

Electropolymerization and Characterization of 3,4-Ethylenedioxy Thiophene on Glassy Carbon Electrode and Study of Ions Transport of the Polymer During Redox Process

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ABSTRACT: Poly(3,4-ethylenedioxythiophene) (PEDOT) films were deposited on glassy carbon (GC) electrodes from organic electrolytes containing the monomer in a solution of acetonitrile (AN). The effect of the supporting electrolyte used during electropolymerization, on the redox behavior, surface morphology, and degree of crystallinity of the films has been investigated by FTIR, cyclic voltammetry, and scanning electron microscopy (SEM) techniques. The use of LiPF_6 leads to a higher electropolymerization efficiency and an

increase of electroactivity and crystallinity of the polymer. On the basis of voltammetric studies of the Nernst and Butler–Volmer equations, we concluded that BF_4^- , ClO_4^- , and PF_6^- anions are the mobile species during the redox process of the PEDOT films. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2407–2416, 2012

Key words: poly (3,4-ethylenedioxythiophene); electropolymerization; morphology; Butler–Volmer equation

INTRODUCTION

Since the discovery in the late 1970s that oxidized polyacetylene could attain a high conductivity,^{1,2} the field of conductive polymers has grown enormously. Conductive polymers have received much attention because of numerous possible applications. To date, polypyridines, polypyrrole, and polyaniline³ have been the most studied polymers. Among the numerous polymers that have been developed over the past years, poly(3,4-ethylenedioxythiophene) (PEDOT) has appeared to be one of the most successful materials since it combines high conductivity with high transparency and excellent stability.^{4,5} PEDOT 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 oxidized state, and high conductivity.⁶ This material has application as anti-static and anti-corrosive coatings,^{7,8} sensors and biosensors,^{9–11} electrochromic devices,^{12–14} and solar cells photoactive component.^{15–17}

This drawback can be circumvented by the introduction of substituent (alkyl, alkoxy or alkoxysulfonate groups) or by polymerization in the presence of a polyelectrolyte such as polystyrenesulfonic (PSS) acid.¹⁸ Despite the commercial success of PEDOT,

little is known about the scope and limitations of the electronic properties of PEDOT derivatives. One of the most important challenges for PEDOT in the near future is to increase the control over its conductive properties. PEDOT may be synthesized chemically using $\text{Fe}_2(\text{SO}_4)_3$ as an oxidant,¹⁹ or electrochemically using an aqueous electrolyte.²⁰ Because of the low solubility of 3,4-ethylenedioxythiophene (EDOT) monomer in pure water, polymerization is usually carried out in the presence of a surfactant.²¹ Organic electrolytes, like solutions of alkylammonium or lithium salts in acetonitrile,^{22–24} have been proposed as an alternative for PEDOT electrosynthesis. The anions used for the electrosynthesis and the following electrochemical experiments could be divided into three groups: (1) small inorganic anions such as Cl^- , Br^- , ClO_4^- , NO_3^- , BF_4^- , and PF_6^- , (2) medium-sized anions such as benzenesulfonate, dodecylsulfonate, and *p*-toluenesulfonate, and (3) large polymeric anions such as polyvinylsulfonate and polystyrenesulfonate. The resulting polymer will exhibit different conductive, mechanical, or electrochemical properties depending on the incorporated anion. The ions interchanged with the solution during the redox switching are also influenced by the doping anion of the polymer. The main goal of this research was to perform the electrosynthesis of PEDOT in acetonitrile-based electrolytes under galvanostatic conditions, and to investigate the role of a few lithium salts, i.e., LiBF_4 , LiClO_4 , and LiPF_6 as the supporting electrolyte. The morphology of the

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deposits was subsequently inspected by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The EDOT_h monomer (Sigma-Aldrich Chemie GmbH, München, Germany), was distilled under a reduced pressure before electropolymerization. All other reagents included acetonitrile (Aldrich, 99.93%), and the supporting electrolytes: lithium hexafluorophosphate (LiPF₆, Alfa Aesar, purity > 98%), lithium perchlorate (LiClO₄, Fluka Chemie GmbH, Buchs, Switzerland), purity > 99%), and lithium tetrafluoroborate (LiBF₄, Merck, Darmstadt, Germany), purity > 99%) were used without any treatment or further purification.

Electrode preparation and electropolymerization

The working electrode used was a glassy carbon (GC) electrode. A Pt-grid was employed as the counter electrode, and an Ag/AgCl/KCl (saturated) electrode was utilized as the reference electrode. The GC electrode surface was cleaned by successive polishing with 0.05- μ m alumina slurry. After the polishing treatment, the electrode was carefully washed with the solvent. PEDOT_h films were electrochemically grown in a conventional three-electrode cell at 120 mV s⁻¹ in a solution of 50 mM EDOT_h in acetonitrile (AN). The supporting electrolyte concentration was fixed at 0.1 M. Prior to the electrochemical tests and measurements, the solutions were deaerated by bubbling N₂ (high purity, dried) for 20 min. The potential was cycled during the 120 cycles, between -0.95 V and 1.26 V. After electrodeposition, the films were washed with AN three times. To estimate the level of doping, the films were electrochemically characterized in the same electrolyte solution without a monomer in the potential range from -0.85 V to 1.10 V at 50 mV s⁻¹.

Instrumentation and procedure used

Electrochemical measurements were performed in a one-compartment cell with a three-electrode configuration. Cyclic voltammetry (CV) tests are carried out using the potentiostat/galvanostat EG&G Model 263A (USA) with a PC and electrochemical setup that controlled with M270 software. The morphology of the modified electrodes was analyzed using the SEM. The images of the produced doped films were taken with the use of the VEGA-TESCAN (Czech Republic) instrument at various magnifications. Sample films were grown on the GC electrode. A Fourier transform infrared (FTIR) spectroscopy study was carried out with a Bruker spectrophotometer (Vector 22, Bremen, Germany) which was equipped with the OPUS software to analyze data.

