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Electrosynthesis and Characterisation of Poly(3,4-Ethylenedioxythiophene) Films Incorporating Ferrocene

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Abstract

Poly(3,4-ethylenedioxythiophene) (PEDOT) films were potentiostatically and potentiodynamically prepared on Pt electrodes from acetonitrile monomer solutions containing $TBAPF_6$ or $FcPF_6$ (or both). The polymer modified electrodes obtained with different growth charges were characterized electrochemically by cyclic voltammetry in a monomer free solution. The results point to the effective immobilization of the ferrocenium ion inside the PEDOT matrix by entrapment during the polymer synthesis in potentiostatic mode. It is discussed the influence of the presence of the organometallic cation in the polymerization solution in the growth process and the efectiveness of the incorporation of the metallocene is analysed on the basis of the electrochemical data collected for the films redox conversion.

Keywords: conducting polymers, ferrocene, immobilization.

Introduction

Metallocenes are characterised for exhibiting properties that allow their use as catalysts (e.g., reduction of ketones, olefins polymerization) in homogeneous [1] and heterogeneous [2] conditions, justifying the intense investigation in view of their potential applications in many areas such as electrocatalysis [3] and biosensors [4].

The immobilisation of such metallocomplexes in a suitable solid support presents as major advantages the fact of not having restrictions on the solubility of the catalyst, its low losses and facile separation from reaction products [5].

From the most noteworthy materials used for the metallic centre incorporation we can distinguish inert matrices such as silica [2] or polymeric resins [6], and electroactive supports such as electronically conducting polymers (ECPs) [7-13], being the latter route the approach followed in the present work. Compared with

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other host supports for the catalytic centres, the electrochemically prepared ECPs exhibit several advantageous characteristics such as the control of the film thickness and morphology [14] by the electrochemical mode [15-18] and conditions employed in the polymerization [19-21], the direct formation of the polymer in the conducting state onto a variety of substrates [22-25] and the possibility to modulate the redox state of the catalyst by electrical conditioning [5, 7, 26]. Moreover, being a porous material, does not restrict the catalytic activity to the film surface, allowing the access of reactants to the organometallic centres immobilized in the interior of the polymer as well as the withdraw of the reaction products to the bathing solution [26, 27].

The more effective methodology to immobilize catalytic centres inside conducting polymers consists in the electropolymerization of specially prepared funcionalized monomers [7, 27]. However, this approach presents some drawbacks being the organic synthesis of the tailored monomers not the less important one. Also, a derivatized monomer usually displays electrochemical properties significantly different from those of the parent pristine monomer [28] rendering often very difficult or even impossible the electroformation of a polymer with significant conductivity [29, 30]. In this work it was adopted a simpler methodology relying with the incorporation of the organometallic complex during the electropolymerization of a conventional monomer. However, for this immobilization process, there is a few literature available [3] and the electrochemical response of the metallocene in the modified polymer has not been reported so far.

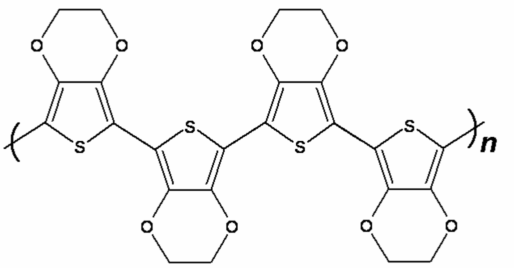


Figure 1. Polymeric structure of the PEDOT polymer [8].

Poly(3,4-ethylenedioxythiophene) (PEDOT), having the backbone structure illustrated in Fig. 1, was the conducting polymer used in the present study in light of its several advantageous properties as compared to other polythiophene derivatives: it combines a low oxidation potential and moderate bandgap with good stability in the oxidized state, in addition to a high conductivity (> 300 S cm^{-1}) [31, 32]. Furthermore, both the PEDOT polymer and the metallocene used in this work (ferrocene), exhibit electrochemical response in the same potential window, allowing the modulation of the catalytic center properties [7].

In this work, we assess the benefit of the important feature of the incorporation of the supporting electrolyte ions into the polymer film during its formation, being the electrochemical properties of the polymer affected by the nature of the electrolyte employed, namely by the ferrocenium ions.

