

## THE OPTIMIZATION OF THE ELECTROCHEMICAL PREPARATION OF PEDOT-PRUSSIAN BLUE HYBRID ELECTRODE MATERIAL AND APPLICATION IN ELECTROCHEMICAL SENSORS

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The electrochemical preparation, characterization and analytical applications of a hybrid material consisting of poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymer and Prussian Blue (PB; iron(III) hexacyanoferrate(II)) are presented. The hybrid material was prepared by a two-steps method. In a first step, the organic conducting polymer coating was deposited onto platinum electrode surface from an aqueous solution containing the monomer and ferricyanide ions. In the second step, the resulted modified electrode Pt|PEDOT-FeCN was immersed in an aqueous solution containing  $\text{Fe}^{3+}$  ions and the electrode potential was cycled between 0.6 and  $-0.4$  V. The in situ formation of PB inside the PEDOT matrix has been demonstrated using cyclic voltammetry and electrochemical quartz crystal microbalance. The hybrid material maintains the electrochemical features of each component, i.e. organic and inorganic components. The inorganic component showed electrochemical activity only for the Prussian blue/Everitt's salt redox system. The hybrid material displayed electrocatalytic activity towards dopamine oxidation in the presence of a large excess of ascorbic acid.

**Keywords:** Electrochemistry; Mixed-valent compounds; Neurotransmitters; Polymers; Platinum; Sensors; Hybrid material; Conducting polymer; Prussian blue; Dopamine; Electrochemical quartz crystal microbalance; Cyclic voltammetry.

Polymers have been extensively used in the last decade in electrochemical sensors thanks to their electrocatalytic, electrochromic and permselective properties. In particular conducting, polymers deposited on bare metallic and carbon-based electrodes, such as polyanilines, polypyrroles and polythiophenes, have proved to afford better selectivity and sensitivity with respect to metallic unmodified electrodes<sup>1-6</sup>. The doping of conducting polymers with various anions has revealed to improve the electrocatalytic

and electrochromic properties of the polymeric selective layers<sup>7-9</sup>. Various procedures for the preparation of inorganic-organic hybrid material coatings have been recently reported<sup>10</sup>. In this frame, Prussian Blue (PB; iron(III) hexacyanoferrate(II)) has been extensively studied in electrochemical sensors applications due to its optical properties and electrocatalytic activity<sup>11-17</sup>. The inorganic-organic materials have been prepared in two geometries, one consisting of an inorganic inner layer and an organic outer layer, and the opposite one where the outer inorganic layer is deposited on top of the inner conducting organic layer<sup>18-24</sup>. It is well known that the stability of PB film in neutral and alkaline aqueous solution is not satisfactory due to the decomposition with iron(III) hydroxide formation<sup>25</sup>. As a consequence new strategies for the preparation of hybrid materials consisting of conducting polymers doped with inorganic redox materials have been investigated<sup>26,27</sup>. Among the different conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has been extensively studied because of its excellent stability and conducting properties<sup>28-33</sup>. PEDOT coatings can also be prepared by electrochemical polymerization in aqueous solution<sup>29</sup>, and this allows the direct incorporation of various water soluble anions, like ferricyanide ions<sup>34</sup>.

In this work, the optimization of the preparation procedures for the in situ formation of an inorganic-organic hybrid material consisting of PB and PEDOT is presented. The PEDOT-PB coating has been prepared by a two steps method. Firstly, the PEDOT film was electrodeposited onto the electrode surface by potentiodynamic polymerization in aqueous solution in the presence of ferricyanide ions. Then, the resulted ferricyanide-doped PEDOT film was transferred in  $\text{Fe}^{3+}$  ions containing aqueous solution where the electrode potential was cycled from 0.6 to  $-0.4$  V. During this potential cycling, the PB was formed inside the PEDOT matrix due to the reaction between iron ions and ferricyanide counter anions. The PEDOT-PB hybrid modified electrode was investigated in neutral aqueous solutions using cyclic voltammetry (CV) and electrochemical quartz crystal microbalance (EQCM). The electrocatalytic activity of the hybrid material towards dopamine (DA) oxidation has been also investigated.

## EXPERIMENTAL

### Reagents

All chemicals:  $\text{FeCl}_3$  (Merck),  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (Merck), HCl (Merck), KCl (Carlo Erba),  $\text{KClO}_4$  (Merck),  $\text{K}_2\text{HPO}_4$  (Merck),  $\text{KH}_2\text{PO}_4$  (Merck) and 3,4-ethylenedioxythiophene (EDOT, Aldrich)

were used without any further purification. Deionized water was always used to prepare aqueous solutions.

### Apparatus

The electrochemical experiments were carried out with an Autolab PGSTAT 30 potentiostat/galvanostat (Ecochemie) coupled to a PC running the GPES software, using a single-compartment, three-electrode cell, at room temperature. A 3-mm diameter Pt disk electrode (Metrohm) was used as a working electrode, a saturated silver|silver chloride electrode (Amel) was used as a reference electrode and a platinum wire (Metrohm) was used as an auxiliary electrode. Before each electrochemical test, the surface of the working electrode was polished subsequently with 1 and 0.3  $\mu\text{m}$  alumina powder to a mirror finish, and then rinsed with deionized water. The microelectrogravimetric measurements were performed with an electrochemical quartz crystal microbalance (EQCM, Metler Toledo) coupled to the potentiostat. The working electrode was a quartz crystal covered with a Pt layer. The geometric surface area of the quartz electrode was of 0.2  $\text{cm}^2$ . The working quartz crystal electrode was washed with deionized water and left to dry prior to measurements. All the solution used for the electrochemical measurements were bubbled with Ar for 10 min and an Ar flow was maintained over the solutions during the experiments.

