a more direct link to the microscopic processes. Until recently, VRH was approached either by the Mott model [$\alpha = 1/(1+d)$, where d is the effective dimensionality of the system][5] or by the Efros-Shklovskii (ES) model ($\alpha = 1/2$ regardless of d).[6] Conducting polymers are three-dimensional networks of one-dimensional conductors, so $d = 3$ (strong interchain coupling) or $d = 1$ (weak interchain coupling), unless it is intervened by special methods of shaping the samples. Hence, the above models predict that α for polymers can be $1/4$ or $1/2$ only. These values (including crossovers between them as a function of doping)[11] were observed indeed. However, there were also reports on α assuming $2/5$,[7,8] *i.e.*, a value taking place in the FTS theory naturally.[9] The FTS model addresses a generalised system of coupled conducting chains, relying on the ES picture where an exciton-like effect is considered: when an electron hops, it experiences Coulomb interaction with the positive charge left behind, and the density of states for charge excitations of an energy E close to the Fermi energy E_{F} acquires a form $g(E) \propto |E - E_{\mathrm{F}}|^{\mu}$. This leads to $\alpha = (1+\mu)/(1+\mu+d)$, with $\mu = 0, 1, 2$. Note that this expression permits not only $\alpha = 1/2$ and $1/4$ but also some other values, including $2/5$. At $|E - E_{\mathrm{F}}| \approx \Delta_{\mathrm{C}}$, where Δ_{C} is termed the ("soft") Coulomb gap, $g(E)$ saturates towards $g(E) = \mathrm{const.}$ of the Mott law (in turn, $\alpha = 1/4$ can be observed even if $\mu \neq 0$, see later). The FTS theory also predicts a possibility that VRH can change into nearest-neighbour hopping corresponding to $\alpha = 1$; in the latter case, σ exhibits an Arrhenius behaviour which is also frequently observed in disordered systems.

The question of the applicability of the FTS theory to conducting polymers is at present largely open to debate. We here point out some rather serious arguments in favour of this possibility. The Mott and ES approaches have been used for explaining experimental results on conducting polymers no less than for other disordered conductors. Since the FTS theory tackles essentially the same physics – but in the presence of additional effects – we see no obvious reason for its inappropriateness. This conclusion holds in spite of some ingredients of the FTS theory not completely resembling the actual situation (*e.g.*, the chains are modelled to be straight and parallel). Our experimental results, addressed in this paper and elsewhere,[12,13,14] suggest that the FTS approach holds reasonably well for doped PANI and – by implication – perhaps beyond this particular class of conducting plastics. The discrepancies are neither numerous nor crucial, and are in fact expected because specificities of polymers (*e.g.*, entanglement of the chains) are not included into the model.

PREPARATION OF SAMPLES AND CONDUCTIVITY MEASUREMENTS

A standard method of preparing PANI-EB powder ready for controlled doping was used.[15] We first synthesised PANI-HCl through the oxidative polymerisation of aniline $C_6H_5NH_2$ by ammonium peroxydisulphate $(NH_4)_2S_2O_8$ in a ≈ 1 M aqueous HCl solution, and then converted it into PANI-EB by a deprotonation in a ≈ 1 M aqueous NH_4OH solution. In the subsequent HCl doping of thus obtained PANI-EB, the control parameter was pH of the aqueous HCl doping solution, correlated with the doping level $Y = [Cl^-]:[N]$ in a known way.[12,15] The precise role of experimental parameters of the doping by DBSA is a subject of ongoing investigations;[13] in this work, the control parameter was $p = n(\text{DBSA}) / n(\text{EB})$, where n(DBSA) and n(EB) were the amounts of DBSA and of one mer of PANI-EB in a 80 ml aqueous solution, respectively. The processing through different solutions always involved prolonged equilibration, thorough drying, and gentle grinding by hand in an agate mortar. The described method leads to a control over around ten orders of magnitude in the room temperature (r.t.) conductivity $\sigma_{\text{r.t.}}$ for the both dopants.[13,14,15]

Pellets (≈ $8 \times 5 \times 1$ mm^3) were produced by pressing the polymer powder under ≈ 90 MPa. Electrical contacts for four-point transport measurements were made by depositing a thin graphite layer onto the contact area before a silver paste was applied. Samples were biased by a constant direct current (1 μA or less, *i.e.*, the current density being maximum 0.1 A m^{-2}), whereas the voltage drop was recorded by a high-input-impedance (≈ 10 GΩ) nanovoltmeter. Temperature sweeps were carried out using a ^{4}He cryostat. Thermal voltages were cancelled out by measuring the signal for two opposite current directions. No effect of thermal cycling on $\sigma(T)$ was found.

