



Electrochemical behavior of poly-bithiophene, poly-3,4-ethylendioxythiophene and poly-3,4-*ortho*-xylendioxythiophene in EtOH/H₂O (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/H₂O (1:1) mixture using 0.1 M LiClO₄ as supporting electrolyte and AcOH/AcONa to buffer pH. PBTh suffers fast degradation, whereas PEDOT and PXDOT show reasonable stability in the EtOH/H₂O mixture. A strong interaction between the 3,4-alkoxythiophene polymers and the EtOH/H₂O mixture was evidenced by a charge/discharge process limited by ionic movement and slow electron transfer (as signaled by a large ΔE_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/H₂O 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/H₂O 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/H₂O 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 β -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 σ -

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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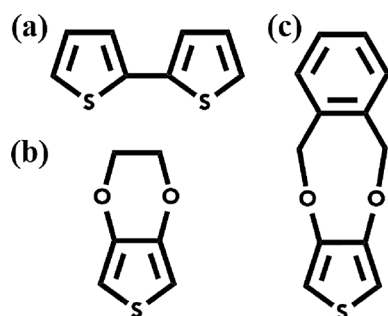


Fig. 1. Chemical structures of (a) bithiophene, (b) 3,4-ethylenedioxythiophene, and (c) 3,4-ortho-xylendioxythiophene monomers.

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., Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and As^{2+}) in aqueous media is feasible using conducting polymers (PTh and PEDOT) [19,20], but the use of EtOH/ H_2O 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/ H_2O (1:1) mixture, using 0.1 M 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/ H_2O 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

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/ H_2O mixture was prepared using a 0.1 M LiClO_4 , AcOH/AcONa buffer (0.05 M/0.008M) at pH = 4, in an EtOH/ H_2O (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 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

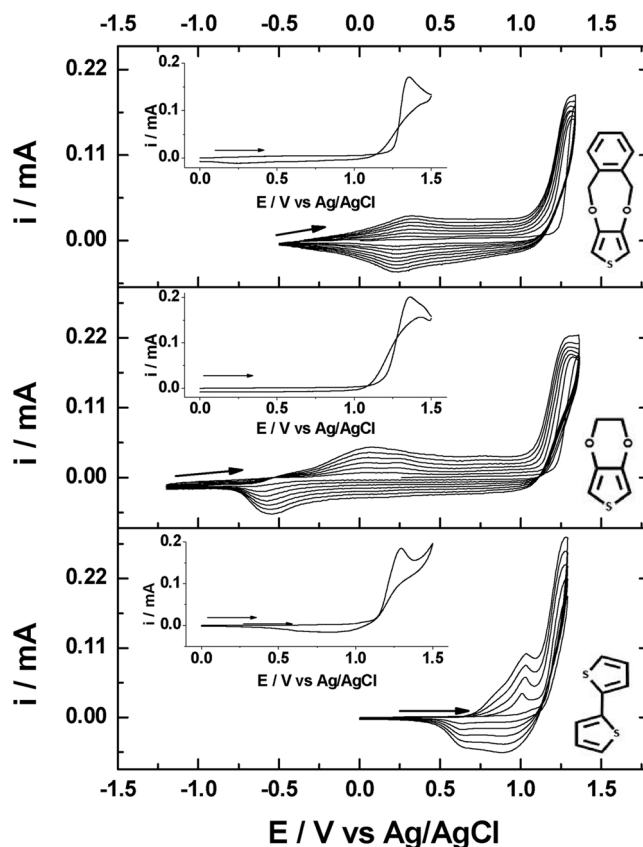


Fig. 2. Potentiodynamic polymerization of 5 mM solutions of BTh (5 cycles), EDOT (7 cycles), and XDOT (8 cycles) in ACN/0.1 M LiClO_4 , $\nu = 25 \text{ mV/s}$. WE: GC, CE: Pt. The inset shows the potentiodynamic oxidation of each monomer. $E_\lambda = 1.5 \text{ V vs. Ag/AgCl}$.

performed with cyclic voltammetry using the GC electrode dipped in a 0.1 M 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_{polym}) for BTh, EDOT, and XDOT, respectively, indicated in the inset of Fig. 2). All the electropolymerizations were performed under a N_2 atmosphere. The electrochemical behavior of the films thus obtained was evaluated by cyclic voltammetry and double pulse chronocoulometry in the EtOH/ H_2O solution described above (Section 2.1). Equivalent experiments were performed with freshly electropolymerized materials in a 0.1 M LiClO_4 solution in ACN for comparison. These polymeric films were also used for the anodic stripping voltammetric experiments performed in the EtOH/ H_2O mixture in the presence of different 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/ LiClO_4 system, showing in the first reverse cycle of the voltammogram the typical trace-crossing effect observed during the electrochemical polymerization of π -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

