

# Effect of the electropolymerisation conditions on the electrochemical, morphological and structural properties of PEDOT<sub>h</sub> films

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**Abstract** Poly(3,4-ethylenedioxythiophene) (PEDOT<sub>h</sub>) films were deposited on platinum electrodes by consecutive potential scanning from acetonitrile solutions with 50 mM EDOT<sub>h</sub>. The effect of the supporting electrolyte used during electropolymerisation, namely LiClO<sub>4</sub>, TBAClO<sub>4</sub> and TBAPF<sub>6</sub>, in the redox behaviour, surface morphology and degree of crystallinity of the films has been investigated by cyclic voltammetry, X-ray diffraction analysis and scanning electron microscopy, respectively. The use of LiClO<sub>4</sub> leads to a higher electropolymerisation efficiency and an increase of electroactivity and crystallinity of the polymers. This electrolyte promotes the formation of a more compact morphology with clusters of different sizes. The film porosity increases when Li<sup>+</sup> is substituted by a larger cation, TBA<sup>+</sup>. The PEDOT<sub>h</sub> layer obtained with PF<sub>6</sub><sup>-</sup> as counter ion is more porous than the obtained with ClO<sub>4</sub><sup>-</sup> and presents a fibrillar aspect. The influence of the scan rate was also studied for films obtained in TBAClO<sub>4</sub>, and high electropolymerisation efficiency and an increase of crystallinity were observed for a low scan rate. PEDOT<sub>h</sub> films with different number of growing cycles were obtained in LiClO<sub>4</sub>, pointing their redox behaviour to structural rearrangement during thickening; the thicker film presents higher structural

organization. It was possible to prepare films in different conditions, but with the same electroactivity, showing the same structural arrangement.

**Keywords** Poly(3,4-ethylenedioxythiophene) · Electropolymerisation · X-ray diffraction · Morphology

## Introduction

In the last decades, poly(3,4-ethylenedioxythiophene) (PEDOT<sub>h</sub>) has been the subject of both fundamental and applied research due to its unique and well-known properties such as low oxidation potential, good stability in the oxidised state and high conductivity [1]. This material has application as anti-static and anti-corrosive coatings [2, 3], sensors and biosensors [4–7], electrochromic devices [8–10] and solar cells photoactive component [11–13].

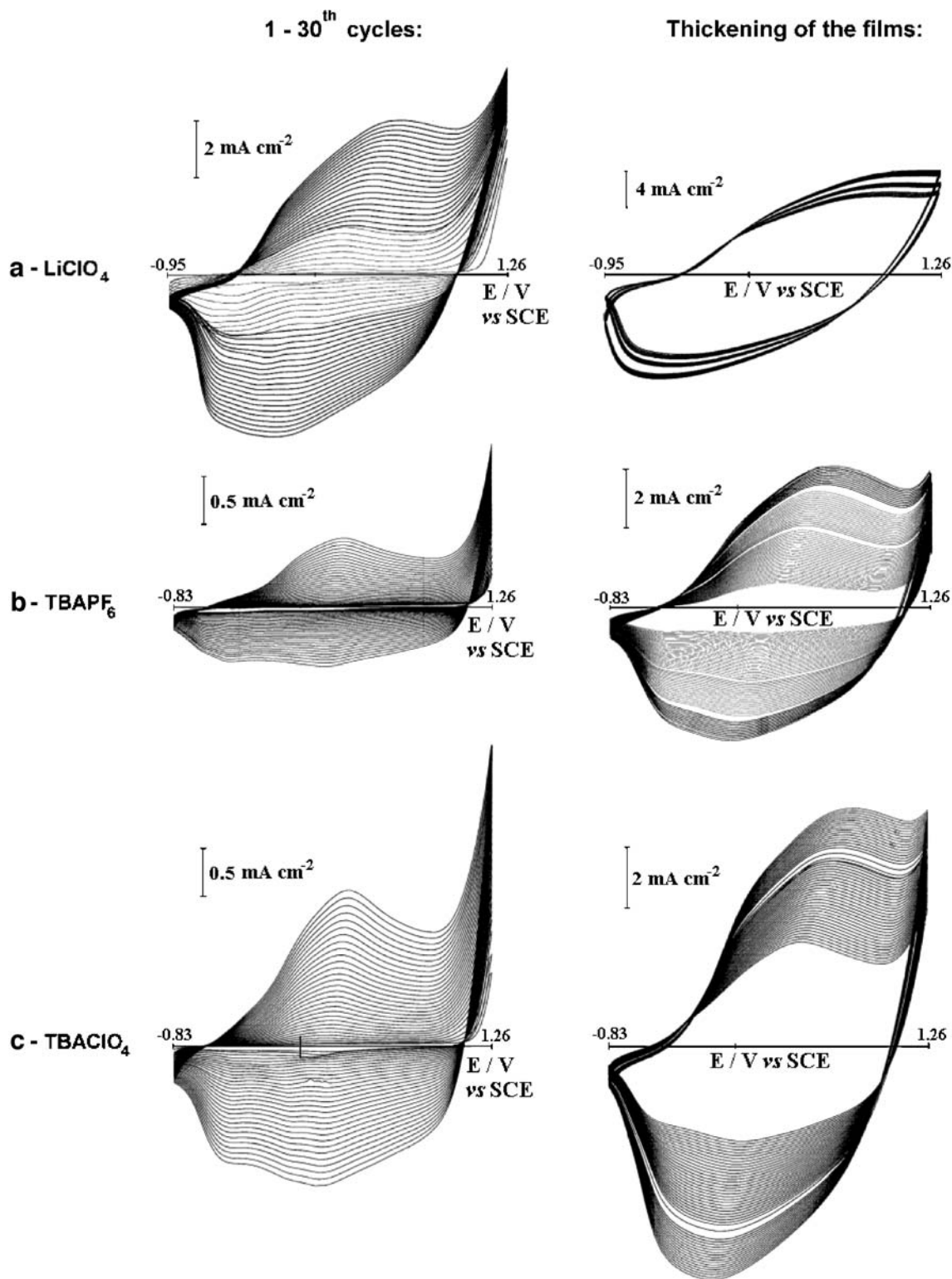
In contrast to other polymers, just a few studies have been concerned to the role of polymerisation conditions on the properties of PEDOT<sub>h</sub> films. The relationship of the conductivity of PEDOT<sub>h</sub> to the polymerisation potentials, in aqueous solution, has been retrieved from resistance measurements [14]; the drastic influence of the potential chosen for the polymer growth has been revealed by ellipsometry [15].

Studies on the galvanostatic polymerisation of EDOT<sub>h</sub> in organic media have shown the influence of the supporting electrolyte, namely the counter-anion nature on the polymer morphology; it has been observed that the PEDOT<sub>h</sub> granules size increases with the molar mass of the anion [16]. The effect of the counter-anion type on the conductivity of the obtained polymer has also been reported [17].

