Electrical conduction mechanism in conjugated polymers studied using Flicker noise spectroscopy

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Abstract

We have performed detailed analysis of the fluctuations of the electrical current in electrochemically deposited conductive polymers (CP) using as example polyaniline and poly(3-methylthiophene). These heterogeneous and disordered materials cannot be analyzed in terms of classical conduction mechanisms (like Schottky or Poole-Frenkel emission). Instead, the electrical transport in CPs is to be considered as a stochastic process with large component of noise. We have been able to distinguish several modes of the conduction process in CPs by applying Flicker Noise Spectroscopy. Thus, we have established that the transport of charge carriers in highly doped CPs is much less correlated than in non-doped ones at the same electric field strength. While applied electric field increases, correlations become lower in a sequence of elementary events contributing to the conductivity of CP. Apparently, the change in the correlation length corresponds to changing mechanism of the electrical conduction. The lower correlation in highly doped sample can be attributed to various factors including change in CP conformation, enhancement in interchain charge transfer and generation of polaron lattice.

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1. Introduction

Electrical conductivity of conducting polymers (CPs) including polyaniline (PANI) has been studied extensively [1-3]. Various models have been proposed for explaining the conduction mechanism: granular metal, variable range hopping model, quasi-one-dimensional conductor with 3D metallic states and quantum resonance hopping between metallic grains, to mention but a few [2, 4-6]. Two dominating models to explain the conduction mechanism are polaron lattice and bipolaron ones [7-10]. Still there is no commonly accepted point of view, which mechanism is the most realistic and therefore new experimental findings and theoretical approaches are necessary to identify the real conduction mechanism.

According to our previous studies on the mobilities of charge carriers in PANI films, the polaron lattice model is a suitable choice [11]. There we were acquiring smoothened conductivity data with noise component of the signal not taken into consideration. However, the noise component is expected to be significant in these disordered and heterogeneous materials. So, here we concentrate on the precise analysis of noise components of the electrical conductivity in CPs. The purpose is to get a deeper insight into the mechanism of the electrical conduction in CPs with varying doping degrees. By analysis of fine structure of stochastic signals, it is possible to get additional information on the dynamics of microscopic events occurring in the heterogeneous system, which is in continuous exchange of energy between the parts of the system and with environment.

2. Experimental & Data Processing Methods

To perform the conductivity measurements in CP of varying doping levels, the following procedure has been used. First, the CP film was deposited at the surface of two-band Pt microelectrode as reported previously [12]. This electrode was prepared by placing an insulating mica film of 5 μm thickness between two sheets of Pt foil (0.13 x 5 mm) and sealing this assembly with epoxy resin. The surface of electrode was planarized and cleaned by polishing it with fine emery paper and alumina.

PANI was deposited by cycling a potential between -0.2 V and 1.0 V vs. Ag/AgCl/NaCl(satd) at a sweep rate of 100 mV s^{-1} in a 2.3 M perchloric acid solution with 1.3 M aniline. This solution has been chosen since it yields highly conductive PANI films [13]. As a result of this polymerization procedure the CP film was bridging the contacts of Pt bi-electrode. Subsequently, the films were dedoped at -0.2 V in the same solutions, rinsed thoroughly with distilled water and dried in air. The electrode with CP film on it was transferred to acetonitrile

(MeCN) solution containing 0.1M tetraethylammonium perchlorate (TEAP). The two-band electrode was then polarized by applying different potentials (in the range of –0.7 to +0.3 V). Sufficient time (5 min) was allowed to ensure complete oxidation of the polymer at each potential. Hereafter, these potentials will be referred to as a doping potential (U_d).

After polarizing the electrode at a given U_d, the polarization potential (U_p) was applied between the two Pt contacts in a range of 0.1-10 mV and the electric current flowing through the system was measured as a function of time. Similar procedure was adopted for galvanostatic polarization regime: while the fixed polarization current (I_p) in the range of 1-50 nA was applied, fluctuation of voltage was registered as a function of time. In both in galvanostatic and potentiostatic modes, we have recorded two measurements each time with different polarity of voltage at the two-band electrode. No rectification behavior was noticed during the measurements.