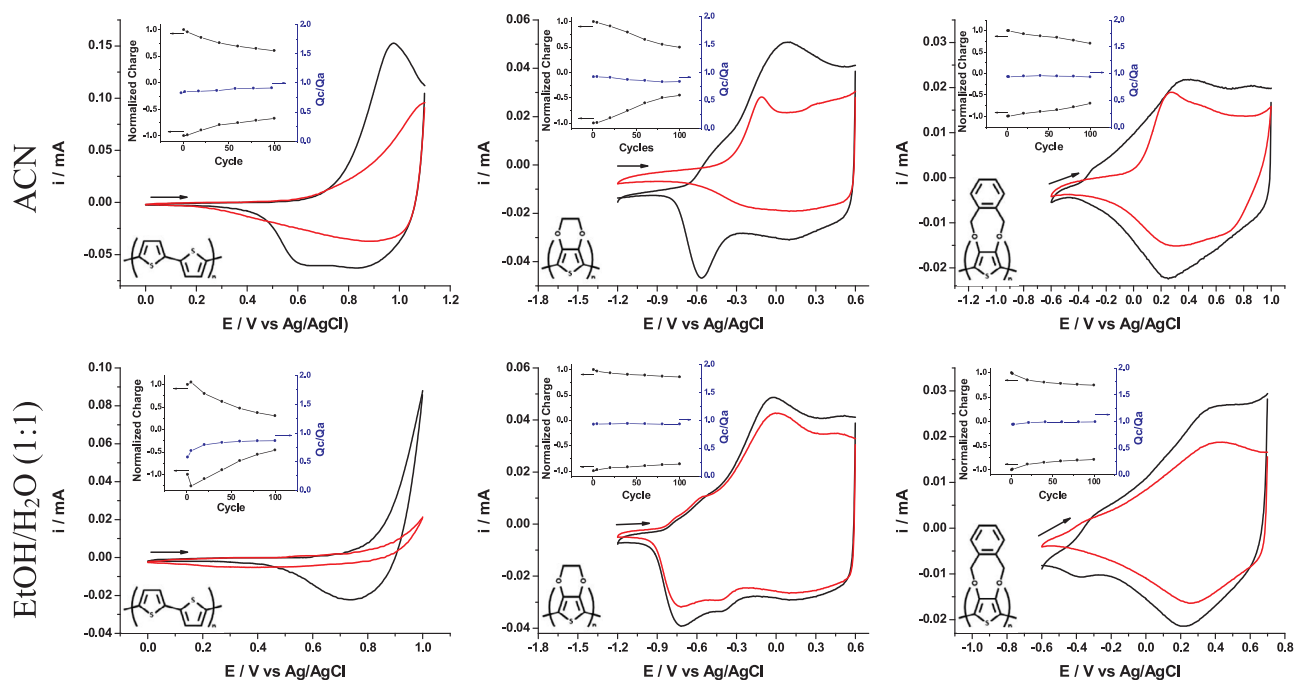


Fig. 3. Cyclic voltammetry of PBTh, PEDOT, and PXDOT films deposited on vitreous carbon electrodes using the conditions indicated in Fig. 2: before (black line) and after (red line) 100 charge/discharge cycles in a monomer free 0.1 M LiClO₄ ACN solution, and 0.1 M LiClO₄ in acetic acid/sodium acetate buffer (0.05 M/0.008M) EtOH/H₂O (1:1) solution. $v = 25$ mV/s. The inset shows the variation of the normalized charge (left axis, black curve) and the Q_c/Q_a variation (right axis, blue curve) during the 100 cycles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

electrochemical response before the stability studies for PBTh and PEDOT films in ACN agrees with that reported in previous works [24,25]. Polymerization under the present conditions allowed the attainment of 21.33 ± 0.88 , 18.75 ± 0.29 , and 17.98 ± 1.41 doping level percentages for PBTh, PEDOT, and PXDOT, respectively. These values were obtained with the methodology reported by Bose et al. [26], that includes potentiodynamic electropolymerization, integration of the corresponding i vs. t curves, and the use of Eq. (1). Two assumptions are required for its use; a) the cathodic charge (Q_c) is equal to the anodic charge (Q_a), and b) the charge in both cases is only due to the response of the polymer grown on the electrode. Three independent experiments were performed, and the value reported here is their average. The standard deviation for each polymer is reported after this average.

