ELECTROCHEMICAL BEHAVIOR OF POLY(3,4-ETHYLENEDIOXY)-THIOPHENE DOPED WITH HEXACYANOFERRATE ANIONS IN DIFFERENT ELECTROLYTE MEDIA

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Dedicated to the memory of Professor Jaroslav Heyrovský on the occasion of the 50th anniversary of the Nobel Prize for polarography.

This paper describes in detail the electrochemical properties of potentiodynamically synthesized poly(3,4-ethylenedioxy)thiophene (PEDOTh) modified by the entrapment of hexacyanoferrate anions ($Fe(CN)_6^{3-}$). Cyclic voltammetric data clearly shows that during polymer redox conversion/immobilized anion reduction and re-oxidation, charge compensation occurs at the expenses of the insertion–deinsertion of appropriate cations from solution. In aqueous electrolyte mainly protons are involved whereas in organic media the process requires small highly mobile ions such as lithium. PEDOTh/Pt and PEDOTh/$Fe(CN)_6^{3-}$/Pt have been used for the detection of ascorbic acid (AA) in mixed medium (0.1 M $TBAPF_6$ in acetonitrile + 8% H_2O). Compared to that of bare platinum electrode, the analyte oxidation peak potential occurs at significant less positive values at both modified electrodes, revealing their good electrocatalytic activity. For the polymer incorporating ferricyanide ion, the observed decrease in the AA oxidation onset potential along with the fading away of $Fe(CN)_6^{3-}$ reduction signal, supports a mechanism taking into account the mediator character of the embedded anion.

Keywords: Polymer film modified electrodes; Poly(3,4-ethylenedioxy)thiophene; Polythiophenes; Hexacyanoferrate anions; Mixed electrolyte solution; Ascorbic acid; Voltammetry; Electrochemistry.

Aiming to build up new functional materials, conducting polymer film coated electrodes have been widely used to incorporate large inorganic anions[1]. As a result of electrostatic interaction between these species and the positively charged polymer chains, the insertion–deinsertion of anions involved in the redox conversion of conventional conducting polymers is

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suppressed and thus the immobile anions induce new properties to the modified electrode[1,2].

In the field of electrochemical sensors, recent reported work focusing the suitability of conducting polymer based electrodes for the voltammetric analysis of neurotransmitters, devotes specific notice to the identification and detection of ascorbic acid (AA) in real samples[3]. The performance of polyaniline (PAni), polypyrrole (PPy), polythiophene (PTh) and their derivatives is well documented[4] as well as the behavior of other polymers such as poly(5-carboxylic acid indole), poly-*p*-phenylene and poly(4-allyl-2-metoxyfenol)[3a]. The role of negatively charged functionalities attached to the polymeric layer, e.g. the electrochemically active hexacyanoferrate anions ($Fe(CN)_6^{3-}$), in the enhancement of the electrocatalytic activity towards the ascorbic acid oxidation, has also been discussed with particular emphasis in PPy based systems[3b,4b,5].

Due to its high conductivity and stability, poly(3,4-ethylenedioxy)thiophene (PEDOTh) has revealed as a strong candidate for the construction of sensing devices. Recently it has been used for the determination of uric acid in the presence of excess of AA [6] and the simultaneous detection of dopamine and AA [4d,7] employing PEDOTh film coated electrodes. To the best of our knowledge, there are just few studies[8] concerning the attachment of ferricyanide to PEDOTh, being the anion incorporated during the polymer potentiostatic or potentiodynamic electrosynthesis. The authors claim that the embedded $Fe(CN)_6^{3-}$ acts as a redox mediator for the oxidation of AA [8b]. However, data elucidating the behavior of pristine PEDOTh under similar conditions are missing and thus no complete explanation of the electrocatalytic activity of the modified electrode can be retrieved.

The pathways describing the oxidation of AA depend on the nature of the electrolyte solution. In aqueous electrolytes, ascorbic acid exhibits a two-electron oxidation (two deprotonation steps with pK_a = 4.17 and 11.57)[3a], involving the release of two protons

$$C_6H_8O_6\ (AA) \rightarrow C_6H_6O_6\ (DHA) + 2\ H^+ + 2\ e^- . \qquad (1)$$

The mono deprotonated anion $C_6H_7O_6^-$ (AA^-), the species present in neutral medium, is irreversibly oxidized on Pt, Au or glassy carbon electrodes at potentials higher than 0.300 V vs SCE [4c,8b,9] yielding dehydroascorbic acid (DHA). At pH > 5 DHA is unstable and undergoes irreversible hydrolysis with formation of $C_6H_7O_7$ (ADCG)[10].