Structural investigations on thin films of tosylate-doped PEDOT<sub>h</sub> lead to a model consisting of a pseudo-ortho-

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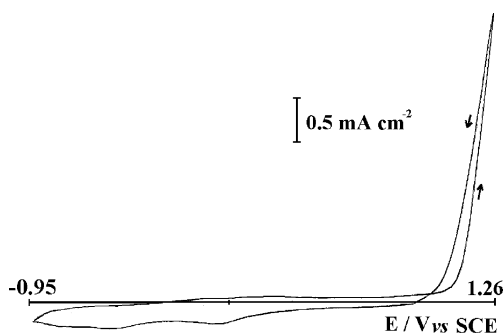
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**Fig. 1** Cyclic voltammograms of the growth of PEDOT films formed upon Pt in 50 mM EDOT + ACN, using different supporting electrolytes,  $v=100 \text{ mV s}^{-1}$

rhombic unit cell [18]; the structure has been described as a paracrystalline one, where the lattice parameters represent mean values of probability distribution, and thus assumes a decay of the crystalline order as the distance increases.

Since no significant structural changes appear to occur upon tosylate–PEDOT doping and dedoping, the authors conclude that the redox process might be balanced by small ions, sized to fit into the existing paracrystalline lattice.



**Fig. 2** Cyclic voltammogram (first scan) of EDOT polymerisation in Pt, from a 50 mM EDOT + 0.1 M LiClO<sub>4</sub> + ACN solution,  $\nu=100 \text{ mV s}^{-1}$

It is expected that the degree of crystallinity of PEDOT films is induced by several parameters of the electrochemical polymerisation. X-ray diffraction spectra of polymer layers potentiodynamically made by potential cycling, keeping the initial potential and the scan rate but varying the anodic limit, and employing different number of potential cycles in order to grow films with similar electroactivity, have shown that depending on the chosen anodic potential limit PEDOT can present amorphous, ordered structure or crystalline domains dispersed in amorphous regions [19]. The X-ray data analysis of PEDOT obtained in the presence of 2-naphthalene sulfonic acid sodium salt has also indicated a higher order of polymer chains when the monomer concentration in the polymerisation solution is increased [20]. Moreover, evidence has been given to the effect of the organic solvent on the structural properties of PEDOT-tosylate; prepared from ketones, the polymer displays an amorphous character whereas from alcohols presents crystalline phases [21].

Since the degree of crystallinity of the polymer film influences the conductivity, the rate of redox conversion, the surface roughness as well as the incorporation/immobilisation of functional species (e.g. biomolecules, inorganic complexes), a detailed study on the influence of the supporting electrolyte, scan rate and film thickness on the electrochemical behaviour, surface morphology and degree of crystallinity of PEDOT deposited on platinum electrodes by consecutive potential scanning from acetonitrile solutions and using salts providing ClO<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> as counter-ions and cations (Li<sup>+</sup>, TBA<sup>+</sup>) of different sizes is presented in this work, aiming to contribute to the enlightenment of the relationship between the electrosynthesis parameters and the properties of the obtained PEDOT films in order to optimise its performance.

## Experimental

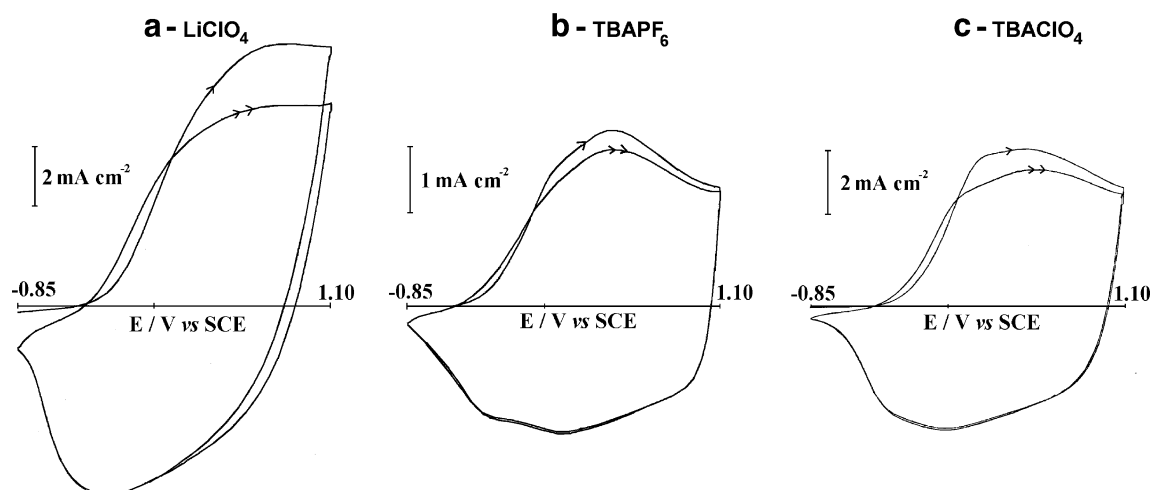
The monomer 3,4-ethylenedioxythiophene, EDOT (Aldrich), was distilled under reduced pressure prior to use. The solvent, acetonitrile, ACN (HPLC grade, Aldrich 99.93%),

was previously dried in calcium hydride and distilled with phosphorus pentoxide under N<sub>2</sub> atmosphere. The supporting electrolytes tetrabutylammonium hexafluorophosphate, TBAPF<sub>6</sub> (Fluka, puriss. ≥99%), and tetrabutylammonium perchlorate, TBAClO<sub>4</sub> (Fluka, puriss. ≥99%), were previously recrystallised from ethanol. Highly pure lithium perchlorate, LiClO<sub>4</sub> (Riedel-de Hën, p.a. ≥99%), was used as received. Prior to the measurements, the solutions were deaerated by bubbling N<sub>2</sub> (high purity, dried) for 20 min. Working electrodes of 200 nm of platinum evaporated on glass with a pre-layer of 2–4 nm of chromium (Arrandee, GmbH) were used in all the experiments. The substrates were cleaned in “piranha” solution for a few minutes, rinsed with water and dried under a nitrogen flux. A Pt foil and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. PEDOT films were potentiodynamically grown in a conventional three-electrode cell, at a sweep rate ( $\nu$ ) of 100 mV s<sup>-1</sup>, in a solution of 50 mM EDOT + ACN in 0.1 M of several supporting electrolytes: LiClO<sub>4</sub>, TBAClO<sub>4</sub> and TBAPF<sub>6</sub>. The potential was cycled, during 200 cycles, between -0.83 and 1.26 V for the films formed in the last two electrolytes, and between -0.95 and 1.26 V for the ones obtained in LiClO<sub>4</sub>. PEDOT films were also electrosynthesised in 0.1 M TBAClO<sub>4</sub> at  $\nu=10 \text{ mV s}^{-1}$  with 50 cycles and in 0.1 M LiClO<sub>4</sub> at  $\nu=100 \text{ mV s}^{-1}$  with different number of cycles (30 to 200 cycles). After polymerisation, the films were electrochemically characterised in the same electrolyte solution used in the growth but without monomer (0.1 M of supporting electrolyte in ACN), using a two-compartment cell, in the potential range [-0.85; 1.10] V at  $\nu=50 \text{ mV s}^{-1}$ . The equipment used for the electrochemical experiments were a voltage scan generator (Wenking Model VSG 83, Bank Elektronik), a potentiostat (Wenking LB75 L Laboratory Model) and a X-Y recorder (Omnigraphic 2000 Houston Instruments).