All electrochemical measurements were performed using a computer-controlled potentio-galvanostat (Hokuto-Denko model HZ-3000). During the measurements it was important to differentiate between the noises coming from the measurement system (operational amplifiers of the potentio-galvanostat, discrete signal processing by computer, etc.) and the noise associated with the charge-transport mechanisms in CP. We have therefore performed a control polarization of a high-stability resistor possessing the same effective resistance (1-1.5 MΩ) as that of the sample. These measurements have shown that the internal noise of the circuitry is at least one order of magnitude lower and the structure of noise is different from that acquired in conductivity measurements of the PANI films. We have used the same measurement parameters (current range, precision and other potentiostat-related variables) for all measurements performed with polymer samples in order to maintain factors associated with equipment the same in all experiments.

The raw data on current and voltage noise I(t) and U(t) in the system were analyzed by calculating well-known power spectra of autocorrelation function (ACF)

$$S(f) \xrightarrow[T \to \infty]{} \left| \int_{-T/2}^{T/2} \langle V(t)V(t + t_1) \rangle \cdot \exp(2\pi i f t_1) dt_1 \right| \qquad (1)$$

and difference moments of second order

$$\Phi^{(2)}(\tau) = \left\langle \left[V(t) - V(t + \tau) \right]^2 \right\rangle \qquad (2)$$

where V(t) is a signal to be analyzed. These functions allow to quantify the presence of correlation links in a sequence of individual events contributing to the stochastic component of the measured signal

After calculating and plotting $S(f)$ and $\Phi^{(2)}(\tau)$, further analysis was performed using an approach known as Flicker Noise Spectroscopy (FNS) [14]. This methodology of the analysis of

stochastic signals has been applied by us to the analysis of the kinetics of different electrochemical processes and properties of heterogeneous materials (like porous silicon, thin film oxides, etc.) [15,16]. The FNS methods allows to quantify the correlation memory in the system through introducing the following approximations for the functions (1) and (2):

$$S(f) \approx \frac{S(0)}{1+(2\pi f T_0)^n} \tag{3}$$

$$\Phi_{(p)}(\tau) \approx g(p) \cdot \sigma^{p} \cdot \left[1 - \Gamma^{-1}(H) \cdot \Gamma(H, \tau/T_1) \right]^{p}, \tag{4}$$

The parameters, which enter in the Eqs. (3) and (4) are T_0, $S(0)$, n, σ, H, and T_1 are the characteristic parameters of the system describing the "memory" towards a sequence of stochastic events [14]. $S(0)$ is a saturation value for the $S(f)$ function at null frequency and it characterizes the mean amplitude of noise present in the signal, T_0 is a time interval within which some correlations between stochastic events still exist, etc. For example, the lower the values of the n and H parameters the lower is a rate of the memory loss in the system (stochastic events "remember" their predecessors longer) [14]. The application of FNS in the present case consisted of the approximation of experimental $S(f)$ and $\Phi^{(2)}(\tau)$ data with model functions (3) and (4) and obtaining corresponding values of characteristic parameters of the system.