RESULTS AND DISCUSSION

Electropolymerization and the redox behavior

The cyclic voltammograms for the EDOT_h electropolymerization on the GC electrode in different electrolytes were presented in Figure 1(a-c). An increase of the anodic current, corresponding to the beginning of the EDOT_h oxidation, was observed at about 1.26 V. In the following cycles [Fig. 1(a-c)], an anodic wave was seen, where a constant current increment occurs from cycle to cycle. It was attributed to the polymer oxidation indicating the film growth. The better polymerization efficiency was obtained in the LiPF₆ electrolyte since a higher current increment per cycle was observed for this electrolyte (see Table I). During the initial cycles, the oxidation potential of the polymer was shifted to more anodic values according to the following order: $E(\text{LiClO}_4) < E(\text{LiBF}_4) < E(\text{LiPF}_6)$.

The different features that were observed in the cyclic voltammograms during the EDOT_h electropolymerization in different electrolytes must be due to the nature of the anions or cations used. It is generally accepted that during electropolymerization, the formation of polaron-anion ionic pairs can occur and these species may be immobilized in the polymer matrix.^{25,26} Considering the effect of the counter-anion in the EDOT_h electropolymerization at the same scan rate, we can suppose that a more mobile anion will be more quickly replaced by the monomer molecules during polymerization than a less mobile one, increasing the rate of polymer growth. Since PF₆⁻ presents higher mobility than ClO₄⁻ and BF₄⁻ a higher current increment was seen for the film formed in LiPF₆ compared to the other electrolytes.

The doping and undoping reactions of conducting polymers (the change between two oxidation states of the polymer) are always followed by the transfer of dopants between the film matrix and the bulk solution (Fig. 2). The cyclic voltammograms of the polymer recorded in the monomer-free solutions are presented in Figure 3(a-c). These voltammograms were taken from +1.1 to -0.85 V on PEDOT_h films in the solutions having 0.1M supporting electrolyte at 50 mV s⁻¹.

The shape of the CV curves is apparently similar. The most essential differences appear in the case of PF₄⁻ anions. The charge needed for the reduction or oxidation of the PEDOT_h/PF₆⁻ film is remarkably larger. The charge measured by integration of the anodic peak for PEDOT_h/PF₄⁻ film was 2.915 mC/cm². The values for PEDOT_h/BF₄⁻ and PEDOT_h/ClO₄⁻ films were found to be 2.83 mC/cm² and 1.00 mC/cm², respectively. This could be described according to the level of the doping or efficiency of the electrodeposition. Comparing the redox behavior of the produced films in Figure 3(a-c), the more mobility of

