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Polythiophene films on gold electrodes: a comparison of bulk and contact resistances in aqueous and organic media

Ulrich Lange · Vladimir M. Mirsky

Abstract Recently, developed technique for separated analysis of bulk and contact resistance was applied for the investigation of polythiophene films electropolymerized in boron trifluoride diethylether. Kinetics of polymer resistance and for the first time of the contact resistance during polymer oxidation and reduction were characterized. Influence of electrochemically controlled oxidation state on the polymer bulk and the polymer/metal contact resistance was measured in aqueous and organic environment. Variation of the electrical potential from −0.2 to 1.1 V vs. Ag/AgCl (sat) leads to an increase of the polymer conductivity for about three orders of magnitude and to a decrease of the contact resistance for about three orders of magnitude. The potential dependence of the two resistances was different, especially at high anodic potentials. In organic solution, the change of both resistances was more than six orders of magnitude. The results were compared with electrochemical and spectroelectrochemical data, a difference in the material behavior depending on the electrolyte solvent was observed. The influence of electrical potential on polymer resistance in aqueous solution was explained quantitatively by a three-state model with the values of oxidation potential +0.3 and +1.2 V.

U. Lange
Institute of Analytical Chemistry, Chemo- and Biosensors,
University of Regensburg,
93040 Regensburg, Germany

V. M. Mirsky (✉)
Nanobiotechnology–Faculty of Natural Sciences, Lausitz
University of Applied Sciences,
01968 Senftenberg, Germany
e-mail: vmirsky@hs-lausitz.de

Introduction

Although polythiophene is the third one in the rank of the mostly studied conducting polymers [1] and most of its physical and chemical properties are well-known [2], a separated analysis of in situ bulk and contact resistances of this polymer was not performed so far. Meanwhile, this information is crucial for each application exploiting electrical conductivity of this polymer: organic electronics, chemical sensors, [3], electrochromic devices, etc. Recently, we have demonstrated that the measurement configuration based on simultaneous application of two- and four-point techniques [4] provides a possibility to get quantitative information on both bulk and contact polymer resistances [5]. The measurement techniques used for characterization of conductivity of electrochemically active polymers were reviewed recently in Ref. [6]. Here, we report an application of simultaneous measurements of bulk and contact resistances for characterization of polythiophene. The measurements were performed at defined polymer oxidation states by application of an electrical potential versus a reference electrode. The behavior of polythiophene films deposited on metal electrodes can be described as an electrochemical transistor: a variation of the applied potential controls the polymer resistance [7, 8].

Polythiophene films electrodeposited from common solvents, like acetonitrile or propylenecarbonate, usually show reduced chemical and physical properties [9]. The deposition of polymer films in this work was performed by electropolymerization of thiophene in boron trifluoride

diethylether (BFEE) resulting in polymer films of higher quality [10–12] containing probably $[BF_3OH]^-$ as a dopant ions [12]. Such films were characterized earlier by cyclic voltammetry, Fourier transform infrared spectroscopy, and spectroelectrochemistry, but mainly in organic media [10–12]. To our knowledge, no data on in situ conductivity of these films was reported and only a few publications describe electrochemical behavior of polythiophene in aqueous media [13–15]. However, for some applications of this material, such data are important. Therefore, the measurements were carried out in 0.1 M NaCl solution buffered at pH 2 by phosphate. Acidic pH value was chosen to minimize alkalic polymer degradation. Here, we have compared electrochemical and spectroelectrochemical behavior of these films in aqueous and organic solvents and investigated the influence of the oxidation state on the polymer gold contact and bulk polymer conductivities.

Experimental

Interdigitated four-contact gold electrodes were used for simultaneous two- and four-point measurements. The outer electrodes had a width of 10 μm, the inner electrodes of 5 μm, and the gap between the electrodes was 5 μm. The electrodes were "folded" on the surface into the compact structure of the size 0.4×0.4 mm so that the same outer electrode was common for the inner electrodes placed on both of its sides (see [4] for details). Prior to electropolymerisation, the gold electrodes were cleaned by a successive treatment in chloroform (Merck), acetone (Merck), water, piranha solution (1:3 mixture of 30% H_2O_2/conc. H_2SO_4, v/v), and finally thoroughly rinsed with deionised water. Indium tin oxide (ITO) slides were cleaned with piranha solution and rinsed thoroughly with deionised water.