Results

In Figure 1, the time variation of the electrical current flowing through the two-band Pt electrode with PANI film preliminarily modified at U_d= -0.7 and +0.1 V is shown. Figure 1a corresponds to U_d = -0.7 V where PANI is in completely dedoped state and therefore highly resistive, whereas at U_d= +0.1V, the polymer is in highly doped state corresponding to 29% oxidation level (Figure 1b). The current in this case is one order of magnitude larger than in dedoped sample. Large current transients are observed for both the doping potentials, probably due to charging of interface traps at electrolyte/PANI interface. The nature of these transients is more complicated in the case of highly doped PANI (Figure 1b) where current achieves the maximum before starting decreasing.
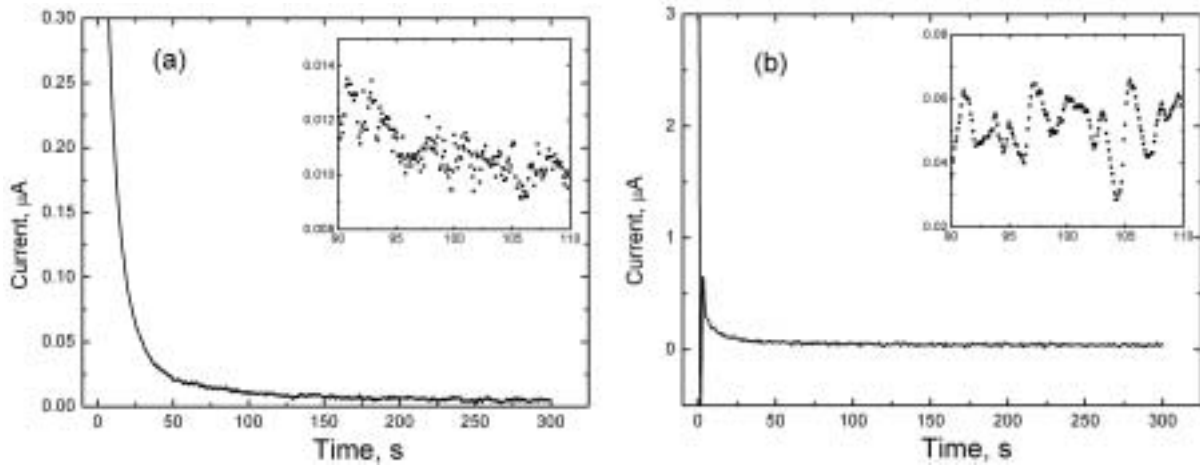
Figure 1. Time variation of the electrical current in PANI samples dedoped at -700 mV (SCE) – (a) and doped at +100 mV (SCE) (b). Measurements are performed at the potentiostatic polarization mode (U_p = 5 mV) applied between the contacts of two-band Pt electrode. The inserts show fine structure of noise in these two cases.

Besides, the doped sample reveals much higher amplitude of stochastic component. Furthermore, not only the amplitude but also the structure of the noise is different in both the cases as revealed in the inset of Figure 1.

Fast Fourrier transform (FFT) of the data in Figure 1 is presented in Figure 2. It shows that in the case of highly doped PANI several characteristic frequencies in the range of 0.05-0.3 Hz are present (curve 1), while the signal is rather random in the case of dedoped PANI (curve 2).
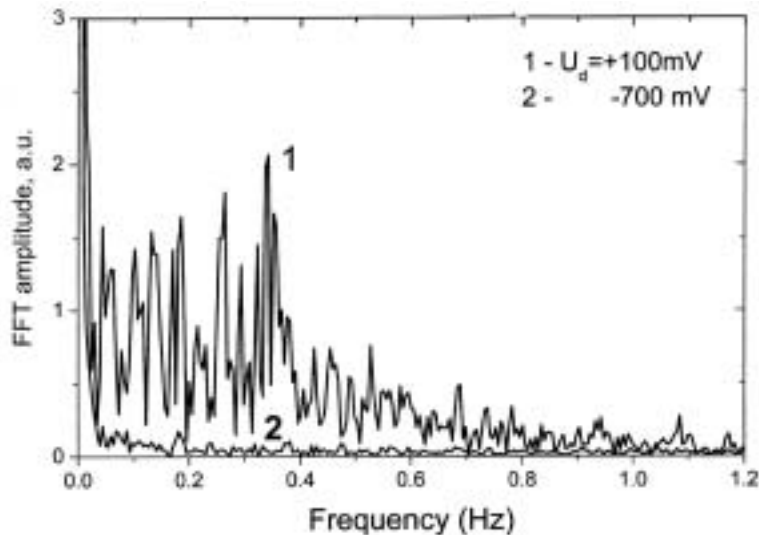

Figure 2. FFT amplitude of the current transients presented in the Figure 1.