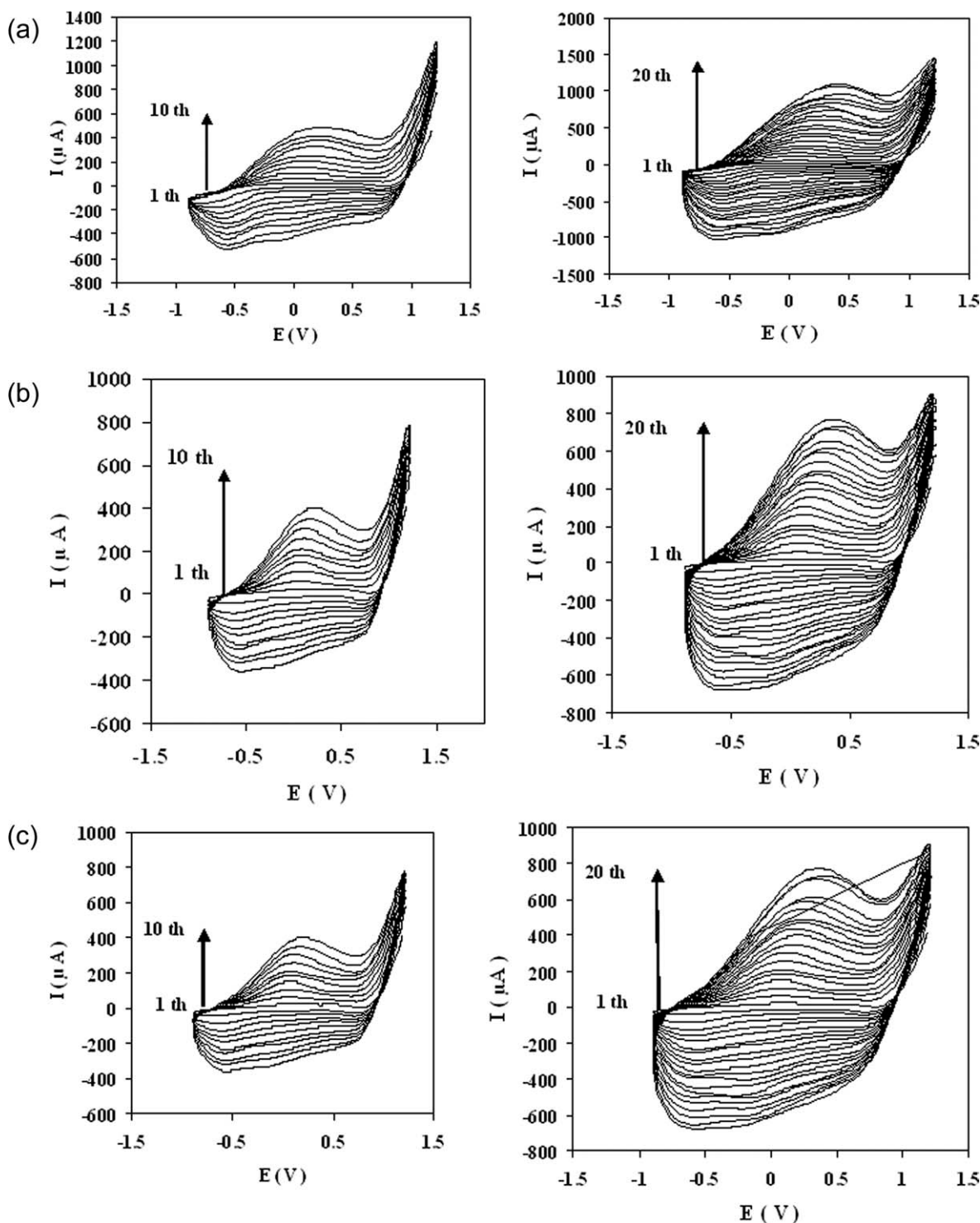


Figure 1 Cyclic voltammograms of the growth of PEDOT_h films formed on GC electrode in 50 mM EDOT_h + AN, using different supporting electrolytes, $\nu = 100 \text{ mV s}^{-1}$, with 10, 20 cycles.

PF₆⁻ anion and the charge distribution could promote the easier migration of the anion inside the polymer matrix in order to balance the charge in the oxidized states. Continuing with the electrochemical behavior of PEDOT_h films in an AN medium, when more-negative potentials (-1.6 or -2.0 V) are reached, noticeable changes in their voltammetry behavior were

observed. This means that higher anodic peaks and greater anodic charges were obtained.

In Figure 4 the influence of potential replacement on the redox process of PEDOT_h was shown for the three anions. The initial potential (E_i) was fixed at +1.1 V, but values of -2.0, -1.6, and -1.2 V were applied as the final potential. Noticeably, when the

TABLE I
Current Increment and Potential Peak Values During the Electropolymerization (First 20 Cycles) of PEDOT_h Films on GC Electrode in 50 mM EDOT_h/ACN at 100 mV s⁻¹

Electrolyte	Current increment at $E = 0.28 \text{ V} (\mu\text{A cm}^{-2}/\text{cycle})$	$E_{\text{Max},0}$ (V) vs. Ag/AgCl
LiClO ₄	591	0.318
LiBF ₄	564	0.385
LiPF ₆	1124	0.408

potential ultimate ranges were more negative, the shift of the anodic peak height and potential was increased. However, when the final potential was fixed at -1.6 V , the anodic peak height and replacement was maximum in the case of PF₆⁻ anion. These observations could be explained according to the changes that carried out in the polymer structure by increasing the potential range. It means that the deposited film will have further time for oxidation.

Therefore, during the redox process, longer lengths of the polymer chains will be oxidized which results in the formation of further pin holes having positive charges. The positive charges accelerate the diffusion of the electrolyte anions to be incorporated into the polymer chains in order to neutralize the positively charged structures. Indeed, this charge development will increase the height of the anodic peak and potential shift.

Effect of the scan rate on the redox behavior of PEDOT_h films

Figure 5 shows the influence of the different scan rates on the redox behavior of PEDOT_h films in a solution including 0.1M of various supporting electrolytes in AN.

The data obtained from this study is presented in Table II, and the changes are considerable. As can be seen in Figure 5, a linear relation exists between the anodic current and scan rate. This means that by increasing the scan rate, the polymer oxidation was increased. As a result, anion transfer to the electrode surface during the polymer oxidation was increased, and further ion penetration into the polymer attained. Among the three anions, the value of polymer oxidation rate is substantial for the case of PF₆⁻.

Effect of the concentration of counter ions

Figure 6 shows the effect of the concentration of PF₆⁻, BF₄⁻, and ClO₄⁻ anions on the anodic peak current. Concentrations of 0.01, 0.03, 0.1, and 0.2M of PF₆⁻, BF₄⁻, and ClO₄⁻ anions were used. As shown by the figure, increasing the anion concentration led to an increase in the anodic current for the resultant polymeric films. The increase in the anodic current was due to an increase in the electroactive surface

area of the resulting polymers that were deposited at higher current densities.

Evidence for anionic transport

In addition to the above observations, there is substantial experimental evidence pointing to prevailing BF₄⁻, ClO₄⁻, PF₆⁻ anions interchange during the redox process of the PEDOT_h films in AN solution. Voltammetric peaks corresponding to the insertion of mobile ions have been considered to be more sensitive to the scan rate. Thus, the insertion of ionic species occurs in the anodic process. Considering the fact that Li⁺ insertion could not be assumed in the anodic process, there must be an uptake of BF₄⁻, ClO₄⁻, PF₆⁻ anions during oxidation revealing a shift in the anodic peaks. This is only possible if BF₄⁻, ClO₄⁻, and PF₆⁻ anions could be entered into a compacted polymeric matrix at an anodic potential and it is expelled from the polymer to the solution at a cathodic potential.