RESULTS AND DISCUSSION

Qualitatively, $\alpha = 2/5$ appears at T below 200−250 K in samples with $\sigma_{\text{r.t.}}$ higher than ≈ 1 S m^{-1}, both for PANI-HCl and for PANI-DBSA. The overall development of α with the doping level and temperature in PANI-HCl, which is the simplest system in the doped-PANI class, is as follows.[12] Below $T^* \approx 200$ K, there are two doping-dependent values of α: $1/2$ (VRH, $\mu = 2$) at low-to-moderate doping ($Y < 0.3$), and $2/5$ (VRH, $\mu = 1$) at high doping ($Y > 0.3$). For $T > T^*$, α equals $1/4$ (VRH, $\mu = 0$) irrespective of its low-T value, except for almost fully doped samples where $\sigma(T > T^*)$ becomes steeper (*i.e.*, α apparently increases instead of decreasing) and thus implies a trend towards a mechanism different from VRH. The above behaviour can be understood from the FTS theory for $d = 3$ when the disorder level, VRH energy scales and thermal energy are taken into account.[12] We henceforth skip details of these results in order to pay attention to a comparison between selected PANI-HCl and PANI-DBSA samples that exhibit $\alpha = 2/5$, *i.e.*, we extend the analysis to a technologically more interesting material.

In Figure 2(a), we compare $\sigma(T)$ of PANI-HCl ($Y = 0.44$, $\sigma_{\text{r.t.}} = 54$ S m^{-1}) and PANI-DBSA ($p = 3$, $\sigma_{\text{r.t.}} = 73$ S m^{-1}) samples of similar $\sigma_{\text{r.t.}}$. In these plots, the experimental data (symbols) for $30 \text{ K} < T < 200$ K exhibit a linear dependence (solid lines, guides to the eye) remarkably well and with almost the same $T_0 \approx 38\,500$ K. This is also seen in the inset to Figure 2(a), where the symbols represent logarithm of $W = \partial \ln \sigma / \partial \ln T$ plotted against $\log T$ for the PANI-DBSA sample. For the both samples, the prediction $\log W \propto \text{const.} - \alpha \log T$ of Eq. (1) holds with $\alpha = 2/5$ up to $T^* \approx 200$ K, above which $\log W$ decreases with increasing $\log T$ faster (*i.e.*, the $\sigma(T)$ dependence is stronger).

In Figure 2(b), we compare $\sigma(T)$ of PANI-HCl and PANI-DBSA samples with the highest obtained $\sigma_{\text{r.t.}}$ for the doping procedure employed. For PANI-HCl, this corresponds to $Y = 0.47$, *i.e.*, 94 % of the maximum possible protonation ($Y = 0.5$), and $\sigma_{\text{r.t.}} = 102$ S m^{-1}. For PANI-DBSA, $p = 10$ and $\sigma_{\text{r.t.}} = 337$ S m^{-1}. As mentioned before, effects of p are currently under investigation,[13] being still controversial because $\sigma_{\text{r.t.}}(p = 10) > \sigma_{\text{r.t.}}(p = 3)$ despite the expectation that already $p = 2$ should give the full protonation. For this work, it is more important that the data shown in Figure 2(b) again reveal $\alpha = 2/5$, with $\log W$ *vs.* $\log T$ plots (not shown) giving similar outcomes to that in the inset to Figure 2(a). Quantitatively, $T^* \approx 200$ K and $T_0 = 41\,800$ K for the PANI-HCl sample, whereas $T^* \approx 250$ K and $T_0 = 14\,000$ K for the PANI-DBSA sample.