The morphology of the modified electrodes was analysed by scanning electron microscopy (SEM) performed with a JEOL JSM-5200 LM system at an accelerating

**Table 1** Current increment and potential peak values during the electropolymerisation (first 30 cycles) of PEDOT formed upon Pt in 50 mM EDOT/ACN using different supporting electrolytes at 100 mV s<sup>-1</sup>

Electrolyte	Current increment at $E=0.280 \text{ V}$ ( $\text{mA cm}^{-2}/\text{cycle}$ )	$E_{O_1}/\text{V}$ vs SCE	$E_{R_2}/\text{V}$ vs SCE	$E_{R_3}/\text{V}$ vs SCE
LiClO <sub>4</sub>	0.167	0.485	-0.180	Peaks overlapped
TBAPF <sub>6</sub>	0.021	0.300	0.200	-0.455
TBAClO <sub>4</sub>	0.050	0.323	0.150	-0.480



**Fig. 3** Cyclic voltammograms of PEDOT films in a monomer-free solution of **a** 0.1 M LiClO<sub>4</sub>, **b** 0.1 M TBAPF<sub>6</sub> and **c** 0.1 M TBAClO<sub>4</sub>;  $\nu=50 \text{ mV s}^{-1}$ ; initial polarisation at  $E=-0.85 \text{ V}$  for 300 s. Films

formed upon Pt in 50 mM EDOT + ACN, at  $100 \text{ mV s}^{-1}$ , with 100 cycles, in **a** 0.1 M LiClO<sub>4</sub>, **b** 0.1 M TBAPF<sub>6</sub> and **c** 0.1 M TBAClO<sub>4</sub>

voltage of 20 keV. The structural characterisation of the so obtained films was done by X-ray powder diffraction in a Siemens D5000 diffractometer by means of Glancing Incidence Geometry (GIXRD) with an incidence angle  $\alpha=1^\circ$ . The X-ray patterns were obtained in the  $2\theta$  range of  $3^\circ$  to  $30^\circ$ , using a  $0.04^\circ$  step size, operating with Cu K $\alpha_1$  radiation ( $\lambda=1.5406 \text{ \AA}$ ).

## Results and discussion

### Electropolymerisation and redox behaviour

The cyclic voltammograms of the EDOT electropolymerisation upon Pt in different electrolytes, corresponding to distinct growing stages, are presented in Fig. 1a to c. Figure 2 shows the first scanning cycle of polymerisation for the film growth in LiClO<sub>4</sub>. An increase of the anodic current, corresponding to the beginning of EDOT oxidation, is observed at about 1.1 V, followed by the formation of an anodic peak at 1.26 V, value at which the direction of the sweep is reversed. In TBAClO<sub>4</sub> and TBAPF<sub>6</sub>, the monomer oxidation starts at more positive potential values (1.12 and 1.13 V, respectively). In the reverse scan, the current decreases and the current crossover at about 0.970 V indicate the beginning of the nucleation process. On the following cycles (Fig. 1a to c), an anodic wave is observed, where a constant current increment occurs from cycle to cycle, attributed to the polymer oxidation and indicating the film growth. The better polymerisation efficiency is obtained in LiClO<sub>4</sub>, since it is observed that there is a higher current increment per cycle in this electrolyte (Table 1). During the initial cycles, the oxidation potential of the polymer is shifted to more anodic values according to the electrolyte used, in the order  $E(\text{TBAPF}_6) < E(\text{TBAClO}_4) < E(\text{LiClO}_4)$  (in Table 1 are

presented the redox potential values for the 30th cycle). The voltammograms show two reduction peaks during the initial stages of polymerisation; as the films become thicker, the peaks overlapped probably due to structural rearrangement similar to what happens for 3-methylthiophene [22].

During the thickening of the film (until the 100th cycle in Fig. 1), the current increment from cycle to cycle is maintained when TBAPF<sub>6</sub> is used; however, for LiClO<sub>4</sub> and TBAClO<sub>4</sub>, it decreases relatively to the initial cycles (approximately to 0.05 and 0.03 mA cm<sup>-2</sup>/cycle, respectively), denoting the deposition of a small amount of polymer on the electrode during the thickening process. After 100 growing cycles, the oxidation of the monomer is hardly visible in LiClO<sub>4</sub>, while in TBAClO<sub>4</sub> and TBAPF<sub>6</sub> the current continues to increase.

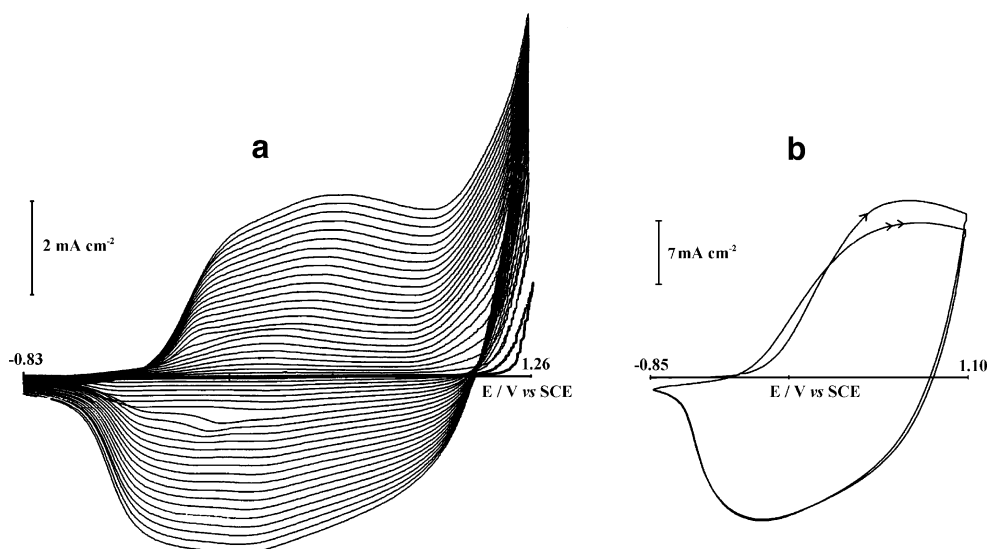
The different features observed in the cyclic voltammograms during PEDOT electropolymerisation in different electrolytes shall be due to the nature of the anion or cations, since all the other experimental conditions were maintained.