### Preparation Procedures of PEDOT-PB Hybrid Films

The hybrid coatings have been prepared by in situ deposition of PB inside the PEDOT matrix using three different preparation procedures:

A) The PEDOT film has been electrogenerated starting from an aqueous solution containing  $5 \times 10^{-3}$  M EDOT,  $1 \times 10^{-3}$  M  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , 0.05 M  $\text{KClO}_4$ , 0.05 M KCl and 0.005 M HCl by potential cycling from -0.6 to 1.0 V at a scan rate of 0.05  $\text{V s}^{-1}$  for 10 successive scans. In this way, a PEDOT film doped with ferricyanide ions, denominated as PEDOT-FeCN, was obtained. Then, the modified electrode was immersed in  $2 \times 10^{-3}$  M  $\text{FeCl}_3$ , 0.1 M KCl and 0.01 M HCl aqueous solution, and the electrode potential was scanned from 0.6 to -0.4 V at a scan rate of 0.05  $\text{V s}^{-1}$  for 5 successive scans. During this potential cycling, the in situ formation of PB layer took place.

B) The PEDOT coating has been obtained by electrochemical electropolymerization from an aqueous solution containing 0.01 M EDOT and 0.1 M  $\text{K}_3[\text{Fe}(\text{CN})_6]$  as supporting electrolyte by potential cycling from -0.6 to 1.0 V at a scan rate of 0.05  $\text{V s}^{-1}$  for 6 successive scans. Consequently, a PEDOT film doped with ferricyanide ions, denominated as PEDOT-FeCN, was obtained. Then, the Pt|PEDOT-FeCN modified electrode was immersed in  $5 \times 10^{-3}$  M  $\text{FeCl}_3$  and 0.01 M HCl aqueous solution, and the electrode potential was scanned from 0.6 to -0.4 V at a scan rate of 0.05  $\text{V s}^{-1}$  for 10 successive scans.

C) Another preparation procedure consisted in the transfer of the Pt|PEDOT-FeCN modified electrode, prepared according to the preparation procedure B), in 0.1 M phosphate buffer solution of pH 7.2, where it has been characterized by CV. Then the PEDOT-FeCN modified electrode was immersed in  $5 \times 10^{-3}$  M  $\text{FeCl}_3$  and 0.01 M HCl aqueous solution, and the electrode potential was scanned from 0.6 to -0.4 V at a scan rate of 0.05  $\text{V s}^{-1}$  for 10 successive scans. After the formation of the hybrid PEDOT-PB coating, the modified electrode was rinsed with deionized water and then immersed in the 0.1 M  $\text{KClO}_4$  aqueous solution, where it has been characterized using CV and EQCM.

## RESULTS AND DISCUSSION

*Potentiodynamic Growth of Ferricyanide-Doped PEDOT Coating*

## Procedure A

Figure 1 shows the cyclic voltammograms and the corresponding frequency signal recorded during the preparation of the hybrid coating using the procedure A. In the first scan, a large peak appears at ca. 0.25 V, which decreases over the subsequent scans. Due to the negative starting potential value for the very first cycle, i.e.  $-0.6$  V, it is possible that ferricyanide ions are reduced to ferrocyanide, which is oxidized back to ferricyanide during the potential scan towards positive potential values. From the frequency plot (right axis of Fig. 1), it can be seen that at ca. 0.25 V potential value starts a deposition process. The decrease of the frequency, which is associated with an increase in the mass of the coating deposited onto the electrode surface, is higher when the electrode potential reaches the anodic

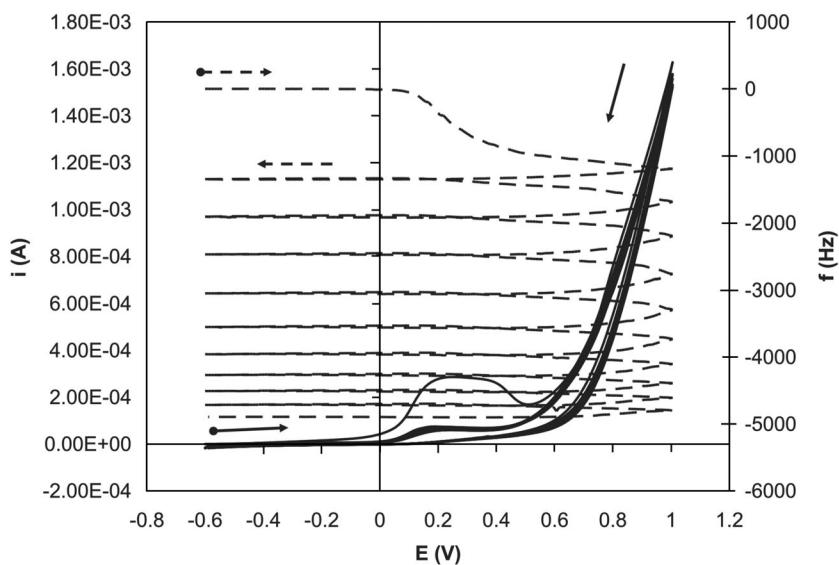


FIG. 1

Cyclic voltammograms (solid line) and frequency changes (dashed line) recorded during the electrochemical polymerization of EDOT at Pt electrode in an aqueous solution containing  $5 \times 10^{-3}$  M EDOT,  $1 \times 10^{-3}$  M  $K_3[Fe(CN)_6]$ , 0.05 M  $KClO_4$ , 0.05 M KCl and 0.005 M HCl. Potential scan rate  $0.05$  V  $s^{-1}$ . The first 10 successive scans are depicted (preparation procedure A, first step)