The reaction expressed by Eq. (*1*) is not favored in non-aqueous electrolytes. In acetonitrile and propylene carbonate, both reduction and oxida-

tion reactions have been observed[11], suggesting that the reduction of AA originates a radical anion (AA$^{\bullet}$), which is stable enough in organic media to be re-oxidized to AA

$$C_6H_8O_6 + e^- \rightarrow C_6H_8O_6^{\bullet -} (AA^{\bullet}) . \quad (2)$$

To offer new insights into the possible cooperative effect of the polymer film and the incorporated anion towards the detection of ascorbic acid, as well as on the role of the electrolyte nature and composition, this work reports the electrochemical behavior of as-obtained potentiodynamically synthesized PEDOTh and of PEDOTh/$Fe(CN)_6^{3-}$, the later prepared using a post-polymerization approach for the anion incorporation. Cyclic voltammetry has been used to study the electrocatalytic activity of both modified electrodes, in 0–10 mM ascorbic acid containing aqueous, organic and mixed (acetonitrile + 8% H_2O) media, in the presence of different supporting electrolytes.

EXPERIMENTAL

The electrochemical experiments were carried out on a CH Instruments electrochemical analyser, model 600A, controlled by a personal computer. The morphology of the PEDOTh films was analysed by scanning electron microscopy (SEM) performed with a JEOL model JSM-5200 LV using an accelerating voltage of 25 kV.

The monomer 3,4-ethylenedioxythiophene (EDOTh; Aldrich) was distilled under reduced pressure prior to use. The solvent, acetonitrile (ACN; HPLC grade, Aldrich 99.93%), was dried using calcium hydride and distilled with phosphorus pentoxide under N_2 atmosphere. The supporting electrolyte tetrabutylammonium hexafluorophosphate ($TBAPF_6$; Fluka, puriss. ≥ 99%) was recrystallized from ethanol prior to use. Highly pure lithium perchlorate ($LiClO_4$; Riedel-de Haën, p.a. ≥ 99%) was used as received. For the incorporation of the metallic complex, potassium hexacyanoferrate(II) ($K_4[Fe(CN)_6]\cdot 3H_2O$; Merck, p.a.) and potassium chloride (KCl; Panreac, p.a. 99.5%), were used. $K_3[Fe(CN)_6]$ (Merck, p.a), L(+)-ascorbic acid ($C_6H_8O_6$; Riedel-de Haën, p.a. 99.7%), sodium dihydrogen phosphate monohydrate ($NaH_2PO_4\cdot H_2O$; Merck, p.a. 99%) and anhydrous disodium hydrogen phosphate (Na_2HPO_4; Merck, p.a. 99%) were used as received. Ultra-pure Milli-Q water was used for the preparation of some solutions.

A platinum disk (area 0.196 cm^2) sealed with epoxy resin into a Teflon holder was used as a working electrode. A Pt foil and a saturated calomel electrode (SCE) were used as a counter and a reference electrode, respectively. For each experiment, a fresh mirror-finish surface was generated by hand-polishing the working electrode in an aqueous suspension of successively finer grades of alumina (down to 0.05 μm). Prior to the measurements, the solutions were deaerated by bubbling N_2 (high purity, dried) for 20 min.

PEDOTh films were potentiodynamically grown in a conventional three-electrode cell, at a sweep rate v = 100 mV s^{-1} using a solution of 0.05 M EDOTh in 0.1 M $TBAPF_6$ acetonitrile. The potential was cycled between –0.83 and 1.26 V vs SCE. After the electro-

polymerization, the films were washed first with acetonitrile, in order to remove any supporting electrolyte, and then with ultra-pure Milli-Q water. Subsequently, they were transferred to a three compartment electrochemical cell containing a solution of x M $K_4Fe(CN)_6$ (x = 0–0.5) in 0. 1 M KCl, polarized at –0.80 V for 300 s, followed by the incorporation of $Fe(CN)_6^{3-}$ by potentiostatic deposition, applying a potential pulse between –0.80 V and E_f (E_f = 0.3–0.7 V) during 60 s.

The modified electrodes (PEDOTh and PEDOTh/$Fe(CN)_6^{3-}$) were electrochemically characterized at v = 50 mV s^{-1} using a two-compartment cell in different solutions: phosphate buffer solution (pH 7) with and without ascorbic acid, 0.1 M $TBAPF_6$ acetonitrile solution, 0.1 M $TBAPF_6$ acetonitrile with 8% H_2O solution with and without ascorbic acid, 0.1 M $LiClO_4$ acetonitrile solution with and without 8% H_2O.

RESULTS AND DISCUSSION

The cyclic voltammetric characteristics of PEDOTh preparation from 0.05 M EDOTh in 0.1 M $TBAPF_6$ acetonitrile solution are illustrated in Fig. 1. Within [–0.8, +1.26] V vs SCE potential window, the polymer redox conversion, involving PF_6^- entrance and exit for charge compensation, is clearly seen. As SEM images show (Fig. 2), the oxidized film (E = 1.26 V, Fig. 2A) presents a loose morphology, consequence of anion penetration in the layer, whereas after anion diffusion out from the polymer, i.e. the neutral PEDOTh (E = –0.83 V, Fig. 2B) appears compact and granular.