$$\delta = \frac{2Q_c}{Q_{pol} - Q_c} \quad (1)$$

The electrochemical stability of the three polymers was evaluated in both media (i.e., the EtOH/H₂O mixture, and ACN) by comparing the cyclic voltammetric response before and after 100 charge/discharge cycles using double pulse chronocoulometry [27]. This involved the application of an anodic (E_{Qa}) and cathodic (E_{Qc}) potential pulse program (i.e., $E_{Qa} = 1.1$ V and $E_{Qc} = 0.2$ V for PBTh, $E_{Qa} = 0.6$ V and $E_{Qc} = -1.2$ V for PEDOT, and $E_{Qa} = 0.7$ V, and $E_{Qc} = -0.6$ V for PXDOT; pulse time = 10 s) as depicted in Fig. 3. The analysis and comparison of these results show that when the EtOH/H₂O mixture is used, PBTh completely loses its electrochemical response, whereas that of the poly-3,4-dialkoxythiophene polymers is maintained. Nonetheless, a slight current decrease was observed even here after 100 charge/discharge cycles.

An anodic current decrease of $6.1 \mu\text{A}$ and its corresponding cathodic decrease of $7.6 \mu\text{A}$ for PEDOT were observed and a similar behavior for PXDOT (i.e., $8.1 \mu\text{A}$ and $5.2 \mu\text{A}$, respectively). Such a decrease is attributed to: a) the loss of electroactive material (i.e., low molecular weight oligomers) from the electrode surface, and b) some of the charges formed during the oxidation of the film in the discharge process that stay trapped inside the polymer matrix. Such phenomenon is known as “charge

trapping” [28–30] and it may occur in an oligomer chain or between neighboring oligomer chains, forming the so-called “ σ -dimers” [7] whose formation occurs either during the electropolymerization process [8], or during the charge/discharge process [6]. To expel these trapped charges a very negative potential is required (i.e., near the n -doping level of the polymer). In order to analyze this phenomenon, the cathodic behavior of both poly-3,4-dialkoxythiophenes was studied in ACN and in the EtOH/H₂O mixture (Fig. 4).

The formation of σ -dimers in the present processes can be ignored due the absence of the characteristic reduction signal around -0.1 V [7] in both media. The discharge of the charge trapped during the p -doping of the polymers in ACN was observed around -1.96 V and -1.75 V vs. Ag/AgCl for PEDOT and PXDOT, respectively. n -doping was not obtained for these polymers since no oxidation peaks associated to this process were observed [4,30–32]. These results reveal that the p -response change during the second potentiodynamic cycle for both poly-3,4-dialkoxythiophenes is due to a polymeric structural change caused by the release of anions during the discharge of the trapped charge [29,30]. The discharge of the charge trapped during the p -doping of the polymers in the hydro-alcoholic mixture was not observed, since the cathodic barrier here is the production of hydrogen located at -1.75 V vs. Ag/AgCl.

The charge trapping in the polymer matrix (Fig. 5a) and the short chain oligomer dissolution (Fig. 5b) affect the current obtained because there are fewer electroactive sites available to perform the charge/discharge faradaic process during the cycling process (Fig. 5). The formation of these trapped charges and the dissolution of low molecular weight oligomers in EtOH/H₂O are incomplete, contrary to what occurs during the equivalent charge/discharge processes in ACN. For the PBTh films the complete electroactivity loss it is very likely attributed to the nucleophilic attack of the H₂O molecule on the cationic species formed during PBTh oxidation. This reaction causes the loss of conjugation with the concomitant conductivity decrease [33]. Due to the higher potential required to charge PBTh, the cationic species obtained are more prone to react with nucleophiles and therefore the polymer chain is destroyed in this solvent mixture.