Polythiophene films were prepared at a constant potential of 1.35 V vs. a silver wire from a 0.05 M solution of thiophene (Merck) in 90% BFEE (Sigma) 10% acetonitrile (Baker, HPLC grade). The oxidation charge was about 1,200 mC/cm^2 for conductivity measurements and 25 mC/cm^2 for the spectroelectrochemical measurements. Cyclic voltammetry was performed on a General Purpose Electrochemical System Autolab PGSTAT-12 (EcoChemie). A one-compartment cell with three electrodes, working electrode, platinum wire counter electrode, and either silver chloride electrode (Ag/AgCl, sat. KCl in water) for aqueous solutions or a silver nitrate electrode (Ag/AgNO$_3$, 10 mM AgNO$_3$, 0.1 M tetrabutylammonium hexafluorophosphate (NBu$_4$PF$_6$, Fluka, electrochemical grade) in acetonitrile) for acetonitrile solutions was used. The potential of the silver nitrate electrode against the silver chloride reference electrode was +0.344 mV. All potentials obtained in organic solutions were recalculated to the silver chloride reference. Measurements in

aqueous media were done in 10 mM pH 2 phosphate (Merck) buffer containing 0.1 MNaCl (Merck). Deionised water additionally purified by Millipore Milli-Q system was used. For measurements in acetonitrile a solution of 0.1 M tetrabutylammonium hexafluorophosphate was used. All measurements were performed at room temperature. In situ conductivity measurements were performed using simultaneous two- and four-point measurement (s24)-technique [4]. The measurement time was 3.4 s per data point. Within this time, a resistance value was calculated from the current of two opposite voltage pulses. The polymer potential was controlled versus the reference electrodes described above. The same reference electrodes were used also for spectroelectrochemical measurements. These measurements were performed in two-electrode configuration using a Cary 50 Bio spectrophotometer from Varian. The value of the contact resistance was obtained from simultaneous two- and four-point measurement according to the approach described earlier [5, 6, 16]. Shortly, this approach is based on the subtraction of the value of four-point resistance, which is multiplicated to geometrical factor characterizing the ratio of effective polymer lengths between external and internal electrodes, from the value of two-point resistance. In the case of the electrodes, used in this work the geometrical factor is 3. A validation of this approach performed by comparison with impedance spectroscopy was reported in Ref. [5]. In this work, we applied this approach for the first time also for kinetic measurements.

Results and discussion

The potentiostatic electropolymerisation of thiophene from 90% BFEE/10% acetonitrile at 1.35 V vs. a Ag-wire yields smooth homogeneous films, which cover the gaps between the sensing strips completely and show a good stability and adhesion to the electrode (Fig. 1). At a high polymerization charge used for the coating of interdigitated electrodes this film has some surface inhomogeneities (Fig. 1a, b) while at the lower polymerization charge used for ITO coating for spectroelectrochemical measurements, an optically smooth coating was obtained (Fig. 1c), containing only a few bigger defects which may result from washing or damages of the ITO-electrode. A similar effect was observed earlier with polymerization of poly-N-methlyaniline [17]: that polymer was smooth up to a polymerization charge of 800 C/m^2 while a further increase of the polymerization charge led to formation of grains and cracks.

After washing with acetonitrile and drying under nitrogen flow, the films were cycled in a 50 mM phosphate pH 2 buffer containing 0.1 M NaCl. The resulting voltammogram can be seen in Fig. 2. The anodic cycling
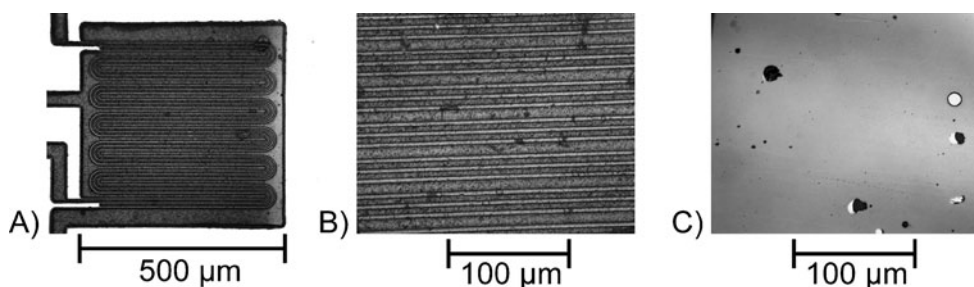
Fig. 1 Interdigitated gold electrode coated by polythiophene by electro-polymerization at +1.35 V from BFEE, polymerization charge 1.2 C/cm² (**a**). The same image under higher magnification (**b**) demonstrates some surface inhomogeneities which are not present in the sample obtained on ITO surface at polymerization charge 25 mC/cm² (**c**)