It is generally accepted that during polymerisation the formation of polaron-anion ionic pairs can occur and these species may be immobilised in the polymer matrix [23]. The charge compensation of these pairs during reduction is

**Table 2** Oxidation and reduction charges of the PEDOT films formed with 100 growing cycles in different electrolytes

State of the film	Electrolyte	$Q_O$ (mC cm <sup>-2</sup> )	$Q_R$ (mC cm <sup>-2</sup> )	$Q_O/Q_R$
Discharged 5 min at -0.85 V	LiClO <sub>4</sub>	190	154	1.23
	TBAPF <sub>6</sub>	57	55	1.04
	TBAClO <sub>4</sub>	110	102	1.08
Not discharged	LiClO <sub>4</sub>	160	160	1
	TBAPF <sub>6</sub>	53	54	0.98
	TBAClO <sub>4</sub>	99	102	0.97

**Fig. 4** **a** Cyclic voltammograms of a PEDOT film growth in 50 mM EDOT + 0.1 M TBAClO<sub>4</sub> + ACN,  $v=10 \text{ mV s}^{-1}$ , with 50 cycles. **b** Cyclic voltammograms of the obtained film in 0.1 M TBAClO<sub>4</sub> monomer-free solution,  $v=50 \text{ mV s}^{-1}$ ; initial polarization at  $E=-0.85 \text{ V}$  for 300 s

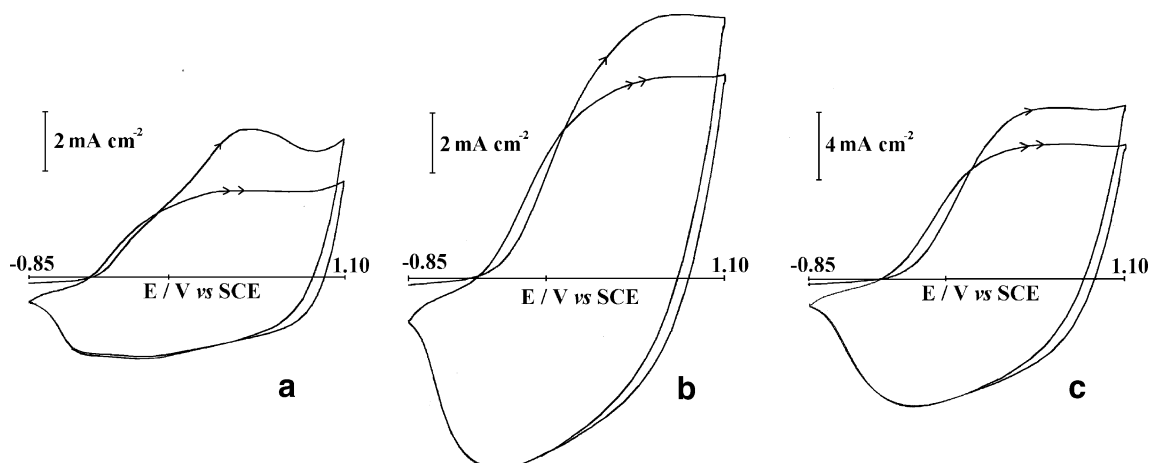


achieved by the insertion of cations from the electrolyte. The big cations will be difficultly accommodated by the film, leading to its incomplete reduction. If big cations will be substituted by smaller ones, the number of electroactive centres in the film that can be reduced and again oxidised increases. This fact can explain the higher polymerisation efficiency obtained when LiClO<sub>4</sub> is used comparatively to TBAClO<sub>4</sub>. On the other hand, and concerning the effect of the counter-anion in the PEDOT polymerisation, for the same scan rate, we can suppose that a more mobile anion will be faster replaced by monomer molecules during polymerisation than a less mobile one, increasing the rate of polymer growth. Since ClO<sub>4</sub><sup>-</sup> presents higher mobility than PF<sub>6</sub><sup>-</sup> [24], the higher current increment concerning the film formed in TBAClO<sub>4</sub> compared to TBAPF<sub>6</sub> is in accordance with what was discussed above.

As expected, the electrochemical characterisation of the films (Fig. 3) revealed different electroactivity according to the electrolyte used: better definition of the oxidation and

reduction peaks is observed in TBAPF<sub>6</sub> (Fig. 3b), two oxidation steps are observed at  $E_{pa}=0.050$  and  $0.435 \text{ V}$ ; and two reduction steps at  $E_{pc}=-0.125$  and  $-0.300 \text{ V}$ . These peaks corresponding to the two redox processes lost definition when TBAClO<sub>4</sub> is used (Fig. 3c) and an increase of the irreversibility of the system is visible, since a shift to more positive values of the oxidation potential peaks and to more negative values for the reduction peaks ( $E_{pa}=0.180$  and  $0.575 \text{ V}$ ;  $E_{pc}=-0.013$  and  $-0.338 \text{ V}$ ) can be observed. The shifts reveal that the polymer formed and characterised in TBAClO<sub>4</sub> is more difficult to oxidise and reduce. In LiClO<sub>4</sub> (Fig. 3a), the two redox processes seem to have overlapped.

For films formed with the same number of growing cycles, their oxidation and reduction charges depend on the electrolyte used (Table 2). The film formed in LiClO<sub>4</sub> exhibits higher currents and thus a higher electroactivity. This indicates better swelling of the polymer in this medium and faster ion transport probably due to the small size and higher mobility of Li<sup>+</sup> compared to TBA<sup>+</sup> and to ClO<sub>4</sub><sup>-</sup>



**Fig. 5** Cyclic voltammograms of PEDOT films in 0.1 M LiClO<sub>4</sub> + ACN,  $v=50 \text{ mV s}^{-1}$ . Films formed in a solution of 50 mM EDOT + 0.1 M LiClO<sub>4</sub> + ACN,  $v=100 \text{ mV s}^{-1}$ , with **a** 30, **b** 100 and **c** 150 cycles; initial polarization at  $E=-0.85 \text{ V}$  for 300 s



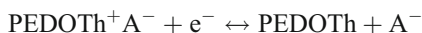
**Table 3** Redox charges of the PEDOT<sub>h</sub> films in 0.1 M LiClO<sub>4</sub>/TBAPF<sub>6</sub>/TBAClO<sub>4</sub> in ACN