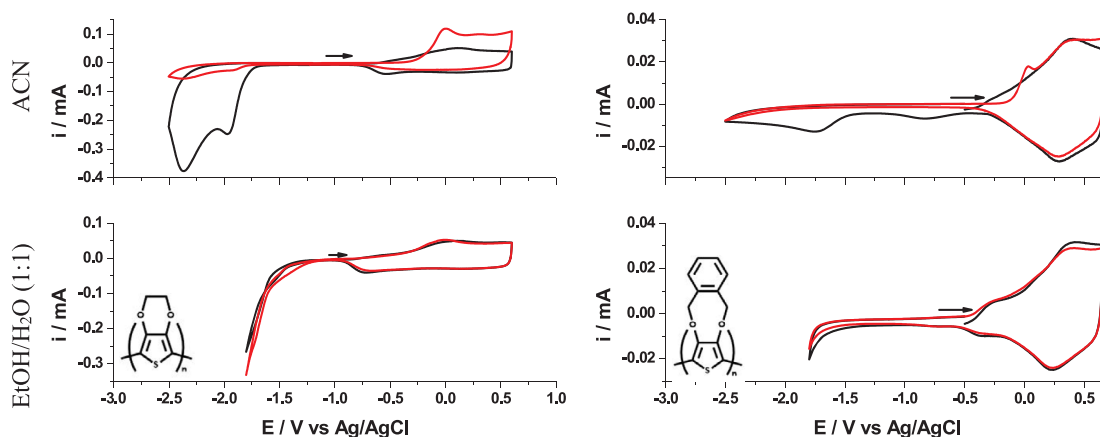


Fig. 4. Cyclic voltammetry of PEDOT and PXDOT films on vitreous carbon electrodes obtained using the conditions indicated in Fig. 2 in a monomer free 0.1 M LiClO₄, ACN solution and a 0.1 M LiClO₄ in acetic acid/sodium acetate buffer (0.05 M/0.008M) EtOH/H₂O (1:1) solution, $\nu = 25$ mV/s. 1st. cycle (black line), and 2nd cycle (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

The percentages of anodic and cathodic charge recovery (% Q_a and % Q_c , respectively) and the Q_c/Q_a ratio give further information about the charge/discharge process (see Table 1). PEDOT showed better stability than PBTh and PXDOT in EtOH/H₂O (i.e., $Q_c/Q_a = 0.931 \pm 0.023$, % $Q_a = 88.15\% \pm 2.45$, and % $Q_c = 87.73\% \pm 2.22$ from three independent experiments), even when the PXDOT showed the highest reversibility (i.e., $Q_c/Q_a = 0.992 \pm 0.12$, % $Q_a = 76.23\% \pm 2.29$, and % $Q_c = 79.88\% \pm 0.97$). Since these experiments were performed by applying a potential where the over-oxidation of the films and β - β coupling (i.e., alkoxy groups in the 3,4 positions of the thiophene ring for PEDOT and PXDOT) cannot occur, these changes may be attributed to the different interactions of the solvent with the oligomers and the chemical structure of the monomers.

The potential difference between the main peaks, ΔE_p changed from 693 to 722 mV for PEDOT, and from 261 to 168 mV for PXDOT. Studies of the electrochemical behavior of PEDOT in *tris* buffer media carried

out by Spires et al. showed that the change in ΔE_p is due to an inhibition of the doping/de-doping process caused by a shrinkage of the film's microstructure [14]. The same authors proposed that the stability of PEDOT in aqueous media is due to the possibility of solvation of the oligomeric chains. This means that charge stabilization may occur not only by the presence of the 3,4-dialkoxy groups, but also because of the formation of a solvation sphere around the positive charges present in the polymeric chain during the *p*-doping process. The formation of this stable type of solvation structure in the EtOH/H₂O mixture may explain the slowness of the charge transfer kinetics (i.e., a high ΔE_p) and the "charge trapping" inhibition, in contrast to the electrochemical behavior of these films in ACN where faster charge transfer kinetics (i.e., lower ΔE_p) were observed (Fig. 6). This indicates that LiClO₄ solvation is more effective in ACN than in EtOH as evidenced by the conductivity values of 0.1 M solutions in both solvents (i.e., $\kappa[\text{H}_2\text{O}] = 0.01059$ S/cm [34], $\kappa[\text{ACN}] = 0.00807$ S/cm [35], $\kappa[\text{EtOH}/\text{H}_2\text{O} 1:1] = 0.00398$ S/cm

