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An ellipsometric study of poly(3,4-ethylenedioxythiophene) electrosynthesis – from the initial stages to thick layers formation

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ABSTRACT

The electropolymerization of 3,4-ethylenedioxythiophene (EDOTh) on platinum, under both potentiostatic and potentiodynamic control, has been analysed by electrochemical and ellipsometric measurements, simultaneously recorded. The experimental procedure for the acquisition of ellipsometric data, developed to follow the electrode surface modification along the whole process, allowed to collect information on the evolution of the polymer film properties with time and also as function of the electrode potential. A two-homogeneous phase model has been successfully used to describe the ellipsometric experimental parameters enabling to obtain from the azimuth angle Ψ and phase shift Δ, simultaneously the thickness and the complex refractive index of poly(3,4-ethylenedioxythiophene) (PEDOTh) films at different growth stages and at various doping levels. Since both electropolymerization methods originate two-layered films, the calculated optical parameters (for the inner and outer layers) are an adequate basis of analysis which have been used in the interpretation of the structural modifications occurring during the growth of PEDOTh films (up to a thickness of about 200 nm) as well as of those induced by the electrode potential, during and after the redox conversion of polymer films with different thicknesses.

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1. Introduction

Although during the last decades much work has been devoted to describe the fascinating properties of electronically conducting polymers (ECP) [1–3], the preparation conditions and the influence of various factors on the polymerization process and on the features of the produced material only recently are receiving increasing attention [4–7].

Most of the envisaged applications of ECP rely on the use of modified electrode surfaces [8–11] and thus, a complete understanding of the electropolymerization process is of the upmost importance. It demands to consider a large variety of parameters, e.g. monomer concentration, nature of supporting electrolyte and solvent, deposition time, applied potential/current, and their critical role in determining the polymer physicochemical properties.

As a consequence of its remarkable properties (low oxidation potential, high conductivity and good stability in the oxidized state [12]), poly(3,4-ethylenedioxythiophene), PEDOTh, is among the most popular ECPs. Studies of EDOTh polymerization have shown morphological diversity of PEDOTh as a function of synthesis conditions, fibre-like or granular nature when prepared under potentiodynamic or potentiostatic control, respectively [13,14]. It has also been reported that the polymer degree of crystallinity [15] and conductivity [16] are mainly imparted by the nature of counter-ions. Though scarce there is some information on the role of different cations both in the electropolymerization process [15] and in the PEDOTh redox conversion [17].

The coupling of electrochemical and optical techniques has been often used to gather a deeper knowledge of the electrosynthesis process [18–20]. In particular, in situ ellipsometry has already been successfully employed for the study of the electropolymerization of thiophene and its derivatives [18,21,22], as well as in the analysis of the redox properties of the deposited films [23].

Ellipsometry is based on the measurement of the change of the polarization state of the light, which is modulated upon specular reflection from the surface under study, allowing to monitoring the transformations in properties of the sample. Being very sensitive to variations of both the amplitude and the phase of the probed light, this technique is the ideal tool to evaluate the modifications of the refractive index and thickness of a conducting polymer film along its deposition and growth or during the redox conversion processes.

The information on the dielectric constants of PEDOTh is rather limited, since most of the published data concerns the characterization of chemically prepared polymers [24,25]. Notwithstanding, the formation of a homogeneous material up to a thickness of about 100 nm, has been claimed for PEDOTh electrosynthesis from aqueous solution [26].

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Ellipsometric investigations on the electropolymerization of other thiophene derivatives from organic media, revealed the occurrence of structural polymer modifications upon thickening [21,27,28], feature that has also been observed for other ECP [29–31]. Thus, the homogeneous or heterogeneous character of PEDOTh film prepared from non-aqueous solution is a open question.

Aiming a correlation of the PEDOTh optical properties with the selected growth conditions, the useful approach of combining in situ ellipsometry and electrochemical measurements has been followed in the present work. For a better appraisal on the influence of the electrochemical parameters, the electropolymerization of EDOTh under both potentiostatic and potentiodynamic control and using different supporting electrolytes, namely distinct cations (tetrabutylammonium, TBA^+, or Li^+) has been considered to obtain information on polymer thickness, porosity, electrolyte solution content, and film homogeneity along thickening. Since ellipsometry is particularly responsive to the electrode coverage and to the evolution of the dielectric constants of the probed material, the collected data provided the optical properties of the deposited film not only at different stages of the polymerization process but also on the structural transformations involved in the PEDOTh redox conversion.

The significant change in the polymer optical properties observed after a critical thickness, which value is dependent on the electrochemical mode selected for the electrosynthesis, is well described by modeling the film structure as consisting of a polymer formed by two distinct homogeneous phases.

2. Experimental

The monomer 3,4-ethylenedioxythiophene, EDOTh (Aldrich), was distilled under reduced pressure prior to use. The solvent, acetonitrile, ACN (HPLC grade, Aldrich 99.93%), was previously dried in calcium hydride and distilled with phosphorus pentoxide under N_2 atmosphere. The supporting electrolyte tetrabutylammonium perchlorate, $TBAClO_4$ (Fluka, purity $\geqslant$99%) was previously recrystallized from ethanol. Highly pure lithium perchlorate, $LiClO_4$ (Riedel-de Häen, p.a. $\geqslant$99%), was used as received. Prior to the measurements, the solutions were deoxygenated directly in the cell by bubbling N_2 (high purity, dried) for 20 min.