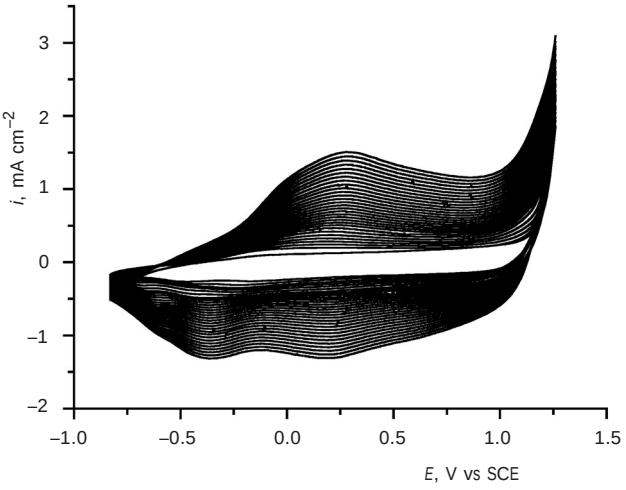

FIG. 1
Cyclic voltammograms collected during the growth of a PEDOTh film prepared on Pt under potentiodynamic control (30 cycles) from 0.05 M EDOTh + 0.1 M $TBAPF_6$ acetonitrile solution; v = 100 mV s^{-1}

After PEDOTh film immersion in the $K_4Fe(CN)_6$ containing solution, the electrode was first kept at a constant negative potential of –0.8 V for 300 s assuring the ejection of hexafluorophosphate ions, and then a potential pulse to values E_f (E_f = 0.3–0.7 V, 60 s) promoting the polymer oxidation has been applied to entrap the $Fe(CN)_6^{3-}$ anions in the PEDOTh matrix. $Fe(CN)_6^{4-}$ got oxidized during the potential pulse. The presence of hexacyanoferrate anions in the polymer has been confirmed by XPS analysis, as reported elsewhere[12]. As pointed out before[8b], the electrostatic interaction between the positively charged film and those anions is the driving force for the incorporation. Moreover, due to their multi-negative charge and large volume[13], $Fe(CN)_6^{3-/4-}$ deinsertion is difficult. Therefore, supporting electrolyte cations play an important role in the overall charge compensation.

Figure 3A shows the voltammetric scan of PEDOTh/$Fe(CN)_6^{3-}$ in aqueous phosphate buffer solution (pH 7). During negative potential scan both the polymer and the entrapped ferricyanide ion undergo reduction, requiring the insertion of cations from solution (protons, potassium and sodium ions) for the charge compensation. Those processes are reversible and thus, during ferrocyanide re-oxidation, ejection of cations must take place. It is worth noticing that the separation of the redox peaks due to the iron complex (E_{red} = –0.130 V, E_{ox} = 0.205 V) is much higher than that observed for $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in solution at naked Pt (E_{red} = 0.125 V, E_{ox} = 0.275 V) (Fig. 3B) which is attributable to anion diffusion control by the polymer film thickness.

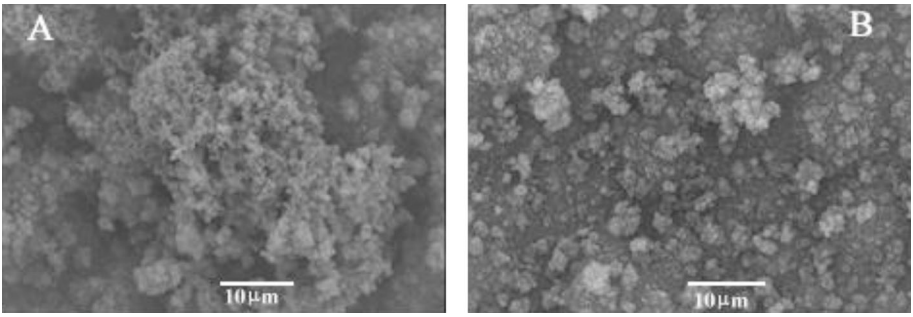

FIG. 2
SEM images of PEDOTh/Pt potentiodynamically prepared from 0.05 M EDOTh + 0.1 M $TBAPF_6$ acetonitrile solution (50 cycles) at v = 100 mV s^{-1}, when the synthesis ceases at 1.26 V (A) and at –0.830 V (B)

Although the irreversible attachment of hexacyanoferrate anions to PEDOTh has been reported[8b], the electrochemical properties of the modified polymer strongly depend on the electrolyte solution nature and on the type of supporting electrolyte cations which must participate in the ionic motion to compensate the excess charge on $Fe(CN)_6^{3-/4-}$ and over the polymer film upon reduction.