Electrolyte	No. of cycles in the polymerisation	$Q_O$ (mC cm <sup>-2</sup> )	$Q_R$ (mC cm <sup>-2</sup> )	$Q_O/Q_R$
LiClO <sub>4</sub>	30	108	76	1.42
TBAPF <sub>6</sub>	145	104	94	1.10
TBAClO <sub>4</sub>	100	110	102	1.08

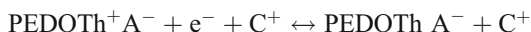
Films formed in 50 mM EDOT<sub>h</sub> with 0.1 M LiClO<sub>4</sub>, TBAPF<sub>6</sub> or TBAClO<sub>4</sub>, respectively, in ACN, with distinct number of cycles. Values of charge after initial polarisation at  $E = -0.85$  V for 300 s.

compared with PF<sub>6</sub> [24, 25]. In addition, the electroactivity increase observed for the film grown with higher polymerisation efficiency points to a more successful growth process in LiClO<sub>4</sub>; i.e., in this medium a lower probability should exist to occur collateral or secondary reactions simultaneous to the electropolymerisation process, such as degradation, crosslinking, electrolyte adsorption onto the electrode surface [26]; the competition between the nucleophilic solvent and the radical cation intermediate to couple with the growing polymer [27] and the formation of soluble oligomers and their diffusion in the bulk solution [22].

It is accepted that the redox behaviour of the polymer, namely polypyrrole [23, 28], poly(1-naphthol) [29] and polythiophenes [30, 31], involves the exchange of anions and cations. Let us consider that during the electrochemical oxidation–reduction processes of PEDOT<sub>h</sub> the electroneutrality of polymer is reached by moving of anions A<sup>-</sup> (free anions):



and/or by cation insertion, C<sup>+</sup>, if anions are blocked (bound anions):



Concerning the redox behaviour of films formed in LiClO<sub>4</sub> and TBAClO<sub>4</sub>, Fig. 3a and c, the differences may be explained considering that during reduction the bound anions immobilised inside the polymer phase may be compensated via insertion of Li<sup>+</sup> cations, TBA<sup>+</sup> (Fig. 3c) could not participate in this charge compensation process due to its large size [29, 32]. In addition, the Li<sup>+</sup> small size favours electrostatic attraction with ClO<sub>4</sub><sup>-</sup> leading to ion-pair formation inside the film, promoting the cation insertion on reduction [30].

Comparing Fig. 3b and c, the slightly small ionic size of ClO<sub>4</sub><sup>-</sup> compared to that of PF<sub>6</sub><sup>-</sup> [32], associated to its tetrahedral structure instead of the hexahedral structure of PF<sub>6</sub><sup>-</sup>, could promote the easier migration of the former anion inside the polymer matrix in order to balance the charge in the oxidised film, leading to a higher oxidation

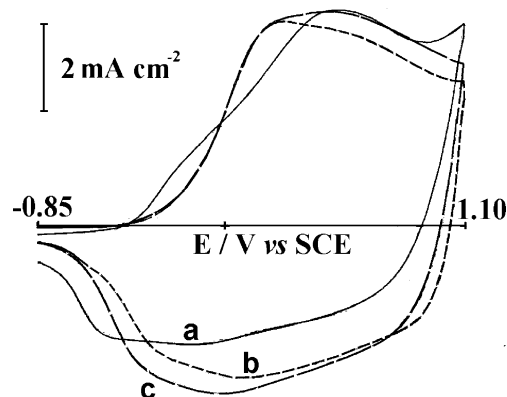
level for the film formed and characterised in TBAClO<sub>4</sub> (Fig. 3c and Table 2).

The ratio  $Q_O/Q_R$  for the discharged films (at  $-0.85$  V, for 300 s) is higher than 1; being almost equal to the unity in the films not discharged in TBAPF<sub>6</sub> and TBAClO<sub>4</sub>, indicating a good reversibility of the redox processes. However, in LiClO<sub>4</sub>, an increase of the irreversibility of the doping and undoping process is observed, since the ratio between  $Q_O$  and  $Q_R$  is higher; the cation seems to have a more significant influence on the PEDOT<sub>h</sub> redox behaviour than the anion. The decrease of the oxidation charge between the discharged and not discharged films was 16% when LiClO<sub>4</sub> was used, 7% in TBAPF<sub>6</sub> and 10% in TBAClO<sub>4</sub>.

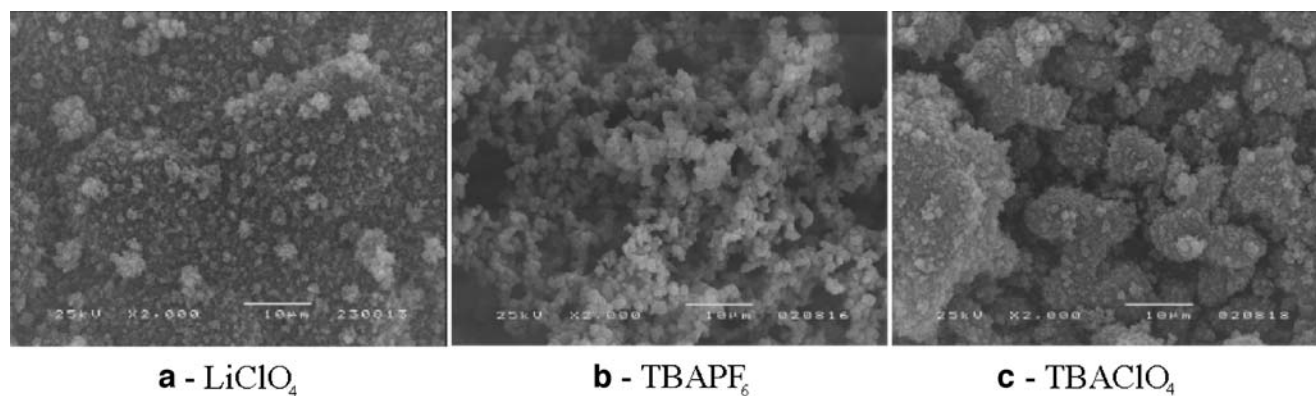
A memory effect [33, 34] is visible in the three films formed in different electrolytes, since in the second redox cycle after the discharge, the polymers recover the behaviour they have before the film was discharged.

The influence of the scan rate on the redox behaviour of PEDOT<sub>h</sub> films was studied in TBAClO<sub>4</sub>. The electropolymerisation of a film at a low scan rate (10 mV s<sup>-1</sup>; Fig. 4a) points to the presence of two oxidation waves instead of the one observed at 100 mV s<sup>-1</sup> (Fig. 1c). However, the reduction processes are worst defined at a low scan rate. The polymerisation efficiency during the first cycles at this scan rate is higher (current increment of 0.130 mA cm<sup>-2</sup>/cycle) than the observed for the film formed at 100 mV s<sup>-1</sup> (0.050 mA cm<sup>-2</sup>/cycle) and close to the value observed for the electropolymerisation in LiClO<sub>4</sub> at 100 mV s<sup>-1</sup> (0.167 mA cm<sup>-2</sup>/cycle).