limit of 1.0 V. In the potential range from 0.75 to 1.0 V, the electrochemical polymerization of EDOT takes place and therefore the PEDOT layer is growing on the electrode surface. The mass increase on the electrode surface is well evident for the first 7 cycles and then a small increase is observed; this behavior is due to the enhanced thickness of the deposited polymer film which reduces the deposition rate of new material onto electrode surface, i.e. the diffusion path for both electrons and ions increases with the potential cycles resulting in a decrease of the deposition rate. Only a small quantity of ferricyanide ions is incorporated into the PEDOT film since its concentration is much smaller than that of  $\text{ClO}_4^-$  anions. This hypothesis is demonstrated by the shape of the cyclic voltammograms which clearly shows that there is no redox wave associated with the ferri/ferrocyanide redox couple.

This fact is more evident when the modified electrode is immersed in the transfer solution containing 0.1 M  $\text{KClO}_4$  solution. Therefore this preparation procedure is not suitable for the preparation of conducting polymers doped with inorganic redox materials.

### Procedure B

The preparation procedure B provides a simply and very efficient way to prepare hybrid coatings on electrode surfaces. Figure 2a reports the cyclic voltammograms and the corresponding frequency changes recorded during the electropolymerization of the EDOT monomer in the presence of ferricyanide ions. In this case, the PEDOT film has been electrodeposited starting from an aqueous solution containing  $1 \times 10^{-2}$  M EDOT and 0.1 M  $\text{K}_3[\text{Fe}(\text{CN})_6]$  as a supporting electrolyte.

The shape of the frequency plot indicates that the mass increases cycle after cycle, evidencing the formation of a film on the electrode. The electropolymerization process is less visible with respect to the procedure A, considering only the current trace: the signal of the ferro/ferricyanide redox couple, present at higher concentration is much more intense with respect to that of the monomer oxidation and of the polymer p-doping. During the very first scan, we can observe that the frequency starts to decrease at ca. 0.84 V, indicating the beginning of the deposition process of PEDOT on the electrode. No frequency change is observed in correspondence of the current peak at +0.4 V, confirming that the relevant oxidation process is not related to a deposition process (see Fig. 2b). The deposition process takes place until the potential value of +0.8 V is reached in the backward scan.