Further evidence of different physical conditions realized in the samples with different doping level was obtained through calculation of power spectra of ACF (Figure 3) and structural function of the second order (Figure 4).
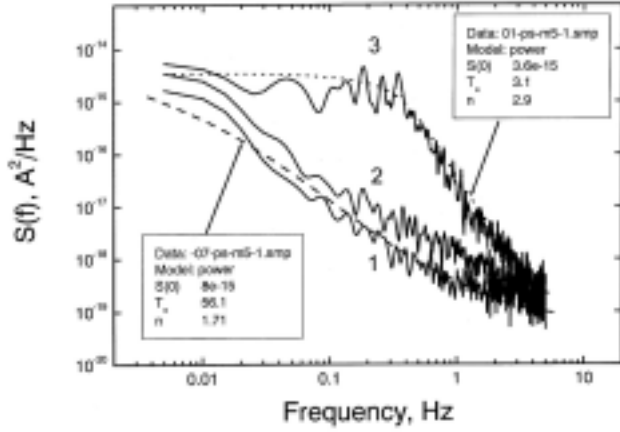
Figure 3. Power spectra of ACF for the electrical current corresponding to U_d = -700 (1), -400 (2) and +100 mV (3). The inserts show the values of parameters ensuring the best fit of the data using Eq.(3).
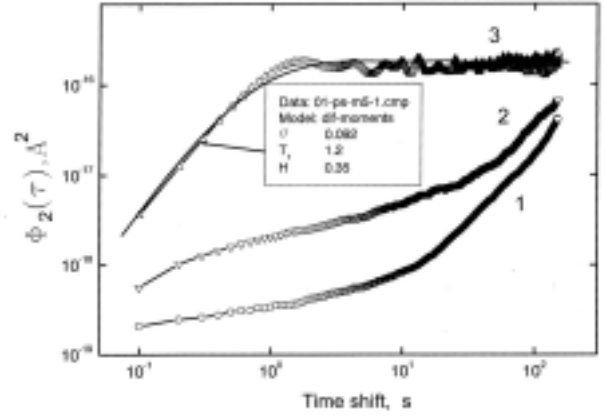
Figure 4. Structural functions of a second order for the current curves corresponding to U_d = -700 (1), -400 (2) and +100 mV (3). The insert shows the values of parameters ensuring the best fit of the data using Eq.(4).

Figure 3 shows power spectra of noise corresponding to different values of U_d. These spectra were obtained after removal of gradually changing component of a current (in order to reveal a stochastic component better). There is a drastic change in the shape of $S(f)$ when the polarization potential is shifted from -400 mV to +100 mV (curve 2 and 3). In case of highly doped sample, one can easily calculate characteristic parameters ($S(0)$ = 3.6 x 10^{-15} A^2/Hz, T_o = 3.1 s and n = 2.9) by fitting the curve obtained at +100 mV with approximation (3). On the contrary, in case of less doped samples (U_d=-700mV and -400 mV) there is no saturation in the $S(f)$ and only reliable n value one can extract is 1.7.

In terms of the FNS, higher value of n means lower correlation in a sequence of stochastic events associated with the conductivity of PANI. Thus the value of n apparently increases from 1.7 to 2.9 while the doping level of the PANI is increasing. Then we can conclude that the transport of charge carriers in heavily doped PANI is much less correlated than in less doped PANI. This conclusion is also supported by the calculation of the structural function of the second order (Figure 4). Slope of the $\Phi(\tau)$ function and its shape are quite different between less doped and heavily doped films. For highly doped sample, the experimental curve can be easily fitted using Eq. (4) as it is shown in Figure 3. On the other hand, for less doped films the fitting is not so straightforward in the whole range of time shift values. Most probably, at low time shift values some influence of the equipment noise can be imposed onto the results. Absolute values of current flowing through the system become small in the case of less doped samples (tenths of nano-amperes) so that the contribution of the artifacts related with the equipment is enhanced.

In order to get more insight into conduction mechanisms in PANI film, we have measured electrical conductivity of PANI at a fixed doping level by varying a polarization voltage (U_p) or a

polarization current (I_p). After acquiring the experimental data, the $S(f)$ and $\Phi(\tau)$ functions were calculated similarly to the cases shown in Figures 3 and 4. The experimental curves were further fitted with the approximations (3) and (4) to obtain the values of the FNS characteristic parameters.