In organic media, e.g. 0.1 M $TBAPF_6$ in acetonitrile usual for conducting polymers characterization[14], no redox couple attributable to $Fe(CN)_6^{4-}$/$Fe(CN)_6^{3-}$ conversion is detected in voltammograms of PEDOTh/$Fe(CN)_6^{3-/4-}$ (Fig. 4A). Actually, the only available cations TBA^+ are too large[15] to penetrate in the film, as observed for PPy/$Fe(CN)_6^{3-}$ modified electrodes[16]. Under such conditions, hexacyanoferrate anions are expulsed from the polymer, which electroactivity drastically decreases, even considering that a gradual replacement by PF_6^- from solution may occur. In similar solution but after a small addition of water (8%), the electrochemical behavior of the modified electrodes clearly reveals the compliant role of protons (Fig. 4B). The cyclic voltammograms exhibit a well defined pair of current peaks (–0.305 V/0.115 V), which correspond to hexacyanoferrate reduction/oxidation. It should also be noted that the redox couple potentials are shifted to more negative values and show a better reversibility, when compared with the data recorded in phosphate buffer (Table I). This can be assigned to the easy diffusion of protons in the polymer matrix to accomplish the required charge compensation.

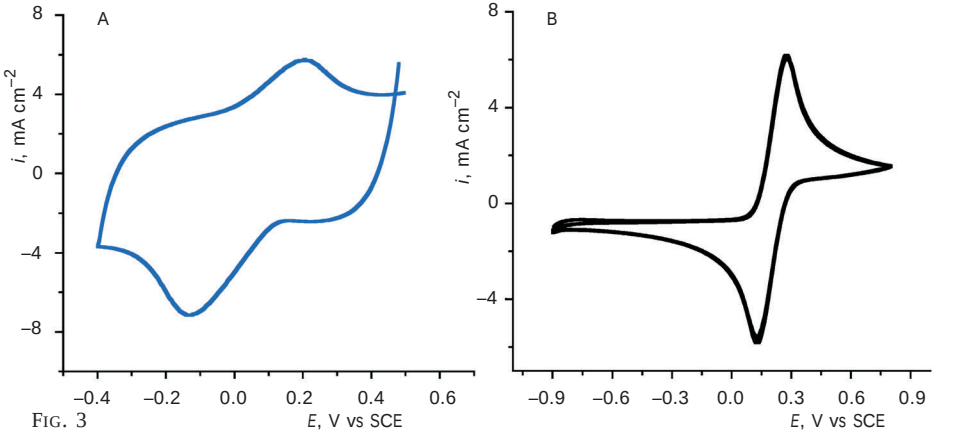

FIG. 3

Cyclic voltammograms of PEDOTh/$Fe(CN)_6^{3-}$ in 0.1 M phosphate buffer (pH 7) (A) and 0.025 M $K_4Fe(CN)_6$ + 0.025 M $K_3Fe(CN)_6$ at bare Pt electrode (B); v = 50 mV s^{-1}. PEDOTh prepared with 60 cycles, $Fe(CN)_6^{3-}$ incorporated at E_f = 0.7 V

A further evidence on the role of supporting electrolyte cations on the electrochemical behavior of PEDOTh/ferricyanide films has been obtained by analysing the voltammetric responses of the modified electrodes in both pure organic and mixed electrolyte solution containing a small cation, $LiClO_4$. The $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple responses can be observed in Fig. 5. When compared to TBA^+, the smaller volume and higher mobility of Li^+ cations[15b,17], convey their participation through the polymer charge compensation even in pure organic medium (Fig. 5A). In the presence of water (Fig. 5B), either protons and solvated Li^+ might be involved in the process and much higher peak currents are observed in comparison with Fig. 4B. Notwithstanding, the potential shift (Table I) observed for the hexacyanoferrate anion conversion suggests some replacement of $Fe(CN)_6^{3-}$ by ClO_4^-, which is also compensated by the insertion of Li^+ and might lead to the formation of ion pairs inside the film[18].

An additional advantage of using the above mentioned mixed medium (acetonitrile + 8% H_2O) is its appropriateness for studying the electrocatalytic activity of the modified electrodes for the determination of different important analytes.

Aiming to explore such properties of PEDOTh/$Fe(CN)_6^{3-}$ electrodes, the preparation conditions to reach the highest anion content in the polymer have been investigated. The effect of polymer film thickness, concentration of the $K_4Fe(CN)_6$ solution and pulse potential height applied to perform the