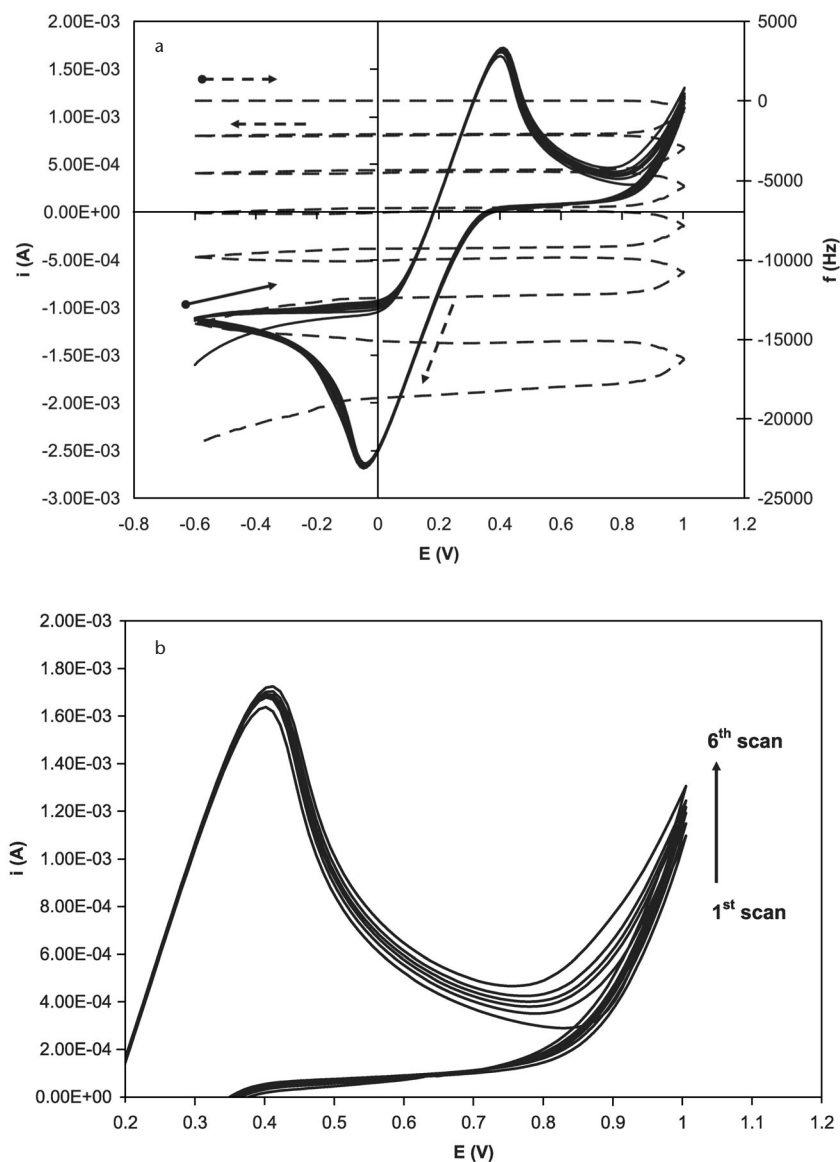


FIG. 2

a Cyclic voltammograms (solid line) and frequency changes (dashed line) recorded during the electrochemical polymerization of EDOT at Pt electrode in an aqueous solution containing 0.01 M EDOT and 0.1 M  $K_3[Fe(CN)_6]$  as a supporting electrolyte. Potential scan rate  $0.05 \text{ V s}^{-1}$ . b In-zoom of the anodic peak region of the cyclic voltammograms from Fig. 2a. The first 6 successive scans are depicted (preparation procedure B, first step)

Only in this small potential range (+0.85  $\rightarrow$  +1.0  $\rightarrow$  +0.85 V), a linear trend in the  $\Delta f$  vs  $Q$  plot is visible, as it can be seen from Fig. 3.

At the end of the first potential scan, a frequency change of  $-2200$  Hz was recorded. The mass changes of the quartz crystal can be calculated on the basis of the changes in the resonant frequency using the Sauerbrey equation<sup>35</sup>, under the hypothesis of a rigid deposit

$$\Delta f = -\frac{2f_0^2 \Delta m}{nA\sqrt{\rho\mu}} \quad (1)$$

where  $f_0$  is the resonant frequency (in Hz) of the QCM resonator once dipped inside the solution, without addition or removal of any mass  $\Delta m$  (in g),  $n$  is the harmonic number of the oscillation ( $n = 1$ ),  $\rho$  is the density of quartz ( $\rho = 2.648 \text{ g cm}^{-3}$ ),  $\mu$  is the shear modulus of quartz ( $\mu = 2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2}$ ) and  $A$  is the geometric area (in  $\text{cm}^2$ ). Considering the resonant frequency of 10 MHz and the electrode area of  $0.2 \text{ cm}^2$ , a mass change of  $\sim 1.94 \mu\text{g}$  can be computed. In the subsequent scans, the frequency variation in the deposition region remains very similar to that observed in the first scan. At the end of the six scans,  $\sim 12 \mu\text{g}$  have been deposited. How-

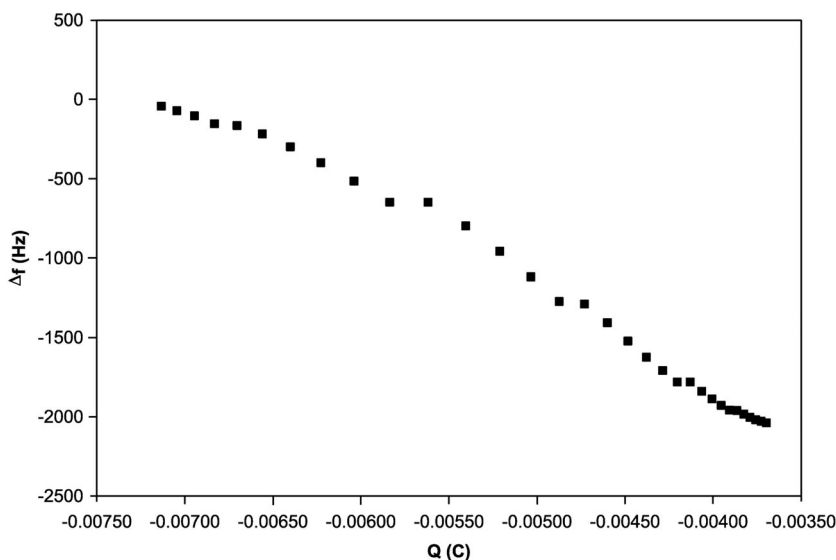


FIG. 3

The dependence of the frequency on the charge consumed during the EDOT electropolymerization. Experimental conditions as indicated in Fig. 2

ever, scan after scan a decrement of frequency, i.e. an increment of mass, in the negative potential range is more and more evident. This is an unexpected behavior, since in this potential range PEDOT should be neutral and then it should expel negative counterions in order to reach electroneutrality. Actually, ferricyanide anions are likely trapped inside PEDOT matrix, so that potassium cations have to enter into the polymer during the dedoping process in order to maintain the electroneutrality. These results clearly demonstrate that this preparation procedure allows the formation of the ferricyanide doped PEDOT films.