potential was limited to +1.1 V. An application of a higher potential led to overoxidation and corresponding loss of electrochemical activity. A similar effect was described in [13] for various polythiophenes. The current response in aqueous solution was much lower than in acetonitrile (Fig. 2, right). This effect can be explained by low penetration of highly hydrophilic ions from aqueous solution into the highly hydrophobic film of polythiophene [18]. It can be formally described as an increase of the oxidation potential of polythiophene in aqueous environment; however, the potential value required for the polymer oxidation cannot be reached because of limited polymer stability.

Spectroelectrochemical measurements of polythiophene films deposited onto ITO electrodes (Fig. 3) were consistent with the results obtained by cyclic voltammetry. The behavior of these films in acetonitrile (Fig. 3a) corresponds to the data reported in [12], while at the same potential scale in aqueous solution only slight optical changes were observed (Fig. 3b). The results confirmed that polythiophene is more stable against oxidation in aqueous environment than in acetonitrile: the potential increase for 1.1 V leads to about 50% decrease of the concentration of reduced state of polythiophene in acetonitrile but to only about 12% decrease in aqueous environment.

The results of the in situ conductivity measurements (Fig. 4) at anodic potentials are consistent with the results obtained from cyclic voltammetry. It can be seen that the total change of conductivity in the aqueous solution is about three to four orders of magnitude but it increases up to over six orders of magnitude in the acetonitrile solution. In the reduced state, the polythiophene film shows a higher conductivity in the aqueous solution; however, the conductivity in acetonitrile is higher at potentials more than +0.8 V. A suppression of the potential effect on polymer conductivity after polymer transfer from organic to aqueous medium was reported earlier for poly(3-methyl)thiophene [14, 15]. The difference in response was controlled by anion used in the polymer synthesis [15]. It has to be noted that the resistance values differed slightly between different samples, but the observed trend was always the same. A slight increase in resistance, especially in the low-resistance region occurred usually at repeated measurements at the same electrode.

The potential influence on polythiophene resistance in aqueous media indicates clearly that the polymer has at least three potentially dependent states. Some polymer oxidation at +0.25 V leads to increase of the polymer conductance for about one order of magnitude (Fig. 4). However, this oxidation is followed by very low changes of the polymer charge which can be hardly observed in voltammetric curve.
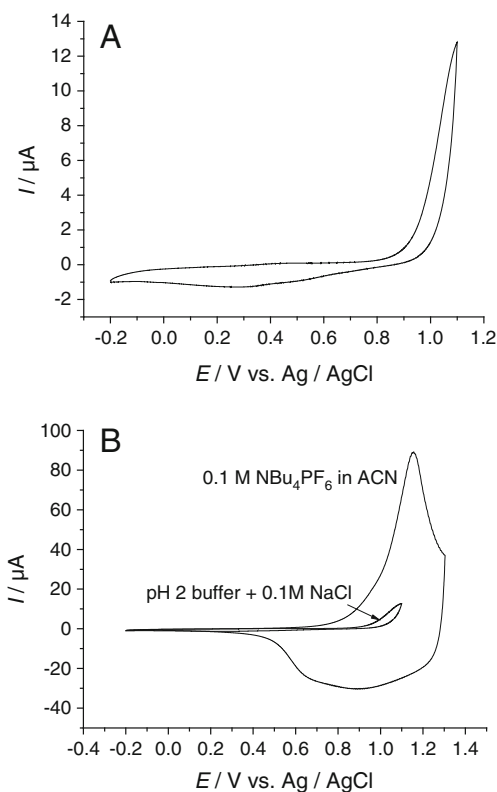