Hence, even though there are some quantitative differences, qualitatively the same overall behaviour of σ suggests the same microscopic processes in the two materials. Notably, $\alpha = 2/5$ connotes $d = 3$, which is in our case reasonable because the chains are much shorter than the sample length and an appreciable conductivity requires a strong interchain coupling. Another condition for $\alpha = 2/5$ in the FTS theory is a weak-to-moderate disorder, which in principle implies a relatively high $\sigma_{\text{r.t.}}$ – in agreement with our observation. That disorder leaves a fingerprint in $\sigma_{\text{r.t.}}$ follows from the known fact that $\sigma_{\text{r.t.}}$ in PANI-HCl at a same Y can vary considerably in response to the method of synthesis as well as to other sample history.

In our samples, the VRH seems to be influenced by a homogeneous disorder rather than by structural heterogeneities originating in a possible partial crystallisation of the polymer. Namely, X-ray diffraction patterns of the discussed PANI-HCl samples exhibit peaks

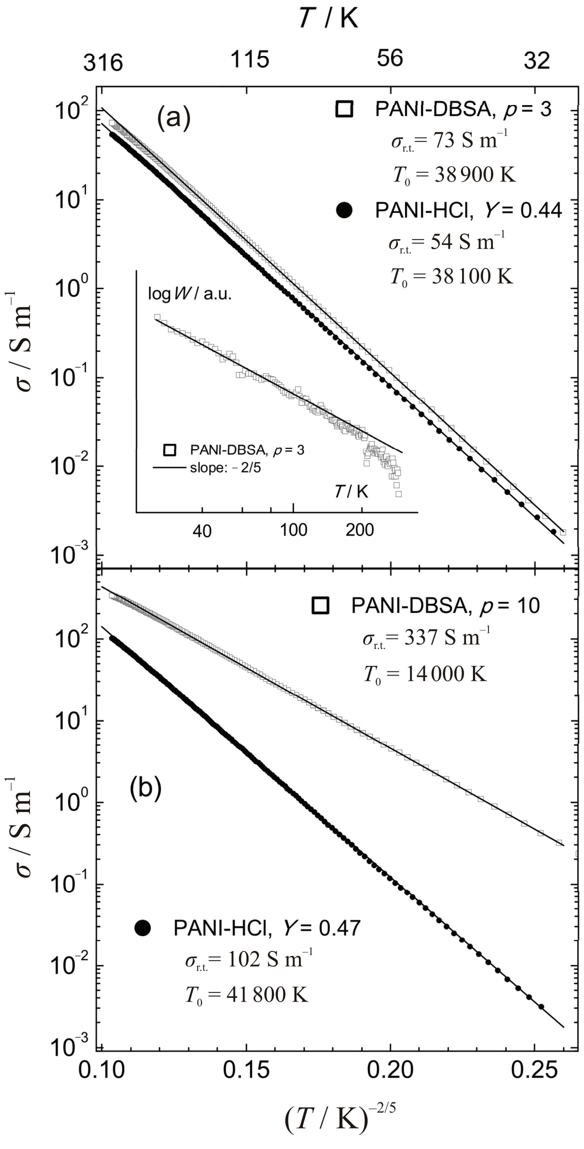

Figure 2. (a) log σ *vs.* $T^{-2/5}$ for PANI-DBSA (open squares, $p = 3$, $\sigma_{\mathrm{r.t.}} = 73$ S m^{-1}) and PANI-HCl (solid circles, $Y = 0.44$, $\sigma_{\mathrm{r.t.}} = 54$ S m^{-1}) samples of similar $\sigma_{\mathrm{r.t.}}$. The solid lines depict $\log\sigma \propto T^{-2/5}$ dependence. Inset: log-log plot of W, in arbitrary units (a.u.), *vs.* T for the PANI-DBSA sample (symbols). The solid line corresponds to $\log W \propto \mathrm{const.} - (2/5)\log T$. (b) log σ *vs.* $T^{-2/5}$ for the best-conducting PANI-DBSA (open squares, $p = 10$, $\sigma_{\mathrm{r.t.}} = 337$ S m^{-1}) and PANI-HCl (solid circles $Y = 0.47$, $\sigma_{\mathrm{r.t.}} = 102$ S m^{-1}) samples produced by the doping methods used.