Experimental

Chemicals and apparatus

The monomer 3,4-ethylenedioxythiophene (EDOT – Sigma-Aldrich) was vacuum distilled before use. The HPLC grade acetonitrile (ACN – Aldrich 99,93 %) was firstly dried during 2 days with CaH_2 before being distilled under N_2 in the presence of P_2O_5. The electrolytes tetrabutylammonium hexafluorophosphate ($TBAPF_6$ – Fluka, purity ≥ 99%) and ferrocenium hexafluorophosphate ($FcPF_6$ – Sigma-Aldrich) were used as received. A standard Potentiostat/Galvonostat/ Voltage Scan Generator - Wenking PGS81R Model combined with a XYt Recorder Omnigraphic 2000 Houston Instrument and a conventional two-compartment three-electrode cell were used for the electrochemical measurements. A specpure platinum disk electrode (apparent area 0.1772 cm^2) was used as working electrode. The Pt electrode was hand polished until a mirror-like finishing, in aqueous suspension of successively finer grades of alumina down to 0.3 μm. A Pt foil (1 cm^2) and a saturated calomel electrode (SCE) were employed as counter electrode and reference electrode, respectively. All potential values in this work are reported versus SCE. The electrolyte solutions were deoxygenated directly in the cell with a stream of nitrogen (purity > 99.99997%) for at least 20 min prior to each experiment. All the experiments were performed at room temperature.

Electrode modification

Polymer films were obtained from ACN solutions containing 0.02 mol dm^{-3} of the monomer (EDOT) + 0.1 mol dm^{-3} $TBAPF_6$ or 0.02 mol dm^{-3} $FcPF_6$ or a mixture of both electrolytes. The films were grown potentiodynamically at ν = 0.1 V s^{-1} in the potential range of [-0.83;+1.25] V and potentiostatically at E_g = 1.25 V with different growth charges.

After electrodeposition, the films were thoroughly rinsed with ACN and dried with N_2 for further use. All the modified electrodes were held, for 10 minutes, at -0.83 V in a monomer-free solution (0.1 mol dm^{-3} $TBAPF_6$ in ACN), to assure the films complete discharge (polymer in its reduce state), before their characterization by cyclic voltammetry in the potential range of [-0.83;+0.83] V at ν = 0.05 V s^{-1}.

Results and discussions

The typical electrochemical response of a bare and PEDOT modified Pt electrode in $TBAPF_6$ + $FcPF_6$ in ACN is depicted in Fig. 2. On the Pt electrode the ferrocene electrochemical conversion takes place with a small peak separation ($E_a \approx 0.42$ V; $E_c \approx 0.32$ V), while an increase of the irreversible character of the redox process is observed when the reactions occur over a thin PEDOT film ($E_a \approx 0.71$ V; $E_c \approx -0.13$V). It is worth mentioning that the redox response of the PEDOT film in $TBAPF_6$/ACN was recorded before and after the voltametric run displayed in Fig. 2, and no modifications were detected in the voltammograms. This fact indicates that the organometallic centres were not incorporated in the film during the PEDOT electrochemical conversion in a Fc^+ containing medium, and that the presence of ferrocene in the bathing solution does not degraded the polymer. The typical electrochemical response of the polymer is not apparent in Fig. 2 (dashed line) due to the low currents involved in the film conversion (very thin film) compared with those resulting from the ferrocene oxidation and reduction.

