

# Electrochemical behavior of poly-bithiophene, poly-3,4-ethylendioxythiophene and poly-3,4-*ortho*-xylendioxythiophene in EtOH/H<sub>2</sub>O (1:1) mixture

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## ABSTRACT

This paper describes the electrochemical behavior of poly-bithiophene (PBTh), poly-ethylene-3,4-dioxythiophene (PEDOT), and poly-3,4-*ortho*-xylendioxythiophene (PXDOT) in an EtOH/H<sub>2</sub>O (1:1) mixture using 0.1 M LiClO<sub>4</sub> as supporting electrolyte and AcOH/AcONa to buffer pH. PBTh suffers fast degradation, whereas PEDOT and PXDOT show reasonable stability in the EtOH/H<sub>2</sub>O mixture. A strong interaction between the 3,4-alkoxythiophene polymers and the EtOH/H<sub>2</sub>O mixture was evidenced by a charge/discharge process limited by ionic movement and slow electron transfer (as signaled by a large  $\Delta E_p$ ). Both of these processes were faster in ACN. The stability of the prepared films was studied through 100 charge/discharge cycles in ACN and in the EtOH/H<sub>2</sub>O mixture. Considerable electroactivity loss for PEDOT and PXDOT was observed in ACN, which may be caused by charge trapping phenomena and oligomer release. This loss diminished substantially in the EtOH/H<sub>2</sub>O mixture showing a current higher than 75% of the initial value and an electrochemical reversibility (i.e., the  $Q_c/Q_a$  ratio) higher than 90%. Due to the stability of the PEDOT and PXDOT films in the EtOH/H<sub>2</sub>O mixture, it was possible to use them in modified electrodes for Cu (II) detection using anodic stripping voltammetry, where concentration-dependent current signals were observed.

## 1. Introduction

Poly-3,4-ethylendioxythiophene (PEDOT) is one of the conducting polymers that has reached the commercial stage due to its excellent properties including thermal stability, good conductivity, and high chemical stability [1]. Its polythiophene backbone plays an important role in its electrical and physical properties, and the inclusion of electrodonating groups in the  $\beta$ -positions of the thiophene ring decreases its oxidation potential and improves its solubility and stability [2]. The family of the 3,4-alkoxythiophenes is of great interest for commercial applications as hole transport materials for LED's, to improve the charge transfer rate in photovoltaic cells, and in sensors due to their stability in different solvents [3]. The charge/discharge process in such polymers can be explained using different theories as the bipolaron model or the mixed-valence conductivity [4,5]. Vorotyntsev and Heinze proposed that the charge/discharge process is due to the formation of two subsystems that coexist during the oxidation of the conducting polymers (i.e., the radical cation subsystem and a subsystem of intermolecular bonds between neighbor oligomeric chains, forming  $\sigma$ -

dimers) [6–8]. The solvent also plays an important role during the charge/discharge process due to its nucleophilic properties, as well as its influence on the ionic transport required to compensate the charges generated by the redox reactions; therefore, the solvent directly affects the charge transfer and the polymeric chain stability of the thus materials generated. The influence of the solvent in the charge/discharge process has been studied using the electrochemical stimulated conformational relaxation model (ESCR) [9,10], which shows that a better polymer/solvent interaction enables a faster polymeric expansion process. Hillman's group demonstrated that solvent transfer in PEDOT electrodes depends on the solvent used [11,12]. In fact, in ACN a rapid solvent exchange between the polymeric matrix and the dissolution occurs at high oxidation potentials [13]. PEDOT and its derivatives show larger shrinkage of the film microstructure in aqueous media than in other solvents [14,15]. When polar organic solvents are used for PEDOT-PSS deposits, changes are observed in the morphology that improve their conductivity [16]. The use of pure alcohols with different chain lengths as solvents during the charge/discharge process of PEDOT has been reported [17]. These studies show that the conductivity