The electrochemical behaviour of the PEDOT<sub>h</sub> film formed with 50 cycles at 10 mV s<sup>-1</sup> in a monomer-free solution (Fig. 4b) presents an increase in electroactivity (much more high currents) and the overlap of the two redox process compared to the film formed at 100 mV s<sup>-1</sup> (Fig. 3c). The  $Q_O/Q_R \sim 1$  for the discharged film (Fig. 4b) what indicates a good reversibility of the doping and dedoping process. A



**Fig. 6** Cyclic voltammograms of PEDOT<sub>h</sub> films in 0.1 M LiClO<sub>4</sub> (a) / TBAPF<sub>6</sub> (b) / TBAClO<sub>4</sub> (c) + ACN,  $v = 50$  mV s<sup>-1</sup>. Films formed in 50 mM EDOT<sub>h</sub> + 0.1 M LiClO<sub>4</sub> (a) / TBAPF<sub>6</sub> (b) / TBAClO<sub>4</sub> (c) + ACN, with distinct number of cycles (see Table 1). Initial polarisation at  $E = -0.85$  V for 300 s



**Fig. 7** Scanning electronic micrographs of the PEDOT films formed upon Pt in a solution of 50 mM EDOT + 0.1 M of  $\text{LiClO}_4$  (a)/ $\text{TBAPF}_6$  (b)/ $\text{TBAClO}_4$  (c) + ACN,  $v=100 \text{ mV s}^{-1}$ , with 200 cycles

memory effect in the electrochemical film behaviour is also observed under these experimental conditions.

With the aim of the studying the influence of thickness in the electrochemical properties, PEDOT films were grown in a solution of 50 mM EDOT + 0.1 M  $\text{LiClO}_4$  + ACN, at  $100 \text{ mV s}^{-1}$ , with 30, 100 and 150 cycles. Their redox behaviour is presented in Fig. 5. The cyclic voltammogram corresponding to the 150th cycle of electropolymerisation is similar to the obtained after 100 cycles (Fig. 1a—thickening) and will not be presented.

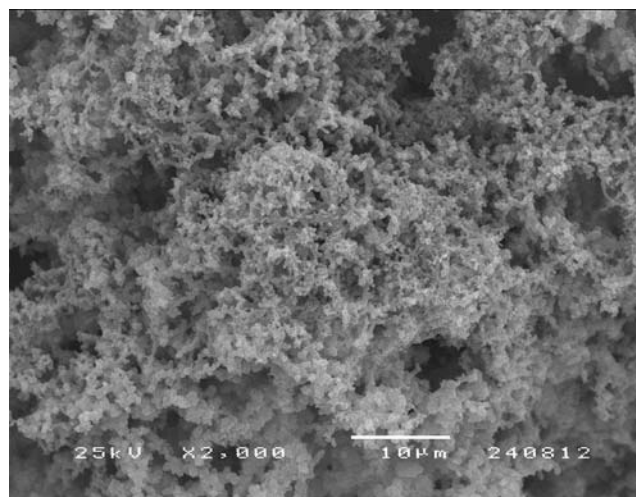
The thin film presents a well-defined anodic wave, and two reduction processes can be distinguished (Fig. 5a). For the films formed with 100 and 150 cycles, the anodic peak loses definition and it is not possible to distinguish separately the two reduction steps. The same phenomena can be observed for  $\text{TBAClO}_4$ , the film formed at  $10 \text{ mV s}^{-1}$  (Fig. 3c) could be thicker than that formed at  $100 \text{ mV s}^{-1}$  (Fig. 4b). This observation can be related to the structural rearrangement of the films with their thickening, which is similar to what happens to 3-methylthiophene [22]. However, in  $\text{LiClO}_4$ , this change in the electrochemical behaviour with the increase of the number of growing cycles can also be related with the increase of the cation participation in the polymerisation process of the film, namely with its increasing insertion in the polymer matrix, leading to structural changes.

In order to obtain films with the same oxidation charge formed in different electrolytes, the films were prepared with different number of cycles in each medium. Indeed, the films formed in  $\text{LiClO}_4$  with 30 cycles, in  $\text{TBAPF}_6$  with 145 cycles and in  $\text{TBAClO}_4$  with 100 cycles have approximately the same oxidation charge ( $104\text{--}110 \text{ mC cm}^{-2}$ ; Table 3, Fig. 6). However, the reduction charges are different according to the electrolyte used. The redox process seems more irreversible in  $\text{LiClO}_4$ , as already concluded when comparing the redox behaviour of films formed with 100 cycles in each of the electrolytes (Fig. 3 and Table 2). Probably in this medium, the  $\text{Li}^+$  cations are inserted in the polymer upon reduction as charge compensators of anions that can stay bound/enclosed

in the interior of the film, blocking the electroactive centres and, consequently, decreasing  $Q_R$ .

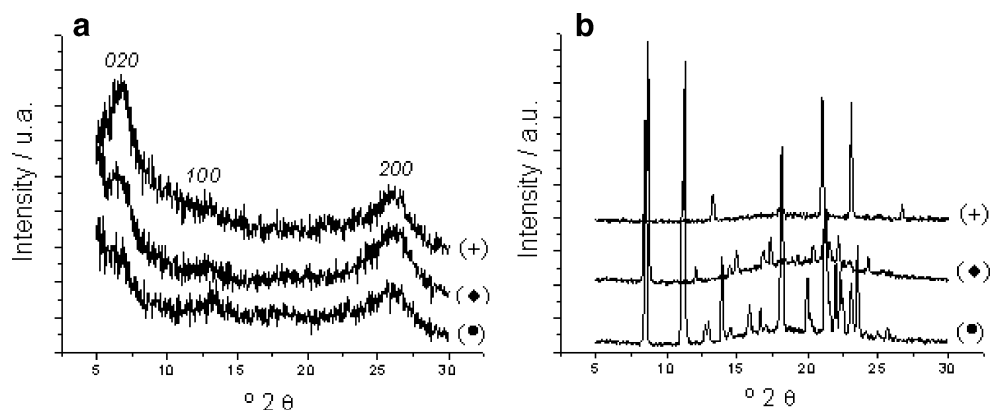
#### Morphological characterisation of the films

After the electropolymerisation of the films (finished at the anodic potential limit), the modified electrodes were washed with acetonitrile, dried under  $\text{N}_2$  atmosphere and characterised by SEM. Figure 7 shows the different morphologies of the films electropolymerised in different supporting electrolytes. Using  $\text{LiClO}_4$  (Fig. 7a), a more compact structure is obtained, formed by clusters of different sizes. The porosity of the film apparently increases when  $\text{Li}^+$  is substituted by a larger cation,  $\text{TBA}^+$  (Fig. 7c), although the same basic structure observed in  $\text{LiClO}_4$  is maintained. Probably,  $\text{Li}^+$  can be accommodated inside the polymer matrix during polymerisation occupying possible empty spaces in the chain, leading to a more compact morphology, which is not probable to occur with  $\text{TBA}^+$  [29].