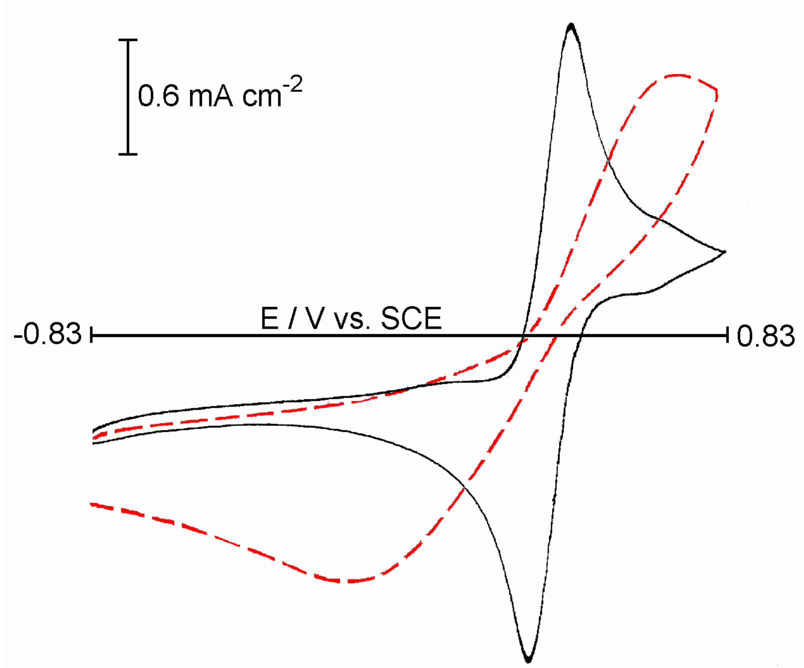
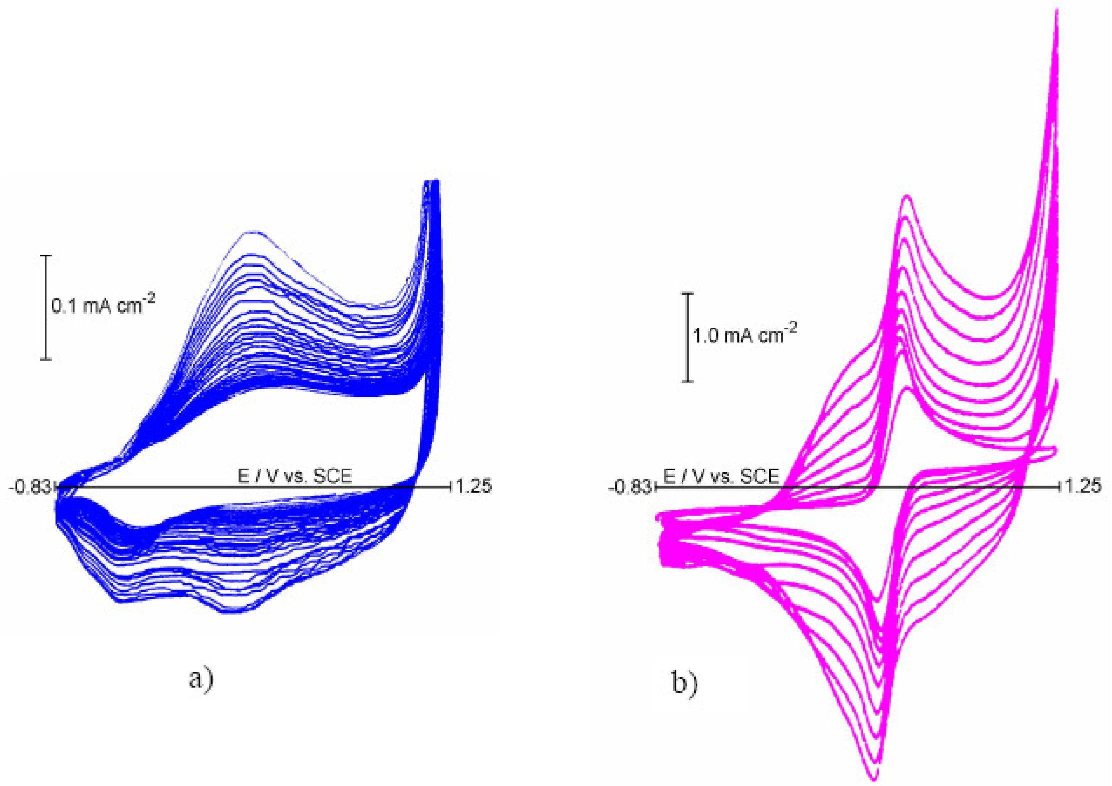