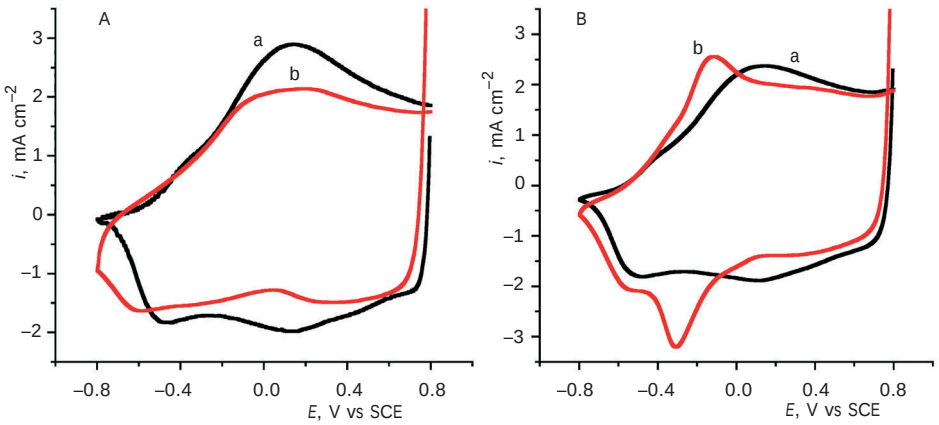

FIG. 4

Cyclic voltammograms of PEDOTh film (a) and PEDOTh/$Fe(CN)_6^{3-}$ (b) in 0.1 M $TBAPF_6$ acetonitrile (A) and in 0.1 M $TBAPF_6$ acetonitrile + 8% H_2O (B); v = 50 mV s^{-1}. PEDOTh prepared with 30 cycles, $Fe(CN)_6^{3-}$ incorporated at E_f = 0.7 V for 60 s

anion incorporation have been analysed via the voltammetric responses (cathodic scans) in 0.1 M $TBAPF_6$ acetonitrile + 8% H_2O (Figs 6–8).

The thickness of the PEDOTh films has no significant influence on the relative amount of entrapped $Fe(CN)_6^{3-}$. Contrasting the data of Fig. 4B (polymer prepared with 30 cycles) to the response collected for PEDOTh synthesized with 60 cycles (see Fig. 6), the increase in charge associated to

TABLE I
Oxidation and reduction peak potentials and ΔE for the redox couple $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ entrapped in PEDOTh in several electrolytes. PEDOTh prepared with 30 cycles, $Fe(CN)_6^{3-}$ incorporated at 0.7 V for 60 s

Supporting electrolyte	Solvent	pH	E_O $Fe(CN)_6^{4-}$ V vs SCE	E_R $Fe(CN)_6^{3-}$ V vs SCE	ΔE, V
Phosphate buffer	H_2O	7.0	0.205	–0.130	0.335
$TBAPF_6$	ACN	3.8	–	–	–
	ACN + 8% H_2O	3.3	–0.115	–0.305	0.190
$LiClO_4$	ACN	1.8	0.230	–0.060	0.290
	ACN + 8% H_2O	3.5	0.325	–0.010	0.335

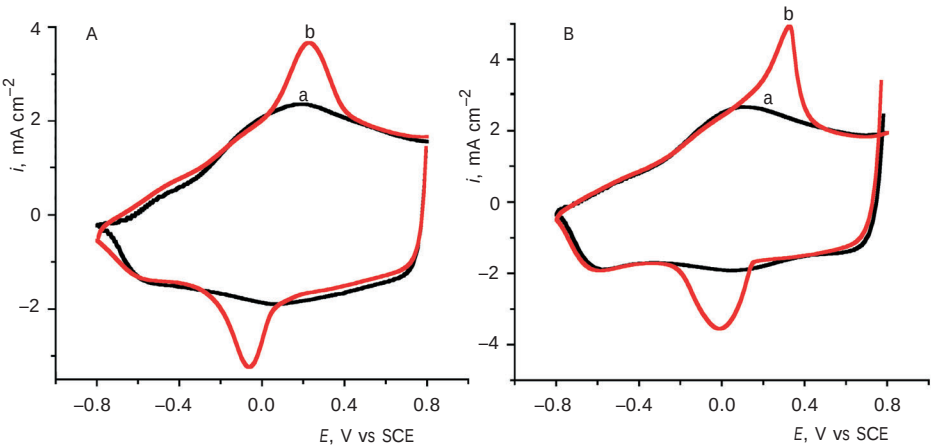

FIG. 5
Cyclic voltammograms of PEDOTh film (a) and PEDOTh/$Fe(CN)_6^{3-}$ (b) in 0.1 M $LiClO_4$ acetonitrile (A) and in 0.1 M $LiClO_4$ acetonitrile + 8% H_2O (B); v = 50 mV s^{-1}. PEDOTh prepared with 30 cycles, $Fe(CN)_6^{3-}$ incorporated at E_f = 0.7 V for 60 s