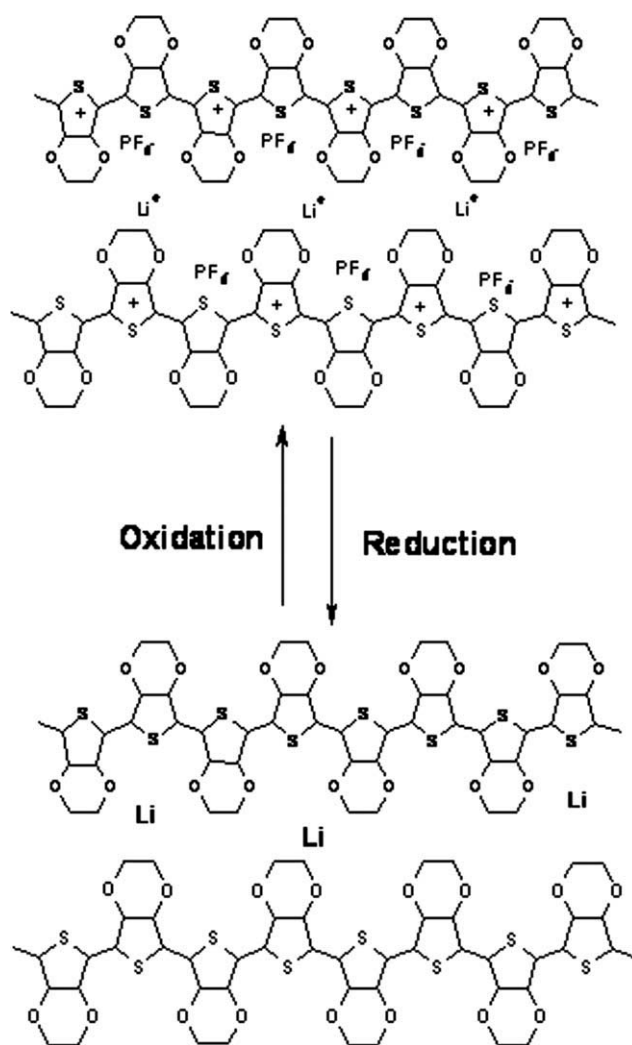


Figure 2 Model for ion insertion during the redox process of PEDOT_h films.

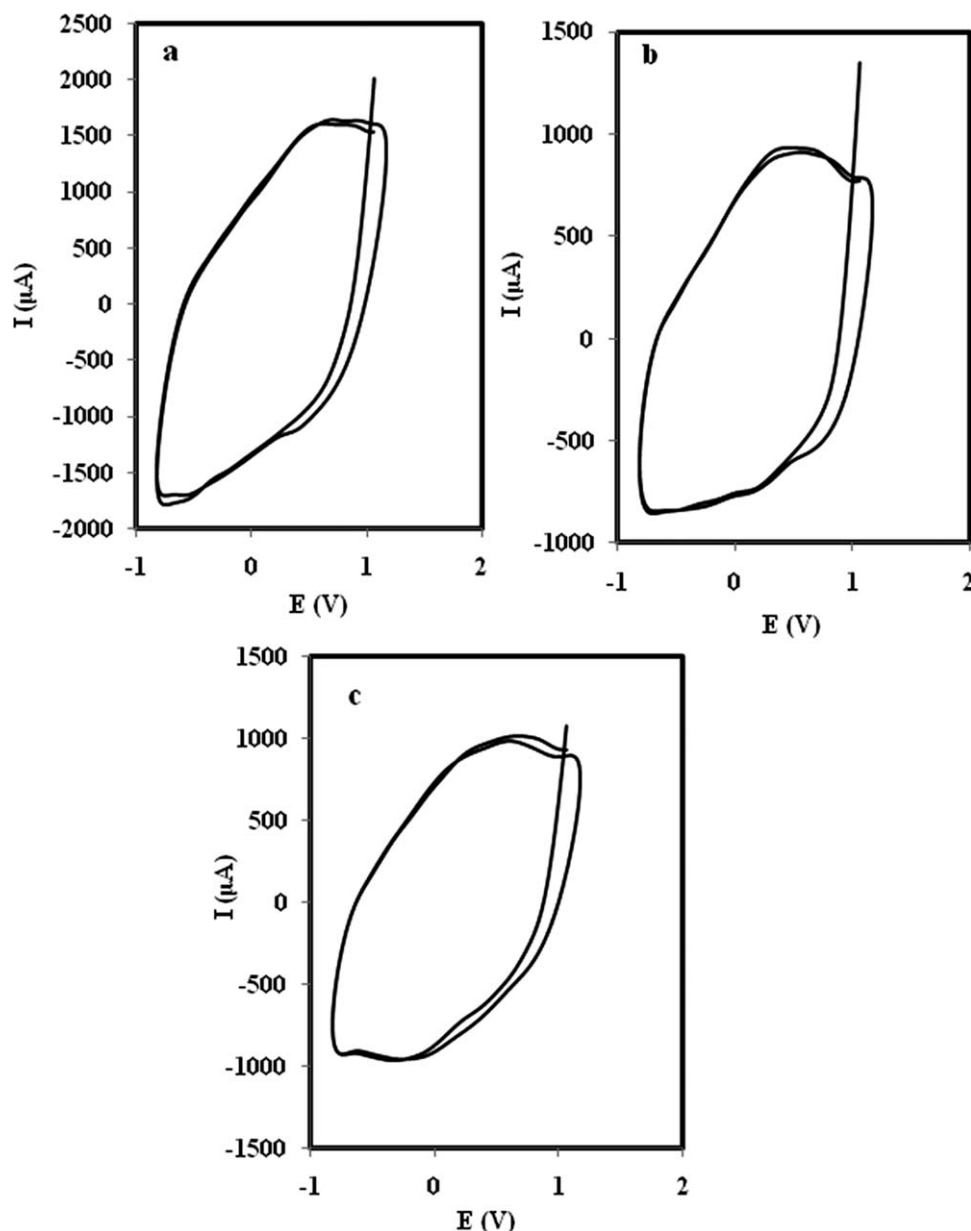


Figure 3 Cyclic voltammograms of PEDOT_h films deposited after 20 cycles in a monomer-free solution of (a) 0.1M LiPF₆, (b) 0.1M LiBF₄, and (c) 0.1M LiClO₄; $\nu = 50 \text{ mV s}^{-1}$; initial polarization at $E = -0.85 \text{ V}$.

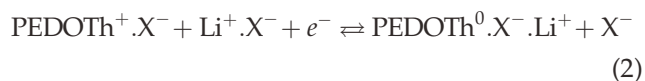
Nernst and Butler–Volmer treatment

As an initial hypothesis, in these types of polyelectrolyte materials, it is not clear which prevailing species, cation or anion, could be transferred during redox processes. Three different possibilities exist:

1. There is a prevailing interchange of cations.
2. There is a prevailing interchange of anions.
3. Both cations and anions participate simultaneously in the redox process.