characteristic of a partial crystalline ordering,[12] whereas the PANI-DBSA samples are fully amorphous.[13,16] Defects corresponding to such a homogeneous disorder can arise from bending and twisting of the chains, as well as from local properties of their entanglement. This may or may not result in the appearance of (quasi) crystallinity, although any crystalline ordering certainly suppresses the above-mentioned defects by straightening the chains. The conclusion on the decisive role of the homogeneous disorder on the VRH in doped PANI supports the applicability of the FTS model further, since this assumption is used therein.[9]

The reason for $\alpha = 2/5$ being limited to $T < T^*$ can be elucidated by considering the roles of relevant energy and length scales. These are: the energy range $|E - E_{\mathrm{F}}| = \varepsilon \approx k_{\mathrm{B}}T(T_0/T)^{\alpha}$ that contributes to the VRH (k_{B} is the Boltzmann constant), the T-independent Δ_{C}, and the average hopping length.[9] If ε is smaller than Δ_{C}, the inconstancy of $g(E)$ is of importance and α differs from $1/4$ of the Mott law (which corresponds to $g(E) = \mathrm{const.}$). Since ε increases with increasing T, eventually $\varepsilon >> \Delta_{\mathrm{C}}$, $g(E) \approx \mathrm{const.}$, and $\alpha \approx 1/4$ regardless of its low-T value. This picture holds as long as VRH is the relevant transport mechanism, and it was confirmed for our PANI-HCl samples in the doping regime $Y < 0.4$ (*i.e.*, low-to-moderate $\sigma_{\mathrm{r.t.}}$).[12] However, for the high-$\sigma_{\mathrm{r.t.}}$ results shown here, $\sigma(T > T^*)$ exhibits an opposite trend – it depends on T stronger than below T^* – but this also does not contradict the FTS model. For a weak disorder (implicitly, high $\sigma_{\mathrm{r.t.}}$), the dominating effect at high T is a reduction of the average hopping length, so the observed behaviour may signify a tendency towards hopping between nearest neighbours. Namely, these hops are more frequent than in VRH and σ is consequently enhanced, having a T dependence (corresponding to $\alpha = 1$) stronger than for any VRH exponent.[9]

CONCLUSIONS

We present and discuss our experimental finding of the exponent $\alpha = 2/5$ in the temperature (T) dependence of the variable-range-hopping (VRH) conductivity (σ) in own-made doped polyaniline pellets. We observe $\alpha = 2/5$ from ≈ 30 K up to $T^* \approx 200-250$ K for relatively well conducting samples (of room temperature conductivity above ≈ 1 S m^{-1}) doped either by HCl or by dodecylbenzenesulphonic acid. The theoretical framework for understanding $\alpha = 2/5$ is given in a recent theory of Fogler, Teber and Shklovskii.[9] The charge transport corresponds to the VRH in a three-dimensional network of chain-like conductors in the presence of a "soft" Coulomb gap around the Fermi energy, the density of states for charge excitations exhibiting a power law with the exponent 1. Another implication of the presented results is that the VRH in our samples is dominated by a homogeneous disorder. For the results shown, the $\sigma(T)$ dependence at $T > T^*$ strengthens, which is ascribed to a gradual transition form variable-range to nearest-neighbour hopping. An alternative behaviour in this regime is VRH with $\alpha = 1/4$, which was observed for HCl-doped samples of lower σ. All the findings presented and/or discussed meet a reasonably good description within the FTS model.

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SAŽETAK

Novi aspekti vodljivosti skakanjem promjenjivog dosega u dopiranom polianilinu

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Diskutirana je temperaturna, T, ovisnost električne vodljivosti, σ, tableta polianilina pripravljenih u našem laboratoriju, visokodopiranih ili s HCl ili s dodecilbenzensulfonskom kiselinom. Za oba je dopanta ispod $T^* \approx 200-250$ K nađen eksponent skakanja promjenjivog dosega jednak 2 / 5. Taj je rezultat moguće razumjeti u okviru nedavne teorije Foglera, Tebera i Shklovskiija, koja uzima u obzir kulonske korelacije u trodimenzionalnom sustavu lančastih vodiča, predviđajući potencijsku ovisnost gustoće stanja za pobuđenja naboja oko Fermijeve energije. Pri $T > T^*$, $\sigma(T)$ krivulje su strmije, implicirajući tendenciju prema skakanju između najbližih susjeda redukcijom prosječne duljine skoka.