

Mechanistic study of the redox process of an in situ oxidatively polymerised poly(3,4-ethylene-dioxythiophene) film

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Abstract

The redox process mechanism responsible for the colour change in poly(3,4-ethylene-dioxythiophene) (PEDOT) was investigated in order to understand the nature and the role of the chemical species involved. PEDOT layers were obtained by chemical polymerisation with iron (III) *p*-toluenesulphonate. The films were then cycled several times in LiClO₄/propylene carbonate (PC) electrolyte. The chemical composition of ‘as-prepared’ and cycled films (in the reduced and oxidised state) was studied by means of EDX and XPS ex situ analysis. The results point out the fundamental role the electrolyte anion plays in the process and provide quantitative information about the extent of anion exchange.

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1. Introduction

Poly(3,4-ethylene-dioxythiophene) (PEDOT) was developed during the second half of the 1980s in the Bayer AG research laboratory in Germany [1] and became one of the most interesting electroactive polymers for both fundamental investigations and practical applications. It has several advantageous properties when compared to other polythiophene-based polymers; in fact, it shows low oxidation potential, high stability in the oxidised state, high conductivity (up to 400–600 S/cm) and high transparency in thin films [2–6]. Due to this property profile PEDOT is used for different purposes: antistatic and electrostatic equipment, solid state capacitor electrodes, substrate for metal deposition in printed circuit boards, carrier conducting material in organic light emitting diodes (OLED) and electrode for inorganic electroluminescent lamps [2,7–9]. PEDOT can be produced from 3,4-ethylene-dioxythiophene (EDOT) by both chemical oxidative or electrochemical polymerisation. Electropolymerisation is a proper way to produce small samples with reproducible

quality on a laboratory scale and requires only small amounts of starting material. For the coating of larger substrates the in situ oxidative polymerisation process, i.e., the oxidative polymerisation of the monomer solution during or after its application to the substrate, has turned out to be more viable. In fact, besides the intrinsic scaling up problems related to electropolymerisation process, the electropolymerised film homogeneity largely depends on the quality of the conductive substrate.

A remarkable PEDOT characteristic is its electrochromic behaviour, which makes it an attractive electrode material in electrochromic devices such as smart windows [10,11]. In fact, PEDOT shows colour change from highly transmissive light sky blue to dark blue when reduced from the oxidised to the neutral state. In general, the colour changes in an electrochromic polymer are due to electrochemical doping–undoping redox processes, which involve ion transport into and out of the polymer matrix to balance the electronic charge (Fig. 1) [12]. The freshly polymerised layer (in its ‘as-prepared’ state) is a mixture of positively charged polymer backbone and anions entering the material during oxidative polymerisation [13]. When cathodic polarisation is applied (in the absence of monomers), the anions are driven from the layer to the

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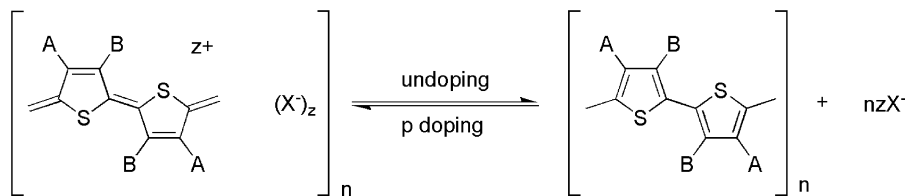


Fig. 1. Redox mechanism responsible for the colour change in polythiophene derivatives. A, B are generic substituents of a polythiophene selectively polymerised at the 2–5 positions; X^- and z^+ are the counterion and polymeric chain net charge, respectively.

electrolyte leaving the polymer backbone in its insulating darkened neutral state. Due to the reaction reversibility, anodic polarisation induces the re-entering of anions from the electrolyte (p-doping) and the polymer becomes conductive and bleached again. However, this process may be more complicated depending both on the nature of involved anions and on the electrolyte chemical composition; it can also involve cation motion. Whereas, the electrical, optical and spectro-electrochemical properties of PEDOT have been widely investigated in the last 15 years [9], only little basic research work was performed to understand the redox process. The knowledge in composition, structure and morphology changes should be very important for PEDOT-based electrochromic device design, predominantly with respect to the electrolyte to be used.