On the basis of voltammetric studies of the Nernst and Butler–Volmer equations, we concluded that BF₄⁻, ClO₄⁻, and PF₆⁻ anions are the mobile species during the

redox process of the PEDOT_h films. Considering that the polyelectrolyte remains fixed inside the polymeric material, two basic redox reactions for the prevailing interchange of cations or anions can be proposed:



In the simplest approximation and considering an equilibrium condition, the electrochemical potential for these reactions could be described by the Nernst equation:

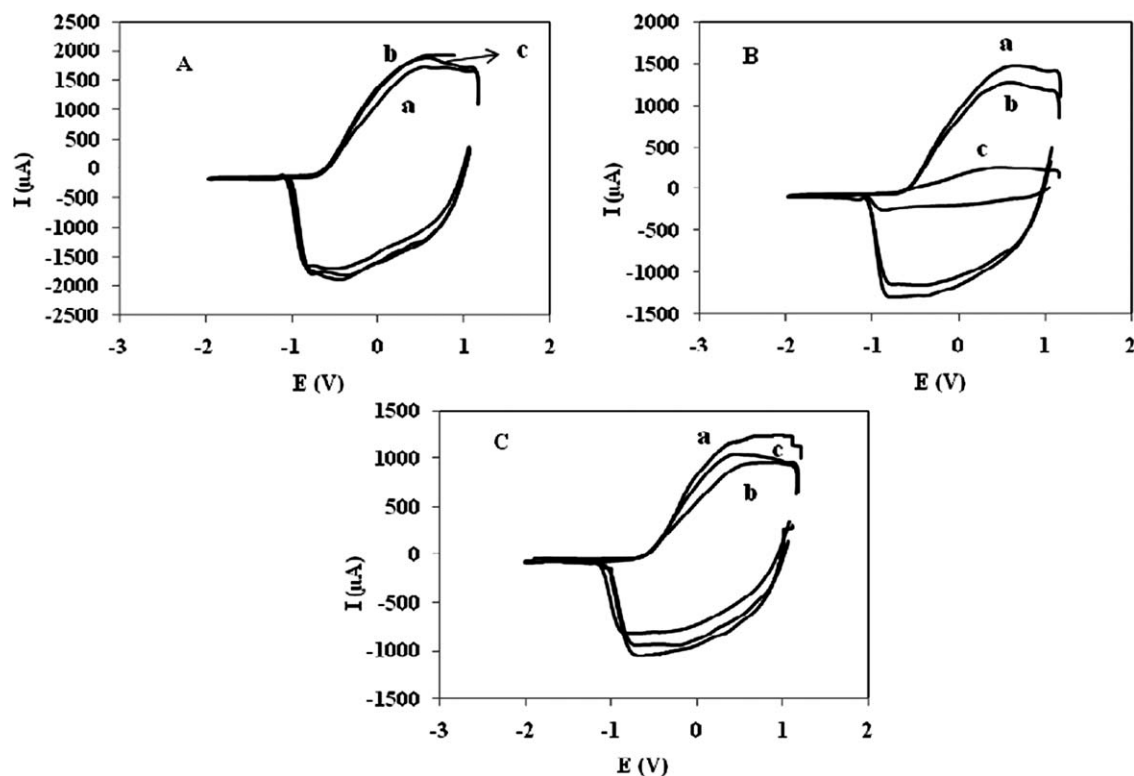


Figure 4 Influence of potential replacement on the redox process of poly (3,4-ethylenedioxythiophene) for three anions: (A) PF_6^- , (B) BF_4^- , (C) ClO_4^- in the potential range: [(a) = -2.0 V, (b) = -1.6 V, (c) = -1.2 V].

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{PEDOT}^+ \cdot \text{X}^-][\text{Li}^+]}{[\text{PEDOT}^0 \cdot \text{X}^- \times \text{Li}^+]}$$

$$= E^0 + \frac{RT}{nF} \ln \frac{[\text{PEDOT}^+ \cdot \text{X}^-]}{[\text{PEDOT}^0 \cdot \text{X}^- \times \text{Li}^+]} + \frac{RT}{nF} \ln [\text{Li}^+] \quad (3)$$

$$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{PEDOT}^+ \cdot \text{X}^- \times \text{Li}^+ \times \text{X}^-]}{[\text{PEDOT}^0 \cdot \text{X}^- \times \text{Li}^+][\text{X}^-]}$$

$$= E^0 + \frac{RT}{nF} \ln \frac{[\text{PEDOT}^+ \cdot \text{X}^- \times \text{Li}^+ \times \text{X}^-]}{[\text{PEDOT}^0 \cdot \text{X}^- \times \text{Li}^+]} - \frac{RT}{nF} \ln [\text{X}^-] \quad (4)$$

These equations describe the evolution of the redox potential as a function of the electrolyte con-

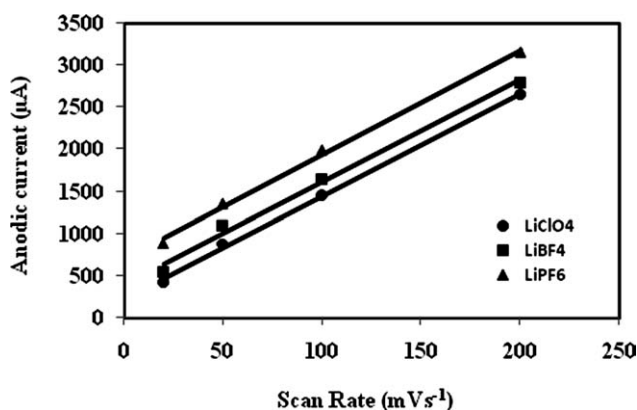


Figure 5 Effect of scan rate on the level of doping for PEDOT films in various electrolytes (0.1M in AN).