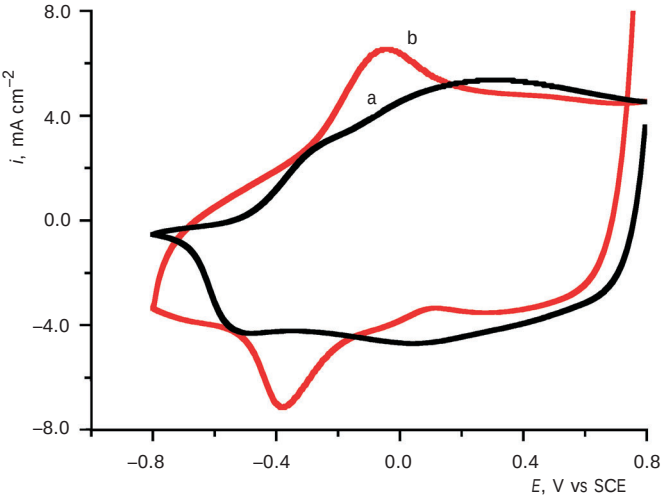

FIG. 6
Cyclic voltammograms of PEDOTh film (a) and PEDOTh/$Fe(CN)_6^{3-}$ (b) in 0.1 M $TBAPF_6$ acetonitrile + 8% H_2O; v = 50 mV s^{-1}. PEDOTh prepared with 60 cycles, $Fe(CN)_6^{3-}$ incorporated at E_f = 0.7 V for 60 s

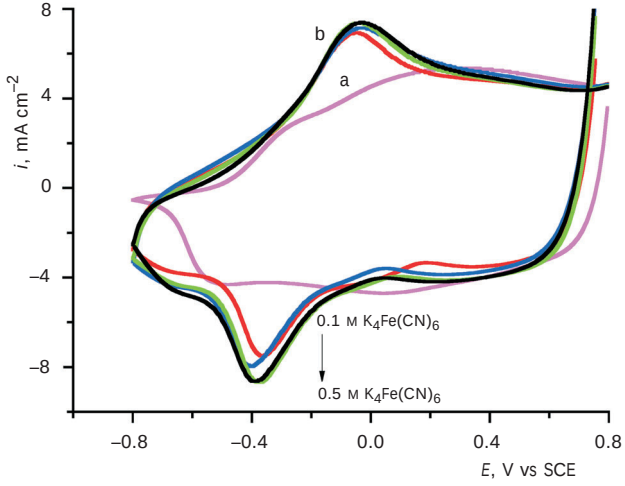

FIG. 7
Cyclic voltammograms of PEDOTh (a) and PEDOTh/$Fe(CN)_6^{3-}$ (b) prepared from solutions of different $K_4Fe(CN)_6$ concentration. Electrolyte solution: 0.1 M $TBAPF_6$ in acetonitrile + 8% H_2O; v = 50 mV s^{-1}. PEDOTh prepared with 60 cycles, $Fe(CN)_6^{3-}$ incorporated at E_f = 0.5 V for 60 s

the redox conversion (Table II) just reveals the presence of more material of identical composition.

Figure 7 illustrates the influence of $K_4Fe(CN)_6$ concentration in solution employed for the anion incorporation. In all cases, the modified PEDOTh displays the above mentioned voltammetric features promoted by the entrapped complex (cathodic wave at about –0.400 V and anodic counter part at –0.040 V). It can be observed that the reduction currents and associated charges increase with the concentration of hexacyanoferrate ion up to 0.1 M, being unimportant the differences thereafter (Table III).

TABLE II

Oxidation and reduction charges retrieved from voltammograms in Figs 4B and 6 for PEDOTh/$Fe(CN)_6^{3-}$

Number of cycles (polymer synthesis)	Q_O, mC cm^{-2}	Q_R, mC cm^{-2}
30	58.1	56.7
60	116.3	112.2

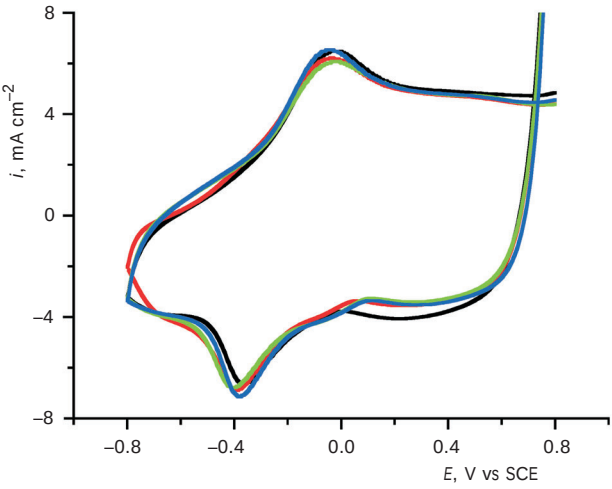

FIG. 8

Cyclic voltammograms of PEDOTh/$Fe(CN)_6^{3-}$ obtained using different potentials for the incorporation of $Fe(CN)_6^{3-}$ for 60 s. Electrolyte solution: 0.1 M $TBAPF_6$ in acetonitrile + 8% H_2O; v = 50 mV s^{-1}. PEDOTh prepared with 60 cycles

In what concerns the anodic limit of the potential pulse (E_f) to induce the anion incorporation in PEDOTh films providing a value within the potential range where the polymer undergoes oxidation, no remarkable effect is observed for E_f between 0.3 and 0.7 V (see Fig. 8). Thus, the subsequent essays have been carried out using E_f = 0.7 V.