Figure 5a and b demonstrates the dependence of power coefficient n on U_p for dedoped and highly doped samples, respectively. In both the cases we observe an increase of the n values with voltage although the trends are different from each other. For less doped films, the value of n changes just within the narrow interval (from 1.7 to 1.8). In contrast, highly doped film reveals much larger growth in n value (from 1.6 to 2.2 and more). This indicates that the correlations in a sequence of conductivity events are stronger at lower voltages while they are becoming weaker with the growth of the electric field. This in its turn shows that the conduction mechanism in PANI film through the positive charge carriers is changing with the increase in the applied voltage.
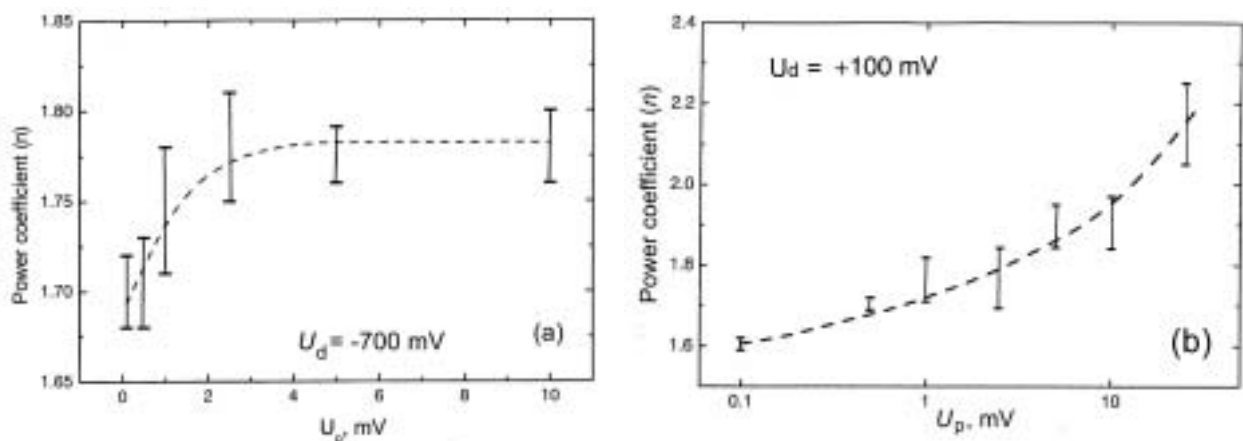

Figure 5. Dependence of the power coefficient on the polarization voltage for dedoped (a) and highly doped (b) PANI

Other FNS parameters which enter into the approximations (3) and (4) also exhibit systematic change while the doping level of the polymer is changing or when the voltage applied to the system is increasing.

We have also performed a study of the voltage noise in the PANI while fixing a polarization current flowing through the polymer. Figure 6 shows the influence of polarization current on structural function of the second order. Lower polarization currents (curve 2 in Figure 6) reveal much more extended saturation of $\Phi_2(\tau)$ function at low time shift values due to equipment limitations. Fitting the experimental curves, we obtained H values of 0.67 and 0.58 for I_p= 50 and 5 nA, respectively. Again, higher current value corresponds to lower dynamic memory in elementary acts of the electrical conduction of PANI.