centrations. If cationic interchange prevails, the redox potential versus the electrolyte concentration plots will exhibit a semi-logarithmic increase in the potential with the electrolyte concentration. On the contrary, a negative slope is expected when the interchange of BF_4^- , ClO_4^- , and PF_6^- anions prevails. To describe a process kinetically, the Butler-Volmer equation is more appropriate for the anodic branch of the voltammograms. In regard to the oxidation part of the general process, $\text{R} \leftrightarrow \text{O} + n\text{e}^-$, the Butler-Volmer equation can be expressed by:

$$E = E^0 + \frac{1}{(1-\alpha)n_s f} \ln \frac{i_a}{nFAk^0} - \frac{1}{(1-\alpha)n_s f} \ln C_R^* \quad (5)$$

where, E^0 , α , k^0 , n_s , and C_R^* are the standard potential, the transfer coefficient, the standard rate constant, the n value of the rate-determining step, and

TABLE II
Current Increment Values During the Doping Process of PEDOT Formed on GC Electrode at Different Scan Rates

Electrolyte	20 mV s^{-1}	50 mV s^{-1}	100 mV s^{-1}	200 mV s^{-1}
	I (μA)	I (μA)	I (μA)	I (μA)
LiClO_4	421	875	1450	2650
LiBF_4	546	1096	1560	2800
LiPF_6	879	1350	1987	3150

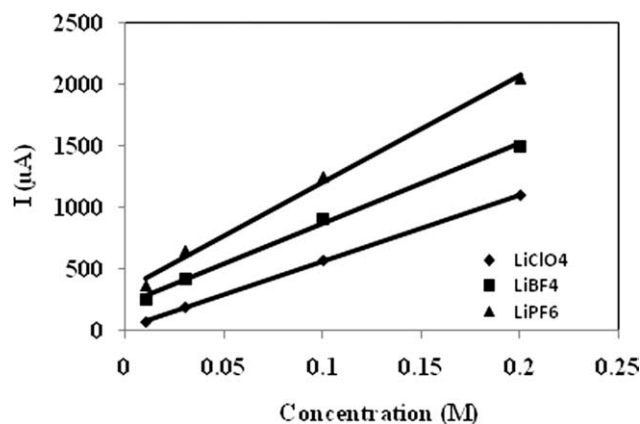


Figure 6 Effect of the electrolyte concentration on the level of doping for PEDOT films in various electrolytes.

the reactive compounds concentration inside the polymer and the anions are interchanged in the redox process. Equation (5) can be rearranged according to the following form:

$$E = E^{0'} \frac{1}{(1-\alpha)n_s f} \ln \frac{i_a}{nFAk^0} - \frac{1}{(1-\alpha)n_s f} \ln[\text{PEDOT}^0 \cdot X^- \times \text{Li}^+] - \frac{1}{(1-\alpha)n_s f} \ln[X^-] \quad (6)$$

Hence, we can postulate that after cycling in LiX, Li^+ cations will be stabilized inside the reduced PEDOT polymers probably forming ion pairs and balancing the $X^- = \text{BF}_4^-, \text{ClO}_4^-, \text{PF}_6^-$ negative charge. However, when the polymer is oxidized, they will remain inside the oxidized polymer as stable pairs with the interchange of X^- prevailing to maintain the charge balance during the redox process. Obviously, the potential value (E) is proportional to $\ln[X^-]$. It means that by increasing electrolyte concentration (X^- anion), the potential value (E) will decrease. To prove which ion will be doped into the polymer, the solutions having 0.01, 0.03, 0.1, and 0.2M of lithium salts in acetonitrile were prepared and voltammetric tests during the fifth cycles performed. Then, the values of potential were obtained where the anodic current was maximum. The result of our analysis is reported in Table III. From these

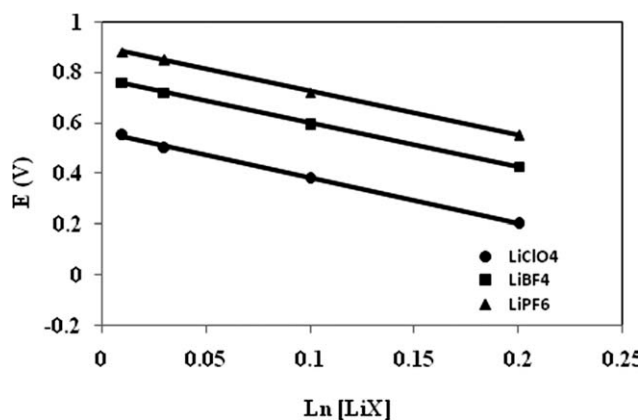


Figure 7 Values of the oxidation peak potentials as a function of the electrolyte concentration.

data, the linear plots of potential versus $\ln[\text{LiX}]$ were produced. Clearly, a negative slope means that the potential will be decreased by increasing the lithium salts concentration. According to this observation and eq. (6), it was implied that the X^- anions are the main intervened species during the polymer oxidation (see Fig. 7).

Spectroscopic characterization of the films

Typical FTIR spectra of the PEDOT films produced in LiPF_6 were depicted in Figure 8. The characteristic peaks vibration of the C—S bond in the thiophene ring can be seen at 940 and 843 cm^{-1} . Vibrations at 1513, 1414, and 1356 cm^{-1} were attributed to the stretching modes of C=C and C—C in the thiophene ring of PEDOT. The bands at 1144 and 1057 cm^{-1} were seen and assigned to the stretching modes of the ethylenedioxy group. Also, the band around 920 cm^{-1} was due to the ethylenedioxy ring deformation mode. However, the vibration peaks at 850, 761, and 624 cm^{-1} were related to the FTIR spectra of the PEDOT doped films with $\text{PF}_6^-, \text{BF}_4^-,$ and ClO_4^- anions, respectively.

Morphological characterization of the produced films

After electropolymerization, the modified electrodes were washed with acetonitrile and then characterized by SEM. Figure 9 shows SEM images of the films produced in different supporting electrolytes.