The electrocatalytic activity of PEDOTh towards the oxidation of AA and its determination in the presence of other interfering molecules have been the subject of several studies[4d,6,7,8b,11,19]. It is well known that ascorbic acid in aqueous solution yields a single irreversible oxidation peak[4b,8b,9], showing that the oxidized form of AA reacts with water. Compared with the performance of bare usual electrodes, the oxidation of AA at PEDOTh occurs at less negative potentials and displays a much higher peak current, which increases with the increasing concentration of AA, as illustrated in Fig. 9. The observed behavior has been attributed to the electrostatic attraction between the ascorbate anion and the oxidized polymer chains[4d,6,10a] resulting in a pre-concentration of the analyte in the polymer matrix. Conducting polymer layers doped with ferrocyanide anion have also been reported as displaying electrocatalytic properties. It has been considered that the incorporated anions can act as mediators for the oxidation of ascorbic acid[5a,8b,20]. In this study, due to the catalytic behavior revealed by the PEDOTh films, the oxidation of the AA in aqueous media occurs before that of the incorporated anions, and thus, that effect is not confirmed. In non-aqueous electrolyte solutions, it has been found a quasi-reversible electrochemical reduction of ascorbic acid producing a relatively stable radical anion $AA^{\bullet}$, which re-oxidizes to AA [11].

The electrochemical behavior of bare Pt has been analysed in ascorbic acid containing mixed electrolyte solution (0.1 M $TBAPF_6$ in acetonitrile +

TABLE III
Cathodic peak currents and potentials and reduction charges retrieved from voltammograms in Fig. 7

$[K_4Fe(CN)_6]$, M	I_{pc}, mA cm^{-2}	E_{pc}, V vs SCE	Q_R, mC cm^{-2}
0.01	2.56	–0.365	11.4
0.05	2.98	–0.400	125.5
0.10	3.84	–0.385	135.7
0.50	4.27	–0.390	135.7

8% H_2O) (see Fig. 10). In [–0.3, +0.8] V potential domain (Fig. 10 A, voltammogram b), the anodic process starting at about 0.300 V and displaying a current peak at 0.670 V, can be assigned to the oxidation of AA to DHA. When the potential limits are enlarged (Fig. 10 B, voltammogram b), the

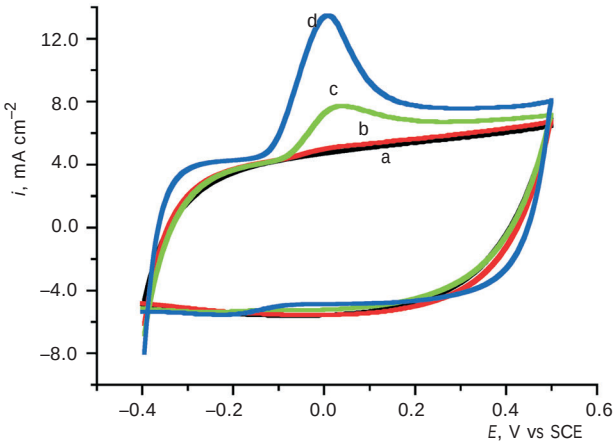

FIG. 9

Cyclic voltammograms of PEDOTh/Pt in aqueous phosphate buffer solution with 0 (a), 1 (b), 5 (c) and 10 (d) mM ascorbic acid; v = 50 mV s^{-1}

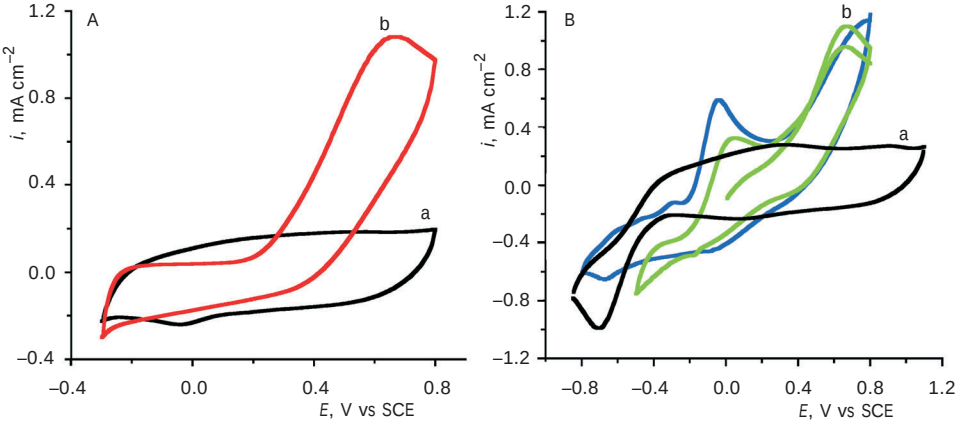

FIG. 10

Cyclic voltammograms of Pt electrode within different potential domains [–0.3, +0.8] V (A) and [–0.85, +1.10] V (B) in 0.1 M $TBAPF_6$ acetonitrile + 8% H_2O (a) and 5 mM AA + 0.1 M $TBAPF_6$ acetonitrile + 8% H_2O (b); v = 50 mV s^{-1}

cathodic wave at about –0.65 V is very likely due to the above mentioned AA reduction to $AA^{\bullet}$, since its counterpart (anodic peak at ca. –40 mV) is observed only when the potential is scanned to enough negative values. Thus the radical anion appears to be stable in the mixed media considered in this work.