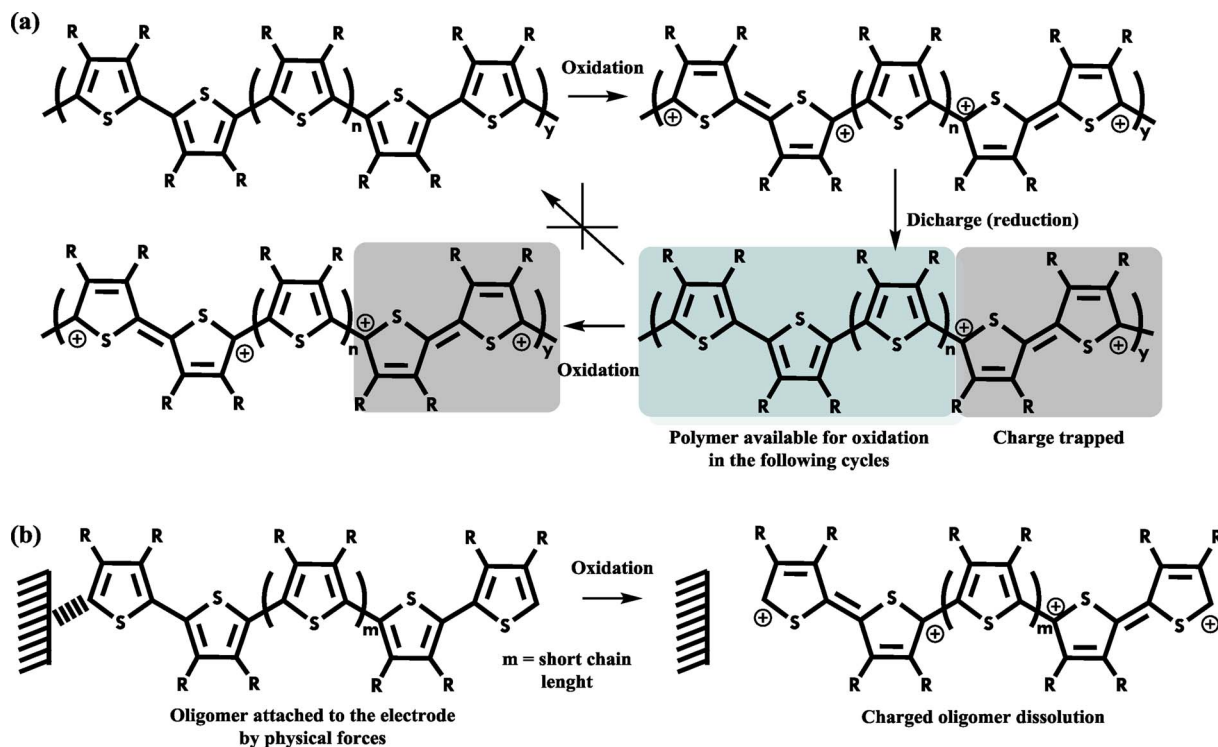


Fig. 5. (a) Charge trapping process during two cycles of charge/discharge for a polythiophene of "y" repetitive units. (b) Dissolution process of low molecular weight charged oligomers in the bulk of the solution.

Table 1

% Q_a , % Q_c recovery, and Q_c/Q_a values for PBTh, PEDOT and PXDOT films obtained by double pulse chronocoulometry (100 cycles) in ACN and later analyzed in EtOH/H₂O (from the inset graphs in Fig. 3). The most stable polymer in the EtOH/H₂O mixture is in bold.

Polymer	ACN			EtOH/H ₂ O		
	% Q_a	% Q_c	Q_a/Q_c	% Q_a	% Q_c	Q_a/Q_c
PBTh	63.38 ± 2.05	68.41 ± 0.55	0.912 ± 0.005	29.02 ± 2.87	36.39 ± 3.66	0.864 ± 0.11
PEDOT	50.20 ± 4.73	45.68 ± 6.49	0.836 ± 0.011	88.15 ± 2.45	87.73 ± 2.22	0.931 ± 0.023
PXDOT	76.56 ± 3.25	76.15 ± 2.38	0.933 ± 0.007	76.23 ± 2.29	79.88 ± 0.97	0.992 ± 0.12

[34]). Nevertheless, the charges in the films are better stabilized by the protic solvent mixture.

A further comparison of the behavior of films in ACN vs. the EtOH/H₂O mixture showed a slight decrease in oxidation potential for the 3,4-dialkoxy substituted polymers, and an increase for PBTh. This indicates that for PBTh, the oxidation process is limited by the low penetration of the ClO₄⁻ ions (solvated with protic solvents) into the hydrophobic film [25,36]. This agrees well with the ESCR model, which predicts an interaction between the PEDOT and PXDOT charged species and the EtOH/H₂O mixture [10] due to the presence of the ether groups in the thiophene rings, and to the possibility of a coulombic interaction with the solvent similar to that in solvation sphere of cations in protic solvents. To have a better understanding of the ClO₄⁻ diffusion process into the polymeric matrix, the apparent ion diffusion coefficient (D_{app}) was evaluated in both media before and after the 100 charge/discharge cycles using chronocoulometry and the corresponding integrated Cottrell equation Eq. (2) [37]. The D value is potential dependent, and therefore this equation can only yield a D_{app} . Steady state conditions attainable by electrochemical impedance spectroscopy need to be used to obtain more accurate D values (D_{eff}) [38,39].