TABLE III
Values of the Anodic Peak Current and Potential at Different Concentrations

Electrolyte	0.01M		0.03M		0.1M		0.2M	
	I (μA)	E (V)	I (μA)	E (V)	I (μA)	E (V)	I (μA)	E (V)
LiClO_4	0.0660	0.55	0.1668	0.51	0.1987	0.38	1.053	0.21
LiBF_4	0.1081	0.76	0.6887	0.72	0.9357	0.59	1.212	0.428
LiPF_6	0.1007	0.882	0.1265	0.85	0.1672	0.72	2.076	0.55

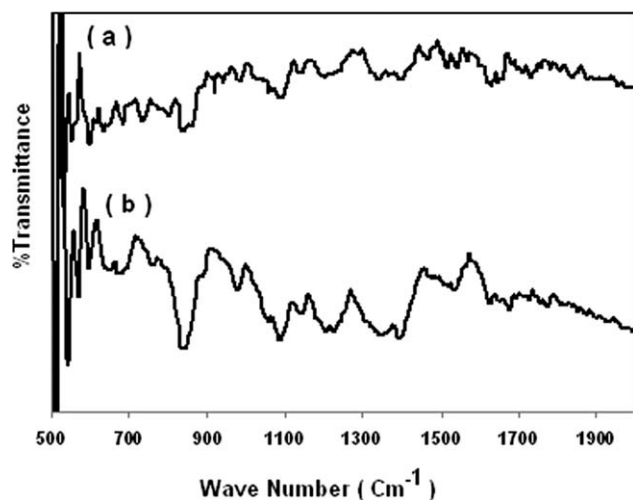


Figure 8 FTIR spectra: transmittance (%) versus wave number (cm^{-1}) for PEDOT films: (a) undoped and (b) doped with PF_6^- .

Figure 10 shows the scanning electron micrograph of the doped PEDOT films. During doping of the films, the inclusion of anions on the matrix is to be expected. The uniform bright portion in the pictures shows the homogeneity of doping. This result seems to agree with the electrochemical behavior of the films. Since a more porous structure with a higher superficial area could promote the ions exchange between the film and the electrolyte during the film growth, the doping of PEDOT/ PF_6^- polymeric film was more feasible than the other doping agents.

CONCLUSIONS

The EDOT electropolymerization process presents different features dependent on the electrolyte used. The beginning of the EDOT oxidation occurs at

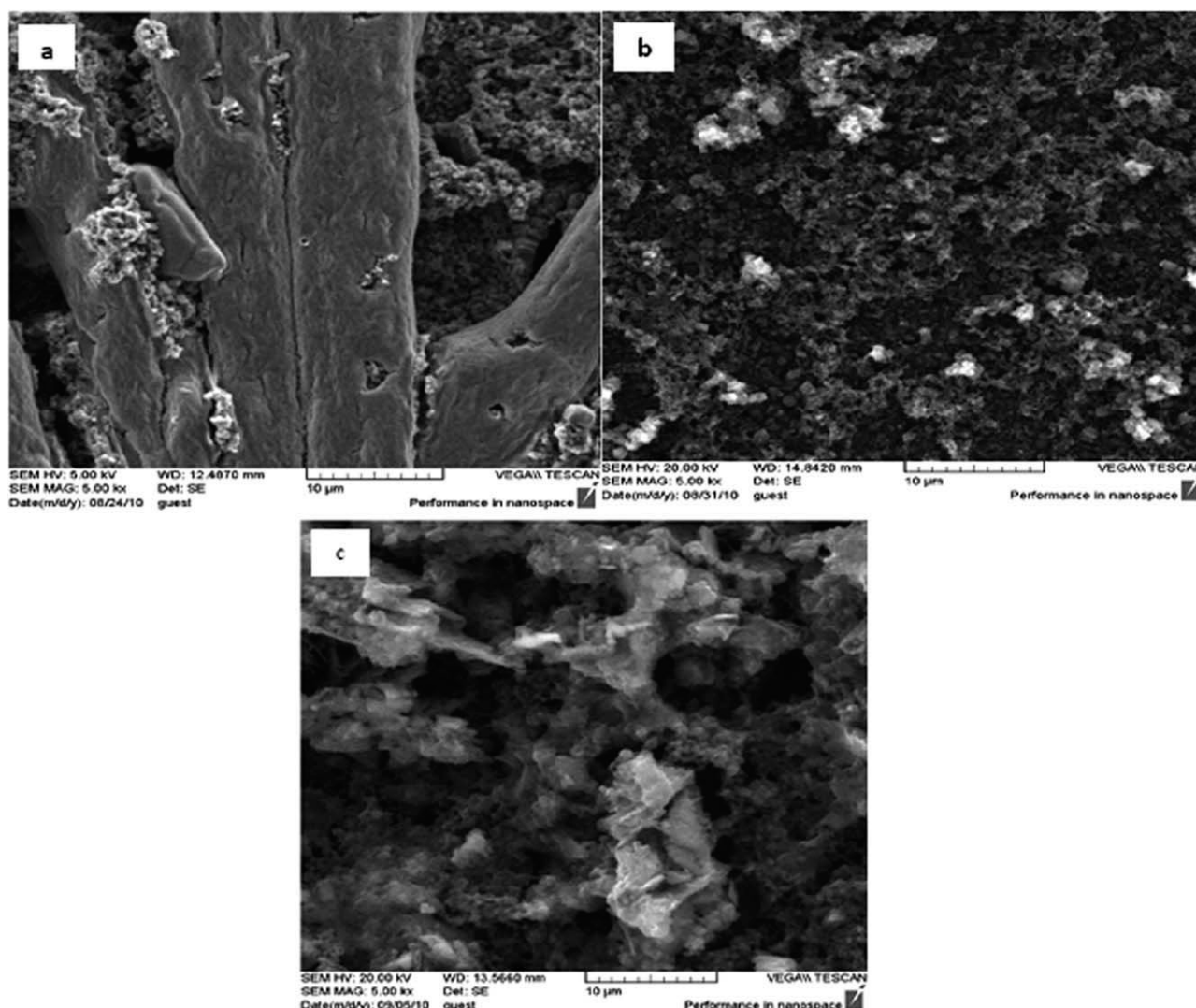


Figure 9 Scanning electron micrographs of the PEDOT films produced on GC electrode in a solution of 50 mM EDOT + 0.1M of (a) LiClO_4 (b) LiBF_4 (c) $\text{LiPF}_6 + \text{AN}$, $v = 120 \text{ mV s}^{-1}$, with 120 cycles.