Fig. 2 Cyclic voltammetry of polythiophene coated gold electrodes in aqueous solution (left and inner curve in the right diagram) of phosphate buffer (10 mM, pH 2) and in acetonitrile solution of 100 mM NBu₄PF₆ (right, outer curve). *Sweep rate* 100 mV/s
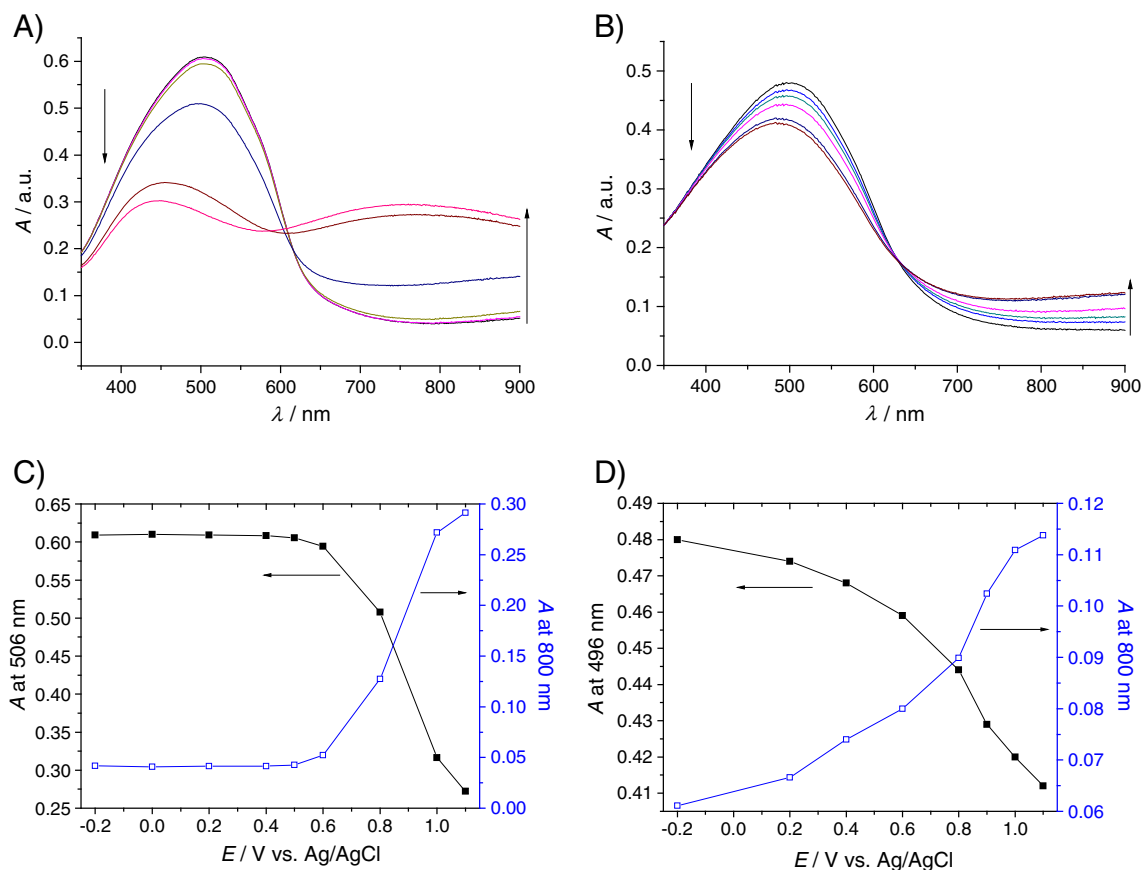
A)

B)

C)

D)

Fig. 3 Influence of electrical potential on optical absorbance of polythiophene films on ITO electrodes in acetonitrile solution of 100 mM NBu$_4$PF$_6$ (**a**) and in aqueous solution of 10 mM phosphate buffer at pH 2 containing 0.1 M NaCl (**b**). The *arrows* on the figure indicate an increasing of the potential. The potential values recalcu-

lated to the potentials vs. Ag/AgCl (sat.) are −0.2, 0.4, 0.6, 0.8, 1.0, and 1.1 V. The dependence of the absorbance at two wavelength (800 and 506/496 nm) on potential is shown for acetonitrile solution in **c** and for the aqueous solution in **d**

The potential influence on the bulk polymer resistance can be described quantitatively by a simple three-state model. Let us suggest that there is an equilibrium between three states A↔B↔C corresponding to three states of the
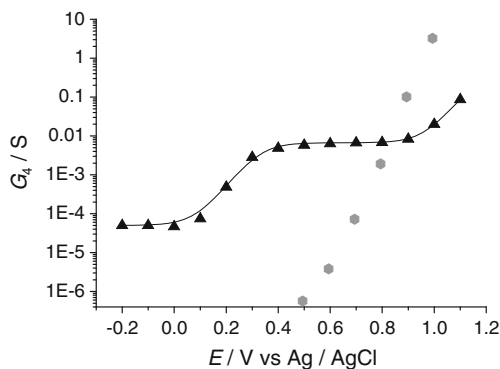