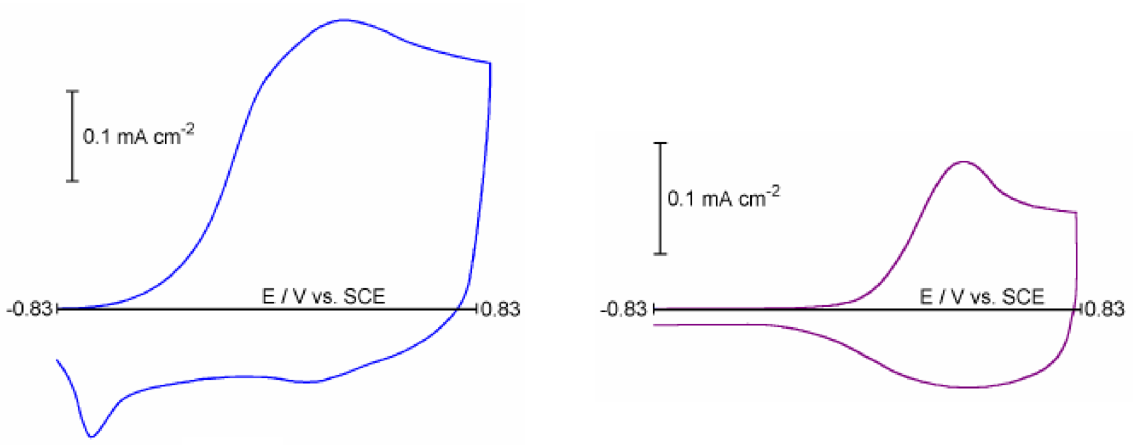
Figure 2. Cyclic voltammograms of the redox response in 0.1 mol dm^{-3} TBAPF$_6$ with 0.02 mol dm^{-3} FcPF$_6$ in ACN solution, at ν = 0.05 V s^{-1}. (—) bare Pt; and (- - -) PEDOT potentiodynamically prepared.

PEDOT films were potentiodynamically prepared on Pt electrodes from organic solutions of 0.02 mol dm^{-3} EDOT and 0.1 mol dm^{-3} TBAPF$_6$, with and without the presence of ferrocenium ions (0.02 mol dm^{-3} FcPF$_6$), being representative cyclic voltammograms shown in Fig. 3. The continuous increase of the current with the cycle number in both synthesis solutions reveals the formation and expansion of a conducting phase at the electrode surface. During the PEDOT growth in the Fc$^+$ free solution, it is observed the development of an anodic peak at $E_a \approx 0.23$ V and two cathodic waves at $E_{c1} \approx 0.14$ V and $E_{c2} \approx -0.44$ V in agreement with the expected behaviour for PEDOT films electrodeposited by this method in the presence of TBAPF$_6$ [20, 33]. For the polymer grown in the presence of the organometallic complex, in addition to the redox process of the ferrocene, it is worth noting the polymer formation and oxidation by the development of an anodic wave starting at potentials just before that of the Fc anodic process. Also in the cathodic scans it is clearly observed the progressive contribution of the current of the polymer reduction which is added to that of the Fc$^+$ reduction. Therefore, it was possible to confirm that both PEDOT and ferrocene are electroactive in the same range of potentials and that the presence of the metallocene does not hinder the polymer growth and conversion.



a) b)

Figure 3. Cyclic voltammograms, at ν = 0.1 V s^{-1}, of PEDOT growth from solutions consisting of: a) 0.02 mol dm^{-3} EDOT and 0.1 mol dm^{-3} $TBAPF_6$ in ACN, during 30 cycles; b) 0.02 mol dm^{-3} of both monomer and metallocene (EDOT and $FcPF_6$, respectively) and 0.1 mol dm^{-3} $TBAPF_6$ in ACN, during 28 cycles.



a) b)

Figure 4. Cyclic voltammograms of the redox response in 0.1 mol dm^{-3} $TBAPF_6$, at ν=0.05 V s^{-1}, of PEDOT films potentiodynamically electropolymerised from solutions consisting of: a) 0.02 mol dm^{-3} EDOT and 0.1 mol dm^{-3} $TBAPF_6$ in ACN, during 30 cycles; b) 0.02 mol dm^{-3} of both monomer and metallocene (EDOT and $FcPF_6$, respectively) and 0.1 mol dm^{-3} TBAPF6 in ACN, during 28 cycles.