$$Q = \frac{2zFACD_{app}^{1/2}}{\pi^{1/2}} t^{1/2} \quad (2)$$

The main difference between the application of the Cottrell equation and the ESCR model to evaluate ion diffusion coefficients in conducting polymer systems is that the former does not take into account the structural changes in the polymer for the analysis of the Q vs. t plots [37]. The present work focuses more on evaluating the apparent ion diffusion coefficients and comparing the values for the charge/discharge processes in both media, than on comparing the accuracies of both models. The apparent ion diffusion coefficients for all the polymers in the two solvents were found to be on the order of 10⁻⁶ cm²/s (see Table 2), which are consistent with those reported in previous works involving conducting polymers and the Cottrell equation [37,40]. For the three polymers studied, the highest D_{app} values were obtained in ACN, which may be attributed to the shrinking of the polymeric matrix in the EtOH/H₂O mixture as was observed in PEDOT [17]. The value of D_{app} obtained for PBTh in EtOH/H₂O confirms the limited displacement of ClO₄⁻ ions inside the hydrophobic polymer matrix, and thus this charging process is more restricted than in ACN [25]. A comparison between D_{app} values obtained before and after the 100 charge/discharge cycles showed that the ClO₄⁻ ion displacement

Table 2

Apparent ion diffusion coefficients for PBTh, PEDOT, and PXDOT films obtained by double pulse chronocoulometry and the integrated Cottrell equation before and after 100 charge/discharge cycles in ACN and EtOH/H₂O.

Polymer	ACN		EtOH/H ₂ O	
	$D_{app} / 10^6 \text{ cm}^2 / \text{s}$ (Before)	$D_{app} / 10^6 \text{ cm}^2 / \text{s}$ (After)	$D_{app} / 10^6 \text{ cm}^2 / \text{s}$ (Before)	$D_{app} / 10^6 \text{ cm}^2 / \text{s}$ (After)
PBTh	1.902 ± 0.228	0.622 ± 0.079	0.082 ± 0.023	0.007 ± 0.003
PEDOT	5.497 ± 0.292	2.157 ± 0.387	3.773 ± 2.192	3.545 ± 2.041
PXDOT	4.211 ± 0.751	1.904 ± 0.984	0.633 ± 0.047	0.541 ± 0.006

through the polymeric network substantially decreases in the ACN medium, whereas they remain approximately constant in the EtOH/H₂O mixture. Such a D_{app} decrease in ACN is probably caused by conformational changes within the polymer matrix, which limit the movement of solvated anions [12,13]. The stabilization of the positive charges presents in the polymeric chain during p -doping occurs, through the formation of a solvation sphere by the protic solvents (Fig. 6) that limits the conformational changes. This is probably the reason behind the higher reversibility, stability, and small D_{app} change during the charge/discharge process of these polymers in EtOH/H₂O. It is worth mentioning that lithium ions may form complexes in this solvent mixture (solvation number is 6 for Li⁺ in H₂O and EtOH) [41], however since the polymer is positively charged during the p -doping and there is no excess of ClO₄⁻ anions inside the polymer matrix, their diffusion is considered negligible.

The variation of peak current as a function of scan rate can provide more information about the charge/discharge process. The poly-3,4-dialkoxythiophene films showed a linear dependence of peak current on scan rate in ACN, which is consistent with the existence of a well-adhered redox film on the surface of the GC; this behavior is also observed in the EtOH/H₂O mixture. A linear dependence is observed when the redox species are adhered to the electrode and the mass transfer process is not governed by diffusion but by a thin-layer process [42]. The ΔE_p increase with scan rate in the EtOH/H₂O mixture for the PEDOT films is attributed to the strong solvent/polymer interaction and is consistent with the results obtained during the stability experiments. The log of peak current was plotted versus the log of scan rate for the films in both solvents (Fig. 7). From the slope in these plots it is possible discern in a qualitative way, whether the mobility of the electrolyte ions ($m \approx 1$) or the electron transfer rate through the π -conjugated chain ($m \approx 0.5$) is

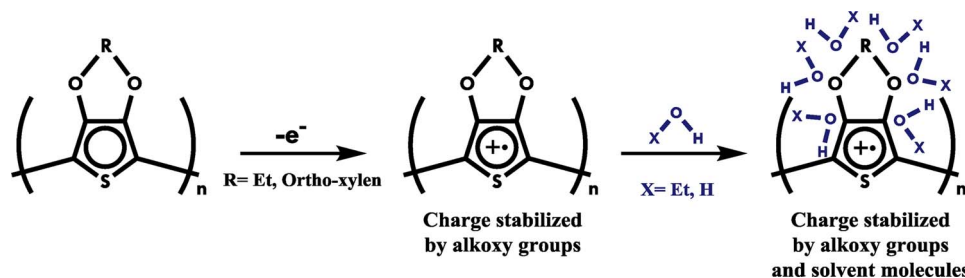


Fig. 6. Solvation and stabilization process of charged poly-3,4-dialkoxythiophenes.