Fig. 4 In situ conductivity of polythiophene measured in acetonitrile solution of 100 mM NBu$_4$PF$_6$ (*circle*) and in aqueous solution of 10 mM phosphate buffer containing 0.1 M NaCl at pH 2 (*triangle*). The *continuous line* indicates a fitting of the experimental dependence by three-state model (see the text for details)

polymer (reduced, slightly oxidized, strongly oxidized). The polymer units have charges n_x and molar conductivities g_x, where the index x indicates the state A, B, or C. The behavior of different units is assumed to be independent. The total conductivity of the polymer between electrodes is the sum of conductivites of all polymer states: $G = c_A g_A + c_B g_B + c_C g_C$, where c_x are the molar fraction of the corresponding species x. Electrochemical potentials of all these states in equilibrium are equal, therefore: $\widetilde{\mu}_A = \widetilde{\mu}_B = \widetilde{\mu}_C$. A substitution of $\widetilde{\mu}_x = \widetilde{\mu}_{0,x} + RT \ln a_x + n_x EF$ (here, a_x is the activity, E is the electrical potential, and R, T, and F have the usual meaning), and an approximation of activities by concentrations gives the equation:

$$G = \frac{g_C + \left[g_B + g_A \exp\left((E_{AB}^0 - E)\frac{(n_B - n_A)F}{RT}\right)\right] \exp\left((E_{BC}^0 - E)\frac{(n_C - n_B)F}{RT}\right)}{1 + \left[1 + \exp\left((E_{AB}^0 - E)\frac{(n_B - n_A)F}{RT}\right)\right] \exp\left((E_{BC}^0 - E)\frac{(n_C - n_B)F}{RT}\right)}$$

where $E_{AB}^0 = \frac{\mu_{0,A} - \mu_{0,B}}{(n_B - n_A)F}$ and $E_{BC}^0 = \frac{\mu_{0,B} - \mu_{0,C}}{(n_C - n_B)F}$ and have the physical meaning of the redox potential of the reactions A↔B and B↔C. The two oxidized polymer states can correspond for example, to polaron and bipolaron states.

Physically, the model is close to that suggested in [19] for the description of the spectroelectrochemical activity of polypyrrole. A similar approach was applied recently to describe potential influence on electrical conductivity of PEDOT [20] but a two-state model was used in that case.

The model was applied for fitting of experimental results in aqueous solution (pH 2). Taking into account that in the reduced state the polymer is not charged, the value n_A was postulated to be zero. The values of n_B and n_C were fixed to 0.5 and 1.0. The fitting results are shown by continuous line in Fig. 4. A quantitative description of experimental data was obtained by fixation of the electrode potentials at 330 and 1,180 mV. Some electrochemical activity at these potentials is observed in voltammetry measurements (Fig. 2, left). The obtained ratio of molar conductivities is $g_A/g_B/g_C=1:130:10,000$.

The kinetics of resistance changes induced by variation of electrode potential to anodic and to cathodic direction is shown in Fig. 5. The results demonstrate that the oxidation in aqueous solution is faster than the reduction. The steady state resistance is about 13 kOhms, which is much lower than the resistance of the reduced film in acetonitrile. Therefore, we suggest that at least at thick films, used for in situ resistance measurements, the reduction in aqueous media at the used potentials is incomplete. The kinetic of resistance changes due to potential changes in acetonitrile was faster than in aqueous solution (not shown here).

