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Non-linearity in the *I–V* characteristic of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) due to Joule heating

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Abstract

Deviations from Ohm's law are reported for electrical conduction in thin films of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS). A bridge method is used with two independent currents: a 'pump' current flowing through mainly one resistive part and a small 'probe' current. Changes in resistance are independent of the probe current, but linearly proportional to the electrical power delivered by the pump current. The change in resistance is interpreted in terms of Joule heating and a constant relating the relative change in resistance to the heat production is extracted: $\alpha_s = 8 \times 10^{-8} \sqrt{s}\,cm^3/J$.
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In the past decades the performance of conducting, π-conjugated polymers has advanced to such a level that they can now be incorporated in plastic electronic circuitry [1–7]. In these applications, polymers rendered conductive by deliberate oxidative doping are used as current carrying wires and in some cases also as active element. Poly(3,4-ethylenedioxythiophene) (PEDOT) has developed into one of the most successful materials [8]. It combines a low oxidation potential with good stability in the oxidized state [9]. Unfortunately, PEDOT is an insoluble polymer. This drawback can be circumvented by polymerization in combination with a water-dispersible polyelectrolyte such as poly(styrenesulfonic acid) (PSS).

A major difference between PEDOT:PSS and normal metals is that, near room temperature, the resistivity *decreases* with temperature [10] ($d\rho/dT < 0$). This fact may cause a thermal instability. Joule heating of the polymeric conductor will result in a lowering of the resistance, as $d\rho/dT < 0$. Hence, the power dissipation will increase with time when a constant voltage is applied to the material. If the heat produced cannot be transported at a sufficient rate, a thermal runaway will

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occur which may eventually result in a breakdown of the material. Therefore, it seems of importance to study the effect of electrical currents on the resistivity of PEDOT: PSS and to evaluate the transport of heat from the polymer film to its surroundings.

Previously, we have studied the effect of infrared (IR) radiation on the electrical conductivity of PEDOT:PSS. We found that upon pulsed irradiation with IR light, a transient reduction of the resistance ($\Delta R(t)$) of PEDOT:PSS occurs [11,12]. This transient decays back to its equilibrium value according to $\Delta R(t) \propto 1/\sqrt{t}$ which can be rationalized in terms of diffusion of heat form the polymer film into the substrate. These electro-optical studies provide an indication on how to describe the effect of Joule heating on the electrical resistance of the conducting polymer. Yet, it remains to be proven whether the effect of the infrared light can indeed be fully understood in terms of sample heating or whether the IR photon with its relatively large quantum of energy can induce processes that cannot be initiated by other energy sources.

Here we investigate changes in the resistance of films of PEDOT:PSS induced by electrical current. The method applied uses two currents ('pump' and 'probe'). After presenting the experimental results, we will analyze the observed effects using a model in which changes in resistance result from a rise in temperature in the conducting layer.

Structures with a Wheatstone bridge arrangement of four resistive patches of polymer have been developed (see Scheme 1). Electrode structures were deposited onto glass substrates by thermal evaporation (glass/Cr (thickness ~ 5 nm)/Au(~ 100 nm)). On the patterned substrates, PEDOT:PSS dispersion [12] was spin cast. The polymer was then dried by heating at 120 °C for a few minutes. Layer thickness: 3.8×10^2 nm. Part of the polymer film was removed by scratching to obtain four isolated, resistive parts. Active resistive area per patch: 3×2.7 mm, resistance $R = 1.2 \times 10^2$ Ω. A variable resistor was connected in parallel with one of the resistive parts to compensate for small differences in resistance. Before each measurement, the voltage across the bridge was nulled when only probe current was applied. Probe
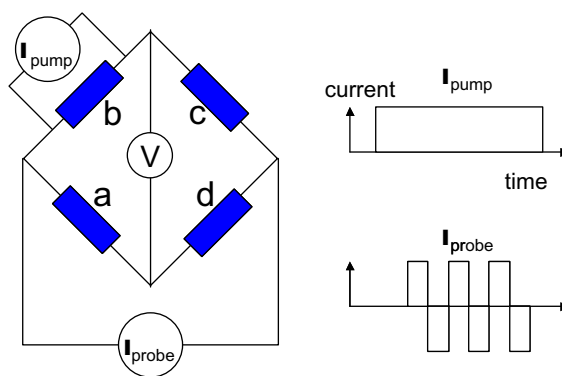
Scheme 1. Schematic layout of the experiment.