**Fig. 8** Scanning electronic micrographs of the PEDOT film formed upon Pt in a solution of 50 mM EDOT + 0.1 M  $\text{TBAClO}_4$  + ACN,  $v=10 \text{ mV s}^{-1}$ , with 50 cycles

**Fig. 9** **a** XRD patterns of PEDOT<sub>h</sub> films electropolymerised in 50 mM EDOT<sub>h</sub> + 0.1 M (*plus sign*) LiClO<sub>4</sub>, (*filled diamond*) TBAClO<sub>4</sub>, (*filled circle*) TBAPF<sub>6</sub> + ACN;  $\nu=100$  mV s<sup>-1</sup>; with 200 cycles. **b** XRD patterns of the respective supporting electrolytes: (*plus sign*) LiClO<sub>4</sub>, (*filled diamond*) TBAClO<sub>4</sub>, (*filled circle*) TBAPF<sub>6</sub>



The PEDOT<sub>h</sub> layer obtained in TBAPF<sub>6</sub> (Fig. 7b) presents a clearly distinct morphology, with a fibrillar aspect, more porous than the film formed in TBAClO<sub>4</sub> (Fig. 7c). During oxidation of the films, the inclusion of anions on the matrix is to be expected. Due to the slightly higher size of PF<sub>6</sub><sup>-</sup>, it will occupy a larger space than ClO<sub>4</sub><sup>-</sup>, leading to a less compact structure. This result seems to agree with the electrochemical behaviour of the film (Fig. 3b) concerning the definition of the redox processes, since a more porous structure with higher superficial area could promote the ions exchange between the film and the electrolyte during the film growth, leading to a better definition of the oxidation and reduction peaks observed in the cyclic voltammogram.

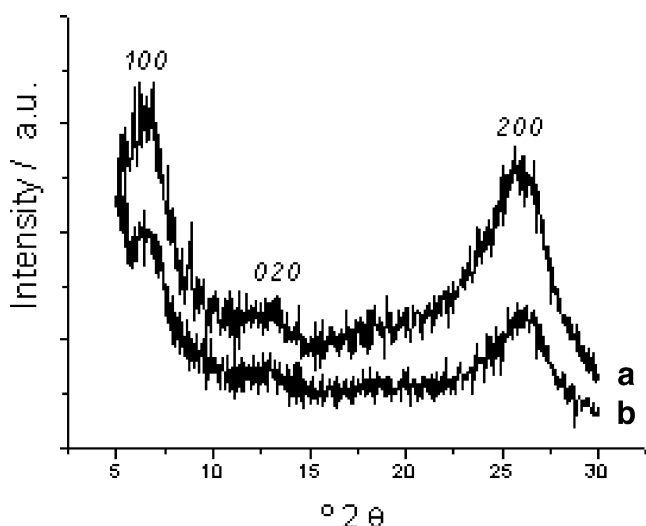
The SEM image of the film formed in TBAClO<sub>4</sub> at a slow scan rate (10 mV s<sup>-1</sup>) with 50 cycles (Fig. 8) shows a more homogeneous surface than that observed when the film is synthesised at 100 mV s<sup>-1</sup> (Fig. 7c); the formation of clusters is not visible, presenting a fibrillar aspect and a more ordered morphology, with a probable increase in the surface area. At a low scan rate, the electrodeposition rate is slower and a more ordered growth could occur; on the other

hand, the higher current increment from cycle to cycle observed during the film growth points to the formation of more material. The higher quantity of the deposited polymer associated to a surface area increase can explain the electroactivity three times higher observed for the film formed at 10 mV s<sup>-1</sup> when compared with that of the film formed at 100 mV s<sup>-1</sup> (Figs. 3c and 4b).

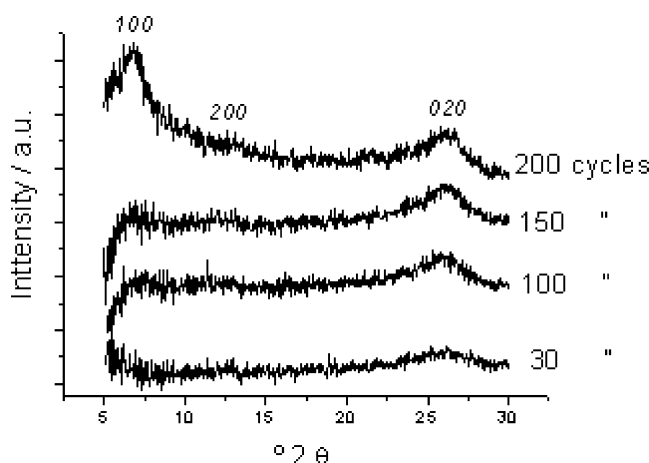
It is worthy to note that, in spite of the described differences in the electroactivity, the polymer films show a redox behaviour with remarkable stability (no change in the respective cyclic voltammograms recorded in monomer-free solution were observed for a large number of potential cycles (over 100).

#### Structural characterisation of the film

The X-ray diffraction of the films formed with 200 cycles in different electrolytes (Fig. 9) shows low crystallinity. Similar to previous XRD analysis of PEDOT<sub>h</sub> samples with orthorhombic structure [35], the diffraction lines at scattering angles  $2\theta \approx 6.8^\circ$ ,  $12.9^\circ$  and  $26^\circ$  can be assigned to 100, 200 and 020 planes. The presence of supporting electrolyte in the films was not detected (Fig. 9b).