The kinetics of contact and bulk resistances on potential changes is quite different: the contact resistance reaches its steady-state value fast in about 30 s (for polymer oxidation) or a couple of minutes (for polymer reduction) while relaxation of bulk polymer resistance is much slower process. This indicates clearly that the values of contact
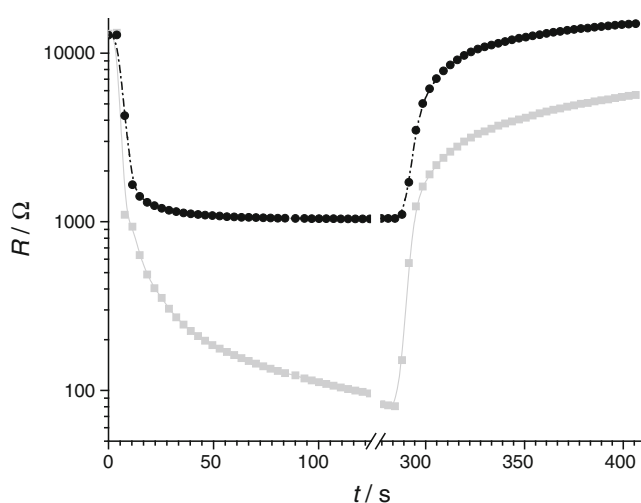
and polymer resistance obtained by analysis of simultaneously measured two- and four-point resistances really correspond to different physico-chemical processes. To our knowledge, this is the first kinetic measurement of the metal/polymer contact resistance.

Earlier, we have shown that s24-technique offers not only the possibility to measure simultaneously the two- and four-point resistance of polymers on electrodes, but also allows to determine quantitatively the contact resistance between electrode and polymer [5]. Figure 6 shows the dependence of the contact resistance calculated from the two-and four-point resistance using a geometrical factor of 3 on the potential in comparison with polymer resistances measured in two- and four-point configurations in aqueous environment and in acetonitrile. It is interesting that while the contact resistance between 0.4 and 0.8 V drops, the polymer resistance remains almost constant. Oppositely, at potentials higher than 0.9 V, the contact resistance is almost constant or displays a small increase while the polymer resistance decreases strongly. We reported a similar behavior earlier for polypyrrole [5]. In acetonitrile, the behavior of the contact resistance is very similar to that of the polymer resistance, but like in aqueous solution it is almost constant at potentials higher
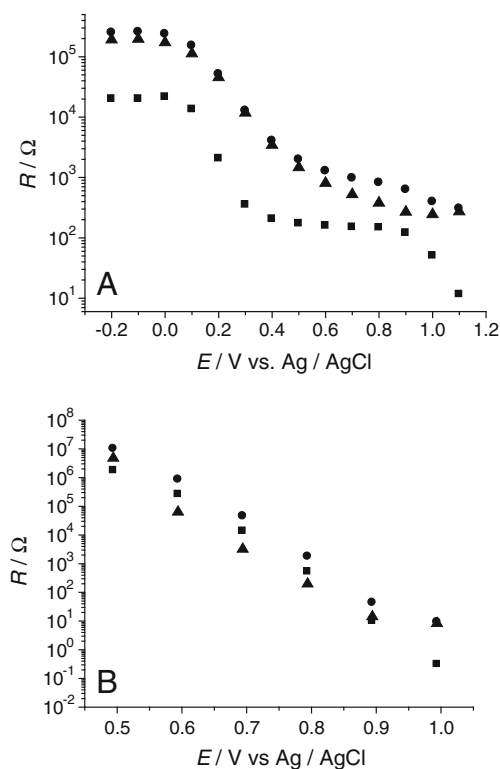

Fig. 6 Potential influence on the resistances of polythiophene films in aqueous solution (10 mM phosphate, pH 2, 0.1 M NaCl) (a) and in acetonitrile (0.1 M NBu$_4$PF$_6$) (b) measured by 2 (circle)- and 4 (square)-point configuration and the contact resistance (triangled) calculated according to Lange and Mirsky [5]

Fig. 5 Kinetics of bulk (square) and contact (circle) film resistances by potential changes from −0.2 to 1.1 V and back in aqueous solution of 10 mM phosphate buffer containing 0.1 M NaCl at pH 2

than 0.9 V. Also, the behavior of the polymer resistance at high potential is very close to that in aqueous solution.

Conclusion

The results demonstrate an influence of polymer oxidation on the metal/polymer contact resistance and show the kinetic change of this resistance upon a potential variation. Kinetics and potential dependence of this value differ essentially from the bulk polymer resistance. These curve are also strongly influenced by the environment, for example the changes of bulk polymer resistance is exponentially dependent on electrode potential and increases for six orders of magnitude for about 600 mV increase of the electrode potential in acetonitrile solution, while these dependencies in aqueous solution have a multiwave shape with a total effect of only three orders of magnitude for total potential changes of 1.3 V.

The potential influence on the polythiophene resistance was described quantitatively by a three-state model. In this model, the potential dependent conductivity is described as a function of the redox state of single polymer units, which can be switched between three states by potential changes.

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