Influence of electrochemical doping on low frequency noise of conducting poly(3-methylthiophene) film

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ABSTRACT

Low frequency noise properties of the poly(3-methylthiophene) film prepared by electrochemical polymerization on two-band Pt electrode are investigated. The relation between flicker noise and conducting properties under different doping potential is discussed on the basis of the Hooge empirical equation. Under light doping state, the Hooge parameter almost remains constant with increasing doping potential. However, in the case of heavy doping, it increases with doping potential. The dependence of the Hooge parameter on doping level reflects the evolution of metallic domains and the transport process of charge carriers. It is believed that the amorphous structure and high carrier concentration in the poly(3-methylthiophene) film lead to a greater Hooge parameter value.

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1. Introduction

Some applications making use of conducting polymers for electronic devices such as field-effect transistors, bipolar transistors, light-emitting diodes have been proposed in recent years [1,2]. However, it is much necessary to understand the physical and chemical mechanisms of the doping of polymers before their final applications. The noise analysis of organic films has attracted a great interest, because the electrical noise reflects sensitively the mechanisms of charge transport in these materials [3–8]. Moreover, the noise analysis turns out to be a superior diagnostic tool for quality assessment of organic semiconductors devices [8,9].

In a variety of dissimilar physical systems, the power spectral density of fluctuation varies approximately as $1/f$, which is named a flicker noise [10–13]. Many of the features of the flicker noise are illustrated by the Hooge phenomenological equation [10]:

$$S_v(f) = \frac{\alpha V_0^{2+\beta}}{N_c f^\gamma} \qquad (1)$$

where $S_v(f)$ is the power spectral density of the voltage fluctuation, V_0 is the dc voltage across constant current bias sample, f is the frequency and N_c is the total number of charge carries in the sample. On the other hand, the resistance fluctuation is also accomplished by analyzing the power spectral density of a current fluctuation at a constant bias voltage.

$$S_I(f) = \frac{\alpha I_0^{2+\beta}}{N_c f^\gamma} \qquad (2)$$

In both equations, the frequency exponent (γ) ranges from 0.8 to 1.5 for stationary condition. If $\beta = 0$, then the noise is produced totally by equilibrium resistance fluctuation of the samples. While $\gamma = 1$ and $\beta = 0$, the Hooge parameter (α) becomes a dimensionless universal constant, 2×10^{-3}. However, further experiments show that the Hooge parameter depends on the quality of materials. It has been reported to vary from 10^{-8} to 10^2 [14]. Specifically, for conducting polymers, α is several orders of magnitude greater than the universal constant of 2×10^{-3} [3,5,8]. It is also found that α depends on the type of conducting polymers. Most of the conducting polymer samples used for noise analysis were prepared by CVD (Chemical Vapor Deposition), PVD (Physical Vapor Deposition) or similar methods, and their conductivities were not changed [4,7,15]. The corresponding noise analysis for conductivity-adjusted polymer samples is rarely published.

The electrical conductivity value of conducting polymers ranges from that of insulator up to a metallic regime, depending on the degree of oxidative or reductive doping. Therefore, it provides us a good opportunity to analyze the Hooge parameter using only one

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sample, which conductivity could be reversibly adjusted over several orders of magnitude. Up to now, no report has been published about this topic.

Polythiophene and its derivatives are typical conducting polymers, and their physical and chemical properties attract much attention [16–20]. We have measured the conductivity and mobility of poly(3-methylthiophene) (PMT) film at different doping potentials by in situ electrochemical method [21]. In the present work, we measured the current fluctuation of PMT films, analyzed its low frequency noise under different doping levels, and then discussed the charge transport mechanism of PMT by comparing its flicker noise parameters and conducting properties. Furthermore, the dependence of the Hooge parameter on the doping potential of conducting polymer was for the first time examined.

2. Experimental

All chemicals were purchased from Tokyo Kasei Co. 3-Methyl-thiophene (MT) and acetonitrile (MeCN) were used after distillation. Tetraethylammonium perchlorate (Et_4NClO_4) was purified by recrystallization from ethanol. Moreover, propylene carbonate (PC) was of reagent grade and used without further purification.

A two-band Pt electrode system was employed to determine in situ conductivities of PMT at different doping potentials as described [21–23]. In this paper, the working electrode was prepared by placing an insulating mica film of 20 μm between two sheets of Pt foil (10 mm × 2.5 mm × 100 μm). The complete system was embedded in a glass tube and glued with epoxy resin. The surface of two-band electrode was first grounded with fine emery papers, and then polished with alumina powder (0.3 μm). The final electrode surface includes two parallel Pt regions (2.5 mm × 100 μm) with a gap of 20 μm.