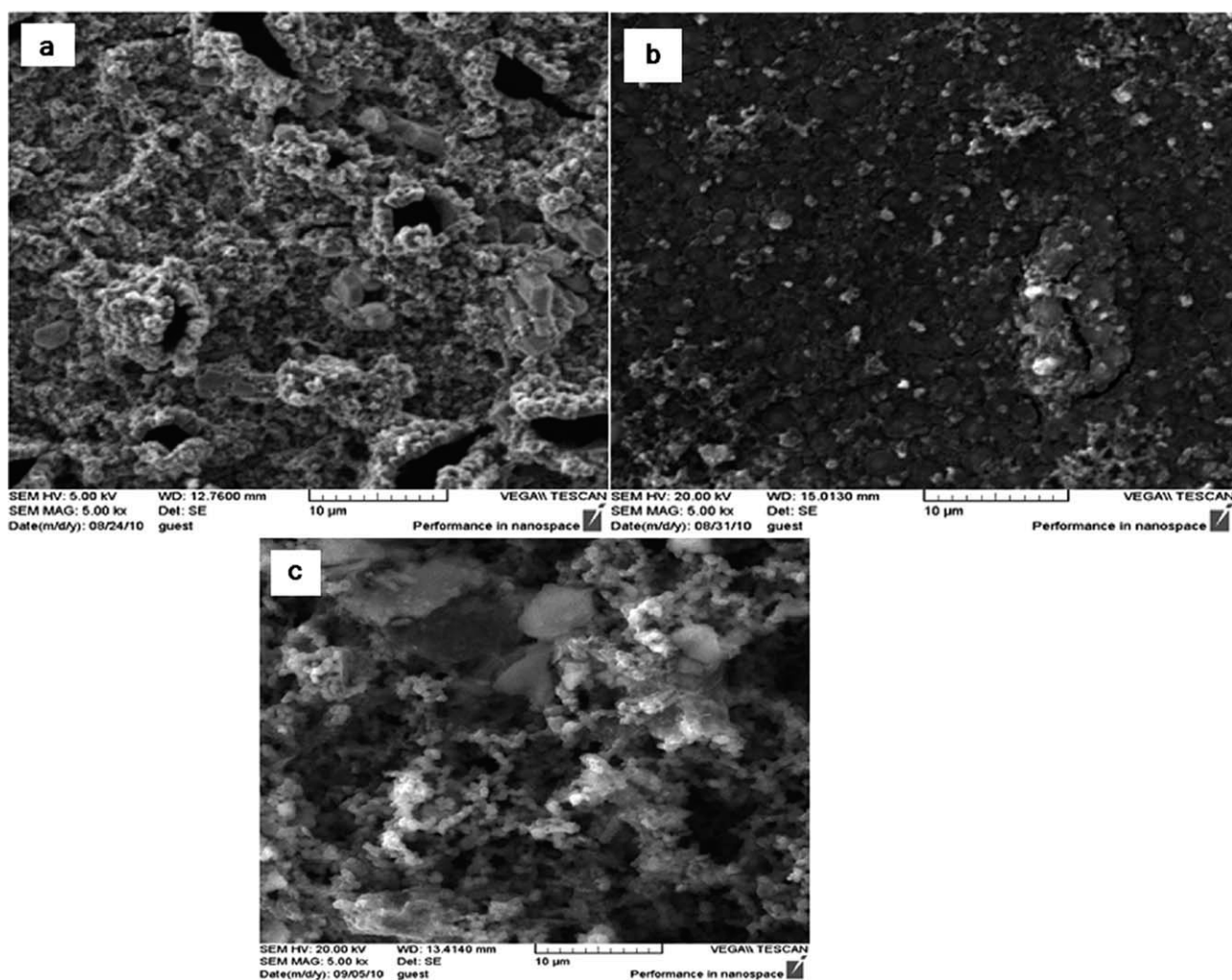


Figure 10 Scanning electronic micrographs of the produced PEDOT films after five cycling in solution of 0.1M of (a) LiClO_4 (b) LiBF_4 (c) $\text{LiPF}_6 + \text{AN}$ (without monomer), $v = 50 \text{ mV s}^{-1}$; initial polarization at $E = -0.85 \text{ V}$.

1.26 V in the presence of the three electrolytes. The oxidation of the polymer occurs at more anodic potential values according to the following order: $E(\text{LiClO}_4) < E(\text{LiBF}_4) < E(\text{LiPF}_6)$. Higher electropolymerization efficiency was obtained in LiPF_6 . The electrochemical characterization of the films formed in the three electrolytes revealed good irreversibility of the redox process of the films. The Nernst and Butler–Volmer equations indicated that anions PF_6^- , BF_4^- , and ClO_4^- were the main mobile species during the redox process. The doping–dedoping reaction consisted of a reversible exchange of anions, and cation exchange seemed to be absent in this case. This study highlights that the morphological and structural properties of PEDOT films can be controlled by the selection of the supporting electrolyte and the electrodeposition condition. These parameters could be used to improve the conductivity of the PEDOT films deposited on the GC electrode. A better crystallinity was obtained when PEDOT electrodeposited on GC surface in LiPF_6 electrolyte.

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