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Fast redox switching into the conducting state, related to single mono-cationic/polaronic charge carriers only in cation exchanger type conducting polymers

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ABSTRACT

Simultaneously performed in situ conductance and spectro-electrochemical measurements—completed by EQCN—proved that fast redox switching can only be expected in cation exchanger type polymers, where the conductance develops promptly with the formation of mono-cationic/polaronic charge carriers—due assumingly to the presence of the charge compensating anions in favorable distribution.

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1. Introduction

Since their discovery at the end of the 1970s, conducting polymers have received a great interest in the last three decades [1-3]. The application of in situ combined electrochemical methods has lead to more and more adequate interpretation of the insulating/conducting transition [4]. By applying techniques such as spectro-electrochemistry in the UV–Vis [5-7] and in the IR [8] or Raman [9,10] regions, the electrochemical quartz crystal nanogravimetry (EQCN) [11-14] or the in situ a. c. impedance or in situ conductance method [15-18], manifold independent information could be obtained from the complex phenomenon of the redox transformation, involving multiple electron transfers, combined with structural modifications, due to ionic and solvent movements [19]. As a result, different charge carriers have been identified, called as polarons/monocations or bipolarons/di-cations.

Later, the simultaneous combination of two in situ techniques has brought new advantages, by delivering information about the process from different aspects [20-22]. Recently, the application of simultaneously performed in situ UV–Vis-NIR spectro-electrochemical and a. c. conductance measurements has been introduced [23]. This combination is able to deliver direct evidence for what an extent a given type of charge carrier is responsible for the development of the conductance in the originally insulating or semi-conducting layers. The method is based on correlating the conductance increase with the absorbance increase at a given wavelength ($G-\mathrm{d}A/\mathrm{d}t$) in the selfsame film. On the grounds of such correlations, the evolution of the conducting state i. e. the development of the name-giving property of these organic materials can be related to optically distinguishable charge carriers.

These studies revealed that the simultaneous application of these two in situ electrochemical techniques was efficient not only for indicating what kind of species were primarily responsible for the development of the conductive state, but it could also demonstrate opposite cases: in the different systems, the formation of either monocationic or di-cationic species can specifically initiate the onset of measurable, finite conductance [24]. Since separate polarons or monocations form right away at the beginning of the redox transformation, while interacting polarons or bipolarons appear only later, i. e. above a certain charge-carrier density, the onset of the conducting state occurs in different stages of the electrochemical transformation. These alternatives are of high importance from practical points-of-view, when the rate of the switching time is a primary factor, determining the adequate functioning of an instrument or a conjugated polymer based device.

2. Experimental

3,4-ethylenedioxythiophene, EDOT (Bayer AG), 3-hexylthiophene, HT (Sigma-Aldrich), solubilizing agent sodium-dodecyl-sulphate, SDS (Sigma-Aldrich) and 3-glycidoxypropyl-trimethoxysilane (Sigma-Aldrich) as adhering material were used as received.

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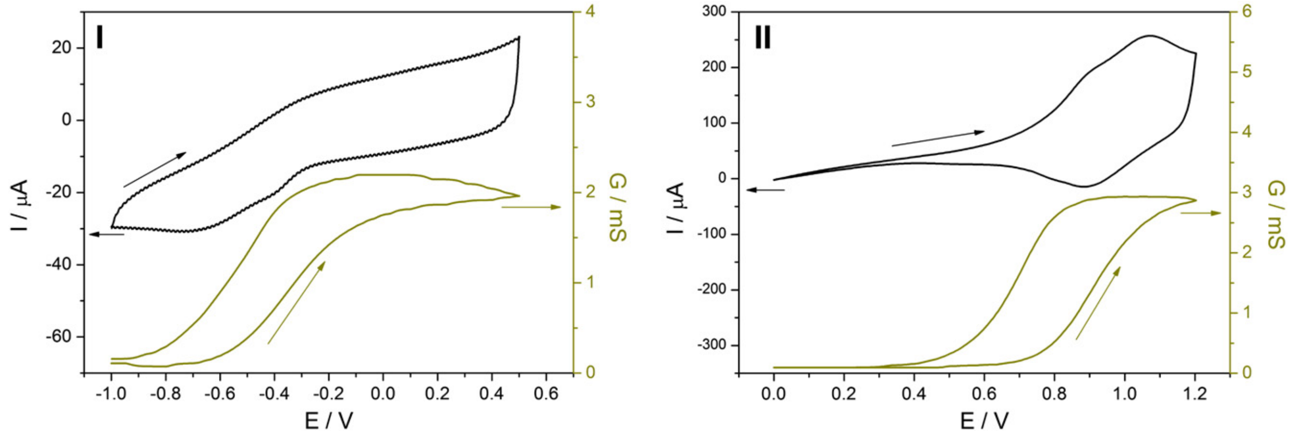

Fig. 1. The cyclic voltammograms (left axis) and the change of the conductance (right axis) of the PEDOT (I.) and the PHT film (II.).