**Fig. 10** XRD patterns of PEDOT<sub>h</sub> films formed in 50 mM EDOT<sub>h</sub> + 0.1 M TBAClO<sub>4</sub> + ACN, at  $a$  10 mV s<sup>-1</sup> with 50 cycles and  $b$  100 mV s<sup>-1</sup> with 200 cycles



**Fig. 11** XRD patterns of PEDOT<sub>h</sub> films formed in 50 mM EDOT<sub>h</sub> + 0.1 M LiClO<sub>4</sub> + ACN, at 100 mV s<sup>-1</sup> with 30 to 200 cycles



The polymer formed in  $\text{LiClO}_4$  shows an increase of crystallinity and presents a more pronounced peak at low angle ( $2\theta \approx 6.83^\circ$ ) indicating a preferential film growth for the 100 direction in this electrolyte. The lattice parameters for this film are  $a=14.4 \text{ \AA}$ ,  $b=6.8 \text{ \AA}$  and  $c=7.8 \text{ \AA}$  similar to Kim et al. [21]. This increase in crystallinity does not correspond to a better definition of the oxidation and reduction processes observed during the electropolymerisation; this film presents more irreversible behaviour during growth. This fact can be understood considering that the reversibility of the redox processes implies the existence of a flexible structure in order to allow the easier ingress and egress of charge-compensating ions during polymerisation which, naturally, is incompatible with a rigid and well-defined structure. On the other hand, during polymerisation the  $\text{Li}^+$  cation could participate in the potentiodynamic electropolymerisation and can be probably inserted in the polymer matrix (as charge compensator or due to the formation of ionic pairs with  $\text{ClO}_4^-$ ) leading to a conformational situation that promotes the PEDOT<sub>h</sub> preferential growth in the 100 plane. Indeed, Alemán et al. [36] showed that the  $\text{Li}^+$  atom is able to distort the ideal conformation of oligomers containing 2 and 3 EDOT<sub>h</sub> units and also the planar conformation of the thiophene ring.

Concerning the effect of the anion, the film electropolymerised on  $\text{TBAClO}_4$  presents sharper peaks than those obtained on  $\text{TBAPF}_6$ , suggesting an increase in crystallinity and a better ordered structure on the first. The smaller anion,  $\text{ClO}_4^-$  [32], could facilitate more compact packing of the PEDOT<sub>h</sub> chains during electropolymerisation.

The X-ray patterns for PEDOT<sub>h</sub> films formed in  $\text{TBAClO}_4$  at 10 and 100  $\text{mV s}^{-1}$  are shown in Fig. 10. Three scattering angles  $2\theta \approx 6.8^\circ$ ,  $12.8^\circ$  and  $26^\circ$  are observed for the two scan rates assigned to 100, 200 and 020 reflections. A better peak definition and intensity, and consequently an increase in crystallinity, is observed for the film formed at 10  $\text{mV s}^{-1}$ , as expected. The increasing of 020 reflection shows a preferential growth also for this direction.

The influence of the number of growing cycles in the crystallinity of the films is presented in Fig. 11. PEDOT<sub>h</sub> films were grown in a 50 mM EDOT<sub>h</sub> + 0.1 M  $\text{LiClO}_4$  + ACN solution, at 100  $\text{mV s}^{-1}$ , with different number of polymerisation cycles. A better definition of the peaks in the diffractogram obtained with 200 cycles is visible due, probably, to an increase of the crystallites, once the film is thicker.

The XRD patterns show an essentially amorphous nature. For thin films, a preferential growth for the 020 direction is observed, corresponding to the diffraction peaks at  $2\theta \approx 26^\circ$ ; for the thicker film (200 cycles), two peaks are clearly visible (at  $6.8^\circ$  and  $26^\circ$ ), indicating a higher organization of the film structure, being the diffraction

peak at low angle ( $6.8^\circ$ ) more pronounced and suggesting a preferential growth in the 100 plane.

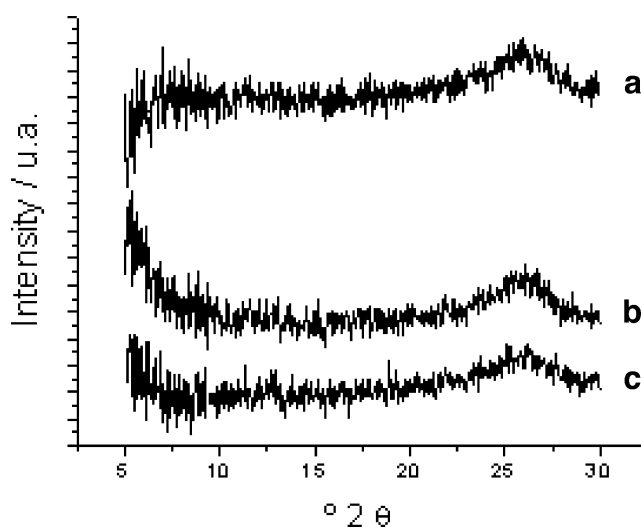
PEDOT<sub>h</sub> films were synthesised in  $\text{LiClO}_4$ ,  $\text{TBAPF}_6$  and  $\text{TBAClO}_4$  with different number of cycles in order to have the same oxidation charge in their redox characterisation in the respective monomer-free electrolyte solution. The XRD patterns of these films are presented in Fig. 12 (the diffractogram of the substrate is also shown).

The amorphous character of the films is observed. A slight preferential growth occurs in a crystallographic direction corresponding to a scattering angle  $2\theta \approx 26^\circ$  for all the films; structural characteristics are similar. Films prepared in different supporting electrolytes and with different number of cycles, in order to display the same electroactivity, exhibit the same structural arrangement.

## Conclusions

The PEDOT<sub>h</sub> electropolymerisation process presents different features dependent on the electrolyte used. The beginning of the EDOT<sub>h</sub> oxidation occurs at 1.1 V in  $\text{LiClO}_4$  but shifts to more positive potential values in  $\text{TBAClO}_4$  and  $\text{TBAPF}_6$  (to 1.12 and 1.13 V, respectively). The oxidation of the polymer occurs at more anodic potential values in the reverse order:  $E$  in ( $\text{TBAPF}_6$ ) <  $E$  ( $\text{TBAClO}_4$ ) <  $E$  ( $\text{LiClO}_4$ ). Higher electropolymerisation efficiency was obtained in  $\text{LiClO}_4$ .

The electrochemical characterisation of the films formed in the three electrolytes in this study has revealed good reversibility of the redox process and memory effects of the films.



**Fig. 12** XRD patterns of PEDOT<sub>h</sub> films formed in 50 mM EDOT<sub>h</sub> + 0.1 M *a*  $\text{TBAClO}_4$ /*b*  $\text{TBAPF}_6$ /*c*  $\text{LiClO}_4$  + ACN, at  $v=100 \text{ mV s}^{-1}$  with *a* 100, *b* 145 and *c* 30 cycles, respectively. All the films have approximately the same oxidation charge ( $104\text{--}110 \text{ mC cm}^{-2}$ )

The morphological and structural properties of PEDOT films can be controlled by the selection of the supporting electrolyte and the scan rate used during electrochemical polymerisation. The use of TBA<sup>+</sup>, PF<sub>6</sub><sup>-</sup> and high scan rates increases the film porosity. A better crystallinity was obtained with LiClO<sub>4</sub>, probably because Li<sup>+</sup> could participate in the potentiodynamic electropolymerisation leading to a conformational situation that promotes the PEDOT preferential growth in the 100 plan corresponding to the diffraction peak at 6.8°; an increase in crystallinity was obtained for film formed at low scan rates.

In this work, it was possible to prepare films in different experimental conditions with the same electroactivity, presenting similar crystallinity.

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