and pump currents were generated by a Keithley 220 current source and a 2400 source meter. The latter was also used to measure the voltage.

A constant pump current is applied via the contacts on one resistive part of the bridge (R_b, see Scheme 1). The waveform of the alternating probe current is illustrated and its period is set to 20 s. The voltage V is monitored and some typical results are illustrated in Fig. 1. From the voltage traces a linear baseline has been subtracted and in this way we compensate for the voltage across the bridge due to the pump current and for slow drift in the resistance R_b.

Fig. 1 illustrates that upon a sudden change of the probe current, the voltage responds quite slowly. Previous measurements of changes in resistance upon irradiation with short pulses of infrared light revealed very short RC times for
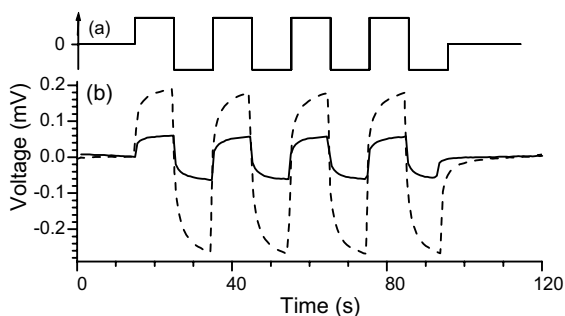

Fig. 1. (a) Waveform of the probe current modulation. (b) Voltage V over the bridge recorded with a $I_{pump} = 9$ mA and $I_{probe} = \pm 2$ mA (dashed line), and ± 0.5 mA (solid line).

similar devices [12]. After detuning the bridge, the voltage responds within the time resolution of the measurement to a change in probe current when no pump current is applied. These observations rule out capacitive effect as an explanation for the slow time constant in the response to the probe voltage modulation.

From Fig. 1, it can be seen that the amplitude of the voltage with 2 mA probe current amplitude is nearly four times higher than with 0.5 mA. We have investigated the dependence on the magnitude of the probe current further. The relative change in resistance R_b was calculated using

$$\frac{\Delta R}{R} = \frac{\Delta V}{2I_{probe}} \frac{4}{R}. \tag{1}$$

Here I_{probe} is the amplitude of the probe current waveform and hence $2I_{probe}$ the total peak-to-peak amplitude. ΔV is the difference in voltage between the maximum of V in the up period and the minimum in the down period. The factor 4 results from the use of a bridge (see below). For various values of I_{probe} we have determined $\Delta R/R$ and the results are shown in part (a) of Fig. 2. The value of $\Delta R/R$ is virtually independent of the magnitude of the probe current. Also the dependence of the change in resistance on the pump current has been investigated (Fig. 2b). We observe a linear relationship between $\Delta R/R$ and the electrical power delivered by the pump current (approximated by $I_{pump}^2 R_b$).

The waveform of the alternating part of the voltage V depends in a peculiar manner on the ratio of pump and probe currents. This is illustrated in Fig. 3(a). Here normalized voltage traces recorded for various pump currents with the same probe current are displayed. The waveform of the downward half of the modulation does not change to a significant extent when I_{pump} is varied while the upper half period changes considerably. Fig. 3(b) shows results of theoretical modeling of the voltage.