Tetraethylammonium hexafluorophosphate, Et_4NPF_6 (Fluka) was dried at 60 °C, in vacuum. Acetonitrile, AN (Sigma-Aldrich) was dried by activated molecular sieves (3 Å) (Sigma-Aldrich). The water content of the non-aqueous solutions was controlled by coulometric Karl Fisher titration (Metrohm 684), and it was kept below 30 ppm.

All electrochemical measurements were performed on a PGSTAT 302 (Autolab) instrument, in a classical three-electrode electrochemical cell. The reference electrode was a Ag/AgCl/3 M NaCl electrode, having a potential 0.200 V vs. SHE, the counter electrode was a rectangular Pt wire. EQCN measurements have been carried out by using a quartz crystal resonator and analyzer EQCM-Oscillator (Autolab module). The crystals ($f_0 = 6$ MHz) were gold coated, and had an overall diameter of 1.36 cm, while the piezoelectrically active area (identical with the geometric area) of the Au working electrode was 0.352 cm^2.

The poly(3,4-ethylenedioxythiophene) (PEDOT) was deposited potentiostatically at $E = +1.1$ V potential from 0.01 M EDOT and 0.05 M SDS containing aqueous solution. The poly(3-hexylthiophene) (PHT) was deposited at a potential of $E = +1.7$ V from anhydrous AN solution containing, 0.1 M HT and 0.1 M Et_4NPF_6.

The details of the electrochemical, the simultaneous in situ UV–vis-NIR spectroscopic and a. c. impedance measurements have been recently described [23]. The ITO-coated glass electrode (IAME, Abtech) used in one experiment was a double band type electrode with a gap of 15 µm width between neighboring electrode parts.

When the polymer layer is forming on the ITO needle-shaped electrode, the film can grow over the gap, forming electrical contact between the parts, so that conductance can be measured [15]. Electrodeposition to the specially shaped ITO with a small area (0.0516 cm^2) could be achieved. Cyclic voltammograms registered at a sweep rate of 50 mV/s are presented.

3. Results and discussion

The present results, shown in Figs. 1, 2, demonstrate further examples for that the development of the conductance may be connected to either the appearance of the first, evidently monocationic species—case I for the PEDOT/SDS/aqueous system—or the formation rate of the dications, detectable only in a later stage of the redox transformation—case II. obtained with the PHT/Et_4NPF_6/AN film. As a consequence of the Lambert–Beer law, the rate of the absorbance increase is proportional with the formation rate of the chromophore, hence the slope of a $G - dA/dt$ curve expresses the effect of its formation on the development of the conductance. The fundamental difference between the two cases manifests in the opposite relation of the slopes of the $G - dA/dt$ curves for the different charge carriers in Fig. 2: in PEDOT none of the large formation rates of species absorbing at the high wavelength range (950 nm) causes conductance increase, while in PHT this statement is valid for the rate of the absorbance change at the intermediate wavelength region (i. e. at 800 nm). The sharp horizontal change on curve b in Fig. 2 case I. clearly demonstrates that the intensive increase at 950 nm at the end of the oxidation is not coupled with conductance increase. Curve b in Fig. 2 case II. represents that G approaches to the saturation value at the end of the oxidation. In both cases the sharp decrease causing a loop is

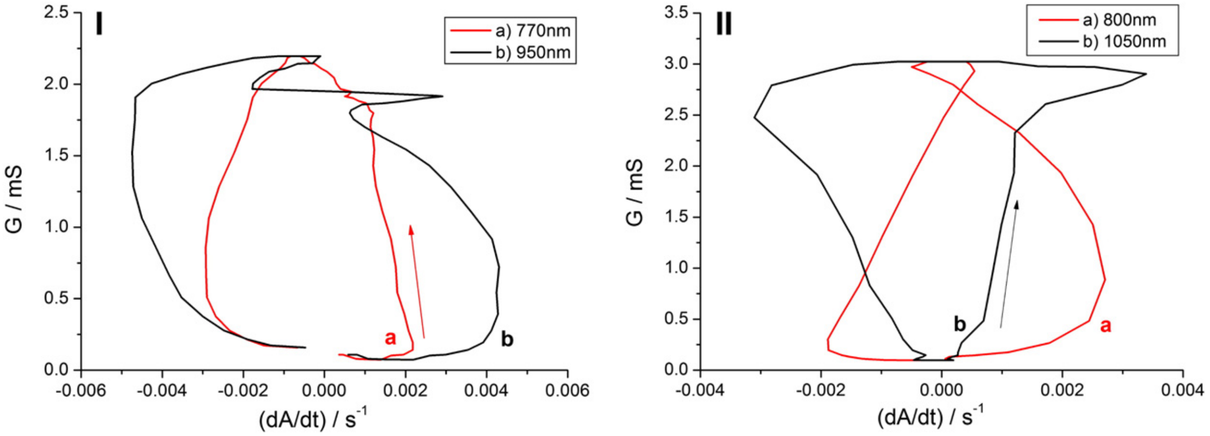

Fig. 2. The in situ conductance vs. the rate of the increase and/or decrease (d*A*/d*t*) of the absorbing species at the characteristic wavelength values (a, b) during the redox process in Fig. 1, I: PEDOT; II: PHT.

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