The properties of PEDOTh and PEDOTh/$Fe(CN)_6^{3-}$ modified electrodes towards the ascorbic acid oxidation are enlighten by the data presented in Fig. 11. The irreversible oxidation of AA on PEDOTh starts at 0.320 V and the current peak can be seen at 0.500 V (Fig. 11A). In mixed electrolyte solution, it is unlikely the presence of ascorbate ion and thus there is no analyte pre-concentration in the polymer as referred for aqueous media. This explains the observed increase in potential for the AA oxidation with respect to that shown in Fig. 9. On PEDOTh/$Fe(CN)_6^{3-}$, the AA oxidation revealed by the current peak at 0.470 V (Fig. 11B) is much better defined than at pristine PEDOTh. As expected, the cathodic peak corresponding to the reduction of $Fe(CN)_6^{3-}$ vanishes and the anodic counterpart is greatly diminished, supporting a mediated oxidation of AA.

Based on the obtained data, it is plausible to assume the following scheme to describe the mechanism for AA oxidation on PEDOTh/$Fe(CN)_6^{4-/3-}$ in the mixed electrolyte.

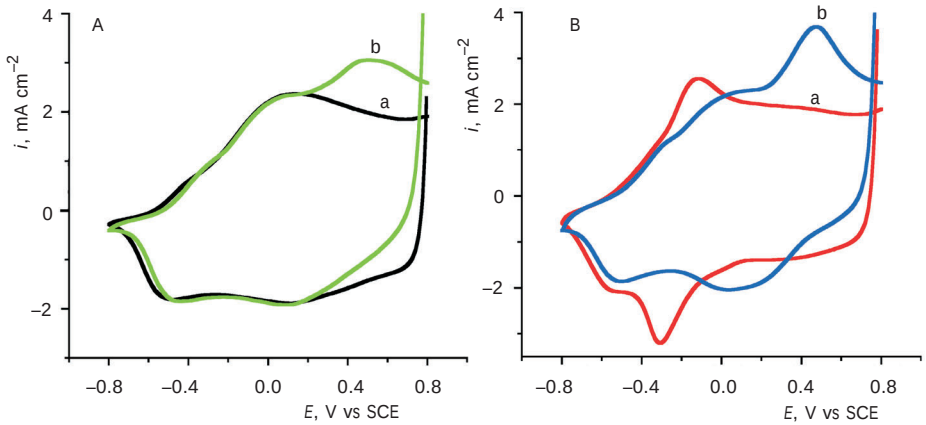

FIG. 11

Cyclic voltammograms of PEDOTh (A) and PEDOTh/$Fe(CN)_6^{3-}$ (B) in 0.1 M $TBAPF_6$ acetonitrile + 8% H_2O solution in absence (a) and presence (b) of 5 mM AA; v = 50 mV s^{-1}. PEDOTh prepared with 30 cycles, $Fe(CN)_6^{3-}$ incorporated at E_f = 0.7 V for 60 s

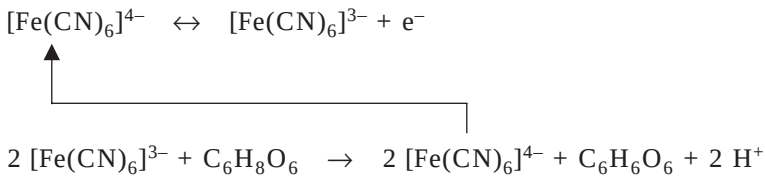

Table IV summarizes the performance of Pt and PEDOTh modified electrodes in the different electrolytes taken into account in the present work with respect to AA oxidation. In aqueous solution, both polymer electrodes are better catalysts than Pt, whereas in mixed medium, PEDOTh/$Fe(CN)_6^{3-}$ appears as more efficient. The observed potential shift to less positive values is small but it can be relevant in simultaneous analysis of related substances.

TABLE IV
Peak and onset potentials for the ascorbic acid oxidation at different electrodes in 0.1 M aqueous phosphate buffer (pH 7) and mixed medium with 5 mM ascorbic acid

Electrode	Ascorbic acid oxidation		
	aqueous sol	mixed medium	
	E_p^O, V vs SCE	oxidation onset, V vs SCE	E_p^O, V vs SCE
Pt	0.370	0.300	≈0.670
PEDOTh/Pt	0.060	0.320	0.500
PEDOTh/$Fe(CN)_6^{3-}$/Pt	0.060	0.220	0.470

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