Straightforward analysis of the circuit drawn in Scheme 1 results in the following expression for the voltage V across the bridge as a function of pump and probe currents:
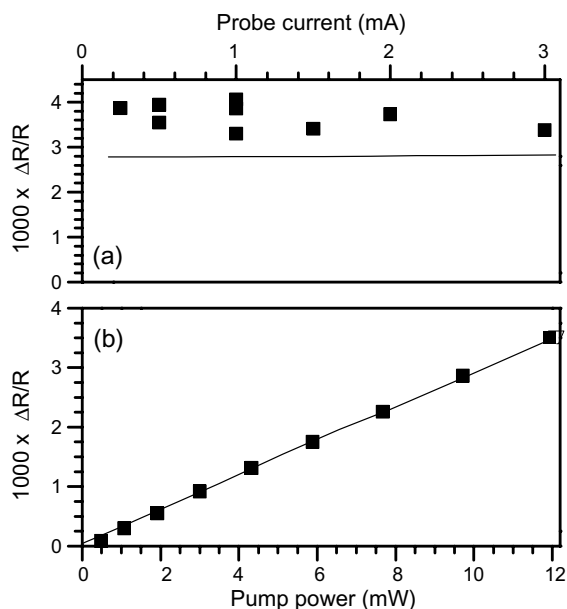

Fig. 2. (a) Relative change in resistance for various probe current amplitudes. $I_{pump} = 9$ mA delivering $\sim$9.7 mW power on a surface area 8 mm^2. (b) Dependence of the change in resistance on pump power. $I_{probe} = \pm 3$ mA. Solid lines: predictions from Eqs. (2) and (4).
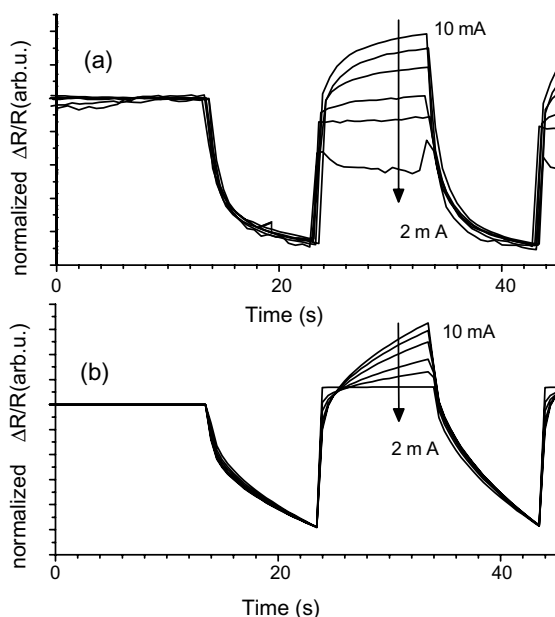

Fig. 3. (a) Voltage waveform as a function of I_{pump} (10, 8, 6, 4, 3 and 2 mA). $I_{probe} = \pm 3$ mA. (b) Modeling using Eqs. (2) and (4).

$$V(I_{\text{pump}}, I_{\text{probe}})$$

$$= \frac{(R_a R_c - R_b R_d)I_{\text{probe}} + R_b(R_c + R_d)I_{\text{pump}}}{\sum R}, \quad (2)$$

where $\sum R = R_a + R_b + R_c + R_d$.

We assume that the resistance R_b depends on the current flowing through it (I_b) and, for the sake of simplicity, that the other resistors have fixed values. The current I_b flowing through R_b can be expressed as

$$I_b = \frac{(R_a + R_d)I_{\text{probe}} + (R_a + R_c + R_d)I_{\text{pump}}}{\sum R}. \quad (3)$$