A homemade two-compartment Teflon cell with two optical windows at 20° from the bottom plane was employed. The working electrode was a "specpure" platinum disk with an exposed area of 0.196 cm^2. For each experiment a fresh mirror-finish surface was generated by hand-polishing the electrode in an aqueous suspension of successively finer grades of alumina (down to 0.05 μm), sonicated in Millipore water for 10 min and dried under high purity nitrogen flux. A large area platinum grid and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively.

The electrodeposition of EDOTh was performed under potentiodynamic and potentiostatic modes, in a solution containing 0.02 mol dm^{-3} EDOTh and 0.1 mol dm^{-3} supporting electrolyte ($TBAClO_4$ or $LiClO_4$) in acetonitrile. The potentiodynamic deposition was made by cycling the potential between -0.800 and +1.235 V for the first five cycles, then lowering the anodic limit to 1.207 V for the following cycles, at a sweep rate (v) of 50 mV s^{-1}. PEDOTh films were also potentiostatically (E_g) prepared at 1.11 and 1.20 V in the solutions containing $LiClO_4$ and $TBAClO_4$, respectively. The working electrode potential was first switched from 0 to 0.85 V and held for 10 s to allow the double-layer charging of the Pt|solution interface, aiming to minimize the distortion of the polymerization current transient [32]; the polymerization was achieved by a second potential pulse from 0.85 V to the growth potential, E_g.

In situ ellipsometric data were collected during the EDOTh electropolymerization with a SENTECH SE 400 ellipsometer working in PCSA mode, fitted with a He–Ne laser (λ = 632.8 nm) at 70° incident angle, programmed to sampling speed of 1.1 s^{-1} and 1.6 s^{-1} for the potentiodynamic and potentiostatic growth, respectively.

The electrochemical measurements were controlled by a potentiostat/galvanostat EG&G PAR model 273a, coupled to an X–Y–t register YOKOGAWA model 2023.

3. Results and discussion

Fig. 1 displays the current transients recorded during the potentiostatic electropolymerization of EDOTh from $LiClO_4$ and $TBAClO_4$ containing solutions, being the distinct growth potential values selected with the purpose of observing fairly similar transient traces. It is worthwhile to notice that the use of $LiClO_4$ as supporting electrolyte, when compared to $TBAClO_4$, requires lower potential to reach a given polymerization rate, pointing to an effect of the cation nature on the first steps of the electrosynthesis, namely on the monomers/oligomers oxidation. Thus it is plausible to assume that the interaction of the oxygen atoms of EDOTh molecule with the ammonium group of TBA^+ cation promotes the monomer stabilization, and thus renders more difficult its oxidation and/or the combination of the radical cations hitherto generated.

As discussed elsewhere [33], the lettering in Fig. 1 refers to the different stages of the deposition process: double layer region (AB), polymer nucleation and coalescence of nuclei (BCD) and film growth (DEF). For the purpose of the present work, it must be emphasized that the base electrode is only covered by a polymer layer after the current inflection (point D), which is only attained after a charge consumption of 3.2 mC cm^{-2} and 4.2 mC cm^{-2}, in the presence of $LiClO_4$ and $TBAClO_4$, respectively. Assuming that in both cases the total coverage involves the same amount of polymeric material, that difference in charge reveals a lower efficiency of the polymer film deposition (distinguishing polymer that attaches to the electrode surface from the oxidized species which remains in solution) when $TBAClO_4$ is employed, in agreement with the occurrence of the above suggested interaction, namely among TBA^+ and the radical cation created by monomer oxidation.

It is well known [22,34–37] that the analysis of the ellipsometric parameters (azimuth angle, Ψ, and phase shift, Δ) as function of the deposition time is a powerful tool to obtain details of polymerization process as well as information on the polymer characteristics. As depicted in Fig. 2, simultaneously to current transients, the evolution of the ellipsometric parameters has been noted down. The overall shape of the curves, very distinct of data reported for

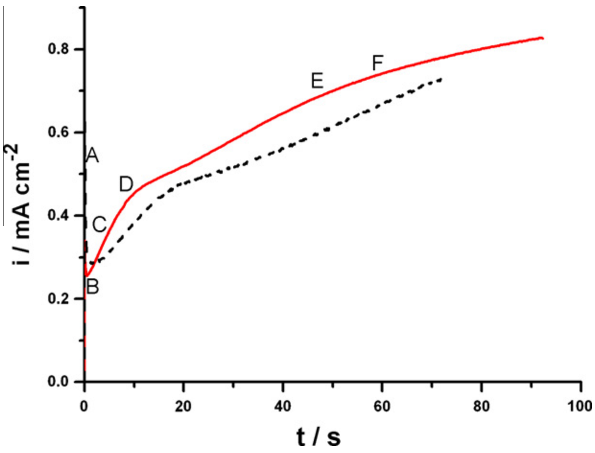

Fig. 1. Current transients recorded during the potentiostatic polymerization of EDOTh on Pt at E_g = 1.200 V (- - -) and E_g = 1.110 V (——) from 0.02 M EDOTh in acetonitrile solution containing 0.1 M $TBAClO_4$ and 0.1 M $LiClO_4$ respectively.

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