The electrosynthesized films were washed with ACN and subsequently discharged by applying a potential of -0.83 V for 10 min in a $TBAPF_6$/ACN solution to assure the egress to the solution of mobile species present within the polymer film and hence to avoid their possible interference during succeeding assays.

Fig. 4 illustrates the representative electrochemical characterisation of both modified Pt electrodes by cyclic voltammetry in monomer free solution. It is clear from the figure that polymers electrodeposited under a potentiodynamic regime reveal differentiated electroactivities according to the electrolyte used in the polymer growth, being the film redox conversion affected by the presence of the $FcPF_6$ in the synthesis solution. The higher oxidation peak potential recorded for the film obtained in the presence of ferrocenium ions (Fig. 4b) may indicate a shorter conjugation length of the polymeric segments indicating that the metallocomplex may disturb the regular growth of the polymer backbone. On the other hand, the higher reversibility (evaluated through the ratio Q_{ox}/Q_{red}) found for this polymer (Q_{ox}/Q_{red} = 1.2 and Q_{ox}/Q_{red} = 2.7 for the films grown in the presence and absence of Fc^+, respectively) suggests a more open structure caused by the presence of the metallocene in the synthesis solution, allowing an easier movement of electrolyte species (namely doping ions) into and out of the polymer. This feature is reinforced by the absence of the cathodic peak at high negative potentials (common to every film prepared in the presence of ferrocenium) which is usually ascribed to the reduction of the denser (inner) layer of the polymer [10]. Nevertheless, there is no evidence of the effective entrapment of the metallocene into the polymer by this method.

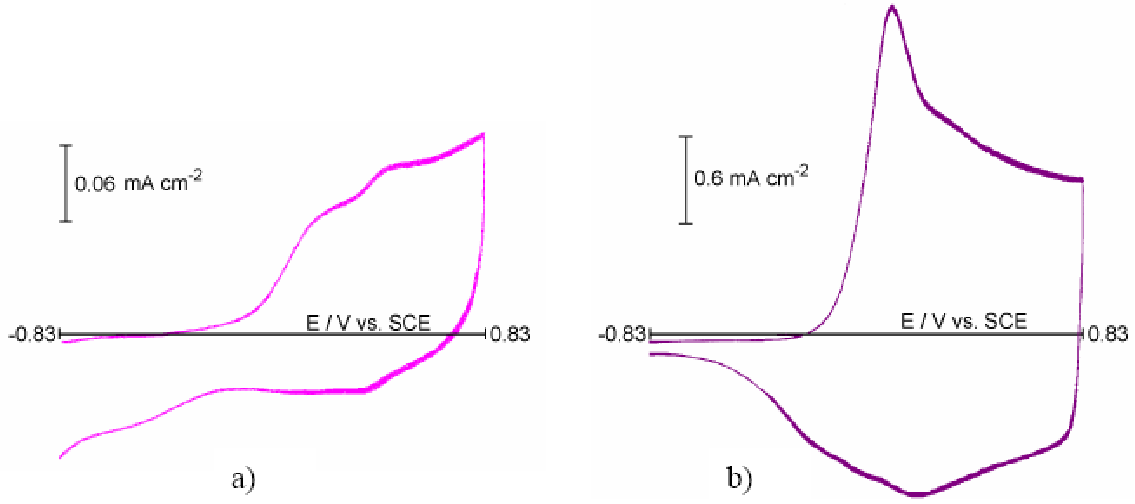


Figure 5. Cyclic voltammograms of the redox response in 0.1 mol dm^{-3} $TBAPF_6$, at ν=0.05 V s^{-1}, of PEDOT+Fc films potentiostatically electropolymerised from solutions consisting of 0.02 mol dm^{-3} of both monomer and metallocene (EDOT and $FcPF_6$, respectively) and 0.1 mol dm^{-3} TBAPF6 in ACN with a) 14 and b) 159 mC cm^{-2} growth charge.