### Procedure C

In the case of the preparation procedure C, the PEDOT coating has been electrogenerated starting from an aqueous solution containing 0.01 M EDOT and 0.1 M  $K_3[Fe(CN)_6]$  as supporting electrolyte. After the PEDOT deposition, the modified electrode was dipped in 0.1 M phosphate buffer aqueous solution of pH 7.2 and the electrode potential was cycled in the

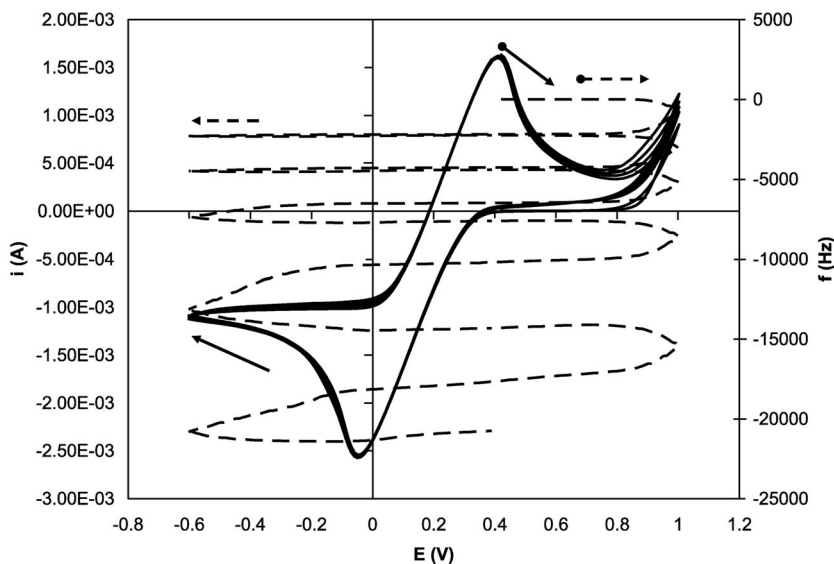


FIG. 4

Cyclic voltammograms (solid line) and frequency changes (dashed line) recorded during the electrochemical polymerization of EDOT at Pt electrode in an aqueous solution containing 0.01 M EDOT and 0.1 M  $K_3[Fe(CN)_6]$  as a supporting electrolyte. Potential range from 0.4 to 1.0 V and reversed back to  $-0.6$  V. Potential scan rate  $0.05 \text{ V s}^{-1}$ . The first 5 successive scans are represented (preparation procedure C, first step)



potential range from  $-0.3$  to  $+0.6$  V for 5 successive scans, at a scan rate of  $0.05$  V s $^{-1}$ .

Figure 4 shows the cyclic voltammograms traces and the corresponding frequency change recorded during the electrochemical polymerization of the EDOT monomer in the presence of ferricyanide ions. The trend is quite similar to the case of procedure B for the first three scans; then the increase of mass during the subsequent scans is higher. The difference in the frequency response for these two coatings is less than 6000 Hz, while the anodic currents are almost identical. This difference in the frequency change can be ascribed to a slightly different doping level of PEDOT coatings.

### Formation of PB Inside the PEDOT Matrix

#### Procedure A

After the preparation of ferricyanide-doped PEDOT coating according to the preparation procedure A, the modified electrode was transferred into an

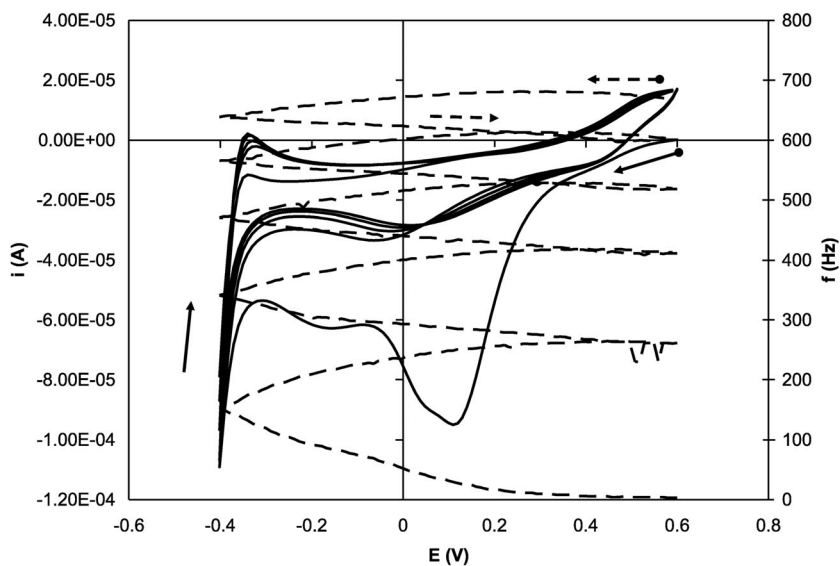


FIG. 5

Cyclic voltammograms (solid line) and the corresponding frequency changes (dashed line) recorded at a Pt|PEDOT-FeCN modified electrode during the in situ formation of the PB layer in a solution containing 2 mM FeCl $_3$ , 0.1 M KCl and 0.01 M HCl. Potential scan rate  $0.05$  V s $^{-1}$ . The first 5 successive scans are depicted (preparation procedure A, second step)

aqueous solution containing  $\text{Fe}^{3+}$  ions, where the electrode potential was cycled from 0.6 to  $-0.4$  V, at a sweep rate of  $0.05 \text{ V s}^{-1}$ . Figure 5 reports the cyclic voltammograms and the frequency change recorded during the potential cycling. Due to the presence of  $\text{Fe}^{3+}$  ions into the solution, the reduction of these ions takes place at the polymer|solution interface and the resulted  $\text{Fe}^{2+}$  ions react with ferricyanide present inside the PEDOT matrix. As a result of this reaction, the formation of PB is expected during the potential cycling.