We now propose that the resistance R_b is lowered because of a rise in temperature ΔT induced by the Joule heating resulting form I_b. In first approximation one expects that ΔT is related to the electrical power dissipated at R_b($I_b^2 R_b$). However, the rise in temperature at time t_1 can only depend to a limited extent on the power dissipated at time t_2 ($t_1 > t_2$) because part of the heat generated at t_2 will have been lost at t_1. To account for this we use the expression

$$R_b(I_{\text{pump}}, I_{\text{probe}}, t)$$

$$= R_{b,0}\left(1 - \alpha \int_0^{t^*} R_{b,0} I_b^2(I_{\text{pump}}, I_{\text{probe}}, t - \tau)\frac{1}{\sqrt{\tau}}\,d\tau\right). \quad (4)$$

Here, the factor $1/\sqrt{\tau}$ in the integrand symbolizes the assumption that the heat generated by, e.g., a short electrical pulse at t_1 will disappear due to heat transport with the remaining thermal energy decaying according to $1\sqrt{t}$ [11]. This time dependence is consistent with a one dimensional diffusion of heat out of the polymer film into the substrate. t^* is a cutoff time and has been set to 10 s in our simulations. The inclusion of such a cutoff time allows for thermal equilibrium to be established. α is a constant which depends on many parameters including the heat capacity and conductivity of polymer and substrate and also the temperature coefficient of the resistivity of the polymer ($d\rho/dT$). It has been treated as an adjustable parameter in our modeling.

Results of the modeling are illustrated in Fig. 2(b) (solid line). The linear dependence of the change in resistivity on the electrical power deli-vered by the pump beam can be reproduced by Eqs. (2) and (4). α is set at 2.6×10^{-2} $\sqrt{s}$/J. It may be anticipated that α is proportional to the volume of the resistive part and taking this into account, one obtains $\alpha_s = 8 \times 10^{-8}$ $\sqrt{s}\,cm^3$/J. Using the same value for α we have also modeled the dependence of the voltage across the bridge on the probe current and results are illustrated in Fig. 2(a). The insensitivity of $\Delta R/R$ to the magnitude of the probe current is born out. The absolute magnitude of the effects cannot be reproduced accurately with $\alpha = 2.6 \times 10^{-2}$, although the agreement is better at high values of the probe current. Part of the discrepancy may be due to irreversible aging effects of the polymer film. Interestingly, experiments on the same films in which the resistance is modified by IR irradiation [12] yield $\alpha_s = 6 \times 10^{-8}$ $\sqrt{s}\,cm^3$/J, in good agreement with the purely electrical measurements.

In Fig. 3(b) we have modeled the waveform of the voltage across the bridge. The modeling reveals that the slow rise and decay times of the voltage signal can be interpreted in terms of diffusion of heat out of the polymer film with its $1/\sqrt{t}$ time dependence. The experimental voltage traces seem to level off more quickly after a sudden change in the current than the theoretical curves. The agreement between theoretical prediction and experiment can be improved by assuming a steeper response function (e.g. $1/\tau^{0.7}$ instead of $1/\sqrt{\tau}$). Alternatively, also a reduction of the cutoff time t^* induces a faster saturation. We mention that a very similar curvature for the voltage traces is observed when the resistance of one of the patches is modified by irradiating with IR light [12]. This indicates that the discrepancy between model and experiment is the result of a poor modeling of the heat transport and does not primarily result from interfering electrical effects.

From Fig. 3(b), it can be seen that voltage across the bridge for $I_{\text{probe}} = \pm 2$ mA remains almost constant during one half period. Under these conditions the current I_b approaches zero during this part of the cycle and hence the voltage across the bridge is completely determined by the other resistances R_a, R_c and R_d and depends only indirectly on the actual value of R_b. Experimentally, this flat response condition seems to be met

already at a probe current of 3 mA and the value of the plateau in voltage is lower than predicted by Eqs. (2) and (4).

In conclusion, deviations from Ohm's law occur for PEDOT:PSS films due to Joule heating. The slow response of the resistance to changes in the current can be explained by slow transport of heat out of the polymer film.

Acknowledgements

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