PEDOT-based electrodes can be cycled in both aqueous and non-aqueous electrolytes; the former are easy to obtain and to handle, but they usually have small electrochemical window stability and might adversely affect the electrode lifetime. The latter, non-aqueous electrolytes, are much more stable at lower potentials and the use of lithium salt opens the way to the production of electrochromic windows equipped with lithium intercalation compounds as counter-electrodes.

Aasmundtveit et al. [14] investigated (in situ by X-ray glazing incidence diffraction) the redox mechanism of PEDOT/tosylate (*para*-toluene sulfonate, $p\text{-CH}_3\text{C}_6\text{H}_4\text{-SO}_3^-$) films (PEDOT/OTs) in LiPF_6 solution. They proposed both the electrolyte cations and anions to be involved in the doping–undoping process without any participation of the tosylate anions, which stay in the polymer layer.

Changes in the chemical composition were investigated by means of energy dispersive X-ray (EDX) analysis and X-ray photoelectron spectroscopy (XPS) on PEDOT/OTs films (obtained by in situ chemical polymerisation with iron (III) tosylate) cycled in LiClO_4 /propylene carbonate (PC) electrolyte, to confirm this hypothesis. The measurements were performed ex situ on samples in different oxidation states. It is important to note that in reduced samples oxidation might occur upon exposition to ambient atmosphere, in case changing the oxygen content only.

In this paper, electrochemical and spectro-electrochemical properties are related to changes in morphology and surface chemistry before and after the cycling process.

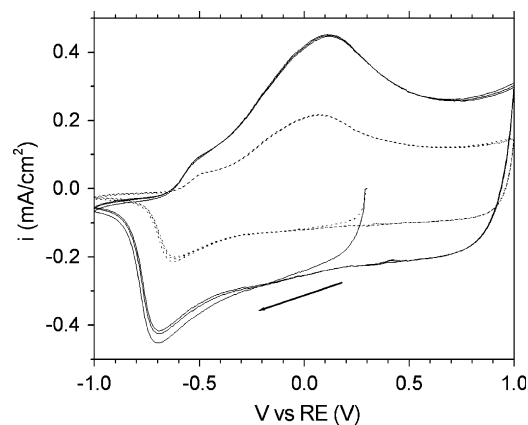


Fig. 2. CV curves at different scan rates. Continuous and dashed lines refer to 100 and 50 mV/s, respectively.

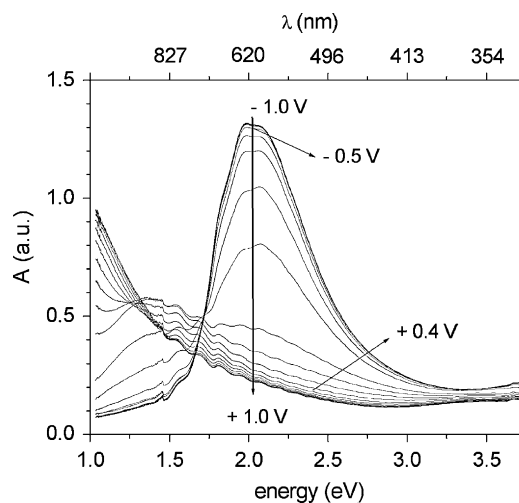


Fig. 3. NIR–vis absorbance spectra detected at different applied potentials: $-1.0\text{ V} < V < 1.0\text{ V}$; $\Delta V = 0.1\text{ V}$.

2. Experimental

2.1. Layer deposition

EDOT monomer (Baytron[®] M, H.C. Starck, Germany) was chemically polymerised on ITO glass according to the procedure described by Ha et al. [15]. Thin films were prepared on ITO-coated glass substrates ($5 \times 5\text{ cm}^2$) by means of spin coating at room temperature. Thermal curing was performed at $120\text{ }^\circ\text{C}$ for 20 min. The excess of

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