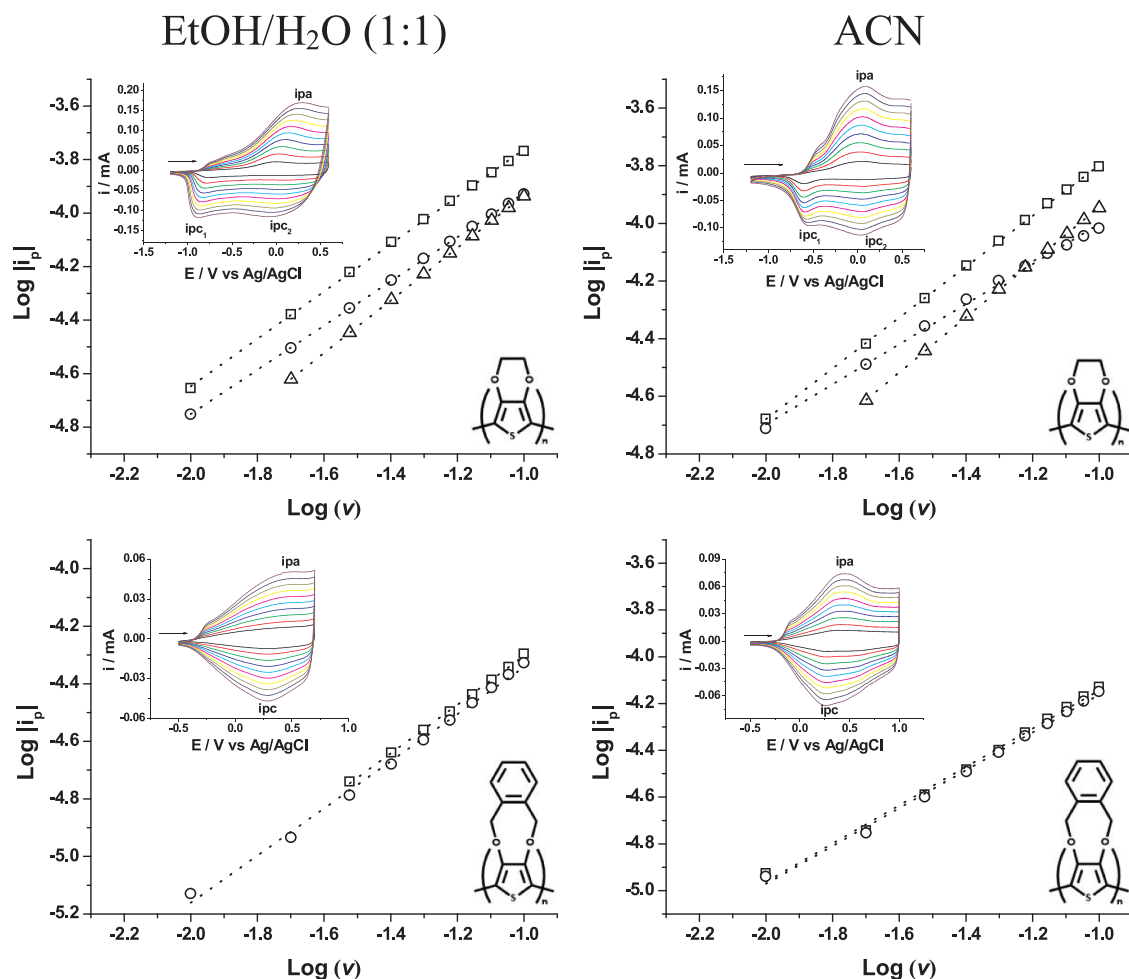


Fig. 7. Plot of $\log |i_p|$ vs. $\log (v)$ for PEDOT and PXDOT films obtained using the conditions indicated in Fig. 2. Left: in a monomer free 0.1 M LiClO₄ in acetic acid/sodium acetate buffer (0.05 M/0.008M) EtOH/H₂O (1:1) solution, and Right: 0.1 M LiClO₄, ACN solution. (□) i_{pa} , (○) i_{pc1} and (Δ) i_{pc2} . Inset shows the scan rate study for each film from 10 to 100 mV/s.