PMT films were prepared on the two-band electrode by a controlled-potential electrolysis in a PC solution containing 0.1 M MT and 0.1 M Et_4NClO_4 at 0 °C. The electrochemical polymerization of MT was carried out at +0.85 V with respect to the reference electrode of $Ag/AgClO_4$ (10 mM), Et_4NClO_4 (0.1 M) in PC. The detailed description was given in Ref. [21]. The film thickness was about 40 μm, estimated by adjusting focus of optical microscope. After polymerization, the PMT films were rinsed with MeCN, and then dedoped at −0.4 V for 30 min in MeCN solution containing 0.1 M Et_4NClO_4. The film-coated electrode was polarized at different potentials ranging from −0.4 V to +0.6 V, chosen according to the conductivity and doping level relation [21]. This applied potential is referred to as the doping potential.

After doping at a given potential, a polarization potential of 10 mV was applied between the two Pt bands, and the current through the PMT film immersed in MeCN solution containing 0.1 M Et_4NClO_4 was recorded as a function of time. Then the current fluctuation is obtained from the current signal. Each measurement was made for at least 5 min. Because PMT in MeCN solution is more stable than in air, the current fluctuation measurements were also made in MeCN solution. In fact, the solution influence on current is negligible, and the current is conducted by the polymer film rather than MeCN solution. It was confirmed further that the current between the two Pt sheets at an applied potential of 10 mV is almost zero for the PMT-free electrode. When the doped sample was taken out, rinsed thoroughly with pure MeCN and dried in air, similar noise measurements were also made with the PMT film in air.

All current fluctuation and electrochemical measurements were performed at a room temperature using a computer-controlled Hokuto Denko HZ-3000 automatic polarization system. The power spectral density of current noise, $S_I(f)$, was calculated by Fourier transform of autocorrelation function of current fluctuation under constant bias voltage [10,24]. High-stability resistors with the

same resistance as the doped film ($1\,\Omega^{-1}\,M\Omega$) as the doped film were subjected to the current fluctuation measurement by a procedure similar to the case of the PMT film. The measurement carried out in the temperature range of 77–673 K confirms that the obtained current noise generates from the tested sample rather than the polarization system including operational amplifiers of the potentiostat–galvanostat.

3. Results

3.1. Conducting properties of PMT film

In a previous paper, we have determined mobilities of charge carriers in the PMT film over a range of doping levels by combining in situ conductivity measurement and potential-step chrono-coulometry with a two-band Pt electrode [21]. In order to find a quantitative relation between the noise parameters and conducting properties, our previous study will be briefly reviewed.

The absolute value of doping level is rather small when the doping potential is less positive than 0.15 V, although the logarithm of the doping level increases by two orders of magnitude with the potential up to 0.30 V [21]. The doping level increases rapidly when the potential exceeds 0.15 V. The conductivity, σ, in a PMT film has a similar tendency to change with doping potential. The σ increases from $3.9 \times 10^{-6}\,S\,cm^{-1}$ at −0.3 V to $30\,S\,cm^{-1}$ at 0.7 V [21]. When the potential is more positive than 0.15 V (σ = 0.05 S cm^{-1}), the absolute value of σ also increases quickly. The concentration of charge carriers, n_c, is directly calculated from the doping charge, Q. The n_c increases to $1.6 \times 10^{21}\,cm^{-3}$ at 0.7 V. Similarly, the n_c value below 0.15 V is rather small though it improves two orders of magnitude from −0.3 V to 0.15 V [21]. Apparent mobility, μ, calculated from σ and n_c increases by several orders of magnitude with an increase of the doping level [21]. However, at heavy doping states the μ stays almost constant and even slightly decreases with doping level.

3.2. Power spectral density of flicker noise in PMT film

Typical $S_I(f)$–f relation is shown in Fig. 1. Power spectra at different doping potentials and bias voltages, tested in air or solution, exhibited a similar feature.

According to the empirical Eqs. (1) and (2), $S(f)$ will be infinite or zero if f tends to 0 or ∞, respectively. That is not consistent with the measured power spectrum. So these equations cannot be used to fit $S(f)$ in the whole frequency range [10]. Some models have been proposed to solve this problem. Timashev and coworkers proposed a flicker noise spectroscopy (FNS) to analyze the fine structure of noise by decomposing it into elementary components (spikes,
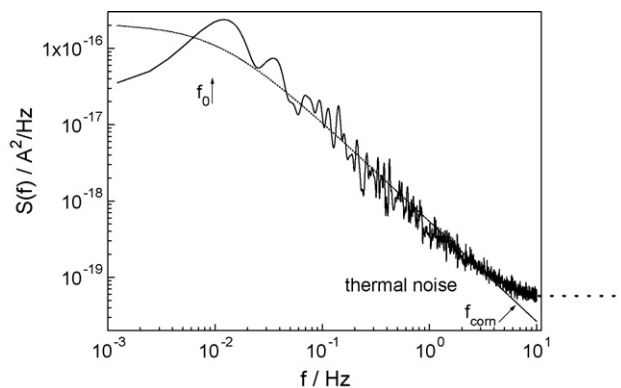

Fig. 1. Power spectral density of current noise of PMT film doped at +0.15 V. Tested at 10 mV bias voltage in 0.1 M Et_4NClO_4 + MeCN solution.