In the case of procedure *A*, due to the small quantities of entrapped ferricyanide ions, there is no evidence for PB formation, as it can be seen from the trace of the cyclic voltammograms. One could observe only a high cathodic wave located at ca.  $+0.15$  V due to the reduction of  $\text{Fe}^{3+}$  ions. The frequency signal shows that in the potential range from 0.15 to  $-0.4$  V a mass decrease takes place, which can be associated with the exit of counterions from the PEDOT layer. On the backward scan towards positive potential values, an increase in the frequency signal attests the entrance of counterions to maintain the electroneutrality. The shape of the cyclic voltammograms and the corresponding frequency plot clearly demonstrates that PB can not be prepared in situ under these experimental conditions. Therefore, it is well evident that the preparation procedure *A* it is not suitable for the preparation of the envisaged hybrid coating.

### Procedure *B*

As mentioned already above, the preparation procedure *B* seems to be more appealing for this purpose. In this case, the Pt|PEDOT-FeCN modified electrode prepared according to the procedure *B* was dipped in aqueous solution containing  $\text{Fe}^{3+}$  ions and the electrode potential was scanned from 0.6 to  $-0.4$  V at a scan rate of  $0.05 \text{ V s}^{-1}$  for 10 successive scans (Fig. 6). During the first potential cycle one can observe two reduction peaks located at ca. 0.2 and 0.05 V, respectively. The first cathodic peak is associated with the reduction of  $\text{Fe}^{3+}$ , while the last one is ascribed to the reduction of ferricyanide ions entrapped inside of PEDOT matrix. The PB is formed in situ by precipitation of  $\text{Fe}^{2+}$  ions with ferrocyanide anions.

As to the frequency signal, a high decrease is observed during the first potential cycle, probably due to the PB formation. Then, the frequency trend remains constant cycle after cycle. At the same time, one can observe that the current signal reaches a stationary state from the 2nd scan onward, as it can be seen from Fig. 6. This behavior is due to the ions exchange during the potential cycling in order to maintain the electroneutrality.

After the formation of PB inside the PEDOT matrix, the modified electrode was immersed in aqueous solution containing 0.1 M  $\text{KClO}_4$ , where it has been investigated by CV and EQCM. Figure 7 reports the cyclic voltammogram and the frequency change recorded during the potential cycling in the range from 0.6 to  $-0.4$  V at a scan rate of  $0.05 \text{ V s}^{-1}$ . The hybrid modified electrode displays a redox wave with a value for the anodic peak potential of 0.2 V and a corresponding cathodic peak potential of 0.1 V, respectively. This wave can be ascribed to the redox process associated with the PB/Everitt's salt (ES) redox system.

Considering the frequency signal, there is a decrease of frequency in the potential range from  $+0.6$  to  $+0.25$  V. In this region, there are at least two processes taking place: the reduction of PB and the de-doping of PEDOT. Since a linear trend in the  $\Delta f$  vs  $Q$  plot was obtained (see Fig. 7b), the molecular weight (MW) of the species that causes the variation of mass can be calculated using the following equation:

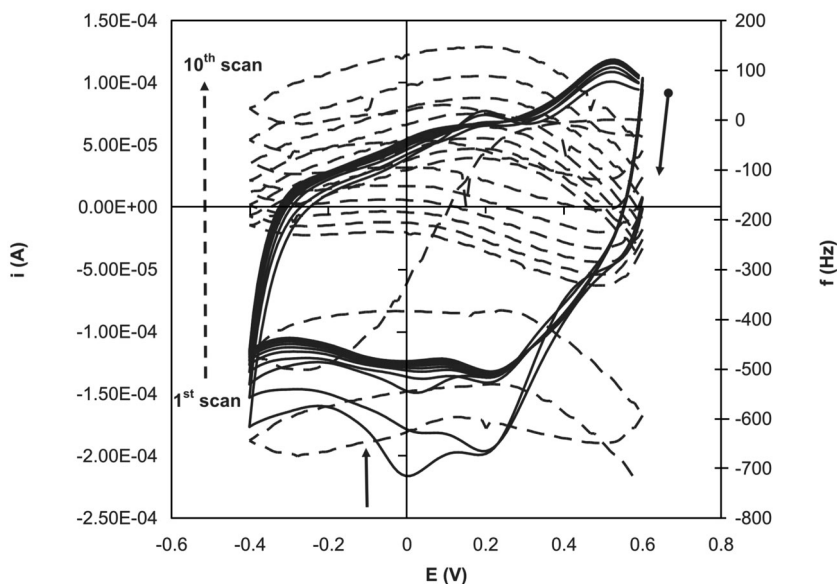


FIG. 6

Cyclic voltammograms (solid line) and the corresponding frequency changes (dashed line) recorded at a Pt|PEDOT-FeCN modified electrode during the in situ formation of the PB layer in a solution containing 5 mM  $\text{FeCl}_3$  and 0.01 M HCl. Potential scan rate  $0.05 \text{ V s}^{-1}$ . The first 10 successive scans are represented (preparation procedure B, second step)