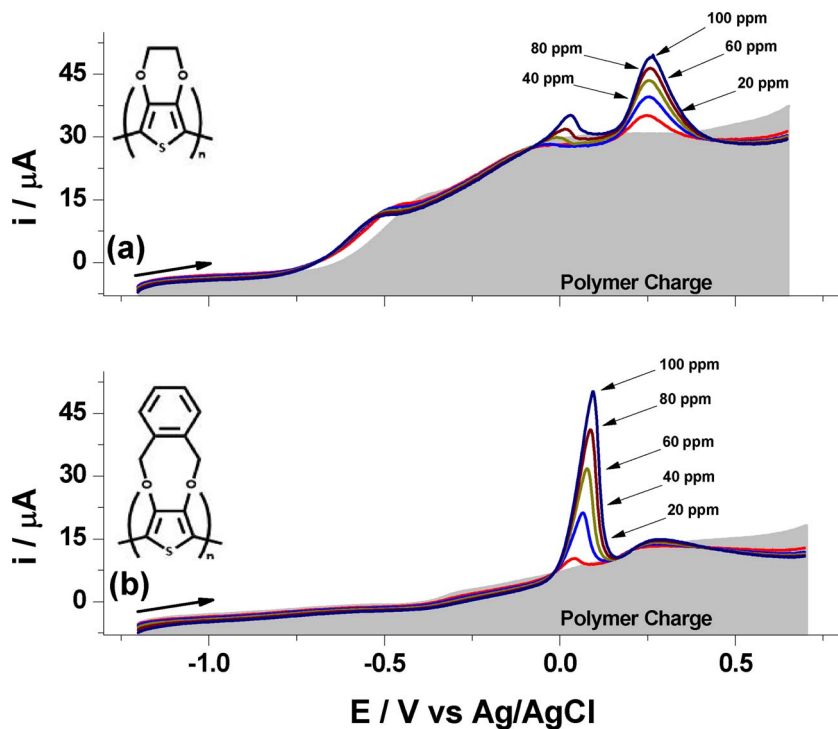


Fig. 8. Anodic stripping voltammetry of different Cu (II) concentrations (20–100 ppm) using PEDOT and PXDOT films on vitreous carbon electrodes obtained using the conditions indicated in Fig. 2. Monomer free 0.1 M LiClO₄ in acetic acid/sodium acetate buffer (0.05 M/0.008M) EtOH/H₂O (1:1) solution, $v = 25$ mV/s. The polymer's background charge current is in gray.

the limiting phenomenon during the charge/discharge process [31,43,44]. Therefore, the analysis of the corresponding slopes for the PEDOT and PXDOT films in the EtOH/H₂O mixture ($m > 0.8$ in all cases) implies a process limited by the ionic mobility inside the polymeric matrices.

In view of the outstanding electrochemical behavior of PEDOT and PXDOT in EtOH/H₂O, these films were considered candidates for the quantification of metallic ions in alcoholic beverages. One of the most ubiquitous cases is the detection of copper in different types of distilled spirits [45]. Therefore, anodic stripping voltammetry was used with the PEDOT and PXDOT covered GC electrodes in EtOH/H₂O 1:1 solutions containing Cu (II) concentrations in the 20–100 ppm range (Fig. 8). Two well-defined peaks were observed with PEDOT, and a single peak with PXDOT; both are concentration dependent. These preliminary results stimulated the study of possible applications of these electrodes to the quantification of Cu (II) ions in alcoholic beverages that is under way in our laboratory.

4. Conclusions

The study of the electrochemical behavior of polybithiophene, poly-3,4-ethylenedioxythiophene, and poly-3,4-*ortho*-xylendioxythiophene conducting polymer films deposited on vitreous carbon electrodes in a 1:1 EtOH/H₂O mixture showed that only the last two polymers are stable at least during 100 charge/discharge cycles. From the D_{app} and ΔE_p values obtained in this solvent mixture, the charge/discharge process is limited by ClO₄⁻ anion transport inside the polymeric matrix that leads to slower charge transfer kinetics; both processes are faster in ACN. The formation of a solvation sphere in the protic solvents that provides more stability to the positive charges generated during the polymer oxidation is proposed as the reason for the stability of the polymeric chain in the EtOH/H₂O mixture. These results prove that 3,4-dialkoxythiophene films have a good solvent/polymer interaction in this medium, whereas the absence of alkoxy groups in the 3,4 position (PBTh) provokes a fast electroactivity loss. Using the PEDOT and PXDOT covered GC electrodes, anodic stripping voltammetry experiments in EtOH/H₂O 1:1 solutions containing Cu (II) yielded concentration dependent oxidation peaks. This allows to propose the use of these conducting polymer modified electrodes for analytical purposes in alcoholic beverages and liquors.

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