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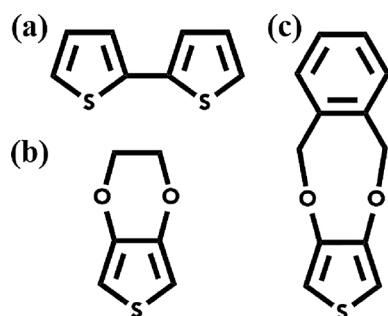


Fig. 1. Chemical structures of (a) bithiophene, (b) 3,4-ethylenedioxythiophene, and (c) 3,4-ortho-xylendioxythiophene monomers.

decreases as the alcohol chain length increases due to changes in hydrogen bonding between the alcoholic solvent and the counter ion inside the PEDOT matrix. The study of solvent/polymer interactions allows to obtain information about the solvation level, and to envisage possible applications of these materials. Even though symmetrical ethers have been obtained *via* acid catalysis when alcohols are refluxed in hexane in the presence of PEDOT, this reaction can be largely disregarded in the present investigation because our study was performed at room temperature [18]. The quantification of different metallic ions (e.g.,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{As}^{2+}$ ) in aqueous media is feasible using conducting polymers (PTh and PEDOT) [19,20], but the use of EtOH/ $\text{H}_2\text{O}$  mixtures that simulate alcoholic beverages has not been reported to date. In this work, the electrochemical behavior of PBTh, PEDOT, and poly-3,4-*ortho*-xylendioxythiophene (PXDOT) (Fig. 1) was studied in an EtOH/ $\text{H}_2\text{O}$  (1:1) mixture, using 0.1 M  $\text{LiClO}_4$  as supporting electrolyte in AcOH/AcONa (0.05 M/0.008M) buffer at pH = 4, and the observed response was compared to that in a typical solvent (i.e., acetonitrile, ACN). This EtOH/ $\text{H}_2\text{O}$  mixture may serve as a model for alcoholic beverages and it is expected that this study could open the door for the use of modified conducting polymer electrodes for metallic ion analysis in liquors without requiring sample pretreatment.

## 2. Experimental

### 2.1. Reagents

$\text{LiClO}_4$  (Aldrich, 99.9%), absolute ethanol (Aldrich, 99.8%), glacial acetic acid (Aldrich, 99.7%), sodium acetate (Aldrich, ACS reagent), 3,4-ethylenedioxythiophene (Aldrich, 97%), bithiophene (Aldrich, 99%), and anhydrous ACN (Aldrich, 99.9%) were used as received. All the solutions were prepared with deionized water (MilliQ Direct-Q®). The 3,4-*ortho*-xylene-dioxythiophene was synthesized in our laboratory following a published methodology for the synthesis of 3,4-alkoxythiophenes [21]. The EtOH/ $\text{H}_2\text{O}$  mixture was prepared using a 0.1 M  $\text{LiClO}_4$ , AcOH/AcONa buffer (0.05 M/0.008M) at pH = 4, in an EtOH/ $\text{H}_2\text{O}$  (1:1) solution.

### 2.2. Electrochemical syntheses and characterization of the conducting polymer films

A single compartment three-electrode cell, equipped with a glassy carbon (GC) working electrode (geometric area =  $0.07 \text{ cm}^2$ , Bioanalytical Systems), a large surface Pt wire as auxiliary electrode, and a Ag/AgCl (in 3 M KCl) reference electrode (Bioanalytical Systems), was used. The reported potential values do not require liquid-junction potential corrections, because the typical shifts observed when the solvent is exchanged between ACN and EtOH are below 40 mV [22]. All the electrochemical experiments were performed with a BAS100B potentiostat (Bioanalytical Systems, USA). The corresponding background voltammograms for both media studied are available in the Supporting Information section. The electropolymerization experiments were