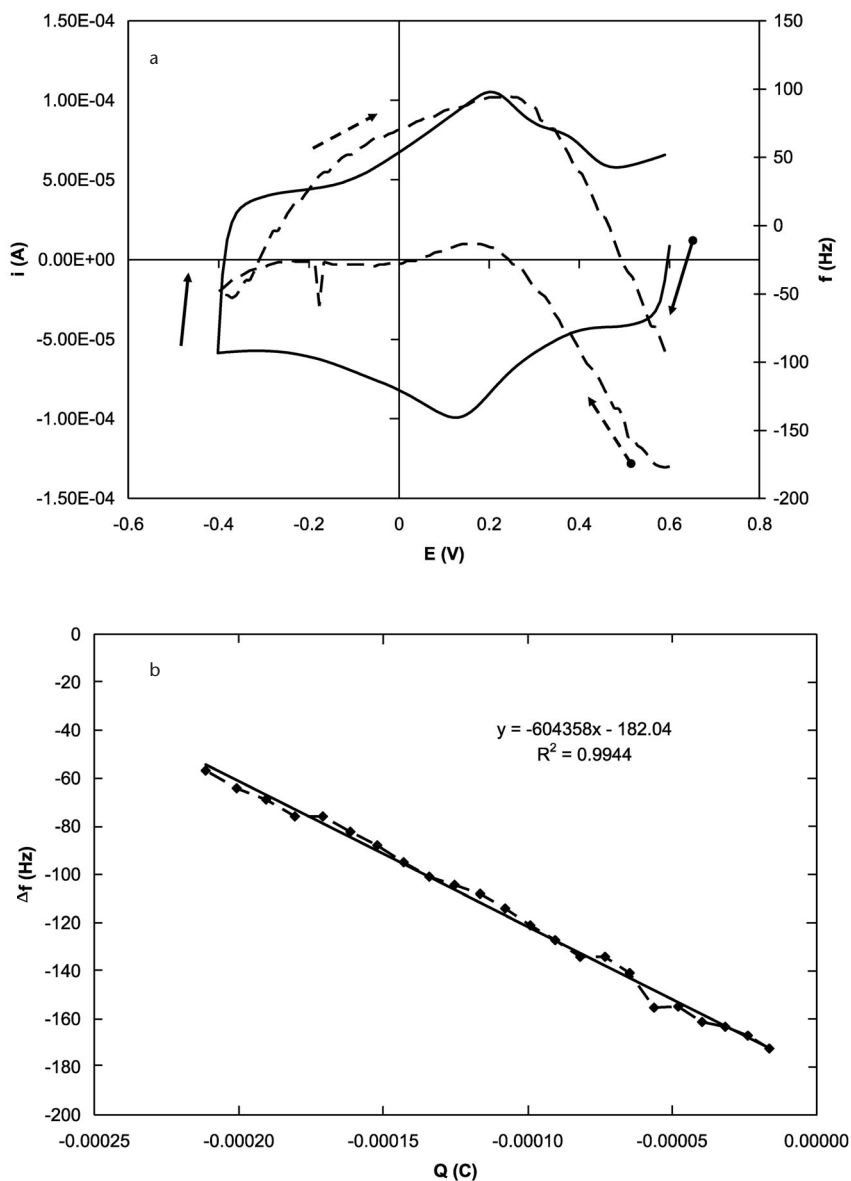


FIG. 7

a Cyclic voltammogram (solid line) and the corresponding frequency change (dashed line) recorded at a Pt|PEDOT-PB hybrid modified electrode in a solution containing 0.1 M KClO<sub>4</sub>. Potential scan rate 0.05 V s<sup>-1</sup>. b The dependence of the frequency change on the charge

$$\Delta f = -\frac{MW' \times C_f Q}{nF} \quad (2)$$

were  $C_f = 2 f_0^2 / nA(\rho\mu)^{1/2}$ ,  $n$  is the number of electrons transferred and  $F$  is the Faraday constant. The value of the molar mass computed is  $\sim 52 \text{ g mol}^{-1}$ , which is compatible with the exit of  $\text{ClO}_4^-$  anion ( $MW = 99.5 \text{ g mol}^{-1}$ ) due to the de-doping of PEDOT and the ingress of  $\text{K}^+$  ( $MW = 39.1 \text{ g mol}^{-1}$ ) cation due to the PB reduction. In the same potential range, during the reverse scan a molar mass value of  $\sim 52 \text{ g mol}^{-1}$  was computed, that can be explained taking into account the same processes but in opposite directions. The investigation of the modified electrode in  $0.1 \text{ M KClO}_4$  aqueous solution aimed to study the ions exchange during the potential cycling. The choice of such supporting electrolyte was based on the difference in molecular weight of the cation and the anion, respectively. This approach provides the determination of the molecular weight of the ionic species involved in the ions transport in the composite film. Furthermore, it should be noted that the electrode potential is cycled around the PB/ES redox system, which corresponds to the "soluble" form of PB. The term "soluble" refers to the peptization process of the potassium salt and does not indicate that this form of PB is soluble; actually both forms of PB are practically insoluble. Therefore, the change in the frequency should be related only to the ion exchange processes that occur during the potential cycling.

### Procedure C

In the case of the modified electrode prepared according to the preparation procedure *C*, the electrochemical properties of this hybrid material revealed little changes with respect to the coating prepared according to the preparation procedure *B*, therefore our interest was focused on the hybrid material prepared according to the procedure *B*, especially for analytical applications.

### *Analytical Performances of PEDOT-PB Hybrid Materials*

The electrochemical properties of the hybrid materials presented above suggested that only the hybrid material PEDOT-PB prepared according to the preparation procedure *B* seems to be appealing for analytical applications. To this purpose, we have investigated the electrocatalytic activity of this

hybrid material towards the DA oxidation in the presence of an excess of ascorbic acid (AA). Figure 8 shows the square wave voltammograms recorded at Pt|PEDOT-PB modified electrode in aqueous 0.1 M phosphate buffer solution for various DA concentrations ranging from 20–1000  $\mu\text{mol l}^{-1}$ .