Since, during the potentiodynamic growth of a polymer, the electrolyte species are continuously inserted and expelled in the film every cycle (simultaneously with the polymer oxidation/reduction) the chances of the enclosure of the ferrocenium (that enters the film together with an anion as an ionic pair) are very low. In order to overcame this difficulty and looking for an effective entrapment of the organometallic centre, the film growth in a continuous regime under potentiostatic control was studied.

Polymer films grown potentiostatically at E_g = 1.25 V with different growth charges (0.014 C m^{-2} < Q_g < 0.159 C cm^{-2}) from organic monomer solutions containing both $TBAPF_6$ and $FcPF_6$ were obtained, being their redox behaviour in $TBAPF_6$/ACN illustrated in Fig. 5 for the thinner and thicker films. While, for very thin films (Fig. 5a), the ferrocene conversion is clearly visible ($E_a \approx 0.44$ V; $E_c \approx 0.38$ V), for the thicker ones these feature is masked by the PEDOT electrochemical conversion and only an anodic shoulder is depicted at potentials slightly positive than that of the polymer oxidation peak – Fig. 5b. Despite the low amount of the metallocene in the film, these voltammograms are reproducible even after several film discharge processes which demonstrates the effectiveness of ferrocenium immobilization in the polymer by this method.

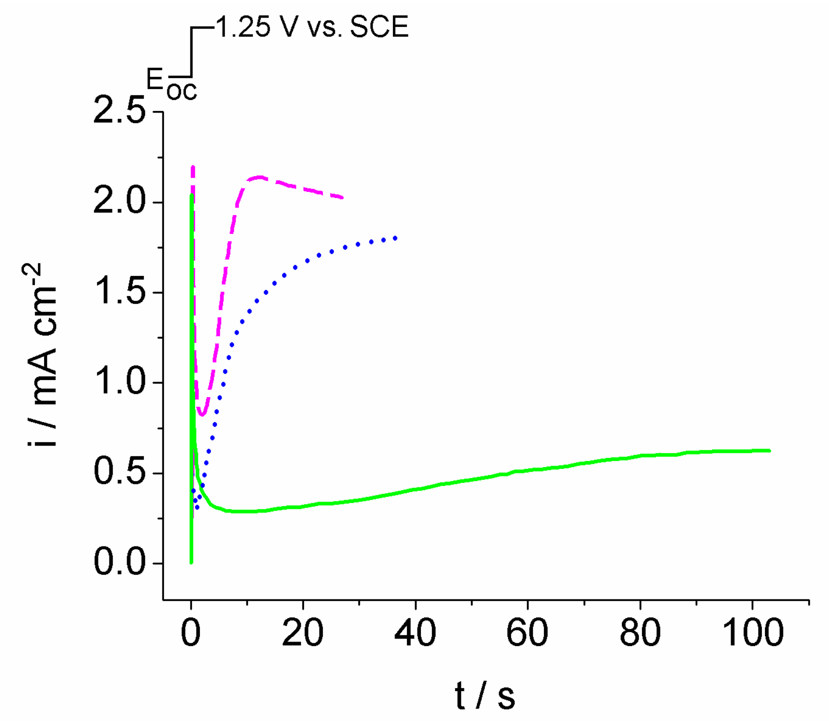


Figure 6. Current transients of the electropolymerization from solutions containing: (••••••) 0.02 mol dm^{-3} EDOT and 0.1 mol dm^{-3} $TBAPF_6$ in ACN; (- - -) 0.02 mol dm^{-3} both monomer and metallocene (EDOT and $FcPF_6$, respectively) and 0.1 mol dm^{-3} $TBAPF_6$ in ACN; (——) 0.02 mol dm^{-3} EDOT and 0.02 mol dm^{-3} $FcPF_6$. Eg = 1.25 V; Q_g = 0.05 C cm^{-2}.