The data obtained by employing poly(3-methylthiophene) (PMT) appeared to be somewhat less convincing as compared with those corresponding to the case of PANI. Though general tendency of electrical transport through the system becoming less correlated with the growth of the doping level and polarization voltage is remaining the same as in the case of PANI, the scatter of the experimental data is still very high to allow for correct fitting of the experimental data. It seems that further work is needed to ensure reproducible properties of PMT .
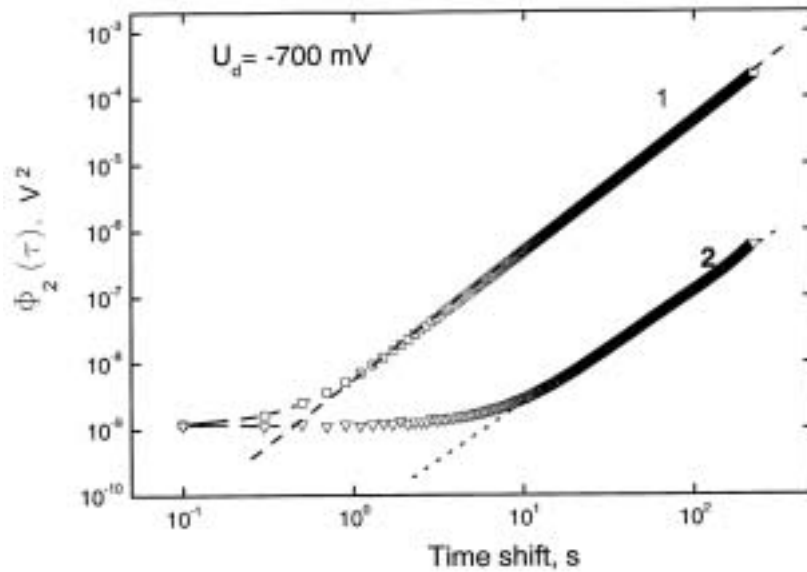

Figure 6. Structural functions of a second order for the polarization voltage curves corresponding to the PANI sample dedoped at -700 mV and polarization currents 50 nA (1) and 5 nA (2).

Discussion

From the data obtained in the present work we can discuss possible conduction mechanisms in PANI films at different doping levels and different stepping voltages. Our data mainly emphasize the following issues.

As our data indicate, with increasing doping level the individual events contributing to the conductivity of PANI film become less correlated. This probably means that more parallel channels for the conductivity are opened with the increasing doping level. Many channels act simultaneously to ensure uncorrelated electronic transport.

As mentioned in the introduction we have recently reported mobilities of charge carriers in PANI films [11]. In that report, the variation in mobility as a function of oxidation level has been explained with the help of conformational change of PANI chains as well as the formation of polaron lattice. The results obtained in the present work can be considered as a further development of this point.

While changing the doping potential from -0.7 V to +0.1 V, we observe the loss of correlation in a sequence of elementary conductivity acts that can be related to factors like a conformational change from coil to expanded coil, formation of polaron lattice and enhancement in the interchain hoping of electrons.

If the voltage applied to the sample is growing, then according to our results, the correlations in the transport of the carriers are weaker. Again we can speculate here that while the electric field in the materials is increasing, more parallel channels for the electrical conduction are opened thus providing paths for uncorrelated electron passage.

One interesting point, which should be addressed to further studies, is a non-monotonic behaviour of the current transients in doped samples. Figure 1(b) shows that at the beginning of the polarization process the current drops to negative value and then rises again to achieve second maximum and finally reduces to some steady state value. This behaviour is apparently associated with relaxation processes at initial stages of polarization and needs further inquiry using transient experimental techniques.

Generally, the analysis of the noise accompanying the electrical current flow in CPs allows to obtain valuable information on the conduction mechanisms through the disordered network of polymeric chains. Apparently, one of the immediate applications of this method in studies of the CPs might be a diagnostics of the degree of the order in these polymers.

Conclusions

1. We have studied the electrical conductivity of the PANI films with different doping levels and at varying electric field in the polymer using a method of Flicker Noise Spectroscopy.

2. Fine structure of the electrical noise assisting the electrical current flow in PANI is changing while the doping level of the polymer is increasing. The noise becomes less correlated thus indicating the changing mechanism of electrical conductivity.

3. Higher electric fields make the electrical noise less correlated. The effect is stronger in the doped samples. This clearly reveals that at higher electric fields any mechanism suggesting a correlated transport (like bipolaron conductivity, space charge limited currents, etc.) is less probable.

4. Flicker Noise Spectroscopy is a useful tool for elucidating conduction mechanism in PANI and the method can be extended to other polymers.

Acknowledgements

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