The DA oxidation produces an anodic peak at 0.26 V, while the AA oxidation occurs at a potential value of 0.08 V. These anodic peaks are located at less positive potential values than in the case of unmodified electrodes. Furthermore, the hybrid coating is able to solve the close voltammetric peaks of both analytes present simultaneously in the sample by providing a peak potential difference of about 180 mV, which is large enough to assure the simultaneous determination of these analytes. The anodic peak current for DA increased linearly with increasing DA concentration (Fig. 9), with a correlation coefficient of 0.9921, a sensitivity of 0.0348  $\mu\text{A } \mu\text{mol l}^{-1}$  and an intercept of 1.7676  $\mu\text{A}$  (after background correction). The intercept of the calibration plot indicates the influence of AA on DA oxidation. A detection limit of 2.2  $\mu\text{mol l}^{-1}$  ( $3\sigma$ ,  $n = 6$ ) was also obtained.

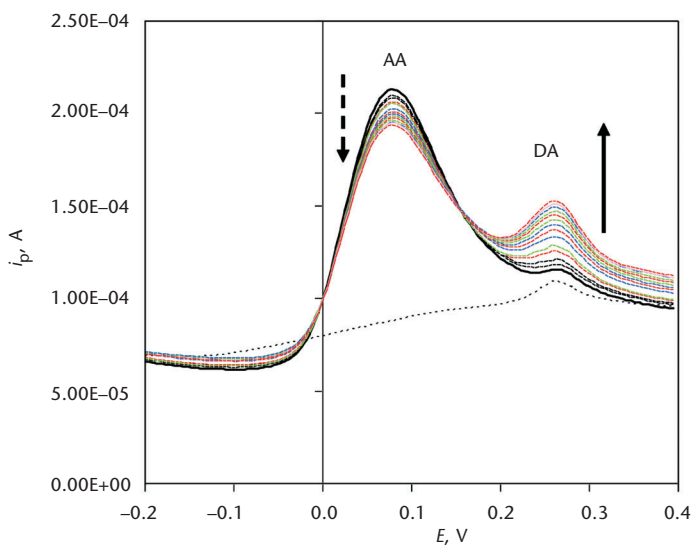


FIG. 8

Square wave voltammograms recorded at a Pt|PEDOT-PB modified electrode in 0.1 M aqueous phosphate buffer solution of pH 7.2 at different dopamine concentrations ranging from 20 to 1000  $\mu\text{mol l}^{-1}$  in the presence of 0.01 M ascorbic acid. Pulse step 0.005 V, pulse amplitude 0.02 V, frequency 10 Hz

The modified electrode was able to sense the lowest concentration of DA ( $20 \mu\text{mol l}^{-1}$ ) in the presence of a large excess of AA ( $10 \text{mmol l}^{-1}$ ) that is 500 times difference in both concentrations, which is similar to the concentration difference of DA and AA under physiological conditions<sup>36</sup>. These results demonstrate that the selective and sensitive voltammetric determination of DA in the presence of a high excess of AA can be achieved at this PEDOT-PB modified electrode.

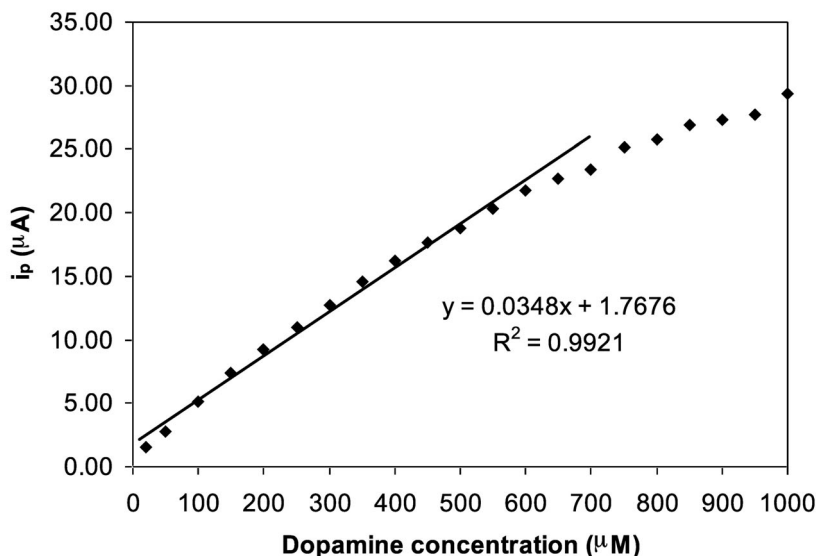


FIG. 9

The linear dependence of the square wave anodic peak current on dopamine concentration in the range  $20\text{--}600 \mu\text{mol l}^{-1}$

## CONCLUSIONS

The PEDOT-PB hybrid coating displayed good electrochemical stability under various experimental conditions. The good stability of the hybrid film is attributed to the electrostatic stabilization of the negatively charged PB by the positive PEDOT backbone, thus preventing the PB dissolution and decomposition in neutral aqueous solutions. The hybrid material maintains the electrochemical activity of PB corresponding to the high spin iron atoms. The EQCM measurements provided good estimation of the molar mass of the counter ions transferred in and out from the hybrid film during

electrochemical polarization. The hybrid material prepared according to the preparation procedure *B* exhibited electrocatalytic activity towards DA oxidation and moreover it allows the selective and sensitive determination of DA in the presence of a high excess of AA.

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