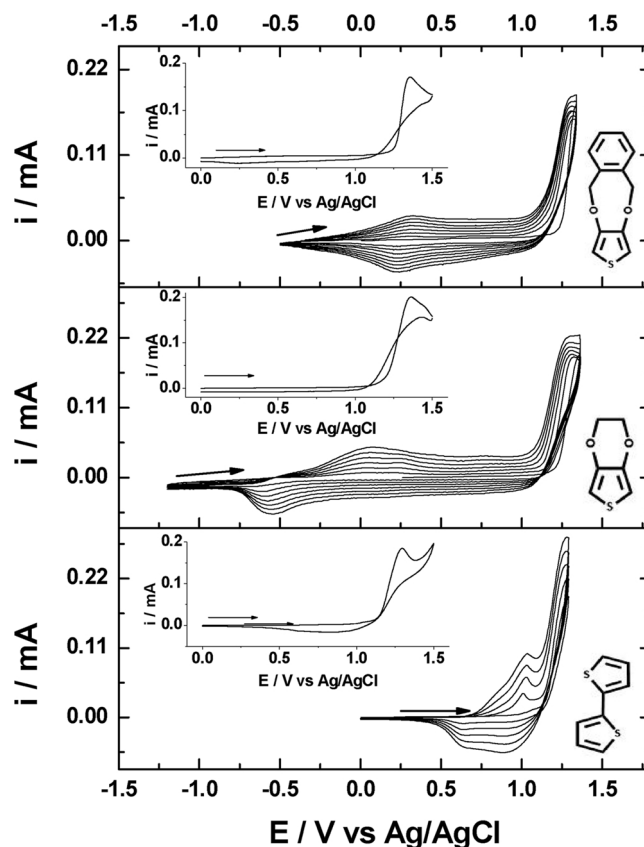


Fig. 2. Potentiodynamic polymerization of 5 mM solutions of BTh (5 cycles), EDOT (7 cycles), and XDOT (8 cycles) in ACN/0.1 M  $\text{LiClO}_4$ ,  $\nu = 25 \text{ mV/s}$ . WE: GC, CE: Pt. The inset shows the potentiodynamic oxidation of each monomer.  $E_\lambda = 1.5 \text{ V vs. Ag/AgCl}$ .

performed with cyclic voltammetry using the GC electrode dipped in a 0.1 M  $\text{LiClO}_4$ , 5 mM monomer solution in ACN (anhydrous, Aldrich),  $\nu = 25 \text{ mV/s}$ , and  $E_\lambda = E_{\text{polym}}$  (where 1.29 V, 1.37 V, and 1.35 V vs. Ag/AgCl are the monomer peak potential oxidation values ( $E_{\text{polym}}$ ) for BTh, EDOT, and XDOT, respectively, indicated in the inset of Fig. 2). All the electropolymerizations were performed under a  $\text{N}_2$  atmosphere. The electrochemical behavior of the films thus obtained was evaluated by cyclic voltammetry and double pulse chronocoulometry in the EtOH/ $\text{H}_2\text{O}$  solution described above (Section 2.1). Equivalent experiments were performed with freshly electropolymerized materials in a 0.1 M  $\text{LiClO}_4$  solution in ACN for comparison. These polymeric films were also used for the anodic stripping voltammetric experiments performed in the EtOH/ $\text{H}_2\text{O}$  mixture in the presence of different  $\text{Cu}^{2+}$  concentrations (i.e., 20, 40, 60, 80 and 100 ppm). A deposition potential,  $E_{\text{dep}} = -1.0 \text{ V vs. Ag/AgCl}$  was applied during 40 s prior to each experiment, with an equilibration step of 10 s and a scan rate of 25 mV/s in the anodic direction.

## 3. Results and discussion

The three monomers: BTh, EDOT, and XDOT (5 mM) presented an irreversible oxidation process on the surface of the GC electrode in the ACN/ $\text{LiClO}_4$  system, showing in the first reverse cycle of the voltammogram the typical trace-crossing effect observed during the electrochemical polymerization of  $\pi$ -conjugated systems (see inset in Fig. 2) [23]. A current increase of the anodic and cathodic signals, which is characteristic of the growth of this type of polymers (Fig. 2), was observed. The oxidation potential for the 3,4-alkoxythiophenes (ca. 1.35 V vs. Ag/AgCl) contrasts with that observed for thiophene ( $\approx 1.7 \text{ V vs. Ag/AgCl}$ ), due to the presence of the alkoxy groups that stabilize the radical cation formed during the oxidation process [3]. The

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