Since the potentiostatic mode has given promising results, the potentiostatic growth of polymer films from monomer organic solutions containing only $FcPF_6$ as supporting electrolyte was also carried out aiming a higher amount of organometallic centre entrapped with respect to the polymer. Fig. 6 shows a representative set of current transients recorded during the synthesis of polymer films (with the same growth charge, Q_g = 50 mC cm^{-2}) in ACN/monomer solutions containing 0.02 mol dm^{-3} $FcPF_6$ (full line), 0.02 mol dm^{-3} $FcPF_6$ + 0.1

mol dm^{-3} TBAPF$_6$ (dashed line) and 0.1 mol dm^{-3} TBAPF$_6$ (dotted line) as supporting electrolytes. It is noteworthy that the polymer electropolymerised just in presence of the FcPF$_6$ requires more growing time to attain the aforesaid Q$_g$, in consequence of the low concentration of electrolyte used in this experiment.

The three types of polymer modified electrodes obtained with the same charge at this electrosynthesis regime were characterized electrochemically by cyclic voltammetry in a monomer free solution (ACN/TBAPF$_6$), being the redox responses depicted in Fig. 7. Despite the lower electroactivity, the occurrence of two anodic processes at potentials very close to each other of the films prepared in the presence of the ferrocenium must be stressed. The first of the two anodic waves would correspond to the polymer matrix anodic conversion while the second one can be assigned to the ferrocene oxidation. Under continuous cycling in this solution (of the film corresponding to the full line in Fig. 7) there is a small current increase and better definition of the wave corresponding to the polymer oxidation but that of the metallocene oxidation remains unchangeable, confirming that it corresponds to a process independent of the polymer matrix transformation. So, the results point to the effective immobilization of the ferrocenium ion inside the PEDOT matrix, by entrapment during the polymer synthesis. Working is currently in progress to elucidate how the polymer structure is affected by the incorporation of the metallocene.

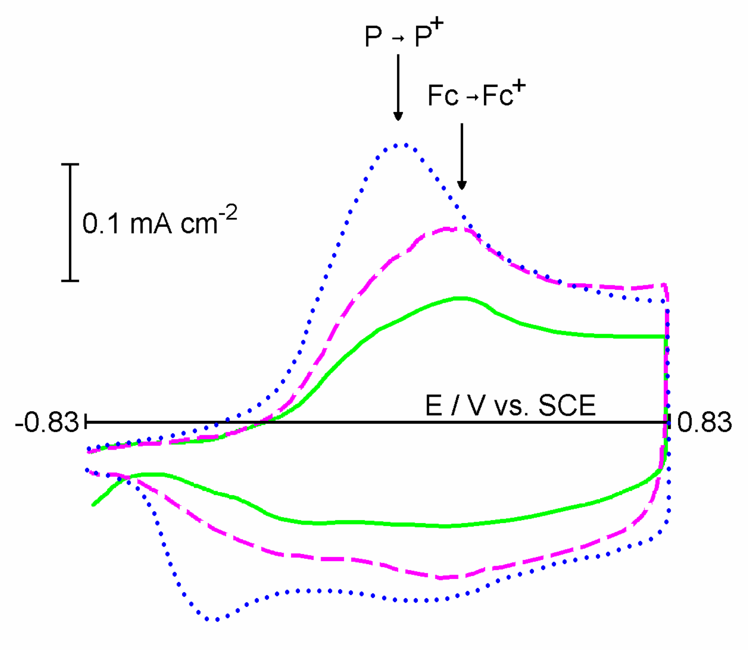


Figure 7. Cyclic voltammograms of the redox response in 0.1 mol dm^{-3} TBAPF$_6$, at ν=0.05 V s^{-1}, of films potentiostatically electropolymerised from solutions consisting of: (••••••) 0.02 mol dm^{-3} EDOT and 0.1 mol dm^{-3} TBAPF$_6$ in ACN; (- - -) 0.02 mol dm^{-3} both monomer and metallocene (EDOT and FcPF$_6$, respectively) and 0.1 mol dm^{-3} TBAPF$_6$ in ACN; (——) 0.02 mol dm^{-3} EDOT and 0.02 mol dm^{-3} FcPF$_6$.

Conclusions

The present work allowed concluding that the ferrocene moiety can be effectively immobilized inside a PEDOT by entrapment during the potentiostatic electropolymerisation of EDOT from solutions containing the ferrocenium ion in the presence or absence of another supporting electrolyte. This procedure permits the development of new metallocene containing polymer based modified electrodes, whose polymeric matrix and organometallic centre exhibit electroactivity in the same range of potentials.

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